Carbon-Bridged Cyclopentadienyl Amido Group 4 Metal Complexes

Ligand Tuning and Olefin Polymerization

Piet-Jan Sinnema

The photograph on front cover shows a ‘Skûtsje’, an ancient Frisian sailing ship, in action during the annual race across the Frisian lakes. The ‘Skûtsje’ displayed here is representing Sneek, a local center in the south-west of Friesland
Photographs taken by J.D. de Jong.

Leden van de beoordelingscommissie:

Prof. dr. B.L. Feringa
Prof. dr. P.W.N.M. van Leeuwen
Prof. dr. J. Okuda

The research for this dissertation was carried out within the scope of NIOK, the Netherlands Institute for Catalysis Research.

Het onderzoek voor dit proefschrift is uitgevoerd in het kader van NIOK, het Nederlands Insituut voor Onderzoek van Katalyse.

RIJKSUNIVERSITEIT GRONINGEN

Carbon-Bridged Cyclopentadienyl Amido Group 4 Metal Complexes

Ligand Tuning and Olefin Polymerization

Proefschrift

ter verkrijging van het doctoraat in de
Wiskunde en Natuurwetenschappen
aan de Rijksuniversiteit Groningen
op gezag van de
Rector Magnificus, dr. D.F.J. Bosscher
in het openbaar te verdedigen op
vrijdag 23 april 1999
om 16.00 uur

door

Piet Jan Sinnema

geboren op 30 november 1963
te Delft

Promotor: Prof. dr. J.H. Teuben

Co-promotor: dr. B. Hessen

ISBN 90-367-1038-3

Voor mijn familie

List of Abbreviations:

Me = $-CH_3$, methyl

Et = $-CH_2CH_3$, ethyl

n-Pr = $-CH_2CH_2CH_3$, n-propyl

i-Pr = $-CH(CH_3)_2$, *iso*-propyl

t-Bu = $-C(CH_3)_3$, *tert*-butyl

Ad = adamantyl

Ph = $-C_6H_5$, phenyl

Cp = η^5-C_5H_5, cyclopentadienyl

Cp* = η^5-C_5Me_5, pentamethylcyclopentadienyl

THF = C_4H_8O, tetrahydrofuran

MAO = $[MeAlO]_n$, methylaluminoxane

Np = $-CH_2C(CH_3)_3$, neopentyl

Nf = $-CH_2C(CH_3)_2C_6H_5$, neophyl

Contents.

1 General Introduction.

Transition metal catalysed olefin polymerization is one of the most fascinating area's in modern chemistry.[1] The field is still expanding rapidly and has shown to be highly surprising both in scientific breakthroughs and in proven commercial importance.[2] In the last 10-15 years, completely new insights have developed and the field has grown from essentially serendipity driven catalyst development to rational catalyst design on the basis of advanced theoretical methodology.[3]

The developments in catalytic olefin polymerization very clearly form the most illustrative example of the enormous potential organometallic chemistry has for catalysis. The origin of this and of many other applications is the unique character of the (transition) metal-carbon bond.

1.1 The Transition Metal-Carbon Bond.

Since metal atoms are more electropositive than carbon, organometallic compounds have polar bonds $M^{\delta+}$-$C^{\delta-}$. The polarity of the M-C bond of transition metal complexes is in general larger than the C-Cl bond[4] but reverse in charge distribution. In organic chemistry the C-Cl bond is considered to be quite polar and many reactions of organo-chloro compounds can be understood on that basis. Mechanistic investigations of organic reactions indicate that beside the well known S_N1 or S_N2 mechanisms, many reactions proceed through concerted four- or six-center transition states with partial charges on the atoms. Similarly a synchronous four-center or six-center transition state (Figure 1) has been suggested for reactions of metal-carbon bonds with polar substrates.

The polarity of the M-C bond varies strongly. Not only the metal (nature and valence state) but also the ligand surroundings influence the polarity dramatically. In addition to electronic factors, the reactivity of the metal center is strongly determined by the steric aspects of the total ligand set.

Due to these variables, organometallic compounds show a broad spectrum of reactivity with various substrates. This has lead to interesting possibilities for C-C, C-O, C-N, C-X and C-H bond formation or activation. This reactivity has been shown to be very useful in organic

synthesis. Applications of these principles in transition metal mediated organic chemistry, both stoichiometric and catalytic, are well known[5].

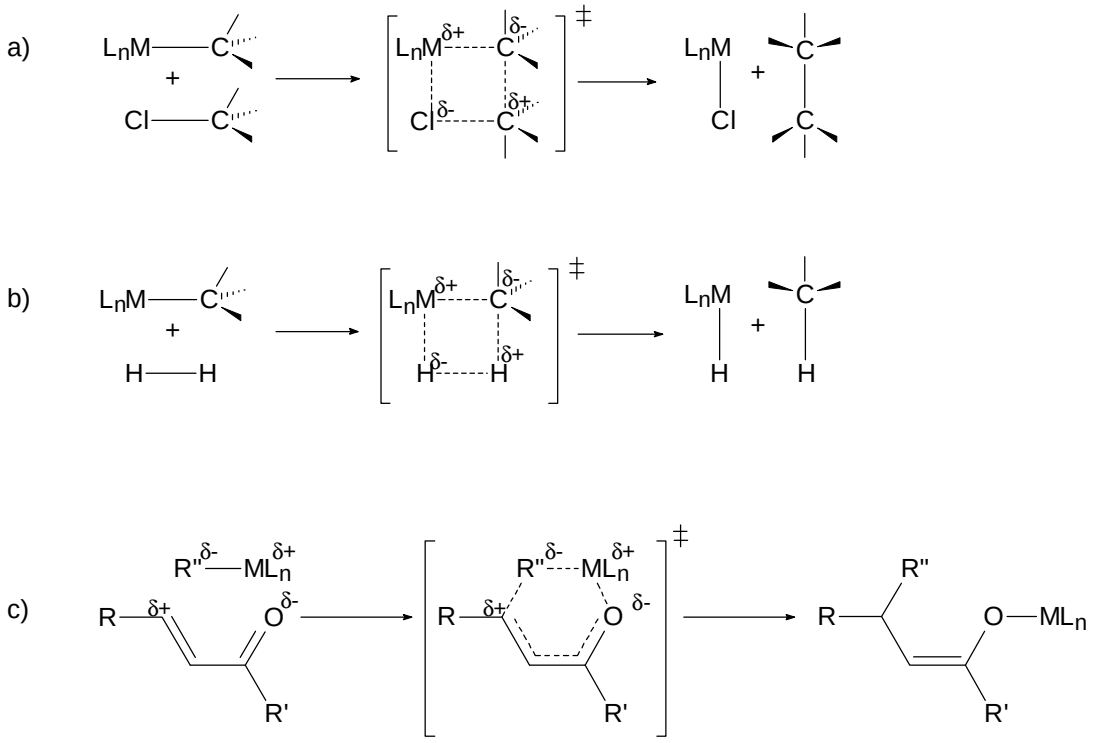


Figure 1. Four and six center transition states in transition metal mediated chemistry: a) Reaction of an organometallic compound with an alkyl halide; b) Hydrogenolysis of a metal-carbon bond; c) Michael addition (M = Li, Mg, Cu and Zn).

1.2 Catalysis and Olefin Polymerization.

Nowadays, nearly all processes with a production of >10,000 ton/year are catalytic. Catalytic processes make up about 30% of the industrial chemical productivity of the western countries[6]. The high performances (activity/selectivity) and high atom efficiency (reduction of waste) of the catalysts results in feedstock and energy savings and high product efficiency. Additionally, highly selective, catalyzed processes contribute to a lower burdening of the environment. The possibility of developing efficient and clean synthetic procedures on the basis of organometallic catalysts is in fact the *raison d'être* for further development of organometallic chemistry.

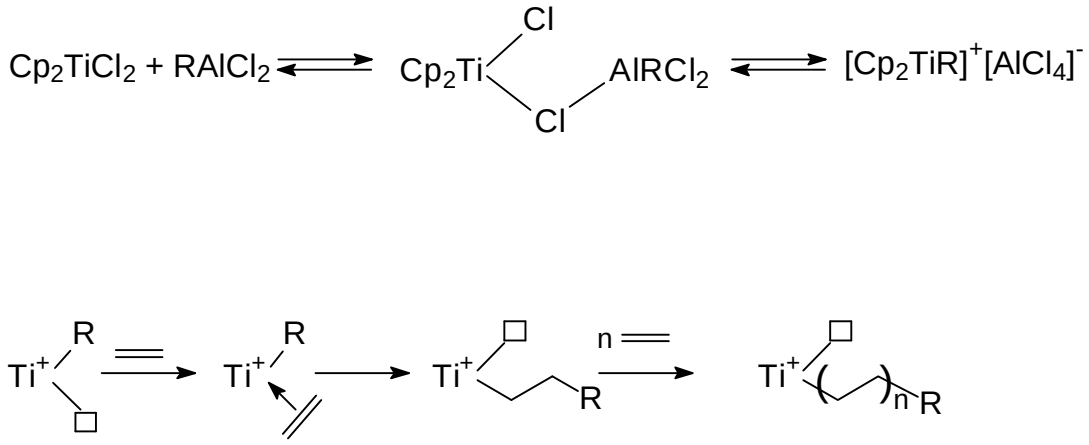
Among the huge number of different polymers available, polyethene and polypropene are by far the most used nowadays and their consumption is still increasing. The total volume of polymers used (110 mln m^3) already exceeds the volume of steel (90 mln m^3) and aluminium (6 mln m^3) combined.[7]

Untill 1953 only low melting and highly branched polyethene with a broad molecular weight distribution was available by radical polymerization at very high pressure (1000-3000 atm) and high temperature (150-230 ^oC).[8] Polymerization of propene (2800 atm at 80 ^oC) yielded atactic, low molecular weight material[9] and high molecular weight stereoregular polyolefins could not be synthesized at all.

A strong impulse for the rapid development of polyolefins was the discovery by Ziegler that polymerization of ethene to high molecular weigth linear polyethene could be achieved at mild reaction conditions using $TiCl_4$ in the presence of aluminium alkyls.[10] Shortly afterwards Natta showed that it was possible to polymerize propene to isotactic polypropene at mild conditions as well using the same type of catalysts.[11]

1.3 Homogenous Metallocene Catalyzed Olefin Polymerization.

In homogeneous catalysis ancillary ligands are used to stabilize the metal center and to tune the electronic properties and steric crowding around the metal. The choice of the ligand is all-important for the stability, activity and selectivity. In early transition metal chemistry cyclopentadienyl ligands are frequently used and especially bis-cyclopentadienyl (metallocene) complexes have been studied extensively. These complexes have shown to be very valuable in various catalytic processes. A major breakthrough in the homogeneous polymerization of α-olefins was made by Sinn and Kaminsky. They used Cp_2ZrMe_2 in combination with methylaluminoxane (MAO) and obtained an extremely active catalyst for the polymerization of ethene.[12] Additionally, it was possible to polymerize propene as well. Kinetic studies on the homogeneous Group 4 metal Ziegler-Natta system $Cp_2TiRCl/AlR'Cl_2$ suggested that two subsequent equilibria lead to the active catalytic species (Scheme 1).[13] Crucial for this mechanism is the formation of a cationic group 4 metal center having a vacant coordination site.[14] Polymerization was proposed to involve coordination of olefin to the vacant site of this activated Ti-R species and subsequent insertion into the Ti-R bond (the Cossee-Arlman mechanism[15]). The essential steps of this mechanism are still generally accepted though modifications involving effects such as α-agostic hydrogen interactions have been proposed.[16]

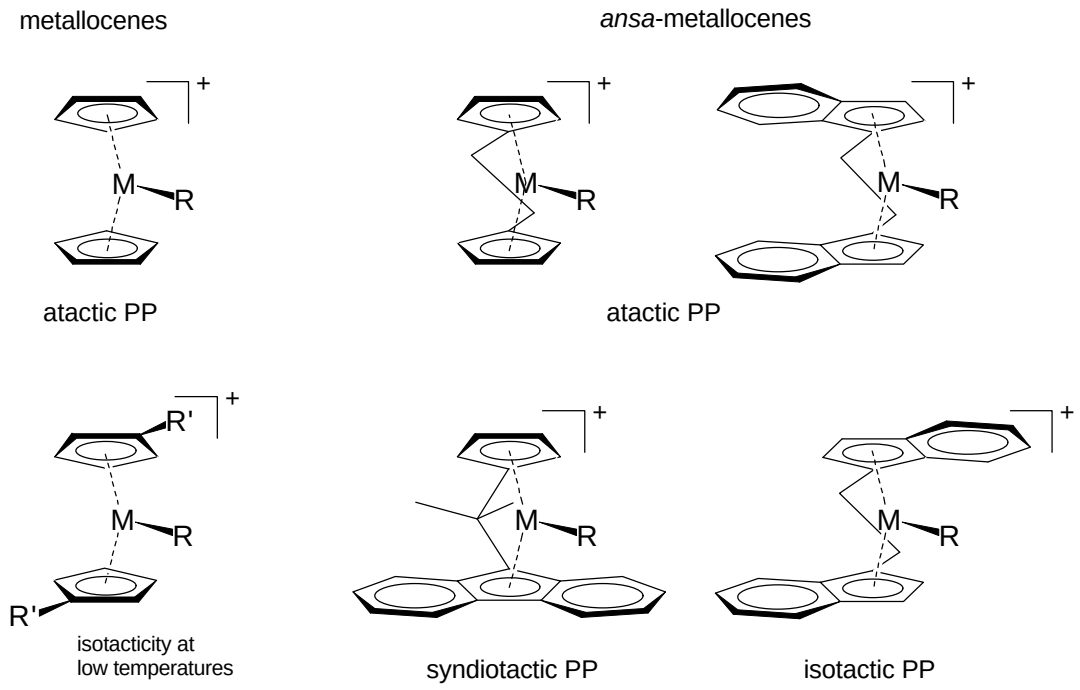


Scheme 1. Insertion of olefins according to the Cossee-Arlman mechanism

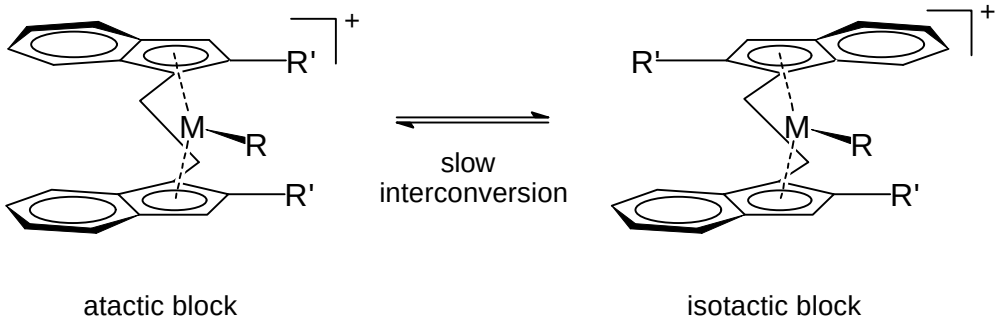
Cationic group 4 metallocene complexes $[Cp'_2MR]^+$ are *iso*-electronic with the neutral group 3 and lanthanide complexes (Cp'_2LnR, Cp' = C_5Me_5, R = H, alkyl) which are among the most active homogeneous catalysts for the polymerization of ethene known to date.[17]

Whereas polymerization of propene with traditional metallocene catalysts only results in low melting, atactic polymers, formation of stereo regular isotactic and syndiotactic polypropene is possible with catalysts with a specific geometry. Brintzinger addressed this problem by bridging the two indenyl ligands (*ansa*-metallocenes, Scheme 2). The initial results, using C_2-symmetric *rac*-(ethylene-*bis*-indenyl) titanium complexes, were encouraging and partial isotactic polypropene was obtained[18] With the zirconium analogue highly isotactic polypropene was produced [19] although the polymerization had to be performed at low temperature. The isotacticy of the polypropene drops dramatically at higher tempratures (70-80 ^oC, the prefered temperature in industrial processes).[20] Introduction of large substituents at the 4 position of the indenyl ring raised the isotacticity to over 95%, even at high temperatures (70-80 ^oC).[21]

Syndiotactic polypropene is obtained with a C_s-symmetric fluorenyl linked cyclopentadienyl zirconium catalyst.[22] Substitution of the cyclopentadienyl moiety at the β-position can dramatically influence the properties of the polypropene produced. When a methyl substituent is present at the β-position of the cyclopentadienyl moiety, hemi-isotactic polypropene is formed[23] while with a *t*-Bu group isotactic polypropene is obtained.



Scheme 2. Polypropene tacticity *vs* catalyst symmetry



Scheme 3. Interconversion of complex symmetry resulting in stereoblock polymerization of α-olefins.

Polypropene with unique rubber-like properties can be obtained using the untied bis-(2-phenyl-indenyl)zirconium dichloride. Slow interconversion between the *rac* and the *meso* form in comparision with the fast propagation results in stereoblock polymers with alternating atactic and isotactic blocks[24] (Scheme 3). It may be clear that polymer properties are related to their molecular structure and thus strongly depend on the catalyst used.

The use of group 4 (*ansa*-)metallocenes is not limited to catalytic polymerization of olefins but they can also be used as reagents in organic synthesis. They can mediate in (catalytic) C-C, C-H, C-N, C-O and C-X bond forming reactions like hydro amination of alkynes,[25a]

allylation of aldehydes and coupling of alkynes to ketones,[25b-d] functionalization of pyridines,[25e] cyclopolymerization of dienes,[25f,g] asymmetric Diels-Alder reactions,[25h,i] carbomagnesation reactions,[25j,k] hydrogenation of olefins,[25l,m] hydrogenation of imines,[25n-p] hydrogenation of enamines,[25q,r] hydrosilylation of ketones,[25s] epoxidation of alkenes,[25t] hydrosilylation of olefins[25u] and hydrosilylation of imines.[25v] In short, the scope of the reactions mediated or catalyzed by group 4 (*ansa*-)metallocenes is still extending which emphasizes the importance of these complexes.

1.4 Ancillary Ligands Systems.

As mentioned before, the ancillary ligand system around the metal center is very important. It controls the reactivity of the metal center in various ways. The ligands facilitate the formation (if ligands of appropriate size are used) of (mononuclear) species and the electronic properties and reaction apertures can be tuned by altering the ligand system (electron withdrawing or releasing and sterically more or less demanding ligands). The bis-cyclopentadienyl ligand system, being capable to stabilize the metal center, in particular the early transition metals, has dominated the organometallic chemistry from the beginning on. By donating 6 electrons for each cyclopentadienyl (anion), the metal centers are electronically stabilized and sterically properly shielded. Additionally, the complete delocalization of the electrons in the π-system of the cyclopentadienyls makes these ligands aromatic and therefore chemically relatively inert. For these reasons, scientists have worked mainly on changing the substituents on the cyclopentadienyl ligands to get complexes with the desired reactivity profile.[26] However, bis-cyclopentadienyl ligand systems in combination with group 4 metals always result in 16 electron species and the overall effect of electron releasing or withdrawing properties of the substituents on the Cp ligands are rather limited. For complexes with electronic and/or steric properties that can not be achieved by traditional metallocenes, other ligands systems have been developed. The alternative ligand systems available up to now can be distinguished in three classes. A brief presentation and discussion of the most important representatives is given in the next section.

A: The so-called "Cp-look alikes" (Figure 2), have a formal steric and electronic analogy with cyclopentadienyls but not so much with respect to the elemental or functional composition. They are mono-anionic ligands which donate up to 6 electrons and may occupy three coordination sites of the metal center. Examples are aryldiamine[27] (A), amido-diphosphine[28] (B), tris(pyrazolyl)borate[29] (C) and diphosphinomethanide[30] (D). The study of the chemistry

of the complexes equiped with these ligands has been mainly explorative and so far few catalytic studies have been reported.

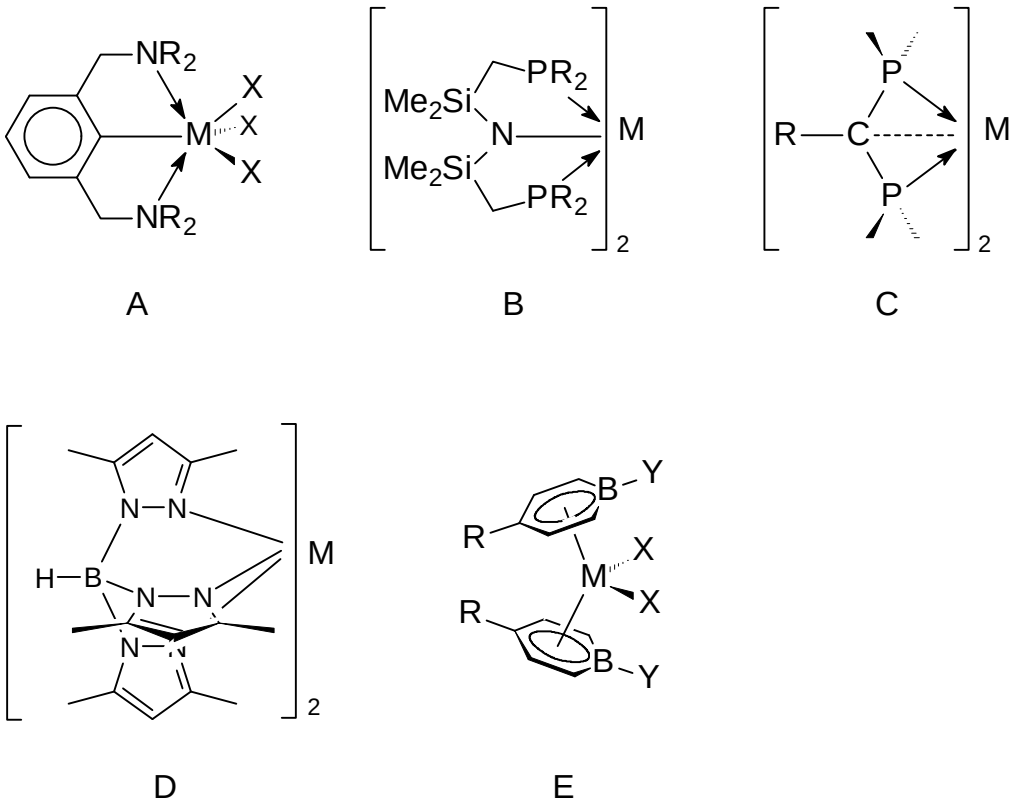


Figure 2. Cp-look alikes: (A) aryldiamines, (B) amidodiphosphines, (C) diphospinomethanide, (D) tris(pyrazolyl)borate, (E) boratabenzene.

Very promising is the boratabenzene ligand (E).[31] The electronic properties of this ligand can be varied widely by substituents on the boron atom or the *para*-carbon. The electronic effects of boron substitution appear to be stronger than those achieved by altering substituents on the normal cyclopentadienyl system. MAO activated $[\eta^6\text{-4-R-}C_5H_4BR')_2ZrCl_2$ (R = H, *t*-Bu; R' = H, N(*i*-Pr)$_2$, Ph, OEt) polymerizes ethene. Chain termination for this system is β-H transfer and it appears that the propagation/termination ratio strongly depends on the boron substituent. Complete different products can be obtained, varying from high molecular weight polyethene for R = H and R' = N(*i*-Pr)$_2$ to short α-olefins (C_{10} to C_{20}) for R' = OEt.[31b]

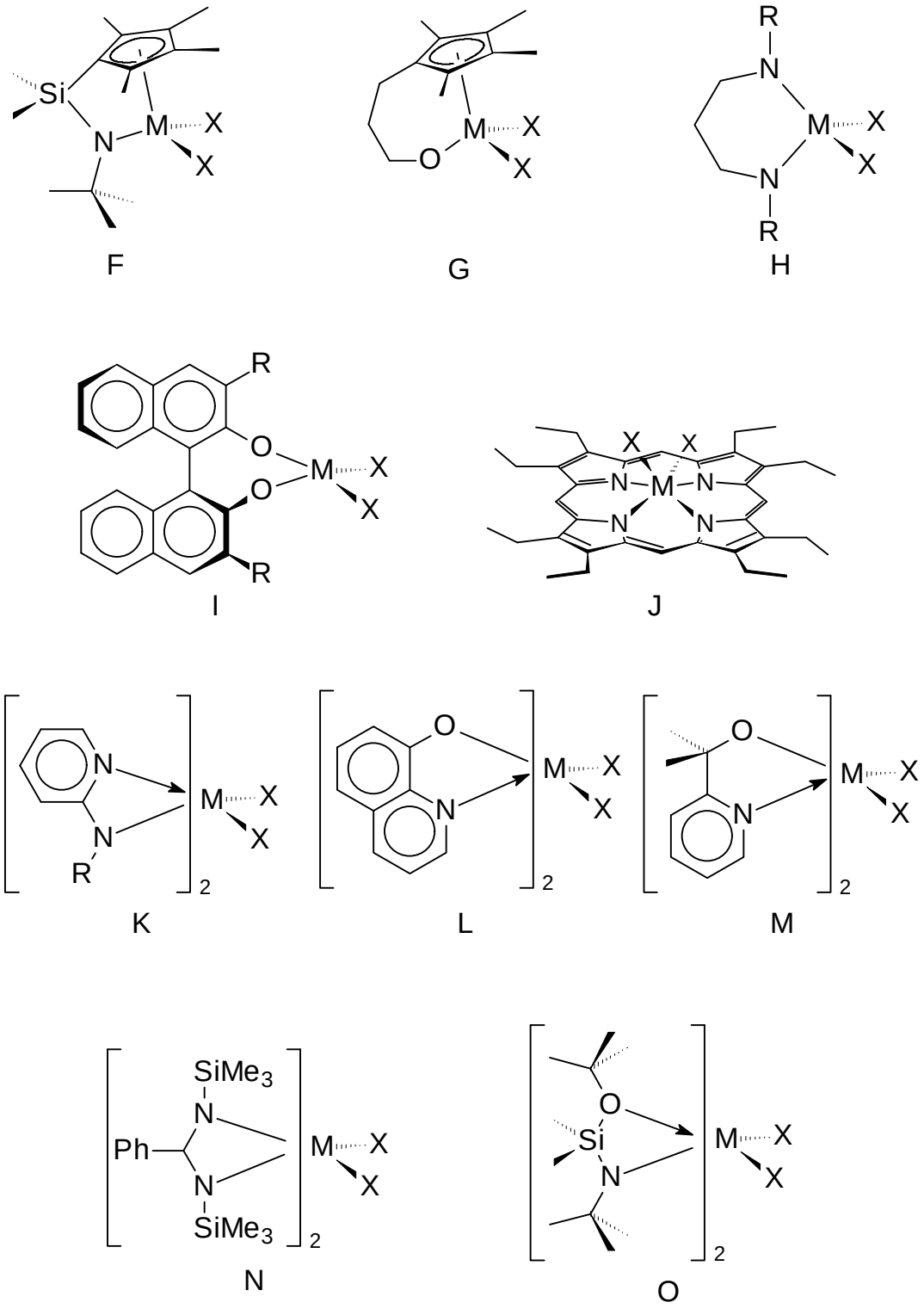
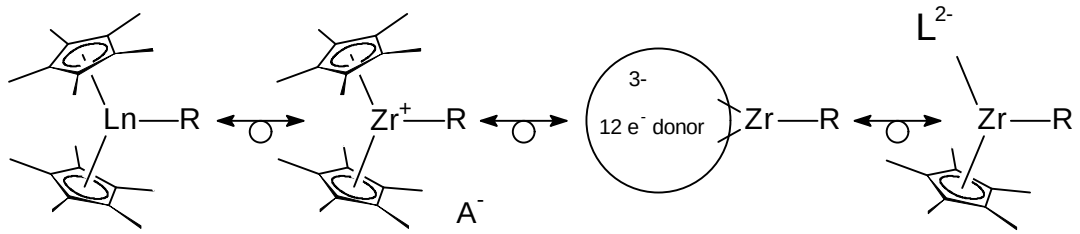


Figure 3. Examples of ligand systems leading to electron deficient complexes: (F) amido linked cyclopentadienyl, (G) oxo linked cyclopentadienyl, (H) diamido, (I) binaphtholate, (J) (octaethyl)porphyrin, (K) aminoptridinato, (L) 8-quinolinolato, (M) pyridine alkoxide, (N) benzamidinate, (O) alkoxysilylamido.

B: Low electron count ligand systems form complexes in which the ligand donates less than 12 electrons to the metal center (Figure 3). The metal center can easily be electronically and coordinatively less saturated than in metallocene systems. Hence the complex will be more electrophilic and the availability of more coordination sites will facilitate the precomplexation of substrates. For example one or two Cp ligands can be replaced by alkoxides or amides. In the last ten years cyclopentadienyls with a pendant amido[32] (F) or oxo[33] (G) function have been introduced to replace the (*ansa*-)metallocene ligand systems. In particular, the group 4 linked cyclopentadienyl amido complexes have been and still are investigated intensively because they are extremely good catalists for the copolymerization of ethene and higher olefins. Replacement of the other cyclopentadienyl by an alkoxide or an amide has been investigated as well. Linked bis-amido[34] (H) and binaphtolate[35] (I) complexes have been reported. Noteworthy are also the porphyrin[36] (J), aminopyridinato[37] (K), 8-quinolinolato[38] (L), pyridine alkoxide[39] (M), (benz)amidinate[40] (N) and the alkoxysilylamido ligands[41] (O). Some of these complexes are active in olefin polymerization. However, the complexes show low catalytic activities in ethene polymerization and frequently ancillary ligand transfer to aluminum is observed when MAO is used as co-catalyst.



Scheme 4. Isolobality of neutral group 3 (and lanthanides), cationic Cp^*_2 group 4 and neutral group 4 complexes.

C: Dianionic ligands (Figure 4): When realizing that the group 3 (and lanthanides) metallocenes and the cationic group 4 metal complexes with a non-coordinating anion are isolobal, one could state as a general rule that a catalytically active group 4 complex requires in total a tri-anionic ligand system donating at most 12 electrons to the metal center (Scheme 4). A way to achieve this, is to replace one of the cyclopentadienyls by a di-anionic, 6 electron donating ligand. A step in the direction of this strategy is the connection of an anionic borate moiety to one of the Cp' ligands in the reaction of $Cp^*(\eta^1,\eta^5\text{-}C_5Me_4CH_2)ZrX$ (X = Cl, Ph) with $B(C_6F_5)_3$.[42] In this way the $[C_5Me_4CH_2B(C_6F_5)_3]^{2-}$ (P) moiety can be regarded as a dianionic 6 electron donating ligand. Polymerization tests with ethene

showed nearly the same activity as the non zwitterionic $Cp^*_2ZrR^+$ systems.[42] Other dianionic, 6 electron ligands have been explored, like carborane (*i.e.*, *nido*-$[2,3\text{-}R_2C_2B_4]^{-2}$, R = H, Me, $SiMe_3$)[43] (Q), (η^5-$C_2B_9H_{11}$)[44] (R), aminoborollide ($C_4H_4BNR_2$, R = ^{i}Pr)[45] (S), trimethylenemethane[46] (T) and butadiene[47] (U). Although all the neutral complexes do polymerize α-olefins, the activities are low and low molecular weight polymers are obtained. A reason for the low activity may be that, although the use of dianionic ligands indeed results in a electrophilic metal center, the extend of charge separation is still smaller than in the cationic complexes with weakly coordinating counter ions. Another disadvantage of these complexes is their rather low thermal stability which makes that some of the ligands tend to interfere with the polymerization reaction giving inactive species.

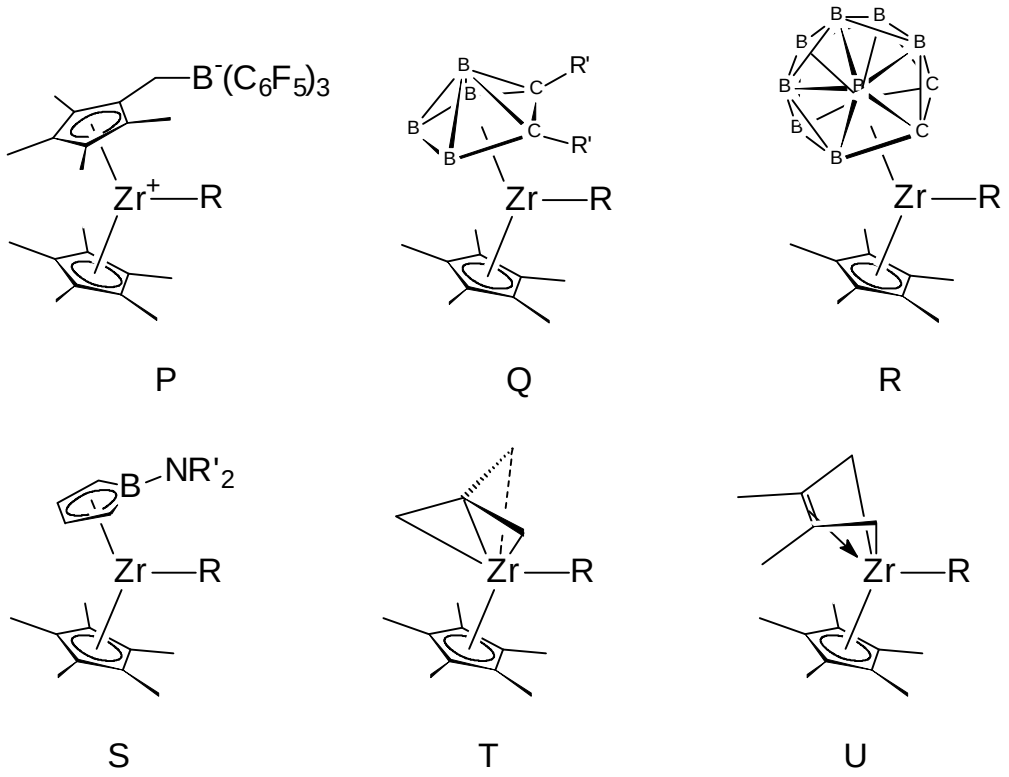


Figure 4. Examples of catalytically active neutral group 4 metal complexes with dianionic 6 electron donating ligands: (P) $[C_5Me_4CH_2B(C_6F_5)_3]^{2-}$, (Q) *nido* $[\eta^5\text{-}2,3\text{-}R_2C_2B_4]^{2-}$, (R) $[\eta^5\text{-}C_2B_9H_{11}]^{2-}$, (S) aminoborolide, (T) trimethylenemethane, (U) butadiene.

A general problem of tri coordinated group 3 (and lanthanides), cationic and neutral group 4 metal complexes, is that they are coordinatively highly unsaturated and have high affinity for all types of substrates. They tend to dimerize, form salt bridges or have cation-anion interactions. In some cases they have to be stabilized by the addition of Lewis bases. This

results in the loss of the free coordination site and consequently the loss of activity. Larger ligands help solve these problems only to a certain extend and usually create new ones. It may be clear that the design of different kinds of alternative ligands is in general accompanied by their own specific problems.

1.5 Scope of this thesis.

Of the alternative ligands presented, only a few are really promising. In particular the linked Cp-amido[32] and in lesser extend the linked Cp-oxo[33] ligands show interesting catalytic possibilities. The linked Cp-amido ligand $[C_5Me_4SiMe_2N\text{-}t\text{-}Bu]^{2-}$ was introduced by Bercaw and co-workers.[32a] A few years later patents on copolymerization of ethene with higher olefins using $[C_5R_4(SiMe_2)_nNR]MCl_2$/MAO were filed by Dow Chemical Co.[32c] and Exxon Chemical Co.[32d] A commercial plant for polyolefins has been build using catalysts based on $[C_5Me_4SiMe_2NR]MCl_2$/MAO. This clearly demonstrates the relevance of the Cp-amido group 4 metal complexes. In the last five years, academic and industrial groups have intensively explored this and related systems.[32] However so far, the main interest has been towards systems with respect to their performances in catalytic olefin polymerizations. Despite the large number of Cp-amido complexes described, a clear relation between ligand parameters (cyclopentadienyl substitution patern, bridge length and nitrogen substituent) and catalyst performance is still lacking. We decided to investigate the Cp-amido group 4 metal chemistry in a broader scope, comparing their chemistry and reactivity with those known for (*ansa*)-metallocene complexes.

The linked Cp-amido and Cp-oxo ligands are related to the *ansa*-bis cyclopentadienyl system in the sense that they adopt a restricted geometry around the metal center (Figure 5). The amido or oxo functions are anionic, and like the Cp moieties, strongly bind to the metal whicht results in a bidentate coordination. The amido and oxo functions donate 2 electrons by σ-bonding and an additional 2 electrons can be donated by the lone pairs on the nitrogen or oxygen respectively. Compared to the group 4 (*ansa*)-metallocene dichlorides Cp_2MCl_2, the Cp-amido or Cp-oxo complexes have at least two electrons less around the metal center. In consequence the compounds are expected to be more reactive and have one vacant site more. The oxo part, in principle, is able to donate the second free electron pair in bonding to the metal center as well. The extend to which this happens is a matter of debate. In our discussion this aspect will be considered as of minor importance.

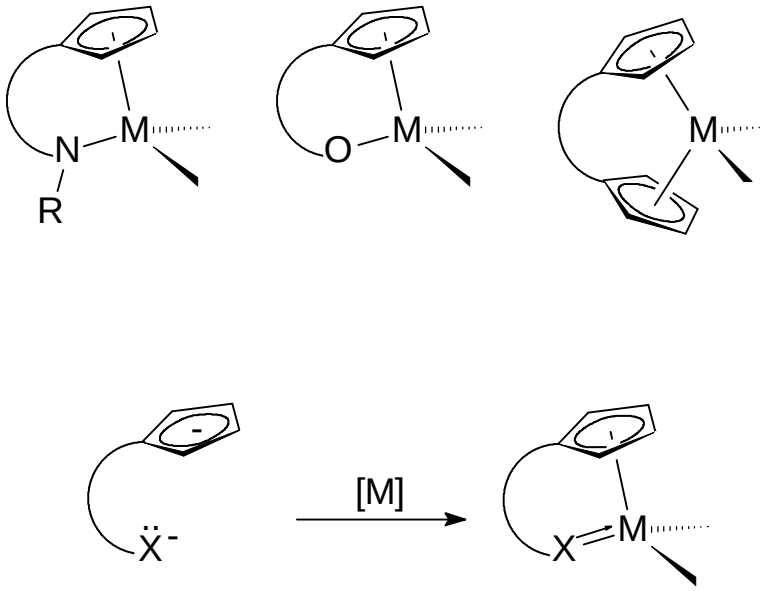
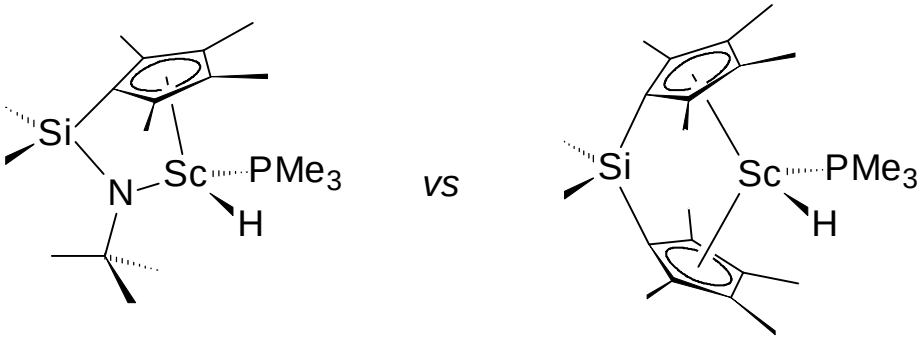


Figure 5. Comparison of the linked Cp-amido and Cp-oxo complexes with (*ansa*)-metallocenes. Bonding of the Cp-amido(oxo) ligand to the metal center

When this project was started, it was assumed that a Cp-amido ligand would stabilize the metal center better than a Cp-oxo ligand. The substituent on the nitrogen can sterically shield the metal center and in combination with the link and (substituted) cyclopentadienyl moiety, there are more possibilities for (fine) tuning of the steric and electronic properties of the complexes than with the Cp-oxo ligand system.

The replacement of a bis-cyclopentadienyl ligand system by an cyclopentadienyl amido ligand can have dramatic effects. Whereas the dimethylsilyl bridged bis-tetramethylcyclopentadienyl scandium hydride complex $[(C_5Me_4)_2SiMe_2]ScH.PMe_3$[48] catalyses the dimerization of α-olefins, polymerization was observed with the dimethylsilyl linked Cp-amido analogue $[\eta^5,\eta^1\text{-}C_5Me_4SiMe_2N\text{-}t\text{-}Bu]ScH.PMe_3$[32a] (Figure 6). The system $[\eta^5,\eta^1\text{-}C_5Me_4SiMe_2N\text{-}t\text{-}Bu]TiCl_2$/MAO co-polymerizes ethene and a wide range of α-olefins (including styrene) with a substantial incorporation of the higher olefins and also homo-polymerization of higher olefins can be achieved. In sharp contrast with this is the inactivity of $[Cp^*_2TiMe(L)]^+[BPh_4]^-$ (L = THF, Et_2O, PhOMe).[49] More surprizing is the fact that no data have been reported for the $Cp^*_2TiCl_2$/MAO system.[50]



10 electrons — polymerizes α-olefins

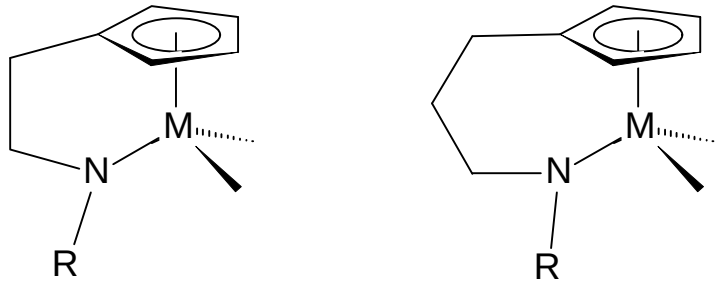
12 electrons — dimerizes α-olefins

Figure 6. Catalytic behavior of $[\eta^5,\eta^1\text{-}C_5Me_4SiMe_2N\text{-}t\text{-}Bu]ScH.PMe_3$ *versus* $[(C_5Me_4)_2SiMe_2]ScH.PMe_3$

1.6 Choice of Cyclopentadienyl-Amido ligands and Metals. Aim of this Thesis.

Although, according to the patent literature[32c,d] the catalytic potential of the $[C_5R_4\text{-}Y\text{-}NR]MCl_2$ system is impressive, the chemistry and especially the similarities and differences with complexes stabilized by two Cp ligands or other ligands is hardly investigated. In addition, despite the large number of complexes tested for catalytic activity, a clear understanding of the relation between structure and performance is still lacking. For the titanium system an acute bite angle Cp-Ti-N together with four methyl substituents on the cyclopentadienyl moiety has been found to give the highest catalytic activity.[32c] This may be the reason that by far most attention has been focused on Cp-amido ligands with a $SiMe_2$ bridge. Only a few examples of complexes with longer links ($SiMe_2SiMe_2$, CH_2CH_2, $CH_2CH_2CH_2$) have been reported.[51]

In the search for a systematic approach to get more insight in the consequences of using Cp-amido systems with different sterically demanding Cp-amido ligands (*i.e.* opening and closing of the Cp-M-N angle and the use of smaller or larger amido substituents), we started to investigate group 4 (Ti and Zr) Cp-amido complexes with CH_2CH_2 (C_2) and $CH_2CH_2CH_2$ (C_3) bridges and a selection of amido substituents (Figure 7).



M = Ti, Zr

Figure 7. C_2 and C_3 bridged Cp-amido group 4 metal complexes

In order to have a relatively inert ligand, it was decided to use an unsubstituted cyclopentadienyl rather than an alkyl substituted one, like for example tetramethylcyclopentadienyl. The aim was to study how the stability, reactivity and catalytic activity depend on the bridge length and the substituent on the nitrogen. Not only the dichloro complexes, but also the mono and bis carbyl complexes are studied since, despite the large number of dichloro complexes, relatively few carbyl complexes have been reported and the reactivity of these has been sparingly investigated.[51a,52] One particularly interesting feature is the inertness of the Cp-amido ligands used. For example, the cyclopentadienyl and in particular the pentamethylcyclopentadienyl ligands in metallocene complexes seldomly behave as strictly inert spectator ligands as they frequently interfere in reactions between ligands and substrates at the metal center.[53] Sometimes this reactivity is reported as a side process. For example in the cationic species $Cp^*_2ZrR^+$ chain transfer by activation of a Cp* ligand is found to interfere with the insertion of olefin.[49,54] In the reaction of the cationic $Cp^*_2ZrMe^+$ with 2-alkenyl-1,3-dithianes, evidence was found for the Cp* ligand being involved in C-H activation giving the cationic fulvene species [η^5,η^1-$C_5Me_4CH_2$]Cp*Zr.[54b] A similar process was observed in the gas phase reaction of $Cp^*_2ZrMe^+$ with ethene.[54c]

Other substituted Cp ligands like *tert*-butyl or trimethylsilyl cyclopentadienyl show ligand participation as well.[55] Up to now, very little information is available on the intrinsic reactivity of the Cp-amido ligand. Recently an example of C-H activation in a linked tetramethylcyclopentadienyl-amido complex has been reported.[52j]

Reaction of the spectator ligand system leads to modification of the catalyst and consequently to a change of catalyst performance. In extreme cases dramatic lowering of activities or even complete deactivation are observed. When designing a catalyst, it should be kept in mind that the ligand used may interfere in the catalytic cycle. Therefore, if a

catalytic process is to be developed, it is very important to have information about the intrinsic reactivity of the ligand.

A study of the thermal stability of the Cp-amido complexes can give clear information about the inertness of the Cp-amido ligand system in relation to the ligand parameters (bridge length and amido substituent) and it is interesting to compare the chemistry with that of the metallocene complexes. The catalytic performance of the complexes on olefin polymerization will be investigated in relation to the Cp-amido ligand used and, if possible, compared with the Dow system ([η^5,η^1-$C_5Me_4SiMe_2N$-*t*-Bu]Ti(Zr)Cl_2).

1.7 Survey of this Thesis.

Chapter 2 describes the synthesis and characterization of [$C_5H_4(CH_2)_nNR$]$TiCl_2$ complexes. The spectroscopic and structural consequences of variation of the bridge length and steric bulk of the amido substituent are determined. Furthermore, a cyclovoltammetry study on the dichlorides is performed in order to compare their redox potentials with other titanium compounds.

Chapter 3 covers the synthesis and characterization of a wide range of Cp-amido titanium carbyl complexes [$C_5H_4(CH_2)_nNR$]Ti(R'$_x$)Cl_{2-x} (x = 1, 2). The thermal stability of the carbyl complexes is studied in relation to ligand variations and in particular attention is focused on the question whether and how the R' and Cp-amido ligands are involved in C-H activation processes. Where possible, the products obtained from the thermolysis of the Cp-amido titanium carbyls were isolated and characterized.

Chapter 4 focuses on one of these thermolysis products, the benzyne complex [$C_5H_4(CH_2)_2N$-*t*-Bu]Ti(C_6H_4)(PMe_3). The synthesis and molecular structure structure is described together with a reactivity study of this complex towards unsaturated substrates. Some of the (unexpected) products obtained are studied in more detail.

Chapter 5 presents the chemistry of Cp-amido zirconium complexes [$C_5H_4(CH_2)_nNR$]$ZrCl_2$/R'$_2$. Various methods of preparation are described and a comparison is made with the corresponding Cp-amido titanium compounds. To determine whether zirconium carbyl complexes show the same C-H activation processes as their titanium analogues, the thermolysis of a selection of Cp-amido zirconium carbyls is studied in detail.

Chapter 6 deals with cationic Cp-amido titanium/zirconium complexes and catalytic olefin polymerization. To get deeper insight in the steric congestion of the Cp-amido ligand for complexes in solution, the interaction between the cationic benzyl complexes {[$C_5H_4(CH_2)_nNR$]$Zr(CH_2Ph)$}$^+$ and the borate anion [$PhCH_2B(C_6F_5)_3$]$^-$ are investigated. The

complexes are tested as catalysts for olefin polymerization using MAO or tris(pentafluorophenyl)borane $B(C_6F_5)_3$. The relations between ligand parameters versus catalyst activity, molecular weight and micro structure of the polymers obtained, are studied.

1.8 References and Notes.

(1) (a) *Chemical & Engineering News*, **1997**, April 28 and October 6. (b) Chemisch Weekblad, **1997**, *93*, June 21.

(2) (a) Vogt, E. *Chemisch Magazine*, **1995**, 549. (b) Duivenvoorde, F.; van der Veen, L.; Zuideveld, M.A. *Chemisch Magazine*, **1995**, 368. (c) Aulbach, M.; Küber, F. *Chemie in unsere Zeit*, **1994**, *28*, 197.

(3) (a) Horton, A.D. *Trends in Polymers* **1994**, *2*, 158. (b) Brintzinger, H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255

(4) In particular the M-C bonds of the early transition metal complexes are considered to have high ionic character.

(5) (a) *Organometallics in Synthesis*, Schlosser, M., Ed., Wiley & Sons, West Sussex, UK, 1994. (b) *Transition Metal Organometallics in Organic Synthesis*, Alper, H., Ed., Academic Press, New York, USA, 1976, Vol. 1, 1978, Vol. 2. (c) *Handbook of Palladium-Catalyzed Organic Reactions*, Malleron, J.-L.; Flaud, J.-C.; Legros, J.-Y., Eds., Academic Press, San Diego, USA, 1997. (d) *Iron Compounds in Organic Synthesis*, Pearson, A.J., Ed., Academic Press, London, UK, 1994. (e) *Lanthanides in Organic Synthesis*, Imamoto, T., Ed., Academic Press, London, UK, 1994. (f) Sheldon, R.A.; Kochi, J.K. *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, USA, 1981.

(6) A nice overview of catalysis in industrial processes is given in: Moulijn, J.A.; Van Leeuwen, P.W.N.M.; Van Santen, R.A. *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, Elsevier, Amsterdam, 1993.

(7) Source: *Chem. Econ. Handb. (SRI) BAYER*, **1991**.

(8) Gavens, P.D.; Bottril, M.; Kelland, J.W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F.G.A.; Abel, E.W., Eds.: Pergamon Press: Oxford, 1982; Vol. 3, Chapt. 22.5.

(9) Osugi, J.; Hamanowne, K.; Tachibana, T. *Rev. Phys. Chem. Jpn.* **1968**, *38*, 96.

(10) Ziegler, K.; Holzkamp, E.; Breil, H. *Angew. Chem.* **1955**, *67*, 541.

(11) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708.

(12) (a) Sinn, H.; Kaminsky, W.; Volmer, H.J.; Woldt, R. *Angew. Chem.* **1980**, *92*, 396. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(13) (a) Fink, G.; Zoller, W. *Makromol. Chem.* **1981**, 3265. (b) Schnell, D.; Fink, G. *Angew. Makromol. Chem.* **1974**, *39*, 131. (c) Fink, G.; Schnell, D. *Angew. Makromol. Chem.* **1982**, *105*, 15. (d) Fink, G.; Schnell, D.; *Angew.omol. Chem.* **1982**, *105*, 31. (e) Fink, G.; Fenzl, W.; Mynott, R. *Z. Naturforsch.* **1985**, *40b*, 158. (f) Mynott, R.; Fink, G.; Fenzl, W. *Angew. Makromol. Chem.* **1987**, *154*, 1.

(14) (a) Dyachkovskii, F.S.; shilova, A.K.; Silov, A.E. *J. Polym. Sci., Part C*, **1967**, *16*, 2333 and references therein. (b) Eisch, J.J.; Plotrowsky, A.M.; Brownstein, S.K.; Gabe, E.J.; Lee, F.L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (c) Jordan, R.F.; Bajgur, C.S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

(15) (a) Cossee, P. *J. Catal.* **1964**, *3*, 80. (b) Arlman, E.J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.

(16) (a) Brookhardt, M.; Green, M.L.H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Chawson, L.; Soto, J.; Buchwald, S.L.; Steigerwald, M.L. *J. Am. Chem. Soc.*, **1985**, *107*, 3377. (c) Burger, B.J.; Thompson, M.E.; Cotter, W.D.; Bercaw, J.E. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (d) Piers, W.E.; Bercaw, J.E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (e) Roll, W.; Brintzinger, H.H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (f) Krauledat, H.; Brintzinger, H.H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412.

(17) For references see: (a) Watson, P.L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Watson, P.L.; Roe, D.C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (c) Watson, P.L.; Parshall, G.W.; *Acc. Chem. Res.* **1985**, *18*, 51. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Swepton, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8001. (e) Thompson, M.E.; Baxter, S.M.; Bulls, A.R.; Burger, B.J.; Nolan, M.C.; Santarsiero, B.D.; Schaefer, W.P.; Bercaw, J.E. *J. Am. Chem. Soc.* **1987**, *109*¸ 203. (f) Bunel, E.; Burger, B.J.; Bercaw, J.E. *J. Am. Chem. Soc.* **1988**, *110*¸ 976. (g) Burger, B.J.; Thompson, M.E.; Cotter, W.D.; Bercaw, J.E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

(18) Wild, F.R.W.P.; Zsolnai, L.; Huttner, G.; Brintzinger, H.H. *J. Organomet. Chem.* **1982**, *232*, 233.

(19) Kaminsky, W.; Külper, K.; Wild, F.R.W.P.; Brintzinger, H.H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507.

(20) Mallin, D.T.; Rausch, M.D.; Chien, J.C.W.; Rieger, B.; Mu, X. *Macromolecules*, **1990**, *23*, 3559.

(21) Spaleck, W.; Küber, F.; Bachmann, B.; Antberg, M.; Dolle, V.; Rohrmann, J.; Winter, A.; Paulus, E.F. *Organometallics*, **1994**, *13*, 954.

(22) (a) Ewen, J.A.; Jones, R.L.; Razavi, A.; Ferrara, J.D. *J. Am. Chem. Soc.* **1988**, *110*, 6256. (b) Ewen, J.A.; Elder, M.J.; Jones, R.L.; Curtis, S.; Cheng, H.N. In *Catalytic Olefin Polymerization: Proceedings of the International Symposium on Recent Developments in Olefin Polymerization Catalysts*, Keii, T.; Soga, K. Eds., Elsevier, Amsterdam, 1989, 439. (c) Razavi, A.; Atwood, J.L. *J. Organomet. Chem.* **1993**, *459*, 117.

(23) Ewen, J.A.; Elder, M.J. *Eur. Pat. Appl.* **1993**, EP-A 0537130.

(24) Coates, G.W.; Waymouth, R.M. *Science*, **1995**, *267*, 217.

(25) (a) Grossmann, R.B.; Davis, W.M.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 2321. (b) Corey, E.J.; Jones, G.B.; *Tetrahedron Lett.* **1991**, *32*, 5713. (c) Corey, E.J.; Cimprich, K.A. *J. Am. Chem. Soc.* **1994**, *116*, 3151. (d) Keck, G.E.; Krishnamurthy, D.; Chen, X. *Tetrahedron Lett.* **1994**, *35*, 8323. (e) Rodewald, S.; Jordan, *J. Am. Chem. Soc.* **1994**, *116*, 4491. (f) Coates, G.W.; Waymouth, R.M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (g) Coates, G.W.; Waymouth, R.M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (h) Hong, Y.; Kuntz, B.A.; Collins, S. *Organometallics*, **1993**, *12*, 964. (i) Jaquith. J.B.; Guan, J.; Wang, S.; Collins, S. *Organometallics*, **1995**, *14*, 1079. (j) Morken, J.P.; Didiuk, M.T.; Hoveyda, A.H. *J. Am. Chem. Soc.* **1993**, *113*, 6997. (k) Morken, J.P. Didiuk, M.T.; Visser, M.S.; Hoveyda, A.H. *J. Am. Chem. Soc.* **1994** *116*, 3123. (l) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. (m) Broene, R.D.; Buchwald, S.L. *J. Am. Chem. Soc.* **1993**, *115*, 12569. (n) Willoughby, C.A.; Buchwald, S.L. *J. Am. Chem. Soc.* **1992**, *112*, 7562. (o) Willoughby, C.A.; Buchwald, S.L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. (p) Willoughby, C.A.; Buchwald, S.L. *J. Am. Chem. Soc.* **1994**, *116*, 11703. (q) Lee, N.E.; Buchwald, S.L. *J. Am. Chem. Soc.* **1994**, *116*, 5985. (r) Noyori, A. *Asymmetric Catalysis in Organic synthesis*, Wiley, New York, 1994, pp 33. (s) Carter, M.B.; Schiott, B.; Gutierrez, A.; Buchwald, S.L. *J. Am. Chem. Soc.* **1994**, *116*, 11667. (t) Coletti, S.L.; Halterman, R.L. *Tetrahedron Lett.* **1992**, *33*, 1005. (u) Kesti, M.R.; Waymouth, R.M. *Organometallics*, **1992**, *11*, 1095. (v) Verdaguer, X.; Lange, U.E.W.; Reding, M.T.; Buchwald, S.L. *J. Am. Chem. Soc.* **1996**, *118*, 6784.

(26) For reviews concerning substituted cyclopentadienyl ligands see: (a) Okuda, J. *Topics in Current Chemistry*, Springer-Verlag, Berlin, Heidelberg, 1991, Vol. 160, pp 97. (b) Halterman, R.L. *Chem. Rev.* **1992**, *92*, 965.

(27) Donkervoort, J.G.; Jastrzebski, J.T.B.H.; Deelman, B.-J.; Kooijman, H.; Veldman, N.; Spek, A.L.; Van Koten, G. *Organometallics* **1997**, *16*, 4174.

(28) (a) Fryzuk, M.D.; Williams, H.D.; Rettig, S.J. *Inorg. Chem.* **1983**, *22*, 863. (b) Fryzuk, M.D.; Haddad, T.S.; Rettig, S.J. *Organometallics* **1992**, *11*, 2967.

(29) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Maunder, G.H.; Sella, A.; Tocher, D.A. *J. Chem. Soc., Chem. Commun.* **1994**, 2689. (c) Mashima, K.; Oshiki, T.; Tani, K. *Organometallics* **1997**, *16*, 2760.

(30) Karsch, H.H.; Ferazin, G.; Kooijman, H.; Steigelmann, O.; Schier, A.; Bissinger, P.; Hiller, W. *J. Organomet. Chem.* **1994**, *482*, 151.

(31) (a) Bazan, G.C.; Rodriguez, G.; Ashe III, A.J.; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (b) Bazan, G.C.; Rodriguez, G.; Ashe III, A.J.; Al-Ahmad, S.; Kampf, J.W.; *Organometallics* **1997**, *16*, 2492. (c) Herberich, G.E.; Englert, U.; Schmitz, A. *Organometallics* **1997**, *16*, 3751. (d) Rogers, J.S.; Bazan, G.C.; Sperry, C.K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (e) Ashe III, A.J.; Al-Ahmad, S.; Kampf, J.W.; Young, Jr, V.G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2014.

(32) (a) Shapiro, P.J.; Bunel, E.; Schaefer, W.P.; Bercaw, J.E. *Organometallics*, **1990**, *9*, 867. (b) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649. (c) Stevens, J.C.; Timmers, F.J.; Rosen, G.W.; Knight, G.W.; Lai, S.Y. (Dow Chemical Co.), *Eur. Pat. Appl.* EP 0416815 A2, 1991. (d) Canich, J.A.M. (Exxon Chemical Co.), *U.S. Patent* 5,026,78, 1991. (e) Piers, W.E.; Shapiro, P.J.; Bunel, E.; Bercaw, J.E. *Synlett.* **1990**, *2*, 74. (f) Shapiro, P.J.; Cotter, W.D.; Schaefer, W.P.; Labinger, J.A.; Bercaw, J.E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (g) Mu, Y.; Piers, W.E.; MacDonald, M.-A.; Zaworotko, M.J. *Can. J. Chem.* **1995**, *73*, 2233. (h) Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1993**, *12*, 1936. (i) Stevens, J.C. *Metcon 93,* Houston, **1993**, pp. 157. (j) Herrmann, W.A.; Morawietz, M.J.A. *J. Organomet. Chem.* **1994**, *482*, 169. (k) Ciruelos, S.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organomtallics*, **1995**, *14*, 177. (l) Okuda, J.; Schattenmann, F.J.; Wocadlo, S.; *Organometallics*, **1995**, *14*, 789. (m) Du Plooy, K.E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics*, **1995**, *14*, 3129. (n) Devore, D.D.; Timmers, F.J.; Hasha, D.L.; Rosen, R.K.; Marks, T.J.; Deck, P.A.; Stern, C.L. *Organometallics*, **1995**, *14*, 3132. (o) Spence, R.E.v.H.; Piers, W.E. *Organometallics*, **1995**, *14*, 4617. (p) Kloppenburg, L.; Petersen, J.L. *Organometallics*, **1996**, *15*, 7. (q) Carpenetti, D.W.; Kloppenburg, L.; Kupec, J.T.; Petersen, J.L. *Organometallics*, **1996**, *15*, 1572.

(33) (a) Fandos, R.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1991**, *10*, 59. (b) Rieger, B. *J. Organomet. Chem.* **1991**, *420*, C17. (c) Herrmann, W.A.; Morawietz, M.J.A.; Priermeier, T. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1946. (d) Trouvé, G.; Laske, D.A.; Meetsma, A.; Teuben, J.H. *J. Organomet. Chem.* **1996**, *511*, 255.

(34) (a) Canich, J.A.M.; Turner, H.W. (Exxon Chemical Co.), *PCT Int. Appl.* WO 92/12162, 1992. (b) Warren, T.H.; Schrock, R.R.; Davis, W.M. *Organometallics*, **1996**, *15*, 562. (c) Scollard, J.D.; McConville, D.H.; Vittal, J.J. *Organometallics*, **1995**, *14*, 5478. (d) Geurin, F.; McConville, D.H.; Vittal, J.J. *Organometallics*, **1995**, *14*, 3154. (e) Scollard, J.D.; McConville, D.H.; Payne, N.C.; Vittal, J.J. *Macromolecules*, **1996**, *29*, 5241. (f) Clark, H.C.S.; Cloke, F.G.N.; Hitchcock, P.B.; Love, J.B.; Wainwright, A.P. *J. Organomet. Chem.* **1995**, *501*, 333. (g) Cloke, F.G.N.; Geldbach, T.J.; Hitchcock, P.B.; Love, J.B. *J. Organomet. Chem.* **1996**, *506*, 343. (h) Horton, A.D.; De With, J.; Van der Linden, A.J.; Van de Weg, H. *Organometallics*, **1996**, *15*, 2672. (i) Horton, A.D.; De With, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1375.

(35) (a) Oliva, L.; Longo, P.; Pellecchia, C. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 51. (b) Aaltonen, P.; Seppälä, J.; Matilainen, L.; Leskelä, M. *Macromolecules* **1994**, *27*, 3136. (c) Matilainen, L.; Klinga, M.; Leskelä, M. *J. Chem. Soc., Dalton Trans.* **1996**, 219. (d) Kakugo, M.; Miyatake, T.; Mizunuma, K. *Chem. Express* **1987**, *2*, 445. (e) Miyatake, R.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Makromol. Chem., Rapid Commun.* **`1988**, *9*, 51. (f) T. Miyatake, T.; Mizunuma, K.; Kakugo, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203. (g) Van der

Linden, A.; Schaverien, C.J.; Meijboom, N.; Ganter, C.; Orpen, A.G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.

(36) (a) Arnold, J.; Hoffman, C.G.; Dawson, D.Y.; Hollander, F.J. *Organometallics* **1993**, *12*, 3645. (b) Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655.

(37) (a) Kempe, R.; Arndt, P. *Inorg. Chem.* **1996**, *35*, 2644. (b) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742.

38 (a) Bei, X.; Swenson, D.C.; Jordan, R.F. *Organometallics* **1997**, *16*, 3282. (b) Tsukahara, T.; Swenson, D.C.; Jordan, R.F. *Organometallics*, **1997**, *16*, 3303.

(39) Kim, I.; Nishihara, Y.; Jordan, R.F.; Rogers, R.D.; Rheingold, A.L.; Yap, G.P.A. *Organometallics* **1997**, *16*, 3314.

(40) (a) Gómez, R.; Duchateau, R.; Chernega, A.N.; Meetsma, A.; Edelmann, F.T.; Teuben, J.H.; Green, M.L.H. *J. Chem. Soc., Dalton Trans.* **1995**, 217. (b) Gómez, R.; Duchateau, R.; Chernega, A.N.; Teuben, J.H.; Edelmann, F.T.; Green, M.L.H. *J. Organomet. Chem.* **1995**, *491*, 153. (c) Duchateau, R.; Meetsma, A.; Teuben, J.H. *Organometallics* **1996**, *15*, 1656. (d) Duchateau, R.; Van Wee, C.T.; Meetsma, A.; Van Duijnen, P.Th.; Teuben, J.H. *Organometallics* **1996**, *15*, 2279. (e) Duchateau, R.; Van Wee, C.T.; Teuben, J.H. *Organometallics* **1996**, *15*, 2291.

(41) (a) Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F.T. *J. Organomet. Chem.* **1991**, *415*, 315. (b) Duchateau, R.; Tuinstra, T.; Brussee, E.A.C.; Meetsma, A.; Van Duijnen, P.Th.; Teuben, J.H. *Organometallics* **1997**, *16*, 3511.

(42) Sun, Y.; Spence, R.E.v.H.; Piers, W.E.; Parvez, M.; Yap, G.P.A. *J. Am. Chem. Soc.* **1997**, *119*, 5132.

(43) (a) Houseknecht, K.L.; Stockman, K.E.; Sabat, M.; Finn, M.G.; Grimes, R.N. *J. Am Chem. Soc.* **1995**, *117*, 1163. (b) Hosmane, N.S.; Wang, Y.; Zhang, H.; Lu, K.-J.; Maguire, J.A.; Gray, T.G.; Brooks, K.A.; Waldhör, E.; Kaim, W.; Kremer, R.H. *Organometallics* **1997**, *16*, 1366.

(44) (a) Crowther, D.J.; Baenzinger, N.C.; Jordan, R.F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Crowther, D.J.; Jordan, R.F. *Makromol.Chem., Macromol. Symp.* **1993**, *66*, 121. (c) Kreuder, C.; Jordan, R.F. *Organometallics* **1995**, *14*, 2993. (d) Yoshida, M.; Crowther, D.J.; Jordan, R.F. *Organometallics* **1997**, *16*, 1349.

(45) Quan, R.W.; Bazan, G.C.; Kiely, A.F.; Schaefer, W.P.; Bercaw, J.E. *J. Am. Chem. Soc.* **1994**, *166*, 4489.

(46) Bazan, G.C.; Rodriguez, G.; Cleary, B.P. *J. Am. Chem. Soc.* **1994**, *116*, 2177. (b) Rodriguez, G.; Bazan, G.C. *J. Am. Chem. Soc.* **1997**, *119*, 343.

(47) Hessen, B.; Van der Heijden, H. *J. Am. Chem. Soc.* **1996**, *118*, 11670.

(48) Parkin, G.; Bunel, B.; Burger, B.J.; Trimmer, M.S.; Van Asselt, A.; Bercaw, J.E. *J. Mol. Cat.* **1987**, *41*, 21.

(49) Eshuis, J.J.W. thesis, 1991, R.U. Groningen.

(50) For a closely related system $[\eta^5\text{-}C_5Me_4\text{-}i\text{-}Pr]_2TiCl_2$/MAO some data are reported: 0.7 kg PE mol^{-1} [Ti] atm^{-1} ethene h^{-1} at 50 ^oC compared with 41 kg PE mol^{-1} [Ti] atm^{-1} ethene h^{-1} at 50 ^oC for Cp_2TiCl_2 see Kaminsky, W. *Macromol. Chem. Phys.* **1996**, 3907.

(51) (a) Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1993**, *12*, 1936. (b) Hughes, A.K.; Marsh, S.M.B.; Howard, J.A.K.; Ford, P.S. *J. Organomet. Chem.* **1997**, *528*, 195. (c) Antonelli, D.M.; Green, M.L.H.; Mountford, P. *J. Organomet. Chem.* **1992**, *438*, C4. (d) Fandos, R.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1991**, *10*, 59. (e) Rasika Dias, H.V.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77. (f) Rieger, B. *J. Organomet. Chem.* **1991**, *420*, C17. (g) Ewen, I.M.; Ahlberg, P. *J. Am. Chem. Soc.* **1992**, *114*, 106869. (h) Dais, H.V.R.; Wang, Z.; Bott, S.G. *J. Organomet. Chem.* **1996**, *508*, 91. (i) Witte, P.T.; Meetsma, A.; Hessen, B.; Budzelaar, P.H.M. *J. Am. Chem. Soc.* **1997**, *119*, 10561. (j) Schwink, L.; Knochel, P.; Eberle, T.; Okuda, J. *Organometallics* **1998**, *17*, 7.

(52) (a) Shapiro, P.J.; Cotter, W.D.; Schaefer, W.P; Labinger, J.A.; Bercaw, J.E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (b) Mu, Y.; Piers, W.E.; MacQuarrie, D.C.; Zaworotko, M.; Young, Jr, V.G. *Organometallics*, **1996**, *15*, 2720. (c) Okuda, J.; Schattenmann, F.J.; Wocadlo, S.; Mass, W. *Organometallics*¸**1995**, *14*, 789. (d) du Plooy, K.E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics*, **1995**, *14*, 3129. (e) Kloppenburg, L.; Petersen, J.L. *Organometallics*, **1997**, *16*, 3548. (f) Kloppenburg, L.; Petersen, J.L. *Organometallics*, **1996**, *15*¸ 7. (g) Rasika Dias, H.V.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77. (h) Okuda, J.; Eberle, T.; Spaniol, T.P. *Chem. Ber./Requeil*, **1997**, *130*¸209. (i) McKnight, A.L.; Masood, Md.A.; Waymouth, R.M.; Straus, D.A. *Organometallics*, **1997**, *16*, 2879. (j) Chen, Y.-X.; Marks, T.J. *Organometallics*, **1997**, *16*, 3649. (k) Devore. D.D.; Timmers, F.J.; Hasha, D.L.; Rosen, R.K.; Marks, T.J.; Deck, P.A.; Stern, C.L. *Organometallics*, **1995**, *14*, 3132.

(53) (a) Bercaw, J.E.; Marvich, R.H.; Bell, L.G.; Brintzinger, H.H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (b) McDade, C.; Green, J.C.; Bercaw, J.E. *Organometallics*, **1982**, *1*, 1629. (c) Pattiasina, J.W. Thesis, R.U. Groningen, **1988**. (d) Pattiasina, J.W.; Hissink, C.E.; De Boer, J.L.; Meetsma, A.; Teuben, J.H.; Spek, A.L. *J.Am. Chem. Soc.* **1985**, *107*, 7758. (e) Pattiasina, J.W.; Van Bolhuis, F.; Teuben, J.H. *Angew. Chem.* **1987**, *99*¸ 342. (f) Luinstra, G.A.; Ten Cate, L.C.; Heeres, H.J.; Pattiasina, J.W.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1991**, *10*, 3227. (g) Abugideiri, F.; Kelland, M.A.; Poll, R.; Rheingold, A.L. *Organometallics*, **1992**, *11*, 1309. (h) Gibson, V.C.; Kee, T.P.; Carter, S.T.; Sanner, R.D.; Clegg, W. *J. Organomet. Chem.* **1991**, *418*, 197. (i) Sinnema, P.-J.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1993**, *12*, 184. (j) Schock, L.E.; Brock, C.P.; Marks, T.J. *Organometallics*, **1987**, *6*, 232. (k) Bulls, A.R.; Schaefer, W.P.; Serfas, M.; Bercaw, J.E. *Organometallics*, **1987**, *6*, 1219. (l) De Wolf, J.M.; Blaauw, R.; Meetsma, A.; Teuben, J.H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A.L. *Organometallics*, **1996**, *15*, 4977.

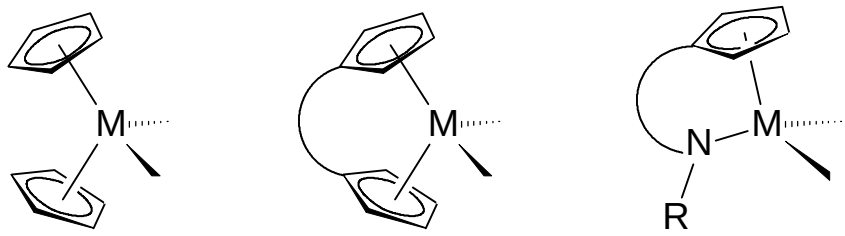
(54) (a) Horton, A.D. *Organometallics*, **1992**, *11*, 3271. (b) Bijpost, E.A. Thesis, R.U. Groningen, **1996**.

(55) (a) Amor, J.I.; Cuenca, T.; Galakhov, M.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *J. Organomet. Chem.* **1997**, *535*, 155. (b) Yang, X.; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (c) Hessen, B. submitted to *J. Am. Chem. Soc.* (d) Horácek, M.; Hiller, J.; Thewalt, U.; Polásek, M.; Mach, K. *Organometallics* **1997**, *16*, 4185.

2 Linked Cyclopentadienyl Amido Titanium Dichlorides. Molecular Structures of $[C_5H_4(CH_2)_nN\text{-}i\text{-}Pr]TiCl_2$, (n = 2, 3) and $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]TiCl_2$.*

2.1 Introduction.

The replacement of the conventional bis-cyclopentadienyl auxillary ligand system by linked cyclopentadienyls (*ansa*-metallocenes) or by bidentate ligands combining a cyclopentadienyl with a amido or oxo function through a chain of variable length (Figure 1), has opened up an interesting and rapidly growing field of organometallic chemistry.



Cp_2M ***ansa*-Cp_2M** **CpNM**

Figure 1.

These new ligand systems offer very promising perspectives for rational design and modification of organometallic compounds with high and selective catalytic activity. [1] At the moment scientific attention is focused on catalyst tuning for olefin polymerisation,[2] but other applications are emerging rapidly.[3]

There seems to be one major problem in experimentally carrying out intended modifications of ligand systems and in introducing these onto the metal. In practice the synthesis of specifically designed ligands and metal complexes appears to be a cumbersome process. Often long, multistep synthetic procedures with frustratingly low overall yields are reported.

* *The X-ray structure determinations described in this Chapter were carried out by A. Meetsma (University of Groningen), N. Veldman and A.L. Spek (University of Utrecht). The cyclovoltammetric measurements were performed by H. Roedelof.*

To introduce *ansa*-type ligands or otherwise functionalized (oxo, amido) cyclopentadienyls normally the salt metathesis route (eqn 1) is used.[1,4]

$$n\ Cp'M' + MX_m \longrightarrow Cp'_nMX_{m-n} + n\ M'X \quad (1)$$

An attractive alternative is dehalosilylation/stannylation of metal halides with silylated or stannylated ligands (eqn 2). This is a very selective method which normally proceeds under mild conditions and leads to high yields.[5]

$$n\ Cp'SiMe_3 + MX_m \longrightarrow Cp'_nMX_{m-n} + x\ Me_3SiX \quad (2)$$

These two methods require reactive ligand derivatives as intermediates that normally have to be synthesized from less reactive precursors like the neutral (protonated) ligands following a long and complicated route. It is clear that methods starting directly from neutral ligands are preferred.

Recently Hughes *et al.* developed a high yield synthesis for the introduction of amido-functionalized cyclopentadienyl ligands $[Cp'\text{-}(CH_2)_3\text{-}NR]^{2-}$ by protolysis of zirconium and hafnium tetra-amides starting from the neutral ligands $Cp'H\text{-}(CH_2)_3\text{-}NRH$ (eqn 3).[6]

$$Cp'H\text{-}(CH_2)_3\text{-}NRH + M(NMe_2)_4 \longrightarrow Cp'\text{-}(CH_2)_3\text{-}NRM(NMe_2)_2 + 2\ Me_2NH \quad (3)$$

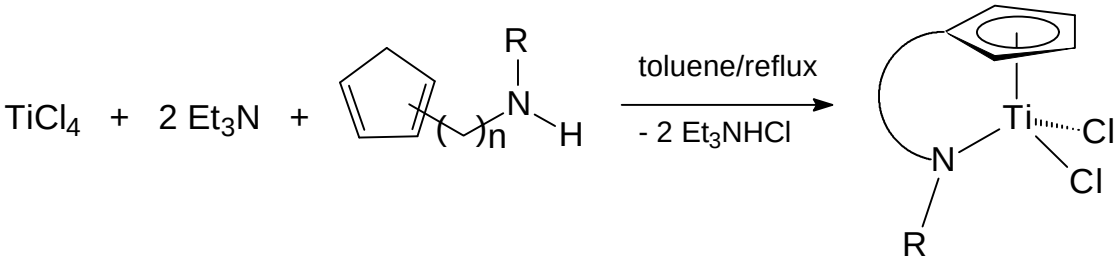
This route appears to be quite general and has been used for other ligand systems and metal amides and metal alkyls as well.[7] In essence, this method consists of transfer of an active proton from the neutral ligand to amide or alkyl anions to form a neutral molecule (R_2NH, RH). The disadvantage of the method is that it seems to be limited to amine and alkyl leaving groups and cannot be used for alkoxy or halide ligands. To extend this method to halide ligands an additional driving force has to be employed. It is known that chloride ligands in $TiCl_4$ can be substituted by cyclopentadienyls, alkoxides and sulfides by base mediated dehydrochlorination with the corresponding cyclopentadiene,[8] alcohol[9] or thiol[10] (eqn 4):

$$n\ Cp'H + n\ Base + TiCl_4 \longrightarrow Cp'_nTiCl_{4-n} + n\ Base.HCl \quad (4)$$

As will be described in this chapter, the base driven dehydrochlorination route (4) appears to be very effective for the synthesis of amido functionalized cyclopentadienyl titanium dichlorides.

2.2 Synthetic Methodology.

The general procedure that appeared to give the best results was combination of stoichiometric amounts of the cyclopentadiene-amine ligand precursor, triethylamine (2 eq.) and $TiCl_4$ added in toluene. The mixture was refluxed to give a clear orange to red solution and a tarry brown residue. Work-up of the solution by crystallization after concentration or by vacuum sublimation after evaporation of the solvent gave the complexes in moderate to high yields (Table 1).



Scheme 1.

The method appears to be quite tolerant with respect to the length of the bridge and the substituent on the amido function. In this way complexes containing $-CH_2CH_2-$ (C_2) and $-CH_2CH_2CH_2-$ (C_3) bridges and with various amido substituents like methyl, ethyl, *iso*-propyl, *tert*-butyl, adamantyl (Ad) and phenyl were synthesized (Scheme 1). In general, the change of a C_2 to a C_3 bridge gave somewhat lower yields (Table 1). Variation of the amine substituent was generally readily achieved, although the yield for $C_5H_5(CH_2)_nN(H)Ph$ was considerably lower.

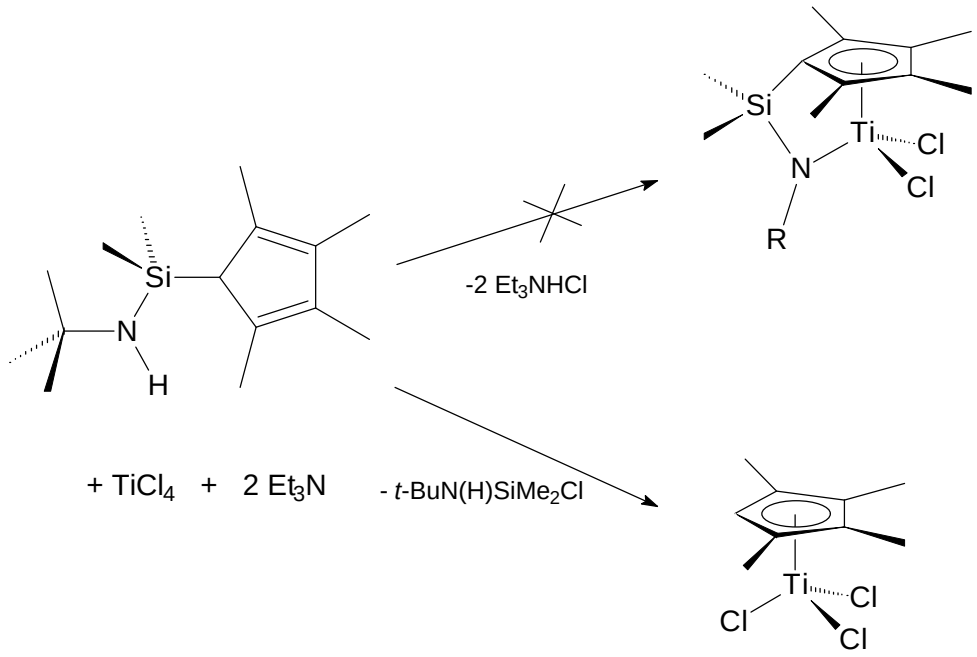
Table 1. Cp-amido titanium dichloride complexes $[C_5H_4(CH_2)_nNR]TiCl_2$ (**1**-**12**)

Complex	Yield (%)	Complex	Yield (%)
$[C_5H_4(CH_2)_2NMe]TiCl_2$ (**1**)	62	$[C_5H_4(CH_2)_3NMe]TiCl_2$ (**7**)	56
$[C_5H_4(CH_2)_2NEt]TiCl_2$ (**2**)	56	$[C_5H_4(CH_2)_3NEt]TiCl_2$ (**8**)	42
$[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**)	61	$[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**)	57
$[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**)	60	$[C_5H_4(CH_2)_3N$-*t*-Bu$]TiCl_2$ (**10**)	[a]
$[C_5H_4(CH_2)_2NAd]TiCl_2$ (**5**)	61	$[C_5H_4(CH_2)_3NAd]TiCl_2$ (**11**)	[a]
$[C_5H_4(CH_2)_2NPh]TiCl_2$ (**6**)	37	$[C_5H_4(CH_2)_3NPh]TiCl_2$ (**12**)	21

[a]) no product isolated.

For the combination of a long (C_3) bridge and a bulky amido substituent (*t*-Bu, Ad) the method is less suitable. With $C_5H_5(CH_2)_3N(H)$-*t*-Bu and $C_5H_5(CH_2)_3N(H)$Ad dark oils were obtained of which the composition could not be determined. Probably the bulk of these ligands prevents the formation of the desired products $[C_5H_4(CH_2)_3NR]TiCl_2$ (R = *t*-Bu, Ad).[11] In some cases a change in reaction conditions led to higher yields. For example in the case of $C_5H_5(CH_2)_2N(H)$-*t*-Bu the procedure as described above gave $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) in 30% yield, whereas a significantly higher yield (60%) was obtained when the order of addition was reversed and the crude product crystallized from diethylether. This indicates that it may well be possible to improve the yield of individual syntheses by careful optimalization of the reaction conditions.

A thorough knowledge of the mechanism of formation of the complexes may be essential when syntheses need to be optimised but so far this has not been considered necessary. Although we have not observed a clear indication for stepwise introduction of the bidentate ligand it may be assumed by analogy with the related synthesis of Cp_2TiCl_2 from $TiCl_4$ and CpH in the presence of Et_2NH that first the amine function coordinates to titanium.[12] On warming, the cyclopentadienyl function will be introduced first because of the greater acidity of the cyclopentadiene hydrogen compared to the amine.[13]



Scheme 2.

Since alcohols react with $TiCl_4$ liberating HCl,[5] the same route was also attempted to introduce alkoxy-functionalized cyclopentadienyls by reaction of $TiCl_4$ with $C_5H_5(CH_2)_2OH$ and $C_5H_5(CH_2)_3OH$. The expected products $[C_5H_4(CH_2)_2O]TiCl_2$[9a] (**13**) and $[C_5H_4(CH_2)_3O]TiCl_2$[9b] (**14**) were indeed obtained, but in low yields (<1% resp 8%). Changing the reaction conditions, for example the reaction temperature or use of different amounts of Et_3N (0, 1 or 3 equiv.) did not improve the yield, indicating that this method is less suited for this type of ligands.

In the literature most of the chemistry concerning group 4 metals Cp-amido catalysts deals with dimethyl silyl bridged ligands. In particular $[C_5Me_4SiMe_2N$-*t*-Bu$]TiX_2$ has been thoroughly investigated and for this complex a number of synthesis routes have been described[1c,d,7c-e,g-1,14] but the reported yields (10 - 40%) are modest and variable. Therefore we attemped to synthesize $[C_5Me_4SiMe_2N$-*t*-Bu$]TiCl_2$ using the base driven dehydrochlorination reaction. However, $C_5Me_4HTiCl_3$ was formed[15] (60% yield) indicating dehalosilylation instead of the intended dehydrochlorination. Apparently, the silylated cyclopentadiene acts as a Cp transfering species and the very strong Si-Cl bond may thermodynamically favor the splitting of the silicon carbon bond of the $[C_5Me_4SiMe_2N$-*t*-Bu] ligand (Scheme 2).

2.3 Characterization of the Dichlorides $[C_5H_4(CH_2)_nNR]TiCl_2$.

The complexes **1**-**12** are thermally robust and can in most cases be vacuum sublimed (0.01 torr, 180-200 ^oC). In contrast to Cp_2TiCl_2, which is stable in air, the cyclopentadienyl-amido titanium dichlorides readily hydrolyze and are in this sense more comparable with $CpTiCl_3$. In general, the complexes are very soluble in aromatic solvents (benzene, toluene) and THF though only sparingly soluble in diethyl ether and alkanes. The mass spectra confirm that the complexes are monomeric in the gas phase. The ^1H and ^{13}C NMR spectra (Table 2) show very similar general features for all complexes. The cyclopentadienyl (C_5H_4) part forms an A_2B_2 system with two sets of proton resonances as pseudo triplets and the protons of the C_2 bridge appear as an A_2B_2 system showing two regular triplets. The C_3 bridge is observed in the ^1H NMR spectra as an $A_2B_2C_2$ spin system with three well separated multiplets and has almost the same characteristics as observed for $[C_5H_4(CH_2)_3NMe]M(NMe_2)_2$ (M = Ti, Zr, Hf).[6a,b]

Table 2. ^{1}H and ^{13}C NMR data of the cyclopentadienyl-amido titanium dichlorides **1**-**12**.

Compound	C_5H_4	$C_5H_4\underline{CH_2}$	NCH_2	$NC\underline{CH_2}$	NR	C_5H_4	$C_5H_4\underline{CH_2}$	NCH_2	$NC\underline{CH_2}$	NR
1	6.01, 5.84	2.42	3.53		3.49	145.61[i], 118.00, 115.26	28.09	80.08		47.54
2	6.05, 5.85	2.50	3.65		4.16, 0.89	145.46, 118.01, 115.38	28.35	75.51		52.44, 11.46
3	6.05, 5.78	2.42	3.57		5.92, 0.86	144.92[i], 117.67, 115.58	28.67	68.15		54.59, 17.78
4	6.19, 5.90	2.37	3.66		1.42	144.10[i], 118.12, 118.04	29.72	69.96		64.59, 28.82
5	6.22, 5.90	2.38	3.70		2.19, 1.97, 1.51					
6	6.11, 5.96	2.39	4.03		7.53[o], 7.22[m], 6.93[p]					
7	6.31, 5.53	2.12	2.29	1.48	3.82	129.68[i], 119.23, 114.58	29.60	62.22	25.69	45.62
8	6.35, 5.56	2.25	2.48	1.60	4.55, 1.01	136.36[i], 119.26, 114.92	30.75	57.84	26.04	49.43, 11.55
9	6.36, 5.47	2.16	2.43	1.46	6.57, 1.02	130.36[i], 119.35, 114.91	32.34	50.36	26.23	50.64, 17.93
12	6.33, 5.72	2.23	2.92	1.61	7.48[o], 7.22[m], 7.01[p]					

[i]) C_5H_4-*ipso.*

Although ^{1}H and ^{13}C NMR spectra of the complexes **1**-**12** are very similar, some notable differences have to be mentioned. The difference between the two ^{1}H NMR resonances of the C_5H_4 group (A_2B_2 spin system) is considerably larger for the C_3 bridged complexes compared to their C_2 bridged homologues (Figure 2). Also the chemical shift of the NCH_2 fragment of the C_3 bridge containing complexes is found at higher field than that of the C_2 bridged complexes. In the ^{13}C NMR spectrum a clear up-field shift (10-15 ppm) for the resonances for C_5H_4-*ipso* and NCH_2 of the C_3 bridge complexes compared to the C_2 bridge complexes is found. The differences in both ^{1}H NMR and ^{13}C NMR spectra can be explained by the fact that the long chain in the $C_5H_4(CH_2)_3NR$ ligands allows an unstrained fitting of the ligand on the metal center. The molecular structures of compounds **3** and **9** (*vide infra*) very clearly support this view and also the structure of $\{[C_5H_4(CH_2)_3NMe]Zr(CH_2Ph)(\mu\text{-}Cl)\}_2$ underlines this.[6a]

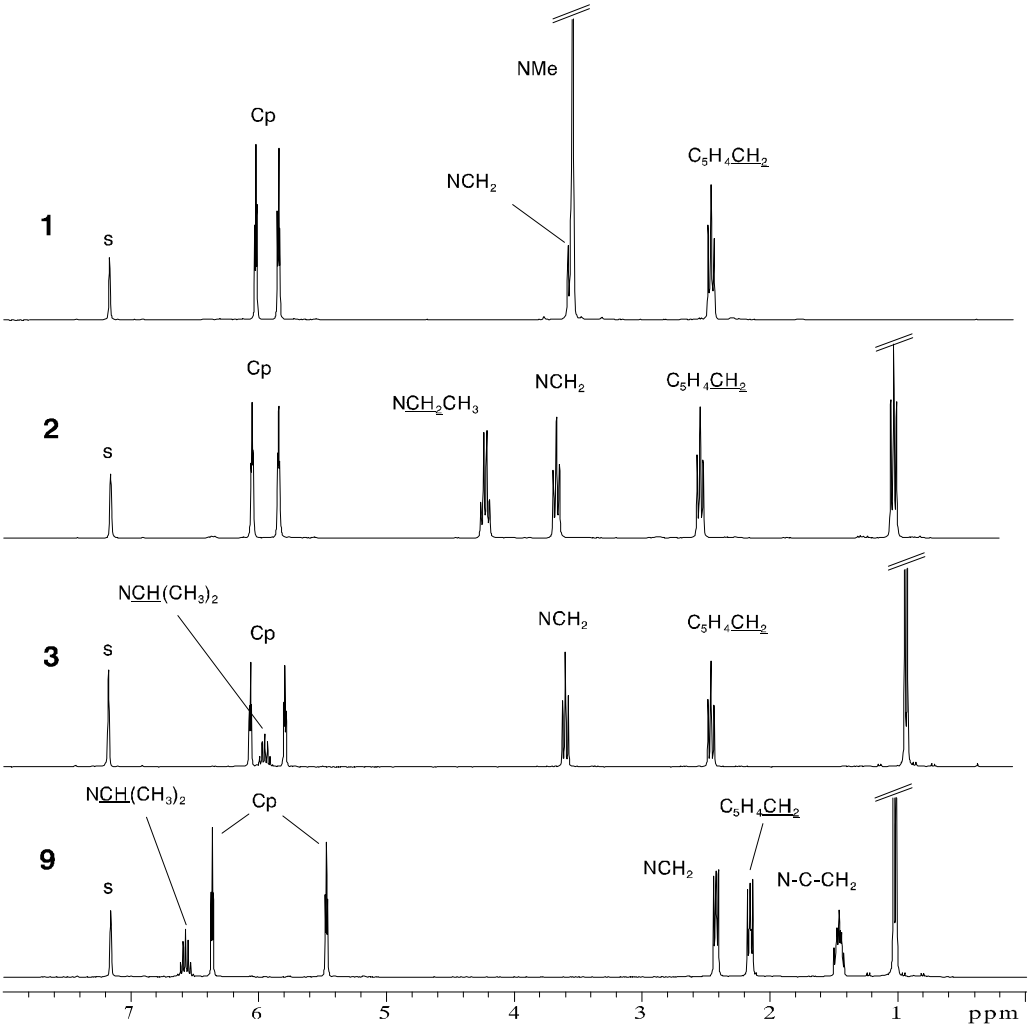


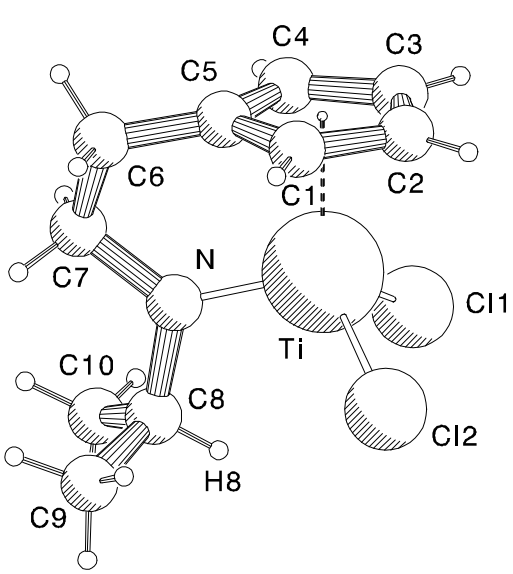
Figure 2. ^{1}H NMR spectra of $[C_5H_4(CH_2)_2NMe]TiCl_2$ (**1**), $[C_5H_4(CH_2)_2NEt]TiCl_2$ (**2**), $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**).

Another remarkable trend is observed in the proton resonances of the α-carbon of the nitrogen subsituent R, which show a significant downfield shift going from **1**, **2** to **3** (resp 3.49, 4.14 and 5.92 ppm). For the corresponding C_3 bridged complexes **7**, **8** and **9** the same trend is found and with resonances at 3.82, 4.55 and 6.47 ppm respectively, this downfield shift is even more pronounced. Especially the large downfield shifts of the α-protons of the *iso*-propyl group of the complexes **3** and **9** to resp 5.92 and 6.57 ppm is striking because they are still aliphatic protons which is demonstrated by the ^{13}C NMR resonances (54.59, 50.63 ppm) and the coupling constants ($^3J_{HH}$ = 6.41, 5.98 Hz resp, $^1J_{CH}$ = 133.7 and 128.9 Hz resp). This strong downfield shift is attributed to steric repulsion within the complexes which forces the α-proton of the isopropyl group on nitrogen in a position very close to the Lewis acidic metal center (*vide infra*).

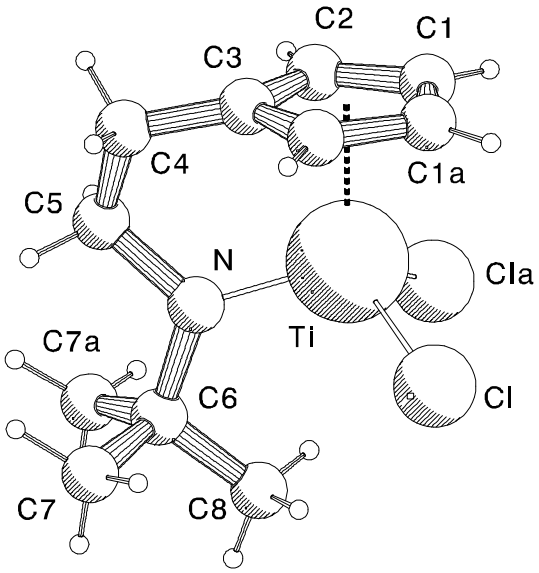
2.4 Molecular Structure of $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (3), $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (4) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (9).

Suitable crystals of $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**) were grown by slowly cooling toluene solutions (saturated at 40-45 °C) to 20 °C. Complex **3** crystallizes in the triclinic space group $P\ \bar{1}$ with *a* = 7.6327(11) Å, *b* = 7.810(2) Å, *c* = 10.716 Å, α = 102.821(10)°, β = 102.618(10)°, γ = 101.211(10)°, *V* = 587.7(2) Å^3 and *Z* = 2 whereas **4** and **9** crystallized in the monclinic space groups $P2_1/m$ and $P2_1/c$ resp. with for **4**: *a* = 7.295(1) Å, *b* = 10.563(1) Å, *c* = 8.526(1) Å, β = 102.640(4)°, *V* = 641.07(13) Å^3, *Z* = 2 and for **9**: *a* = 8.5385(5) Å, *b* = 12.9690(7) Å, *c* = 11.9157(6) Å, β = 108.722(4)°, *V* = 1249.08(12) Å^3, *Z* = 4. Molecular structures of **3**, **4** and **9** with numbering schemes are shown in Figure 3. Bond distances and bond angles are given in Tables 3 and 4.

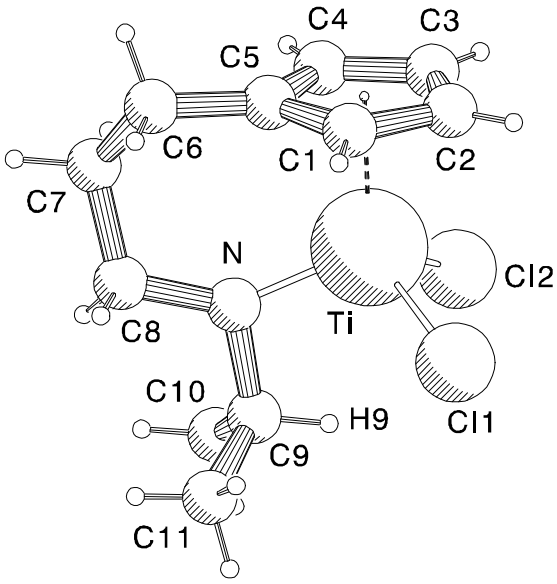
All three compounds are monomeric with a distorted tetrahedral surrounding of the metal centers. Compounds **3** and **4** are clearly more deformed than **9** which adopts an almost ideal piano-chair conformation with about equal Cg-Ti-Cl1 (112.9(1)°), Cg-Ti-Cl2 (115.8(1)°) and Cg-Ti-N (112.6(1)°) angles. These values compare well with those found for $CpTiCl_3$ (112.5-114.7°).[16] For **3** and **4**, the Cg-Ti-N bite-angles (104.4(1)°, 106.60(6)° resp.) are considerably smaller than for **9**. The Cg-Ti-Cl angles in **3** are larger (118.3(1) and 118.5(1)°), illustrating the smaller bite-angle of the $C_5H_4(CH_2)_2N$-*i*-Pr ligand.



3



4



9

Figure 3. Structures of $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**).

Table 3. Selected bond distances in $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**).

3	distance (Å)	**4**	distance (Å)	**9**	distance (Å)
Ti - Cl1	2.2996(12)	Ti - Cl	2.2849(7)	Ti - Cl1	2.2849(5)
Ti - Cl2	2.2752(11)	Ti - Cla	2.2849(7)	Ti - Cl2	2.3025(6)
Ti - N	1.864(2)	Ti - N	1.901(1)	Ti - N	1.8668(15)
Ti - Cg	2.008(4)	Ti - Cg	2.019(3)	Ti - Cg	2.027(2)
Ti - H8	2.67			Ti - H9	2.38
C7 - N	1.470(5)	C5 - N	1.520(4)	C8 - N	1.461(2)
C8 - N	1.476(4)	C6 - N	1.503(4)	C9 - N	1.495

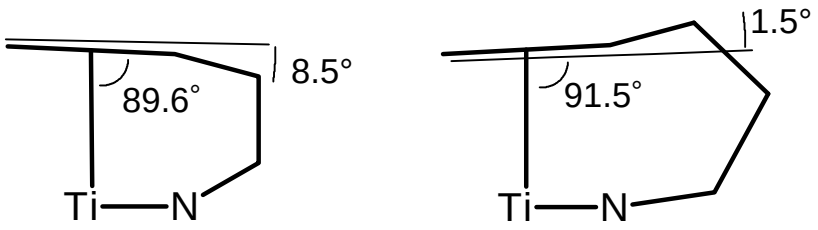
Cg denotes center of gravity of the cyclopentadienyl moieties of **3**, **4** and **9**.

Table 4. Selected bond angles in $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**).

3	Angles (^{o})	**4**	Angles (^{o})	**9**	Angles (^{o})
Cl1-Ti-Cl2	103.01(4)	Cl-Ti-Cla	105.23(3)	Cl1-Ti Cl2	103.40(3)
Cl1-Ti-N	104.98(8)	Cl-Ti-N	108.35(5)	Cl1-Ti-N	105.67(5)
Cl2-Ti-N	106.53(7)	Cla-Ti-N	108.35(5)	Cl2- Ti-N	105.54(5)
Cg-Ti-Cl1	118.3(1)	Cg-Ti-Cl	114.05(5)	Cg-Ti-Cl1	112.9(1)
Cg-Ti-Cl2	118.5(1)	Cg-Ti-Cla	114.05(5)	Cg-Ti- Cl2	115.8(1)
Cg-Ti-N	104.4(1)	Cg-Ti-N	106.6(1)	Cg-Ti-N	112.6(1)
Ti-N-C7	129.2(2)	Ti-N-C5	122.43(19)	Ti-N-C8	142.08(13)
Ti-N-C8	114.23(19)	Ti-N-C6	124.13(18)	Ti-N-C9	104.47(10)
C7-N-C8	116.4(3)	C5-N-C6	111.0(2)	C8-N-C9	112.98(14)

Cg denotes center of gravity of the cyclopentadienyl moieties of **3**, **4** and **9**.

The different chain lengths also have consequences for the methylene groups adjacent to the cyclopentadienyls. In the case of **3** and **4**, the C_{ipso}-CH_2 bonds bend (8.5(2)^o and 9.5(1)^o resp.) towards to the metal center whereas for **9** the C_{ipso}-CH_2 bond bends 1.5(2)^o upwards. The C_5H_4 moieties themselves are also tilted somewhat with respect to the Cg-Ti bond (see Figure 4). For the complexes **3** and **4** the Ti-Cg-C_{ipso} angles are 89.6(1)^o and 89.1(1)^o resp. whereas this angle in compound **9** is 91.5(1)^o.



3 **9**

Figure 4. Illustration of the bending of the C_{ipso}-CH_2 bond in **3** and **9** with respect to the C_5H_4 and the tilt of the C_5H_4 moiety.

The smaller bite-angle of the $C_5H_4(CH_2)_2$N-*i*-Pr ligand forces the C_5H_4 part somewhat closer to the metal center than in the $C_5H_4(CH_2)_3$N-*i*-Pr ligand (Ti-Cg 2.008 Å *vs* 2.027 Å). The Ti-N distances (**3**: 1.864(2) Å, **9**: 1.8668(15)) are equal within experimental error. However this distance in **4** is somewhat longer (1.901(1) Å) and this is probably due to sterical hindrance caused by the *t*-Bu group. The Ti-N distances in all complexes are consistent with a Ti-N double bond. When comparing the structures of **3**, **4** and **9** with other cyclopentadienyl amido titanium complexes, some aspects have to be mentioned. The Ti-N bond lengths of **3** and **9** are similar to those found for CpTi(N(*i*-Pr)$_2$)Cl$_2$ (1.865(2) Å) and Cp*Ti[N(*i*-Pr)$_2$]Cl$_2$ (1.865(5) Å),[17] but are shorter than the Ti-N bond of CpTi[N(SiMe$_3$)$_2$]Cl$_2$ (1.879(3) Å).[18] The Ti-N bond distance in **4** resemble those in Ti[N(SiMe$_3$)$_2$]$_3$Cl (1.940(10) Å) and Cp*Ti(NMe$_2$)$_3$ (1.912(9), 1.923(14) Å).[19]

Some notable observations can be made concerning the Ti-N-C and C-N-C angles in **3**, **4** and **9**. Of those three compounds, **4** displays the smallest Ti-N-C_{chain} (112.43(19)^o) and C_{chain}-N-$C_{subst.}$ (111.0(2)^o) angles and the largest Ti-N-$C_{subst.}$ (124.13(18)^o) angle. This is clearly a consequence of the steric repulsion of the bulky *t*-Bu group which is pushed away from the metal center.

Although the Ti-N-C and C-N-C angles in **3** and **9** deviate considerably from 120^o (this is to a lesser extent the case for **4**), the nitrogen atom can best be represented as having a planar sp^2 hybridization (sum of the Ti-N-C and C-N-C angles ≈ 360^o). As can be concluded from the N-Ti distance (1.86-1.90 Å), the out-of-plane N lone pair is involved in a significant N(p_π) $\rightarrow$M(d_π) interaction.

Table 5. Selected interatomic distances and bond angles for related cyclopentadienyl titanium complexes.

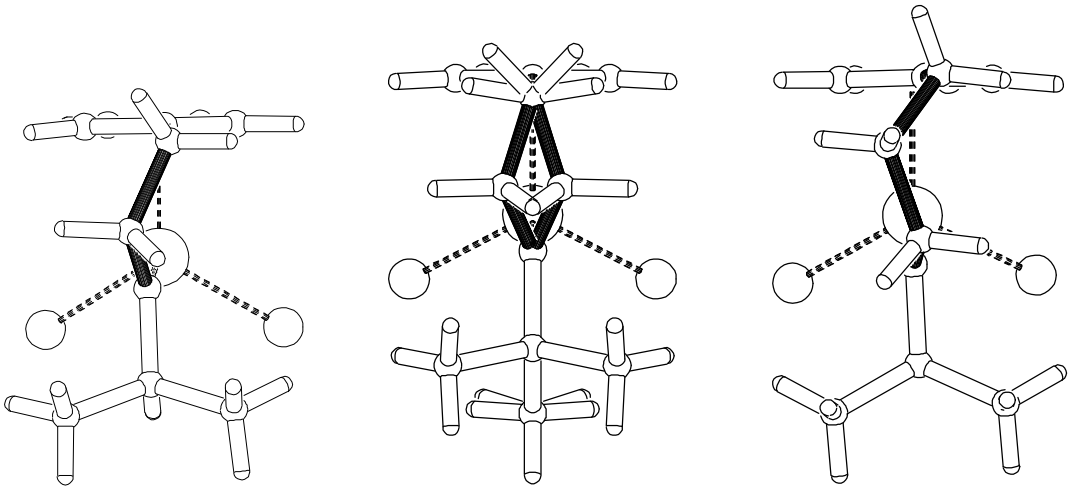
Compound	Cg-Ti-N (°)	Ti-Cg (Å)	Ti-N (Å)	Ti-Cl (Å)	ref.
$[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]TiCl_2$ (**3**)	104.4(1)	2.008(4)	1.864(2)	2.2874	[a]
$[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]TiCl_2$ (**4**)	106.6(1)	2.019(3)	1.901(1)	2.2849(7)	[a]
$[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]TiCl_2$ (**9**)	112.6(1)	2.027(2)	1.8668(15)	2.2937	[a]
$[C_5H_4SiMe_2N\text{-}i\text{-}Pr]TiCl_2$	105.5	2.017	1.878(2)	2.2659(6)	20
$[C_5H_4SiMe_2N\text{-}t\text{-}Bu]TiCl_2$	107.0	2.019	1.901(3)	2.264	21
$[C_5H_4SiMe_2NCH_2(2,5\text{-}C_6H_3F_2)]TiCl_2$	-	-	1.890(2)	2.2581	20
$[C_5H_4SiMe_2N\text{-}t\text{-}Bu]Ti(NMe_2)_2$	105.5	2.083	1.972(4)	-	21
$[C_5Me_4SiMe_2N\text{-}t\text{-}Bu]TiCl_2$	107.6	-	1.909(5)	2.262(2)	22
$[C_5Me_4(CH_2)_2N\text{-}t\text{-}Bu]TiCl_2$	107.9	-	1.909(5)	2.282(2)	22
$CpTi[N(i\text{-}Pr)_2]Cl_2$	116.2	2.035	1.865(2)	2.298	17
$Cp^*Ti[N(i\text{-}Pr)_2]Cl_2$	114.5	2.191	1.988(4)	2.410	17
Cp_2TiCl_2	130.9	2.06	-	2.364	23
$CpTiCl_3$	-	2.04	-	2.30	16

[a]) this work.

The Ti-Cg distances of **3** (2.008(4) Å), **4** (2.019(3) Å) and **9** (2.027(4) Å) are slightly shorter than the Ti-Cg distance in $CpTi[N(i\text{-}Pr)_2]Cl_2$ (2.035 Å),[17] $Cp^*Ti[N(i\text{-}Pr)_2]Cl_2$ (2.191 Å),[17] $CpTiCl_3$ (2.04 Å)[16] and Cp_2TiCl_2 (2.06 Å).[23] With a difference of only 0.02 Å the Ti-Cl distances in **3** (2.2752(11), 2.2996(12) Å), **4** (2.2849(7) Å) and **9** (2.2849(5), 2.3025(6) Å) are nearly identical. These distances are close to the Ti-Cl distances found for $CpTiCl_3$ (2.30 Å)[16] and $CpTi[N(i\text{-}Pr)_2]Cl_2$ (2.298 Å).[17] but are substantially shorter than those of Cp_2TiCl_2 (2.364 Å),[23] $[CH_2(C_5H_4)_2]TiCl_2$ (2.34 Å),[24] $[(CH_2)_2(C_5H_4)_2]TiCl_2$ (2.35 Å),[24] $[(CH_2)_3(C_5H_4)_2]TiCl_2$ (2.368 Å)[25]. and $Cp^*Ti[N(i\text{-}Pr)_2]Cl_2$ (2.410 Å).[17] The shorter Ti-Cl distances found for the Cp-amido titanium complexes and $CpTiCl_3$ compared to the (*ansa*) metallocenes may be a consequence of lower electron count number ($CpNTiCl_2$, 14 e; $CpTiCl_3$, 12 e *vs* Cp_2TiCl_2, 16 e). The lower electron density at the metal allows the chlorine atoms closer to the metal.

The Cl1-Ti-Cl2 angles (**3**: 103.01(4)°, **4**: 105.23(3)° and **9**: 103.40(3)°) are comparable to the Cl-Ti-Cl angles of $CpTiCl_3$ (103.1°)[16] and $CpTi[N(i\text{-}Pr)_2]Cl_2$ (103.4°)[17] but are larger than those found for $Cp^*Ti[N(i\text{-}Pr)_2]Cl_2$ (99.2°),[17] Cp_2TiCl_2 (94.5°)[23] and the *ansa*-metallocene analogues $[(CH_2)_n(C_5H_4)_2]TiCl_2$ (n = 1: 97.2°, n = 2: 94.8°, n = 3 : 93.7°).[24,25] The larger Cl-Ti-Cl angles, found for **3**, **4** and **9**, are presumably a consequence of the lesser steric demands of the

$[C_5H_4(CH_2)_n)$N-*i*-Pr] ligands (n = 2, 3) compared to the pentamethylcyclopentadienyl di-isopropylamido ligand system, the Cp_2 ligand system and its *ansa*-metallocene analogues.



3 **4** **9**

Figure 5. Puckering of the carbon backbone in **3**, **4** and **9**.[26]

In all complexes, the *ipso*-carbon atom of the cyclopentadienyl, the carbon atoms of the chain and the nitrogen atom are not in one plane but display a zigzag pattern (Figure 5). Due to this, the complexes have a chiral center of which the enantiomers are related to each other by the symmetry operations in the unit cells. However, the ^{1}H and ^{13}C spectra (benzene-d_6) of the complexes have a symmetric appearance (Figure 2) indicating that both isomers interconvert very rapidly. Even at -100 ^{o}C simple ^{1}H and ^{13}C NMR spectra (toluene-d_8) were observed for the dichlorides.

In the complexes **3** and **9** the *iso*-propyl groups are similarly oriented with the methine proton pointed towards the metal center whereas in **4** one methyl of the *t*-Bu group is directed to the metal. In the case of **3** and **4** no significant Ti-H interactions are found (**3**: Ti-H8 = 2.67 Å, **4**: Ti-H8 = 2.83 Å) while for **9**, the longer chain forces the methine proton closer to the metal center and the Ti-H9 distance (2.38 Å) is significantly shorter than the sum of the van der Waals radii (2.6-2.7 Å). This indicates an agostic interaction.[27] However, the NMR data, in particular the normal coupling constants ($^{3}J_{HH}$ = 5.98 Hz, $^{1}J_{CH}$ = 128.9 Hz) do not confirm this and suggest that the methine proton in **9** is forced into this particular position by steric reasons. The origin of the strong down-field shifts observed for the methine protons of **3** and **9** and the short Ti-H9 distance in **9** still remains a question. The explanation could be that these chemical shifts are strongly influenced by local fields generated by electrons in orbitals of the metal center or the ligands.

2.5 Cyclovoltammetry.

It is relevant to study the redox properties of the $[C_5H_4(CH_2)_nNR]TiCl_2$ complexes since they are intended to be used as precursors for the synthesis of Cp-amido titanium carbyl complexes. The synthesis of Ti(IV) carbyl compounds, both neutral and cationic, is often hampered by reduction of the metal. In order to get insight into the reduction resistance of these species compared to the traditional (*ansa*) titanocenes, cyclovoltammetry measurements were performed.

In THF, complex $[C_5H_4(CH_2)_2NMe]TiCl_2$ (**1**) showed a reversible 1 electron reduction at -1.78 V *vs* the Cp_2Fe/Cp_2Fe^+ couple. No second reduction within the applied voltage sweep (-3.5 - 2 V) was observed. The reduction potential did not depend substantially on the length of the backbone or the nitrogen substituent: for $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) and $[C_5H_4(CH_2)_3NMe]TiCl_2$ (**7**) similar reduction potentials were found (Table 6).

Table 6. Reduction potentials of various titanium (IV) complexes *vs* the Cp_2Fe/Cp_2Fe^+ couple.

Complex	1st red. (V)	2nd red. (V)	ref.
$[C_5H_4(CH_2)_2NMe]TiCl_2$ (**1**)	-1.78	-	this work
$[C_5H_4(CH_2)_2N$-t-Bu$]TiCl_2$ (**4**)	-1.73	-	this work
$[C_5H_4(CH_2)_3NMe]TiCl_2$ (**7**)	-1.77	-	this work
Cp_2TiCl_2	-1.32	-2.52	28
$CpTiCl_3$	-0.86	-	29
$[(CH_3)_4C_2(C_5H_4)_2]TiCl_2$	-1.44	-3.05	30
$[SiMe_2(C_5H_4)_2]TiCl_2$	-1.31	-	31
$CpTi(O$-i-Pr$)Cl_2$	-1.28	-	29
$CpTi(O$-C_6H_3-2-t-Bu-6-$PPh_2)Cl_2$	-1.31	-	32
$[C_5Me_4(CH_2)_3O]TiCl_2$	-1.69	-	33
$[C_5Me_4$6-MeO-C_6H_3-2-O$]TiCl_2$	-1.46	-3.30	34

Compared with other titanium (IV) chloride complexes the Cp-amido system is by far the most stable with respect to reduction.[28-34] Only $[C_5Me_4(CH_2)_3O]TiCl_2$ (-1.69 V) shows a comparable reduction potential. The consequence of this property will be illustrated in the next chapter where the synthesis of titanium alkyl and aryl complexes will be described. It will be shown that certain carbyl species, unknown for the traditional titanocene systems due to reduction, are stabilized by the Cp-amido ligand.

2.6 Concluding Remarks.

The amido functionalized cyclopentadienyl titanium dichlorides, $[C_5H_4(CH_2)_nNR]TiCl_2$ are fairly accessible from the reaction of $TiCl_4$ with the neutral ligand $C_5H_5(CH_2)_nN(H)R$ using an amine as HCl-trapping agent. This method has no restriction for the nitrogen substituents using ligand with a C_2-bridge. For the C_3-bridge however, the choice was limited to the smaller nitrogen substituents.

The method works as well but is less suitable for the synthesis of oxo functionalized cyclopentadienyl titanium dichlorides. However, using a bridged Cp-amido ligand with a silyl function adjacent to the cyclopentadienyl results in splitting of the silyl carbon bond of the ligand giving $C_5Me_4HTiCl_3$ rather than the formation of the desired $[C_5Me_4SiMe_2N$-*t*-Bu$]TiCl_2$.

The molecular structures of $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**) show that the main structural consequence from changing a C_2- to a C_3-bridge is the larger bite-angle of the Cp-amido ligand which results in narrowing of the coordination aperture of the metal center. Other structural parameters like the Ti-Cg, Ti-N and Ti-Cl distances and Cl-Ti-Cl angles are hardly affected. The use of the larger nitrogen substituent R (*t*-Bu) in $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) causes a significant elongation of the Ti-N bond and closing of the Cg-Ti-Cl angles. For $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**), a Ti-$H_{methine}$ distance of 2.38 Å, shorter than the sum of the VanderWaals radii, suggests some Ti-H interaction. However, the spectral data of **9** oppose the existence of an agostic interaction, although both $[C_5H_4(CH_2)_nN$-*i*-Pr$]TiCl_2$ (n = 2, 3) complexes show a characteristic down-field shifted $H_{methine}$ resonance.

Cyclovoltammetry shows a single electron reduction for the complexes tested. The reduction potential appeared to be nearly invariant for bridge length and size of the nitrogen substituent. The Cp-amido stabilized titanium dichloro complexes $[C_5H_4(CH_2)_nNR]TiCl_2$ are significantly more resistent against reduction than other cyclopentadienyl containing titanium complexes.

2.7 Experimental Section.

General Considerations. All compounds are extremely air sensitive and manipulations were performed under nitrogen atmosphere using Schlenk glassware, Glovebox (Braun MB-200) or vacuum line techniques. Solvents and reagents (toluene, benzene, triethylamine, THF, ether, pentane, hexane, cyclohexane) were purified by distillation from potassium or sodium/potassium melt. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded in sealed tubes using Varian Gemini-200, Varian VXR-300 or Varian Unity 500 spectrometers. The chemical shifts are reported relative to TMS or standard samples (^{31}P: H_3PO_4 /H_2O, ^{19}F: CHF_3) and the resonances of residual protons in chloroform-d_1 ($CDCl_3$), benzene-d_6 (C_6D_6), cyclohexane-d_{12} (C_6D_{12}), bromobenzene-d_5 (C_6D_5Br), toluene-d_8 (C_7D_8), methylcyclohexane-d_{14} (C_7D_{14}) and THF-d_8 were used as references. IR spectra were recorded as Nujol mulls between KBr discs (unless mentioned otherwise) on a Mattson Galaxy 4020 spectrophotometer. Elemental analysis were performed at the Microanalytical Department of this laboratory. Each value given is the average of at least two independent determinations. GC-MS analyses were preformed on a Hewlett Packard Gas Chromatograph using a HP 5 MS (crosslinked 5% PHME siloxane, 30 m, 0.25 mm, film thickness 0.25 μm) connected to a Hewlett Packard 5973 Mass Selective Detector. Cyclovoltammetry measurements were performed with a Potentiostat/Galvanostat Model 273 (EG&G Princeton Applied Research) using approximately 1 mM solutions in THF (electrolyte: Bu_4NPF_6, 0.1 M). Mass spectra were recorded on an AE1 MS 902 mass spectrometer.

General procedures for the synthesis of $C_5H_5(CH_2)_nN(H)R$. The neutral Cp-amine ligands were prepared according to Hughes *et al*.[6a] by treating $Br(CH_2)_nN(H)R.HBr$ with excess CpNa in THF. The bromine-hydrobromide salts $Br(CH_2)_nN(H)R.HBr$ were prepared by reacting the chloro alcohol $Cl(CH_2)_nOH$ with large excess (8-10 eq.) of RNH_2 followed by treatment with excess HBr. A description of the syntheses of $Br(CH_2)_nN(H)Me.HBr$ and $C_5H_5(CH_2)_nN(H)Me$ (n = 2, 3) are given. For all bromine-hydrobromide salts and Cp-amine ligands the yields are tabulated (Table 7). All Cp-amine ligands with exception of $C_5H_5(CH_2)_2N(H)$-*t*-Bu exist as two isomers i.e. the 1,2 and 1,3 isomers in about equal amounts (^{1}H NMR). $C_5H_5(CH_2)_2N(H)$-*t*-Bu exists as the 1,1, 1,2 and 1,3 isomers in about 0.5:1:1 ratio. Together with the products, a small amount of dimerized cyclopentadiene was present (3-5%, ^{1}H NMR) but the ligands could be used without further purification.

Table 7.

	$Br(CH_2)_nN(H)R.HBr$ Yield (%)		$C_5H_5(CH_2)_nN(H)R$ Yield (%)	
	n = 2	n = 3	n = 2	n = 3
R = Me	70	73	64	73
R = Et	70	71	71	69
R = *i*-Pr	74	75	79	69
R = *t*-Bu	70	83	80	73
R = Ad	90	82	63	80
R = Ph	69	58	34	25

Synthesis of $Br(CH_2)_2N(H)Me.HBr$. A mixture of 50 mL (0.75 mol) $HO(CH_2)_2CL$ and 350 mL 40% $MeNH_2$ (aq) was stirred for 16 h. GC-analysis revealed completion of the reaction. The excess amine and water were removed under vacuum using a water-bath (100 ^oC) leaving a colorless oil. To the oil 250 mL of 47% HBr (aq) was added and the mixture was refluxed for 1 hour. Then a 30 cm Vigreux column was fitted to the flask and the mixture was slowly (4-5 hours) distilled until 235 mL of liquid was collected. A light brown oil remained in the destillation flask. This oil was further purified and freed from water by adding acetone (200 mL) and heating the mixture to reflux. Cooling of the two layer system to -20 ^oC resulted in solidification of the product. The liquids were decanted from the solid and the procedure was repeated by adding fresh acetone (200 mL). The acetone was finally removed in vacuum by heating the product in a water-bath (100 ^oC). 116.2 g (0.53 mol, 70%) of cream-colored crystals were obtained. ^1H NMR (200 MHz, D_2O): δ 3.65 (t, $^3J_{HH}$ = 5.86 Hz, 2H, $BrCH_2CH_2N$); 3.46 (t, $^3J_{HH}$ = 5.86 Hz, 2H, $BrCH_2CH_2N$); 2.70 (s, 3H, NMe).

Synthesis of $Br(CH_2)_3N(H)Me.HBr$. A mixture of 65.6 g (0.69 mol) of $HO(CH_2)_3Cl$ and 650 mL of 40% $MeNH_2$ solution in water was stirred for 16 h. The excess amine and water was removed in vacuum yielding a colorless oil. GC-analysis showed completion of the reaction. Without further purification of the product, 350 mL 47% HBr (aq) was added. The flask was mounted to a destillation apparatus equiped with a 30 cm Vigreux and the mixture was refluxed for 1 h. Slowly destilling off the water, HCl and excess HBr during 4-5 h yielded a brown liquid residue in the destillation flask. The residu was cooled and mixed with 70 mL of acetone to give a homogeneous mixture. Cooling to -20 ^oC gave off-white crystals. Isolation of the crystalline material and recrystallisation of the mother liquor yielded in total 118.6 g (0.51 mol, 73%) of $Br(CH_2)_3N(H)Me.HBr$. A ^1H NMR spectrum of the product showed it to be identical with that reported by Hughes *et al.*[6a]

Synthesis of $C_5H_5(CH_2)_2N(H)Me$. to To a solution (0 ^oC) of 53 g (0.60 mol) of CpNa in 300 mL of THF 44 g (0.20 mol) of $Br(CH_2)_2N(H)Me.HBr$ was added. After addition the temperature was raised to 50 ^oC. The solution became cloudy and a white solid precipitated. The mixture was stirred for 2 h and then quenched with 100 mL of water. The clear solution was diluted with 250 mL of light petroleum

and the organic layer was separated. The aqueous layer was extracted with 100 mL of light petroleum and the combined organic layers were washed with 100 mL of brine, dried on Na_2SO_4 and filtered. The solvents were removed in vacuum, the crude product (28.7 g) was vacuum transferred at 1 torr Hg and 25-30 ^oC. 15.7 g (0.13 mol, 64%) of $C_5H_5(CH_2)_2N(H)Me$ was obtained as a colorless oil existing as a ca. 1 : 1 mixture of the 1,2 and 1,3 isomers. ^1H NMR (200 MHz, $CDCl_3$): δ 6.32 (overlapped m, 3H, 2 x CH of C_5H_5 ring 1,2 isomer, 1 x CH 1,3 isomer); 6.15 (m, 1H, CH of C_5H_5 ring 1,3 isomer); 6.10 (m, 1H, CH of CH ring 1,3 isomer); 5.96 (m, 1H, CH of C_5H_5 ring 1,2 isomer); 2.85 (m, 2H, CH_2 of C_5H_5 ring isomer 1); 2.78 (m, 2H, CH_2 of C_5H_5 ring isomer 2); 2.67 (t, 2H, $^3J_{HH}$ = 6.8 Hz, NCH_2); 2.65 (t, 2H, $^3J_{HH}$ = 6.8 Hz, NCH_2); 2.48 (m, 4H, 2 x $C_5H_5CH_2$); 2.33 (s, 6H, 2 x NMe); 0.93 (s, 2H, 2 x NH).

Synthesis of $C_5H_5(CH_2)_3N(H)Me$. To a solution of 133 g (1.51 mol) of CpNa in 1L of THF, 118 g (0.51 mol) of $Br(CH_2)_3N(H)Me.HBr$ was added. The solution became turbid and was stirred for 4 hours. The reaction mixture was quenched with 300 mL of water. The organic layer was separated and the aqueous layer was extracted twice with 300 mL ether. The combined organic layers where washed with 150 mL of brine and dried over Na_2SO_4. The volatiles were removed in vacuum leaving a pale brown residue. Distillation at 39-42 ^oC (0.05-0.1 torr) gave a light coloured oil which was collected in a cooled receiver (-30 ^oC). Yield: 51.6 g (0.37 mol, 73%) of $C_5H_5(CH_2)_3N(H)Me$. The ^1H NMR spectrum was identical to that reported by Hughes *et al.*[6a]

Synthesis of $[C_5H_4(CH_2)_2NMe]TiCl_2$ **(1).** To a solution of 1.78 g (9.38 mmol) of $TiCl_4$ in 40 mL of toluene, 1.4 g (11.4 mmol) of $C_5H_5(CH_2)_2N(H)Me$ and 2.6 mL (18.8 mmol) of Et_3N were quickly added giving a dark brown mixture. The mixture was refluxed for 1 h to give an orange solution with a tarry brown residue. The orange solution was decanted from the residue and the solvent was removed in vacuum. Sublimation of the orange residue at 160-180 ^oC and 10^{-2} torr gave 1.38 g (5.8 mmol, 62%) of $[C_5H_4(CH_2)_2NMe]TiCl_2$. ^1H NMR (200 MHz, C_6D_6): δ 6.01 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.84 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.53 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 3.49 (s, 3H, NMe); 2.42 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$). ^{13}C NMR (50 MHz, C_6D_6): δ 145.61 (s, C_5H_4-*ipso*); 118.00 (d, $^1J_{CH}$ = 175.8 Hz, C_5H_4); 115.26 (d, $^1J_{CH}$ = 177.8 Hz, C_5H_4); 80.08 (t, $^1J_{CH}$ = 140.6 Hz, NCH_2); 47.54 (q, $^1J_{CH}$ = 137.4 Hz, NMe); 28.09 (t, $^1J_{CH}$ = 129.9 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3109 (w), 3101 (m), 2787 (m), 1836 (w), 1801 (w), 1749 (w), 1713 (m), 1664 (w), 1491 (s), 1429 (m), 1408 (s), 1384 (m), 1342 (m), 1312 (m), 1285 (vw), 1234 (s), 1196 (w), 1170 (m), 1085 (s), 1066 (m), 1051 (m), 1036 (m), 1007 (s), 966 (s), 922 (m), 881 (s), 831 (vs), 719 (m), 642 (s), 569 (s), 524 (m). Anal. Calcd. for $C_8H_{11}Cl_2NTi$: C, 40.04; H, 4.62; Ti, 19.96. Found: C, 40.18; H, 4.58; Ti, 19.86. Mass spec.: 239 [M^+, 70.5%, correct isotope pattern for Ti and Cl], 161 [M^+-$C_5H_4CH_2$, 78.3%] (100% = [M^+-CH_2NMe]).

Reverse order of addition. Addition of 3.4 mL 1 M (3.4 mmol) of $TiCl_4$ in toluene to a solution of 500 mg (4.05 mmol) of $C_5H_5(CH_2)_2N(H)Me$ and 1 mL (7.2 mmol) of Et_3N in 25 mL of toluene and subsequent refluxing for 1 h resulted in a red-orange solution and a tarry brown residue. Filtration, concentration at 80-90 ^oC and crystallisation at -18 ^oC yielded 0.47 g (1.96 mmol, 58%) of **1**.

Slow addition of reagents. Addition of a solution of 460 mg (3.7 mmol) of $C_5H_5(CH_2)_2N(H)Me$ and 0.95 mL of Et_3N in 10 mL of toluene during 1 h, to a hot solution of 3.4 mmol of $TiCl_4$ in 20 mL of toluene resulted after workup (*vide supra*) in 0.50 g (2.08 mmol, 61%) product

***Synthesis of [$C_5H_4(CH_2)_2NEt$]$TiCl_2$* (2).** To a hot (70 ^oC) solution of 11.9 g (86.7 mmol) of $C_5H_5(CH_2)_2N(H)NEt$ and 25 mL (180 mmol) of Et_3N in 250 mL of toluene, a solution of 9.5 mL (86 mmol) of $TiCl_4$ in 50 mL of toluene was added in 5 min. The mixture turned dark brown. After the addition had been completed, the mixture was heated at 120-125 ^oC. After 1 h a red-orange solution and a tarry brown residue had been formed. The solution was filtered into a sublimation vessel and the volatile components were removed in vacuum. The remaining red-orange residue was sublimed at 10^{-2} torr and 190-200 ^oC yielding 12.30 g (48.4 mmol, 56%) of product. ^1H NMR (300 MHz, C_6D_6): d 6.05 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.85 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 4.16 (q, $^3J_{HH}$ = 6.87 Hz, 2H, $\underline{CH_2}CH_3$); 3.65 (t, $^3J_{HH}$ = 7.14 Hz, 2H, NCH_2); 2.50 (t, $^3J_{HH}$ = 7.14 Hz, 2H, $C_5H_4\underline{CH_2}$); 0.89 (t, $^3J_{HH}$ = 6.87 Hz, 3H, $CH_2\underline{CH_3}$). ^{13}C NMR (75.4 MHz, C_6D_6): d 145.46 (s, C_5H_4-*ipso*); 118.01 (d, $^1J_{CH}$ = 174.6 Hz, C_5H_4); 115.38 (d, $^1J_{CH}$ = 177.0 Hz, C_5H_4); 75.51 (t, $^1J_{CH}$ = 137.3 Hz, NCH_2); 52.44 (t, $^1J_{CH}$ = 134.3 Hz, $\underline{CH_2}CH_3$); 28.35 (t, $^1J_{CH}$ = 130.6 Hz, $C_5H_4\underline{CH_2}$); 11.46 (q, $^1J_{CH}$ = 127.4 Hz, $CH_2\underline{CH_3}$). IR (cm^{-1}): 3107 (w), 3094 (w), 3084 (m), 2725 (w), 1855 (w), 1817 (w), 1766 (w), 1728 (m), 1680 (w), 1491 (m), 1423 (w), 1373 (s), 1340 (s), 1288 (m), 1253 (w), 1226 (m), 1172 (m), 1161 (m), 1099 (s), 1068 (w), 1057 (m), 1043 (m), 1018 (s), 972 (s), 927 (vw), 916 (w), 889 (s), 841 (vs), 787 (m), 723 (w), 702 (m), 642 (s), 586 (s), 532 (s), 451 (m), 426 (m).

***Synthesis of [$C_5H_4(CH_2)_2N$-*i*-Pr]$TiCl_2$* (3).** To a hot (70 ^oC) solution of 11.3 g (74.7 mmol) of $C_5H_5(CH_2)_2N(H)$-*i*-Pr and 21 mL (152 mmol) Et_3N in 250 mL of toluene, a solution of 8.5 mL (77 mmol) of $TiCl_4$ in 100 mL toluene was added in 10 min. The mixture became dark brown and after the addition was complete, the mixture was heated at 120-125 ^oC for 2 h. A red-orange solution and a tarry black residue had formed. The hot solution was filtered from the residue and concentrated to $\pm$ 50 mL (at 100-110 ^oC). Slowly cooling to room temperature gave11.1 g of orange crystals. Concentration of the mother liquor gave a second crop (1.11 g), yielding in total 12.2 g (45.6 mmol, 61%) of product. ^1H NMR (200 MHz, C_6D_6): δ 6.05 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.92 (hept, $^3J_{HH}$ = 6.41 Hz, 1H, $\underline{CH}Me_2$); 5.78 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.57 (t, $^3J_{HH}$ = 7.05 Hz, 2H, NCH_2); 2.42 (t, $^3J_{HH}$ = 7.05 Hz, 2H, $C_5H_4\underline{CH_2}$); 0.86 (d, $^3J_{HH}$ = 6.41 Hz, 6H, $CH\underline{Me_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 144.92 (s, C_5H_4-*ipso*); 117.67 (d, $^1J_{CH}$ = 175.2 Hz, C_5H_4); 115.58 (d, $^1J_{CH}$ = 177.6 Hz, C_5H_4); 68.15 (t, $^1J_{CH}$ = 137.6 Hz, NCH_2); 54.59 (d, $^1J_{CH}$ = 133.7 Hz, $\underline{CH}Me_2$); 28.67 (t, $^1J_{CH}$ = 130.6 Hz, $C_5H_4\underline{CH_2}$); 17.78 (q, $^1J_{CH}$ = 127.0 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3097 (m), 3084 (m), 1836 (w), 1801 (w), 1757 (w), 1739 (w), 1722(w), 1707 (w), 1680 (w), 1667 (w), 1645 (w), 1493 (m), 1425 (sh, Nujol), 1385 (m), 1362 (m), 1340 (s), 1315 (w), 1292 (w), 1256 (w), 1230 (m), 1170 (s), 1155 (s), 1113 (m), 1070 (m), 1060 (m), 1041 (s), 1020 (m), 985 (s), 966 (m), 927 (w), 918 (w), 881 (s), 856 (vw), 839 (s), 821 (vs), 723 (w), 698 (m), 642 (s), 621 (w), 528 (m). Anal. Calcd for $C_{10}H_{15}Cl_2NTi$: C, 44.81; H, 5.64; Ti, 17.87. Found: C, 44.80; H, 5.48; Ti, 17.75. Mass spec.: 267 [M^+, 8.2%, correct isotope pattern for Ti and Cl_2], 252 [M^+-Me, 100%].

***Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]$TiCl_2$* (4).** To a hot (70 ^oC) solution of 32.3 g (0.195 mol) of $C_5H_5(CH_2)_2N(H)$-*t*-Bu and 55 mL (0.40 mol) of Et_3N in 450 mL of toluene, a solution of 22 mL (0.20 mol) of $TiCl_4$ in 250 mL of toluene was added under vigorous stirring in 20 min. The solution turned brown and a tarry black residue formed. After addition, the mixture was refluxed for 3 h resulting in a deep red solution and a black residue. After cooling to room temperature the red solution was separated from the black residue. The toluene was removed under reduced pressure yielding a dark red crystalline product which was extracted with ether. After the ether was removed in *vacuo*, a red micro-crystalline product was obtained which was washed two times with 100 mL of pentane. Drying in vacuum gave 33.65 g (119 mmol, 60%, based on $C_5H_5(CH_2)_2N(H)$-*t*-Bu) of **4**. An analytical pure sample of **4** was obtained after recrystallization from ether. ^1H NMR (200 MHz, C_6D_6): δ 6.19 (m, J_{HH} = 2.56 H, 2H, C_5H_4); 5.90 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.66 (t, $^3J_{HH}$ = 6.87 Hz, 2H, NCH_2); 2.37 (t, $^3J_{HH}$ = 6.87 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.42 (s, 9H, *t*-Bu). ^{13}C NMR (50 MHz, C_6D_6): δ 144.10 (s, C_5H_4-*ipso*); 118.12 (d, $^1J_{CH}$ = 171.9 Hz, C_5H_4); 118.04 (d, $^1J_{CH}$ = 178.7 Hz, C_5H_4); 69.96 (t, $^1J_{CH}$ = 137.4 Hz, NCH_2); 64.59 (s, $\underline{C}Me_3$); 29.72 (t, $^1J_{CH}$ = 130.2 Hz, $C_5H_4\underline{CH_2}$); 28.82 (q, $^1J_{CH}$ = 126.2 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3102 (m), 1756 (w), 1709 (w), 1664 (w), 1656 (w), 1562 (w), 1498 (w), 1469 (sh, Nujol), 1447 (sh, Nujol), 1425 (w), 1392 (w), 1360 (m), 1344 (w), 1319 (m), 1246 (m), 1238 (m), 1224(m), 1205 (w), 1176 (s), 1159 (sh), 1082 (sh), 1070 (s), 1043 (m), 1024 (sh), 1014 (w), 981 (s), 918 (s), 873 (m), 841 (sh), 829 (vs), 763 (m), 721 (w), 694 (m), 640 (m), 567 (m), 535 (s), 482 (s), 426 (s), 416 (sh). Anal. Calcd. for $C_{11}H_{17}Cl_2NTi$: C, 46.84; H, 6.08; Ti, 16.98. Found: C, 46.88; H, 6.09; Ti, 16.90. Mass spec.: 281 [M^+, 4.4%, correct isotope pattern for Ti and Cl_2] (100% = [M^+-Me]).

***Synthesis of [$C_5H_4(CH_2)_2$N-Ad]$TiCl_2$* (5).** To a warm solution (45 ^oC) of 5.0 g (21 mmol) of $C_5H_5(CH_2)_2N(H)$Ad and 6 mL (42 mmol) of Et_3N in 50 mL of toluene, a solution of 3.92 g (21 mmol) of $TiCl_4$ in 50 mL of toluene was added in 30 min. The mixture was stirred under reflux for 2 h. A tarry black residue and a dark red brown solution had formed. The solution was decanted from the residue and the solvent was removed in vacuum leaving a red-brown solid. The solid was extracted with 40 mL of THF and filtered. After removal of the THF in vacuum, the remaining solid was washed three times with 25 mL of cold (-20 ^oC) ether. Drying gave 4.61 g (12.8 mmol) of $[C_5H_4(CH_2)_2N$-Ad]$TiCl_2$. ^1H NMR (300 MHz, C_6D_6): δ 6.22 (m, J_{HH} = 2.50 Hz, 2H, C_5H_4); 5.90 (m, J_{HH} = 2.50 Hz, 2H, C_5H_4); 3.70 (t, $^3J_{HH}$ = 6.61 Hz, 2H, NCH_2); 2.38 (t, $^3J_{HH}$ = 6.61 Hz, 2H, $C_5H_4\underline{CH_2}$); 2.19 (d, $^3J_{HH}$ = 2.8 Hz, 6H, 3x $C\underline{CH_2}CH$); 1.97 (m, 3H, 3x $CH_2\underline{CH}CH_2$); 1.51 (m, 6H, 3x $CH\underline{CH_2}CH$).

***Synthesis of [$C_5H_4(CH_2)_2$NPh]$TiCl_2$* (6).** To a hot (80 ^oC) mixture of 4.00 g (21.6 mmol) of $C_5H_5(CH_2)_2N(H)$Ph and 6.0 mL (43.2 mmol) Et_3N in 50 mL of toluene, a solution of 2.3 mL (20.8 mmol) of $TiCl_4$ in 40 mL of toluene was added in 20 min. The dark brown mixture was then refluxed for 3 h. The solution turned dark red-orange and a black tar separated. After cooling to room temperature the red-orange solution was filtered and the toluene was removed in vacuum to leave an oily residue. This was extracted with 40 mL of THF and the solution was evaporated to dryness. The sticky solid was washed three time with 30 mL of cold (-20 ^oC) ether to leave an orange-yellow powder. Yield; 2.31 g (7.65 mmol, 37%) of $[C_5H_4(CH_2)_2NPh]TiCl_2$. ^1H NMR (200 MHz, C_6D_6): δ 7.53 (m, 2H, *o*-Ph); 7.22 (m,

2H, *m*-Ph); 6.93 (m, 1H, *p*-Ph); 6.11 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.96 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 4.03 (t, $^3J_{HH}$ = 6.84 Hz, 2H, NCH_2); 2.39 (t, $^3J_{HH}$ = 6.84 Hz, 2H, $C_5H_4\underline{CH_2}$).

***Synthesis of [$C_5H_4(CH_2)_3NMe$]$TiCl_2$* (7).** To a solution (room temperature) of 10.47 g (55.2 mmol) of $TiCl_4$ in 250 mL of toluene 7.5 g (54.7 mmol) of $C_5H_5(CH_2)_3N(H)Me$ and 15.3 mL (110 mmol) of Et_3N were quickly added. The solution turned black immediately. Refluxing for 3 h gave a orange-red solution with a tarry black residue. The solution was separated from the residue and the solvent was removed in vacuum to give an orange-red solid. Sublimation at 200 ^oC and 10^{-2} torr gave an orange-red crystalline solid. Yield: 7.88 g (31.0 mmol, 56%) of $[C_5H_4(CH_2)_3NMe]TiCl_2$. ^1H NMR (200 MHz, C_6D_6): δ 6.31 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.53 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.82 (s, 3H, NMe); 2.29 (m, 2H, NCH_2); 2.12 (m, 2H, $C_5H_4\underline{CH_2}$); 1.48 (m, 2H, $\underline{CH_2}CH_2N$). ^{13}C NMR (50 MHz, C_6D_6): δ 129.68 (s, C_5H_4-*ipso*); 119.23 (d, $^1J_{CH}$ = 177.3 Hz, C_5H_4); 114.58 (d, $^1J_{CH}$ = 181.2 Hz, C_5H_4); 62.22 (t, $^1J_{CH}$ = 135.5 Hz, NCH_2); 45.62 (q, $^1J_{CH}$ = 137.4 Hz, NMe); 29.6 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$); 25.69 (t, $^1J_{CH}$ = 129.3 Hz, $\underline{CH_2}CH_2N$). IR (cm^{-1}): 3103(m), 2704(vw), 1419(m), 1406(m), 1336(m), 1267((m), 1248(m), 1184(m), 1097(m), 1070(m), 1053(w), 1033(m), 981(m), 935(m), 902(s), 875(m), 837(s). Anal. Calcd. for $C_9H_{13}Cl_2NTi$: C, 42.55; H, 5.16; Ti, 18.86. Found: C, 42.42; H, 5.16; Ti, 18.76. Mass spec.: 253 [M^+, 14% correct isotope pattern for Ti and Cl_2], 217 [M^+-HCl, 59%] (100% = [M^+-CH_3NCH_2.HCl]).

***Synthesis of [$C_5H_4(CH_2)_3NEt$]$TiCl_2$* (8).** A solution of 8.0 mL (72 mmol) of $TiCl_4$ in 100 mL of toluene was added in 10 min to a hot (70 ^oC) solution of 10.9 g (72.1 mmol) of $C_5H_5(CH_2)_3N(H)Et$ and 20 mL (144 mmol) of Et_3N in 250 mL of toluene. A dark reaction mixture was formed which became a red-orange soluion and a tarry, dark-brown residue upon refluxing for 3 h. The hot solution was separated from the residue and the solvent was removed in vacuum leaving a red-orange residue which was sublimed (190-200 ^oC, 10^{-2} torr). Yield: 8.17 g (30.48 mmol, 42%) of **7**. ^1H NMR (300 MHz, C_6D_6): δ 6.35 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.56 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 4.55 (q, $^3J_{HH}$ = 6.59 Hz, 2H, $\underline{CH_2}CH_3$); 2.48 (m, 2H, NCH_2); 2.25 (m, 2H, $C_5H_4\underline{CH_2}$); 1.60 (m, 2H, $NCH_2\underline{CH_2}$); 1.01 (t, $^3J_{HH}$ = 6.59 Hz, 3H, $CH_2\underline{CH_3}$). ^{13}C NMR (75.4 MHz, C_6D_6): d 136.36 (s, C_5H_4-*ipso*); 119.26 (d, $^1J_{CH}$ = 177.0 Hz, C_5H_4); 114.92 (d, $^1J_{CH}$ = 174.6 Hz, C_5H_4); 57.84 (t, $^1J_{CH}$ = 136.1 Hz, NCH_2); 49.43 (t, $^1J_{CH}$ = 135.5 Hz, $\underline{CH_2}CH_3$); 30.75 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$); 26.04 (t, $^1J_{CH}$ = 128.8 Hz, $NCH_2\underline{CH_2}$); 11.55 (q, $^1J_{CH}$ = 127.4 Hz, $CH_2\underline{CH_3}$). IR (cm^{-1}): 3107 (w), 3099 (w), 3078 (m), 2725 (w), 1894 (w), 1849 (w), 1813 (w), 1743 (w), 1664 (w), 1494 (m), 131366 (m), 1346 (s), 1290 (m), 1275 (m), 1244 (m), 1230 (w), 1161 (s), 1105 (m), 1072 (s), 1057 (m), 1033 (s), 1004 (s), 937 (s), 883 (w), 869 (w), 854 (sh, 835 cm^{-1}), 835 (vs), 788 (m), 723 (m), 673 (m), 60.3 (m), 580 (s), 542 (m), 453 (s), 434 (s).

***Synthesis of [$C_5H_4(CH_2)_3N$-*i*-Pr]$TiCl_2$* (9).** To a hot (70-75 ^oC) solution of 12.0 g (72.6 mmol) of $C_5H_5(CH_2)_3N(H)$-*i*-Pr and 21 mL (151 mmol) of Et_3N in 250 mL of toluene, a solution of 8 mL (73 mmol) of $TiCl_4$ in 100 mL of toluene was added in 10 min. After addition the dark mixture was refluxed for 2 h. A red solution with a tarry black residue formed. The red solution was filtered and concentrated to ± 50 mL at 100-110 ^oC. Slow cooling to room temperature yielded 9.63 g red crystalline product. A second crop was obtained by concentrating the mother liquor, (1.99 g) giving a total yield of 11.62 g (41.2

mmol, 57 %) of **9**. ^{1}H NMR (200 MHz, C_6D_6): 6.57 (hept, $^{3}J_{HH}$ = 5.98 Hz, 1H, $\underline{CH}Me_2$); 6.36 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.47 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 2.43 (m, 2H, NCH_2); 2.16 (m, 2H, $C_5H_4\underline{CH_2}$); 1.46 (m, 2H, $NCH_2\underline{CH_2}$); 1.02 (d, $^{3}J_{HH}$ = 5.98 Hz, 6H, $CH\underline{Me_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 130.36 (s, C_5H_4-*ipso*); 119.35 (d, $^{1}J_{CH}$ = 177.3 Hz, C_5H_4); 114.91 (d, $^{1}J_{CH}$ = 173.8 Hz, C_5H_4); 50.64 (d, $^{1}J_{CH}$ = 128.9 Hz, $\underline{CH}CMe_2$); 50.36 (t, $^{1}J_{CH}$ = 135.5 Hz, NCH_2); 32.24 (t, $^{1}J_{CH}$ = 128.7 Hz, $C_5H_4\underline{CH_2}$); 26.23 (t, $^{1}J_{CH}$ = 128.7 Hz, $NCH_2\underline{CH_2}$); 17.93 (q, $^{1}J_{CH}$ = 127.1 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3111 (w), 3097 (w), 3084 (w), 1844 (w), 1795 (w), 1755 (w), 1697 (w), 1662 (w), 1498 (s), 1417 (s), 1398 (m), 1361 (s), 1330 (m), 1278 (m), 1244 (m), 1226 (m), 1174 (m), 1153 (s), 1116 (m), 1085 (w), 1074 (m), 1057 (m), 1039 (m), 1012 (m), 966 (m), 939 (s), 895 (m), 875 (m), 827 (vs), 800 (s), 661 (m), 609 (m), 536 (s), 447 (vs). Anal. Calcd for $C_{11}H_{17}Cl_2NTi$: C, 46.84; H, 6.08; Ti, 16.98. Found: C, 46.94; H, 6.00; Ti, 16.88. Mass spec.: 281 [M^+, 13%, correct isotope pattern for Ti and Cl_2], 266 [M^+-Me, 100%].

Synthesis of $[C_5H_4(CH_2)_3NPh]TiCl_2$ **(12).** To a hot (70 °C) solution of 5.2 g (25.8 mmol) of $C_5H_5(CH_2)_3N(H)Ph$ and 7.2 mL (52 mmol) of Et_3N in 50 mL of toluene, a solution of 2.8 mL (25.3 mmol) of $TiCl_4$ in 40 mL of toluene was added in 15 min. The mixture was refluxed for 4 h. A dark red-brown solution and a black tar formed. After cooling to room temperature the solution was filtered and the volatiles were removed in vacuum. The dark oily residue was extracted with 40 mL of THF. The extract was pumped to dryness. The resulting sticky solid was washed three times with 20 mL of cold ether leaving a yellow-brown powder. Yield: 1.72 g (5.44 mmol, 21%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.48 (m, 2H, *o*-Ph); 7.22 (m, 2H, *m*-Ph); 7.01 (m, 1H, *p*-Ph); 6.33 (dd, $^{3}J_{HH}$ = 2.86 Hz, $^{4}J_{HH}$ = 2.56 Hz, C_5H_4); 5.72 (dd, $^{3}J_{HH}$ = 2.86 Hz, $^{4}J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 2.92 (m, 2H, NCH_2); 2.23 (m, 2H, $C_5H_4\underline{CH_2}$); 1.61 (m, 2H, $NCH_2\underline{CH_2}$).

Synthesis of $[C_5H_4(CH_2)_2O]TiCl_2$ **(13).** To a solution (room temperature) of 1.97 g (10.3 mmol) of $TiCl_4$ in 40 mL of toluene 1.4 g (12.7 mmol) of $C_5H_5(CH_2)_2OH$ and 3.0 mL (21.6 mmol) of Et_3N were added. The mixture turned black immediately and a tarry black residue precipitated leaving a pale yellow solution. The mixture was refluxed for 2 h giving a yellow solution which was decanted after cooling to room temperature. After removal of the solvent in vacuum a tarry residue was obtained. The residue was sublimed (180-200 °C, 10^{-2} torr) yielding an orange solid (25 mg, 0.11 mmol, 1%). The residue was dissolved in 0.5 mL of C_6D_6 giving a pale yellow solution and a white precipitate. The ^{1}H NMR spectrum shows besides the resonances (6.06, 5.78, 4.67 and 2.17 ppm resp.) characteristic for $\{[C_5H_4(CH_2)_2O]TiCl_2\}_2$[5b], broad resonances (3.5 - 0 ppm) of an unidentified product accounting for more than 80% of the total integral.

Synthesis of $[C_5H_4(CH_2)_3O]TiCl_2$ **(14).** To a cooled (-80 °C) solution of 1.90 g (10.0 mmol) of $TiCl_4$ in 40 mL of toluene 1.3 g (10.6 mmol) of $C_5H_5(CH_2)_3OH$ was added. The mixture became turbid. Addition of 2.8 mL (20.2 mmol) of Et_3N gave a dark mixture which was successively heated at 120 °C for 3 h. A tarry, black residue and a yellow solution was obtained. The yellow solution was decanted and the solvent was removed in vacuum giving a dark yellow oil. Sublimation of the oil (200 °C, 10^{-2} torr) yielded 0.21 g (0.9 mmol, 8%) of **14** as bright yellow crystals. ^{1}H NMR (200 MHz, C_6D_6): δ 6.45 (m, J_{HH}

= 2.78 Hz, 2H, C_5H_4); 5.46 (m, J_{HH} = 2.78 Hz, 2H, C_5H_4); 3.54 (m, 2H, OCH_2); 1.88 (m, 2H, $C_5H_4\underline{CH_2}$); 1.30 (m, 2H, $OCH_2\underline{CH_2}$).

2.8 References and Notes.

(1) (a) Shapiro, P.J.; Bunel. E.E.; Schaefer, W.P.; Bercaw, J.E. *Organometallics* **1990**, *9*, 867. (b) Piers, W.E.; Shapiro, P.J.; Bunel, E.E.; Bercaw, J.E. *Synlett.* **1990**, *2*, 74. (c) Exxon Chemical Co. US Pat. 5,026,798 **1991**, 5,055,438 **1991**. (d) Dow Chemical Co. Europ. Pat. Appl. 0416815 **1991**. (e) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E.F. *Organometallics* **1994**, *13*, 954. (f) Hajela, S.; Bercaw, J.E. *Organometallics* **1994**, *13*, 1147.

(2) (a) Ewen, J.A.; Elder, M.J.; Jones, R.L.; Haspeslagh, L.; Atwood, J.L.; Bott, S.G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253. (b) Brintzinger,H.H.; Fischer, D.; Müllhaupt, R.; Rieger, B.; Waymouth, R.M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907.

(3) Hoveyda, A.H.; Morken, J.P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262.

(4) (a) Weng, W.; Arif, A.M.; Ernst, R.D. *Organometallics* **1993**, *12*, 1537. (b) Sullivan, E.; Setton, R. *J. Organomet. Chem.* **1963**, *4*, 156. (c) King, R.B.; Bisnette, M.B. *J. Organomet. Chem.* **1967**, 8, 287. (d) Samuel, E.; Alt, H.G.; Hrncir, D.C.; Rausch, M.D. *J. Organomet. Chem.* **1976**, *113*, 331. (e) Blenkers, J.; De Liefde Meijer, H.J.; Teuben, J.H. *J. Organomet. Chem.* **1981**, *218*, 383. (f) Evans, W.J.; Peterson, T.T.; Rausch, M.D.; Hunter, W.E.; Zhang, H.; Atwood, J.L. *Organometallics* **1985**, *4*, 554. (g) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (h) Thompson, M.; Baxter, M.; Bulls, A.R.; Burger, B.J.; Nolan, M.C.; Santasiero, B.D.; Schaefer, W.P.; Bercaw, J.E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(5) (a) Antonelli, D.M.; Green, M.L.H.; Mountford, P. *J. Organomet. Chem.* **1992**, *438*, C4. (b) Trouve, G.; Laske, D.A.; Meetsma, A.; Teuben, J.H. *J. Organomet. Chem..* **1996**, *511*, 255.

(6) (a) Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics* **1993**, *12*, 1936. (b) Hughes, A.K.; Marsh, S.M.B.; Howard, J.A.K.; Ford, P.S. *J. Organomet. Chem.* **1997**, *528*, 195. (c) Herrmann, W.A.; Morawietz, M.J.A.; Priermeier, T. *Angew. Chem. Int. Ed.* **1994**, *33*, 1946.

(7) (a) Herrmann, W.A.; Morawitz, M.J.A.; Priermeier, T. *Angew. Chem. Int. Ed. Eng.* **1994**, *33*, 1946. (b) Herrrmann, W.A.; Morawitz, M.J.A. *J. Organomet. Chem.* **1994**, *482*, 169. (c) Diamond, G.M.; Rodewald, S.; Jordan, R.F. *Organometallics* **1995**, *14*, 5. (d) Carpenetti, D.W.; Kloppenburg, L.; Kupec, J.T.; Petersen, J.L. *Organometallics* **1996**, *15*, 1572. (e) Mu , Y.; Piers, W.E.; MacQuarrie, D.C.; Zaworotko, M.J.; Young, V.G. *Organometallics* **1996**, *15*, 2720. (f) Herrmann W.A.; Baratta. W. *J. Organomet. Chem.* **1996**, *506*, 357. (g) Diamond, G.M.; Jordan, R.F.; Petersen, J.L. *Organometallics* **1996**, *15*, 4030. (h) Christopher, J.N.; Diamond, G.M.; Jordan, R.F.; Petersen, J.L. *Organometallics* **1996**, *15*, 4038. (I) Diamond, G.M.; Jordan, R.F.; Petersen, J.L. *Organometallics* **1996**, *15*, 4045.

(8) (a) Birmingham, J.M.; Seyferth, D.; Wilkinson, G. *J. Am. Chem. Soc.*, **1954**, *76*, 4179. (b) Brmingham, J. M. *Adv. Organometal. Chem.* **1964**, *2*, 365.

(9) (a) Bradley, D.C. *Adv. Inorg. Chem. Radiochem.*, **1972**, *15*, 259 and references herein. (b) Wilkinson, G.; Gillard, R.D.; McCleverty, J.A. *Comprehensive Coordination Chemistry;* Volume 3, Pergamon Press: New York, **1987**, pp 333.

(10) Nadasdi, T.T.; Stephan, D.W. *Inorg. Chem.* **1993**, *32*, 5933.

(11) ^{1}H NMR spectra show that complex mixtures had been formed. No unequivocal indication for the presence of the expected complexes **10** and **11** could be obtained. It is well possible that only the cyclopentadienyl ligand has been introduced and that the amine function cannot coordinate to the metal for steric reasons.

(12) The synthesis of Cp_2TiCl_2 is performed in THF. $TiCl_4$ is first added to (0 ^{o}C) THF giving a yellow suspension of $TiCl_4$.2THF. Addition of Et_2NH and CpH results in the formation of a dark green complex of which the composition is not exactly known, however there is evidence for titanium amine complexes.

(13) Stepwise introduction of the Cp-amido ligand to titanium has been observed in the reaction of $C_5H_5(CH_2)_nN(H)Me$ (n = 2, 3) with $Ti(NMe_2)_4$ where $[Me(H)N(CH_2)_nC_5H_4]Ti(NMe_2)_3$ was observed as an intermediate (P.-J. Sinnema, J.H. Teuben, unpublished results). pK_a(methylcyclopentadiene) ≈ 19, pK_a(amine) ≈ 25-35. See: Bordwell, F.G. *Acc. Chem. Res.* **1988**, *21*, 456.

(14) Chen, Y.X.; Marks, T.J. *Organometallics* **1997**, *16*, 3649.

(15) $[C_5Me_4H]TiCl_3$ was identified by ^{1}H, ^{13}C NMR spectra and elemental analysis.

(16) Ganis, P.; Allegra, G. *Atti. Accad. Nazl. Lincei. Rend. Classe. Sci. Fis. Mat. Nat.* **1962**, *33*, 303.

(17) Pupi, R.M.; Coalter, J.N.; Petersen, J.L. *J. Organomet. Chem.* **1995**, *497*, 17.

(18) Bai, Y.; Roesky, H.W.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1991**, *595*, 21.

(19) Airoldi, C.; Bradley, D.C.; Chudzynska, H.; Hursthouse, M.B.; Abdul Malik, K.M.; Raithby, P.R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

(20) Okuda, J.; Eberle, T.; Spaniol, T.P. *Chem. Ber./Recueil* **1997**, *130*, 209.

(21) Carpenetti, D.W.; Kloppenburg, L.; Kupec, J.T.; Petersen, J.L. *Organometallics* **1996**, *15*, 1572.

(22) (a) Stevens, J.C. *Metcon 93*, Houston, 26-28 May, **1993**, 157. (b) Stevens, J.C. *Stud. Surface Sci. Cat.* **1994**, *89*, 277.

(23) Clearfield, A.; Warner, D.K.; Saldarriaga-Molina, C.H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

(24) Smith, J.A.; von Seyerl, J.; Huttner, G.; Brintzinger, H.H. *J. Organomet. Chem.* **1979**, *173*, 175.

(25) Davis, B.R.; Bernal, I. *J. Organomet. Chem.* **1971**, *30*, 75.

(26) In the case of complex **4**, the space group causes the molecules to occupy special possitions in the unitcell. The molecules are bisected by a mirror plane through the atoms Ti, C3, C4, N,

C6 and C8. Atom C5 and the hyrogens on C8 are disordered in two positions with populations of 50% each.

(27) In general agostic interactions are diagnosed by acute M-C_α-C_β angles (like the Ti-C_α-C_β angle of 86^o found for Ti($Me_2PCH_2CH_2PMe_2$)$EtCl_3$), down-field shifts of the agostic protons in the ^{1}H NMR spectra and low values for $^1J_{CH}$, (60-90 Hz for sp^3-CH, 90-125 Hz for sp^2-CH). See ref 21.

(28) Fussing, I.M.M.; Pletcher, D.; Whitby, R.J. *J. Organomet. Chem.* **1994**, *470*, 119.

(29) Fussing, I.M.M.; Pletcher, D.; Whitby, R.J. *J. Organomet. Chem.* **1994**, *470*, 109.

(30) Schwemlein, H.; Tritschler, W.; Kiesele, H.; Brintzinger, H.H. *J. Organomet. Chem.* **1985**, *293*, 353.

(31) Bajgur, C.S.; Tikkanen, W.R.; Petersen, J.L. *Inorg. Chem.* **1985**, *24*, 2539.

(32) Willoughby, C.A.; Duff, R.R. Jr.; Davis, W.M.; Buchwald, S.L. *Organometallics* **1996**, *15*, 472.

(33) (a) Gielens, E.E.C.G. Thesis, Groningen, 1999. (b) Fandos, R. *Unpublished results.*

(34) Vogelzang, J. University of Groningen, Undergraduate research report 1991, unpublished.

3 Cyclopentadienyl Amido Titanium Bis-alkyl and Bis-aryl Complexes $[C_5H_4(CH_2)_nNR]TiR'_2$. A Study of C-H Activation Processes. Stable Alkylidene and Olefin Complexes.

3.1 Introduction.

In the previous chapter a facile route has been described for a wide range of cyclopentadienyl amido titanium dichloro complexes $[C_5H_4(CH_2)_nNR]TiCl_2$. These dichlorides provide a good opportunity to prepare and investigate the Cp-amido titanium carbyl compounds $[C_5H_4(CH_2)_nNR]Ti(Cl)R'$ and $[C_5H_4(CH_2)_nNR]TiR'_2$.

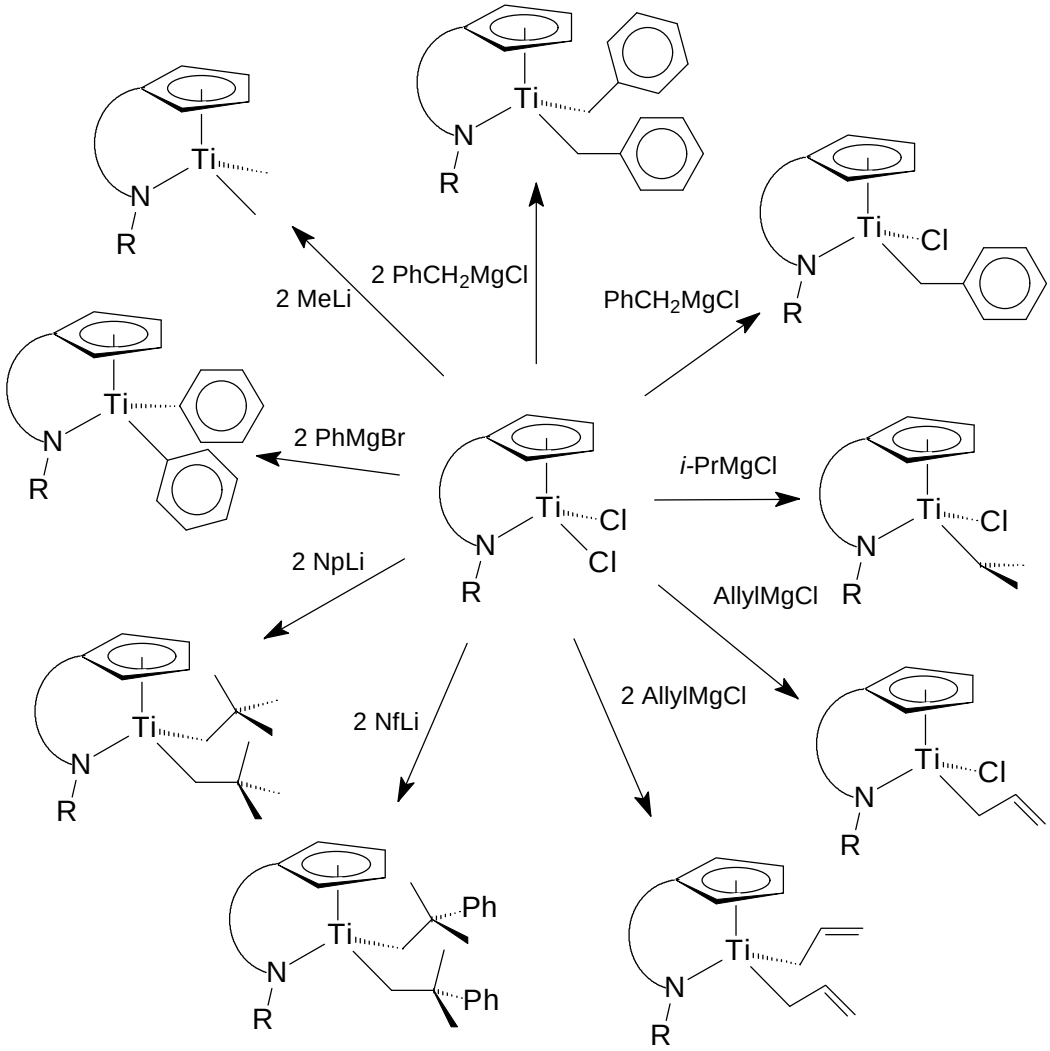
Bis-cyclopentadienyl and bis-pentamethylcyclopentadienyl group 4 metal bis-carbyl complexes, Cp'_2MR_2, are well-known and have been studied extensively but the information on the synthesis and properties of analogues with linked amido (or alkoxy/aryloxy) cyclopentadienyl spectator ligands is scarce.[1] These carbyl complexes can be of scientific and industrial importance since they form sources for cationic species $\{[C_5H_4(CH_2)_nNR]TiR'\}^+$, the active species in catalytic olefin polymerization.[2,3,4]

Furthermore, bis-carbyl complexes Cp'_2MR_2 are known to undergo C-H activation (e.g. yielding alkylidene, aryne/alkyne and olefin complexes), Cp ligand activation and C-X activation and have a very rich and interesting insertion chemistry with unsaturated substrates which gives valuable synthons for organic synthesis.[5] It would be interesting to explore possibilities to make new alkylidene, aryne/alkyne and olefin complexes starting from Cp-amido titanium complexes $[C_5H_4(CH_2)_nNR]TiR'_2$. In addition, the intrinsic reactivity of the Cp-amido ligands is hardly investigated and we want to know whether these Cp-amido ligands can be regarded as truely inert spectator ligands or whether they may bring additional reactivity to the compounds.

Here we report the synthesis and characterization of Cp-amido titanium alkyl and aryl species $[C_5H_4(CH_2)_nNR]TiR'_2$. In the second part of this chapter the thermolyses of a representative selection of bis carbyl compounds $[C_5H_4(CH_2)_nNR]TiR'_2$ will be described and discussed.

3.2 Synthesis of Cp-Amido Titanium Bis(carbyl) Complexes $[C_5H_4(CH_2)_nNR]TiR'_2$.

The amido functionalized cyclopentadienyl titanium dichlorides $[C_5H_4(CH_2)_nNR]TiCl_2$ (Chapter 2) are excellent precursors for the preparation of alkyl and aryl compounds $[C_5H_4(CH_2)_nNR]TiR'_2$ of which a wide range could be obtained in moderate to high yields (Scheme 1, Table 1). The general procedure is the classical but efficient salt metathesis route. The complexes were obtained by adding the appropiate organolithium or Grignard reagents to cooled (-80°C) ether solutions of the dichlorides, $[C_5H_4(CH_2)_nNR]TiCl_2$, followed by work up and crystallization from pentane. Some of the products are oils, but they could be identified satisfactorily by ^1H and ^{13}C NMR spectroscopy.



Scheme 1. Routes to Cp-amido titanium carbyl complexes.

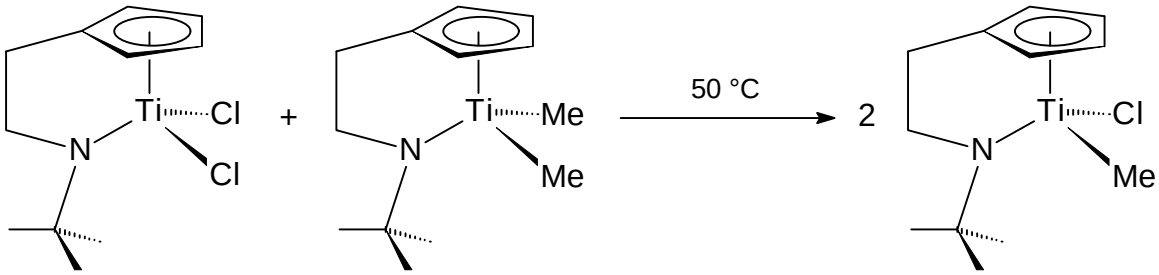
Table 1. Cp-amido titanium carbyl complexes $[C_5H_4(CH_2)_nNR]TiR'_2$.

Complex	Yield(%)	Color	Cryst./Oil
$[C_5H_4(CH_2)_2NMe]TiMe_2$ (**15**)	61	yellow	cryst.
$[C_5H_4(CH_2)_2N$-*i*-Pr$]TiMe_2$ (**16**)	83	yellow	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]TiMe_2$ (**17**)	76	yellow	oil.
$[C_5H_4(CH_2)_3NMe]TiMe_2$ (**18**)	82	yellow	cryst.
$[C_5H_4(CH_2)_3N$-*i*-Pr$]TiMe_2$ (**19**)	77	yellow	cryst.
$[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**20**)	66	red	cryst.
$[C_5H_4(CH_2)_2N$-*i*-Pr$]Ti(CH_2Ph)_2$ (**21**)	84	red	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2Ph)_2$ (**22**)	69	red	oil
$[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)_2$ (**23**)	68	red	oil
$[C_5H_4(CH_2)_3N$-*i*-Pr$]Ti(CH_2Ph)_2$ (**24**)	92	red	oil
$[C_5H_4(CH_2)_2NMe]TiPh_2$ (**25**)	26	yellow-brown	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]TiPh_2$ (**26**)	44	orange-yellow	cryst.
$[C_5H_4(CH_2)_3NMe]TiPh_2$ (**27**)	22	green-yellow	cryst.
$[C_5H_4(CH_2)_2NMe]Ti(CH_2CMe_3)_2$ (**28**)	85	yellow-brown	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2CMe_3)_2$ (**29**)	68	orange-yellow	cryst.
$[C_5H_4(CH_2)_2NMe]Ti(CH_2CMe_2Ph)_2$ (**30**)	60	yellow-brown	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2CMe_2Ph)_2$ (**31**)	67	yellow	cryst.
$[C_5H_4(CH_2)_3NMe]Ti(CH_2CMe_2Ph)_2$ (**32**)	67	yellow	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2Ph)Cl$ (**33**)	69	red	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]T(Me)Cl$ (**34**)	64	brown	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti($i-Pr$)Cl$ (**35**)	74	red	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_3H_5)Cl$ (**37**)	32	red-brown	cryst./oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_3H_5)_2$ (**38**)	75	red	oil

3.3 Synthesis of Cp-amido titanium chloro alkyl complexes $[C_5H_4(CH_2)_nNR]Ti(Cl)R'$.

Reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ with 1 eq. $PhCH_2MgCl$ in ether afforded the mono benzyl chloro complex $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2Ph)Cl$ (**33**) in 69% yield as red crystals. Performing a similar reaction with 1 eq. of MeLi resulted in a mixture of $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$, $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiMe_2$ and the methyl-chloro complex $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(Me)Cl$ (**34**). Heating the reaction mixture at 50 ^oC (benzene) for 24 h resulted in the

desired product $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(Me)Cl (**34**). Complexes **33** and **34** could also be synthesized by synproportionation of the bis(alkyl) and dichloro compounds. When an equimolar mixture of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ (**4**) and $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiMe_2$ (**17**) in C_6D_6 was monitored by ^{1}H NMR spectroscopy virtually no reaction occured at room temperature but at 50 ^{o}C the methyl-chloro complex **34** started to form slowly and after 24 h the conversion was complete (Scheme 2).[6]



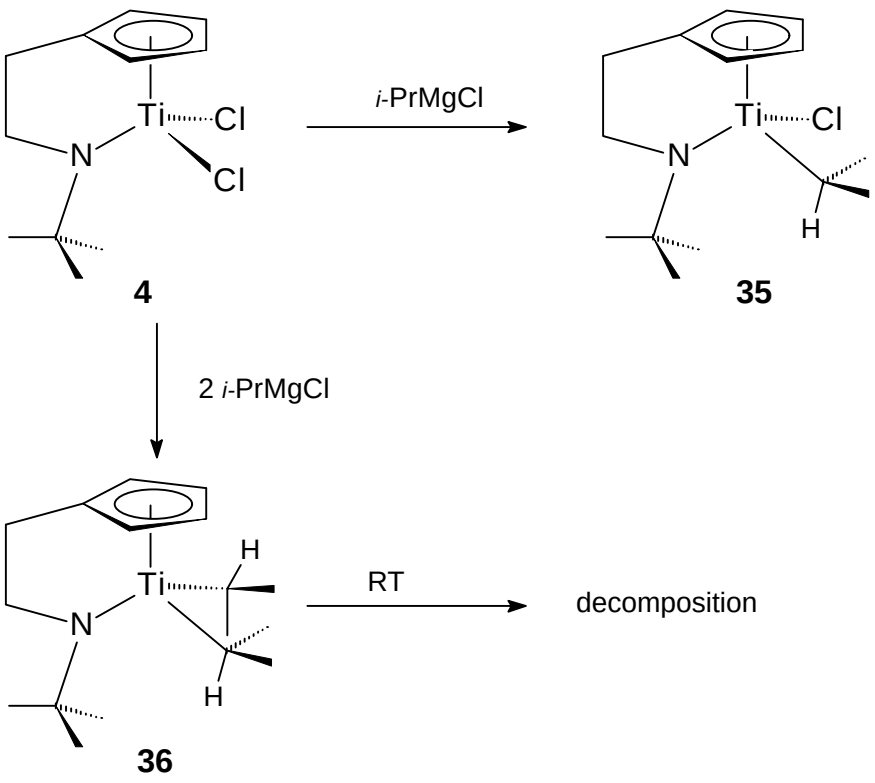
4 **17** **34**

Scheme 2. Synproportionation of **4** and **17** to **34**.

Under similar conditions, the reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ and $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2Ph)_2$ appeared to be considerably slower. After 98 h at 50 ^{o}C the conversion was completed. Attempts to prepare the analoguous chloro phenyl, chloro neopentyl and chloro dimethyl-phenyl-methyl (neophyl) complexes failed. Under these conditions, the thermolysis of the bis(carbyl) compounds (*vide infra*) competes with the synproportionation.

3.4 Stable Titanium(IV) Allyl and *iso*-Propyl Complexes.

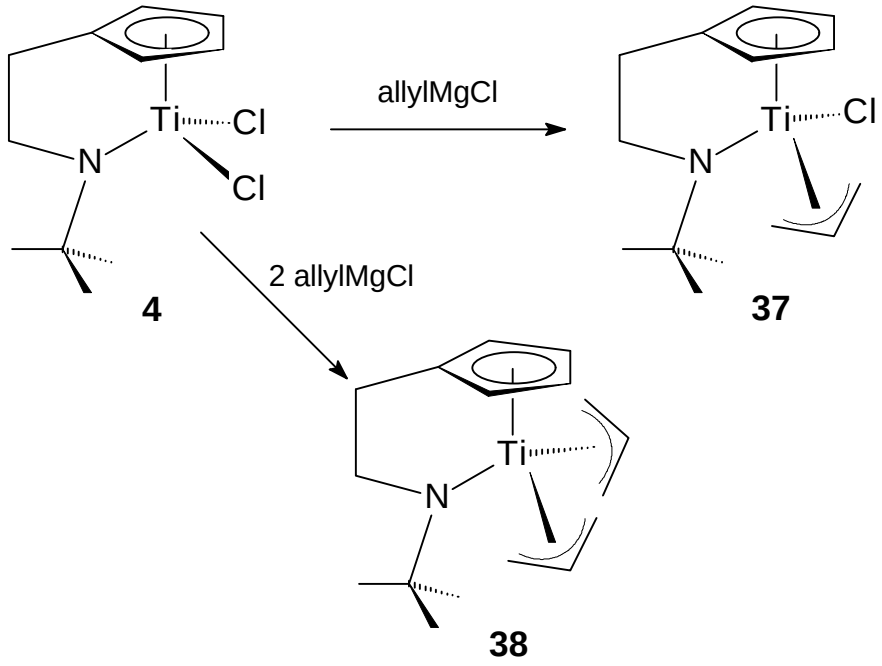
Interestingly, the reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ with 1 eq. of *i*-PrMgCl did not result in the formation of a trivalent titanium species like the formation of Cp_2TiCl by treatment of Cp_2TiCl_2 with *i*-PrMgCl.[11a] Instead a red-brown oil was obtained and a ^{1}H NMR spectrum indicated exclusive formation of the titanium(IV) species $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(*i*-Pr)Cl (**35**) (Scheme 3).



Scheme 3.

Treatment of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ under similar conditions with 2 eq of *i*-PrMgCl gave a dark red solution as expected for $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(*i*-Pr)$_2$ (**36**) but on workup it decomposed and a black tarry product was isolated which could not be identified.[7] However, the location and the narrow line widths of the ^{1}H NMR resonances of the mixture showed that no paramagnetic species had been formed and presumably no reduction had occured. Although the *iso*-propyl group is known to give β-H transfer[8], the *iso*-propyl chloro compound (**35**) is thermally stable and can be heated at 70 ^{o}C for hours without decomposition. A similar lack for β-H transfer has been reported for the *tert*-butyl complex (2,6,-*i*-Pr_2-$C_6H_3O)_3TiCMe_3$.[9]

Similarly, the reaction of $C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ with 1 or 2 eq. of the allyl Grignard did not proceed by reduction of the titanium complex. Diamagnetic dark red oils were obtained which were identified on the basis of their ^{1}H and ^{13}C NMR spectra as the allyl complexes complexes $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(η^3-C_3H_5)Cl (**37**) and $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(η^3-$C_3H_5)_2$ (**38**) (Scheme 4).



Scheme 4.

The reactions of the dichloride **4** with *iso*-propyl and allyl Grignard reagents proceed clearly different from Cp_2TiCl_2. Instead of reduction of the metal center, simple salt metathesis occurred and Ti(IV)-species are obtained. The reactions observed clearly demonstrate the higher resistance of the Cp-amido titanium dichlorides against reduction than their Cp_2Ti congeners and are in accordance with the higher reduction potentials observed for the Cp-amido titanium dichlorides.

Titanium(IV) alkyls Cp_2TiR_2 and $Cp^*_2TiR_2$ are borderline cases with respect to their oxidation/reduction stabilities. They tend to disproportionate to Ti(III) or even Ti(II) species. Photochemical reduction of Cp_2TiMe_2 has been observed[10] whereas the reduction of other titanocene ($Cp^*_2Ti(Cl)R$)[10b] alkyls are thermally induced. Reduction also is often observed when early transition metal halides react with Grignard reagentia and aluminum alkyls.[11,12] As shown, the cyclopentadienyl amido stabilized titanium alkyls $[C_5H_4(CH_2)_nNR]TiR'_2$ and $[C_5H_4(CH_2)_nNR]TiR'Cl$ are substantially more stable against reduction than the bis(pentamethyl)cyclopentadienyl analogues.

3.5 Spectroscopic Characterization.

The ^{1}H and ^{13}C NMR spectra of the carbyl complexes **15**-**37** show for the Cp-amido ligand the same general features as observed for the dichloro compounds. For example, the methine proton of the N-*iso*-propyl groups of $[C_5H_4(CH_2)_2N$-*i*-Pr]$TiMe_2$ (**16**), $[C_5H_4(CH_2)_3N$-*i*-Pr]$TiMe_2$ (**19**), $[C_5H_4(CH_2)_2N$-*i*-Pr]$Ti(CH_2Ph)_2$ (**21**) and $[C_5H_4(CH_2)_3N$-*i*-Pr]$Ti(CH_2Ph)_2$ (**24**) are strongly shifted down-field and an extra CH_2 unit in the backbone results in a larger $\Delta\delta$ of the C_5H_4-A_2B_2 resonances as well as a upfield shift of the NCH_2 resonance (Table 2).

For the dimethyl complexes **15**-**19** the ^{1}H NMR resonances of the two methyl groups bonded to titanium were found at 0.49, 0.42, 0.47, 0.40 and 0.30 ppm respectively, at higher field compared to the 12 electron complex $CpTiMe_3$ (1.16 ppm)[13] but at lower field than for the 16 electron complex Cp_2TiMe_2 (-0.17 ppm). However, care should be taken suggesting a direct relation between electronic structure and chemical shifts in ^{1}H and ^{13}C NMR since the methyl resonance for the 14 electron complex $Cp[CPh(NSiMe_3)_2]TiMe_2$[14] is found at 1.20 ppm and for the 12 electron complex $[CPh(NSiMe_3)_2]_2TiMe_2$[15] at 1.94 ppm. For all benzyl (**20**-**24**), neopentyl (**28** and **29**) and 2-phenyl-2-methyl propyl (neophyl; **30**, **31** and **32**) compounds the protons of the α-carbon of the alkyl groups are diastereotopic (figure 1) giving an AB spin system with $^{2}J_{HH}$ of 9-11.5 Hz.

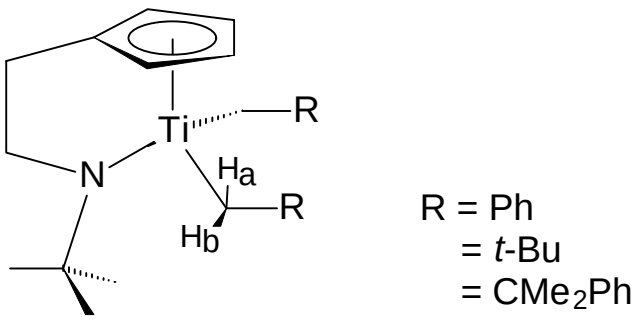


Figure 1. Illustration of the diastereotopic α-protons in **20**-**24** and **28**-**32**,

Table 2. Selected ^{1}H and ^{13}C NMR data of the bis-benzyl compounds **20**-**24**.

Compound	C_5H_4	$C_5H_4\underline{CH_2}$	NCH_2	$NC\underline{CH_2}$	NR	R_2
20	5.93, 5.15	2.23	3.34		3.40	7.19^{m}, 6.90^{p}, 6.80^{o}, 2.40, 2.19
	136.79[a], 117.30, 113.63	28.51	73.70		44.39	75.90 (122.3)
21	5.83, 5.25	2.26	3.41		5.73, 1.03	7.19^{m}, 6.89^{p}, 6.83^{o}, 2.38, 2.17
	136.59[a], 116.85, 115.04	29.06	61.78		51.23, 20.45	74.40 (120.9)
22	5.92, 5.27	2.10	3.29		1.50	7.22^{m}, 6.90^{p}, 6.82^{o}, 2.73, 2.27
	135.67[a], 118.04, 117.42	30.61	62.61		60.96, 30.11	78.04 (120.5)
23	6.21, 4.89	1.96	2.43	1.36	3.87	7.17^{m}, 6.88^{p}, 6.77^{o}, 2.45, 2.20
	124.84[a], 117.59, 114.20	30.87	60.11	26.47	42.55	74.53 (122.4)
24	6.10, 4.96	2.03	2.58	1.40	6.57, 1.22	7.19^{m}, 6.89^{p}, 6.81^{o}, 2.34, 2.15
	125.10[a], 118.84, 114.13	32.79	47.37	26.87	46.91, 20.59	72.88 (120.9)

[a]) *ipso*-C_5H_4

To relieve their electronic unsaturation, early transition metal complexes tend to bind benzyl ligands in a η^2 or η^3 fashion.[1a,16] η^2-Benzyl complexes show some characteristic features in the ^{1}H and ^{13}C NMR spectra: (a) high-field shifts of the ortho ^{1}H (δ < 6.8 ppm, *i.e.* $Ti(CH_2Ph)_4$: 6.42 ppm[16a]) and CH_2 ^{13}C (δ < 75 ppm) resonances and (b) large $^1J_{CH}$ coupling constants for the CH_2 group ($^1J_{CH}$ > 130 Hz).[17] For the bis-benzyl complexes **20**-**24** (Table 3) the ^{1}H resonances of the *ortho* protons (6.77-6.83 ppm) are shifted only slightly up-field indicating a regular η^1-bonded benzyl. Additionally, the ^{13}C NMR spectra of **20**-**24** showed the benzylic resonances between 72 and 78 ppm and the normal values of the coupling constants ($^1J_{CH}$ = 120-122 Hz) exclude significant η^2-bonding of the benzyl ligands. Whether this is due to the fact that these titanium complexes are not very electrophilic or that the η^2-bonding of the benzyl ligands is sterically prohibited in these species is not clear yet.

3.6 Stability of Cp-Amido Titanium Carbyl Complexes; Ligand Activation.

In Cp_2M and Cp^*_2M bis(carbyl) complexes of the early transition metals, many examples are known in which the ligands interfere in processes like α, β, γ and δ C-H activation[18]. Some well defined systems have been used to study these C-H activations of the ligands. These systems can be roughly divided in two classes: (a) complexes with ligands containing β-hydrogen atoms like ethyl or phenyl groups, known to give olefin[19] or aryne species[20], (b) complexes lacking β-hydrogen but with α, γ and δ-hydrogens like methyl, neopentyl or neophyl groups which are sources for alkylidenes[21] and metallacycles[22].

Another point is that the cyclopentadienyl and pentamethylcyclopentadienyl[23] ligands seldom are strictly inert spectator ligands and interfere in reactions between ligands and substrates of choice at the metal center.[24] This can have dramatic consequences for the reactivity and catalytic activity of the complexes. For example, for the cationic $Cp^*_2ZrR^+$, chain transfer by activation of a Cp* ligand is found to interfere with insertion of olefin[25]. Also other substituted Cp ligands like *tert*-butyl cyclopentadienyl show similar ligand activation[26] and other alkyl/aryl substituted cyclopentadienyls may be prone to ligand activation as well. When designing a catalyst, it should be kept in mind that the auxiliary ligand system used may interfere in the catalytic cycle. Therefore, if a stable catalytic process is to be designed it is important to have full information about the intrinsic reactivity of the spectator ligand used.

3.6.1 Thermal Stability: All carbyl complexes **15**-**38** can be handled at room temperature although the (bis)allyl and bis(phenyl) species have to be stored at -30 °C. Cyclohexane-d_{12} solutions of the bis(phenyl) compounds **25**-**27** show thermal decomposition with benzene formation at room temperature. For all alkyl and aryl derivatives formation of RH was observed at elevated temperatures (75-120 °C). A comparison of the thermal stability of $[C_5H_4(CH_2)_2N$-*t*-Bu]TiR'$_2$ versus $Cp_2TiR'_2$ is given in Table 3. Compared to the Cp_2Ti-analogues the bis-methyl **17**, the bis-benzyl **22**, bis-neopentyl **29** and bis-neophyl **31** complexes are thermally considerably more stable. In contrast the bis-phenyl compound **26** is considerably less stable than their Cp_2-analogue.

Table 3. Half life-times ($t_{1/2}$) of a selection of Cp-amido titanium bis(carbyl) complexes $[C_5H_4(CH_2)_nNR]TiR'_2$ compared with bis(carbyl) titanocenes Cp_2TiR. Samples were prepared as ≈ 0.4 M solutions

$[C_5H_4(CH_2)_nNR]TiR'_2$	temp. (°C), $t_{1/2}$, solv.	ref.
$[C_5H_4(CH_2)_2NMe]TiMe_2$ (**15**)	100, 4 h, C_7D_{14}	this work
$[C_5H_4(CH_2)_2N$-*i*-Pr]$TiMe_2$ (**16**)	100, 4.5 h, C_7D_{14}	"
$[C_5H_4(CH_2)_2N$-*t*-Bu]$TiMe_2$ (**17**)	100, 4.5 h, C_7D_{14}	"
$[C_5H_4(CH_2)_3NMe]TiMe_2$ (**18**)	80, 1.3 h, C_6D_{12}	"
$[C_5H_4(CH_2)_3N$-*i*-Pr]$TiMe_2$ (**19**)	80, 14 min, C_6D_{12}	"
$[C_5H_4(CH_2)_2N$-*i*-Pr]$Ti(CH_2Ph)_2$ (**21**)	120, 4.5 h, C_7D_{14}	"
$[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2Ph)_2$ (**22**)	120, 1.7 h, C_7D_{14}	"
$[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)_2$ (**23**)	100, 2 h, C_7D_{14}	"
$[C_5H_4(CH_2)_3N$-*i*-Pr]$Ti(CH_2Ph)_2$ (**24**)	80, 1.5 h, C_6D_{12}	"
$[C_5H_4(CH_2)_2N$-*t*-Bu]$TiPh_2$ (**26**)	75, 7 min, C_6D_{12}	"
$[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2CMe_3)_2$ (**29**)	75, 11 min, C_6D_{12}	"
$[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2CMe_2Ph)_2$ (**31**)	75, 60 min, C_6D_{12}	"
Cp_2TiMe_2	76, 70 min, C_6D_6	27a
$Cp_2Ti(CH_2Ph)_2$	80, 7 h, C_6H_6	27b
Cp_2TiPh_2	74, 2.5 h, C_6H_{12}	27c
$Cp_2Ti(CH_2CMe_3)_2$	20, 56 min, C_6H_{12}	21g

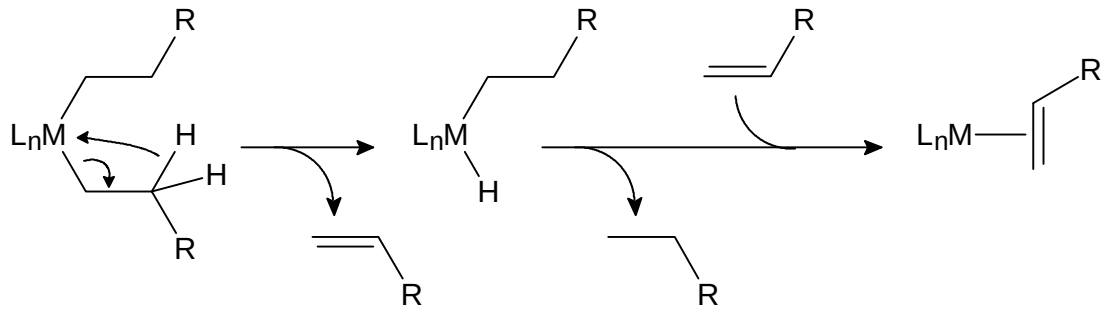
In relation to the different Cp-amido ligands in bis(methyl) and bis(benzyl) compounds some interesting trends in the order of thermal stability can be observed. The amido

substituent R in the C_2-bridged compounds hardly affects the thermal stability. The C_3-bridged complexes are thermally less stable than the C_2-bridged analogues and for the C_3 bridged carbyl complexes the group R of the amide function also affects the thermal stability. The $[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]TiR_2$ compounds are significantly less stable than $[C_5H_4(CH_2)_3NMe]TiR_2$ (R = Me, CH_2Ph) and are the least stable of the series tested.

3.6.2 Light Sensitivity: A number of group 4 metal carbyls have been reported to be light sensitive e.g. Cp_2TiMe_2, Cp_2TiPh_2.[10a,28] Of the complexes discussed here, $[C_5H_4(CH_2)_2NMe]TiMe_2$ (**15**) is sensitive to light and has to be stored in the dark. Sterically more demanding Cp-amido ligands seem to influence the light sensitivity of these complexes. $[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]TiMe_2$ (**16**), $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]TiMe_2$ (**17**), $[C_5H_4(CH_2)_3NMe]TiMe_2$ (**18**) and $[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]TiMe_2$ (**19**) are considerably less light sensitive than **15**.[29] The character of the carbyl is also important: benzyl, neopentyl and neophyl complexes **20**-**32** are light stable.

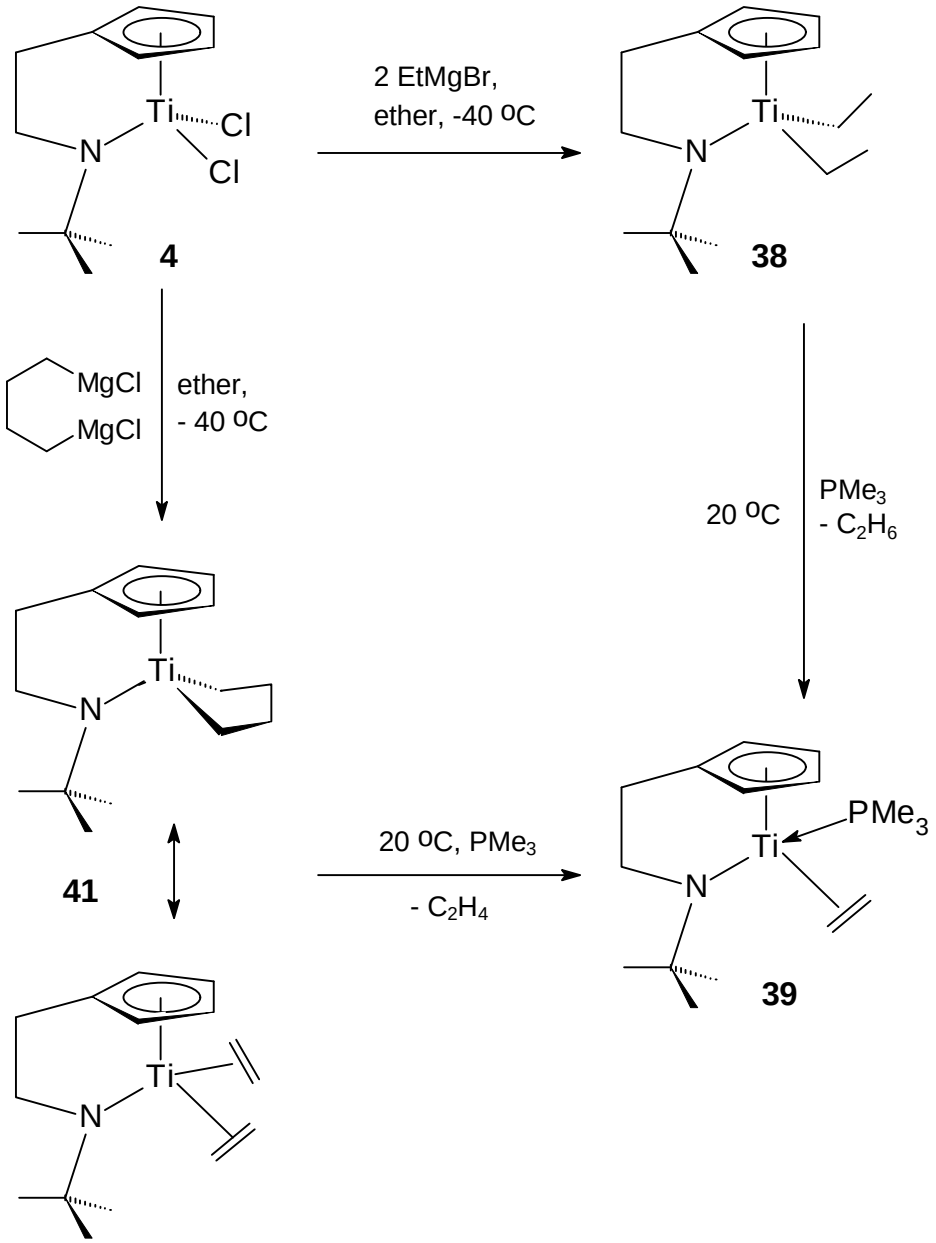
3.7 Synthesis of Cp-Amido Titanium Olefin, Benzyne and Alkylidene Complexes.

Since bis(carbyl) complexes are frequently used as sources for olefin,[19] aryne,[20] alkylidene[21] and metallacycle complexes[22], it was decided to see whether it is possible to prepare these types of compounds starting from the Cp-amido titanium bis(carbyl) species. Because the rather open structure of the Cp-amido complexes, it was expected that the olefin, aryne and alkylidene compounds need to be stabilized with a Lewis-base like PMe_3.[30] Therefore a selection of $[C_5H_4(CH_2)_nNR]TiR'_2$ compounds was thermolyzed in the presence of PMe_3. An exploratory preliminary investigation revealed that $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]TiR_2$ gave the most consistent results.[31]



Scheme 5.

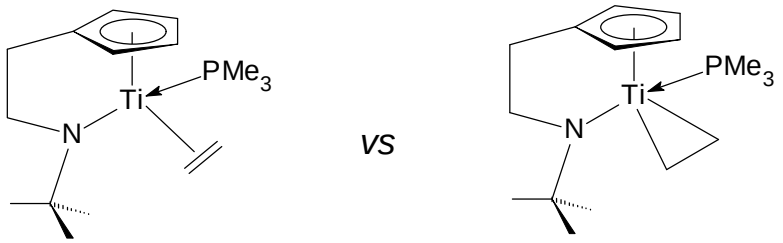
3.7.1 Generation of Olefin Complexes: Complexes with two linear alkyl groups often show β-hydrogen transfer followed by reductive elimination of RH and formation of the olefin complex[19] (Scheme 5), an important reaction for the synthesis of metallacycles and dimerization of alkenes.[32]



Scheme 6.

An *in situ* prepared solution of $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiEt_2$ (**38**) (-40 ^oC) in ether was warmed to room temperature in the presence of PMe_3. The solution became dark purple and evolution of ethane (GC-MS, 1.02-1.03 mol gas/mol Ti) was observed. Workup gave a dark purple oil of which the ^1H NMR spectrum was consistent with the formation of the PMe_3 stabilized ethene complex $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_2H_4)(PMe_3)$ (**39**) by β-hydrogen elimination in the initially formed diethyl complex (**38**) (Scheme 6). The same reaction without phosphine also gave ethane but the organometallic product(s) (a black oil) could not be identified. A ^1H NMR spectrum showed broad resonances in region of 7-0 ppm which could not be assigned to an ethene complex.

The ^1H NMR spectrum (C_6D_6) of **39** shows besides a doublet at 0.86 ppm (9H, PMe_3) and a singlet at 0.82 ppm (9H, *t*-Bu), 12 resonances which integrate each for 1H. A Cosy NMR experiment reveals that these 12 resonances originate from 3 independent ABCD spin systems. Two spin systems at low field (6.6-4.2 and 3.6-2.4 ppm, resp. C_5H_4 and CH_2CH_2) are assigned to the $C_5H_4(CH_2)_2N$ moiety. The remaining ABCD spin system with resonances at resp 2.18, 1.64, 1.39 and 0.35 ppm is assigned to an ethene coordinated to titanium. In the ^{13}C NMR spectrum the resonances for the ethene are found at 49.14 ($^2J_{CP}$ = 10.0 Hz, $^1J_{CH}$ = 145.8 Hz) and 44.45 ppm ($^1J_{CH}$ = 147.5 Hz).



Ti(II)
ethene adduct

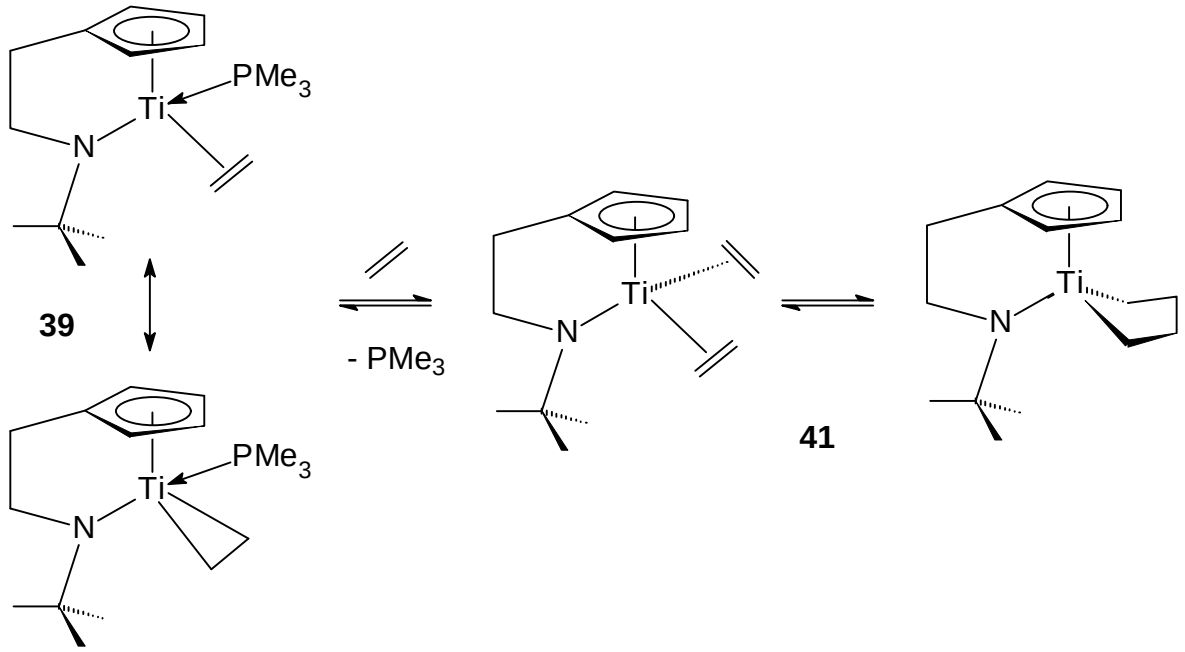
Ti(IV)
titanacyclopropane

Figure 3.

The bonding of the ethene ligand in **39** can be considered either as a coordinated ethene to a divalent titanium or as a metallacyclopropane with two sp^3 carbons (Figure 3). NMR data provides indication of which bonding type prevails. The chemical shifts of the ethene protons (2.2-0.3 ppm) are comparable with, for example, those of the methyl ligands in $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiMe_2$ (0.47 ppm) and the benzylic protons in $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2Ph)_2$ (2.73, 2.27 ppm). Also the ^{13}C resonances for the complexed ethene (49.14 and 44.45 ppm) compare well with the one found for the methyl ligand in $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiMe_2$ (47.14 ppm) but are dramatically shifted upfield compared with $Cp^*_2Ti(C_2H_4)$

(105.1 ppm) [33] and free ethene (123 ppm). Hence the conclusion seems justified that **39** can be best represented as a titanacyclopropane species with oxidation state IV rather than an ethene titanium II complex. An example of separate Ti(II) and Ti(IV) isomers has been observed for the constrained-geometry titanium diene complexes $[C_5Me_4SiMe_2NR]Ti(R'CHCH{=}CHCHR')$.[34] Changing the amido substituent R from *t*-Bu into Ph, the diene fragment changes from predominantly π-bound to partly π-bound and σ-bound.

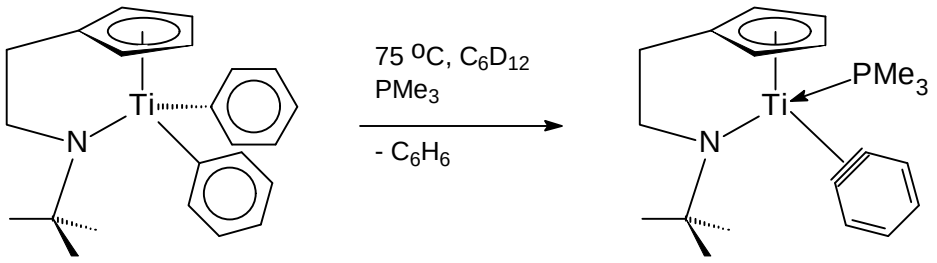
Attemps to substitute the ethene in **39** by propene or to insert propene failed. When a large excess of propene was added **39** remained unchanged. In the ^1H NMR spectrum no resonance of free ethene was observed. The propene complex $[C_5H_4(CH_2)_2N$-*t*-$Bu]Ti(C_3H_6)(PMe_3)$ (**40**) was prepared independently from $[C_5H_4(CH_2)_2N$-*t*-$Bu]TiCl_2$ with 2 eq. of *n*-PrMgCl in the presence of PMe_3. ^1H, ^{13}C and ^{31}P NMR data showed that all 4 possible isomers had been formed. The fact that treatment of **40** with 1 eq. of ethene leads to complete conversion to **39** illustrates the far better affinity of ethene compared to propene. Furthermore, the facile olefin exchange indicates that **39** behaves, at least partly, as a η^2-olefin Ti(II) species, even though NMR spectroscopy suggests otherwise.



Scheme 7. Equilibrium between $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_2H_2)(PMe_3)$ (**39**) and $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2)_4$ (**41**) and PMe_3 in the presence of ethene.

Reaction of **39** with an excess of ethene resulted immediately in a color change from dark purple to brown. ^{1}H NMR spectroscopy showed the mixture to be an equilibrium between **39**, ethene, the metallacylopentane complex $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2)_4$ (**41**) and free PMe_3 (Scheme 7). Titanacyclopentane complexes have been reported for Cp_2Ti[35] and Cp^*_2Ti compounds[33] but were never isolated and no structural data are available. $Cp_2Ti(CH_2)_4$ decomposes already at -30 ^{o}C and $Cp^*_2Ti(CH_2)_4$ is in equilibrium with $Cp^*_2Ti(\eta^2$-$C_2H_4)$ and ethene. When $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ (**4**) was treated at low temperature (-80 ^{o}C) with $ClMg(CH_2)_4MgCl$ a yellow solution was obtained on warming to -40 ^{o}C. Further raising of the temperature resulted in a black solution. The yellow color observed propably can be attributed to the titanacyclopentane complex **41**. At higher temperatures this complex looses ethene and generates the unstable Lewis-base free ethene compound $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_2H_4)$ (**42**). A black solid was obtained which could not be characterized.[36] Performing the reaction of **4** with $ClMg(CH_2)_4MgCl$ in the presence of PMe_3 gave **39** and ethene (Scheme 6).[37]

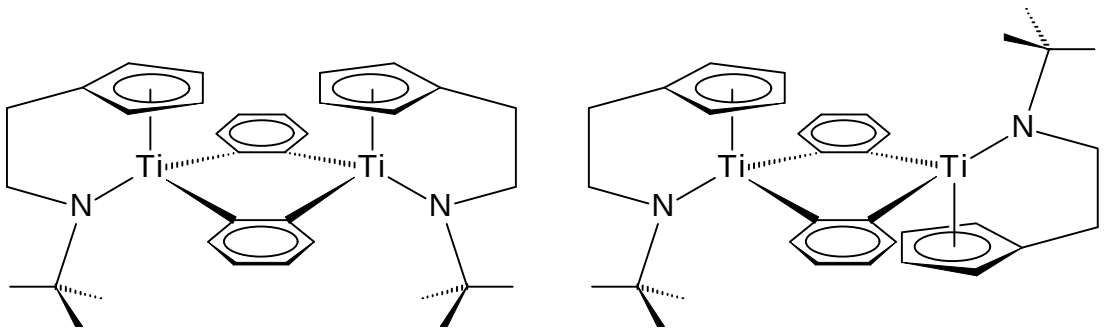
3.7.2 Generation of Benzyne Complexes: Heating (75 ^{o}C, 30 min.) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiPh_2$ in C_6D_{12} in the presence of PMe_3 resulted in the formation of the benzyne complex $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**) (Scheme 8) and 1 eq. of benzene (^{1}H NMR). A preparative synthesis yielded 53% of pure material. The complex was fully characterized with ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. The structure was elucidated by single crystal X-ray diffraction. A full discussion concerning the synthesis, structure and reactivity towards unsaturated substrates like alkenes, alkynes, nitriles and ketones will be given in the next chapter.



26 **43**

Scheme 8.

In the absence of a Lewis-base, thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiPh_2$ (**26**) in cyclohexane (55-60 ^oC, 5 h) gave an orange precipitate. ^1H and ^{13}C NMR spectra (C_6D_{12}) reveal the formation of a highly symmetric complex. Resonances are found at 7.92, 7.00, 6.19, 4.87, 4.05, 2.85 and 0.73 ppm which integrate in 2 : 2 : 2 : 2 : 2 : 2 : 9 ratio. This suggests the formation of a Lewis-base free benzyne complex and this observation is supported by the ^{13}C NMR spectrum which show resonances in the aromatic part at 188.71 (s), 139.60 (d) and 133.48 (d) ppm indicative for a benzyne or *o*-phenylene ligand.



A B

Figure 4. Two possible structures for $\{[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)\}_2$ (**44**).

From the low solubility of the orange compound in organic solvents, the complex was tentativily formulated as a dimer $\{[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)\}_2$ (**44**) with two *ortho*-phenylene moieties bridging between the metal centers, but higher associations cannot be excluded. Adopting a dinuclear species for **44**, two structures are possible (Figure 4). Thermolysis of **26** first generates the monomeric $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)$ (**45**) which dimerizes to **44**. That **44** must have at least a dimeric stucture is indicated by its slow reaction with PMe_3 (10 h, 75 ^oC) to **43** in contrast to the fast formation of **43** by thermolysis of **26** in the presence of PMe_3, under the same conditions.

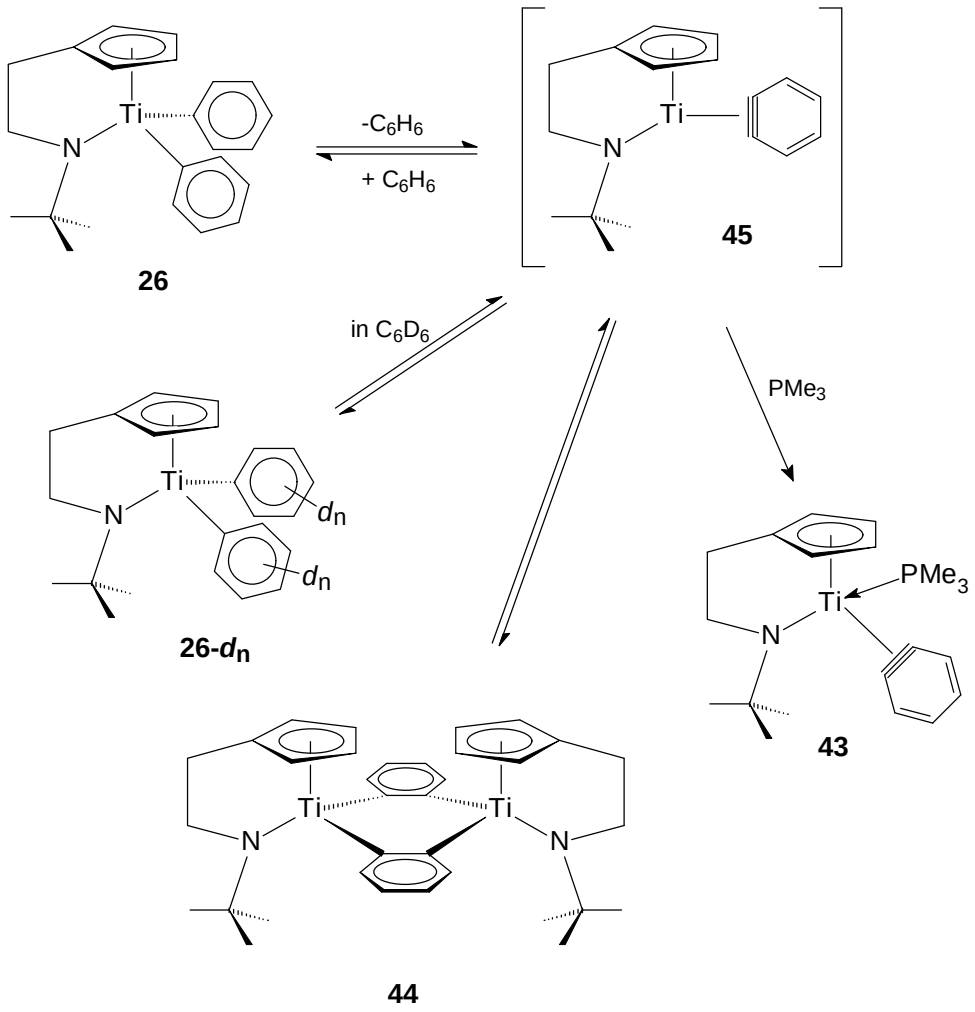
Table 4. Selected ^1H and ^{13}C NMR data for some *o*-phenylene compounds compared with complexes **26**, **43** and **44**.

Compound	H_3, H_6	H_4, H_5	C_1, C_2	ref
$\{[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)\}_2$ (**44**)	7.93	7.00	188.71	
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)(PMe_3)$ (**43**)	7.82, 7.64	7.16	190.73, 184.53	
$[C_5H_4(CH_2)_2N$-*t*-Bu$]TiPh_2$ (**26**)			C_{ipso}: 192.50	

$[Mg_4(C_6H_4)_4](THF)_4$	8.12	7.23	189.1	38
$[Zn_2(C_6H_4)_2](THF)_4$	7.37	6.28	169.3	40

The quarternary carbons of the *ortho*-phenylene moiety of **44** show shifts similar as found for **43** (190.73, 184.53 ppm) and **26** (192.50 ppm). Several polynuclear *ortho*-phenylene compounds have been reported for magnesium,[38] mercury[39] and zinc.[40] The NMR data of **44** resemble those of the tetrameric *ortho*-phenylene magnesium compound $[Mg_4(C_6H_4)_4](THF)_4$ (Table 4). The formation of Lewis base free *ortho*-phenylene titanium **44** is unprecedented and has not been reported for Cp_2Ti and Cp^*_2Ti systems.

The thermolysis of $[C_5H_5(CH_2)_2N$-*t*-Bu]$TiPh_2$ (**26**) was studied in detail in C_6D_6 and C_6D_{12} at 55 ^oC. In C_6D_6 **44** and benzene were formed. First, a rather rapid decrease of **26** and a simultaneous increase of **44** and benzene was observed but after 10 hours the ratio of **26** and **44** did not change further and the system appeared to reach an equilibrium. Further heating resulted in slow decomposition of **26** and **44** (products not identified). In C_6D_{12}, at similar concentrations, a rapid and complete conversion of **26** within 6 h was observed together with the formation of **44** (55 %), benzene and unidentified decomposition products. Further heating resulted in further decomposition of **44**.

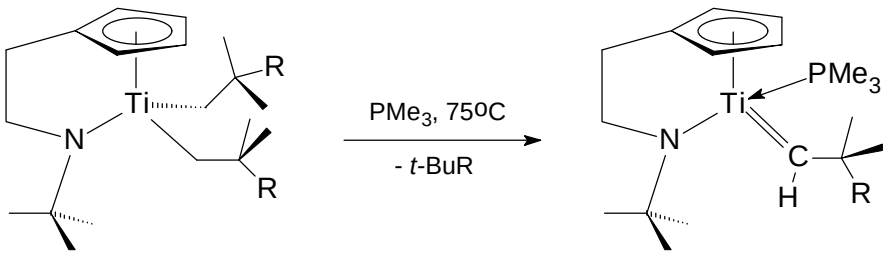


Scheme 9. Reversible decomposition of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiPh_2$ (**26**) and trapping of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)$ with PMe_3.

The difference in behavior of **26** in C_6D_6 and C_6D_{12} can be rationalized by assuming that **44** is in equilibrium with $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(C_6H_4) (**45**) which reacts with C_6D_6 to give the partially phenyl deuterated **26** (Scheme 9). In addition, the integral of the phenyl and *o*-phenylene resonances decreased with respect to those of the $[C_5H_5(CH_2)_2N$-*t*-Bu] ligand and benzene. This indicates that complex **44** is involved in σ-bond metathesis with C_6D_6 giving deuterated $[C_5H_5(CH_2)_2N$-*t*-Bu]Ti(Ph-$d_n)_2$. The formation of a mixture of **26** and **44** after heating of **44** in C_6D_6 (75 ^oC) is a strong evidence for an equilibrium between **26** and **44** in benzene.[41] In C_6D_{12} **26** is converted into **44** and other decomposition products which presumably are formed by another reaction path from **26** and/or the hypothetical monomeric species $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(C_6H_4) (**45**).

3.7.3 Generation of Alkylidenes: When a yellow solution of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti($CH_2CMe_3)_2$ (**29**) was heated at 75 ^oC in C_6D_{12} in the presence of 2 equivalents of PMe_3 it turned red-brown. After 1.5 h, ^1H NMR spectroscopy showed the exclusive formation of one organometallic product and neopentane. In the Cp range (6.8-4.8 ppm) 5 resonances were present integrating for 1H each. One resonance (d, 6.28 ppm) displayed a small coupling of 1.37 Hz, which is attributed to a J_{PH} coupling.[42] This proton was tentatively assigned to the α-proton of the alkylidene species $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti=C(H)$CMe_3(PMe_3)$ (**46**). This alkylidene is proposed to be formed by α-H abstraction from one of the neopentyl groups of the bis(neopentyl) complex **29** (Scheme 10).

Thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti($CH_2CMe_2Ph)_2$ (**31**) proceeded much slower reaching completion only after 8.5 hours (NMR). The ^1H NMR spectrum showed the same general features as **46** and it is reasonable to indentify this as the neophylidene complex $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti=C(H)$CMe_2Ph(PMe_3)$ (**47**).



29: R = Me
31: R = Ph

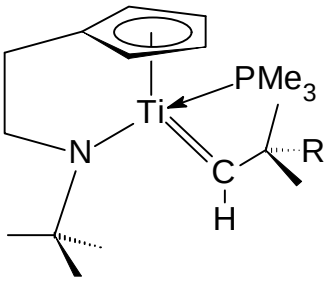
46: R = Me
47: R = Ph

Scheme 10.

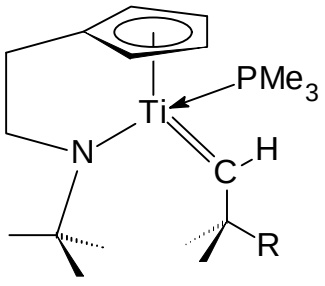
The thermolysis of **29** proceeds similar to that of $Cp_2Ti(CH_2CMe_3)_2$ and $CpV(CH_2CMe_3)_2(PMe_3)$ giving the alkylidene complex **46**. In contrast to $CpV(CH_2CMe_2Ph)_2(PMe_3)$[22] which shows δ-H activation of a phenyl group on the alkyl ligand, producing a metallacycle, **31** undergoes exclusively α-hydrogen abstraction affording the neophylidene complex **47**.

The alkylidene complexes **46** and **47** are easily prepared on multigram scale as red-brown crystalline solids in resp 68 and 66% yield. In C_6D_6, the ^{1}H NMR spectrum show the =C(*H*)CMe_2R (R = Me, Ph) resonances (6.39 and 6.44 ppm resp.) as phosphorus coupled doublets ($^3J_{PH}$ = 1.70, 1.28 Hz resp). The Cp-amido ligand resonances in the ^{1}H NMR spectra of **46** and **47** have roughly the same appearance as those of the ethene (**39**) and the benzyne (**43**) complexes showing four resonances for the Cp protons and a ABCD spin system for the C_2-bridge. ^{13}C and ^{1}H-coupled ^{13}C NMR spectra show the carbene resonances at resp 251.39 ppm ($^1J_{CH}$ = 83.1 and $^2J_{CP}$ = 13.1 Hz) and 245.96 ppm ($^1J_{CH}$ = 88.0 and $^2J_{CP}$ = 12.8 Hz).

Analogous to a C-C double bond, the double bond of metal alkylidenes is fixed and has a high barrier for rotation around metal-carbon axis. For Cp_2 metal alkylidenes, the p-orbital of the alkylidene is generally believed to be perpendicular to the plane through the metal and the cyclopentadienyl centroids.[43] This fixed orientation of the alkylidene ligand causes, in the case of **46** and **47**, two possible orientations (Figure 4). ^{1}H, ^{13}C and ^{31}P NMR spectra show for each compound that one rotamer is present and NOESY NMR experiments suggest structure **A** as the most likely.



A



B

Figure 4. Possible rotamers for **46** and **47**.

Both **46** and **47** show small $^{1}J_{CH}$ coupling constants (83.1 and 88.0 Hz resp.) for the α-carbon of the alkylidene which indicate an agostic interaction between this α-proton and titanium. Such interactions have also been reported for [η^5-C_5H_3-1,3-($SiMe_2CH_2P(i$-$Pr_2)$)$_2$]Zr=C(H)Ph(Cl),[44] $CpTi(OC(CMe_2C_6H_4CMe_2)CH_2PMe_2C(H)CMe_3$[45] and $CpV=C(H)CMe_3(DMPE)$.[22]

Table 5. Selected NMR data of group IV alkylidene complexes

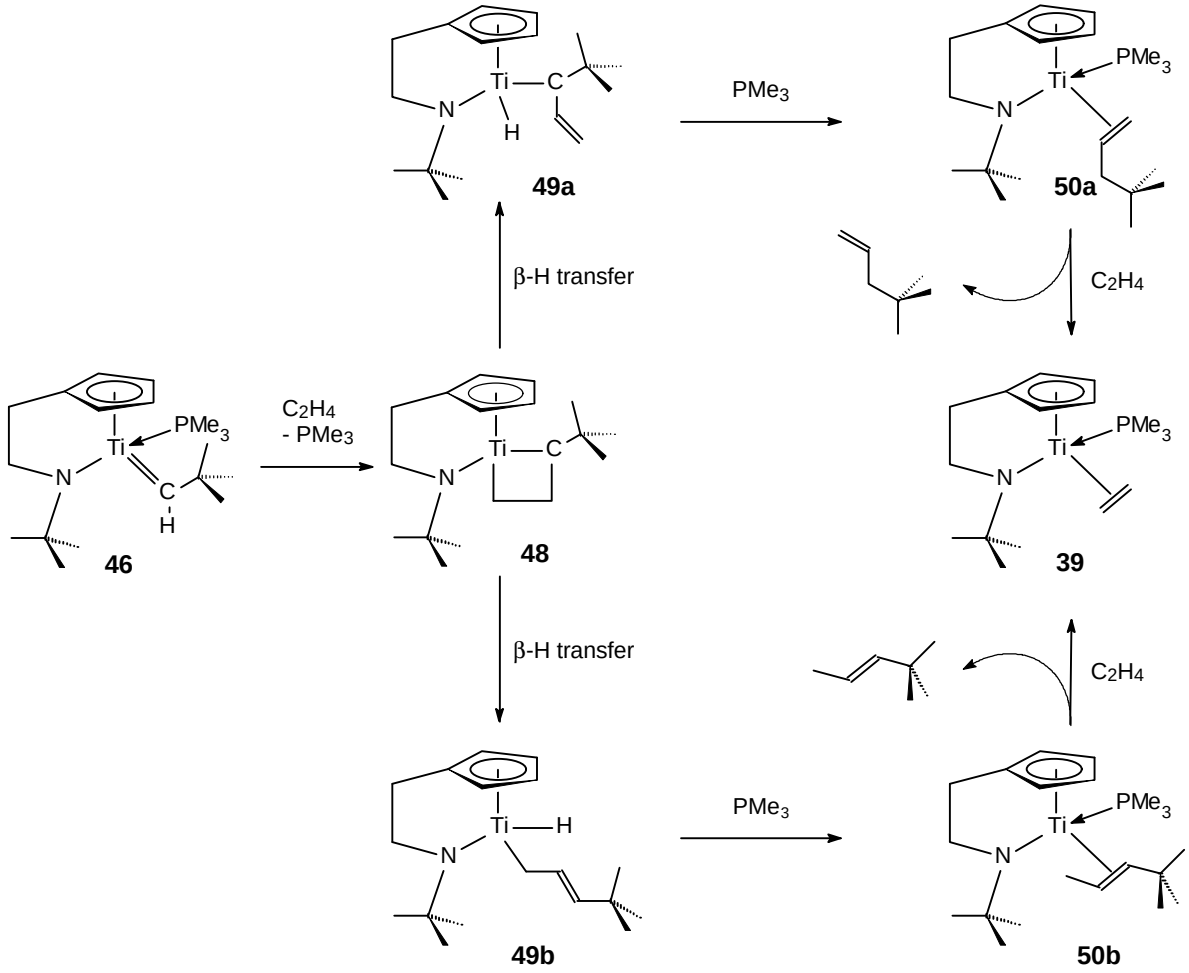
Compounds	δ M=C*H*	δ M=*C*H	$^{1}J_{CH}$ (Hz)	$^{2}J_{CP}$ (Hz)	ref.
$[C_5H_4(CH_2)_2N$-*t*-Bu]Ti=C(H)$CMe_3(PMe_3)$ (**46**)	6.39	251.39	83.1	13.1	-
$[C_5H_4(CH_2)_2N$-*t*-Bu]Ti=C(H)$CMe_2Ph(PMe_3)$ (**47**)	6.44	245.96	88.0	12.8	-
$Cp_2Ti=CH_2(PMe_3)$	12.1	286	127	31.7	21f
$Cp_2Ti=C(H)CMe_3(PMe_3)$	12.32	312.9	110	27	21g
$Cp_2Ti=C(H)CMe_2C(H)=CH_2$	12.06	306.9	111	26.6	46
$CpTi(OC(CMe_2C_6H_4CMe_2)CH_2PMe_2)=C(H)CMe_3$	11.92	278.1	95	12.2	45
$Cp_2Zr=CH_2(PPh_3)$	11.0	248	121	14.6	47
[η^5-C_5H_3-1,3-($SiMe_2CH_2P(i$-$Pr_2)$)$_2$]Zr=C(H)Ph(Cl)	8.08	229.4	86.8	8.0	44

Compared to the NMR data with other group 4 metal alkylidene complexes, the resonance of the α-proton of **46** and **47** shows a large upfield shift (Table 5). The electronic unsaturation of the 16 electron complexes can not be the main reason for the upfield shift. In the related 16 electron complex $CpTi(OC(CMe_2C_6H_4CMe_2)CH_2PMe_2)=C(H)CMe_3$, the α-H resonance is observed at 11.92 ppm.[45] Possibly this strong upfield shift is due to anisotropic effects but without further structural data available no definite conclusions are possible.

3.7.3.1 Insertion of Olefins: To check if the complexes **46** and **47** are active in ROMP catalysis they were reacted with an excess of norbornene but no catalytic activity was observed (25 to 80 ^{o}C). In an additional experiment the neopentylidene complex **46** was reacted with 2 eq. of ethene (50 ^{o}C) but showed no metathesis. Instead formation of the ethene complex $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti$(C_2H_4)(PMe_3)$ was observed.[48] Apparently, the insertion product **48** undergoes fast β-hydrogen transfer followed by reductive elimination and coordination of 4,4-dimethyl-1-pentene or 4,4-dimethyl-2-pentene yielding the phosphine

olefin adducts **50a-b**. A second ethene molecule replaces the 4,4-dimethyl-1-pentenes giving the ethene complex **39** (Scheme 11).

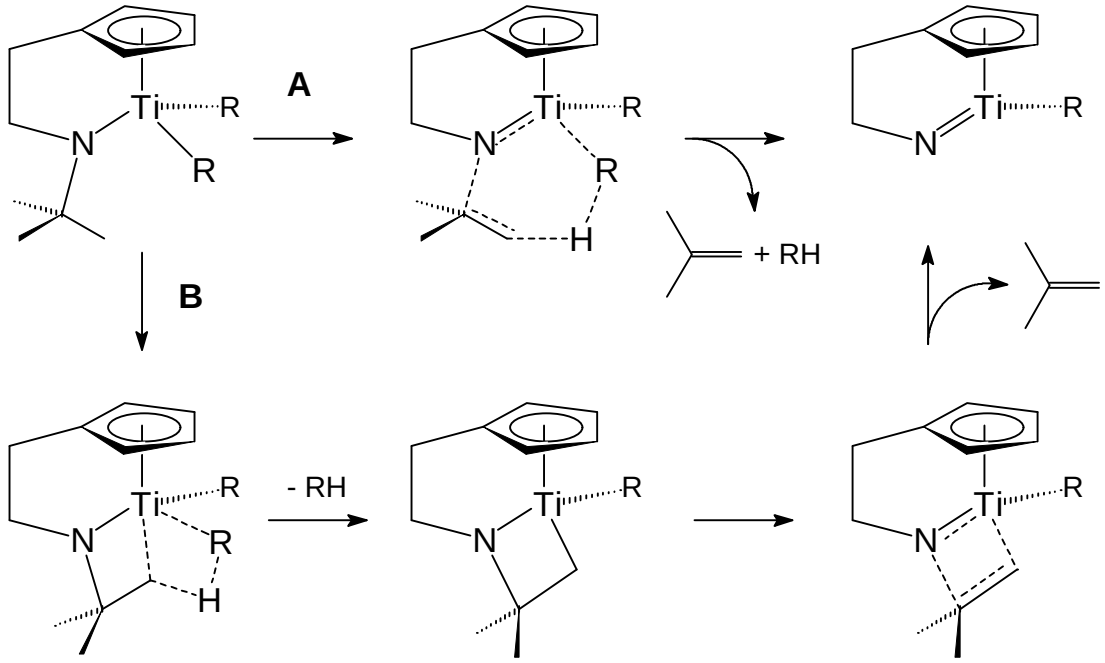
A similar preference for β-hydrogen transfer has been observed for the related complex $CpTi(OC(CMe_2C_6H_4CMe_2)CH_2PMe_2)=C(H)CMe_3$ although this process is much slower and the metallacyclobutane species could be isolated and fully characterized.[45] The two systems mentioned here differ remarkably from the well known Tebbe reagent[49] which is an excellent precursor for a catalytically active species in olefin metathesis, ROMP catalysis and the living polymerization of norbornene.[50]



Scheme 11. Reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti=C(H)$CMe_3(PMe_3)$ (**46**) with ethene resulting in the formation of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti$(C_2H_4)(PMe_3)$ (**39**), 4,4-dimethyl-1-pentene and 4,4-dimethyl-2-pentene.

3.8 Activation of the Cp-Amido Ligands:

Thermolysis of the complexes $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiMe_2$ (**17**) (100 ^oC) and $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2Ph)_2$ (**22**) (120 ^oC) in the presence of PMe_3 did not proceed by α-hydrogen abstraction of the carbyl ligands. When monitored by ^1H NMR spectroscopy, formation of methane (toluene) and, in both cases, *iso*-butene (^1H NMR, GC-MS) was observed. No information about the identity of the organometallic product(s) could be obtained as the ^1H NMR spectra showed broad resonances in the region of 7-4 and 3-1 ppm. Similar observations were made during the thermolysis of $[C_5H_4(CH_2)_2N$-*i*-Pr]$Ti(CH_2Ph)_2$ (**21**) (120 ^oC). In this case toluene and propene were liberated. However, in the case of $[C_5H_4(CH_2)_2N$-*i*-Pr]$TiMe_2$ (100 ^oC) only methane was found and ^1H NMR showed further the usual broad resonances at 7-4 and 3-1 ppm. As already mentioned before, the C_3-bridged *iso*-propyl amido titanium dimethyl and dibenzyl complexes **19** and **24** are far less stable than the C_2-bridged complexes.



Scheme 12. Two possible mechanism for C-H activation of the amido alkyl group in $[C_5H_4(CH_2)_2N$-*t*-Bu]TiR_2 complexes (R = Me, CH_2Ph).

The elimination of propene and *iso*-butene indicates activation of the amido substituent, most probably by γ-H transfer generating imido-like species. Two routes are possible (Scheme 12), one with a six membered transition state inwhich RH, *iso*-butene and the imido species are formed in one step (**A**) or a two-step process with a metalla-aza-cyclobutane compound as intermediate (**B**). The imido species may decompose or form

dimers or higher aggregates. In fact, activation of the amido substituents is not so surprising since especially the *t*-Bu group can point a methyl towards the metal center, so that C-H activation becomes feasible. This may be also the case for *i*-Pr substituents and gives a reasonable explanation for the decreased stability of the C_3-bridged carbyl complexes, since the amido group is pushed closer to the metal than in the C_2-bridged analogues (*cf.* Chapter 2).

The possibility that $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)(PMe_3)$ (**43**) is generated via the metalla-aza cyclobutane intermediate can be excluded. Only a minor amount of C_6D_5H was obtained (<5%, ^{1}H NMR) by thermolysis of deca-deutero $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti($Ph-$d_5)_2$ (**26-d_{10}**)[51] in the presence of excess PMe_3 (C_6D_{12}, 65 ^oC)[52]. Considering the reaction conditions, it is very likely that also the alkylidenes **46** and **47** are generated directly from the corresponding bis alkyl complexes without the metalla-aza cyclobutane intermediate.

The participation of the iso-propyl and tert-butyl group of the $[C_5H_4(CH_2)_{2(3)}N$-*i*-Pr] and $[C_5H_4(CH_2)_2N$-*t*-Bu] ligands respectively in the thermolyses of $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiMe_2$ and $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$ (R = *i*-Pr, *t*-Bu) is a clear indication that the Cp-amido ligands are chemically not inert. This may have important consequences for the use of these Cp-amido complexes as catalysts, especially at higher temperatures. From the thermolyses of the $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiR_2$ complexes (R = Me, Et, CH_2Ph, Ph, CH_3CMe_3, CH_2CMe_2Ph), a fair estimate can be made about the thermal stability limit for $[C_5H_4(CH_2)_2NR]$ ligands. Below 100 ^oC the $[C_5H_4(CH_2)_2NR]$ ligands do not interfere in C-H activation processes but this becomes increasingly important at higher temperatures. The temperature limit for C_3-bridged Cp-amido ligands is according to Table 3 considerably lower than 100 ^oC.

3.9 Concluding Remarks.

The amido functionalized cyclopentadienyl titanium dichlorides $[C_5H_4(CH_2)_nNR]TiCl_2$ are good precursors for the preparation of mono and bis(carbyl) complexes $[C_5H_4(CH_2)_nNR]TiR'_2$. The successful isolation of stable Ti(IV) *iso*-propyl and allyl compounds from the reaction with the corresponding Grignard reagents clearly demonstrates the better resistance against reduction of the dichlorides.

The bis-alkyl complexes$[C_5H_4(CH_2)_2N$-*t*-Bu$]TiR'_2$ are thermally more stable than the Cp_2Ti analogues. In contrast, the bis-aryl complexes are less stable. In general, the thermal stability of the bis carbyl compounds strongly depends on the nature of the Cp-amido

ligands. The C_2-bridged complexes are considerably more stable than the C_3-bridged analogues.

Like the Cp_2TiR_2 and $Cp^*_2TiR_2$ systems, the $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiR_2$ complexes undergo C-H activation processes. Phosphine stablilized olefin, aryne and alkylidene complexes can be isolated and studied. It was possible to isolate a Lewis base free benzyne species $\{[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)\}_2$ but stable Lewis base free olefin $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_nH_{2n})$ and alkylidene complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti{=}C(H)R$ could not be isolated. The alkylidene complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti{=}C(H)R(PMe_3)$ (**46**, R = *t*-Bu; **47**, R = CMe_2Ph) are not active in ROMP catalysis. Instead of olefin metathesis, the metallacyclobutane complex undergo fast β-hydrogen elimination giving olefin coordinated organometallic species.

From the decomposition studies on the $[C_5H_4(CH_2)_nNR]TiR'_2$ complexes it is evident that the Cp-amido ligands do not behave as inert spectator ligands but can be involved in C-H activation processes. From the thermolyses of the $[C_5H_4(CH_2)_nNR]TiR'_2$ compounds a lower limit of about 100 ^oC is estimated for Cp-amido ligand activation. The resulting organometallic complexes, however, could not be identified and the precise reaction pathway remains to be elucidated.

3.10 Experimental.

For general considerations see Chapter 2.

General procedure for syntheses of $[C_5H_4(CH_2)_nNR]TiR'_2$ complexes: All syntheses were performed in diethylether. Reagents were taken from stock solutions in ether or THF (MeLi, EtMgBr, *n*-PrMgCl, *i*-PrMgCl, C_3H_5MgCl, $PhCH_2Cl$, PhMgBr) or pentane (Me_3CCH_2Li, $PhMe_2CCH_2Li$) and added by means of a syringe or dropping funnel to a cooled (-80 to -40 ^oC) suspension of the titanium dichloride $[C_5H_4(CH_2)_nNR]TiCl_2$. The mixtures were then slowly warmed to room temperature and kept at this temperature for 0.5 h. The volatiles were removed in vacuum and the residue was stripped several times with 5-10 mL of pentane. The residue was extracted with pentane and crystallized by concentrating and subsequent cooling of the solutions. When the products were oils, the pentane was removed in vacuum. Unless mentioned otherwise, the workup was performed at room temperature

$[C_5H_4(CH_2)_2NMe]TiMe_2$ (15): $[C_5H_4(CH_2)_2NMe]TiCl_2$ (1.39 g, 5.8 mmol), MeLi (11.6 mmol) (-80 ^oC, 40 mL, 1.5 h, workup at 0 ^oC). Yield: 0.71 g (3.6 mmol, 61%, yellow crystals). ^1H NMR (200 MHz, C_6D_6): δ 6.21 (m, J_{HH} = 2.58 Hz, 2H, C_5H_4); 5.60 (m, J_{HH} = 2.58 Hz, 2H, C_5H_4); 3.67 (s, 3H, NMe); 3.49 (t, $^3J_{HH}$ = 5.55 Hz, 2H, NCH_2); 2.39 (t, $^3J_{HH}$ = 5.4 Hz, 2H, $C_5H_4\underline{CH_2}$); 0.49 (s, 6H, Me). ^{13}C NMR

(50 MHz, C_6D_6): δ 134.64 (s, C_5H_4-*ipso*); 115.33 (d, $^1J_{CH}$ = 170.0 Hz, C_5H_4); 110.17 (d, $^1J_{CH}$ = 173.1 Hz, C_5H_4); 73.41 (t, $^1J_{CH}$ = 134.4 Hz, NCH_2); 45.71 (q, $^1J_{CH}$ = 118.1 Hz, Me); 42.58 (q, $^1J_{CH}$ = 134.1 Hz, NMe); 28.40 (t, $^1J_{CH}$ = 127.3 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3082 (w), 2782 (m), 2752 (m), 2674 (m), 2178 (w), 1763 (m), 1674 (m), 1615 (m), 1489 (m), 1447 (sh, Nujol), 1435 (sh), 1412 (m), 1389 (m), 1346 (w), 1314 (m), 1256 (w), 1233 (s), 1194 (m), 1167 (m), 1103 (s), 1067 (w), 1051 (s), 1042 (s), 1011 (s), 964 (s), 920 (m), 866 (s), 835 (w), 810 (vs), 724 (w), 696 (s), 646 (s), 590 (s), 544 (s), 498 (m), 422 (m). Anal. Calcd: C, 60.31; H, 8.60; Ti, 24.05. Found: C, 60.23; H, 8.68; Ti, 23.93.

[$C_5H_4(CH_2)_2$N-i-Pr]$TiMe_2$ (16): [$C_5H_4(CH_2)_2$N-*i*-Pr]$TiCl_2$ (1.44 g, 5.37 mmol), MeLi (10.8 mmol) (-50 ^oC, 60 mL, 2 h). Yield: 1.02 g (4.49 mmol, 83%, yellow crystals). ^1H NMR (300 MHz, C_6D_6): δ 6.25 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 6.07 (hept, $^3J_{HH}$ = 6.41 Hz, 1H, $C\underline{H}Me_2$); 5.57 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.50 (d, $^3J_{HH}$ = 6.77 Hz, 2H, NCH_2); 2.38 (d, $^3J_{HH}$ = 6.77 Hz, 2H, $C_5H_4C\underline{H_2}$); 1.11 (d, $^3J_{HH}$ = 6.59 Hz, 6H, $CH\underline{Me_2}$); 0.42 (s, 6H, Me). ^{13}C NMR (75.4 MHz, C_6D_6): δ 134.47 (s, C_5H_4-*ipso*); 115.04 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.41 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 61.26 (t, $^1J_{CH}$ = 138.6 Hz, NCH_2); 50.01 (d, $^1J_{CH}$ = 131.9 Hz, $\underline{CH}Me_2$); 43.44 (q, $^1J_{CH}$ = 118 Hz, Me); 28.99 (t, $^1J_{CH}$ = 128.8 Hz, $C_5H_4\underline{CH_2}$); 20.49 (q, $^1J_{CH}$ = 125.7 Hz, $CH\underline{Me_2}$). IR (cm^{-1}):

[$C_5H_4(CH_2)_2$N-t-Bu]$TiMe_2$ (17): [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiCl_2$ (0.85 g, 3.0 mmol), MeLi (6.0 mmol), (-80 ^oC, 30 mL, 1 h). Yield: 0.55 g (2.3 mmol, 76%, yellow oil). ^1H NMR (200 MHz, C_6D_6): δ 6.30 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 5.64 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 3.41 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.27 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.54 (s, 9H, *t*-Bu); 0.47 (s, 6H, 2 Me). ^{13}C NMR (50 MHz, C_6D_6): δ 133.24 (s, C_5H_4-*ipso*); 114.60 (d, $^1J_{CH}$ = 171.6 Hz, C_5H_4); 113.62 (d, $^1J_{CH}$ = 178.7 Hz, C_5H_4); 62.34 (t, $^1J_{CH}$ = 134.9 Hz, NCH_2); 59.50 (s, $\underline{C}Me_3$); 47.14 (q, $^1J_{CH}$ = 118.9 Hz, Me); 29.88 (q, $^1J_{CH}$ = 125.3 Hz, $C\underline{Me_3}$); 29.46 (t, $^1J_{CH}$ = 128.5 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}, neat): 3088 (w), 2968 (vs), 2933 (vs), 2864 (s), 2835 (s), 2789 (w), 2764 (w), 2673 (w), 1811 (w), 1774 (w), 1720 (w), 1678 (w), 1628 (w), 1494 (w), 1471 (m), 1442 (m), 1388 (m), 1357 (s), 1342 (m), 1321 (w), 1244 (s), 1224 (m), 1194 (vs), 1105 (w), 1074 (s), 1043 (m), 1026 (w), 983 (s), 947 (s), 904 (vw), 868 (s), 844 (m), 815 (vs), 769 (m), 680 (m), 646 (m), 567 (s), 534 (w), 497 (s).

[$C_5H_4(CH_2)_3$NMe]$TiMe_2$. (18): [$C_5H_4(CH_2)_3$NMe]$TiCl_2$ (2.23 g, 8.8 mmol), MeLi (17.5 mmol), (-80 ^oC, 50 mL, 2 h, workup at 0 ^oC). Yield: 1.55 g (7.3 mmol, 82%, yellow crystals). ^1H NMR (200 MHz, C_6D_6): δ (6.19 t, $^3J_{HH}$ = 2.42 Hz, 2H, C_5H_4); 5.33 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 4.07 (s, 3H, NMe); 2.62 (m, 2H, NCH_2); 2.14 (m, 2H, $C_5H_4\underline{CH_2}$); 1.54 (m, 2H, $\underline{CH_2}CH_2N$); 0.40 (s, 6H, Me). ^{13}C NMR (50 MHz, C_6D_6): δ 122.34 (s, C_5H_4-*ipso*); 113.79 (d, $^1J_{CH}$ = 173.9 Hz,, C_5H_4); 111.42 (d, $^1J_{CH}$ = 172.8 Hz, C_5H_4); 59.40 (t, $^1J_{CH}$ = 133.0 Hz, NCH_2); 44.36 (q, $^1J_{CH}$ = 119.0 Hz, Me); 40.56 (q, $^1J_{CH}$ = 134.4 Hz, NMe); 30.86 (t, $^1J_{CH}$ = 126.1 Hz, $C_5H_4\underline{CH_2}$); 26.62 (t, $^1J_{CH}$ = 127.3 Hz, $\underline{CH_2}CH_2N$). IR (cm^{-1}): 3111 (w), 3097 (w), 2823 (sh, Nujol), 2789 (m), 2715 (w), 2700 (m), 1805 (w), 1763 (w), 1713 (w), 1668 (m), 1616 (m), 1494 (m), 1440 (s), 1411 (m), 1394 (m), 1367 (m), 1334 (m), 1273 (m), 1253 (s), 1186 (s), 1163 (m), 1109 (s), 1084 (w), 1072 (m), 1051 (m), 1031 (s), 987 (s), 931 (s), 906 (s), 880 (w), 860 (s), 845

(w), 810 (vs), 661 (m), 611 (m), 547 (s), 505 (vs), 439 (w). Anal. Calcd: C, 61.98: H, 8.98; Ti, 22.47. Found: C, 62.30; H, 8.89; Ti, 22.58.

[$C_5H_4(CH_2)_3$N-i-Pr]$TiMe_2$ (19): [$C_5H_4(CH_2)_3$N-i-Pr]$TiCl_2$ (1.45 g, 5.14 mmol), MeLi (10.3 mmol) (-50 ^oC, 60 mL, 2h). Yield: 0.96 g (3.98 mmol, 77%, yellow crystals). ^1H NMR (300 MHz, C_6D_6): δ 7.00 (hept, $^3J_{HH}$ = 6.13 Hz, 1H, C*H*Me_2); 6.53 (m, J_{HH} = 2.38 Hz, 2H, C_5H_4); 5.29 (m, J_{HH} = 2.38 Hz, 2H, C_5H_4); 2.61 (m, 2H, NCH_2); 2.17 (m, 2H, $C_5H_4\underline{CH_2}$); 1.28 (d, $^3J_{HH}$ = 6.23 Hz, 6H, $CH\underline{Me_2}$); 0.30 (s, 6H, Me). ^{13}C NMR (75.4 MHz, C_6D_6): δ 122.51 (s, C_5H_4-*ipso*); 114.12 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 111.30 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 46.57 (t, $^1J_{CH}$ = 133.1 Hz, NCH_2); 45.43 (d, $^1J_{CH}$ = 125.7 Hz, $\underline{CH}Me_2$); 41.94 (q, $^1J_{CH}$ = 118.8 Hz, Me); 32.44 (t, $^1J_{CH}$ = 126.4 Hz, $\underline{CH_2}CH_2N$); 26.95 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$); 20.54 (q, $^1J_{CH}$ = 126.1 Hz, $CH\underline{Me_2}$).

[$C_5H_4(CH_2)_2$NMe]$Ti(CH_2Ph)_2$ (20): [$C_5H_4(CH_2)_2$NMe]$TiCl_2$ (1.02 g, 4.25 mmol), $PhCH_2MgCl$ (8.5 mmol), (-80 ^oC, 30 mL, 3 h). Yield: 0.99 g (2.82 mmol, 66%, red crystals). ^1H NMR (200 MHz, C_6D_6): δ 7.19 (m, 4H, 2 x *m*-Ph); 6.90 (m, 2H, 2 x *p*-Ph); 6.80 (m, 4H, 2 x *o*-Ph); 5.93 (t, $^3J_{HH}$ = 2.78 Hz, 2H, C_5H_4); 5.15 (t, $^3J_{HH}$ = 2.78 Hz, 2H, C_5H_4); 3.40 (s, 3H, NMe); 3.34 (t, $^3J_{HH}$ = 6.84 Hz, 2H, NCH_2); 2.40 (d, $^2J_{HH}$ = 9.83 Hz, 2H, 2 x $Ph\underline{CH_2}$); 2.23 (t, $^3J_{HH}$ = 6.84 Hz, 2H, $C_5H_4\underline{CH_2}$); 2.19 (d, $^2J_{HH}$ = 9.83 Hz, 2H, 2 x $Ph\underline{CH_2}$). ^{13}C NMR (50 MHz, C_6D_6): δ 149.08 (s, Ph-*ipso*); 136.79 (s, C_5H_4-*ipso*); 128.50 (d, $^1J_{CH}$ = 168.2 Hz, *m*-Ph); 125.68 (d, $^1J_{CH}$ = 153.5 Hz, *o*-Ph); 121.55 (d, $^1J_{CH}$ = 156.3 Hz, *p*-Ph); 117.30 (d, $^1J_{CH}$ = 172.3 Hz, C_5H_4); 113.63 (d, $^1J_{CH}$ = 165.9 Hz, C_5H_4); 75.90 (t, $^1J_{CH}$ = 122.3 Hz, $\underline{CH_2}Ph$); 73.70 (t, $^1J_{CH}$ = 135.4 Hz, NCH_2); 44.39 (q, $^1J_{CH}$ = 134.6 Hz, NMe); 28.51 (t, $^1J_{CH}$ = 128.8 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3059 (m), 3014 (m), 2775 (w), 1938 (w), 1851 (w), 1803 (w), 1793 (w), 1776 (w), 1722 (w), 1691 (w), 1591 (s), 1479 (m), 1446 (w), 1406 (w), 1311 (sh, Nujol), 1288 (w), 1257 (vw), 1234 (w), 1211 (s), 1178 (m), 1149 (w), 1089 (m), 1064 (w), 1049 (m), 1037 (vw), 1026 (m), 1008 (s), 983 (m), 962 (s), 918 (m), 873 (s), 839 (w), 815 (vs), 796 (w), 744 (vs), 696 (vs), 646 (m), 584 (m), 561 (m), 540 (m), 528 (w), 515 (w), 457 (m), 423 (s). Anal. Calcd.: C, 75.21; H, 7.17; Ti, 13.63. Found: C, 75.14; 7.14; Ti, 13.58.

[$C_5H_4(CH_2)_2$N-i-Pr]$Ti(CH_2Ph)_2$ (21): [$C_5H_4(CH_2)_2$N-*i*-Pr]$TiCl_2$ (1.08 g, 4.03 mmol), $PhCH_2MgCl$ (8.4 mmol), (0 ^oC, 30 mL, 3 h). Yield: 1.31 g (3.45 mmol, 84%, red oil). ^1H NMR (300 MHz, C_6D_6): δ 7.19 (t, $^3J_{HH}$ = 7.51 Hz, 4H, *m*-Ph); 6.89 (t, $^3J_{HH}$ = 7.33 Hz, 2H, *p*-Ph); 6.83 (d, $^3J_{HH}$ = 7.32 Hz, 4H, *o*-Ph); 5.83 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.73 (sept, $^3J_{HH}$ = 6.50 Hz, 1H, $C\underline{H}Me_2$); 5.25 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.41 (t, $^3J_{HH}$ = 6.78 Hz, 2H, NCH_2); 2.38 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $C\underline{H_2}Ph$); 2.26 (t, $^3J_{HH}$ = 6.78 Hz, 2H, $C_5H_4C\underline{H_2}$); 2.17 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $C\underline{H_2}Ph$); 1.03 (d, $^3J_{HH}$ = 6.50 Hz, 6H, $CH\underline{Me_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 149.99 (s, *ipso*-Ph); 136.59 (s, *ipso*-C_5H_4); 128.52 (d, $^1J_{CH}$ = 153.8 Hz, *o*-Ph); 125.72 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 121.38 (d, $^1J_{CH}$ = 156.3 Hz, *p*-Ph); 116.85 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 115.04 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 74.40 (t, $^1J_{CH}$ = 120.9 Hz, $Ph\underline{C}H_2$); 61.78 (t, $^1J_{CH}$ = 135.5 Hz, NCH_2); 51.23 (d, $^1J_{CH}$ = 130.6 Hz, $\underline{C}HMe_2$); 29.06 (t, $^1J_{CH}$ = 129.4 Hz, $C_5H_4\underline{C}H_2$); 20.45 (q, $^1J_{CH}$ = 126.1 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3069 (m), 3055 (m), 3015 (s), 2965 (s), 2926 (s), 2853 (s), 2770 (vw),

1933 (w), 1846 (w), 1790 (w), 1717 (w), 1593 (s), 1487 (s), 1449 (m), 1385 (m), 1358 (m), 1339 (m), 1300 (m), 1209 (s), 1177 (m), 1154 (m), 1107 (w), 1055 (m), 1040 (m), 1028 (m), 990 (s), 876 (w), 855 (w), 818 (s), 745 (s), 698 (s), 646 (m), 619 (w), 561 (w), 521 (w), 449 (m), 424 (m), 409 (m).

[$C_5H_4(CH_2)_2$N-*t*-Bu]Ti($CH_2Ph)_2$ (22): [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiCl_2$ 1.21 g (4.3 mmol), $PhCH_2MgCl$ (8.6 mmol), (0 °C, 30 mL, 2h). Yield: 1.15 g (3.0 mmol, 69%, red oil). ^{1}H NMR (200 MHz, C_6D_6): δ 7.22 (m, 4H, 2 x *m*-Ph); 6.90 (m, 2H, 2 x *p*-Ph); 6.82 (m, 4H, 2 x *o*-Ph); 5.92 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 5.27 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 3.29 (t, $^3J_{HH}$ = 6.63 Hz, 2H, NCH_2); 2.73 (d, $^2J_{HH}$ = 9.40 Hz, 2H, Ph$\underline{CH_2}$); 2.27 (d, $^2J_{HH}$ = 9.40 Hz, 2H, Ph$\underline{CH_2}$); 2.10 (t, $^3J_{HH}$ = 6.63 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.50 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 150.70 (s, Ph-*ipso*); 135.67 (s, C_5H_4-*ipso*); 128.45 (d, $^1J_{CH}$ = 154.0 Hz, *o*-Ph); 125.73 (d, $^1J_{CH}$ = 153.1 Hz, *m*-Ph); 121.59 (d, $^1J_{CH}$ = 156.3 Hz, *p*-Ph); 118.04 (d, $^1J_{CH}$ = 173.7 Hz, C_5H_4); 117.42 (d, $^1J_{CH}$ = 171.4 Hz, C_5H_4); 78.04 (t, $^1J_{CH}$ = 120.5 Hz, $\underline{CH_2}$Ph); 62.61 (d, $^1J_{CH}$ = 135.4 Hz, CH_2N); 60.96 (s, $\underline{C}Me_3$); 30.16 (t, $^1J_{CH}$ = 129.0 Hz, $C_5H_4\underline{CH_2}$); 30.11 (d, $^1J_{CH}$ = 125.3 Hz, $C\underline{Me_3}$). IR (cm^{-1}, neat): 3084 (m), 3061 (m), 3026 (m), 2966 (s), 2916 (m), 2837 (s), 2702 (w), 1946 (w), 1863 (w), 1805 (w), 1805 (w), 1662 (w), 1595 (s), 1493 (s), 1450 (s), 1388 (m), 1359 (s), 1302 (w), 1240 (m), 1203 (vs), 1097 (vs), 1072 (vs), 1026 (m), 983 (m), 945 (m), 908 (w), 868 (m), 842 (sh), 815 (vs), 746 (vs), 698 (vs), 682 (sh), 656 (m), 605 (w), 561 (m), 459 (m).

[$C_5H_4(CH_2)_3$NMe]Ti($CH_2Ph)_2$ (23): [$C_5H_4(CH_2)_3$NMe]$TiCl_2$ (1.86 g, 7.35 mmol), $PhCH_2MgCl$ (14.7 mmol), (-80 °C, 30 mL, 3 h). Yield: 1.83 g (5.0 mmol, 68%, red oil). ^{1}H NMR (200 MHz, C_6D_6): δ 7.17 (m, 4H, 2 x *m*-Ph); 6.88 (m, 2H, 2 x *p*-Ph); 6.77 (m, 4H, 2 x *o*-Ph); 6.21 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 4.89 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 3.87 (s, 3H, NMe); 2.43 (m, 2H, NCH_2); 2.45 (d, $^2J_{HH}$ = 9.83 Hz, 2H, Ph$\underline{CH_2}$); 2.20 (d, $^2J_{HH}$ = 9.83 Hz, Ph$\underline{CH_2}$); 1.96 (m, 2H, $C_5H_4\underline{CH_2}$); 1.36 (m, 2H, $NCH_2\underline{CH_2}$). ^{13}C NMR (50 MHz, C_6D_6): δ 150.05 (s, Ph-*ipso*); 128.38 (d, $^1J_{CH}$ = 154.1 Hz, *m*-Ph); 125.59 (d, $^1J_{CH}$ = 153.6 Hz, *o*-Ph); 124.84 (s, C_5H_4-*ipso*); 121.46 (d, $^1J_{CH}$ = 155.6 Hz, *p*-Ph); 117.59 (d, $^1J_{CH}$ = 174.2 Hz, C_5H_4); 114.20 (d, $^1J_{CH}$ = 171.2 Hz, C_5H_4); 74.53 (t, $^1J_{CH}$ = 122.4 Hz, Ph$\underline{CH_2}$); 60.11 (t, $^1J_{CH}$ = 135.0 Hz, NCH_2); 42.55 (q, $^1J_{CH}$ = 134.5 Hz, NMe); 30.87 (t, $^1J_{CH}$ = 126.7 Hz, $C_5H_4\underline{CH_2}$); 26.47 (t, $^1J_{CH}$ = 127.7 Hz, $NCH_2\underline{CH_2}$).

[$C_5H_4(CH_2)_3$N-*i*-Pr]Ti($CH_2Ph)_2$ (24): [$C_5H_4(CH_2)_3$N-*i*-Pr]$TiCl_2$ (of 1.22 g, 4.33 mmol), $PhCH_2MgCl$ (8.9 mmol), (0 °C, 30 mL, 3 h). Yield: 1.57 g (3.99 mmol, 92%, red oil). ^{1}H NMR (300 MHz, C_6D_6): δ 7.19 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.89 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.81 (d, $^3J_{HH}$ = 7.69 Hz, 4H, *o*-Ph); 6.57 (sept, $^3J_{HH}$ = 6.11 Hz, C$\underline{H}Me_2$); 6.10 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 4.96 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 2.58 (m, 2H, NCH_2); 2.34 (d, $^2J_{HH}$ = 9.88 Hz, 2H, $C\underline{H_2}$Ph); 2.15 (d, $^2J_{HH}$ = 9.88 Hz, 2H, $C\underline{H_2}$Ph); 2.03 (m, 2H, $C_5H_4C\underline{H_2}$); 1.40 (m, 2H, $NCH_2C\underline{H_2}$); 1.22 (d, $^3J_{HH}$ = 6.11 Hz, 6H, $CH\underline{Me_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 151.39 (s, Ph-*ipso*); 128.44 (d, $^1J_{CH}$ = 153.8 Hz, *o*-Ph); 125.91 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 125.10 (s, C_5H_4-*ipso*); 121.43 (d, $^1J_{CH}$ = 156.3 Hz, *p*-Ph); 118.84 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 114.13 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 72.88 (t, $^1J_{CH}$ = 120.9 Hz, $\underline{C}H_2$Ph); 47.37 (t, $^1J_{CH}$ = 133.1 Hz, NCH_2); 46.91 (d, $^1J_{CH}$ = 124.5 Hz, $\underline{C}HMe_2$); 32.79 (t, $^1J_{CH}$ = 127.0 Hz, $C_5H_4\underline{CH_2}$); 26.87 (t, $^1J_{CH}$ = 127.6

Hz, $NCH_2\underline{CH_2}$); 20.59 (q, $^1J_{CH}$ = 126.2 Hz, $CH\underline{Me_2}$). IR (cm^{-1}, neat): 3069 (m), 3055 (m), 3015 (m), 2967 (m), 2928 (s), 2853 (m), 2774 (vw), 2693 (w), 1933 (w), 1848 (w), 1790 (w), 1723 (w), 1593 (s), 1485 (s), 1449 (m), 1389 (m), 1358 (s), 1302 (vw), 1275 (w), 1244 (w), 1209 (s), 1177 (m), 1155 (m), 1109 (w), 1088 (w), 1072 (w), 1053 (m), 1030 (m), 1015 (m), 984 (m), 937 (m), 899 (m), 870 (w), 822 (s), 808 (s), 746 (s), 698 (s), 615 (w), 559 (w), 521 (m), 449 (m).

[$C_5H_4(CH_2)_2$NMe]$TiPh_2$ (25): [$C_5H_4(CH_2)_2$NMe]$TiCl_2$ (of 1.43 g, 5.96 mmol), PhLi (1.04 g, 12.4 mmol), (-80 °C, 30 mL, 2h, workup at -15 °C). Yield: 0.51 g (1.58 mmol, 26%, yellow-brown crystals). ^{1}H NMR (300 MHz, C_6D_{12}): δ 7.30 (m, 4H, 2 x *m*-Ph); 6.94 (m, 6H, 2 x *o*-Ph + 2 x *p*-Ph); 6.30 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 5.99 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 3.93 (t, $^3J_{HH}$ = 6.60 Hz, 2H, NCH_2); 3.62 (s, 3H, NMe); 2.86 (t, $^3J_{HH}$ = 6.60 Hz, 2H, $C_5H_4\underline{CH_2}$). ^{13}C NMR (75.4 MHz, C_6D_{12}): δ 191.50 (s, Ph-*ipso*); 136.67 (s, C_5H_4-*ipso*); 133.93 (d, $^1J_{CH}$ = 156.4 Hz, *m*-Ph); 127.91 (d, $^1J_{CH}$ = 157.6 Hz, *p*-Ph); 127.10 (d, $^1J_{CH}$ = 154.1 Hz, *o*-Ph); 117.50 (d, $^1J_{CH}$ = 170.7 Hz, C_5H_4); 112.98 (d, $^1J_{CH}$ = 172.2 Hz, C_5H_4); 74.57 (t, $^1J_{CH}$ = 134.0 Hz, NCH_2); 43.74 (q, $^1J_{CH}$ = 134.8 Hz, NMe); 29.43 (t, $^1J_{CH}$ = 128.7 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3105 (w), 3080 (w), 3045 (s), 2787 (m), 2733 (vw), 2681 (w), 1954 (w), 1876 (w), 1817 (w), 1768 (w), 1722 (w), 1687 (w), 1631 (w), 1589 (vw), 1564 (m), 1527 (m), 1487 (w), 1429 (w), 1413 (s), 1348 (m), 1325 (w), 1309 (w), 1288 (w), 1259 (w), 1232 (m), 1190 (m), 1165 (w), 1153 (vw), 1095 (m), 1057 (s), 1039 (w), 1008 (s), 989 (m), 962 (s), 920 (w), 906 (w), 868 (m), 812 (vs), 777 (m), 721 (vs), 700 (vs), 646 (m), 563 (s), 520 (m), 449 (s), 420 (m).

[$C_5H_4(CH_2)_2$N-*t*-Bu]$TiPh_2$ (26): [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiCl_2$ (1.13 g, 4.0 mmol), PhMgBr (8.1 mmol), (-80 °C, 30 mL, 2h, workup at 0 °C). Yield: 0.64 g (1.75 mmol, 44%, orange-yellow crystals). ^{1}H NMR (300 MHz, C_6D_{12}): δ 7.31 (m, 4H, 2 x *m*-Ph); 6.99 (m, 6H, 2 x *p*-Ph + 2 x *o*-Ph); 6.21 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 6.04 (t, $^3J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 4.01 (t, $^3J_{HH}$ = 6.47 Hz, 2H, NCH_2); 2.83 (t, $^1J_{HH}$ = 6.47 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.41 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_{12}): δ 192.50 (s, Ph-*ipso*); 136.49 (s, C_5H_4-*ipso*); 134.25 (d, $^1J_{CH}$ = 154.1 Hz, *m*-Ph); 127.19 (d, $^1J_{CH}$ = 155.1 Hz, *o*-Ph); 126.93 (d, $^1J_{CH}$ = 157.6 Hz, *p*-Ph); 117.84 (d, $^1J_{CH}$ = 175.3 Hz, C_5H_4); 115.18 (d, $^1J_{CH}$ = 174.8 Hz, C_5H_4); 64.07 (t, $^1J_{CH}$ = 134.5 Hz, NCH_2); 61.87 (s, $\underline{C}Me_3$); 30.89 (t, $^1J_{CH}$ = 128.4 Hz, $C_5H_4\underline{CH_2}$); 28.96 (q, $^1J_{CH}$ = 125.4 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3113 (w), 3090 (w), 3043 (m), 1952 (w), 1874 (w), 1726 (w), 1631 (w), 1562 (w), 1552 (w), 1493 (m), 1460 (sh, Nujol), 1411 (m), 1357 (m), 1344 (w), 1325 (w), 1298 (w), 1240 (m), 1207 (sh), 1190 (s), 1074 (s), 1055 (s), 1016 (w), 985 (s), 941 (m), 906 (w), 869 (m), 844 (m), 820 (vs), 773 (m), 727 (vs), 702 (vs), 565 (m), 526 (m), 480 (w), 453 (m). Anal Calcd: C, 75.61; H, 7.45; Ti, 13.11. Found: C, 75.17; H, 7.35; Ti, 12.97.

[$C_5H_4(CH_2)_3$NMe]$TiPh_2$. (27): [$C_5H_4(CH_2)_3$NMe]$TiCl_2$ (1.23 g, 4.84 mmol), PhLi (0.79 g, 9.40 mmol), (-80 °C, 25 mL, 4 h, workup at 0 °C). Yield: 0.36 g (1.07 mmol, 22%, green-yellow crystals). ^{1}H NMR (300 MHz, C_6D_6): δ 7.32 (m, 4H, 2 x *o*-Ph); 7.12 (m, 6H, 2 x *m*-Ph + 2 x *p*-Ph); 6.41 (t, $^3J_{HH}$ = 2.57 Hz, C_5H_4); 5.53 (t, $^3J_{HH}$ = 2.57 Hz, C_5H_4); 3.78 (s, 3H, NMe); 2.61 (m, 2H, NCH_2); 2.24 (m, 2H, $C_5H_4\underline{CH_2}$); 1.68 (m, 2H, $NCH_2\underline{CH_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 191.06 (s, Ph-*ipso*); 134.00 (d, $^1J_{CH}$ = 155.6

Hz, *m*-Ph); 127.10 (d, $^{1}J_{CH}$ = 157.1 Hz, *o*-Ph); 127.00 (d, $^{1}J_{CH}$ = 159.5 Hz, *p*-Ph); 124.19 (s, C_5H_4-*ipso*); 115.96 (d, $^{1}J_{CH}$ = 174.8 Hz, C_5H_4); 113.69 (d, $^{1}J_{CH}$ = 168.6 Hz, C_5H_4); 59.67 (t, $^{1}J_{CH}$ = 134.4 Hz, NCH_2); 40.27 (q, $^{1}J_{CH}$ = 135.3 Hz, NMe); 30.88 (t, $^{1}J_{CH}$ = 126.9 Hz, $C_5H_4\underline{CH_2}$); 26.70 (t, $^{1}J_{CH}$ = 127.4 Hz, $NCH_2\underline{CH_2}$). IR (cm^{-1}): 3111 (w), 3080 (w), 3041 (s), 3020 (sh), 2823 (w), 2789 (w), 2714 (w), 2696 (w), 2002 (w), 1957 (w), 1863 (w), 1807 (w), 1710 (w), 1666 (w), 1622 (w), 1564 (w), 1496 (m), 1440 (m), 1411 (s), 1363 (m), 1334 (w), 1271 (w), 1253 (s), 1186 (s), 1163 (w), 1151 (vw), 1107 (m), 1076 (w), 1057 (s), 1035 (m), 989 (m), 933 (m), 902 (m), 879 (w), 860 (m), 844 (w), 815 (vs), 721 (vs), 698 (vs), 609 (m), 559 (m), 449 (m), 424 (w).

[C$_5$H$_4$(CH$_2$)$_2$NMe]Ti(CH$_2$CMe$_3$)$_2$ (28): $[C_5H_4(CH_2)_2NMe]TiCl_2$ (1.73 g, 7.2 mmol), $LiCH_2CMe_3$ (1.05 g, 13.6 mmol), (-80 °C, 40 mL 3.5 h). Yield: : 1.90 g (6.1 mmol, 85%, yellow-brown oil). ^{1}H NMR (200 MHz, C_6D_6): δ 6.37 (t, $^{3}J_{HH}$ = 2.35 Hz, 2H, C_5H_4); 5.86 (t, $^{3}J_{HH}$ = 2.35 Hz, 2H, C_5H_4); 3.67 (s, 3H, NMe); 3.52 (t, $^{3}J_{HH}$ = 6.84 Hz, 2H, NCH_2); 2.44 (t, $^{3}J_{HH}$ = 6.84 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.65 (d, $^{2}J_{HH}$ = 10.68 Hz, 2H, $\underline{CH_2}CMe_3$); 1.17 (d, $^{2}J_{HH}$= 10.68 Hz, 2H, $\underline{CH_2}CMe_3$); 0.94 (s, 18H, 2 x $CH_2C\underline{Me_3}$). ^{13}C NMR (50 MHz, C_6D_6); δ 133.02 (s, C_5H_4-*ipso*); 116.00 (d, $^{1}J_{CH}$ = 170.1 Hz, C_5H_4); 108.40 (d, $^{1}J_{CH}$ = 171.7 Hz, C_5H_4); 92.61 (t, $^{1}J_{CH}$ = 108.0 Hz, $\underline{CH_2}CMe_3$); 73.60 (t, $^{1}J_{CH}$ = 137.3 Hz, NCH_2); 46.67 (q, $^{1}J_{CH}$ = 134.0 Hz, NMe); 38.04 (s, $CH_2\underline{C}Me_3$); 34.17 (q, $^{1}J_{CH}$ = 123.6 Hz, $CH_2C\underline{Me_3}$); 28.63 (t, $^{1}J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$).

[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ti(CH$_2$CMe$_3$)$_2$ (29): $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (2.97 g, 10.54 mmol), $LiCH_2CMe_3$ (1.65 g, 21.1 mmol), (-80 °C, 90 mL, 2.5 h. workup at 0 °C). Yield: 2.54 g (7.2 mmol, 68%, orange-yellow crystals). ^{1}H NMR (200 MHz, C_6D_6): δ 6.60 (t, $^{3}J_{HH}$ = 2.56 Hz, C_5H_4); 5.90 (t, $^{3}J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 3.41 (t, $^{3}J_{HH}$ = 6.63 Hz, 2H, NCH_2); 2.25 (t, $^{3}J_{HH}$ = 6.63 Hz, 2H, $C_5H_4\underline{CH_2}$); 2.05 (d, $^{2}J_{HH}$ = 11.11 Hz, 2H, $\underline{CH_2}CMe_3$); 1.58 (s, 9H, N-*t*-Bu); 1.00 (s, 18H, 2 x $CH_2C\underline{Me_3}$); 0.97 (d, $^{2}J_{HH}$ = 11.11 Hz, 2H, $\underline{CH_2}CMe_3$). ^{13}C NMR (50 MHz, C_6D_6): δ 131.73 (s, C_5H_4-*ipso*); 115.41 (d, $^{1}J_{CH}$ = 170.2 Hz, C_5H_4); 110.67 (d, $^{1}J_{CH}$ = 173.2 Hz, C_5H_4); 93.94 (t, $^{1}J_{CH}$ = 109.0 Hz, $\underline{CH_2}CMe_3$); 63.04 (t, $^{1}J_{CH}$ = 134.5 Hz,, NCH_2); 60.77 (s, $N\underline{C}Me_3$); 38.31 (s, $CH_2\underline{C}Me_3$); 34.64 (q, $^{1}J_{CH}$ = 123.9 Hz, $CH_2C\underline{Me_3}$); 30.61 (t, $^{1}J_{CH}$ = 128.4 Hz, $C_5H_4\underline{CH_2}$); 30.56 (q, $^{1}J_{CH}$ = 125.4 Hz, $NC\underline{Me_3}$). Anal. Calcd: C, 71.36; H, 11.12; Ti, 13.55. Found: C, 71.31; H, 11.11; Ti, 13.43.

[C$_5$H$_4$(CH$_2$)$_2$NMe]Ti(CH$_2$CMe$_2$Ph)$_2$ (30): $[C_5H_4(CH_2)_2NMe]TiCl_2$ (1.50 g, 6.25 mmol), $LiCH_2CMe_2Ph$ (1.65 g, 11.77 mmol), (-70 °C, 50 mL, 2 h). Yield: 1.64 g (3.76 mmol, 60%, yellow-brown crystals). ^{1}H NMR (200 MHz, C_6D_6): δ 7.33-7.05 (m, 10H, 2 x $CH_2CMe_2\underline{Ph}$); 5.59 (t, $^{3}J_{HH}$ = 2.57 Hz, 2H, C_5H_4); 5.30 (t, $^{3}J_{HH}$ = 2.57 Hz, 2H, C_5H_4); 3.57 (s, 3H, NMe); 3.46 (t, $^{3}J_{HH}$ = 6.84 Hz, 2H, NCH_2); 2.28 (t, $^{3}J_{HH}$ = 6.84 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.84 (d, $^{2}J_{HH}$ = 10.69 Hz, 2H, 2 x $\underline{CH_2}CMe_2Ph$); 1.41 (d, $^{2}J_{HH}$ = 10.69 Hz, 2H, 2 x $\underline{CH_2}CMe_2Ph$); 1.29 (s, 6H, 2 x $CH_2C\underline{Me_2}Ph$); 1.23 (s, 6H, $CH_2C\underline{Me_2}Ph$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 153.03 (s, Ph-*ipso*); 133.21 (s, C_5H_4-*ipso*); 128.05 (d, $^{1}J_{CH}$ = 158.1 Hz, CH_2CMe_2-*o*-Ph); 125.69 (d, $^{1}J_{CH}$ = 155.1 Hz, CH_2CMe_2-*m*-Ph); 125.39 (d, $^{1}J_{CH}$ = 159.6 Hz, CH_2CMe_2-*p*-Ph); 116.96 (d, $^{1}J_{CH}$ = 170.7 Hz, C_5H_4); 109.05 (d, $^{1}J_{CH}$ = 174.3 Hz, C_5H_4); 90.39 (t, $^{1}J_{CH}$ = 109.5 Hz, $\underline{CH_2}CMe_2Ph$);

73.51 (t, $^{1}J_{CH}$ = 134.5 Hz, NCH_2); 46.38 (q, $^{1}J_{CH}$ = 134.0 Hz, NMe); 43.98 (s, $CH_2\underline{C}Me_2Ph$); 35.29 (q, $^{1}J_{CH}$ = 125.4 Hz, $CH_2C\underline{Me_2}Ph$); 32.53 (q, $^{1}J_{CH}$ = 123.4 Hz, $CH_2C\underline{Me_2}Ph$); 28.53 (t, $^{1}J_{CH}$ = 128.4 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3101 (w), 3082 (m), 3059 (m), 3018 (w), 2816 (w), 2793 (w), 2783 (w), 2737 (w), 2721 (w), 2679 (w), 1936 (w), 1866 (w), 1797 (w), 1599 (m), 1493 (s), 1444 (m), 1408 (m), 1357 (s), 1311 (w), 1275 (m), 1259 (w), 1234 (m), 1188 (s), 1168 (m), 1099 (m), 1082 (w), 1053 (m), 1039 (w), 1028 (m), 1010 (s), 964 (m), 920 (w), 904 (w), 871 (m), 854 (w), 839 (m), 810 (vs), 765 (s), 742 (vw), 700 (vs), 648 (m), 596 (s), 574 (m), 555 (m), 520 (m), 491 (m), 464 (m), 424 (m).

[$C_5H_4(CH_2)_2$N-t-Bu]Ti(CH_2CMe_2Ph)$_2$ (31): [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiCl_2$ (1.37 g, 4.85 mmol), $LiCH_2CMe_2Ph$ (1.32 g, 9.42 mmol), (-70 ^{o}C, 50 mL, 2 h). Yield: 1.56 g (3.27 mmol, 67%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.41-7.15 (m, 10H, 2 x $CH_2CMe_2\underline{Ph}$); 5.71 (t, $^{3}J_{HH}$ = 2.35 Hz, 2H, C_5H_4); 5.49 (t, $^{3}J_{HH}$ = 2.35 Hz, 2H, C_5H_4); 3.48 (t, $^{3}J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.28 (d, $^{2}J_{HH}$ = 10.69 Hz, 2H, 2 x $\underline{CH_2}CMe_2Ph$); 2.23 (t, $^{3}J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.65 (s, 9H, *t*-Bu); 1.45 (d, $^{2}J_{HH}$ = 10.69 Hz, 2H, 2 x $\underline{CH_2}CMe_2Ph$); 1.37 (s, 6H, 2 x $CH_2C\underline{Me_2}Ph$); 1.32 (s, 6H, 2 x $CH_2C\underline{Me_2}Ph$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 152.82 (s, $CH_2CMe_2\underline{Ph}$-*ipso*); 131.80 (s, C_5H_4-*ipso*); 128.18 (d, $^{1}J_{CH}$ = 158.6 Hz, CH_2CMe_2-*o*-Ph); 125.81 (d, $^{1}J_{CH}$ = 155.1 Hz, CH_2CMe_2-*m*-Ph); 125.49 (d, $^{1}J_{CH}$ = 160.1 Hz, CH_2CMe_2-*p*-Ph); 116.43 (d, $^{1}J_{CH}$ = 171.2 Hz, C_5H_4); 111.02 (d, $^{1}J_{CH}$ = 174.25 Hz, C_5H_4); 92.59 (t, $^{1}J_{CH}$ = 109.8 Hz, $\underline{CH_2}CMe_2Ph$); 92.53 (t, $^{1}J_{CH}$ = 109.8 Hz, $\underline{CH_2}CMe_2Ph$); 62.88 (t, $^{1}J_{CH}$ = 134.7 Hz, NCH_2); 60.65 (s, $N\underline{C}Me_3$); 44.26 (s, $CH_2\underline{C}Me_2Ph$); 35.68 (q, $^{1}J_{CH}$ = 125.4 Hz, $CH_2C\underline{Me_2}Ph$); 35.64 (q, $^{1}J_{CH}$ = 125.4 Hz, $CH_2C\underline{Me_2}Ph$); 33.37 (q, $^{1}J_{CH}$ = 125.4 Hz, $CH_2C\underline{Me_2}Ph$); 30.56 (q, $^{1}J_{CH}$ = 124.9 Hz, $NC\underline{Me_3}$); 30.44 (t, $^{1}J_{CH}$ = 128.4 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3105 (w), 3082 (m), 3053 (m), 3028 (m), 3016 (w), 1946 (w), 1597 (s), 1493 (s), 1442 (m), 1358 (s), 1344 (sh), 1325 (w), 1276 (m), 1244 (m), 1228 (w), 1184 (vs), 1155 (w), 1116 (m), 1078 (w), 1064 (s), 1040 (s), 1028 (s), 981 (s), 941 (m), 927 (m), 908 (w), 869 (m), 842 (m), 827 (vs), 765 (vs), 702 (vs); 684 (w), 646 (m), 588 (m), 569 (m), 561 (m), 530 (m), 488 (w), 474 (m). Anal. Calcd: C, 77.96; H, 9.08; Ti, 10.03. Found: 77.94; H, 9.04; Ti, 10.12.

[$C_5H_4(CH_2)_3$NMe]Ti(CH_2CMe_2Ph)$_2$ (32): [$C_5H_4(CH_2)_3$NMe]$TiCl_2$ (1.41 g, 5.55 mmol), $LiCH_2CMe_2Ph$ (1.51 g, 10.77 mmol), (-70 ^{o}C, 50 mL, 2h). Yield: 1.59 g (3.54 mmol, 66%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.31-7.08 (m, 10H, 2 x $CH_2CMe_2\underline{Ph}$); 6.03 (t, $^{3}J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 4.99 (t, $^{3}J_{HH}$ = 2.56 Hz, 2H, C_5H_4); 3.94 (s, 3H, NMe); 2.59 (m, 2H, NCH_2); 2.03 (m, 2H, $C_5H_4\underline{CH_2}$); 1.84 (d, $^{2}J_{HH}$ = 11.11 Hz, 2H, 2 x $\underline{CH_2}CMe_2Ph$); 1.51 (m, 2H, $NCH_2\underline{CH_2}$); 1.45 (d, $^{2}J_{HH}$ = 11.11 Hz, 2H, 2 x $\underline{CH_2}CMe_2Ph$); 1.27 (s, 6H, 2 x $CH_2C\underline{Me_2}Ph$); 1.16 (s, 6H, $CH_2C\underline{Me_2}Ph$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 152.94 (s, $CH_2CMe_2\underline{Ph}$-*ipso*); 128.00 (d, $^{1}J_{CH}$ = 158.1 Hz, CH_2CMe_2-*o*-Ph); 125.70 (d, $^{1}J_{CH}$ = 154.6 Hz, CH_2CMe_2-*m*-Ph); 125.32 (d, $^{1}J_{CH}$ = 159.1 Hz, CH_2CMe_2-*p*-Ph); 120.84 (s, C_5H_4-*ipso*); 113.57 (d, $^{1}J_{CH}$ = 170.7 Hz, C_5H_4); 112.17 (d, $^{1}J_{CH}$ = 173.7 Hz, C_5H_4); 87.95 (t, $^{1}J_{CH}$ = 111.0 Hz, $\underline{CH_2}CMe_2Ph$); 60.38 (t, $^{1}J_{CH}$ = 134.7 Hz, NCH_2); 46.05 (q, $^{1}J_{CH}$ = 133.8 Hz, NMe); 44.32 (s, $CH_2\underline{C}Me_2Ph$); 35.45 (q, $^{1}J_{CH}$ = 125.1 Hz, $CH_2C\underline{Me_2}Ph$); 32.14 (q, $^{1}J_{CH}$ = 128.9 Hz, $CH_2C\underline{Me_2}Ph$); 31.01 (t, $^{1}J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$); 26.70 (t, $^{1}J_{CH}$ = 126.7 Hz, $NCH_2\underline{CH_2}$). IR (cm^{-1}): 3101 (m), 3082 (m), 3055 (m), 3028 (w), 3016 (w), 2814 (m), 2793 (sh), 2742 (w), 2727 (w), 1942 (w), 1875 (w), 1800 (w), 1670 (w), 1624 (w), 1599 (s), 1579 (w),

1533 (vw), 1494 (s), 1442 (m), 1411 (w), 1361 (sh, nujol), 1338 (w), 1303 (vw), 1277 (m), 1249 (m), 1182 (s), 1165 (w), 1105 (m), 1078 (m), 1053 (m), 1030 (s), 993 (m), 962 (vw), 939 (m), 908 (m), 875 (w), 858 (m), 835 (w), 814 (vs), 767 (vs), 700 (vs), 667 (w), 607 (m), 570 (s), 553 (w), 468 (m), 430 (m).

[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ti(CH$_2$Ph)Cl (33): [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]TiCl$_2$ (4.05 g, 14.36 mmol), PhCH$_2$MgCl (28.6 mmol), (-40 ^{o}C, 50 mL, 5 h). Yield: 3.34 g (9.89 mmol, 69%, red crystals). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.19 (t, $^{3}J_{HH}$ = 7.69 Hz, 2H, *m*-Ph); 6.96 (d, $^{3}J_{HH}$ = 7.81 Hz, 2H, *o*-Ph); 6.89 (t, $^{3}J_{HH}$ = 7.33 Hz, 1H, *p*-Ph); 6.15 (m, 1H, C$_5$H$_4$); 5.61 (m, 2H, C$_5$H$_4$); 5.41 (m, 1H, C$_5$H$_4$); 3.50 (m, 2H, NCH$_2$); 2.97 (d, $^{2}J_{HH}$ = 9.28 Hz, 1H, PhC<u>H</u>$_2$); 2.80 (d, $^{2}J_{HH}$ = 9.28 Hz, 1H, PhC<u>H</u>$_2$); 2.23 (m, 2H, C$_5$H$_4$C<u>H</u>$_2$); 1.47 (s, 9H, CMe$_3$). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 150.37 (s, Ph-*ipso*); 138.88 (s, C$_5$H$_4$-*ipso*); 128.49 (d, $^{1}J_{CH}$ = 157.2 Hz, *o*-Ph); 126.73 (d, $^{1}J_{CH}$ = 157.8 Hz, *m*-Ph); 122.18 (d, $^{1}J_{CH}$ = 156.71 Hz, *p*-Ph); 118.96 (d, $^{1}J_{CH}$ = 169.5 Hz, C$_5$H$_4$); 117.43 (d, $^{1}J_{CH}$ = 176.0 Hz, C$_5$H$_4$); 115.86 (d, $^{1}J_{CH}$ = 176.0 Hz, C$_5$H$_4$); 114.95 (d, $^{1}J_{CH}$ = 173.7 Hz, C$_5$H$_4$); 76.06 (t, $^{1}J_{CH}$ = 124.4 Hz, Ph<u>C</u>H$_2$); 65.30 (t, $^{1}J_{CH}$ = 136.3 Hz, NCH$_2$); 62.22 (s, <u>C</u>Me$_3$); 30.09 (q, $^{1}J_{CH}$ = 125.9 Hz, C<u>Me$_3$</u>); 29.85 (t, $^{1}J_{CH}$ = 129.7 Hz, C$_5$H$_4$CH$_2$). IR (cm^{-1}): 3111 (vw), 3073 (w), 3045 (vw), 3017 (w), 1946 (vw), 1928 (w), 1863 (vw), 1845 (w), 1800 (vw), 1720 (w), 1657 (w), 1595 (s), 1481 (sh, nujol), 1448 (sh, nujol), 1421 (w), 1392 (m), 1367 (m), 1359 (m), 1340 (w), 1325(vw), 1244 m), 1224 (w), 1205 (m), 1186 (s), 1155 (w), 1070 (m), 1041 (m), 1026 (m), 981 (m), 937 (m), 925 (m), 877 (m), 837 (s), 767 (m), 744 (s), 696 (s), 682 (w), 646 (m), 561 (w), 536 (w), 482 (m), 439 (m). Anal. Calcd for C$_{18}$H$_{24}$ClNTi: C, 64.01; H, 7.16; Ti, 14.18. Found: C, 63.95; H, 7.22; Ti, 14.08.

NMR tube reaction of [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]TiCl$_2$ with [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]TiMe$_2$. A solution of 80.0 mg (0.28 mmol) of [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]TiCl$_2$ in 0.6 mL of C$_6$D$_6$ was added to 68.5 mg (0.28 mmol) of [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]TiMe$_2$. The mixture was transferred to an NMR tube. After 10 min a ^{1}H NMR spectrum was recorded. At this stage no reaction had occured. The NMR tube was heated at 50 ^{o}C and the reaction was monitored at regular intervals with ^{1}H NMR spectroscopy. The reaction was complete after 24 h. One single complex was formed which was identical with [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]Ti(Me)Cl (**34**).

NMR tube reaction of [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]TiCl$_2$ with [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ti(CH$_2$Ph)$_2$. A solution of 78.0 mg (0.28 mmol) of [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]TiCl$_2$ in 0.6 mL of C$_6$D$_6$ was added to 111 mg (0.28 mmol) of [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]Ti(CH$_2$Ph)$_2$ and transferred to an NMR tube. The NMR tube was heated at 50 ^{o}C and the reaction was monitored by ^{1}H NMR spectroscopy. After 98 h 99% conversion to [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]Ti(CH$_2$Ph)Cl had been reached.

Synthesis of [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ti(Me)Cl (34). To a cooled (0 ^{o}C) suspension of 1.02 g (3.62 mmol) of [C$_5$H$_4$(CH$_2$)$_2$N-*t*-Bu]TiCl$_2$ in 50 mL of ether, 4.6 mL 0.88 M (4.0 mmol) of MeLi in ether was added dropwise. The mixture was stirred for 1 h at room temperature. The solvent was removed and the residue was stripped with 30 mL of pentane. The residue was extracted three times with 40 mL of

toluene and the combined solutions were concentrated to 8 mL. The solution was heated at 60-70 ^{o}C for 16 h giving a brown solution. Removal of the toluene in vacuum yielded an oil which solidified which turned solid after stripping twice with 30 mL of pentane. The brown solid was disolved in 50 mL of pentane and filtered. The solution was concentrated at reflux to 5 mL. Slowly cooling to 0 ^{o}C resulted in the formation of red-brown crystals. The crystals were washed with cold (-20 ^{o}C) pentane and dried in vacuum. Yield: 0.61 g (2.33 mmol, 64%) of $[C_5H_4(CH_2)_2N$-t-Bu]Ti(Me)Cl. A ^{1}H NMR spectrum revealed the presence of a small amount (ca 2.5%) of the dichloride complex $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 6.19 (m, 1H, C_5H_4); 6.17 (m, 1H, C_5H_4); 5.73 (m, 1H, C_5H_4); 5.70 (m, 1H, C_5H_4); 3.50 (m, 2H, NCH_2); 2.27 (m, 2H, $C_5H_4C\underline{H}_2$); 1.47 (s, 9H, CMe_3); 0.84 (s, 3H, Me). ^{13}C NMR (75.4 MHz, C_6D_6): δ 138.04 (s, C_5H_4-*ipso*); 116.48 (d, $^{1}J_{CH}$ = 172.1 Hz, C_5H_4); 115.52 (d, $^{1}J_{CH}$ = 177.0 Hz, C_5H_4); 114.47 (d, $^{1}J_{CH}$ = 175.8 Hz, C_5H_4); 114.29 (d, $^{1}J_{CH}$ = 169.9 Hz, C_5H_4); 65.42 (t, $^{1}J_{CH}$ = 136.1 Hz, NCH_2); 61.39 (s, $\underline{C}Me_3$); 48.38 (q, $^{1}J_{CH}$ = 122.9 Hz, Me); 29.75 (t, $^{1}J_{CH}$ = 129.4 Hz, $C_5H_4\underline{C}H_2$); 29.60 (q, $^{1}J_{CH}$ = 125.7 Hz, $C\underline{Me}_3$). IR (cm^{-1}): 3100 (w), 3083 (w), 2776 (w), 1840 (w), 1796 (w), 1694 (w), 1657 (w), 1368 (m), 1358 (s), 1344 (m), 1323 (m), 1244 (m), 1225 (m), 1190 (s), 1107 (w), 1076 (s), 1044 (m), 1026 (w), 984 (s), 941 (s), 922 (w), 876 (s), 825 (vs), 768 (m), 683 (m), 642 (m), 571 (m), 538 (m), 494 (s). Anal. calcd: C, 55.10; H, 7.71; Ti, 18.31. Found: C, 54.96; H, 7.67; Ti, 18.22.

[$C_5H_4(CH_2)_2$N-t-Bu]Ti(i-Pr)Cl (35): $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ (2.53 g, 8.97 mmol), *i*-PrMgCl (8.9 mmol), (-40 ^{o}C, 40 mL, 2 h). Yield: 1.92 g (6.63 mmol, 74%, orange-red oil). ^{1}H NMR (300 MHz, C_6D_6): δ 6.20 (m, 1H, C_5H_4); 6.12 (m, 1H, C_5H_4); 5.68 (m, 1H, C_5H_4); 5.64 (m, 1H, C_5H_4); 3.47 (m, 2H, NCH_2); 2.26 (m, 2H, $C_5H_4C\underline{H}_2$); 2.19 (hept, $^{3}J_{HH}$ = 6.04 Hz, 1H, $C\underline{H}Me_2$); 1.46 (s, 9H, CMe_3); 1.31 (d, $^{3}J_{HH}$ = 5.49 Hz, 3H, $CH\underline{Me}_2$); 1.25 (d, $^{3}J_{HH}$ = 5.86 Hz, 3H, $CH\underline{Me}_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 135.85 (s, C_5H_4-*ipso*); 117.21 (d, $^{1}J_{CH}$ = 179.5 Hz, C_5H_4); 114.73 (d, $^{1}J_{CH}$ = 174.6 Hz, C_5H_4); 114.18 (d, $^{1}J_{CH}$ = 168.5 Hz, C_5H_4); 114.10 (d, $^{1}J_{CH}$ = 174.6 Hz, C_5H_4); 86.05 (d, $^{1}J_{CH}$ = 112.3 Hz, $\underline{C}HMe_2$); 63.25 (t, $^{1}J_{CH}$ = 135.5 Hz, NCH_2); 61.55 (s, $\underline{C}Me_3$); 30.41 (q, $^{1}J_{CH}$ = 125.7 H, $C\underline{Me}_3$); 29.64 (t, $^{1}J_{CH}$ = 127.6 Hz, $C_5H_4\underline{C}H_2$); 29.07 (q, $^{1}J_{CH}$ = 124.5 Hz, $CH\underline{Me}_2$); 25.88 07 (q, $^{1}J_{CH}$ = 124.5 Hz, $CH\underline{Me}_2$). IR (cm^{-1}, neat): 3109 (w), 3090 (w), 2947 (s), 2920 (s), 2868 (s), 2837 (s), 2697 (w), 1821 (w), 1778 (w), 1724 (w), 1692 (w), 1628 (w), 1493 (m), 1456 (s), 1393 (m), 1370 (s), 1360 (s), 1344 (m), 1323 (w), 1244 (s), 1223 (m), 1190 (s), 1163 (w), 1143 (s), 1072 (s), 1044 (m), 1026 (w), 984 (s), 937 (m), 912 (w), 885 (m), 845 (m), 814 (s), 770 (m), 679 (m), 646 (m), 608 (w), 561 (m), 534 (m), 486 (m), 442 (s), 424 (w).

[$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_3H_5)Cl (37): $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ (0.98 g, 3.47 mmol), C_3H_5MgCl (3.5 mmol), (-35 ^{o}C, 30 mL, 2 h, workup at 0 ^{o}C). Yield: 0.32 g (1.11 mmol, 32%, dark red crystals/oil). ^{1}H NMR (300 MHz, C_6D_6): δ 6.19 (m, 1H, C_5H_4); 6.16 (m, 1H, C_5H_4); 6.09 (quint, $^{3}J_{HH}$ = 10.98 Hz, 1H, $CH_2C\underline{H}CH_2$); 5.67 (m, 2, C_5H_4); 3.54 (d, $^{3}J_{HH}$ = 10.98 Hz, 4H, $C\underline{H}_2CHC\underline{H}_2$); 3.42 (m, 1H, NCH_2, the other resonance of NCH_2 is overlappped with the resonance at 3.54 ppm); 2.25 (m, 2H, $C_5H_4C\underline{H}_2$); 1.41 (s, 9H, CMe_3); ^{13}C NMR (75.4 MHz, $C_6D_\wedge$): δ 144.09 (d, $^{1}J_{CH}$ = 146.5 Hz, $CH_2\underline{C}HCH_2$); 138.49 (s, C_5H_4-*ipso*); 119.86, 117.41, 114.99 (C_5H_4); 90.05 (t, $^{1}J_{CH}$ = 141.6 Hz, $\underline{C}H_2CH\underline{C}H_2$); 65.13 (t, $^{1}J_{CH}$ =

138.6 Hz, NCH_2); 62.05 (s, $\underline{C}Me_3$); 29.90 (q, $^1J_{CH}$ = 126.6 Hz, $C\underline{Me_3}$); 29.85 (t, $^1J_{CH}$ = 129.4 Hz, $C_5H_4\underline{C}H_2$). IR (cm^{-1}): 3075 (w), 2726 (w), 2674 (w), 1603 (s), 1497 (w), 1362 (m), 1343 (w), 1323 (w), 1244 (m), 1225 (w), 1188 (s), 1072 (m), 1044 (m), 1017 (m), 982 (m), 937 (m), 862 (m), 845 (w), 826 (s), 770 (m), 739 (w), 723 (w), 681 (w), 646 (m), 593 (w), 534 (w), 484 (m), 459 (w), 428 (m).

[$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_3H_5)$_2$ (38): [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiCl_2$ (1.16 g, 4.11 mmol), C_3H_5MgCl (8.1 mmol), (-50 °C, 30 mL, 2 h, workup at 0 °C). Yield: : 0.91 g (3.10 mmol, 75%, dark red oil). ^{1}H NMR (300 MHz, C_6D_6): δ 5.77 (m, 2H, C_5H_4); 5.74 (quint, $^3J_{HH}$ = 5.61 Hz, 2H, $CH_2C\underline{H}CH_2$); 4.94 (m, 2H, C_5H_4); 3.55 (t, $^3J_{HH}$ = 5.13 Hz, 2H, NCH_2); 3.44 (d, $^3J_{HH}$ = 11.47 Hz, 8H, $C\underline{H_2}CHC\underline{H_2}$); 2.45 (t, $^3J_{HH}$ = 5.13 Hz, 2H, $C_5H_4C\underline{H_2}$); 0.94 (s, 9H, CMe_3). ^{13}C NMR 75.4 MHz, C_6D_6): δ 139.85 (d, $^1J_{CH}$ = 146.6 Hz, $CH_2\underline{C}HCH_2$); 133.60 (s, C_5H_4-*ipso*); 112.67 (d, $^1J_{CH}$ = 176.8 Hz, C_5H_4); 111.32 (d, $^1J_{CH}$ = 174.8 Hz, C_5H_4); 80.01 (t, $^1J_{CH}$ = 145.8 Hz, $\underline{C}H_2CH\underline{C}H_2$); 61.94 (t, $^1J_{CH}$ = 134.4 Hz, NCH_2); 59.76 (s, $\underline{C}Me_3$); 30.78 (t, $^1J_{CH}$ = 129.9.4 Hz, $C_5H_4\underline{C}H_2$); 28.94 (q, $^1J_{CH}$ = 124.4 Hz, $C\underline{Me_3}$). IR (cm^{-1}, neat): 3065 (s), 2970 (s), 2860 (s), 2675 (w), 1639 (w), 1597 (s), 1525 (s), 1496 (m), 1473 (s), 1458 (m), 1388 (m), 1357 (s), 1342 (), 1323 (w), 1288 (w), 1244 (s), 1224 (m), 1188 (s), 1066 (s), 1024 (s), 981 (s), 941 (s), 912 (m), 871 (sh, 830 cm^{-1}), 830 (s), 765 (m), 731 (m), 694 (w), 670 (m), 646 (m), 623 (w), 557 (w), 536 (m), 486 (w), 443 (m).

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_2H_4)(PMe_3) (39). To a cooled (-60 °C) solution of 1.82 g (6.45 mmol) of [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiCl_2$ and 1.5 mL (14 mmol) of PMe_3 in 40 mL of ether, 7.8 mL of 1.65 M (13 mmol) of EtMgBr in ether was added quickly. On warming up the reaction mixture to -40 °C, the solution turned yellow. Further warming to room temperature resulted in darkening of the solution and after 16 h stirring a deep purple solution and an off-white precipitate was obtained. The solvent was removed in vacuum resulting in a dark tarry residue. The residue was stripped with 20 mL of pentane and then extracted with 40 mL of pentane. The solution was concentrated to 5 mL and cooled to -50 °C. Crystallisation of a dark purple compound was observed but on warming to room temperature the crystals melted and the remaining pentane was removed in vacuum. Yield: 1.73 g (5.49 mmol, 85%) of **39**. ^{1}H NMR (300 MHz, C_6D_6): δ 6.59 (m, 1H, C_5H_4); 5.78 (m, 1H, C_5H_4); 4.97 (m, 1H, C_5H_4); 4.27 (m, 1H, C_5H_4); 3.54 (m, 1H, NCH_2); 3.09 (m, 1H, NCH_2); 2.57 (m, 1H, $C_5H_4C\underline{H_2}$); 2.47 (m, 1H, $C_5H_4C\underline{H_2}$); 2.18 (m, 1H, C_2H_4); 1.64 (m, 1H, C_2H_4); 1.39 (m, 1H, C_2H_4); 0.90 (d, $^2J_{PH}$ = 5.38 Hz, 9H, PM_3); 0.87 (s, 9H, N-*t*-Bu); 0.35 (m, 1H, C_2H_4). ^{13}C NMR (50 MHz, C_6D_6): δ 130.38 (s, C_5H_4-*ipso*); 110.58 (d, $^1J_{CH}$ = 170.6 Hz, C_5H_4); 105.43 (d, $^1J_{CH}$ = 172.0 Hz, C_5H_4); 102.80 (d, $^1J_{CH}$ = 167.8 Hz, C_5H_4); 100.21 ($^1J_{CH}$ = 167.6 Hz, C_5H_4); 57.62 (t, $^1J_{CH}$ = 132.9 Hz, NCH_2); 56.51 (s, $N\underline{C}Me_3$); 49.14 (dt, $^1J_{CH}$ = 145.8 Hz, $^2J_{CP}$ = 10.0 Hz, C_2H_4); 44.45 (t, $^1J_{CH}$ = 147.5 Hz, C_2H_4); 31.21 (t, $^1J_{CH}$ = 127.2 Hz, $C_5H_4\underline{C}H_2$); 29.54 (q, $^1J_{CH}$ = 124.5 Hz, $NC\underline{Me_3}$); 16.74 (dq, $^1J_{CH}$ = 128.1 Hz, $^1J_{CP}$ = 13.6 Hz, PMe_3). ^{31}P NMR (80.96 MHz, C_6D_6): δ 6.86 (PMe_3).

Töpler-pump experiment of [$C_5H_4(CH_2)_2$N-t-Bu]$TiCl_2$ with 2 eq EtMgBr and 1 eq. PMe3. A double legged Schlenk vessel (volume 180 mL) was filled with a solution of 571 mg (2.03 mmol) of

$[C_5H_4(CH_2)N$-*t*-Bu$]TiCl_2$ in 20 mL of THF and a solution of 2.8 mL 1.46 M (4.08 mmol) of EtMgBr in THF and 215 μL (2.08 mmol) PMe_3 in 15 mL of THF. The vessel was degassed using 3 freeze pump thaw cycles. Then the two cooled (-60 ^oC) solutions were mixed and slowly warmed to room temperature. The resulting dark purple solution was stirred for 3 h. Then the solution was cooled to -40 ^oC and the evolved gas was pumped through two cold traps (-70 and -115 ^oC) into a calibrated volume and measured. In total, 2.08 mmol of gas was obtained corresponding with 1.03 mole gas/mole Ti. GC Anal.: Ethane, 100%. A second Töpler pump experiment carried out with 528.2 mg (1.873 mmol) of $[C_5H_4(CH_2)N$-*t*-Bu$]TiCl_2$, 2.6 mL 1.46 M (3.80 mmol) of EtMgBr and 200 μL (1.93 mmol) of PMe_3, gave 1.02 mole gas/mole Ti. GC Anal.: Ethane, 100%

Synthesis of $[C_5H_4(CH_2)_2N$-t-Bu$]Ti(C_3H_6)(PMe_3)$. (40). A cooled (-50 ^oC) suspension of 1.77 g (6.27 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ in 35 mL of ether and 2.0 mL (19 mmol) of PMe_3 was reacted with 6.2 mL 2.02 M (12.5 mmol) of *n*-PrMgBr in ether. The mixture turned yellow. When the temperature was raised to -20 ^oC the color changed into dark green. The mixture was stirred overnight at room temperature. The ether was removed in vacuum and the oily residue was stripped with 50 mL of pentane followed by extraction with pentane (2x 50 mL). Complete removal of the solvent yielded a dark oil: 1.80 g (5.46 mmol, 87%) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_3H_6)(PMe_3)$. ^1H, ^{13}C and ^{31}P NMR spectroscopy revealed the presence of 4 isomers of complex **40**.

Reaction of $[C_5H_4(CH_2)_2N$-t-Bu$]Ti(C_2H_4)(PMe_3)$ with excess ethene in C_6D_6. A NMR tube with a solution of 22.0 mg (0.070 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_2H_4)(PMe_3)$ in 0.4 mL of C_6D_6 was charged with 0.31 mmol of ethene. The color changed immediately from purple into brown. ^1H NMR spectroscopy showed the presence of $[C_5H_4(CH_2)_2N$-t-Bu$]Ti(C_2H_4)(PMe_3)$ (**39**) and $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_4H_8)$ (**41**) in a 43 : 57 ratio. ^1H-NMR (300 MHz, C_6D_6) for **41**: δ 6.68 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.47 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.33 (t, $^2J_{HH}$ = 6.47 Hz, 2H, NCH_2); 2.31 (m, 2H, C_4H_8); 2.15 (t, $^2J_{HH}$ = 6.47 Hz, 2H, $C_5H_4C\underline{H}_2$); 2.13 (m, 2H, C_4H_8); 1.74 (m, 2H, C_4H_8); 1.69 (s, 9H, *t*-Bu); 1.26 (m, 2H, C_4H_8). ^{13}C NMR (75.4 MHz, C_6D_6): δ 132.70 (C_5H_4-*ipso*); 114.97 (C_5H_4); 114.63 (C_5H_4); 64.07 (α-$\underline{C}_4H_8$); 60.83 (NCH_2); 59.79 ($\underline{C}Me_3$); 30.42 ($C\underline{Me}_3$); 29.93 (β-$\underline{C}_4H_8$); 29.80 ($C_5H_4\underline{C}H_2$).

Thermolysis of $[C_5H_4(CH_2)_2N$-t-Bu$]TiPh_2$ (26) in the presence of 2 eq. PMe_3. In an NMR tube 45.4 mg (0.124 mmol) of **26** was dissolved in 0.4 mL of C_6D_{12} and 2 eq. of PMe_3 was added. The NMR tube was sealed and heated to 75 ^oC. After 30 min **26** had been converted in to **43**.

Thermolysis of $[C_5H_4(CH_2)_2N$-t-Bu$]TiPh_2$ (26) in C_6D_6.. In an NMR tube a solution of 50.6 mg (0.138 mmol) of **26** in 0.5 mL of C_6D_6 (0.276 M) was prepared and the tube was sealed under nitrogen. The tube was heated at 55.0 ^oC and ^1H NMR spectra were recorded using the following time intervals: first eight spectra with an interval of 15 min, then 8 spectra with an interval of 30 min and at last 18 spectra with an interval of 60 min.

Thermolysis of [$C_5H_4(CH_2)_2$N-t-Bu]$TiPh_2$ (26) in C_6D_{12}. A similar NMR tube experiment as described above was performed using 35.5 mg (0.097 mmol) of **26** in 0.35 mL of C_6D_{12} (0.277 M). Within 6 h **26** was completely converted into **44** (55%), benzene and decomposition products which could not be identified.

Synthesis of {[$C_5H_4(CH_2)_2$N-t-Bu]$Ti(C_6H_4)$}$_2$ (44). A solution of 0.95 g (2.60 mmol) of **26** in 40 mL of hexane was heated at 57 ^oC. The dark-yellow solution became dark and after 30 min. an orange powder started to precipitate. After 5 h the reaction mixture was cooled to room temperature, filtered and the orange residue was washed 3 times with 10 mL of pentane. Yield: 0.26 g (0.91 mmol, 35%) of **44**. ^1H NMR (200 MHz, C_6D_{12}): δ 7.92 (dd, J_{HH} = 5.56 Hz, J_{HH} = 2.99 Hz, 2H, C_6H_4); 7.00 (dd, J_{HH} = 5.56 Hz, J_{HH} = 2.99 Hz, 2H, C_6H_4); 6.19 (t, J_{HH} = 2.56 Hz, 2H, C_5H_4); 4.87 (t, J_{HH} = 2.56 Hz, 2H, C_5H_4); 4.05 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.85 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4C\underline{H_2}$); 0.73 (s, N-*t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_{12}): δ 188.71 (s, C*q*-C_6H_4)); 139.60 (s, C_5H_4-*ipso*); 133.48 (d, $^1J_{CH}$ = 157.4 Hz, C_6H_4); 126.44 (d, $^1J_{CH}$ = 156.0 Hz, C_6H_4); 112.32 (d, $^1J_{CH}$ = 173.2, Hz, C_5H_4); 110.65 (d, $^1J_{CH}$ = 171.84 Hz, C_5H_4); 64.82 (t, $^1J_{CH}$ = 133.3 Hz, NCH_2); 62.35 (s, N$\underline{C}Me_3$); 32.00 (t, $^1J_{CH}$ = 127.8 Hz, $C_5H_4\underline{CH_2}$); 29.11 (q, $^1J_{CH}$ = 125.1 Hz, NC$\underline{Me_3}$). IR (cm^{-1}): 3057 (w), 3030 (w), 3003 (sh, nujol), 1520 (w), 1500 (w), 1354 (m), 1342 (w), 1321 (w), 1269 (w), 1248 (m), 1227 (m), 1194 (s), 1116 (w), 1068 (m), 1044 (w), 1031 (w), 983 (m), 972 (w), 947 (m), 930 (w), 864 (m), 844 (m), 819 (s), 792 (w), 767 (m), 736 (s), 677 (m), 644 (w), 605 (m), 542 (m). Anal. calcd for $C_{17}H_{21}NTi$: C, 71.08; H, 7.37. Found: C, 68.36; H, 7.33.

Thermolysis of [$C_5H_4(CH_2)_2$N-t-Bu]$Ti(CH_2CMe_3)_2$ (29) in C_6D_{12} in the presence of 2 eq. of PMe_3. In an NMR tube, a solution of 42.7 mg (0.120 mmol) of **29** and 25 μL (0.242 mmol) of PMe_3 in 0.4 mL of C_6D_{12} was prepared and the tube was sealed. The tube was heated at 75 ^oC and a ^1H NMR spectrum was recorded every 30 min. After 90 min. **29** was been completely converted into **46**.

Thermolysis of [$C_5H_4(CH_2)_2$N-t-Bu]$Ti(CH_2CMe_2Ph)_2$ (31) in C_6D_6 in the presence of excess PMe_3. A solution of 70.2 mg (0.147 mmol) of **31** and 20 mL of PMe_3 in 0.4 mL of C_6D_6 was sealed in a NMR tube and heated at 75 ^oC. A ^1H NMR spectrum was recorded after resp. 50, 140, 210, 360, 510 min. After 8.5 h the starting material had been completely converted into [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti=C(H)CMe_2Ph).PMe_3 (**47**) and *t*-butylbenzene.

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]$Ti=C(H)CMe_3(PMe_3)$ (46). A solution of 2.50 g (7.07 mmol) of [$C_5H_4(CH_2)_2$N-*t*-Bu]$Ti(CH_2CMe_3)_2$ and 1.5 mL (14 mmol) of PMe_3 in 35 mL of cyclohexane was heated at 75-80 ^oC during 3 h. The yellow-brown solution turned red-brown. The solvent was removed in vacuum and the red-brown residue was stripped with 20 mL of pentane. The residue was extracted with 20 mL of pentane and the solution was concentrated to 5 mL while refluxing. Standing overnight at room temperature, dark purple crystals were formed resulting in 0.45 g (1.26 mmol) of product. Concentration of the mother liquor and cooling to -30 ^oC gave a second crop 1.26 g (3.52 mmol) of

product. Yield: 1.71 g (4.78 mmol, 68%) of **46**. ^{1}H NMR (300 MHz, C_6D_6): δ 7.01 (m, 1H, C_5H_4); 6.39 (d, $^{3}J_{PH}$ = 1.70 Hz, 1H, =C(H)CMe_3); 6.10 (m, 1H, C_5H_4); 5.39 (m, 1H, C_5H_4); 4.98 (m, 1H, C_5H_4); 3.46 (m, 1H, NCH_2); 3.07 (m, 1H, NCH_2); 2.44 (m, 1H, $C_5H_4CH_2$); 2.07 (m, 1H, $C_5H_4CH_2$); 1.37 (s, 9H, N-*t*-Bu); 1.16 (s, 9H, =C(H)CMe_3); 0.91 (d, $^{2}J_{PH}$ = 6.1 Hz, 9H, PMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 251.39 (dd, $^{1}J_{CH}$ = 83.1 Hz, $^{2}J_{PC}$ = 13.1 Hz, =C(H)CMe_3); 127.79 (s, C_5H_4-*ipso*); 105.97 (d, $^{1}J_{CH}$ = 169.2 Hz, C_5H_4); 103.24 (d, $^{1}J_{CH}$ = 172.2 Hz, C_5H_4); 101.39 (d, $^{1}J_{CH}$ = 167.19 Hz, C_5H_4); 100.79 (d, $^{1}J_{CH}$ = 166.2 Hz, C_5H_4); 57.94 (t, $^{1}J_{CH}$ = 132.5 Hz, NCH_2); 56.70 (s, NCMe_3); 45.48 (s, =C(H)CMe_3); 33.63 (dq, $^{1}J_{CH}$ = 124.6 Hz, $^{4}J_{CP}$ = 3.0 Hz, =C(H)CMe_3); 32.79 (q, $^{1}J_{CH}$ = 124.6 Hz, NCMe_3); 31.87 (t, $^{1}J_{CH}$ = 126.9 Hz, $C_5H_4CH_2$); 17.70 (dq, $^{1}J_{CH}$ = 128.9 Hz, $^{1}J_{CP}$ = 17.1 Hz, PMe_3). ^{31}P NMR (80.96 MHz, C_6D_6): δ -6.01 (PMe_3). IR (cm^{-1}): 3117 (vw), 3094 (w), 2814 (w), 2714 (vw), 2675 (m), 1572 (w), 1458 (sh, Nujol), 1420 (m), 1350 (s), 1302 (m), 1279 (s), 1244 (s), 1227 (m), 1190 (s), 1146 (m), 1059 (m), 1045 (m), 1030 s), 984 (w), 972 (w), 951 (vs), 856 (m), 839 (m), 828 (w, 787 (vs), 762 (m), 729 (m), 687 (m), 673 (m), 554 (m), 542(m). Anal. Calcd. for $C_{19}H_{36}NPTi$: C, 63.86; H, 10.15; Ti, 13.40. Found: C, 64.13; H, 9.89; Ti, 13.55.

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti=C(H)CMe_2Ph(PMe_3) (47). A solution of 3.07 g (6.46 mmol) of [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti($CH_2CMe_2Ph)_2$ and 1.6 mL (15 mmol) of PMe_3 in 40 mL of cyclohexane was heated at 80 °C for 8 h. The dark yellow solution became red-brown. The solvent was removed in vacuum and the red-brown residue was stripped three times with 30 mL of pentane and dried in vacuum (10^{-1} torr) for 1 h. The residue was extracted with 50 mL of pentane and the solution was concentrated while refluxing until the complex started to crystallize. Pentane (3 mL) was added. On refluxing all crystals dissolved and the solution was cooled overnight to -30 °C. In a first crop 1.36 g (3.24 mmol) of dark red crystals were obtained. Concentration and slowly cooling of the mother liquor gave a second crop, 0.43 g (1.03 mmol) of product. Yield: 1.79 g (4.27 mmol, 66%) of **47**. ^{1}H NMR (300 MHz, C_6D_6): δ 7.51 (m, 2H, =C(H)CMe_2-o-Ph); 7.23 (m, 2H, =C(H)CMe_2-m-Ph); 7.07 (m, 2H, =C(H)CMe_2-p-Ph); 6.74 (m, 1H, C_5H_4); 6.44 (s, 1H, =C(H)CMe_2Ph); 6.03 (m, 1H, C_5H_4); 5.38 (s, 1H, C_5H_4); 4.94 (m, 1H, C_5H_4); 3.46 (m, 1H, NCH_2); 3.06 (m, 1H, NCH_2); 2.43 (m, 1H, $C_5H_4CH_2$); 2.05 (m, 1H, $C_5H_4CH_2$); 1.55 (s, 3H, =C(H)CMe_2Ph); 1.48 (s, 3H, =C(H)CMe_2Ph); 1.33 (s, 9H, N-*t*-Bu); 0.77 (d, $^{2}J_{PH}$ = 6.35 Hz, 9H, PMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 245.96 (dd, $^{1}J_{CH}$ = 88.0 Hz, $^{2}J_{CP}$ = 12.8 Hz, =C(H)CMe_2Ph); 152.61 (d, $^{4}J_{CP}$ = 3.2 Hz, =C(H)CMe_2Ph- *ipso*); 127.85 (d, $^{1}J_{CH}$ = 155.8 Hz, =C(H)CMe_2-o-Ph) 127.78 (s, C_5H_4-*ipso*); 126.06 (d, $^{1}J_{CH}$ = 153.96 Hz, =C(H)CMe_2-*m*-Ph); 124.77 (d, $^{1}J_{CH}$ = 159.0 Hz, =C(H)CMe_2-*p*-Ph); 106.20 (d, $^{1}J_{CH}$ = 168.2 Hz, C_5H_4); 103.96 (d, $^{1}J_{CH}$ = 172.8 Hz, C_5H_4); 101.94 (d, $^{1}J_{CH}$ = 168.2 Hz, C_5H_4); 101.19 (dd, $^{1}J_{CH}$ = 165.9 Hz, $^{2}J_{CP}$ = 0.9 Hz, C_5H_4); 58.05 (t, $^{1}J_{CH}$ = 132.7 Hz, NCH_2); 57.03 (s, NCMe_3); 52.02 (s, =C(H)CMe_2Ph); 33.35 (dq, $^{1}J_{CH}$ = 125.9 Hz, $^{4}J_{CP}$ = 3.2 Hz, =C(H)CMe_2Ph); 32.78 (q, $^{1}J_{CH}$ = 124.6 Hz, NCMe_3); 32.26 (dq, $^{1}J_{CH}$ = 125.7 Hz, $^{4}J_{CP}$ = 2.3 Hz, =C(H)CMe_2Ph); 31.85 (t, $^{1}J_{CH}$ = 126.9 Hz, $C_5H_4CH_2$); 17.09 (dq, $^{1}J_{CH}$ = 128.9 Hz, $^{1}J_{CP}$ = 17.0 Hz, PMe_3). ^{31}P NMR (80.96 MHz, C_6D_6): δ -7.26 (PMe_3). IR (cm^{-1}): 3151 (vw), 3128 (vw), 3082 (w), 3057 (m), 3020 (w), 2729 (w), 2674 (m), 19469 (w), 1874 (w), 1805 (w), 1753 (vw), 1658 (w), 1593 (s), 1493 (m), 1467 (m), 1421 (w), 1354 (s), 1336 (w), 1309 (w), 1302 (w), 1280 (s), 1246 (m), 1224 (m), 1190

(vs), 1157 (w), 1120 (w), 1091 (m), 1068 (m), 1043 (s), 1028 (s), 1006 (w), 970 (w), 954 (vs), 910 (m), 873 (m), 839 (s), 823 (s), 787 (vs), 765 (s), 727 (m), 700 (s), 682 (m), 578 (s), 559 (w), 540 (m), 489 (w), 468 (m), 445 (vw). Anal. Calcd. for $C_{24}H_{38}NPTi$: C, 68.72; H, 9.13; Ti, 11.42. Found: C, 68.40; H, 9.13; Ti, 11.58.

3.11 References and Notes.7

(1) (a) Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1993**, *12*, 1936. (b) Shapiro, P.J.; Cotter, W.D.; Schaefer, W.P; Labinger, J.A.; Bercaw, J.E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (c) Mu, Y.; Piers, W.E.; MacQuarrie, D.C.; Zaworotko, M.; Young, Jr, V.G. *Organometallics*, **1996**, *15*, 2720. (d) Okuda, J.; Schattenmann, F.J.; Wocadlo, S.; Mass, W. *Organometallics*¸**1995**, *14*, 789. (e) du Plooy, K.E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics*, **1995**, *14*, 3129. (f) Kloppenburg, L.; Petersen, J.L. *Organometallics*, **1997**, *16*, 3548. (g) Kloppenburg, L.; Petersen, J.L. *Organometallics*, **1996**, *15*¸ 7. (h) Rasika Dias, H.V.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77. (i) Okuda, J.; Eberle, T.; Spaniol, T.P. *Chem. Ber./Requeil*, **1997**, *130*¸209. (j) McKnight, A.L.; Masood, Md.A.; Waymouth, R.M.; Straus, D.A. *Organometallics*, **1997**, *16*, 2879. (k) Chen, Y.-X.; Marks, T.J. *Organometallics*, **1997**, *16*, 3649. (l) Devore. D.D.; Timmers, F.J.; Hasha, D.L.; Rosen, R.K.; Marks, T.J.; Deck, P.A.; Stern, C.L. *Organometallics*, **1995**, *14*, 3132. (m) Duda, L.; Erker, G.; Frölich, R.; Zippel, F. *Eur. J. Inorg. Chem.* **1998**, 1153.

(2) For recent reviews see (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans*. **1996**, 255. (c) Brintzinger. H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (d) *Catalyst Design for Tailor-Made Polyolefins*: Soga, K.; Terano, M., Eds. Elsevier: Tokyo, 1994. (e) Möhring, P.C.; Coville, N.J. *J. Organomet. Chem.* **1994**, *479*, 1. (f) Marks, T.J. *Acc. Chem. Rev.* **1992**, *25*, 57. (g) Jordan, R.F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(3) (a) Dyachkovskii, F.S.; Shilova, A.K.; Silov, A.E. *J. Polym. Sci., Part C*, **1967**, *16*, 2333 and references therein. (b) Bochmann, M.; Wilson, L.M. *J. Chem. Soc., Chem. Comm.* **1986**, 1610. (c) Jordan, R.F.; Bajgur, C.S. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (d) Jordan, R.F.; LaPointe, R.E.; Bajgur, C.S.; Echols, S.F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (e) Bochmann, M.; Wilson, L.M.; Hursthouse, M.B.; Short, R.L. *Organometallics*, **1987**, *6*, 2556. (f) Jordan, R.F. *J. Chem. Educ.* **1988**, *65*, 285. (g) Hlatky, G.G.; Turner, H.W.; Eckman, R.R.; *J. Am. Chem. Soc.* **1989**, *111*, 2728. (h) Jordan, R.F.; LaPointe, R.E.; Bradley, P.K.; Baenziger, N. *Organometallics*, **1989**, *8*, 2892. (i) Bochmann, M.; Jaggar, A.J.; Wilson, L.M. Hursthouse, M.B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838. (j) Christ, C.S., Jr.; Eyler, J.R.; Richardson, D.E. *J. A. Chem. Soc.* **1990**, *112*, 596. (k) Jordan, R.F.; Taylor, D.F.; Baenziger, N.C. *Organometallics*, **1990**, *9*, 1546. (l) Park, J.W.; Henling, L.M.; Schaefer, W.P.; Grubbs, R.H. *J. Am. Chem. Soc.* **1990**, *9*, 1650.

(4) (a) Canich, J.M.; Hlatky, G.G.; Turner, H.W. PCT Appl. WO 92-00333, 1992. Canich, J.M. Eur Patent Appl. EP 420 436-A1, 1991 (Exxon Chemical Co.). (b) Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S. Eur. Patent Appl. EP 416 815-A2, 1991 (Dow Chemical Co.).

(5) (a) Buchwald, S.L.; Fischer, R.A.; *Chem. Rev.* **1988**, *88*, 1047. (b) Buchwald, S.L.; Fischer, R.A. *Chem. Scr.* **1989**, *29*, 417. (c) Erker, G.; Kroop, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (d) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (e) Tidwell, J.H.; Senn, D.R.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 4685. (f) Tidwell, J.H.; Buchwald, S.L. *J. Org. Chem.* **1992**, *57*, 6380. (g) Spence, R.E.v.H.; Hsu, D.P.; Buchwald, S.L. *Organometallics*, **1992**, *11*, 3492. (h) Buchwald, S.L.; Fischer, R.A.; Foxman, B.M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 771. (i) Hsu, D.P.; Lucas, E.A.; Buchwald, S.L. *Tetrahedron Lett.* **1990**, *31*¸5563. (j) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495. (k) Coles, N.; Whitby, R.J.; Blagg, J. *Synlett.* **1990**, 271. (l) Grossman, R.B.; Davis, W.M.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 2321. (m) Broene, R.D.; Buchwald, S.L. *Science*, **1993**, *261*, 1696.

(6) The formation of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiMe_2$ may be also due to fact that when the MeLi is added the dichloride is only partially dissolved. The initially formed $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(Me)Cl can react with another equivalent MeLi. Probably $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2Ph)Cl$ is under these conditions much less reactive towards $PhCH_2MgCl$.

(7) When the same reaction was carried out in the presence of excess PMe_3 a tarry brown oil was obtained. ^1H NMR spectroscopy revealed the same resonances as observed for the propene complex $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_3H_6).PMe_3$.

(8) A nice example is the reaction of $Cp^*Zr(C_8H_8)Cl$ with *i*-PrMgCl resulting in the hydride $Cp^*Zr(C_8H_8)H$ by extrusion of propene. Highcock, W.J.; Mills, R.M.; Spencer, J.L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 821.

(9) Noth, H.; Schmidt, M. *Organometallics*, **1995**, *14*, 4601.

(10) (a) Van Leeuwen, P.W.N.M.; Van der Heijden, H.; Roobeek, C.F.; Frijns, J.H.G. *J. Organomet. Chem.* **1981**, *209*, 169. (b) Luinstra, G.A. Thesis, Groningen, 1991.

(11) (a) Martin, H.A. Thesis, Groningen, 1967. (b) Bartlett, P.D.; Seidel, B. *J. Am. Chem. Soc.* **1961**, *83*, 581. (c) Henric-Olivé, G.; Olivé, S. *Angew. Chem.* **1967**, *79*, 764 and references cited therein.

(12) (a) Martin, H.A.; Jellinek, F. *J. Organomet. Chem.* **1967**, *8*, 115. (b) Helmholdt, R.B.; Jellinek, F.; Martin, H.A.; Vos, A. *Recueil*, **1967**, *86*, 1263.

(13) Green, M.L.H.; Lucas, C.R. *J. Organomet. Chem.* **1974**, *73*, 259.

(14) Gómez, R.; Duchateau, R.; Chernega, A.N.; Meetsma, A.; Edelmann, F.T.; Teuben, J.H.; Green, M.L.H. *J. Chem. Soc., Dalton Trans.* **1995**, 217.

(15) Flores, J.C.; Chien, J.C.W.; Rausch, M.D. *Organometallics* **1995**, *14*, 1827.

(16) (a) Davies, G.R.; Jarvis, J.A.J. *J. Chem. Soc., Chem. Comm.* **1971**, 1511. (b) Davies, G.R.; Jarvis, J.A.J.; Kilbourn, B.T.; Pioli, A.J.P. *J. Chem. Soc., Chem. Comm.* **1971**, 677.

(17) Latsky, S.L.; McMullen, A.K.; Niccolai, G.P.; Rothwell, I.P.; Huffman, J.C. *Organometallics*, **1985**, *4*, 902.

(18) *Activation and Functionalization of Alkenes*; Hill, C.L., Ed. Wiley: New York, 1989.

(19) (a) Kool, L.B.; Rausch, M.D.; Alt, H.G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 394. (b), McDermott, J.X.; Whitesides, G.M. *J. Am. Chem. Soc.* **1974**, *96*, 947. (c) McDermott, J.X.; Whitesides, G.M. *J. Am. Chem. Soc.* **1978**, *98*, 6529. (d) Bates, R.B.; Kroposki, L.M.; Potter, D.E. *J. Org. Chem.* **1972**, *37*, 560,. (e) Jung, M.E.; Blum, R.B. *Tetrahedron Lett.* **1977**, *43*, 3791. (f) Hessen, B. *Thesis*, **1989**, Groningen.

(20) (a) Buchwald, S.L.; Campora, J. *Organometallics*, **1993**, *12*, 4182. (b) Koschmieder, S.U.; McGilligan, B.S.; McDermott, G.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3427. (c) Buchwald, S.L.; Watson, B.T. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (d) Churchill, M.R.; Youngs, W.J. *Inorg. Chem.* **1979**, *18*, 1697. McLain, S.J.; Schrock, R.R.; Sharp, P.R.; Churchill, M.R.; Youngs, W.J. *J. Am. Chem. Soc,* **1979**, *101*, 7863.

(21) (a) Schrock, R.R. *J. Am. Chem. Soc.* **1974**, *96*, 6796. (b) Wengrovius, J.H.; Schrock, R.R. *J. Organomet. Chem.* **1981**, *205*, 319. (c) Howard, T.R.; Lee, J.B.; Grubbs, R.H. *J. Am. Chem. Soc.* **1980**, *102*, 6878. (d) Cundari, T.R.; Gordon, M.S. *J. Am. Chem. Soc.* **1992**, *114*, 539. (e) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem.* **1989**, *101*, 647.(f) Meinhart, J.D.; Anslyn, E.V.; Grubbs, R.H. *Organometallics* **1989**, *8*, 583. (g) Van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145. (h) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics*, **1994**, *13*, 4978

(22) Hessen, B.; Buijink, J.K.F.; Meetsma, A.; Teuben, J.H.; Helgesson, G.; Håkansson, M.; Jagner, S.; Spek, A.L. *Organometallics* **1993**, *12*, 2268.

(23) Replacement of cyclopentadienyls by pentamethycyclopentadienyls normaly enhances the thermal stability of the early transition metal carbyl complexes, see: (a) Maitlis, P.M. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Blenkers, J.; de Liefde Meijer, H.J.; Teuben, J.H. *J. Organometal. Chem.* **1981**, *218*, 383. However, Cp* ligands are frequently activated in *intra* molecular processes. See also ref. 24

(24) (a) Bercaw, J.E.; Marvich, R.H.; Bell, L.G.; Brintzinger, H.H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (b) McDade, C.; Green, J.C.; Bercaw, J.E. *Organometallics*, **1982**, *1*, 1629. (c) Pattiasina, J.W. Thesis, R.U. Groningen, **1988**. (d) Pattiasina, J.W.; Hissink, C.E.; De Boer, J.L.; Meetsma, A.; Teuben, J.H.; Spek, A.L. *J.Am. Chem. Soc.* **1985**, *107*, 7758. (e) Pattiasina, J.W.; Van Bolhuis, F.; Teuben, J.H. *Angew. Chem.* **1987**, *99*¸ 342. (f) Luinstra, G.A.; Ten Cate, L.C.; Heeres, H.J.; Pattiasina, J.W.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1991**, *10*, 3227. (g) Abugideiri, F.; Kelland, M.A.; Poll, R.; Rheingold, A.L. *Organometallics*, **1992**, *11*, 1309. (h) Gibson, V.C.; Kee, T.P.; Carter, S.T.; Sanner, R.D.; Clegg, W. *J. Organomet. Chem.* **1991**, *418*, 197. (i) Sinnema, P.-J.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1993**, *12*, 184. (j) Schock, L.E.; Brock, C.P.; Marks, T.J.

Organometallics, **1987**, *6*, 232. (k) Bulls, A.R.; Schaefer, W.P.; Serfas, M.; Bercaw, J.E. *Organometallics*, **1987**, *6*, 1219. (l) De Wolf, J.M.; Blaauw, R.; Meetsma, A.; Teuben, J.H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A.L. *Organometallics*, **1996**, *15*, 4977.

(25) (a) Horton, A.D. *Organometallics*, **1992**, *11*, 3271. (b) Bijpost, E.A. Thesis, R.U. Groningen, **1996**. (c) Eshuis, J.J.W. Thesis, R.U. Groningen, **1991**.

(26) (a) Amor, J.I.; Cuenca, T.; Galakhov, M.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *J. Organomet. Chem.* **1997**, *535*, 155. (b) Yang, X.; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (c) Hessen, B. submitted to *J. Am. Chem. Soc.*

(27) (a) Petasis, N.A.; Fu, D.K. *Organometallics* **1993**, *12*, 3776. (b) Boekel, C.P.; Teuben, J.H.; De Liefde Meijer, H.J. *J. Organomet. Chem.* **1975**, *102*, 317. (c) Boekel, C.P.; Teuben, J.H.; De Liefde Meijer, H.J. *J. Organomet. Chem.* **1975**, *102*, 161.

(28) Alt, H.; Rausch, M.D. *J. Am. Chem. Soc.* **1974**, *96*, 5936.

(29) The photochemically induced decompositions as they are reported are not fully understood. Probably these processes can better be considered as photochemically catalyzed thermal decompositions.

(30) Phosphines are commonly used to stabilize olefin, aryne and alkylidene complexes, see ref. 19, 20 and 21.

(31) Thermolyses of the $[C_5H_4(CH_2)_nNMe]TiR_2$ (n = 2, 3; R = Et, Ph, CH_2CMe_3 and CH_2CMe_2Ph) in the presence of PMe_3 did not result in the formation of olefin, aryne and alkylidene complexes. The aryne complex $[C_5H_4(CH_2)_2N$-*i*-Pr]$Ti(C_6H_4)(PMe_3)$ was obtained on thermolysis of the diphenyl compound in the presence of PMe_3. From this it can be assumed that bulky amido substituents are required to get the desired olefin, aryne and alkylidene complexes.

(32) (a) Mclain, S.I.; Sancho, J.; Schrock, R.R. *J. Am. Chem. Soc.* **1980**, *102*, 5610. (b) Datta, S.; Fischer, M.B.; Wreford, S.S. *J. Organometal. Chem.* **1980**, *188*, 353.

(33) Cohen, S.A.; Auburn, P.R.; Bercaw, J.E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(34) Devore, D.D.; Timmers, F.J.; Hasha, D.L.; Rosen, R.K.; Marks, T.J.; Deck, P.A.; Stern, C.L. *Organometallics* **1995**, *14*, 3132.

(35) (a) McDermott, J.X.; Whitesides, G.M. *J. Am. Chem. Soc.* **1974**, *96*, 947. (b) McDremott, J.X.; Wilson, M.E.; Whitesides, G.M. *J. Am. Chem. Soc.* **1976**, *98*, 6529

(36) A ^{1}H NMR spectrum showed resonances characteristic for a $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti moiety together with some broad resonances but the identity of the complexes formed could not be elucidated.

(37) A Töpler experiment revealed the formation of 0.91 mol C_2H_4/mol Ti.

(38) Tinga, M.A.G.M.; Akkerman, O.S.; Bickelhaupt, F.; Horn, E.; Spek, A.L. *J. Am. Chem. Soc.* **1991**, *113*, 3604.

(39) Wittig, G.; Bickelhaupt, F. *Chem. Ber.* **1958**, *91*, 883.

(40) Schreuder Goedheijt, M. Thesis, Amsterdam, **1996**.

(41) At this stage the NMR tube still contains **44** as a solid, therefore no proper conversion degree of **44** could be estimated.

(42) NOESY experiments revealed that the resonances for **46** (6.28 ppm) and **47** (6.45 ppm) showed no coupling with the other resonances in that region.

(43) Gibson, V.C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1565.

(44) Fryzuk, M.D.; Mao, S.S.H.; Zaworotko, M.J.; MacGillivray, L.R. *J. Am. Chem. Soc.* **1993**, *115*, 5336.

(45) Van Doorn, J.A.; Van der Heijden, H.; Orpen, A.G. *Organometallics* **1995**, *14*, 1278.

(46) Gilliom, L.R.; Grubbs, R.H. *Organometallics* **1986**, *5*, 721.

(47) Schwartz, J.; Gell. K.I. *J. Organomet. Chem.* **1980**, *184*, C1.

(48) At the beginning, the formed $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_2H_4)(PMe_3)$ (**39**) reacts further with the present ethene resulting in the formation of some $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2)_4$ (**41**).

(49) Tebbe, F.N.; Parshall, G.W.; Reddy, G.S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(50) Gilliom, L.R.; Grubbs, R.H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(51) **26-d_{10}** was prepared analoguous to **26** in 66% yield using C_6D_5MgBr.

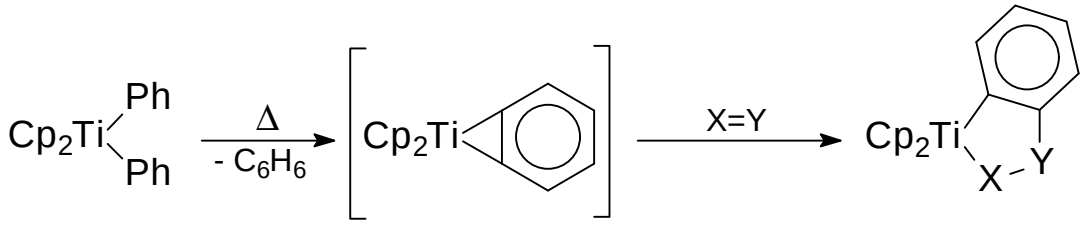
(52) The thermolyses of **26** and **26-d_{10}** (66 ^oC, C_6D_{12}, 3 equiv. PMe_3) obey first order kinetics with $k_H = 4.77 \pm 0.14 \times 10^{-4}$ s^{-1}, $k_D = 1.08 \pm 0.06 \times 10^{-4}$ s^{-1}, $k_H/k_D = 4.4$ at 339 K.

4 Cyclopentadienyl Amido Titanium Benzyne Complexes: Synthesis, Reactivity and Molecular structure of [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4)(PMe_3).*

4.1 Introduction.

Although unknown as a free species, the benzyne molecule has been observed as an intermediate in aromatic substitutions[1]. Benzyne reacts with unsaturated substrates and is a useful building block in organic synthesis.

Vol'pin suggested in 1971 that the formation of a 2,3-diphenyltitanaindene complex, during thermolysis of diphenyl titanocene in the presence of diphenylacetylene, proceeds via a titanium benzyne intermediate.[2,3] Erker *et al.* provided clear evidence for intermediate benzyne complexes in an elegant reactivity study of diphenyl and ditolyl zirconocenes.[4]



Scheme 1. Generation of titanacycles by thermolysis of diphenyl titanocene in the presence of unsaturated substrates.

The benzyne intermediate was found to react with a wide range of unsaturated substrates (Scheme 1) like alkenes,[5] alkynes,[6] CO_2[2], nitriles,[7] and elements like sulphur and selenium.[8] Even dinitrogen can be affected by metal benzyne complexes.[9] The rich insertion chemistry of group 4 metal alkyne/aryne species provides an important tool in metal mediated organic synthesis.[10]

While group 4 metallocene benzyne chemistry has been studied extensively we felt that a more detailed study of the synthesis and reactivity of the Cp-amido titanium benzyne

* *This work was performed in collaboration with L. van der Veen. The X-ray structure determinations described in this chapter were carried out by A. Meetsma (University of Groningen) and S.I. Troyanov (Moscow State University).*

complexes would be worthwhile. In this chapter we present the synthesis and characterization of the C_2-bridged *tert*-butyl amido cyclopentadienyl titanium benzyne complex $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_2H_4)(PMe_3)$ (**43**) and a study of its reactivity towards unsaturated substrates.

4.2 Synthesis and Characterization of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (43).

$[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**) was prepared by thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiPh_2$ (**26**) in the presence of excess PMe_3 and was isolated as dark yellow crystals in 53% yield. The ^{1}H NMR spectrum (C_7D_{14}, 25 ^{o}C) confirms the asymmetric overall structure of **43** (Figure 1). Four resonances (m, 1H) at 6.50, 6.11, 5.19 and 4.42 ppm are observed for the Cp protons and the C_2-bridge appears as an ABCD spin system showing three multiplets at δ 3.91 (1H), 3.72 (1H) and 2.76 (2H). A doublet at 1.43 ppm ($^2J_{PH}$ = 5.98 Hz, 9H) and a singlet (0.64 ppm, 9H) were assigned to a coordinated PMe_3 and the *t*-butyl group respectively.

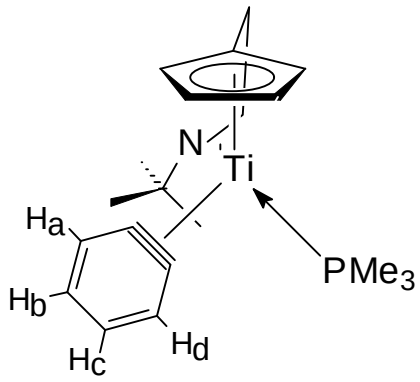


Figure 1. $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**).

For a benzyne ligand with a fixed orientation, four resonances are expected. However at room temperature only two are observed; a broad resonance at 7.65 ppm ($\Delta\nu_{1/2}$ = 20 Hz) and a somewhat better resolved resonance at 7.11 ppm (dd) which indicates fluxional processes. To investigate this, variable temperature ^{1}H and ^{13}C NMR[11] spectroscopy studies were performed (Figure 2).

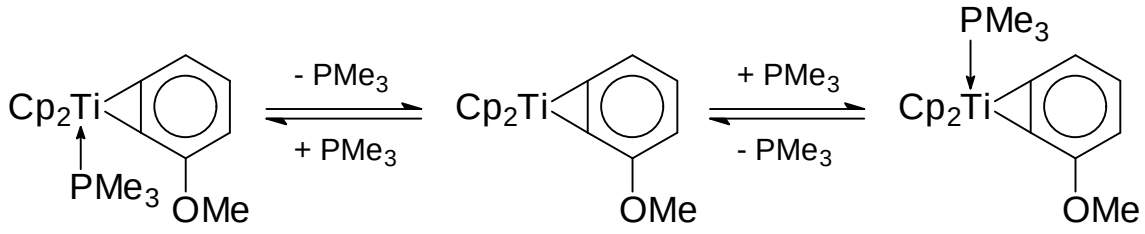
At -30 ^{o}C, the ^{1}H NMR spectrum showed three well resolved resonances assigned to the benzyne ligand at resp 7.80, 7.62 and 7.12 ppm (1 : 1 : 2 ratio). On raising the temperature the resonances at 7.80 and 7.62 ppm coalesced at 19 ± 1 ^{o}C. At 70 ^{o}C one resonance at

7.67 ppm (2H) was found. The resonance at 7.12 ppm showed to be a multiplet at -50 ^{o}C and coalesced at 5 ± 2 ^{o}C. Further raising of the temperature resulted in a double doublet (J_{HH} = 4.88 Hz, J_{HH} = 2.44 Hz) at 25 ^{o}C. Gibbs energies of activation $\Delta G^{\neq}$ = 59.6 ± 0.5 kJ/mol (278 K) and 59.8 ± 0.2 kJ/mol (292 K)[12] were calculated for this fluxional process.

In the range of -70 to 60 ^{o}C the asymmetric overall appearance of complex **43** is retained. Only small shifts were observed for the resonances of the $C_5H_4(CH_2)_2$ moiety. However at higher T these resonances broadened. They coalesced at 80 ^{o}C ($C_5H_4C\mathit{H_2}$), 95 ^{o}C (NCH_2), 100 ^{o}C (C_5H_4) and 105 ^{o}C (C_5H_4) corresponding to the estimated energies of activation $\Delta G^{\neq}$ = 79.2 ± 1 kJ/mol (80 ^{o}C), 76.5 ± 0.3 kJ/mol (95 ^{o}C), 74.6 ± 0.4 kJ/mol (100 ^{o}C) and 73.5 ± 0.5 kJ/mol (105 ^{o}C) respectively.

Using the equation $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$, the activation parameters $\Delta H^{\neq}$ (160 ± 10 KJ/mol) and $\Delta S^{\neq}$ (230 ± 30 J/K mol) were determined. Although the estimation of the parameters is rather crude, the high positive value of $\Delta S^{\neq}$ indicates a dissociative process.

Buchwald and co-workers observed fluxional behavior for $Cp_2Ti(\eta^2\text{-}2\text{-}MeO\text{-}C_6H_3)(PMe_3)$ in which the methoxy group is *cis* or *trans* to the trimethyl phosphine ligand. They propose a mechanism of dissociation and recoordination of PMe_3 with the benzyne ligand in a fixed orientation (Scheme 2).[5a]



Scheme 2. Dissociation mechanism of PMe_3 in $Cp_2Ti(\eta^2\text{-}2\text{-}MeO\text{-}C_6H_3)(PMe_3)$

The fluxional behavior observed for **43** at *low* temperature however, can not be explained by dissociation and recoordination of PMe_3 since this would result in a symmetric intermediate with two resonances for the backbone and two resonances for the cyclopentadienyl ligand. The equalization of the benzyne β and γ proton pairs as observed with ^{1}H NMR spectroscopy, is best rationalized by rotation of the benzyne ligand around its coordination axis (Scheme 3A). Rotation of aryne, olefin or alkyne ligands has been observed for $Cp^*Ta(C_6H_4)Me_2$, $Cp^*Ta(C_2H_4)Cl_2$[13] and various acetylene complexes.[14]

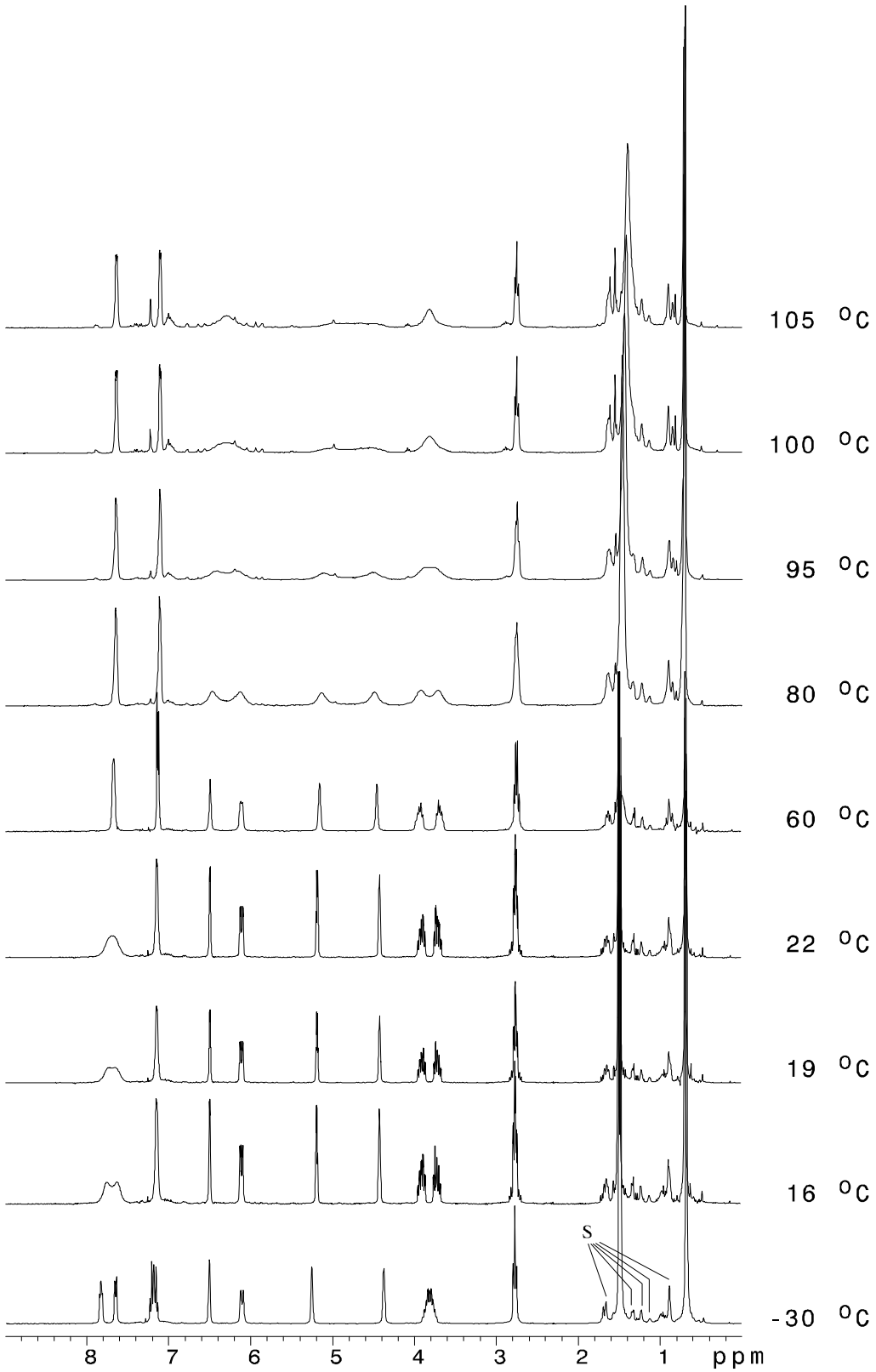
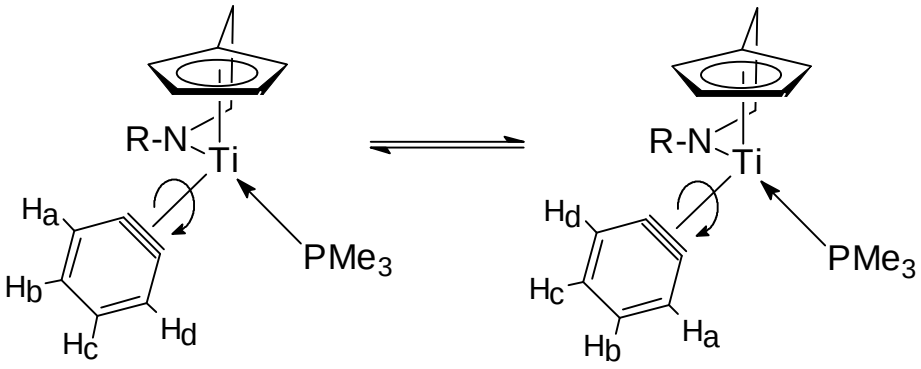
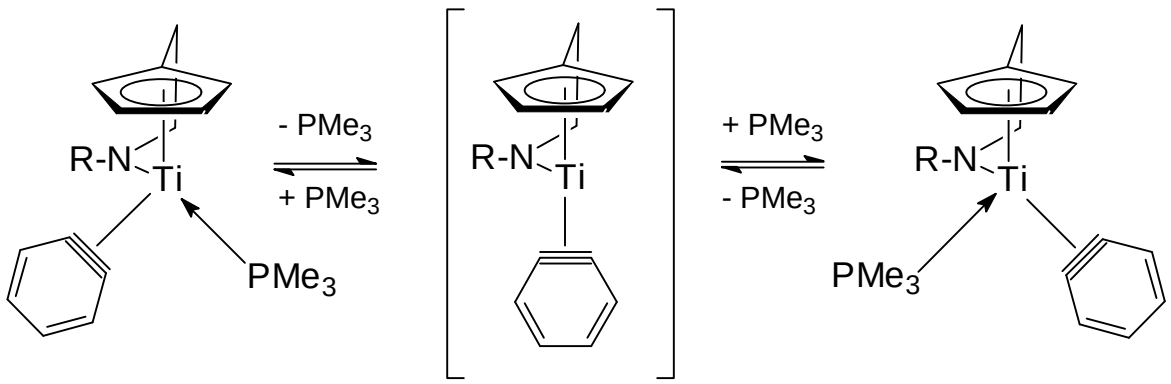


Figure 2. ^{1}H NMR spectra of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(C_6H_4)(PMe_3) (**43**) in methylcyclohexane-d_{14} at different temperatures. (s = solvent).

The *high* temperature fluxional process indeed can be rationalized as PMe_3 migration from one side to the other (Scheme 3B) giving the symmetric intermediate with two resonances for the backbone and two resonances for the cyclopentadienyl ligand.[15] This process has a 14-15 kJ mol^{-1} higher activation barrier than the rotation of the benzyne ligand. The positive $\Delta S^{\neq}$ (230 $\pm$ 30 J/K mol) is a strong indication for a dissociative process.



A



B

Scheme 3. Low (A) and high temperature (B) fluxional processes in $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**)

4.3 Molecular structure of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)(PMe_3)$ (43).

An X-ray structure determination on $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)(PMe_3)$ (**43**) was performed. Suitable crystals were grown by slowly cooling a saturated hexane solution.[16] The structure is shown in Figure 3 and a selection of bond distances and bond angles are given in Table 1.

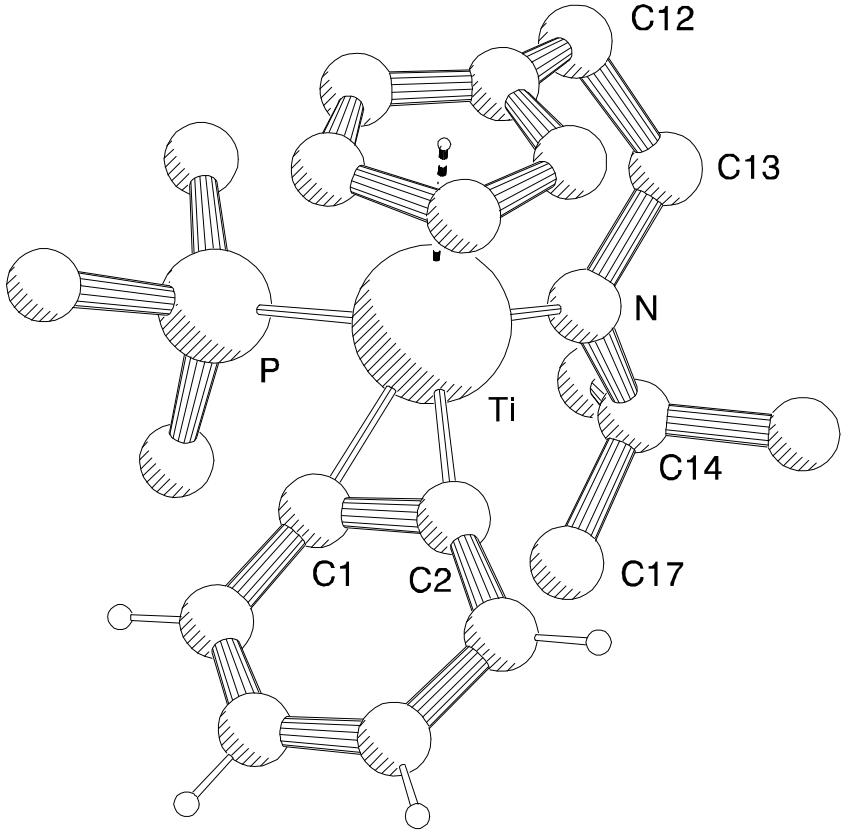


Figure 3. Structure of $[C_5H_4(CH_2)_2N$-*t*-Bu$]T(C_6H_4)(PMe_3)$ (**43**). Non-benzyne hydrogens are omitted for clarity.

The molecular structure shows that **43** has a distorted tetrahedral geometry. The bite-angle of the Cp-amido ligand (∠ N-Ti-Cg = 107.1(4)^o) and P-Ti-Cg (109.8(4)^o) are close to ideal tetrahedral geometry, while the P-Ti-C(bz) angle (97.5(4)^o) and the P-Ti-N angle (97.7(4)^o) are smaller. The largest angles are found for Cg-Ti-C(bz) (119.9(5)^o) and N -Ti-C(bz) (121.1(4)^o). The bite angle of the Cp-amido ligand (107.1(4)^o) in **43** is about the same as in $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) (106.6(1)^o).

Table 1. Selected bond distances and angles for $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(η^2-C_6H_4)(PMe_3) (**43**).

bond lengths (Å)		bond angles (deg.)	
Ti - P	2.517(5)	P - Ti - N	97.7(4)
Ti - N	1.979(14)	P - Ti - Cg	109.8
Ti - C1	2.107(15)	P - Ti - C(bz)	97.5(4)
Ti - C2	2.085(13)	N - Ti - Cg	107.1(4)
Ti - Cg	2.032(13)	N - Ti - C(bz)	121.1(4)
N - C13	1.485(18)	Cg - Ti - C(bz)	119.9(4)
C12 - C13	1.54(2)	C1 - Ti - C2	38.0(6)
C11 - C12	1.49(2)	N - C13 - C12	109.6(12)
C1 - C2	1.36(2)	Ti - N - C13	120.7(10)
C2 - C3	1.42(2)	Ti - N - C14	128.5(10)
C3 - C4	1.42(2)	C13 - N - C14	110.8(12)
C4 - C5	1.40(2)		
C5 - C6	1.31(3)		
C6 - C1	1.39(3)		

Cg and C(bz) denote the centers of gravity of the cyclopentadienyl ring and of the C1-C2 bond respectively

The benzyne ligand is η^2-bonded to titanium and the Ti-C(benzyne) distances (Ti-C1 = 2.107(15) Å and Ti-C2 = 2.085(13) Å) are comparable with normal carbon titanium σ-bonds. The Ti-C distances found for **43** are somewhat shorter than those found for Cp_2TiPh_2[17] (Ti-C(Ph) = 2.272(14) Å) and $Cp^*_2Ti(Me)CH_2Ph$ (Ti-Me = 2.181(3) Å, Ti-CH_2Ph = 2.227(4) Å)[18] but are nearly the same as those found for the titanium alkyne complexes $Cp^*_2Ti(\eta^2$-$Me_3SnC{\equiv}CSnMe_3)$ (2.096(11) Å)[19], $Cp^*_2Ti(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$ (2.124(3) Å) and $Cp_2Ti(\eta^2$-$PhC{\equiv}CSiMe_3)$ (2.118(3), 2.095(3) Å)[20].

The essentially planar benzyne ligand is oriented in the wedge left open by the cyclopentadienyl amido ligand. The six benzyne carbons and the titanium center are in one plane. The benzyne ligand in **43** is similarly oriented as in $CpV(C_6H_4)(PMe_3)$[21] and $Cp_2Zr(C_6H_4)(PMe_3)$.[22] This orientation is in accordance with the postulate proposed by Gibson[23] that in tetrahedral complexes with two strong π-donors (e.g. Cp and amido) the aryne will be directed towards the weakest π-donor (PMe_3).

The Ti-N bond distance (1.979(14) Å) in **43** is considerably longer than in $[C_5H_4(CH_2)_2N$-*i*-Pr]$TiCl_2$ (**3**) (1.864(2) Å), $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ (**4**) (1.901(1) Å) and $[C_5H_4(CH_2)_3N$-*i*-Pr]$TiCl_2$ (**9**) (1.8668(15) Å) (Chapter 2), because **43** is formally a 16 electron complex. Donation of extra electrons to titanium by PMe_3 weakens the Ti-N π-bonding. The nitrogen atom can be considered as sp^2 hybridized (sum of the Ti-N-C and C-N-C angles ≈ 360°). Like in **4**, the *tert*-butyl group in **43** is for steric reasons bent further away from the titanium center (∠Ti-N-C13 = 128.5(10)°) than the isopropyl substituent in **3** (∠Ti-N-C = 114.23(19)°) and the C-N-C angle (110.8(12)°) in **43** is smaller than in **3** (116.4(3)°). The Cp moiety shows the usual features and the distance (Cg-Ti, 2.032(13) Å) to titanium is nearly the same as found for **3** (2.008(4) Å), **4** (2.019(3) Å) and **9** (2.027(2) Å). The Ti-P distance (2.517(5) in **43** is rather short. Ti-P distances of other titanium phosphine complexes are in the range of 2.52-2.65 Å.[24]

Four independent molecules of **43** are present in the unit cell, two pairs of virtually identical molecules can be distinguished. The two pairs differ by the orientation of the backbone of the Cp-amido ligand putting the molecules in two diastereomeric conformations in the crystal lattice (Figure 4). Low temperature ^1H NMR measurements (-80 °C) however, showed only one species in solution and this suggests a low energy barrier and therefore fast interconversion of both diastereomers.[25]

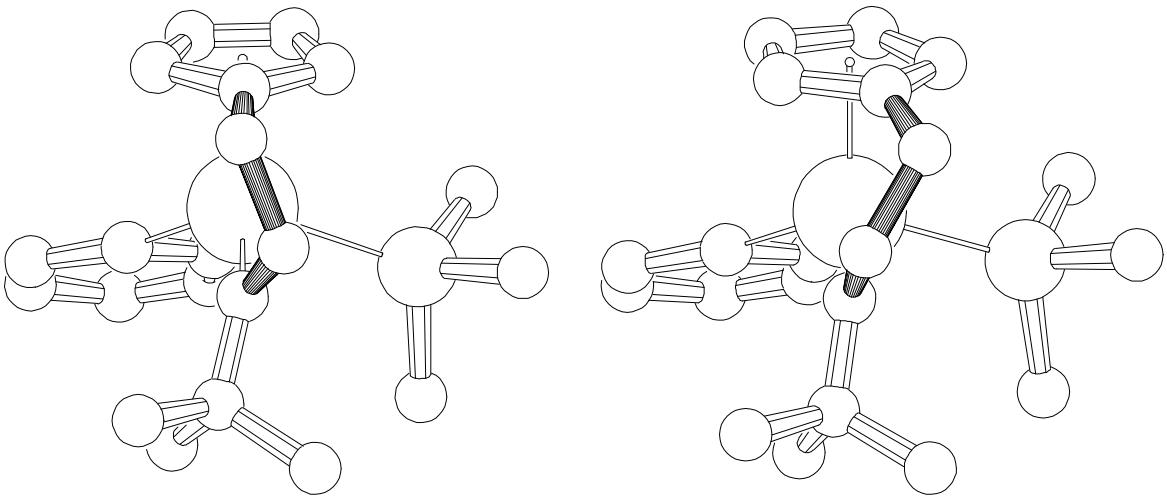
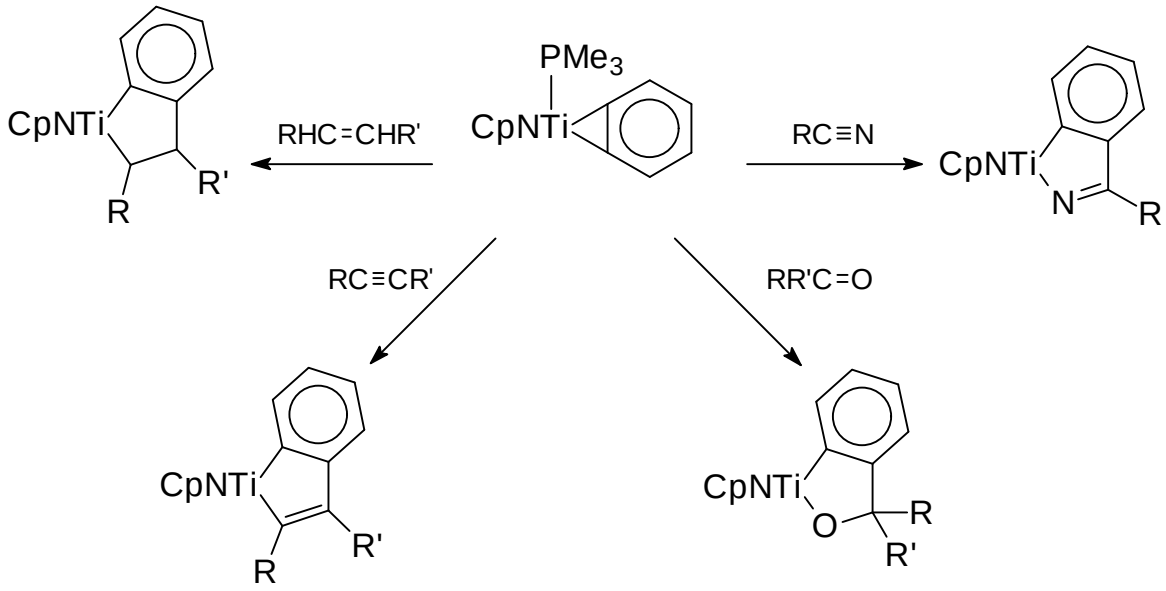


Figure 4. Diastereomeric conformers of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**).

4.4 Reactions of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(C_6H_4)(PMe_3) (43) with Unsaturated Substrates.

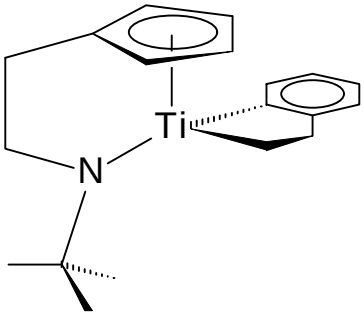
In order to determine whether the reactivity of the phosphine stabilized Cp-amido titanium benzyne complex can be compared with the titanocene analogue, **43** was reacted with various unsaturated substrates (Scheme 4).



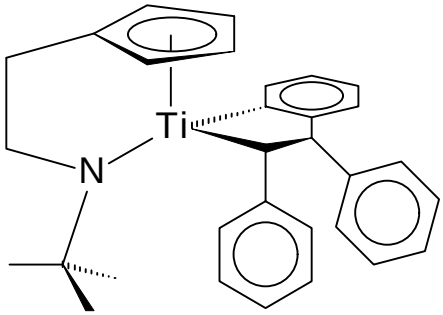
Scheme 4. Insertion chemistry of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(η^2-C_6H_4)(PMe_3) (**43**) with unsaturated substrates. CpN = $[C_5H_4(CH_2)_2N$-*t*-Bu]

4.4.1 Reaction with Alkenes:

Complex **43** reacts with ethene (^{1}H NMR) to give the titanacycle $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-$C_6H_4CH_2CH_2$) (**51**) which was isolated as a red tarry product. From COSY NMR the two triplets for the protons of the inserted ethene group (3.45 (t) and 2.33 (t) ppm resp.) were identified. The reaction of **43** with *cis*-stilbene on NMR scale, produced one distinct insertion product, $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CHPh-CHPh) (**52**). *Cis*-stilbene can coordinate to titanium with the phenyl group directed towards the Cp or to the *tert*-butyl amido. It is reasonable to assume that isomer **52** (Figure 5) is formed with both phenyl groups pointing downwards.[26]



51



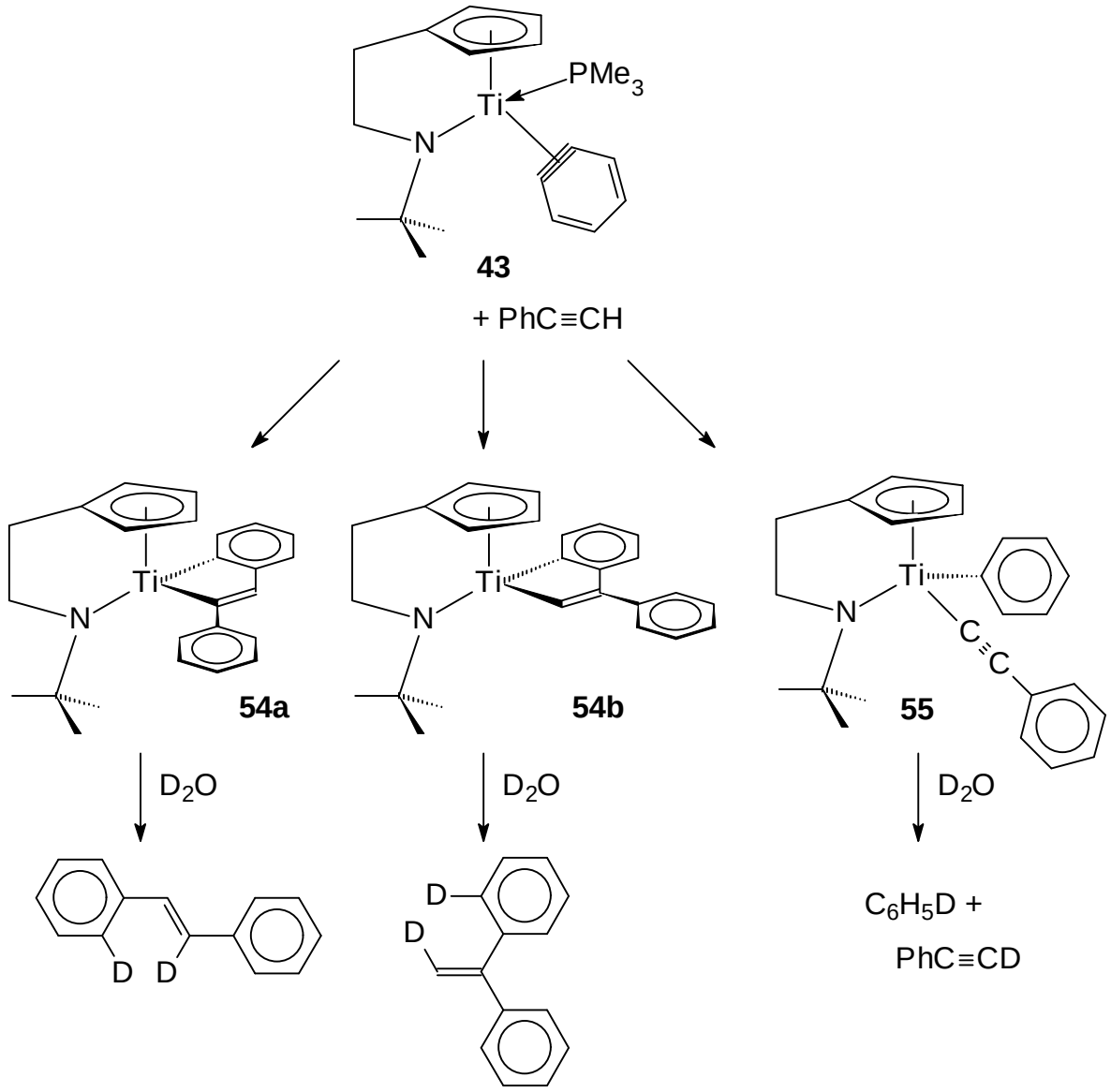
52

Figure 5. Illustration of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-$C_6H_4CH_2CH_2$) (**51**) and $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CHPh-CHPh) (**52**)

4.4.2 Reaction with Alkynes:

Reaction of **43** with diphenylacetylene gave the insertion product $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CPh=CPh) (**53**). On preparative scale **53** was isolated as red crystals in 81% yield and fully characterized (^{1}H, ^{13}C NMR, IR, EA).

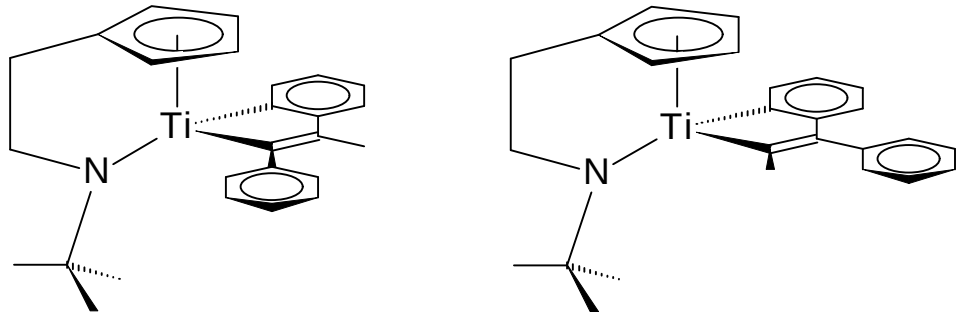
With asymmetric alkynes two different products can be expected. With PhC≡CH indeed two products in a 2 : 1 ratio (^{1}H NMR) were obtained. GC-MS analysis of the product (after quenching with D_2O 1 min after addition of PhC≡CH), indicated the presence of the mono deuterated *trans*-stilbene, 1,1-diphenylethene in a 3 : 1 ratio and minor amounts (≈ 4%) of C_6H_5D and PhC≡CD. *Trans*-stilbene corresponds to the major insertion product $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CH=CPh) (**54a**) and 1,1-diphenylethene to the minor product $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CPh=CH) (**54b**). Apparently also σ-bond metathesis with the acid alkyne proton had occurred (Scheme 5), as can be concluded from the presence of mono deuterated benzene and phenylacetylene liberated from quenching $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(Ph)C≡CPh (**55**) with D_2O.



Scheme 5. Reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(C_6H_4)(PMe_3)$ (**43**) with phenylacetylene

Monitoring the reaction of **43** with PhC≡CH by ^{1}H NMR spectroscopy, the minor product **54b** disappeared in 12 h at room temperature, while simultaneously *iso*-butene was liberated. This indicates activation of the Cp-amido ligand. The organometallic decomposition product(s) could not be identified. The major phenylacetylene insertion product appeared to be much more stable as the amounts of **54a** remained constant. Apparently a selective decomposition of the minor product **54b** had occurred. When in a similar reaction PMe_3 was removed, decomposition of **54b** proceeded much faster. Within 3 h **54b** was decomposed completely. Also in this experiment the major product was not affected and the amount of **56a** remained constant.

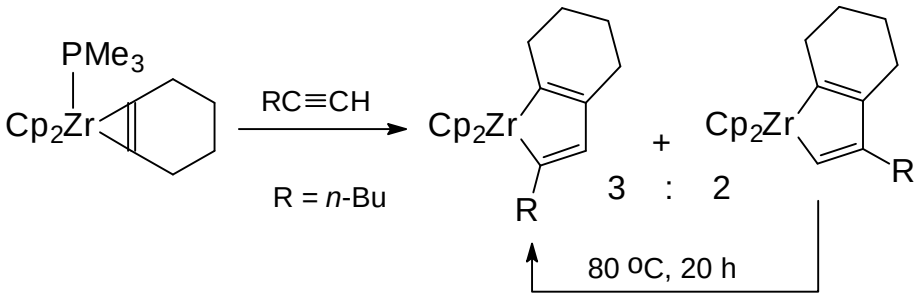
The reaction of **43** with PhC≡CMe is slower than with phenylacetylene, reaching completion after 30 min. (RT). Two products in nearly equal amounts (54 : 46) were obtained as was concluded from ^{1}H NMR spectroscopy. With a NOESY ^{1}H NMR experiment the major product was identified as [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(o-C_6H_4CMe=CPh) (**56a**) and the minor products as [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(o-C_6H_4CPh=CMe) (**56b**) (Figure 6). Also in this case selective decomposition of **56b** was observed though at much lower rate than **54b**.



56a **56b**

Figure 6.

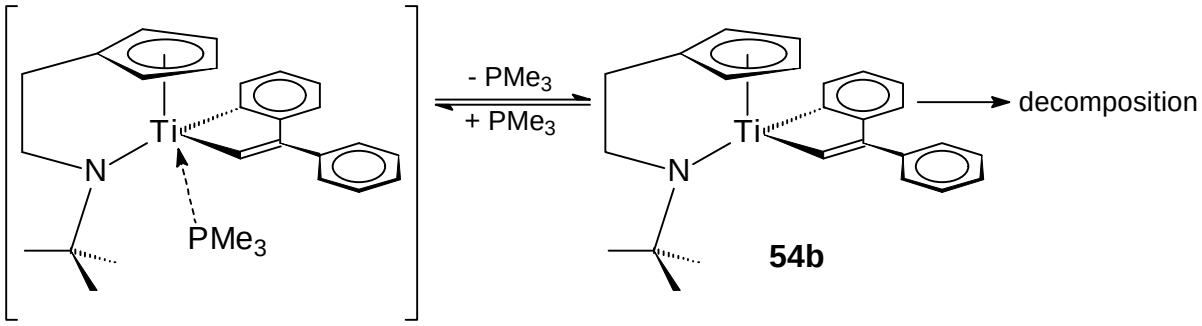
A reason for complex **54a** being the major product, could be that the alkyne substituent is more hindered by the former aryne ligand than by the wedge left open by the Cp-amido ligand. A similar preference was observed by Buchwald *et al.*[5a] in the reaction of $Cp_2Ti(C_6H_3OMe)PMe_3$ with 1-hexyne. However, in this case the insertion is reported to be 100% regiospecific.[27] A similar insertion has been reported for the cyclohexyne complex $Cp_2Zr(C_6H_8).PMe_3$ in the reaction with 1-hexyne. A 3 : 2 mixture of geminal and *trans* insertion products was obtained. In this case a complete isomerization to the geminal insertion product (Scheme 6) was observed at higher temperatures (80 ^{o}C, 20 h).[10]



Scheme 6.

The difference in thermal stability between complexes **54a** and **54b** is remarkable as **54a** is thermally quite stable and **54b** is not. In this respect, complex **54b** is more comparable with $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiEt_2$ (**38**) and the metallacycle $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2)_4$ (**41**) than with other stable $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiR_2$ species. Surprising however, is that the decomposition of **54b** is retarded in the presence of PMe_3. This implies an interaction of the phosphine with the metal center. Another indication for an interaction is the broadened resonance observed for PMe_3 in the ^{1}H NMR spectrum.[28] However, the interaction is weak since PMe_3 can be removed easily, e.g. no phosphorus resonance could be detected when C_6D_6 was removed under vacuum and replaced by fresh solvent.

The rather facile activation of the *tert*-butyl amido in **54b** suggests that the methyl groups of the amido substituent can interact with the metal center. For **54a** such an interaction is blocked by the phenyl group alongside the titanium center. In the case of **56b**, activation of the *tert*-butyl amido is hampered by the presence of the methyl group near titanium. More crowded systems make ligand activation less likely and this is in accordance with the observed inhibition of the process by PMe_3 (Scheme 7).

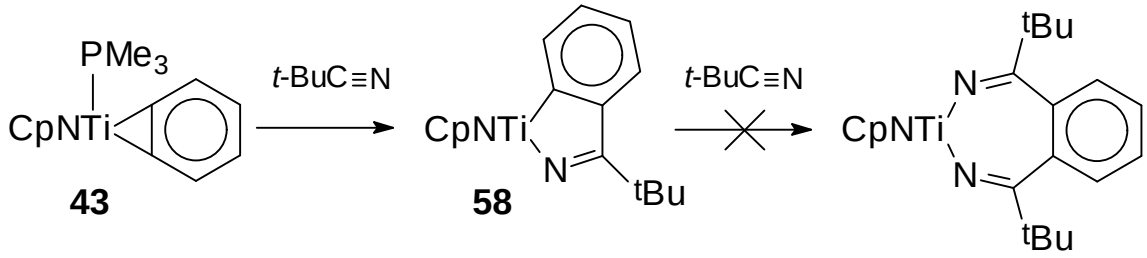


Scheme 7.

4.4.3 Reaction with Nitriles:

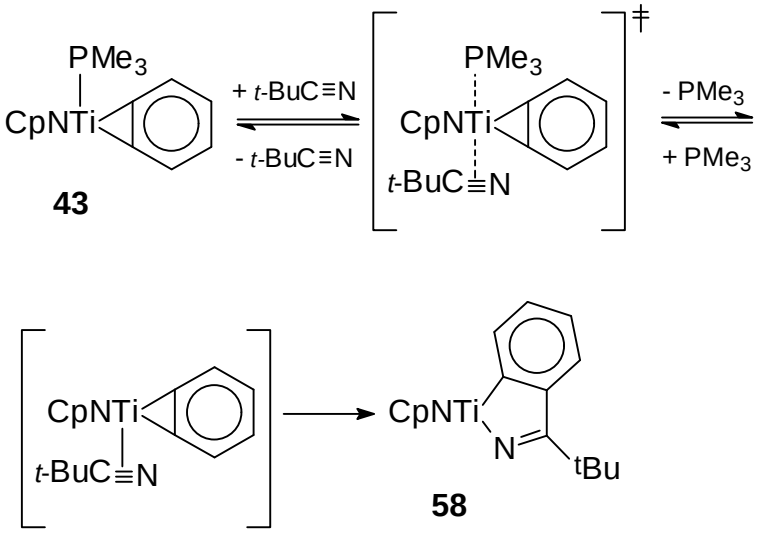
Reaction of **43** with one equivalent of acetonitrile in pentane immediately gave a brown insoluble product. After removal of the solvent in vacuum, a brown powder was obtained. The product appeared to be slightly soluble in THF-d_8 and from the ^{1}H NMR spectrum it was concluded that the mono-insertion product $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(o\text{-}C_6H_4CMe{=}N)$ (**57**) had been formed. With the sterically more hindered *tert*-butyl nitrile the insertion reaction was considerably slower and after 2.5 h (^{1}H NMR) **43** was completely converted into the

metallacycle $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4C(*t*-Bu)=N) (**58**) (Scheme 8). A preparative scale synthesis yielded **58** as a red oil in 86% yield.



Scheme 8.

Insertion of a second nitrile, known to happen for $CpV(\eta^2$-$C_6H_4)(PMe_3)_2$,[21] did not occur. Treating **43** with two equivalents of *t*-BuCN only gave the mono-insertion product **58** and heating at 75°C only resulted in formation of *iso*-butene, *i.e.* decomposition of the mono-insertion product had occurred.



Scheme 9.

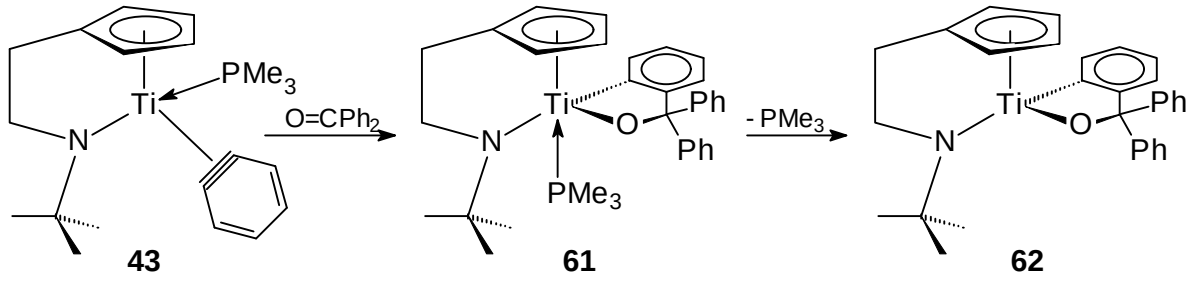
Cámpora and Buchwald observed that the rates of insertion of unsaturated substrates decrease dramatically when excess trimethylphosphine is added. In such a situation the incoming substrate has to compete with phosphine for a coordination site (Scheme 9). To prove that the mechanism suggested by Buchwald is valid for the insertion chemistry of **43** as well, NMR tube reactions of **43** with *t*-BuCN[29] were performed with (10 fold excess) and

without PMe_3. Without PMe_3, the reaction was completed for 83 % after 15 minutes, while with a ten fold excess PMe_3, the same conversion was reached only after 240 minutes. From this it can be concluded that also in the case of **43** the incoming substrates have to compete with the trimethylphosphine for a coordination site on the titanium center (Scheme 9).

4.4.4 Reaction with Ketones:

NMR tube reactions of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)PMe_3$ (**43**) with 1 eq. of acetone or acetophenone at room temperature immediately afforded the oxotitanacyclic complexes $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(-*o*-$C_6H_4C(Me_2)O)$ (**59**) and $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(-*o*-$C_6H_4C(Me)PhO)$ (**60**), the latter as a mixture of two diastereomers **60a** and **60b** in about 1 : 1 ratio. The phenyl and methyl groups of the incoming acetophenone are pointing away from the CpNTi moiety and it seems that steric congestion of the incomming acetophenone does not lead to a preferent insertion reaction.

Performing a preparative reaction of **43** with benzophenone, both ^1H and ^{13}C NMR showed an additional, phosphorus coupled resonance at 0.79 ppm (d, $^2J_{PH}$ = 0.74 Hz) integrating for 9 protons and 15.56 ppm (dq, $^1J_{CP}$ = 6.10 Hz, $^1J_{CH}$ = 128.2 Hz resp. ^{31}P NMR showed a sharp up-field shifted resonance at -58.05 ppm. Hence it is concluded that the trimethylphosphine adduct $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(*o*-$C_6H_4C(Ph)_2O)(PMe_3)$ (**61**) was formed instead of the expected phosphine free species $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(*o*-$C_6H_4C(Ph)_2O)$ (**62**). The ^{31}P resonance at -58.05 ppm, observed for **61**, is to our knowledge the most up-field shift ever reported for a coordinated trimethylphosphine and is rather close to the chemical shift of free PMe_3 (-62.6 ppm) and indicates that the phosphine is weakly coordinating. Attempts to perform an elemental analysis of complex **61** yielded values close to those of the phosphine free complex **62** which clearly showed a different ^1H and ^{13}C NMR spectrum. Analytical pure $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(-*o*-$C_6H_4C(Ph_2)O)$ (**62**) was prepared by stripping $C_5H_4(CH_2)_2N$-*t*-Bu]Ti(-*o*-$C_6H_4C(Ph_2)O)(PMe_3)$ with hot toluene and crystallization of the residue from pentane (Scheme 10).



Scheme 10.

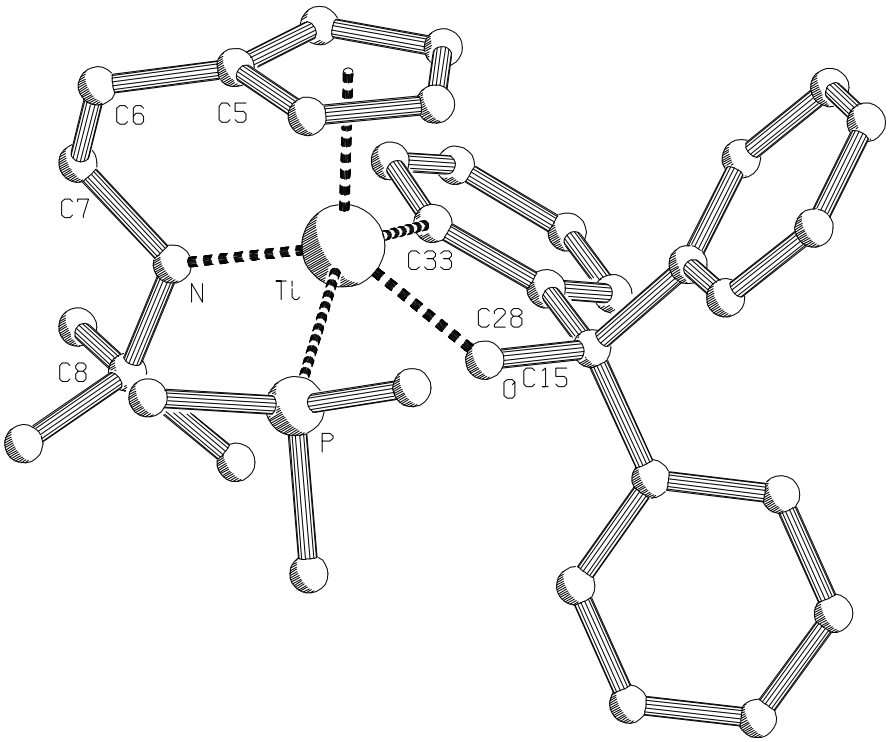


Figure 7. Molecular structure of $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(o\text{-}C_6H_4CPh_2O)PMe_3$ (**61**). Hydrogens have been omitted for clarity.

In order to establish the molecular geometry of both compounds, single crystal X-ray diffraction structure analyses of $[C_5H_4(CH_2)_2N\text{-}t\text{-}u]Ti(\text{-}o\text{-}C_6H_4C(Ph_2)O)(PMe_3)$ and $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(\text{-}o\text{-}C_6H_4C(Ph_2)O)$ were carried out. [30] A PLUTO representation of **61** and **62** is shown (Figure 7 and 8) and selected data are listed in Table 2.

Compound **61** adopts a distorted square based pyramidal geometry with the Cp moiety placed on the top and the metal center lifted from the square plane. Complex **62** has a distorted tetrahedral surrounding of the metal center.

In **61** the Ti-O (1.9396(12) Å) and the Ti-C (2.1780(19) Å) distances are considerably larger than the corresponding distances in **62** (Ti-O = 1.834(4) Å, Ti-C = 2.121(5) Å) while the Ti-N and Ti-Cg distances are almost equal for both complexes (Table 3). The coordinating PMe_3 in **61** increases the electron density at the metal center and consequently elongates the Ti-O and Ti-C(aryl) bonds but not the Ti-N and Ti-Cg bonds.

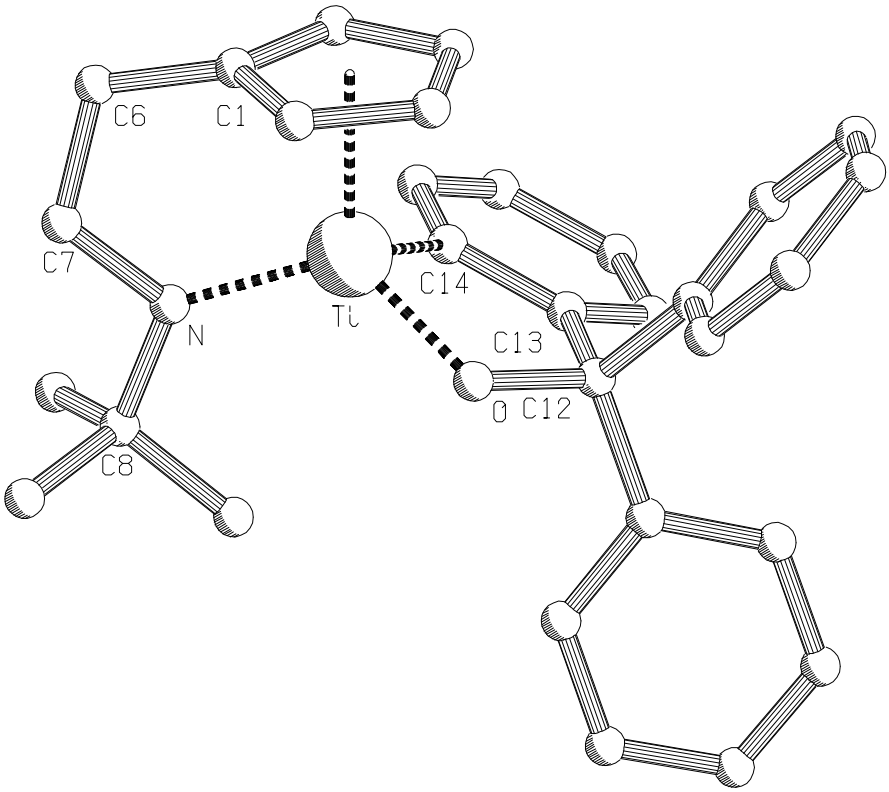


Figure 8. Molecular structure of $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(o\text{-}C_6H_4CPh_2O)$ (**62**)
Hydrogens have been omitted for clarity.

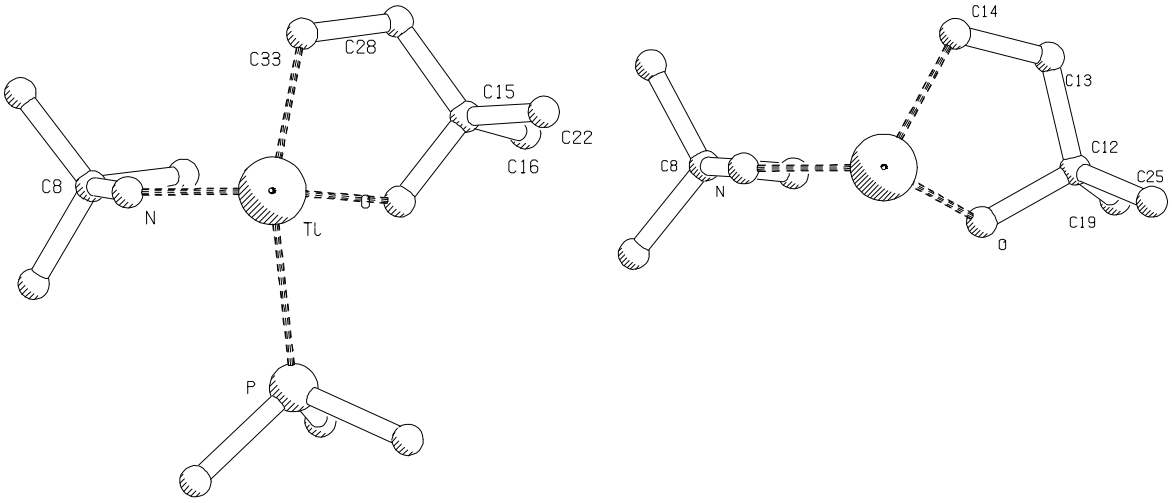


Figure 9. Projection along the Ti-Cg axis of the simplified structures of **61** (left) and **62** (right). The Ti-Cg vectors are directed to the reader.

Table 2. Selected geometric data for $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(o\text{-}C_6H_4CPh_2O)(PMe_3)$ (**61**) and $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(o\text{-}C_6H_4CPh_2O)$ (**62**).

$[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(o\text{-}C_6H_4CPh_2O)(PMe_3)$		$[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(o\text{-}C_6H_4CPh_2O)$	
Bond lengths (Å)			
Ti - P	2.6647(6)		
Ti - O	1.9396(12)	Ti - O	1.834(4)
Ti - N	1.9580(15)	Ti - N	1.941(6)
Ti - Cg	2.061(2)	Ti - Cg	2.035(6)
Ti - C33	2.1780(19)	Ti - C14	2.121(5)
C33 - C28	1.401(2)	C14 - C13	1.408(6)
C28 - C15	1.523(2)	C13 - C12	1.525(6)
C15 - O	1.421(2)	C12 - O	1.437(5)
Bond angles (^{o})			
Cg - Ti - P	104.45(5)		
Cg - Ti - O	121.56(6)	Cg - Ti - O	126.08(17)
Cg - Ti - N	105.71(6)	Cg - Ti - N	107.79(19)
Cg - Ti - C33	106.64(6)	Cg - Ti - C14	109.08(19)
P - Ti - O	73.40(4)		
P - Ti - N	91.32(5)		
P - Ti - C33	144.82(5)		
O - Ti - N	132.47(6)	O - Ti - N	119.27(17)

O - Ti - C33	76.54(6)	O - Ti - C14	79.79(16)
N - Ti - C33	95.73(7)	N - Ti - C14	109.21(17)
Ti - C33 - C28	113.24(12)	Ti - C14 - C13	110.0(3)
C33 - C28 - C15	114.42(15)	C14 - C13 - C12	115.6(4)
C28 - C15 - O	106.73(13)	C13 - C12 - O	105.5(3)
Ti - O - C15	122.86(10)	Ti - O - C12	121.5(2)

Cg denotes the center of gravity of the cyclopentadienyl moiety

From the structures and top-view projections (Figure 9) of both molecules it can be clearly seen that in the case of the phosphine free complex **62**, a rather large space is left open opposite to C14. Coordination of PMe_3 causes a rotation of the oxometallacycle of about 20^o counterclockwise around the Cg-Ti axis towards the amido and in **61** the oxygen is opposite to the amido (N-Ti-Cg-O = 175^o) while the phosphine is almost opposite to C33 (C33-Ti-Cg-P = 163^o). The geometry of the oxometallacycle itself is hardly affected by the coordinated PMe_3.

The large gap in **62** is in fact positioned at the wrong side of the molecule to allow an attack on the remaining titanium carbon bond. Similar structures can be expected for the other insertion products **57**-**60** with a large gap at the hetero atom side and a much smaller one at the titanium carbon bond side. This would explain why the reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**) with *t*-BuCN stops after one nitrile insertion.

The Ti-P bond (2.6647(6) Å) in **61** is, to our knowledge, the longest reported and is clearly longer than the one in the benzyne complex $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)(PMe_3)$ (**43**) (2.517(5) Å) (*vide supra*). Other Ti-P distances of complexes reported are in the range of 2.52-2.65 Å.[24] The Ti-Cg distances (**61**: 2.061(2) Å, **62**: 2.035(6) Å) are normal and well within the range of other Cp titanium(IV) complexes (Chapter 2 and references cited). The Ti-N distances in **61** and **62** (1.9580(15) resp. 1.941(6) Å) are comparable with the one of **43** (1.979(14) Å) but are considerably longer than those of the dichloro species $[C_5H_4(CH_2)_2N$-*i*-Pr]$TiCl_2$ (**3**) (1.864(2) Å), $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ (**4**) (1.901(1) Å) and $[C_5H_4(CH_2)_3N$-*i*-Pr]$TiCl_2$ (**9**) (1.8668(15) Å).[31] The long Ti-N distance in **62** may be due to a strong $O(p_\pi)\rightarrow M(d_\pi)$ interaction that competes with the $N(p_\pi)\rightarrow M(d_\pi)$ interaction. In both complexes the nitrogen geometry is planar, indicative for sp^2 hybridization As can be seen in Table 3, the Ti-O bond is influenced in greatest extent by the coordination of PMe_3, in **62** the Ti-O bond is 1.834(4) Å while this bond in **61** is 0.1 Å longer (1.9396(12) Å). The Ti-O bond length in **62** is comparable with CpTi(O-2 PPh_2- 6-*t*-Bu-C_6H_3)Cl_2 (1.860(5) Å),[24a] $Cp_2Ti(Cl)OEt$ (1855(2) Å)[32a]

and CpTi(OC(CMe_2-*o*-C_6H_4-CMe_2)CH_2PMe_2)=CH-*t*-Bu (1.869(2) Å)[24m] but is longer than the Ti-O bonds in [$C_5H_4(CH_2)_3O$]$TiCl_2$ (1.762(2) Å),[32d] and [$C_5Me_4(CH_2)^3O$]$TiCl_2$ (1.767(1) Å)[32c] Although coordination of PMe_3, like in **61**, is unprecedented in related Cp_2Ti chemistry, it may reflect the consequence of using electronically and sterically more unsaturated complexes. From the molecular structure of **62** it is obvious that the rather large gap between the Cp, the amido and the oxygen allows coordination of Lewis bases. However, as observed for **61**, the coordinated phosphine is easily removed and it is very likely that in the case of the other insertion reactions presented in this chapter, the PMe_3 may have an interaction with the metal center but too weak to allow isolation of the phosphine adducts.[33]

4.4.5 The Reactivity of [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4)(PMe_3) (43) *versus* Titanocene Benzyne Complexes.

In general **43** reacts considerably faster than titanocene benzyne complexes. For example, the reaction of $Cp_2Ti(\eta^2$-2-MeO-$C_6H_3)(PMe_3)$ with ethene requires heating at 80 ^oC for 1.5 hour,[5a] while in the case of **43** the reaction was complete after 2 hours at room temperature. The reaction of **43** with internal alkynes are completed almost immediately whereas the reaction of $Cp_2Ti(\eta^2$-2-MeO-$C_6H_3)(PMe_3)$ with 3-hexyne requires 2 hours at 85 ^oC.[5a] The higher reactivity of **43** is most prrobably a consequence of using electronically and sterically more unsaturated complexes.

4.5 Concluding Remarks.

The benzyne complex [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4)(PMe_3) (**43**) is easily available through thermolysis of the bis phenyl complex [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiPh_2$ in the presence of PMe_3. The molecular structure of **43** shows a regular benzyne ligand. A special feature is the presence of two diastereomers in the crystal lattice which differ in the conformation of the Cp-amido ligand backbone.

In solution **43** is highly fluxional. Variable temperature NMR spectroscopy reveals two distinct processes being simultaneous operative: rotation of the benzyne around its coordination axis ($\Delta G^{\neq}$ = 59.8 ± 0.2 kJ/mol (292 K)) and reversible dissociative rearrangement of the PMe_3 ligand ($\Delta G^{\neq}$ = 73.5 ± 0.5 kJ/mol (378 K)). Rotation of the benzyne ligand proceeds much faster than reversible dissociative rearrangement of the PMe_3 ligand.

Reaction of $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti$(C_6H_4)(PMe_3)$ (**43**) with unsaturated substrate molecules like alkenes, alkynes, nitriles and ketones give insertions like those observed in group 4 metallocene aryne chemistry. In general stable compounds are formed which could be isolated and identified. However, in some cases the stability of the complex formed clearly depends on how the substrate inserts. Compound $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CH=CPh) (**54a**) is more stable than $C_5H_4(CH_2)_2N$-*t*-Bu]Ti(o-C_6H_4CPh=CH) (**54b**). Sterically demanding substituents near the metal center tend to inhibit activation of the Cp-amido ligand. This is also supported by the retarding of this process by PMe_3.

A clear consequence of the electronically and sterically unsaturation of the $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti system, is the availability of an extra coordination site which enhances the reactivity of the complexes. This is clearly demonstrated by the unexpected phosphine adduct of the oxo metallacycle $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti$(OC(Ph)_2C_6H_4)(PMe_3)$ (**61**), obtained by the reaction of **43** with benzophenone.

4.6 Experimental.

For general considerations see Chapter 2. The reagents used in this chapter were purified by distillation and dried over molsieves (4 Å) (phenylacetylene, phenylmethylacetylene, acetonitrile, *t*-butylnitrile, acetone and acetophenone) or recrystallized (cis-stilbene, diphenylacetylene and benzophenone). Deutero phenylacetylene PhC≡CD was prepared hydrolysis of PhC≡CLi with D_2O.

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_6H_4)(PMe_3) (43). To a solution of 1.13 g (3.10 mmol) of [$C_5H_4(CH_2)_2$N-*t*-Bu]$TiPh_2$ in 50 mL of hexane 0.70 mL (6.4 mmol) of PMe_3 was added. The vessel was closed and the brown solution was stirred at 70 ^oC for 1.5 h. The solution turned yellow. Subsequently the mixture was cooled to room temperature and approximately 25 mL of solvent was removed in vacuum. On cooling overnight to -30 ^oC dark yellow crystals separated, yield: 0.59 g (1.63 mmol, 53%). ^1H NMR (200 MHz, C_7D_{14}, -60 ^oC): δ 7.82 (m, 1H, C_6H_4); 7.64 (m, 1H, C_6H_4); 7.16 (m, 2H, C_6H_4); 6.45, 6.00, 5.26, 4.26 (m, 4H, C_5H_4); 3.75 (m, 2H, NCH_2); 2.71 (m, 2H, $C_5H_4\underline{CH_2}$); 1.40 (d, $^2J_{HP}$ = 5.86 Hz, 9H, PMe_3); 0.63 (s, 9H, N-*t*-Bu). ^{13}C NMR (75.4 MHz, C_7D_{14}, -60 ^oC): δ 190.73 (d, $^2J_{CP}$ = 8.06 Hz, C*q*-C_6H_4); 184.53 (d, $^2J_{CP}$ = 35.25 Hz, C*q*-C_6H_4); 131.54, 130.34, 130.12, 129.35 (d, $^1J_{CH}$ = 148.6, 154.1, 155.6, 138.0 Hz, C_6H_4); 129.56 (s, C_5H_4-*ipso*); 111.13, 109.49, 107.75, 100.27 (d, $^1J_{CH}$ = 178.3, 183.3, 175.4, 172.2 Hz, C_5H_4); 62.85 (t, $^1J_{CH}$ = 133.0 Hz, NCH_2); 59.25 (s, N-*C*Me_3); 32.44 (s, N-C$\underline{Me_3}$); 32.24 (t, $^1J_{CH}$ = 126.7 Hz, $C_5H_4\underline{CH_2}$); 19.15 (dq, $^1J_{CH}$ = 126.4 Hz, $^2J_{CP}$ = 15.6 Hz, PMe_3). ^{31}P NMR (80.96 MHz, C_6D_6): δ -3.73 (PMe_3). IR (cm^{-1}): 2726 (w), 2627 (w), 1545 (w), 1420 (w), 1400 (w), 1323 (m), 1300 (m), 1281 (m), 1244 (w), 1192 (m), 1150 (w), 1069 (w), 1053 (w), 986 (w), 978 (m), 951 (s), 936 (m), 849 (w), 835 (w), 799 (m), 793 (m), 735 (s), 681 (w), 556 (w), 436 (w), 411 (w). Anal. Calcd for $C_{20}H_{30}NPTi$: C, 66.11; H, 8.32; Ti, 13.18. Found: C, 66.40; H, 8.38; Ti, 13.12.

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-$C_6H_4CH_2CH_2$) (51). To a cooled (-80 °C) solution of 0.46 g (1.27 mmol) of **43** in 40 mL of hexane, an excess of ethene was added. Upon warming to room temperature, the reaction mixture turned red. It was stirred overnight. The solvent was removed in vacuum and the residue was stripped twice with 15 mL of ether to give a red oil. ^1H NMR (200 MHz, C_6D_6): δ 7.12 - 6.79 (m, 4H, C_6H_4); 6.41, 5.56 (m, 2 x 2H, C_5H_4); 3.45 (t, $^3J_{HH}$ = 6.47 Hz, 2H, $TiCH_2$); 3.19 (m, 2H, NCH_2); 2.33 (t, $^3J_{HH}$ = 6.47 Hz, 2H, $C_6H_4\underline{CH_2}$); 1.90, 1.68 (m, 2 x 1H, $C_5H_4\underline{CH_2}$); 1.40 (s, 9H, *t*-Bu).

NMR tube reaction of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_6H_4)(PMe_3) (43) with cis-stilbene. In an NMR tube 23 μL (0.13 mmol) of *cis*-stilbene was added to a solution of 46 mg (0.13 mmol) of **43** in 0.6 mL of C_6D_6. In two hours at room temperature, the color changed from yellow-brown to dark red. The ^1H NMR spectrum showed the presence of a new product in 20% conversion. Heating at 50 ^oC for 1 d. resulted in almost complete conversion in [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(*o*-C_6H_4C(Ph)H-CH(Ph)) (**52**). ^1H NMR (200 MHz, C_6D_6): δ 7.95, 7.65, 7.31, 7.27, 7.2-7.0 (m, 13H, 2 x C_6H_5 + C_6H_4); 6.70 (m, 1H, C_5H_4); 6.20 (d,

$^3J_{HH}$ = 7.57 Hz, 1H, C_6H_5); 5.85 (m, 1H, C_5H_4); 5.56 (m, 1H, C_5H_4); 5.29 (d, $^3J_{HH}$ = 6.34 Hz, 1H, TiCH(Ph)-C<u>H</u>(Ph)); 4.50 (m, 1H, C_5H_4); 4.02 (d, $^3J_{HH}$ = 6.59 Hz, 1H, TiC<u>H</u>(Ph)); 3.35 (m, 2H, NCH_2); 2.25 (m, 2H, C_5H_4<u>CH_2</u>); 1.26 (s, 9H, *t*-Bu); 0.79 (d, $^2J_{HP}$ = 2.2 Hz, 9H, free PMe_3).

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-C_6H_4CPh=CPh) (53). To a mixture of 0.48 g (2.70 mmol) of diphenylacetylene and 0.99 g (2.72 mmol) of **43**, 50 mL of cyclohexane was added. After 0.5 h the solvent was removed in vacuum and the orange residue was extracted with 100 mL of pentane. Concentration and cooling (-30 °C) gave red crystals. Yield: 1.02 g (2.19 mmol, 81 %). ^{1}H NMR (200 MHz, C_6D_{12}): δ 7.04 - 6.94 (m, 4H, C_6H_4); 6.88 - 6.42 (m, 5H, C_6H_5); 6.83 - 6.58 (m, 5H, C_6H_5); 6.48, 6.43 (m, 2 x 1H, C_5H_4); 5.91, 5.42 (q, 2 x 1H, C_5H_4); 3.91, (m, 2H, NCH_2); 2.78 (t, $^3J_{HH}$ = 6.59 Hz, C_5H_4<u>CH_2</u>); 1.65 (s, 9H, *t*- Bu). ^{13}C NMR (75.4 MHz, C_6D_{12}): δ 205.09 (s, C_q-Ti<u>C</u>=C); 195.24 (s, $^3J_{CH}$ = 4.58 Hz, C_q-TiC_6H_4); 147.77 (s, C_q-TiC=<u>C</u>); 146.65, 144.63, 140.20 (s, $^3J_{CH}$ = 7.63 Hz, C_q-C_6H_4, 2 x C_q-C_6H_5),;137.47 (s, C_5H_4-*ipso*); 130.97, 125.17, 124.04 (d, C_6H_4); 130.57, 128.02, 127.82, 127.25, 126.38, 126.33 (d, 2 x C_6H_5); 118.02, 117.75, 114.83, 114.68 (d, C_5H_4); 62.95 (t, $^1J_{CH}$ = 134.29 Hz, NCH_2); 61.05 (s, <u>C</u>Me_3); 31.15 (t, $^1J_{CH}$ = 128.18 Hz, C_5H_4<u>CH_2</u>); 29.12 (q, C<u>Me_3</u>). IR (cm^{-1}): 2726 (w), 2446 (w), 1694 (w), 1682 (w), 1632 (w), 1589 (m), 1557 (w), 1512 (m), 1317 (m), 1308 (m), 1263 (w), 1242 (w), 1223 (w), 1194 (m), 1171 (m), 1155 (m), 1105 (w), 1071 (m), 1028 (w), 982 (m), 949 (m), 901 (w), 868 (w), 841 (w), 804 (w), 785 (w), 756 (w), 719 (m), 698 (w), 577 (w), 426 (w). Anal. Calcd. for $C_{31}H_{31}$TiN: C, 80.03; H, 6.66; Ti, 10.29. Found: C, 80.03; H, 6.95, Ti, 9.61.

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-C_6H_4CH=CPh) (54a). To a solution of 0.62 g (1.71 mmol) of **43** in 50 mL of pentane, 188 μL (1.71 mmol) of phenylacetylene was added. The dark brown/red solution was stirred for 48 h at room temperature. Another 75 mL of pentane was added and the reaction mixture was filtered. After concentration and cooling (- 30 °C), a brown powder was obtained. Yield: 0.28 g (0.72 mmol, 42 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.46 (s,1H, CH); 7.22, 6.99 (m, 2 x 2H, C_6H_4); 7.07 - 7.03 (m, 2H, C_6H_5); 6.96, 6.89, 6.83 (m, 3 x 1H, C_6H_5); 6.36, 6.25 (q, 2 x 1H, C_5H_4); 5.77 (t, 2H, C_5H_4); 3.61, 3.43 (m, $^3J_{HH}$ = 6.83 Hz, 2 x 1H, NCH_2); 2.44 (m, $^3J_{HH}$ = 6.35 Hz, 2H, C_5H_4<u>CH_2</u>); 1.44 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 203.38 (s, C_q-Ti<u>C</u>=CH); 190.91 (C_q-TiC_6H_4); 146.31, 138.07 (s, C_q-C_6H_4, C_q-C_6H_5); 135.91 (s, C_5H_4-*ipso*); 133.87 (d, TiC=<u>C</u>H); 131.77 - 124.77 (d, C_6H_4, C_6H_5); 117.78, 115.71, 113.65, 112.77 (d, C_5H_4); 62.38 (t, NCH_2); 59.90 (s, <u>C</u>Me_3); 29.62 (t, C_5H_4<u>CH_2</u>); 28.20 (q, C<u>Me_3</u>). IR (cm^{-1}): 2726 (w), 2672 (w), 2361 (w), 1946 (w), 1591 (m), 1192 (m), 1074 (m), 984 (w), 949 (w), 814 (s), 762 (s), 718 (s), 698 (s). Anal. Calcd for $C_{25}H_{27}$TiN: C 77.11; H 6.99; Ti 12.30. Found: C 76.86; H 6.85; Ti 11.72.

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-C_6H_4CD=CPh) (54a-d_1). To a solution of 0.56 g (1.54 mmol) of **43** in 50 mL pentane, 171.4 μL (1.54 mmol) of PhC≡CD was added. The reaction mixture was stirred for 120 h at room temperature, and the solvent was removed in vacuum. Another 100 mL of pentane was added, and the reaction mixture was filtered and concentrated. Cooling (- 30 °C) gave a brown powder. Yield: 0.21 g (0.54 mmol, 35 %). ^{1}H NMR (200 MHz, C_6D_6): δ 7.26 - 6.80 (m, 9H, C_6H_4, C_6H_5);

6.35, 6.24 (q, 2 x 1H, C_5H_4); 5.77 (t, 2H, C_5H_4); 3.62, 3.41 (m, 2 x 1H, NCH_2); 2.41 (m, 2H, $CH_2C_5H_4$); 1.44 (s, 9H, *t*-Bu).

NMR tube reaction of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_6H_4)(PMe_3) (43) with methylphenylacetylene. To a solution of 38.9 mg (0.11 mmol) of **43** in C_6D_6, 13.3 µL (0.11 mmol) PhC≡CMe was added. The color of the solution changed immediately from brown to red. The ^{1}H NMR spectrum showed that two isomers had been formed in a ratio of 54 (**56a**):46 (**56b**). ^{1}H NMR (200 MHz, C_6D_6): δ 7.30 - 6.99, 6.88 - 6.72 (m, 14H, 2 x C_6H_5, 2 x C_6H_4); 6.65, 6.48, 5.62, 5.29 (m, 4 x 1H, C_5H_4); 6.62, 6.61, 5.71, 5.63 (m, 4 x 1H, C_5H_4); 3.47 (m, 2 x 2H, NCH_2); 2.46, 2.34 (m, 2 x 2H, $C_5H_4\underline{CH_2}$); 1.92 (s, 3H, TiC($\underline{CH_3}$), **56a**); 1.52 (s, 3H, TiC(C_6H_5)C($\underline{CH_3}$), **56b**); 1.51 (s, 9H, *t*-Bu, **56a**); 1.49 (s, 9H, *t*-Bu, **56b**). ^{13}C NMR (75.4 MHz, C_6D_6): δ 206.13, 204.92 (s, 2 x C_q-TiC); 194.87, 192.47 (s, 2 x C_q-TiC_6H_4); 147.34, 147.06 (s, 2 x C_q-TiC=$\underline{C}$); 145.15, 144.54, 141.62, 140.33 (s, 2 x C_q-C_6H_4, 2 x C_q-C_6H_5); 137.52, 136.54 (s, 2 x C_5H_4-*ipso*); 131.84, 131.39, 130.94 - 123.23 (d, 2 x C_6H_4, 2 x C_6H_5); 117.81, 117.74, 117.35, 116.12, 114.77, 114.21, 114.01, 112.96 (d, 2 x C_5H_4); 62.39, 62.18 (t, NCH_2 **56a** and **56b**); 60.53, 59.96 (s, $\underline{C}Me_3$ **56a** and **56b**); 30.21 (t, $C_5H_4\underline{CH_2}$ **56a** and **56b**); 28.89, 28.80 (q, $C\underline{Me_3}$ **56a** and **56b**); 22.06, 22.05 (q, CH_3 **56a** and **56b**).

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-C_6H_4CMe=N) (57). To a solution of 0.43 g (1.18 mmol) of **14** in 25 mL of pentane, 61.6 µL (1.18 mmol) of MeCN was added. A brown insoluble product formed immediately. The reaction mixture was stirred overnight at room temperature. After removal of the solvent in vacuum, a brown powder was obtained. Yield 0.25 g (0.76 mmol, 65 %). ^{1}H NMR (200 MHz, THF-d_8): δ 7.59, 7.21 (m, 2 x 1H, C_6H_4); 6.94 - 6.86 (m, 2H, C_6H_4); 6.37, 6.04, 5.80, 5.39 (q, 4 x 1H, C_5H_4); 4.54, 3.79 (m, 2 x 1H, NCH_2); 3.00 (m, 2H, $C_5H_4\underline{CH_2}$); 2.45 (s, 3H, Me); 1.03 (s, 9H, *t*-Bu).

NMR tube reaction of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_6H_4)(PMe_3) (43) with tert-butylnitrile. In an NMR tube 49.2 mg (0.136 mmol) of **43** was dissolved in 0.6 mL C_6D_6 and 15.6 µL (0.136 mmol) of *t*-BuCN was added. The color of the solution changed immediately from brown to red. After 1.5 h the starting material had completely been converted into [$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(o-C_6H_4C(*t*-Bu)=N) (**58**).

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-C_6H_4C(t-Bu)=N) (58). To a solution of 1.01 g (2.78 mmol) of **43** in 40 mL of pentane 0.32 mL (2.78 mmol) of *t*-BuCN was added. The solution turned red and was stirred for 5 h at room temperature to complete the reaction. The solvent was removed in vacuum and the residue was extracted with 40 mL of pentane. Removing the pentane in vacuum left an oily, dark red product. Yield: 0.88 g (2.38 mmol, 86 %). ^{1}H NMR (200 MHz, C_6D_6): δ 7.16 - 6.83 (m, 4H, C_6H_4); 6.52, 6.14 (m, 2 x 1H, C_5H_4); 5.82 (t, $^3J_{HH}$ = 2.56 Hz, 2 x 1H, C_5H_4); 3.60, 3.37 (m, 2 x 1H, NCH_2); 2.51 (m, 2H, $C_5H_4\underline{CH_2}$); 1.33, 1.32 (s, 2 x 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 195.34 (C_q-TiC_6H_4); 189.50, 159.43 (C_q-C_6H_4, C_q-CN); 134.75, 126.95, 124.71, 124.52 (C_6H_4); 137.24 (C_5H_4-*ipso*); 114.86, 113.80, 112.61, 110.76 (C_5H_4); 67.47 (NCH_2); 61.03 ($N\underline{C}Me_3$); 34.74 (N=$\underline{C}Me_3$); 30.28 ($C_5H_4\underline{CH_2}$); 28.74, 28.61 (2 x $C\underline{Me_3}$)

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-$C_6H_4CMe_2O$) (59). To a solution of 0.66 g (1.82 mmol) of **43** in 50 mL of pentane, 133.7 µL (1.82 mmol) of acetone was added. The reaction mixture was stirred overnight at room temperature. 50 mL of pentane was added to the mixture and the brown solution was filtered. About 80 mL of solvent was removed in vacuum. On cooling overnight (- 30 °C) green crystals were obtained. Yield 0.25 g (0.72 mmol, 40 %). ^{1}H NMR (200 MHz, C_6D_6): δ 7.12 - 6.92 (m, 4H, C_6H_4); 6.78, 6.38 (m, 2 x 1H, C_5H_4); 5.74 (m, 2H, C_5H_4); 3.70, 3.46 (m, 2 x 1H, NCH_2); 2.48 (m, 2H, $C_5H_4\underline{CH_2}$); 1.56 (s, 3H, Me); 1.51 (s, 3H, Me); 1.22 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 186.32 (s, C_q-TiC_6H_4); 170.62 (s, C_q-C_6H_4); 138.48 (s, C_5H_4-*ipso*); 133.50, 125.56, 123.80, 123.46 (d, C_6H_4); 114.94, 113.92, 113.58, 107.46 (d, C_5H_4); 86.09 (s, $\underline{C}Me_2$); 63.84 (t, $^1J_{CH}$ = 135.05 Hz, NCH_2); 59.00 (s, $\underline{C}Me_3$); 33.68 (q, Me); 30.11 (q, $C\underline{Me_3}$); 29.74 (t, $^1J_{CH}$ = 128.56 Hz, $C_5H_4\underline{CH_2}$); 28.48 (q, Me).

NMR tube reaction of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(C_6H_4)(PMe_3) (43) with acetophenone. In an NMR tube 36 mg (0.10 mmol) of **43** was dissolved in 0.7 mL C_6D_6 and 11.6 µL (0.10 mmol) of MePhC=O was added. The color of the solution immediately changed from brown to dark yellow. After 25 min, the ^{1}H NMR spectrum showed that two isomers of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-C_6H_4C(Me)PhO) (**60a**-**b**) in approximately 1 : 1 ratio had been formed. ^{1}H NMR (200 MHz, C_6D_6): 7.61, 7.57, 7.45, 7.41, 7.24 - 7.04 (m, 18H, 2 x C_6H_4, 2 x C_6H_5); 6.15, 5.95, 5.92, 5.86, 5.67, 5.59, 5.55, 4.98 (q, 8 x 1H, 2 x C_5H_4); 3.77, 3.46 (m, 4, NCH_2 **60a**-**b**); 2.47 (m, 4H, $C_5H_4\underline{CH_2}$ **60a**-**b**); 1.84, 1.16 (s, 2 x 9H, *t*-Bu **60a**-**b**); 0.75 (s, 9H, free PMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 189.93 (s, 2 x C_q-TiC_6H_4); 165.30, 165.25 (s, 2 x C_q-C_6H_4); 150.49, 147.94 (s, 2 x C_q- C_6H_5); 136.80, 136.38 (s, 2 x C_5H_4-*ipso*); 134.84, 134.30 (dd, 2 x C_6H_4); 127.84 - 123.80 (d, 2 x C_6H_4, 2 x C_6H_5); 115.83, 115.67, 114.11, 113.96, 112.69, 112.21, 107.07, 106.36 (d, 2 x C_5H_4); 91.41, 90.61 (s, 2 x O$\underline{C}$MePh); 63.88, 63.67 (t, 2 x NCH_2); 59.71, 58.95 (s 2 x $\underline{C}Me_3$); 32.78, 29.64 (q, 2 x $C\underline{Me_3}$); 30.68, 29.59 (t, 2 x C_5H_4-$\underline{CH_2}$); 15.06 (dq, free PMe_3).

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-$C_6H_4CPh_2O$)(PMe_3) (61). To 0.96 g (5.27 mmol) of benzophenone and 1.91g (5.27 mmol) of **43**, 125 mL of pentane was added under stirring. After 5 min a yellow powder started to precipitate. The reaction mixture was stirred overnight at room temperature and another 100 mL of pentane was added. The reaction mixture was filtered. The solution was concentrated to 150 mL, and cooling (- 30 °C) overnight gave 1.28 g (2.35 mmol) of orange crystals. Concentration of the mother liquor and cooling (- 30 °C) gave 0.73 g (1.34 mmol) of product. Yield: 2.01 g (3.69 mmol, 70 %). ^{1}H NMR (300 MHz, C_6D_6): δ 7.55 (m, 2H, C_6H_4); 7.33 (m, 2H, 2 x C_6H_5); 7.16 (m, 2H, C_6H_4); 7.22 - 6.95 (m, 8H, 2 x C_6H_5); 5.92, 5.76, 5.67, 4.81 (m, 4 x 1H, C_5H_4); 3.79, 3.49 (m, 2 x 1H, NCH_2); 2.53, 2.40 (m, 2 x 1H, $C_5H_4\underline{CH_2}$); 1.18 (s, 9H, *t*-Bu); 0.79 (d, $^2J_{HP}$ = 0.74 Hz, PMe_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ 191.98 (s, C_q-TiC_6H_4); 164.56 (s, C_q-C_6H_4); 151.66, 150.11 (s, 2 x C_q-C_6H_5); 136.95 (s, C_5H_4-*ipso*); 135.01 (dd, $^1J_{CH}$ = 156.26 Hz, C_6H_4); 128.84 - 124.49 (d, C_6H_4, 2 x C_6H_5); 116.75, 115.12, 112.64, 107.90 (d, C_5H_4); 96.80 (s, O$\underline{C}$(Ph_2); 64.38 (t, $^1J_{CH}$ = 133.98 Hz, NCH_2); 60.11 (s, $\underline{C}Me_3$); 30.33 (q, $^1J_{CH}$ = 125.33 Hz, $C\underline{Me_3}$); 30.25 (t, $^1J_{CH}$ = 128.18 Hz, $C_5H_4\underline{CH_2}$), 15.56 (dq, $^1J_{CH}$ = 128.18 Hz, $^2J_{CP}$ = 6.10 Hz, PMe_3). IR (cm^{-1}), 2726(w), 2674 (w), 2438 (w), 2427 (w), 2413 (w), 2359 (w), 1944 (w), 1914 (w), 1887 (w), 1869 (w), 1809 (w), 1595 (m), 1562 (m), 1352 (m), 1343 (m), 1302

(m), 1275 (m), 1240 (w), 1221 (w), 1190 (m), 1175 (w), 1157 (w), 1069 (w), 1032 (w), 1007 (s), 982 (m), 953 (s), 941 (s), 903 (w), 866 (w), 806 (m), 768 (s), 756 (s), 727 (s), 702 (s), 656 (w), 534 (w), 482 (w), 442 (w).

Synthesis of [$C_5H_4(CH_2)_2$N-t-Bu]Ti(o-$C_6H_4CPh_2O$) (62). A solution of 0.41 g (0.75 mmol) of **61** in 30 mL of toluene, was heated to 100 °C for 2 h and stirred overnight at room temperature. The solvent was removed in vacuum and the residue was stripped with 20 mL of pentane. The residue was extracted with 100 mL of pentane and the solution was concentrated. Cooling to - 30 °C gave orange crystals. Yield: 0.1 g (0.21 mmol, 28 %). ^{1}H NMR (200 MHz, C_6D_6): δ 7.64 (m, 2H, C_6H_4); 7.35 (m, 2H, 2 x C_6H_5); 7.17 (m, 2H, C_6H_4); 7.21 - 6.92 (m, 8H, 2 x C_6H_5); 6.00, 5.69, 5.63, 4.99 (q, 4 x 1H, C_5H_4); 3.58 (m, 2H, CH_2N); 2.46 (m, 2H, $C_5H_4\underline{CH_2}$); 1.25 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 188.93 (s, C_q-TiC_6H_4); 166.72 (s, C_q-C_6H_4); 150.99, 147.90 (s, 2 x C_q-C_6H_5); 139.02 (s, C_5H_4-*ipso*); 133.68 (dd, $^1J_{CH}$ = 156.26 Hz, C_6H_4); 128.09 - 124.31 (d, C_6H_4, 2 x C_6H_5); 115.53, 114.94, 114.01, 109.20 (d, C_5H_4); 93.81 (s, O$\underline{C}$(Ph_2); 63.81 (t, $^1J_{CH}$ = 135.24 Hz, NCH_2); 59.66 (s, $\underline{C}Me_3$); 30.19 (q, $^1J_{CH}$ = 125.89 Hz, C$\underline{Me_3}$); 29.67 (t, $^1J_{CH}$ = 128.37 Hz, $C_5H_4\underline{CH_2}$). Anal. Calcd for $C_{30}H_{34}$TiNO: C 76.75; H 6.66; Ti 10.20. Found: C 76.74; H 6.80; Ti 10.08.

4.7 References and Notes.

(1) (a) Roberts, J.D.; Caserio, M.C. *Basic Principles of Organic Chemistry, 2nd Ed.* World Student Series, W.A. Benjamin, Inc. Menlo Park , California, USA, 19. (b) McMurry, J. *Organic Chemistry*, Brooks/Cole Publishing Company, Monterey, California, USA, 19.

(2) Kolomnikov, I.S.; Lobeeva, T.S.; Gorbachevskaya, V.V.; Aleksandrov, G.G.; Struckhov, Y, T.; Vol'pin, M.E. *J. Chem. Soc., Chem. Commun.* **1971**, 972

(3) Shur, V.; Berkovitch, E.G.; Vol'pin, M.E.; Lorenz, B.; Wahren, M. *J. Organomet. Chem.* **1982**, *228*, C36.

(4) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659.

(5) (a) Cámpora, J.; Buchwald, S.L. *Organometallics* **1993**, *12*, 4182. (b) Erker, G.; Korek, U.; Pettrenz, R.; Rheingold, A.L. *J. Organomet. Chem.* **1991**, *421*, 215. (c) Erker, G.; Korek, U.; Rheingold, A.L. *J. Organomet. Chem.* **1993**, *454*, 113.

(6) Rausch, M.D.; Mintz, E.A. *J. Organomet. Chem.* **1980**, *190*, 65.

(7) (a) Buchwald, S.L.; Sayers, A.; Watson, B.T.; Dewan, J.C. *Tetrahedron Lett.* **1987**, *28*, 3245. (b) Buchwad, S.L.; Watson, B.T.; Lum, R.T.; Nugent, W.A. *J. Am. Chem. Soc.* **1987**, *109*, 7137.

(8) Gautheron, B.; Tainfurier, G.; Pouly, S. *Organometallics* **1984**, *3*, 1495.

(9) Small amounts of ammonia, phenylhydrazine and aniline were found after hydrolysis of a Cp_2TiPh_2 solution heated under a nitrogen atmosphere. (a) Vol'pin, M.E.; Shur, V.B. in *New*

Trends in the Chemistry of Nitrogen Fixation, Chatt, J.; da Cãmarapina, L.M.; Richards, R.L., Ed., Academic Press: London, **1980**, 67. (b) Shur, V.B.; Berkovitch, E.G.; Vasiljeva, L.B.; Kudryavtsev, R.V.; Vol'pin, M.E. *J. Organomet. Chem.* **1974**, *78*, 127. (c) Berkovitch, E.G.; Shur, V.B.; Vol'pin, M.E.; Lorenz, B.; Rummel, S.; Wahren, M. *Chem. Ber.* **1980**, *113*, 70.

(10) Buchwald,S.L.; Nielsen, R.B. *Chem. Rev.* **1988**, *88*, 1047 and references therein.

(11) Variable temperature ^{13}C NMR spectroscopy also revealed two fluxional processes. At -60 ^{o}C two phosphorus coupled resonances (190.73 ppm, $^{2}J_{CP}$ = 8.06 Hz; 184.53 ppm, $^{2}J_{CP}$ = 35.25 Hz) for the quarternary carbons were observed. The other benzyne carbon atoms show resonances at 131.54, 130.34, 130.12 and 129.35 ppm which coalescence at 20 ^{o}C[11]. At high temperature (50 ^{o}C) one quarternary carbon resonance at 186.10 ppm and two CH resonances at 130.84 and 129.95 ppm are observed for the benzyne ligand. In this case an energy of activation $\Delta G^{\neq}$ = 59.0 ± 0.6 kJ/mol (20 ^{o}C) is estimated. The four resonances of the C_5H_4 moiety remain virtually unchanged in the temperature range of -60 - 70 ^{o}C but broaden at higher temperatures and coalesce around 105 ^{o}C[11]. For the high temperature process an energy of activation $\Delta G^{\neq}$ = 74 ± 1 kJ/mol (105 ^{o}C) is estimated

(12) $\Delta G^{\neq}$ is calculated from $\Delta G^{\neq} = 19.1x10^{-3}\ T_c\ (9.97 + \log T_c - \log(\nu_a - \nu_b))$ with T_c = 278 and 292 K and $\nu_a - \nu_b$ = 16 and 57 Hz respectively. Hesse, M.; Meier, H.; Zeeh, B. *Spectroscopische Methoden in der Organischen Chemie* **1991**, Georg Thieme Verlag: Stuttgart.

(13) McLain, S.J.; Schrock, R.R.; Sharp, P.R.; Churchill, M.R.; Youngs, W.J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

(14) Jackman, L.M.; Cotton, F.A. (Ed.), *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1975 and references therein.

(15) Well resolved symmetric ^{1}H and ^{13}C NMR spectra for **43** can not be obtained since substantial decomposition of **43** occurs already at 105 ^{o}C.

(16) Crystal data for **43**: $C_{20}H_{30}NPTi$, M_w = 363.32 g mol^{-1}, orthorhombic, space group *P*bc2_1 with a = 9.627(1) Å, b = 21.286(1) Å, c = 38.089(2) Å, V = 7805.2(10) Å^3, Z = 16 and D_{calc} = 1.237 g cm^{-3}. R_F = 0.0695 for 3436 unique observed reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 853 parameters.

(17) Kocman, V.; Rucklidge, J.C.; O'Brien, R.J.; Santo,W. *J. Chem. Soc., Chem. Commun.* **1971**, 1340.

(18) Luinstra, G.A. Thesis, Groningen, **1991**.

(19) Varga, V.; Mach, K.; Hiller, J.; Thewalt, U.; Sedmera, P.; Polášek, M. *Organometallics* **1995**, *14*, 1410.

(20) Burlakov, V.V.; Polyakov, A.V.; Yanovsky, A.I.; Struchkov, Yu.T.; Shur, V.B.; Vol'pin, M.E.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1994**, *476*, 197.

(21) Buijink, J.K.F.; Kloetstra, K.R.; Meetsma, A.; Teuben, J.H. *Organometallics* **1996**, *15*, 2533.

(22) Buchwald, S.L.; Watson, B.T.; Huffman, J.C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(23) Gibson, V.C. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1565.

(24) Short Ti-P distances are known for chelating complexes, like in $(MeC_5H_4)_2Ti(dmpe)$ (2.527(4) Å, 2.540(4) Å), CpTiCl(dmpe) (2.571(1) Å), CpTiMe(dpme) (2.6021(1) Å), and for the dimer $[Cp_2TiP(CH_3)_2]_2$ (2.613(2) Å, 2.642(2) Å). Long Ti-P bond distance are known for the more bulky PR_3 ligands like in $Cp_2Ti(PhSiH_2)PEt_3$ (2.651(6) Å), due to greater steric crowding of the ligand. (a) Willoughby, C.A.; Duff, Jr., R.R.; Davis, W.M.; Buchwald, S.L. *Organometallics* **1996**, *15*, 472. (b) van Doorn, J.A.; van der Heijden, H.; Orpen, A.G. *Organometallics* **1995**, *14*, 1278. (c) Thiele, K.H.; Windisch, H.; Schumann, H.; Kociok-Köhn, G. *Z. anorg. allg. Chem.* **1994**, *620*, 523. (d) Spaltenstein, E.; Palma, P.; Kreutzer, K.A.; Willoughby, C.A.; Davis, W.M.; Buchwald, S.L. *J. Am. Chem. Soc.* **1994**, *116*, 10308. (e) You, Y.; Wilson, S.R.; Girolami, G.S.; *Organometallics* **1994**, *13*, 4655. (f) Samuel, E.; Mu, Y.; Harrod, J.F.; Promzee, Y.; Jeannin, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3435. (g) Payne, R.; Hachgenei, J.; Frittz, G.; Frenske, D.Z. *Naturforsch.* **1986**, *41b*, 1535. (h) Dawoodi, Z.; Green, M.L.H.; Mtetwa, V.S.B.; Prout, K.; Schultz, A.J.; Williams, J.M.; Koetzie, T.F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629. (i) Kool, L.B.; Rausch, M.D.; Alt, H.G.; Herberhold, M.; Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1986**, *310*, 27. (j) Kool, L.B.; Rausch, M.D.; Alt, H.G.; Herberhold, M.; Wolf, B.; Thewalt, U. *J. Organomet. Chem.* **1985**, *297*, 159. (k) Kool, L.B.; Rausch, M.D.; Alt, H.G.; Herberhold, M.; Thewalt, U. ; Wolf, B. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 394. (l) Girolami, G.S.; Wilkinson, G.; Thornton-Pett, M.; Hunzsthous, M.B. *J. Chem. Soc., Dalton Trans.* **1984**, 2347. (m) van Doorn, J.A.; van der Heijden, H.; Orpen, A.G. *Organometallics* **1995**, *14*, 1278.

(25) The symmetric complexes $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$ (**4**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**) have diastereotopic methylenes in the carbon chain in the solid state, see Chapter 2.

(26) Full characterization of the complex could not be achieved since NOESY NMR experiments did not give conclusive information about which isomer is formed.

(27) The 100% regio-selectivity mentioned here means that 1-hexyne inserts with the alkyl group directing along the titanium center independent of the orientation of the methoxy group of the benzyne ligand.

(28) During the reaction the PMe_3 resonance became broader and less well resolved.

(29) In principle it should be the case for insertions of all unsaturated substrates. In this case we have chosen for the insertion of *t*-BuCN because this reaction is sufficiently slow to follow with ^1H NMR spectroscopy. Reactions with other substrates are almost completed immediately.

(30) Suitable crystals of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(-o$-$C_6H_4C(Ph_2)O)$ **53** were grown by slowly concentrating a pentane solution to which excess of PMe_3 was added. In absence of additional PMe_3 recrystallisation from pentane results in the phosphine free adduct.

Crystal data for **61**: $C_{33}H_{40}NOPTi$, M_w = 545.54 g mol^{-1}, orthorhombic, space group Pbca with a = 18.395(1) Å, b = 16.766(1) Å, c = 18.468(1) Å, V = 5695.7(6) Å^3, Z = 8 and D_{calc} = 1.272 g

cm^{-1}. R_F = 0.0368 for 5045 unique observed reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 494 parameters.

62 crystallizes in two forms; triclinic for **62a** and monoclinic for **62b.** Crystal data for **62a**: $C_{30}H_{31}NOTi$, M_w = 469.45 g mol^{-1}, triclinic, space group P_1 with a = 8.531(6)Å, b = 10.733(4) Å, c = 13.885(8) Å, α = 77.00(3)°, β = 85.935(5)°, γ = 74.36(4)°, V = 1192.8(12) $Å^3$, Z = 2 and D_{calc} = 1.3079 g cm^{-3}, R_F = 0.0665 for 2812 unique observed reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 442 parameters. Crystal data for **62b**: $C_{30}H_{31}NOTi$, M_w = 469.45 g mol^{-1}, monoclinic, space group $P2_1/c$ with a = 11.799(2) Å, b = 23.936(5) Å, c = 8.732(2) Å, β = 100.28(3)°, V = 2426.5(9) A^3, Z = 4 and D_{calc} = 1.289 g cm^{-3}. R_F = 0.0879 for 1309 unique observed reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 301 parameters.

(31) For comparison with other titanium amido complexes see Chapter 2 and references therein.

(32) (a) Huffman, J.C.; Moloy, K.G.; Marsella, J.A.; Caulton, K.G. *J. Am. Chem. Soc.* **1980**, *102*, 3009. (b) van Doorn, J.A.; van der Heijden, H.; Orpen, A.G. *Organometallic* **1994**, *13*, 4271. (c) Fandos, R.; Meetsma, A.; Teuben, J.H. *Organometallics* **1991**, *10*, 59. (d) Trouvé, G.; Laske, D.A.; Meetsma, A.; Teuben, J.H. *J. Organomet. Chem.* **1996**, *511*, 255. (e) Cetinkaya, B.; Hitchcock, P.B.; Lappert, M.F.; Torroni, S.; Atwood, J.L.; Hunter, W.E.; Zaworotko, M.J. *J. Organomet. Chem.* **1980**, *188*, C31. (f) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 66. (g) Curtis, M.D.; Thanedar, S.; Butler, W.M. *Organometallics* **1984**, *3*, 1855. (h) Orpen, A.G.; Brammer, L.; Allen, F.H.; Kennard, O.; Watson, D.G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(33) In several cases some PMe_3 was left after the removal of the solvent and drying under vacuum for a short time. Longer periods of drying in vacuum resulted in complete removement of PMe_3.

5 Cyclopentadienyl Amido Zirconium Chloride and Carbyl Complexes; Synthesis and Reactivity of $[C_5H_4(CH_2)_nNR]ZrX_2$.*

5.1 Introduction.

Zirconocene complexes are increasingly important in catalysis, especially in catalytic polymerization of α-olefins[1] and show in general higher activities than the analogous titanocene or hafnocene compounds.[1b] Some years ago, the development of new catalysts based on linked cyclopentadienyl amido group 4 metal complexes $[C_5R_4\text{-}Y\text{-}NR']MCl_2$ (R= H, Me; Y = $SiMe_2$, $(SiMe_2)_2$, $(CH_2)_2$; R' = *t*-Bu, aryl; M = Ti, Zr) by Dow Chemical and Exxon Chemical[2] gave a strong stimulus for further development of this area. This however, by the time we started this project, has been mainly focused to titanium complexes bearing a relatively narrow class of silyl bridged Cp-amido ligands. For zirconium and hafnium, only a limited number of $SiMe_2$ or otherwise bridged Cp-amido complexes have been described so far and little is known about the more general chemistry of these complexes.[3]

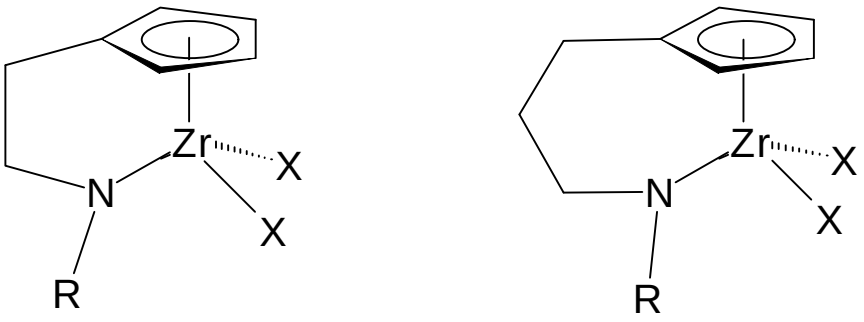


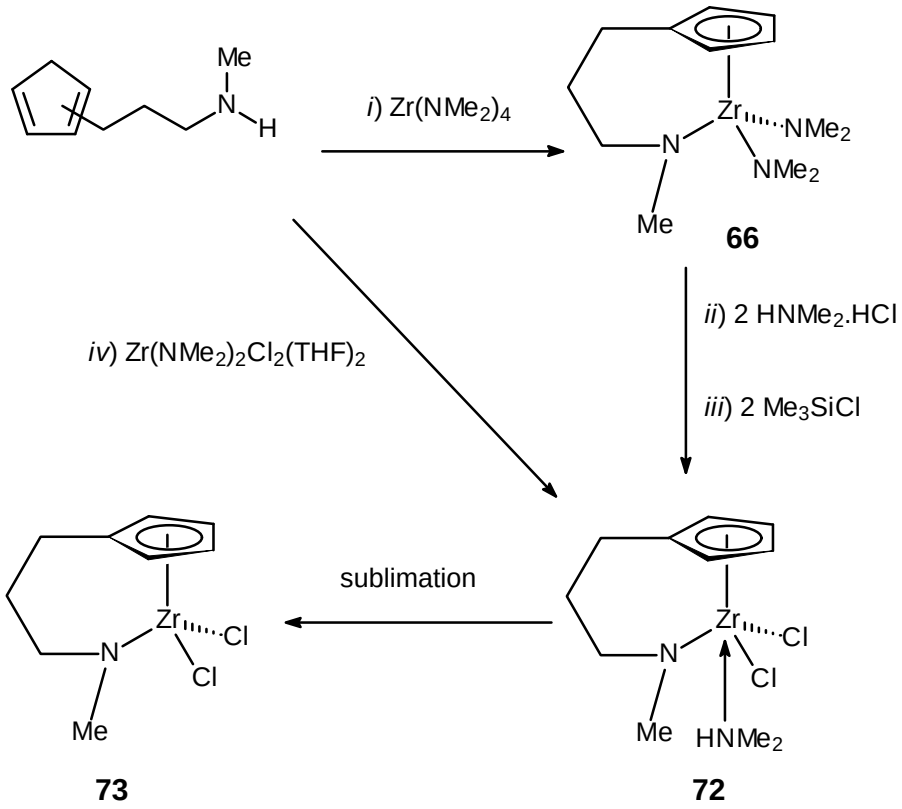
Figure 1.

* *Parts of this work have been performed in collaboration with K. Liekelema, A. Arnold and M. Bouwkamp.*

In order to extend the Cp-amido titanium chemistry described in the previous chapters, we felt it would be worth to explore the analogous zirconium complexes (Figure 1).

5.2 Synthesis and Characterization of Cyclopentadienyl Amido Zirconium Dichlorides $[C_5H_4(CH_2)_nNR]ZrCl_2$.

Attempts to synthesize $[C_5H_4(CH_2)_nNR]ZrCl_2$ complexes using the same route as described for the $[C_5H_4(CH_2)_nNR]TiCl_2$ compounds (Chapter 2) were not successful as unidentifiable oily products were obtained.[4] Aminolysis of homoleptic metal amides, first described by Lappert,[5] appeared to be a better route to introduce Cp-amido ligands to zirconium.[3a,6] For example $[C_5H_4(CH_2)_3NMe]Zr(NMe_2)_2$ was prepared by reacting $Zr(NMe_2)_4$ with the amino-cyclopentadiene, $C_5H_5(CH_2)_3N(H)Me$ (Scheme 1, *i*).[3a] Conversion of such Cp-amido zirconium bis(dimethylamido) complexes to the corresponding dichloro complexes was carried out by reacting the metal amides with $HNMe_2$.HCl (Scheme 1, *ii*). In our experiments, this method gave irreproducible results and often mixtures of products were obtained. Recently Petersen *et al.* developed an elegant route to convert bis-amido complexes to dichlorides using Me_3SiCl.[6] This appeared to be very useful for our systems as well (Scheme 1, *iii*). Independently, we developed an alternative amine-elimination route starting from the mixed bis-amido zirconium dichloride $Zr(NMe_2)_2Cl_2(THF)_2$ (**59**) directly yielding the dichloro complex in a one step synthesis (Scheme 1, *iv*).


Me
N
H
i) $Zr(NMe_2)_4$
Zr
NMe_2
N
NMe_2
Me
66
ii) 2 $HNMe_2$.HCl
iii) 2 Me_3SiCl
iv) $Zr(NMe_2)_2Cl_2(THF)_2$
sublimation
Zr
Cl
N
Cl
Me
73
Zr
Cl
N
Cl
Me
$HNMe_2$
72

Scheme 1.

The introduction of cyclopentadienyl and amido moieties proceeds at different rates. The cyclopentadiene function reacts faster than the amino function with metal amides (^{1}H-NMR). The reactivity of the ligands towards a metal amide depends strongly on the zirconium precursor. For $Zr(NMe_2)_4$ and $C_5H_5(CH_2)_2N(H)$-t-Bu the reaction was complete within 1 h at 50 ^oC (NMR). $Zr(NMe_2)_2Cl_2(THF)_2$ needed more drastic conditions (75 ^oC, 16 h). The $[C_5H_4(CH_2)_nNR]Zr(NMe_2)_2$ complexes (n = 2, R = Me, *t*-Bu; **64**, **65**; n = 3, R = Me, Ad; **66**, **69**) were purified by vacuum distillation and isolated as light green oils in 72-90% yield. With Me_3SiCl (2 eq.) these bis(amido) complexes were cleanly converted into the corresponding dichlorides (**70**-**77**) (Scheme 1, *iii*). The dichlorides could also be prepared in a one pot synthesis by subsequent addition of Me_3SiCl without isolation of the bis(dimethylamido) complexes. The yields thus obtained are comparable to those of the one step synthesis using $Zr(NMe_2)_2Cl_2$.2THF (**63**) (Scheme 1, *iv*, 60-80%). Both routes resulted in formation of the dimethylamine adduct $[C_5H_4(CH_2)_nNR]ZrCl_2(Me_2NH)$, but the Lewis-base free products (**70**-**77**) were obtained by vacuum sublimation.

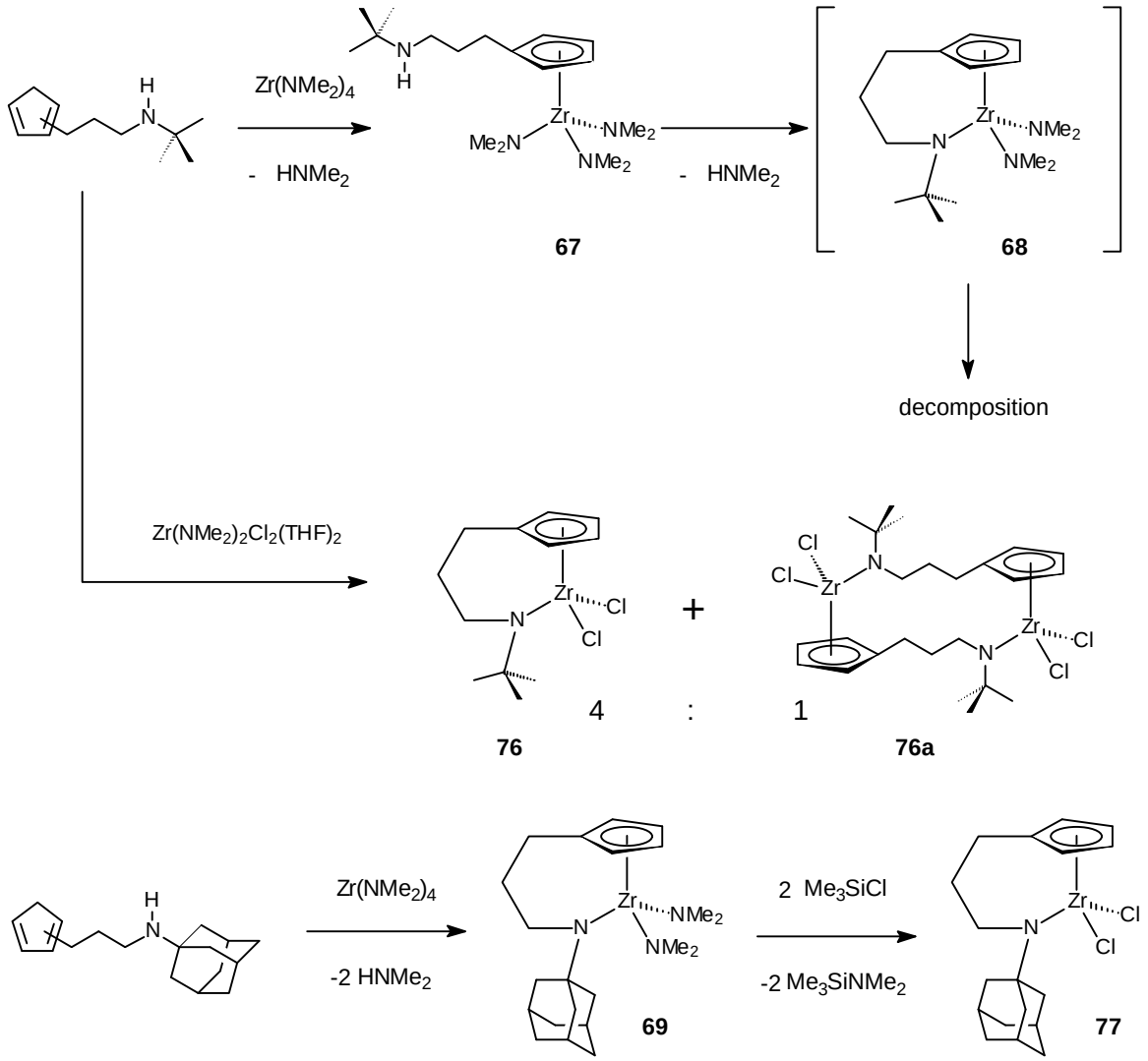
Table 1. Cp-amido Zirconium complexes

Compound	method	yield (%)
$[C_5H_4(CH_2)_2NMe]Zr(NMe_2)_2$ (**64**)	*i*	72
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ (**65**)	*i*	80
$[C_5H_4(CH_2)_3NMe]Zr(NMe_2)_2$ (**66**)	*i*	90[a]
$[C_5H_4(CH_2)_3N(H)$-*t*-Bu$]Zr(NMe_2)_3$ (**67**)	*i*	90
$[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(NMe_2)_2$ (**68**)	*i*	[b]
$[C_5H_4(CH_2)_3NAd]Zr(NMe_2)_2$ (**69**)	*i*	46
$[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrCl_2$ (**70**)	*i+iii/iv*	74
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCl_2$ (**71**)	*i+iii/iv*	69
$[C_5H_4(CH_2)_3NMe]ZrCl_2$ (**73**)	*i+iii*	68
$[C_5H_4(CH_2)_3NEt]ZrCl_2$ (**74**)	*i+iii*	66
$[C_5H_4(CH_2)_3N$-*i*-Pr$]ZrCl_2$ (**75**)	*i+iii/iv*	65/71
$[C_5H_4(CH_2)_3N$-*t*-Bu$]ZrCl_2$ (**76**)	*iv*	59
$[C_5H_4(CH_2)_3NAd]ZrCl_2$ (**77**)	*i+iii*	46

[a]) ref 7; [b]) could not be isolated.

A wide range of Cp-amido ligands can be introduced on zirconium using these methods (Table 1).[6,8] Only for the sterically least hindered aminocyclopentadiene, $C_5H_5(CH_2)_2N(H)Me$, the desired dichloride could not be obtained. Although aminolysis of $Zr(NMe_2)_4$ did result in $[C_5H_4(CH_2)_2NMe]Zr(NMe_2)_2$ (**64**), subsequent reaction with Me_3SiCl gave ill defined products. With $Zr(NMe_2)_2Cl_2(THF)_2$ similar results were obtained. The products are poorly soluble even in coordinating solvents such as THF. This suggests that higher aggregates of $[C_5H_4(CH_2)_2NMe]ZrCl_2$ have been formed. Sterically more demanding Cp-amido ligands, e.g. those containing long backbones in combination with bulky nitrogen substituents, give unexpected reactions as well. The reaction of $C_5H_5(CH_2)_3N(H)$-*t*-Bu with $Zr(NMe_2)_4$ at room temperature ceased with the formation of $[C_5H_4(CH_2)_3N(H)$-*t*-Bu$]Zr(NMe_2)_3$ (**67**). Under more forcing conditions (120 ^oC, 80 h) bonding of the amine function was observed yielding $[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(NMe_2)_2$ (**68**) (NMR), but competitive decomposition (evolution of *iso*-butene) prevented isolation of the complex. A key-feature of the thermolysis of Cp-amido group 4 metal complexes containing a *t*-butyl amido substituent appears to be activation of the *t*-butyl group resulting in evolution of *iso*-butene (Chapter 3). A more detailed thermolysis study is presented elsewhere in this chapter. To circumvent amido activation is using substituents in which activation is inhibited. The, with respect to $[C_5H_4(CH_2)_3N$-*t*Bu], sterically/electronically comparable adamantyl substituted ligand $[C_5H_4(CH_2)_3NAd]$ is a good alternative, since formation of a C=C double bond is highly disfavored in the adamantyl cage. The reaction of $Zr(NMe_2)_4$ with $C_5H_5(CH_2)_3N(H)Ad$ does indeed give the desired complex $[C_5H_4(CH_2)_3NAd]Zr(NMe_2)_2$ (**69**) in fair yield (Scheme 2). Subsequent reaction with 2 eq. of Me_3SiCl also affords the dichloro complex $[C_5H_4(CH_2)_3NAd]ZrCl_2$ (**77**).

With $Zr(NMe_2)_2Cl_2(THF)_2$ as precursor $C_5H_5(CH_2)_3N(H)$-*t*-Bu yielded a mixture of two products in a ratio of 4 : 1. The major product was identified as $[C_5H_4(CH_2)_3N$-*t*-Bu$]ZrCl_2$ (**76**) on the basis of the close similarity of the ^1H- and ^{13}C NMR spectra with those of other propylene bridged complexes (Table 2). The ^1H NMR resonances of the minor product are shifted up-field compared to the major product and the features of the resonances of the backbone differ clearly from those observed for the major product. The internal methylene group of the backbone appears as regular quintet whereas a complex multiplet is observed for all other C_3 bridged complexes. This indicates that the backbone is more flexible and allows the internal methylenes to rotate freely. On the basis of these spectral data a dimeric species $\{[C_5H_4(CH_2)_3N$-*t*-Bu$]ZrCl_2\}_2$ (**76a**) is postulated with the amido function bonded to the other metal center (Scheme 2).



Scheme 2.

The dichlorides (Table 1) are fairly well soluble in THF, $CHCl_3$ and aromatic solvents. The compounds with small nitrogen substituents (Me, Et) are sparingly soluble in aromatic solvents (benzene, toluene). In contrast to $\{[C_5H_4SiMe_2N\text{-}t\text{-}Bu]ZrCl(\mu\text{-}Cl)\}_2$, which was found to be dimeric in both the solid state and in solution (NMR),[8,9] the ethylene bridged complex $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]ZrCl_2$ is a monomer. Also the N-*i*-Pr compound $[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]ZrCl_2$ is monomeric in solution. The C_3-bridged complexes $[C_5H_4(CH_2)_3NMe]ZrCl_2$ (**73**) and $[C_5H_4(CH_2)_3NEt]ZrCl_2$ (**74**), are poorly soluble in benzene and probably are dimers. The X-ray structure of $\{[C_5H_4(CH_2)_3NMe]ZrCH_2Ph(\mu\text{-}Cl)\}_2$[3a] confirms this, although NMR spectra ($CDCl_3$) of the dichlorides **73** and **74** suggest C_s symmetry.

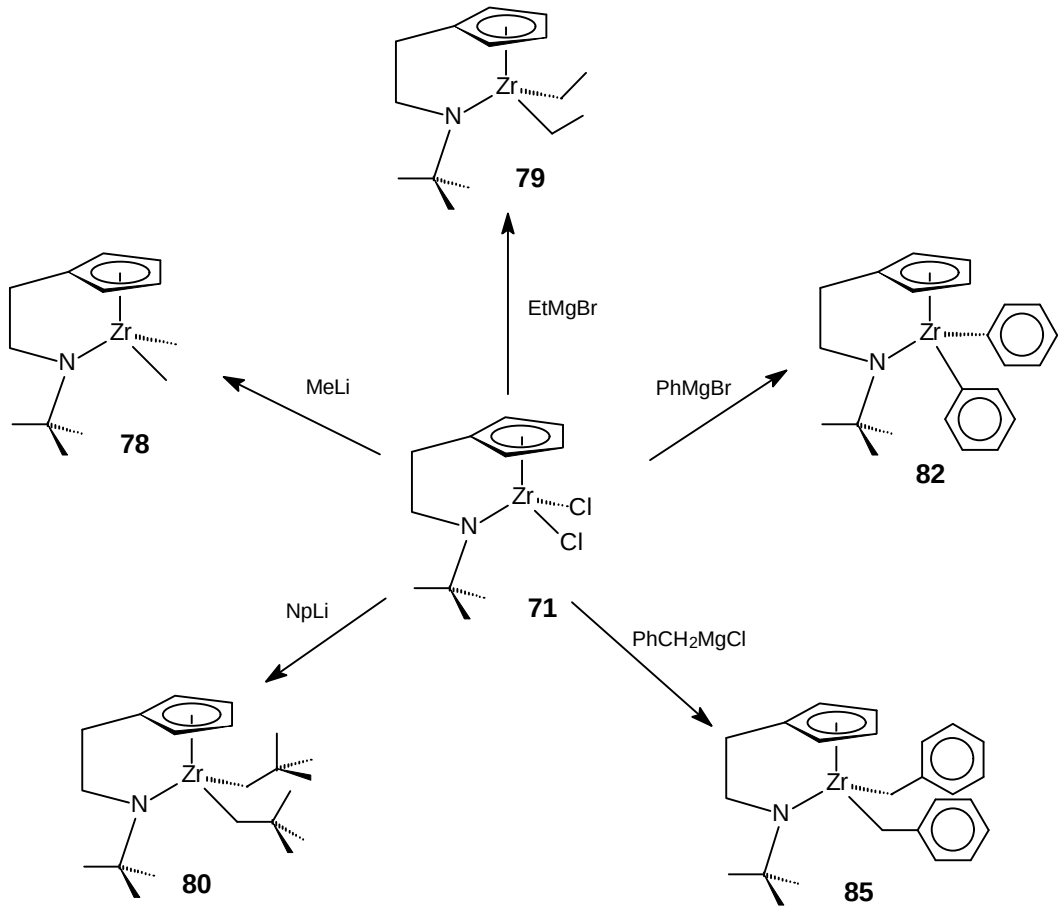
5.3 Synthesis and Characterization of Cp-amido Zirconium Bis(carbyl) Complexes $[C_5H_4(CH_2)_nNR]ZrR'_2$.

The Cp-amido zirconium dichlorides are excellent precursors for bis(alkyl) and bis(aryl) complexes of which a range has been synthesized (Table 2). Attention has been focused on $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ (R = Me, Et, CH_2CMe_3, Ph, CH_2Ph) and $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ (n = 2, 3; R = Me, Et, *i*-Pr, *t*-Bu) complexes for comparison with the titanium analogues. The complexes were prepared by treatment of ether suspensions of the dichlorides with appropriate organo lithium or Grignard reagents (Scheme 3). The carbyl complexes are crystalline compounds (70-85% yield), except $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrMe_2$ (**78**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**) and $[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(CH_2Ph)_2$ (**89**) which were isolated as oils.

Table 2. Cp-amido zirconium carbyl complexes $[C_5H_4(CH_2)_nNR]ZrR'_2$.

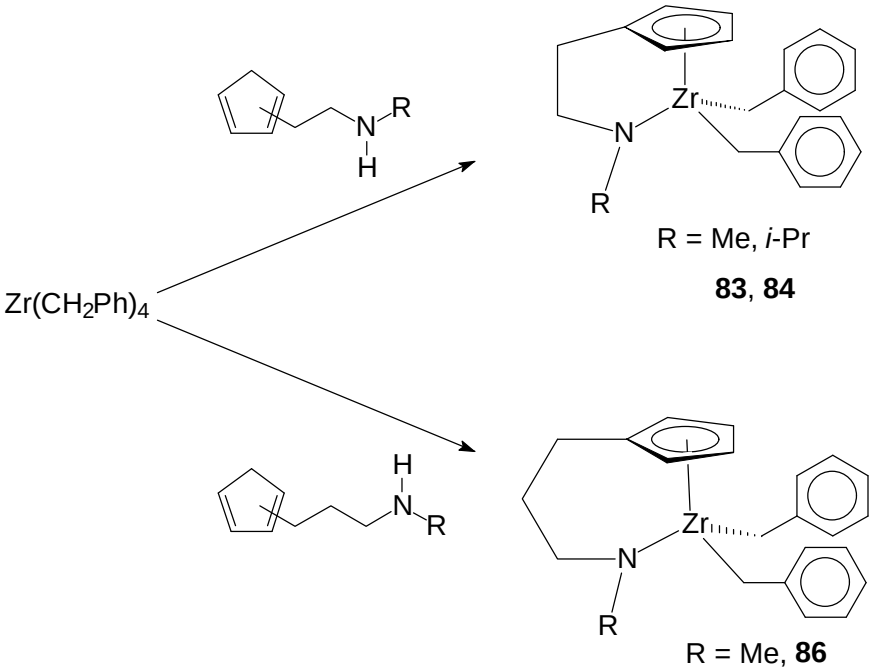
compound	yield (%)	color	cryst./oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrMe_2$ (**78**)	87	white	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**)	86	white	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(CH_2CMe_3)_2$ (**80**)	68	white	cryst.
$[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrPh_2$ (**81**)	45	light brown	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrPh_2$ (**82**)	55	light brown	cryst.
$[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**)	22	brown yellow	cryst.
$[C_5H_4(CH_2)_2N$-*i*-Pr$]Zr(CH_2Ph)_2$ (**84**)	65	brown yellow	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(CH_2Ph)_2$ (**85**)	65	yellow	cryst.
$[C_5H_4(CH_2)_3NMe]Zr(CH_2Ph)_2$ (**86**)	90[a]	yellow	cryst.
$[C_5H_4(CH_2)_3NEt]Zr(CH_2Ph)_2$ (**87**)	65	yellow	cryst.
$[C_5H_4(CH_2)_3N$-*i*-Pr$]Zr(CH_2Ph)_2$ (**88**)	85	yellow	cryst.
$[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(CH_2Ph)_2$ (**89**)	77	orange	oil

[a]) NMR tube experiment.



Scheme 3.

Introduction of ligands by proteolysis of homoleptic metal alkyls[10] is an interesting alternative for the synthesis of linked Cp-amido metal carbyl complexes. For group 4 metals several homoleptic metal alkyls, MR_4 (M = Ti, Zr, Hf; R = CH_2CMe_3,[11] CH_2SiMe_3,[12] CH_2Ph,[13] norbornyl[14]) and mixed metal alkyl chlorides, $M(R)_xCl_{3-x}$ are known.[15] When $Zr(CH_2Ph)_4$ was reacted with $C_5H_5(CH_2)_2N(H)Me$ at room temperature (16 h), formation of the bis-benzyl complex $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**) and 2 eq. of toluene (NMR) was observed (Scheme 4). The sterically more demanding neutral ligands like $C_5H_5(CH_2)_3N(H)Me$ and $C_5H_5(CH_2)_2N(H)$-*i*-Pr required somewhat more drastic conditions (resp. 5 and 16 h at 50 ^oC). However, this route appeared less satisfactorily for $C_5H_5(CH_2)_3N(H)$-*i*-Pr and $C_5H_5(CH_2)_2N(H)$-*t*-Bu. Besides liberation of toluene, complex product mixtures were obtained (NMR). Apparently, the introduction of these ligands require such harsh conditions (> 80 ^oC, 24 h), that thermal decomposition of $Zr(CH_2Ph)_4$ interferes. Nevertheless, this method is a suitable entry for the chemistry of $[C_5H_4(CH_2)_2NMe]ZrR_2$ compounds since the corresponding dichloro precursor, $[C_5H_4(CH_2)_2NMe]ZrCl_2$, is not available (*vide supra*).



Scheme 4.

5.4 Stability of Cp-Amido Zirconium bis(Carbyl) Compounds $[C_5H_4(CH_2)_nNR]ZrR'_2$.

With exception of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**), the bis(carbyl) complexes are fairly stable. They can be stored at room temperature although the bis(methyl) **78** is light sensitive and has to be stored in the dark. Noteworthy is the surprising stability of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**) which can be isolated as a colorless oil but decomposes at ambient temperature ($t_{1/2}$ = 75 min at T = 25 ^oC). Complex **79** is clearly much more stable than $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiEt_2$ which decomposes already at -40 ^oC and Cp_2ZrEt_2 which has to be stored at -80 ^oC.[16]

5.5 Spectroscopic Characterization.

The ^1H and ^{13}C NMR spectra of the dichlorides $[C_5H_4(CH_2)_nNR]ZrCl_2$ **70**-**77** showed the same general features as those of the titanium complexes. The same trends were observed on elongation of the backbone and variation of the nitrogen substituent (Table 3). In the case of $[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrCl_2$ (**70**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]ZrCl_2$ (**75**), substantial down-field shifts of the methine protons were observed (resp. 4.43 and 4.86 ppm) although the shifts are considerable smaller than those of the titanium analogues $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**) (resp. 5.92 and 6.57 ppm, Chapter 2).

The larger atomic radius of zirconium readily explains the smaller down-field shifts observed for the methine protons in **70** and **75**. The smaller Cp-Zr-N bite-angle (107.6°) in {[$C_5H_4(CH_2)_3$NMe]ZrCH_2Ph(μ-Cl)}$_2$ compared to [$C_5H_4(CH_2)_3$N-*i*-Pr]TiCl_2) (112.6°) pulls the nitrogen substituent further away from the metal center. However, the rather small $^1J_{CH}$ coupling constant (117.2 Hz *vs* 128.9 Hz for the titanium analogue) observed for the methine carbon in [$C_5H_4(CH_2)_3$N-*i*-Pr]ZrCl_2 (**75**) could indicate a β-agostic interaction. For the C_2 bridged complex [$C_5H_4(CH_2)_2$N-*i*-Pr]ZrCl_2 (**70**) a higher $^1J_{CH}$ value is observed (129.4 Hz). The chemical shifts of the Cp-CH_2 protons of [$C_5H_4(CH_2)_3$N-*t*-Bu]ZrCl_2 (**76**) and [$C_5H_4(CH_2)_3$NAd]ZrCl_2 (**77**) are shifted down-field with respect to the NCH_2 protons. This is probably related to the steric bulk of the *t*-butyl and adamantyl groups, since this order is reversed in all other dichloro complexes.

Table 3. ^{1}H NMR data of [$C_5H_4(CH_2)_n$NR]ZrCl_2 complexes.[a]

Compound	C_5H_4	NCH_2	$-CH_2-$	Cp-CH_2	R, α	R, β
[$C_5H_4(CH_2)_2$N-i-Pr]ZrCl_2 (**70)**	6.3, 6.3	4.12		3.02	4.43	1.13
[$C_5H_4(CH_2)_2$N-t-Bu]ZrCl_2 (**71**)	6.38, 6.32	4.09		2.92		1.25
[$C_5H_4(CH_2)_3$NMe]ZrCl_2 (**73**	6.46, 6.05	2.95	2.17	2.80	3.27	
[$C_5H_4(CH_2)_3$NEt]ZrCl_2 (**74**)	6.52, 6.02	2.92	2.15	2.81	3.81	1.21
[$C_5H_4(CH_2)_3$N-i-Pr]ZrCl_2 (**75**)	6.52, 5.98	2.85	2.09	2.79	4.86	1.23
[$C_5H_4(CH_2)_3$N-t-Bu]ZrCl_2 (**76a**)[b]	6.51, 6.12	2.73	1.90	3.15		1.55
[$C_5H_4(CH_2)_3$N-t-Bu]ZrCl_2 (**76b**)[b]	6.27, 6.19	2.67	1.69	2.55		1.06
[$C_5H_4(CH_2)_3$NAd]ZrCl_2 (**77**)	6.47, 6.12	2.70	1.85	3.15		

[a]) 300 MHz, $CDCl_3$, 25 °C. [b]) **76a** major compound, **76b** minor compound.

The ^{1}H and ^{13}C NMR spectra (Table 4 and 5) of the carbyl complexes show the same general features as their titanium analogues. The α-protons of the diethyl, bis(benzyl) and bis(neopentyl) are diastereotopic and appear as well separated double doublets.

Organometallic benzyl complexes can release electronic unsaturation of the metal through η^2- or η^3-coordination of the benzyl ligand.[17] This type of coordination shows characteristic high-field shifts of the *ortho* protons and the benzylic carbon and large $^1J_{CH}$ values (Chapter 3).[18] The ^{1}H and ^{13}C NMR spectra of the bis-benzyl complexes (Table 4, 5), exhibit some interesting trends. Complexes with sterically more demanding Cp-amido ligands show smaller upfield shifts of the *o*-Ph protons. The ^{13}C NMR spectra show little variation of the

chemical shifts of the benzylic carbons (around 50 ppm), except for $[C_5H_4(CH_2)_3N$-*t*-Bu]$Zr(CH_2Ph)_2$ (**89**) with a Zr-CH_2 resonance at 63.53 ppm.

Table 4. ^{1}H-NMR data for $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$.[a]

comp	Cp	NCH_2	CH_2-	Cp-CH_2	R, α	R, β	$ZrCH_2$	Ph o-H	Ph m-H	Ph p-H
79	5.72 5.28	3.43		2.43	2.49		1.44, 1.36	6.47	7.11	6.92
80	5.72 5.27	3.48		2.44	3.57	0.94	1.67, 1.05	6.58	7.12	6.94
81	5.57 5.47	3.35		2.24		1.13	1.94, 1.43	6.70	7.11	6.93
82	5.58 5.39	2.48	1.54	2.19	2.66		1.62, 1.26	6.58	7.11	6.93
83	5.60 5.39	2.45	1.53	2.21	3.05	1.00	1.62, 1.22	6.61	7.11	6.94
84	5.59 5.30	2.50	1.58	2.23	4.00	1.12	1.86, 1.01	6.70	7.14	6.95
85	5.79 5.52	2.10	1.31	2.58		1.20	2.15, 1.96	6.92	7.21	6.92

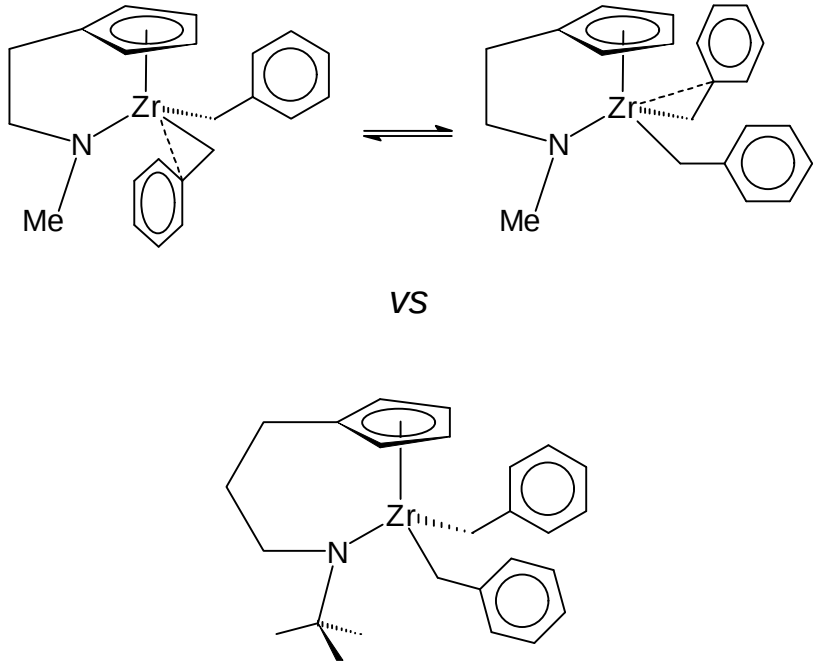
[a]) 300 MHz, C_6D_6, 25 °C.

For the sterically least congested complex, $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**), the *o*-Ph protons show the largest upfield shift (6.47 ppm) and the benzylic carbon the highest $^1J_{CH}$ value (129.4 Hz) while the sterically most demanding complex $[C_5H_4(CH_2)_3N$-*t*-Bu]$Zr(CH_2Ph)_2$ (**89**) shows no upfield shift for the *o*-Ph protons (6.92 ppm) and the lowest $^1J_{CH}$ value (119.6 Hz) is observed for the benzylic carbon. An η^2-bonding mode for at least one of the benzyl ligands is suggested in $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**) while for $[C_5H_4(CH_2)_3N$-*t*-Bu]$Zr(CH_2Ph)_2$ (**89**), the steric bulk of the ligand system seems too large and prevents η^2-bonding of the benzyl ligands. Although η^2-bonding of one of the benzyl ligands is likely in $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**), both ^{1}H and ^{13}C NMR spectra have a symmetric appearance which may be due to the fast flipping of the benzyl groups (Scheme 5). This rearrangement could not be frozen out, low temperature ^{1}H and ^{13}C NMR spectra (toluene-d_8, -90 °C) showed the same symmetric resonances.

Table 5. ^{13}C-NMR data for $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$[a]

comp.	Cp ipso	Cp CH		N-CH_2	-CH_2-	Cp-CH_2	$ZrCH_2$	R, α	R, β	Ph *ipso*	Ph *o*-CH	Ph *m*-CH	Ph *p*-CH
79	135.93	112.92	107.80	71.37		28.89	50.85	37.16		146.14	130.56	125.15	121.80
		(170.9)	(170.9)	(134.3)		(127.6)	(129.4)	(133.1)			(157.5)	(155.0)	(161.1)
80	135.83	113.06	108.64	59.98		29.39	50.34	44.95	21.23	146.53	130.32	125.59	121.85
		(170.9)	(170.9)	(130.0)		(127.6)	(128.2)	(120.9)	(125.7)		(157.5)	(153.8)	(162.4)
81	134.80	113.60	110.98	61.49		29.90	52.86	56.84	28.02	146.24	129.28	126.96	121.79
		(170.9)	(172.1)	(134.3)		(127.6)	(124.5)		(124.5)		(156.3)	(155.0)	(162.4)
82		110.5	110.1	55.5	26.6	29.8	50.2	34.3		145.4	121.8	129.6	126.4
83	122.69	110.64	110.31	39.66	26.77	30.11	49.61	50.72	14.89	145.66	129.51	126.30	121.82
		(170.9)	(170.9)	(127.6)	(125.7)	(126.4)	(127.6)	(132.5)	(126.6)		(157.5)	(153.8)	(162.0)
84	122.63	111.43	110.75	43.49	27.06	30.84	50.98	42.07	21.59	146.51	129.39	126.53	121.77
		(170.9)	(169.7)	(132.5)	(127.0)	(126.4)	(125.1)	(114.8)	(126.1)		(157.5)	(153.8)	(162.4)
85	126.60	114.83	112.55	48.22	28.02	34.14	63.53	57.08	29.65	149.04	128.74	126.66	121.45
		(172.1)	(169.7)	(132.5)	(127.0)	(126.4)	(119.6)		(124.9)		(156.3)	(153.8)	(157.5)

[a]) 75.4 MHz, C_6D_6, 25 ^{o}C, $^{1}J_{CH}$ coupling constants (Hz) in brackets.

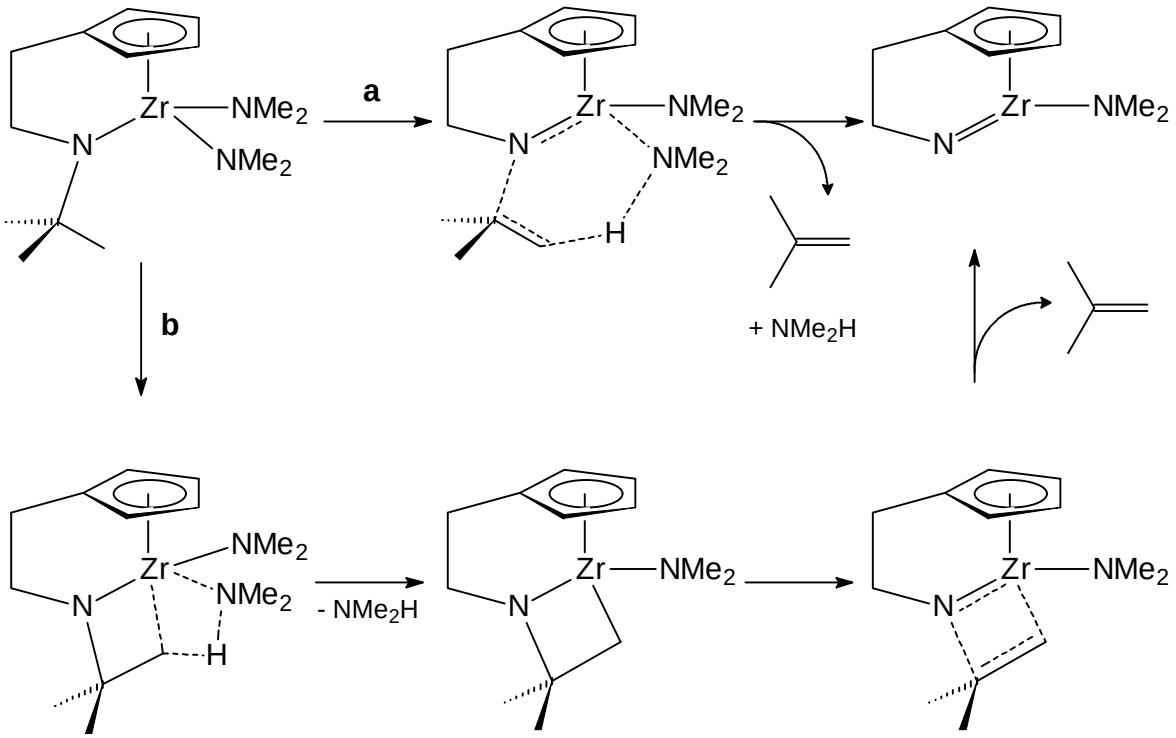


Scheme 5.

5.6 Thermolysis of $[C_5H_4(CH_2)_nN$-*t*-Bu$]Zr(NMe_2)_2$, Ligand Activation.

Intramolecular proteolysis by the amine function in $[C_5H_4(CH_2)_3N(H)$-*t*-Bu$]Zr(NMe_2)_3$ (**68**) was studied in detail. When a benzene-d_6 solution of this compound was heated, the reaction was complete in 80 hours at 120 ^oC giving a dark brown solution.[19] ^1H NMR spectroscopy and GC-MS analysis of the volatiles generated, revealed the presence of *iso*-butene and Me_2NH. The ^1H NMR spectrum of the product mixture formed showed broad signals at 7-5 ppm and 3-2 ppm. Heating of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ (**65**) in benzene-d_6 at 200 ^oC for 24 h resulted in complete decomposition and formation of Me_2NH and *iso*-butene[20] and the ^1H NMR spectrum showed the same broad resonances as observed for the thermolysis of $[C_5H_4(CH_2)_3N(H)$-t-Bu$]Zr(NMe_2)_3$ (**67**). Töpler pump determination of the volatile products of the thermolysis of $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(NMe_2)_2$ (**65**) in benzene-d_6 gave 0.92-0.95 mol *iso*-butene/mol Zr and 1.1-1.33 mol Me_2NH/mol Zr. The formation of *iso*-butene and Me_2NH indicates activation of the *t*-Bu group. A plausible explanation *i.e.* transfer of the hydrogen from the *t*-Bu fragment to the dimethylamido group followed by extrusion of *iso*-butene is given in Scheme 6. Two possible mechanisms are displayed: one with a six membered transition state in which dimethylamine and *iso*-butene are formed in one step (**a**) and a two step mechanism featuring four center transition states (**b**). Group 4 metal complexes

bearing a terminal imido ligand are rare and are prone to give dimers or higher aggregates. Possibly, oligomers of the imido complex are formed.



Scheme 6.

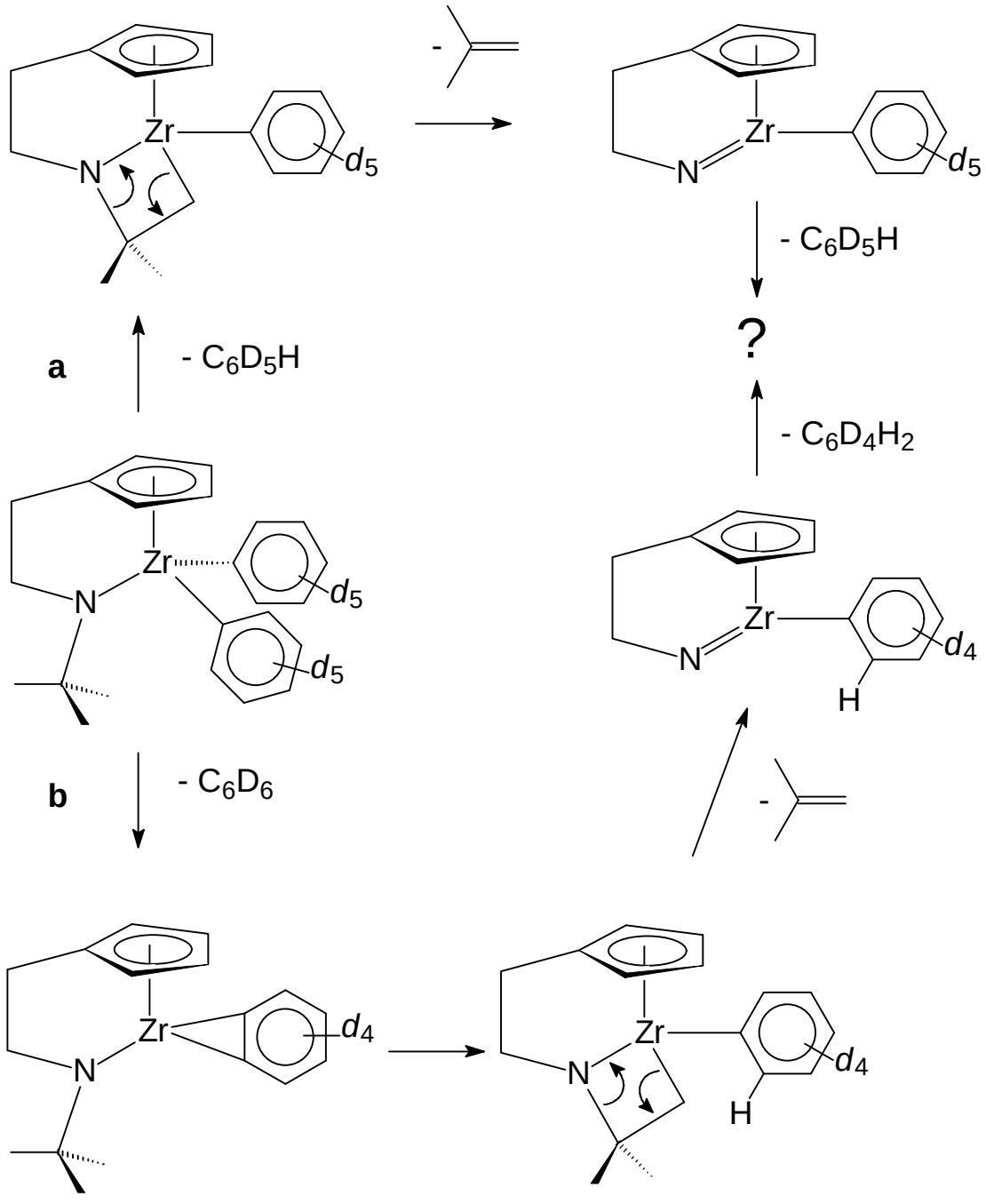
5.7 Thermolysis of Cp amido zirconium bis(carbyl) complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$.

Zirconium bis(carbyl) complexes are known sources for aryne[21,22] and carbene complexes.[23] The bis(alkyl) titanium complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiR_2$ reported earlier in this thesis are useful precursors for aryne, olefin and alkylidene complexes (Chapter 3). Since we have a variety of Cp-amido zirconium bis(alkyl) compounds available it seems worthwile to study whether these can produce the corresponding aryne, olefin and alkylidene species. However, a preliminary investigation was discouraging: when a sample of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrPh_2$ (**82**) in the presence of an excess of PMe_3 was heated (methylcyclohexane-d_{14}, 105 ^oC), formation of benzene and *iso*-butene was observed and the nearly colorless

solution turned dark brown. ^{1}H NMR showed in addition to the resonances of benzene and *iso*-butene broad resonances at 7-5 and 4-1 ppm and part of the product had precipitated. The species formed could not be identified. Thermolysis of the bis(methyl), bis(neopentyl) and bis(benzyl) complexes (**78**, **80** and **85**) proceeded in a similar way: *iso*-butene and RH had been formed together with unidentified products.

The thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrPh_2$ (**82**) was studied in more detail. Attempts to trap the possibly formed benzyne intermediate with diphenylacetylene failed, formation of *iso*-butene was observed instead and the amount of diphenylacetylene remained unchanged. When the deuterated species $[C_5H_4(CH_2)_2N$-*t*-Bu]$Zr(Ph$-$d_5)_2$ (**82-*d*$_{10}$**) was heated under the same conditions described above, the decomposition occurred at nearly the same rate ($k_H/k_D \approx 1.1$) and ^{1}H NMR spectra showed besides *iso*-butene, protonated benzenes. GC-MS analysis revealed formation of C_6D_6, C_6D_5H and $C_6D_4H_2$ in a approximately 1 : 4 : 1 ratio. The ^{1}H NMR spectra showed in addition that two equivalents of RH had been generated.

The liberation of C_6D_6, C_6D_5H and $C_6D_4H_2$ implies that at least two mechanisms are active (Scheme 7). [24] The formation of C_6D_5H and *iso*-butene and the k_H/k_D being close to unity suggest a mechanism in which the *t*–Bu amido fragment becomes directly activated giving C_6D_5H and the azazirconacyclobutane intermediate. This intermediate looses *iso*-butene generating an imido species which decomposes further under evolution of another C_6D_5H molecule (Scheme 7a). The evolution of C_6D_6 and $C_6D_4H_2$ suggests a second mechanism in which a benzyne species and C_6D_6 are generated followed by intramolecular C-H activation and liberation of *iso*-butene. Decomposition of the imido species would result in the evolution of $C_6D_4H_2$ (scheme 7b).



Scheme 7.

Transformation of the *t*-Bu amido group into an imido function, with loss of an organic fragment, has precedents. Direct R-transfer from an amido group has been observed by Green *et al.* for R = $SiMe_3$[25] and by Wolczanski *et al.* for R = H.[26] C-H activation is known for some bis(trimethylsilyl)amido compounds of group IV and V metals and actinides in the presence of hydride, alkyl or amido groups on the metal, giving silylazametallacyclobutanes under elimination of H_2, alkanes or amines.[27] A similar reaction producing an

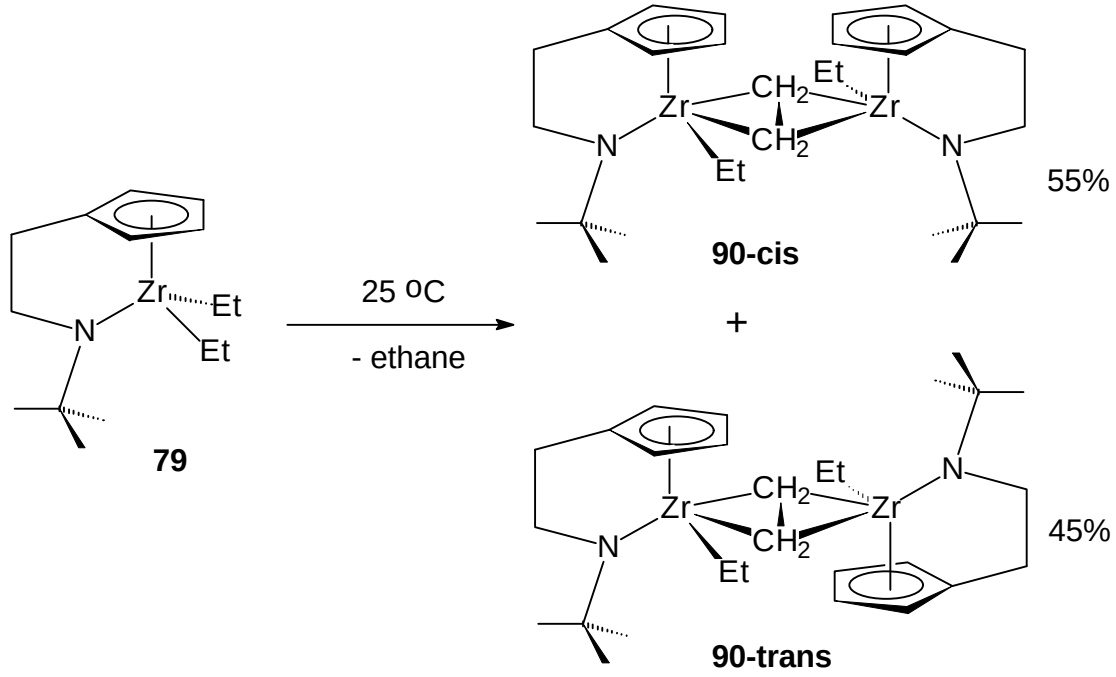
azametallacycle, is observed for (*t*-$Bu_3SiNH)_3ZrCH_3$. Solid state thermolysis resulted in the formation of a silylazametallacyclopentane and methane.[28] Liberation of *iso*-butene is known for complexes bearing the *tert*-butoxysilyl(*tert*-butyl)amido ligands[29] but it has not been reported for complexes with the [$C_5Me_4SiMe_2N$-*t*-Bu] ligand. Instead activation of the tetramethylcyclopentadienyl ligand has been observed.[30]

5.8 Thermolysis of [$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ (79). Formation of the Ethene Bridged Dimer {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4).

The decomposition of [$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ (25 ^oC, C_6D_6, ^1H NMR) was complete in 7 h. The ^1H NMR spectrum of the formed product showed 6 resonances in the Cp region (6.19, 6.15, 5.87, 5.72, 5.40 and 5.17 ppm, an ABCD spin system at 3.8-2.4 ppm, a well resolved triplet at 1.72 ppm (J_{HH} = 7.88 Hz) coupled with a multiplet at 1-0.8 ppm. A sharp singlet at 0.78 ppm was assigned to ethane being formed during the thermolysis. Three high-field resonances were observed, a high order multiplet at 0.47 ppm which couples with another at -0.50 ppm and a singlet at -0.04 ppm which shows no coupling with the other two high field resonances. Two singlets at 1.10 and 1.05 ppm (integrating in 45:55 ratio), assigned to *t*-Bu groups, revealed the formation of two different compounds.

A white product was obtained when performing the reaction on a preparative scale and this was on the basis of ^1H and ^{13}C NMR spectroscopy identified as the ethene bridged dinuclear compound {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4) (**90**). The resonances at 0.47, -0.49 (^1H) and 25.85 ($^1J_{CH}$ = 139.8 Hz) ppm (^{13}C) are assigned to the bridged ethene and from this the isolated complex was identified as the *cis* isomer of {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4) (**90-*cis***) in which the *t*-Bu groups of the two {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt} moieties are directed to the same side (Scheme 8). The other compound mentioned in the thermolysis of [$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ showed one single resonance (-0.04 ppm) for the bridged ethene and was identified as the *trans* isomer **90-*trans***.

The NMR data of **90-*cis*** and **90-*trans*** closely resemble those of a similar scandium complex {[$C_5Me_4SiMe_2$N-*t*-Bu]$ScPMe_3$}$_2$(μ:η^2,η^2-C_2H_4) (^1H NMR: 0.18, -0.54 ppm; ^{13}C NMR: 35.2 ppm, $^1J_{CH}$ = 142 Hz). The molecular structure of the complex showed it to be the *cis*-isomer.[31] Ethene bridged between two transition metals has been reported for the group 4 metals[32] and the formation of such complexes has been shown to be a significant polymerization catalyst deactivation mechanism.[33]



Scheme 8.

Like for the titanium bis(carbyl) complexes (Chapter 3), two thermolysis processes are recognized. At low temperature, a process in which only the carbyl ligands become activated, while at high temperature the Cp-amido ligand becomes involved in the thermolysis. The $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ complexes are thermally more stable than their titanium analogues, very much in the way that Cp_2ZrR_2 compounds are more stable than Cp_2TiR_2. The $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ compounds all decompose in a similar way (except the diethyl complex **79**) at 100 °C, or higher, giving RH, *iso*-butene and unidentified organometallic products.

Apparently, the activation energy for the carbyl ligand extrusion is so high that another thermolysis mechanism starts to compete *e.g.* the activation of the amido group. That zirconium complexes are, compared to titanium, less easily reduced may be an other reason since aryne, alkylidene and olefin complexes can be regarded as having resonance structures in which the metal center is divalent. Like for the corresponding titanium complexes, the studies on the thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ complexes indicate that the $[C_5H_4(CH_2)_2N$-*t*-Bu] ligand can be considered as an inert spectator ligand at temperatures below 100 °C.

5.9 Concluding Remarks.

A facile synthesis route for a range of zirconium dichloro complexes $[C_5H_4(CH_2)_nNR]ZrCl_2$ has been developed. The dichlorides can be obtained in large quantities, in a relatively short time. However, it was not possible to synthesize $[C_5H_4(CH_2)_2NMe]ZrCl_2$.

Two routes to the bis(carbyl) complexes $[C_5H_4(CH_2)_nNR]ZrR'_2$ have been used: salt metathesis starting from the Cp-amido zirconium dichlorides $[C_5H_4(CH_2)_nNR]ZrCl_2$ and proteolysis of tetra(alkyl) zirconium by neutral $C_5H_5(CH_2)_nN(H)R$ ligands. The salt metathesis route is the most conveniently one, making a wide range of $[C_5H_4(CH_2)_nNR]ZrR'_2$ complexes accessible but in some cases proteolysis of tetra(alkyl) zirconium complexes offers relief when the related Cp-amido zirconium dichloro compound is not available as precursor, for example in the case of $[C_5H_4(CH_2)_2NMe]ZrCl_2$.

The bis(carbyl) complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ are more stable than the titanium analogues and except the diethyl compound $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$, all bis(carbyl) complexes are fairly stable in solution up to 100 ^oC.

Thermolysis of the $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ complexes proceeds by two processes: Selective activation of the carbyl ligands proceeds at low temperature as is found for $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ yielding the dinuclear complex $\{[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt\}_2(\mu{:}\eta^2,\eta^2$-$C_2H_4)$ (**90**). At high temperature (> 100 ^oC) direct activation of the *tert*-butyl amido moiety competes with the activation of the carbyl ligands.

C-H activation processes are not limited to bis(carbyl) complexes. The *t*-Bu ligand activation is also observed during the formation of $[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(NMe_2)_2$ by amine elimination. Even $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ is affected in this way although at considerably higher temperature.

5.10 Experimental.

For general information see Chapter 2.

Synthesis of $Zr(NMe_2)_2Cl_2(THF)_2$ (63). To a solution of 5.1 g (19.0 mmol) $ZrCl_4$ in 50 mL of THF, 4.4 g (18.9 mmol) of $Zr(NMe_2)_4$ was added. Subsequently the clear yellow mixture was stirred for 16 h at room temperature. The reaction mixture was filtered and concentrated. Pentane was allowed to condense onto the solution overnight. Clear yellow crystals precipitated and were isolated. Yield: 9.0 g (22.7 mmol; 60%). ^1H NMR (200 MHz, C_6D_6): δ 3.78 (t, 8H, THF); 3.23 (s, 12H, NMe_2); 1.28 (q, 8H,

THF). Anal. Calcd for $C_{12}H_{28}N_2O_2Cl_2Zr$: C, 36.54; H, 7.15; Zr, 23.12. Found: C, 35.95; H, 6.86; Zr, 23.12.

Synthesis of [C$_5$H$_4$(CH$_2$)$_2$NMe]Zr(NMe$_2$)$_2$ (64). To a solution of 1.94 g (7.25 mmol) of $Zr(NMe_2)_4$ in 10 mL of toluene, 1.0 g (8.12 mmol) of $C_5H_5(CH_2)_2N(H)Me$ was added. The solution turned immediately light yellow. It was stirred at room temperature for an additional 2 h. The toluene was removed in vacuum and the remaining oily residue taken up in 10 mL of pentane. After removal of the pentane an oily product was vacuum transferred (150 ^oC and 0.01 torr) as an almost colorless oil. Yield: 1.57 g (5.22 mmol, 72%) $C_5H_4(CH_2)_2NMeZr(NMe_2)_2$. ^1H NMR (200 MHz, C_6D_6): 5.94 (t, 2H, $^3J_{HH}$ = 2.6 Hz, C_5H_4); 5.79 (t, 2H, $^3J_{HH}$ = 2.6 Hz, C_5H_4); 3.68 (t, 2H, $^3J_{HH}$ = 6.7 Hz, NCH_2); 3.04 (s, 3H, NMe); 2.89 (s, 12H, 2 x NMe2); 2.69 (t, 2H, $^3J_{HH}$ = 6.7 Hz, $C_5H_4\underline{CH_2}$). C NMR (50 MHz, C_6H_6): 136.4 (s, C_5H_4-*ipso*); 112.3 (d, $^1J_{CH}$ = 168.3 Hz, C_5H_4); 106.8 (d, $^1J_{CH}$ = 169.6, C_5H_4); 71.5 (t, $^1J_{CH}$ = 132.3 Hz, NCH_2); 43.9 (q, $^1J_{CH}$ = 131.2 Hz, NMe_2); 41.5 (q, $^1J_{CH}$ = 128.7 Hz, NMe); 29.5 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$)

Synthesis of [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Zr(NMe$_2$)$_2$ (65). To a solution of 2.56 g (9.57 mmol) of $Zr(NMe_2)_4$ in 15 mL of toluene, 1.6 g (9.7 mmol) of $C_5H_5(CH_2)_2N(H)$-t-Bu was added. The solution turned immediately yellow. After stirring overnight at 50 ^oC, the toluene was removed in vacuum and the orange oily residue was taken up in 20 mL of pentane and transferred to a distillation apparatus. After removal of the pentane, the remaining brown oil was vacuum transferred (120-130 ^oC and 0.001 torr) to give a light green oil. Yield: 2.7 (7.9 mmol, 81%) $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(NMe_2)_2$. ^1H NMR (200 MHz, C_6D_6): δ 5.90 (t, J_{HH} = 2.4 Hz, 2H C_5H_4); 5.86 (t, J_{HH} = 2.4 Hz, 2H, C_5H_4); 3.63 (t, $^3J_{HH}$ = 6.4 Hz, 2H, NCH_2); 2.81 (s, 12H, 2 x NMe_2); 2.58 (t, $^3J_{HH}$ = 6.4 Hz, 2H, $C_5H_4C\mathit{H_2}$); 1.24 (s, 9H, *t*-Bu). ^{13}C NMR (50 MHz, C_6D_6): δ 135.2 (s, C_5H_4-*ipso*); 111.5 (d, $^1J_{CH}$ = 157.2 Hz, C_5H_4); 107.9 (d, $^1J_{CH}$ = 162.9 Hz, C_5H_4); 60.5 (t, $^1J_{CH}$ = 132.9 Hz, NCH_2); 57.0 (s, $\underline{C}Me_3$); 44.5 (q, $^1J_{CH}$ = 138.7 Hz, NMe_2); 31.1 (t^1J_{CH} = 128.7 Hz, $C_5H_4\underline{CH_2}$); 30.0 (q, $^1J_{CH}$ = 124.1 Hz, $C\underline{Me_3}$). Anal. Calcd for $C_{15}H_{29}N_3Zr$: C, 52.58; H, 8.53; Zr, 26.62. Found: C, 52.51; H, 8.65; Zr, 26.56.

Synthesis of [C$_5$H$_4$(CH$_2$)$_3$N(H)-t-Bu]Zr(NMe$_2$)$_3$ (67). To a solution of 3.07 g (11.5 mmol) of $Zr(NMe_2)_4$ in 20 mL of toluene, 2.3 g (12.8 mmol) of $C_5H_5(CH_2)_3N(H)$-*t*-Bu was added. The solution turned light green. The mixture was stirred for 2 h at room temperature. The toluene was pumped off and the oily residue was stripped twice with 15 mL of pentane. The volatiles were removed in high vacuum (0.001 torr). The oil was not purified further. ^1H NMR (C_6D_6) revealed the presence of some free ligand (5%). ^1H NMR (200 MHz, C_6D_6): δ 6.00 (m, J_{HH} = 2.4 Hz, 2H, C_5H_4); 5.95 (m, J_{HH} = 2.4 Hz, 2H, C_5H_4); 2.94 (s, 18H, 3 x NMe_2); 2.61 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $C_5H_4\underline{CH_2}$); 2.50 (q, $^3J_{HH}$ = 7.7 Hz, 2H, NCH_2); 1.66 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, $NCH_2\underline{CH_2}$); 1.01 (s, 9H, *t*-Bu); 0.25 (s, 1H, NH).

Synthesis of [C$_5$H$_4$(CH$_2$)$_3$NAd]Zr(NMe$_2$)$_2$ (69). A solution of 2.00 g (7.48 mmol) of $Zr(NMe_2)_2$ and 1.90 g (7.44 mmol) of $C_5H_5(CH_2)_3N(H)$Ad in 50 mL of toluene was refluxed for 12 h. The toluene was removed in vacuum and the light brown residue was stripped with 20 mL of pentane. The residue was

extracted with 20 mL pentane and filtered. The solution was concentrated to 10 mL and slowly cooled to -90 °C. Light brown crystals formed. Yield: 1.50 g (3.45 mmol, 46%) of $[C_5H_4(CH_2)_3NAd]Zr(NMe_2)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 6.19 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.83 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.01 (m, 2H, $C_5H_4\underline{CH_2}$); 2.98 (s, 12H, NMe_2); 2.59 (m, 2H, NCH_2); 2.06 (m, 3H, C-CH-C of adamantyl) 1.65 (m, 12H, C-CH_2-C of adamantyl); 1.61 (m, 2H, $NCH_2\underline{CH_2}$).

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-i-Pr]Cl$_2$. (70). To a solution of 2.1 g (5.3 mmol) of $Zr(NMe_2)_2Cl_2\cdot(THF)_2$ in 50 mL of toluene, 0.8 mL (5.3 mmol) of $C_5H_5(CH_2)_2N(H)$-*i*-Pr was added. The reaction mixture was stirred for 18 h at 75 ºC. The yellow solution was filtered and the volatiles were removed in vacuum giving a yellow solid which was stripped with 10 mL of pentane and washed 3 times with 25 mL of pentane. The resulting light yellow solid was dried in vacuum and was identified as the dimethylamine adduct (^{1}H, ^{13}C NMR). After sublimation (0.05 torr, 60 ºC) the amine-free compound was isolated as an off white solid. Yield: 1.2 g (3.9 mmol; 74%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.81 (t, 2H, C_5H_4); 5.74 (t 2H, C_5H_4); 4.55 (m, 1H, $\underline{CH}Me_2$); 3.48 (t, 2H, CH_2N); 2.31 (t, 2H, $C_5H_4\underline{CH_2}$); 0.89 (d, 6H, $CH\underline{Me_2}$. ^{13}C NMR (50.3 MHz, C_6D_6): δ 141.8 (s, C_5H_4-*ipso*); 115.5 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 111.8 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 63.3 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 49.4 (d, $^1J_{CH}$ = 129.4 Hz, $\underline{C}HMe_2$); 28.6 (t, $^1J_{CH}$ = 113.2 Hz, $C_5H_4\underline{CH_2}$); 19.5 (q, $^1J_{CH}$ = 127.8 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3079 (sh), 1378 (s), 1358 (sh), 1342 (sh), 1183 (sh), 1168 (sh), 1159 (s), 1059 (m), 1042 (m), 1024 (m), 991 (s), 885 (m), 826 (sh), 815 (s), 723 (m), 609 (w), 525 (m), 469 (m), 427 (m). Anal. Calcd for $C_{10}H_{15}NCl_2Zr$:: C, 38.58; H, 4.86; Zr, 29.30. Found: C, 38.58; H, 4.81; Zr, 29.20. Mol. weight Calcd for $C_{10}H_{15}NCl_2Zr$: 311.4 g/mol. Found: 350.9 ± 30 g/mol.

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Cl$_2$ (71). To a clear yellow solution of 4.6 g (12.2 mmol) of $Zr(NMe_2)_2Cl_2\cdot(THF)_2$ in 50 mL of toluene, 2.2 mL (12.4 mmol) of $C_5H_5(CH_2)_2N(H)$-*t*-Bu was added. The reaction mixture was stirred for 18 h at 75 ºC. The orange-yellow solution was filtered and the volatiles were removed under vacuum. The orange solid was stripped with 15 mL of pentane and washed 3 times with 25 mL of pentane. The yellow crystals were characterized as the dimethylamine adduct. After sublimation (0.05 torr, 60 ºC) the amine-free compound was isolated as a cream white solid. Yield: 3.1 g (8.4 mmol; 69%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.99 (t, 2H, C_5H_4); 5.79 (t 2H, C_5H_4); 3.47 (t, 2H, CH_2N); 2.23 (t, 2H, $C_5H_4\underline{CH_2}$); 1.25 (d, 9H, t-Bu). ^{13}C NMR (50.3 MHz, C_6D_6): δ 141.4 (s, C_5H_4-*ipso*); 115.7 (d, $^1J_{CH}$= 106.2 Hz, C_5H_4); 113.3 (d, $^1J_{CH}$ = 112.3 Hz, C_5H_4); 64.9 (t, $^1J_{CH}$ = 136.1 Hz, NCH_2); 57.2 (s, $\underline{C}Me_3$); 29.3 (t, $^1J_{CH}$ = 129.4 Hz, $C_5H_4\underline{CH_2}$); 27.7 (q, $^1J_{CH}$ = 125.3 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3077 (sh), 2726 (w), 2679 (w), 1377 (sh), 1365 (sh), 1346 (sh), 1307 (w), 1247 (m), 1199 (w), 1168 (m), 1086 (w), 980 (w), 951 (w), 888 (w), 817 (m), 768 (m), 722 (m), 557 (w), 535 (w), 487 (w). Anal. Calcd for $C_{11}H_{17}NCl_2Zr$: C, 40.60; H, 5.27; Zr, 28.03. Found: C, 40.55; H, 5.27; Zr, 28.13. Mol. weight Calcd for $C_{11}H_{17}NCl_2Zr$: 325.4 g/mol. Found: 332.3 ± 25 g/mol.

Synthesis of [C$_5$H$_4$(CH$_2$)$_3$NMe]ZrCl$_2$.HNMe$_2$ (72). A solution (0 °C) of 6.76 g (25.27 mmol) of $Zr(NMe_2)_4$ in 30 mL of toluene was treated with 3.4 g (24.8 mmol) of $C_5H_5(CH_2)_3N(H)Me$ and stirred for 0.5 h at 50 °C. The resulting light green-yellow solution was cooled to 0 °C and 6.4 mL (50.4

mmol) of Me_3SiCl was added. A light yellow precipitate formed which dissolved upon heating to reflux. After refluxing for 4 h a clear yellow brown solution had been formed. The solvent was removed in vacuum and the residue was washed twice with 30 mL of pentane. After drying in vacuum, the residue was extracted with 60 mL of hot toluene. Concentrating at 80-90 ^oC to 15 mL and slowly cooling to -20 ^oC gave cream colored crystals of $[C_5H_4(CH_2)_3NMe]ZrCl_2.HNMe_2$. Yield: 6.48 g (18.92 mmol, 75%). ^1H NMR (200 MHz, $CDCl_3$): δ 6.20 (m, J_{HH} = 2.68 Hz, 2H, C_5H_4); 6.07 (m, J_{HH} = 2.68 Hz, 2H, C_5H_4); 2.99 (s, 3H, NMe); 2.93 (m, 2H, NCH_2); 2.75 (m, 2H, $C_5H_4\underline{CH_2}$); 2.62 (d, $^3J_{HH}$ = 5.86 Hz, 6H, $HN\underline{Me_2}$); 2.12 (m, 2H, $NCH_2\underline{CH_2}$). Sublimation of 0.95 g of $[C_5H_4(CH_2)_3NMe]ZrCl_2.HNMe_2$ at 150-160 ^oC and 10^{-3} torr yielded 0.75 g (91%) of $[C_5H_4(CH_2)_3NMe]ZrCl_2$ (**73**). ^1H NMR (300 MHz, $CDCl_3$): δ 6.46 (m, J_{HH} = 2.75 Hz, 2H, C_5H_4); 6.05 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.27 (s, 3H, NMe); 2.95 (m, 2H, NCH_2); 2.80 (m, 2H, $C_5H_4\underline{CH_2}$); 2.17 (m, 2H, $NCH_2\underline{CH_2}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 127.64 (s, C_5H_4-*ipso*); 114.17 (d, $^1J_{CH}$ = 174.6 Hz, C_5H_4); 112.31 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 55.85 (t, $^1J_{CH}$ = 134.9 Hz, NCH_2); 37.24 (q, $^1J_{CH}$ = 135.5 Hz, NMe); 28.95 (t, $^1J_{CH}$ = 127.0 Hz, $C_5H_4\underline{CH_2}$); 26.01 (t, $^1J_{CH}$ = 128.2 Hz, $NCH_2\underline{CH_2}$). IR (cm^{-1}): 3102 (m), 3084 (m), 2741 (m), 1800 (w), 1759 (w), 1715 (w), 1670 (w), 1620 (w), 1530 (w), 1497 (m), 1481 (m), 1447 (m), 1433 (m), 1420 (m), 1393 (m), 1333 (m), 1273 (m), 1254 (s), 1231 (w), 1188 (s), 1163 (m), 1121 (s), 1074 (w), 1063 (w), 1042 (s), 1034 (s), 984 (m), 932 (s), 901 (s), 880 (m), 860 (m), 839 (m), 810 (vs), 748 (vw), 729 (vw), 683 (w), 667 (w), 56 (w), 638 (w), 621 (w), 608 (w), 577 (w), 559 (w), 530 (s), 511 (m), 484 (w), 469 (w), 453 (w), 438 (w).

Synthesis of $[C_5H_4(CH_2)_3NEt]ZrCl_2$ (74). To a cooled (0 ^oC) solution of 6.11 g (22.8 mmol) of $Zr(NMe_2)_4$ in 50 mL of toluene, 3.8 g (25 mmol) of $C_5H_5(CH_2)_3N(H)Et$ was added. The solution became light yellow-green upon warming and after refluxing for 15 min the mixture was cooled to 0 ^oC and 5.8 mL (46 mmol) of Me_3SiCl was added while stirring at room temperature for 20 min. the solution became turbid. Refluxing for 10 min. gave a clear deep yellow solution which was filtered and concentrated to 15 mL at reflux. Slowly cooling to 0 ^oC afforded light orange crystals which were washed with 20 mL of pentane. Yield 4.72 g (15.1 mmol, 66%). A pure sample was obtained by sublimation (150-160 ^oC and 10^{-3} torr). ^1H NMR (300 MHz, $CDCl_2$): δ 6.52 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 6.02 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.81 (q, $^3J_{HH}$ = 6.47 Hz, 2H, $N\underline{CH_2}CH_3$); 2.92 (m, 2H, NCH_2); 2.81 (m, 2H, $C_5H_4\underline{CH_2}$); 2.15 (m, 2H, $NCH_2\underline{CH_2}$); 1.21 (t, $^3J_{HH}$ = 6.47 Hz, 3H, $NCH_2\underline{CH_3}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 128.03 (s, C_5H_4-*ipso*); 114.48 (d, $^1J_{CH}$ = 174.6 Hz, C_5H_4); 112.20 (d, $^1J_{CH}$ = 17.1 Hz, C_5H_4); 51.27 (t, $^1J_{CH}$ = 134.9 Hz, NCH_2); 42.93 (t, $^1J_{CH}$ = 130.6 Hz, $N\underline{CH_2}CH_3$); 29.83 (t, $^1J_{CH}$ = 127.0 Hz, $C_5H_4\underline{CH_2}$); 26.31 (t, $^1J_{CH}$ = 128.2 Hz, $NCH_2\underline{CH_2}$); 12.69 (q, $^1J_{CH}$ = 127.4 Hz, $NCH_2\underline{CH_3}$). IR (cm^{-1}): 3102 (m), 3086 (w), 2805 (m), 2701 (m), 2645 (w), 1807 (w), 1767 (m), 1717 (m), 1694 (w), 1682 (w), 1624 (m), 1495 (m), 1437 (m), 1397 (vw), 1339 (s), 1289 (s), 1269 m), 1242 (m), 1227 (s), 1177 (s), 1161 (s), 1113 (s), 1082 (m), 1057 (s), 1040 (s), 1007 (s), 943 (m), 930 (m), 903 (w), 878 (m), 862 (s), 843 (w), 810 (vs), 779 (s), 737 (w), 654 (w) 610 (w), 563 (s), 525 (m) 421 (s), 409 (s).

Synthesis of $Zr[C_5H_4(CH_2)_3N$-i-Pr$]Cl_2$ (75). A solution of 3.9 g (9.9 mmol) of $Zr(NMe_2)_2Cl_2\cdot(THF)_2$ and 1.6 mL (9.9 mmol) of $C_5H_5(CH_2)_3N(H)$-*i*-Pr in 50 mL of toluene was heated for 24 h at 75 ^oC. After

work-up pale yellow crystals were isolated. Yield: 2.30 g (7.0 mmol; 71%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.81 (t, 2H, C_5H_4); 5.74 (t, 2H, C_5H_4); 4.55 (m, 1H, $\underline{CH}Me_2$); 3.48 (t, 2H, NCH_2); 2.31 (t, 2H, $C_5H_4\underline{CH_2}$); 0.89 (d, 6H, $CH\underline{Me_2}$). ^{13}C NMR (50.3 MHz, C_6D_6); δ 114.9 (d, $^{1}J_{CH}$ = 173.4 Hz, C_5H_4); 111.9 (d, $^{1}J_{CH}$ = 174.6 Hz, C_5H_4); 46.5 (d, $^{1}J_{CH}$ = 117.2 Hz, $\underline{CH}Me_2$); 44.2 (t, $^{1}J_{CH}$ = 134.3 Hz, NCH_2); 30.5 (t, $^{1}J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 26.4 (t, $^{1}J_{CH}$ = 127.6 Hz, $NCH_2\underline{CH_2}$); 19.6 (q, $^{1}J_{CH}$ = 127.0 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3106 (sh), 3088 (sh), 2683 (w), 2628 (m), 1769 (w), 1723 (w), 1714 (w), 1690 (w), 1681 (w), 1642 (w), 1627 (w), 1493 (w), 1357 (m), 1348 (m), 1242 (m), 1181 (m), 1171 (m), 1160 (m), 1106 (m), 1087 (m), 1072 (m), 1050 (m), 1033 (m), 866 (m), 813 (s), 802 (s), 609 (m), 597 (m), 456 (m), 442 (m), 417 (m). Anal. Calcd for $C_{11}H_{17}NCl_2Zr$: C, 40.60; H, 5.27; Zr, 28.03. Found: C, 40.66; H, 5.27; Zr, 28.05.

Synthesis of [$C_5H_4(CH_2)_3$N-t-Bu]$ZrCl_2$ (76). To a solution of 4.53 g (11.48 mmol) of $Zr(NMe_2)_2Cl_2(THF)_2$ in 50 mL of toluene, 2.2 mL (11.6 mmol) of $C_5H_5(CH_2)_3N(H)$-*t*-Bu was added and the mixture was stirred for 24 h at 90 °C. A pale green solution was obtained. After cooling to room temperature the solution was filtered and concentrated to about 20 mL. The product was precipitated by adding 80 mL of pentane yielding a cream colored power which was washed 2 times with 50 mL of pentane and dried in vacuum. According to the ^{1}H NMR spectrum coordinated Me_2NH was present together with some other unidentified products (about 15% of total integral). Sublimation (170-190 °C, 0.005 torr) of the crude product gave 2.31 g (6.83 mmol, 59%) white material. A ^{1}H NMR spectrum of the product showed it to be a 4:1 mixture of [$C_5H_4(CH_2)_3$N-*t*-Bu]$ZrCl_2$ (**76a**) and {[$C_5H_4(CH_2)_3$N-*t*-Bu]$ZrCl_2$}$_2$ (**76b**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4, **76a**); 6.27 (m, J_{HH} = 2.42 Hz, 4H, 2x C_5H_4, **76b**); 6.19 (m, J_{HH} = 2.42 Hz, 4H, 2x C_5H_4, **76b**); 6.12 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4, **76a**); 3.15 (m, 2H, $C_5H_4\underline{CH_2}$, **76a**); 2.73 (m, 2H, NCH_2, **76a**); 2.67 (t, $^{3}J_{HH}$ = 7.23 Hz, 4H, 2x NCH_2, **76b**); 2.55 (t, $^{3}J_{HH}$ = 7.41 Hz, 4H, 2x $C_5H_4\underline{CH_2}$, **76b**); 1.90 (m, 2H, $NCH_2\underline{CH_2}$, **76a**); 1.69 (quint, $^{3}J_{HH}$ = 7.34 Hz, 4H, 2x $NCH_2\underline{CH_2}$, **76b**); 1.55 (s, 9H, *t*-Bu, **76a**); 1.06 (s, 18H, 2x *t*-Bu, **76b**).

Synthesis of [$C_5H_4(CH_2)_3$NAd]$ZrCl_2$ (77). A solution of 1.25 g (2.88 mmol) of [$C_5H_4(CH_2)_3$NAd]$Zr(NMe_2)_2$ in 10 mL of toluene was treated with 0.73 mL (5.75 mmol) of Me_3SiCl and the mixture was stirred at 60 °C for 4 h. An off-white precipitate formed. After cooling to 0 °C 10 mL of pentane was added and the precipitate was allowed to settle. The solvents were removed by filtration and the gray residue was washed with pentane and dried in vacuum. Isolated: 0.91 g (2.18 mmol, 75%) of [$C_5H_4(CH_2)_3$NAd]$ZrCl_2$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 6.12 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.15 (m, 2H, $C_5H_4\underline{CH_2}$); 2.70 (m, 2H, NCH_2); 2.18 (m, 9H, Overlapped resonances of C-CH_2-CH and C*H* of adamantyl); 1.85 (m, 2H, $NCH_2\underline{CH_2}$, 6H, CH-CH_2-CH of adamantyl). ^{13}C NMR (75.4 MHz, $CDCl_3$, 50 °C): 131.55 (s, C_5H_4-*ipso*); 116.76 (d, $^{1}J_{CH}$ = 175.8 Hz,C_5H_4); 114.90 (d, $^{1}J_{CH}$ = 173.4 Hz, C_5H_4); 60.30 (s, -C≡ adamantyl); 48.21 (t, $^{1}J_{CH}$ = 134.3 Hz, NCH_2); 40.73 (t, $^{1}J_{CH}$ = 124.5 Hz, CH_2, adamantyl); 37.61 (t, $^{1}J_{CH}$ = 128.0 Hz, $C_5H_4\underline{CH_2}$); 36.33 (t, $^{1}J_{CH}$

= 127.6 Hz, CH_2, adamantyl); 29.45 (d, $^1J_{CH}$ = 131.9 Hz, CH, adamantyl); 26.93 (t, $^1J_{CH}$ = 128.2 Hz, $NCH_2\underline{CH_2}$).

Thermolysis of [C₅H₄(CH₂)₂N-t-Bu]Zr(NMe₂)₂ (65) in C₆D₆. A solution of 89.3 mg (0.244 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ in 0.5 mL of C_6D_6 was sealed in an NMR tube under vacuum. The NMR tube was kept in an oven at 210 °C for 36 hr. The decomposition was monitored by ^{1}H NMR spectroscopy at regular intervals. The ^{1}H NMR spectrum showed the formation of *iso*-butene and Me_2NH, After 24 h, all starting material had disappeared. At the vacuum line the NMR tube was broken under vacuum and all volatiles were condensed to a 0.100 N aqueous solution of HCl (1.665 mmol). The solution was warmed to room temperature and stirred for 30 min. to trap all amine. The solution was degassed using three freeze and thaw cycles at -30 °C and the gas was collected in a trap cooled to -196 °C. The trap was warmed to -30 °C and residual gas was pumped through a cold trap (-70 °C) in a calibrated volume using a Töpler pump. 0.224 mmol (0.92 mol/mol Zr) of *iso*-butane (MS) gas was collected. All condensed residues were transferred back to the aqueous solution. The solution was titrated with NaOH solution (1.340 mmol) yielding 1.33 mol Me_2NH/mol Zr. A second experiment was carried out with 121.6 mg (0.332 mmol) of $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(NMe_2)_2$ yielding 0.315 mmol *iso*-butene (0.95 mol/mol Zr) and 0.365 mmol Me_2NH (1.1 mol/mol Zr).

Synthesis of [C₅H₄(CH₂)₂N-t-Bu]ZrMe₂ (78). A cooled (0 °C) suspension of 1.07 g (3.29 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCl_2$ in 30 mL of ether was treated with 8 mL 0.88 M (7.0 mmol) of MeLi in ether. The mixture was stirred for 3 h at room temperature giving a nearly colorless solution and a white precipitate. After removal of the solvent in vacuum the sticky, off-white residue was stripped with 20 mL of pentane. The residue was extracted with 40 mL of pentane and filtered. Removal of the pentane in vacuum left a nearly colorless oil. Yield 0.82 g (2.88 mmol, 87%) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrMe_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 6.03 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.82 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.44 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.35 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.39 (s, 9H, *t*-Bu); 0.03 (s, 6H, 2 x Me). ^{13}C NMR (75.4 MHz, C_6D_6): δ 133.11 (s, C_5H_4-*ipso*); 112.80 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 109.81 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 60.73 (t, $^1J_{CH}$ = 133.7 Hz, NCH_2); 55.43 (s, $N\underline{C}Me_3$); 31.43 (q, $^1J_{CH}$ = 113.5 Hz, Me); 29.75 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$); 28.62 (q, $^1J_{CH}$ = 124.5 Hz, $NC\underline{Me_3}$). IR (cm^{-1}): 3086 (vw), 2760 (w), 2675 (w), 1667 (w), 1613 (w), 1466 (sh, nujol), 1358 (m), 1344 (vw), 1321 (w), 1246 (m), 1204 (s), 1125 (m), 1088 (s), 1040 (m), 1028 (w), 980 (m), 955 (m), 862 (m), 841 (m), 806 (vs), 766 (m), 681 (m) 644 (m), 557 (m), 527 (w), 461 (s).

Synthesis of [C₅H₄(CH₂)₂N-t-Bu]ZrEt₂ (79). A cooled (-10 °C) suspension of 0.46 g (1.41 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCl_2$ in 30 mL of ether was treated with 2.0 mL 1.54 M of EtMgBr in ether. The mixture was stirred for 1.5 h at -10 °C giving a clear solution and a white precipitate. The work-up procedure was also performed at -10 °C. The solvent was removed in vacuum and the white oily residue was stripped with 20 mL of pentane. The residue was extracted with 50 mL of pentane and after filtration a clear nearly colorless solution was obtained. The solution was concentrated to 10 mL and transferred into a small vessel. Removal of the pentane in vacuum left a nearly colorless oil.

Yield: 0.38 g (1.22 mmol, 86%, based on $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrEt_2$). A ^1H NMR spectrum showed beside the resonances of the bis-ethyl complex also the appearance of the resonances of the decomposition products. ^1H NMR (300 MHz, C_6D_6): δ 5.94 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.86 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.42 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.38 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4CH_2$); 1.36 (t, $^3J_{HH}$ = 8.05 Hz, 6H, $CH_2\underline{CH_3}$); 1.33 (s, 9H, CMe_3); 0.69 (m, 2H, $\underline{CH_2}CH_3$); 0.44 (m, 2H, $\underline{CH_2}CH_3$).

Thermolysis of [C₅H₄(CH₂)₂N-t-Bu]ZrEt₂ (79). An NMR sample of **79** was monitored at 25 °C at regular times. Evolution of ethane (NMR) was observed and after 7 hours the bis ethyl complex had completely been converted into the *cis* and *trans* isomers of $\{[C_5H_4(CH_2)_2N$-*t*-Bu]ZrEt$\}_2(\mu{:}\eta^2,\eta^2\text{-}C_2H_4)$ (**90**) in a 1 to 0.86 ratio.

Synthesis of cis-{[C₅H₄(CH₂)₂N-t-Bu]ZrEt}₂(μ:η², η²-C₂H₄) (90-cis). To a cooled (-10 °C) suspension of 0.61 g (1.87 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrCl_2$ in 30 mL of ether, 2.5 mL 1.54 M (3.8 mmol) of EtMgBr in ether was added and the mixture was stirred for 2 h at -10 °C. After removal of the ether in vacuum the residue was stripped with 20 mL of pentane. The residue was extracted with 50 mL of pentane and filtered. The clear and nearly colorless solution was concentrated to 5 mL and stirred for 3 h at 30 °C. The solution turned orange and an off-white powder precipitated. The powder was isolated on a frit, washed twice with 5 mL of pentane and dried in vacuum. Yield: 0.075 g (0.13 mol, 14%) of $\{[C_5H_4(CH_2)_2N$-t-Bu]ZrEt$\}_2(\mu{:}\eta^2,\eta^2\text{-}C_2H_4)$ (**90**). An NMR sample showed it to be predominantly the *cis* isomer. ^1H NMR (300 MHz, THF-d_8): δ 6.27 (m, 2H, C_5H_4); 6.20 (m, 2H, C_5H_4); 5.75 (m, 2H, C_5H_4); 5.16 (m, 2H, C_5H_4); 3.86 (m, 2H, NCH_2); 3.64 (m, 2H, NCH_2); 2.76 (m, 2H, $C_5H_4\underline{CH_2}$); 2.65 (m, 2H, $C_5H_4\underline{CH_2}$); 1.35 (t, $^3J_{HH}$ = 7.51 Hz, 6H, $CH_2\underline{CH_3}$); 1.10 (s, 18H, *t*-Bu); 0.63 (m, 2H, $\underline{CH_2}CH_3$); 0.49 (m, 2H, $\underline{CH_2}CH_3$); 0.32 (m, 2H, C_2H_4); -0.67 (m, 2H, C_2H_4). ^{13}C NMR (75.4 MHz, d_8-THF): δ 135.27 (s, C_5H_4-*ipso*); 112.97 (d, $^1J_{CH}$ = 166.0 Hz, C_5H_4); 110.82 (d, $^1J_{CH}$ = 166.0 Hz, C_5H_4); 110.12 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 107.06 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 61.81 (t, $^1J_{CH}$ = 133.1 Hz, NCH_2); 57.69 (s, $\underline{C}Me_3$); 33.18 (t, $^1J_{CH}$ = 112.9 Hz, $\underline{CH_2}CH_3$); 32.113 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 28.98 (q, $^1J_{CH}$ = 123.9 Hz, $C\underline{Me_3}$); 25.85 (t, $^1J_{CH}$ = 139.8 Hz, C_2H_4); 18.51 (q, $^1J_{CH}$ = 122.5 Hz, $CH_2\underline{CH_3}$).

Synthesis of [C₅H₄(CH₂)₂N-t-Bu]Zr(CH₂CMe₃)₂ (80). A solution of 0.91 g (2.80 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrCl_2$ and 0.44 g (5.64 mmol) of $LiCH_2CMe_3$ in 30 mL of ether was prepared at -40 °C. The mixture was warmed slowly to room temperature and stirred for 2 h. The solvent was removed in vacuum and the white residue was stripped with 20 mL of pentane. The residue was extracted with 40 mL of pentane and filtered giving a clear colorless solution. The solution was concentrated to 5 mL at room temperature and white crystals were formed on standing overnight at -25 °C. Yield 0.76 g (1.92 mmol, 68%) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Zr(CH_2CMe_3)_2$. ^1H NMR (300 MHz, C_6D_6): δ 6.25 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 6.04 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.44 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.33 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.41 (s, 9H, N-*t*-Bu); 1.09 (s, 18H, 2 x $CH_2C\underline{Me_3}$); 1.05 (d, $^2J_{HH}$ = 12.09 Hz, 2H, $\underline{CH_2}CMe_3$); 0.52 (d, $^2J_{HH}$ = 12.09 Hz, 2H, $\underline{CH_2}CMe_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 131.85 (s, C_5H_4-*ipso*); 113.53 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 108.13 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4);

78.84 (t, $^1J_{CH}$ = 103.2 Hz, $\underline{CH_2}CMe_3$); 61.33 (t, $^1J_{CH}$ = 133.7 Hz, NCH_2); 56.42 (s, $N\underline{C}Me_3$); 36.60 (s, $CH_2\underline{C}Me_3$); 35.54 (q, $^1J_{CH}$ = 123.7 Hz, $CH_2C\underline{Me_3}$); 30.25 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$); 29.35 (q, $^1J_{CH}$ = 124.5 Hz, $NC\underline{Me_3}$). IR (cm^{-1}): 3111 (vw), 3100 (vw), 3081 (vw), 2795 (w), 2747 (vw), 2714 (w), 1780 (w), 1748 w), 1730 (w), 1688 (w), 1655 (w), 1636 (w), 1605 (w), 1491 (m), 1468 (m), 1356 (s), 1323 (w), 1231 (s), 1202 (s), 1171 (w), 1076 (s), 1040 (m), 1030 (w), 1017 (vw), 982 (s), 953 (s), 909 (w), 891 (vw), 858 (s), 841 (s), 804 (s), 766 (m), 750 (s), 681 (m), 642 (m), 554 (s), 525 (w), 500 (m), 473 (m), 434 (w). Anal. Calcd for $C_{21}H_{39}NZr$: C, 63.57; H, 9.91; Zr, 22.99. Found: C, 63.41; H, 9.87; Zr, 22.91.

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-i-Pr]Ph$_2$ (81). To a cooled (-50 °C) solution of 0.7 g (2.3 mmol) of $Zr[C_5H_4(CH_2)_2N$-*i*-Pr$]Cl_2$ in 50 mL of ether, 4.0 mL (4.6 mmol) of a 1.17 M solution PhMgBr in ether was added. After allowing to warm up to 0 °C in 3 h, the ether was evaporated in vacuum. The yellow brown residue was stripped with 10 mL of pentane. Subsequently, the product was extracted 3 times with 20 mL of pentane. The solution was concentrated and after cooling to -30 °C orange brown crystals precipitated. Yield: 0.4 g (1.0 mmol; 45%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.56 (s, 4H, C_6H_5); 7.06 (m, 6H, C_6H_5); 6.13 (t, 2H, C_5H_4); 5.84 (t, 2H, C_5H_4); 4.44 (m, 1H, $\underline{CH}Me_2$); 3.80 (t, 2H, NCH_2); 2.80 (t, 2H, $C_5H_4\underline{CH_2}$); 0.74 (d, 6H, $CH\underline{Me_2}$) .

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ph$_2$ (82). To a cooled (-80 °C) solution of 1.3 g (4.0 mmol) of $Zr[C_5H_4(CH_2)_2N$-*t*-Bu$]Cl_2$ in 40 mL of ether, 7 mL (8.2 mmol) of a 1.17 M solution of PhMgBr in ether was added. The mixture was stirred and allowed to warm to room temperature in 2 h and subsequently stirred for another hour. The ether was removed under vacuum and the brown yellow solid was stripped with 10 mL of pentane and extracted 3 times with 25 mL of pentane. The solution was concentrated and after cooling to - 30 °C brown crystals precipitated. The crystals were dried in vacuum and isolated. Yield: 1.21 g (3.0 mmol; 75%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.64 (double d, 4H, C_6H_5); 7.3 - 7.1 (m, 6H, C_6H_5); 5.99 (t, 2H, C_5H_4); 5.85 (t, 2H, C_5H_4); 3.56 (t, 2H, NCH_2); 2.48 (t, 2H, $C_5H_4\underline{CH_2}$); 1.24 (s, 9H, *t*-Bu). ^{13}C NMR (50.3 MHz, C_6D_6): δ 184.4 (s, C_6H_5-*ipso*); 135.3 (d, $^1J_{CH}$ = 155.0 Hz, *m*-C_6H_5); 134.3 (s, C_5H_4-ipso); 127.4 (d, $^1J_{CH}$ = 157.5 Hz, *o*-C_6H_5); 127.3 (d, $^1J_{CH}$ = 156.3 Hz, *p*-C_6H_5); 114.7 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 111.0 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 61.8 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 56.3 (s, $\underline{C}Me_3$); 29.9 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 27.9 (q, $^1J_{CH}$ = 124.5 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3047 (sh), 2726 (w), 2673 (w), 1359 (sh), 1343 (sh), 1320 (sh), 1204 (w), 1170 (w), 1058 (m), 1040 (m), 979 (w), 955 (w), 808 (s), 719 (s), 700 (s), 555 (w), 472 (w), 439 (w). Anal. Calcd for $C_{23}H_{27}NZr$: C, 67.59; H, 6.66; Zr, 22.32. Found: C, 66.55; H, 6.70; Zr, 22.52.

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu](Ph-d$_5$)$_2$ (82-d$_{10}$). Using the same procedure as for the synthesis of **82**, 1.4 g (3.3 mmol) of $Zr[C_5H_4(CH_2)_2N$-*t*-Bu$]Cl_2$ was reacted with 11.7 mL (6.8 mmol) of a 0.58 M solution of Ph-d_5MgBr in ether. After work-up brown crystals were obtained. Yield: 0.7 g (1.6 mmol; 45%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.99 (t, 2H, C_5H_4); 5.85 (t, 2H, C_5H_4); 3.56 (t, 2H, $C_5H_4CH_2$); 2.48 (t, 2H, CH_2N); 1.24 (s, 9H, $C(CH_3)_3$. ^{13}C NMR (50.3 MHz, C_6D_6); δ 184.2 (s, C_6H_5-*ipso*), 135.2 (s, *m*-

C_6H_5), 134.9 (s, C_5H_4-ipso), 128.0 (s, *o*-C_6H_5), 127.7 (s, *p*-C_6H_5), 114.7 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4), 111.0 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4), 61.7 (t, $^1J_{CH}$ = 133.6 Hz, NCH_2), 56.3 (s, $\underline{C}Me_3$), 29.9 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$), 27.9 (q, $^1J_{CH}$ = 124.6 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3076 (sh), 2726 (w), 2673 (w), 2350 (w), 2259 (m), 2224 (w), 2210 (w), 1359 (sh), 1343 (sh), 1325 (sh), 1243 (w), 1203 (m), 1091 (m), 948 (m), 808 (s), 766 (m), 617 (m), 528 (s), 470 (m).

Synthesis of [$C_5H_4(CH_2)_2$NMe]Zr(CH_2Ph)$_2$ (83). A solution of 1.98 g (4.34 mmol) of $Zr(CH_2Ph)_4$ in 20 mL of toluene was treated with 0.55 g (4.46 mmol) of $C_5H_5(CH_2)_2$ N(H)Me and the mixture was stirred overnight at 50 ^oC, yielding a brown solution. The solvent was removed in vacuum and the remaining oily residue was stripped with pentane. The residue was extracted with 40 mL of ether and filtered. The solution was concentrated to 10 mL and cooled overnight to -25 ^oC. Brown-yellow crystals were obtained. Yield: 0.38 g (0.96 mmol, 22%) of $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$. ^1H NMR (300 MHz, C_6D_6): δ 7.11 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.92 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.47 (d, $^3J_{HH}$ = 7.69 Hz, 4H, *o*-Ph); 5.72 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.28 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.43 (t, $^3J_{HH}$ = 6.78 Hz, 2H, NCH_2); 2.49 (s, 3H, NMe); 2.43 (t, $^3J_{HH}$ = 6.78 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.44 (d, $^2J_{HH}$ = 9.16 Hz, 2H, Ph$\underline{CH_2}$); 1.36 (d, $^2J_{HH}$ = 9.16 Hz, 2H, Ph$\underline{CH_2}$). ^{13}C NMR (75.4 MHz, $C_6D_6$146.14 (s, Ph-*ipso*); 135.93 (s, C_5H_4-*ipso*); 130.56 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 125.15 (d, $^1J_{CH}$ = 155.0 Hz, *m*-Ph); 121.80 (d, $^1J_{CH}$ = 161.1 Hz, *p*-Ph); 112.92 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 107.80 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 71.37 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 50.85 (t, $^1J_{CH}$ = 129.4 Hz, $\underline{CH_2}$Ph); 37.16 (q, $^1J_{CH}$ = 133.1 Hz, NMe); 28.89 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3055 (w), 3005 (w), 2809 (w), 2772 (m), 2674 (w), 1589 (s), 1557 (w), 1478 (s), 1445 (m), 1410 (w), 1348 (vw), 1327 (w), 1298 (w), 1231 (m), 1213 (s), 1192 (m), 1181 (m), 1157 (w), 1113 (s), 1088 (w), 1065 (w), 1047 (m), 1038 (w), 1028 (m), 1005 (s), 978 (s), 964 (m), 903 (m), 868 (m), 837 (s), 810 (vs), 745 (s), 696 (s), 644 (w), 556 (m), 546 (m), 511 (s), 424 (s). Anal. Calcd for $C_{22}H_{25}NZr$: C, 66.95; H, 6.39; Zr, 23.11. Found: C 66.71; H, 6.46; Zr, 23.04.

Synthesis of [$C_5H_4(CH_2)_2$N-*i*-Pr]Zr(CH_2Ph)$_2$ (84). To a cooled (0 ^oC) solution of 1.33 g (2.92 mmol) of $Zr(CH_2Ph)_4$ in 10 mL of toluene, 446 µL (2.99 mmol) of $C_5H_5(CH_2)_2N(H)$-*i*-Pr was added. The mixture was stirred overnight at ambient temperature. After removal of the solvent the sticky residue was stripped with 10 mL of pentane leaving a brown powder which was extracted with ether. Upon concentrating the solution and standing overnight at -20 ^oC 0.55 g crystalline material was obtained. A second crop yielded 0.25 g of product. Total yield: 0.80 g (1.89 mmol, 65%) of $[C_5H_4(CH_2)_2N$-*i*-Pr]Zr(CH_2Ph)$_2$. ^1H NMR (300 MHz, C_6D_6): δ 7.12 (t, ^3J_H = 7.69 Hz, 4H, *m*-Ph); 6.94 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.58 (d, $^3J_{HH}$ = 7.32 Hz, 4H, *o*-Ph); 5.72 (t, $^3J_{HH}$ = 2.57 Hz, 2H, C_5H_4); 5.27 (t, $^3J_{HH}$ = 2.57 Hz, 2H, C_5H_4); 3.57 (h, $^3J_{HH}$ = 6.04 Hz, 1H, $\underline{CH}Me_2$); 3.48 (t, $^3J_{HH}$ = 6.59 Hz, 2H, NCH_2); 2.44 (t, $^3J_{HH}$ = 6.59 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.67 (d, $^2J_{HH}$ = 9.15 Hz, 2H, Ph$\underline{CH_2}$); 1.05 (d, $^2J_{HH}$ = 9.15 Hz, 2H, Ph$\underline{CH_2}$); 0.94 (d, $^2J_{HH}$ = 6.23 Hz, 6H, CHMe_2). ^{13}C NMR (75.4 MHz, C_6D_6): δ 146.53 (s, *ipso*-Ph); 135.83 (s, *ipso*-C_5H_4); 130.32 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 125.59 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 121.85 (d, $^1J_{CH}$ = 162.4 Hz, *p*-Ph); 113.06 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 108.64 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 59.89 (t, $^1J_{CH}$ = 130.0 Hz, CH_2Ph); 50.34 (t, $^1J_{CH}$ = 128.2 Hz, NCH_2); 44.95 (d, $^1J_{CH}$ = 120.9 Hz, $CH(CH_3)_2$); 29.39 (t,

$^1J_{CH}$ = 127.6 Hz, $C_5H_4CH_2$); 21.32 (q, $^1J_{CH}$ = 125.7 Hz, $CH(CH_3)_2$). IR (cm^{-1}): 3063 (w), 3046 (m), 3005 (m), 2683 (w), 2670 (w), 1659 (w), 1643 (w), 1632 (w), 1589 (s), 1559 (m), 1489 (sh, 1478 cm^{-1}), 1478 (s), 1460 (m), 1445 (m), 1418 (m), 1393 (s), 1358 (m), 1343 (m), 1319 (vw), 1298 (m), 1279 (m), 1265 (w), 1246 (w), 1231 (m), 1211 (s), 1190 (m), 1175 (m), 1159 (m), 1146 (w), 1105 (m), 1088 (w), 1067 (w), 1053 (s), 1036 (m), 1026 (s), 1005 (m), 991 (m), 978 (s), 899 (s), 872 (w), 837 (m) (824 (s), 804 (s), 745 (s), 704 (m), 696 (s), 644 (m), 610 (w), 594 (vw), 542 (m), 517 (s), 448 (m), 428 (m), 415 (s). Anal. Calcd for $C_{24}H_{29}NZr$: C, 68.19; H, 6.92; Zr, 21.58. Found: C, 68.44; H, 7.15; Zr, 21.47.

Synthesis of Zr[C₅H₄(CH₂)₂N-t-Bu](CH₂Ph)₂ (85). To a cooled solution (- 40 °C) of 1.7 g (5.2 mmol) of $Zr[C_5H_4(CH_2)_2N$-*t*-$Bu]Cl_2$ in ether, 7.8 mL (10.5 mmol) of a 1.35 M solution of $PhCH_2MgBr$ in ether was quickly added. The mixture was stirred and allowed to warm to room temperature in 3 h. The ether was evaporated in vacuum and the yellow solid residue stripped with 15 mL of pentane. The product was extracted 3 times with 40 mL of pentane. The solution was concentrated and after cooling to - 30 °C brown crystals precipitated. Yield: 1.5 g (3.4 mmol; 65%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.11 (t, 4H, C_6H_5); 6.93 (t, 2H, C_6H_5); 6.70 (t, 4H, C_6H_5); 5.57 (t, 2H, C_5H_4); 5.47 (t, 2H, C_5H_4); 3.35 (t, 2H, CH_2N); 2.24 (t, 2H, $C_5H_4\underline{CH_2}$); 1.94 (d, 1H, $Ph\underline{CH_2}$); 1.43 (d, 1H, $Ph\underline{CH_2}$); 1.13 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 146.24 (s, *ipso*-Ph); 134.80 (s, C_5H_4-*ipso*); 129.28 (d, $^1J_{CH}$ = 156.3 Hz, *o*-Ph); 126.96 (d, $^1J_{CH}$ = 155.0 Hz, *m*-Ph); 121.79 (d, $^1J_{CH}$ = 162.4 Hz, *p*-Ph); 113.60 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.98 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 61.49 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 56.84 (s, $\underline{C}Me_3$); 52.86 (t, $^1J_{CH}$ = 124.5 Hz, $Ph\underline{CH_2}$); 29.90 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 28.02 (q, $^1J_{CH}$ = 124.5 Hz, CMe_3). IR (cm^{-1}): 3169 (sh), 3152 (sh), 3138 (sh), 3131 (sh), 2726 (w), 2675 (w), 1593 (m), 1379 (s), 1302 (sh), 1208 (w), 1169 (w), 980 (m), 810 (s), 793 (s), 766 (m), 536 (w), 519 (w). Anal. Calcd for $C_{25}H_{31}NZr$: C, 68.75; H, 7.15; Zr, 20.89. Found: C, 68.39; H, 7.10; Zr, 20.80.

Synthesis of [C₅H₄(CH₂)₃NEt]Zr(CH₂Ph)₂ (87). To a cooled (0 °C) suspension of 1.63 g (5.24 mmol) of $[C_5H_4(CH_2)_3NEt]ZrCl_2$ in 30 mL of ether, 11.4 mL of a 0.93 M solution of $PhCh_2MgCl$ in ether was added. On warming to room temperature the mixture became light yellow. After stirring for 3 h at room temperature the solvent was removed in vacuum and the light yellow residue stripped with 30 mL of pentane. The solids were extracted with 40 mL of hot hexane. Concentrating the hot solution to ± 10 mL and cooling to 0 °C yielded 1.44 g (3.41 mmol, 65%) $[C_5H_4(CH_2)_3NEt]Zr(CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.11 (t, $^3J_{HH}$ = 7.51 Hz, 4H, *m*-Ph); 6.94 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.61 (d, $^3J_{HH}$ = 7.33 Hz, 4H, *o*-Ph); 5.60 (m, J_{HH} = 2.75 Hz, 2H, C_5H_4); 5.39 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.05 (q, $^3J_{HH}$ = 6.47 Hz, 2H, $N\underline{CH_2}CH_3$); 2.45 (m, 2H, NCH_2); 2.21 (m, 2H, $C_5H_4\underline{CH_2}$); 1.62 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$); 1.53 (m, 2H, $NCH_2\underline{CH_2}$); 1.22 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$); 1.00 (t, $^3J_{HH}$ = 6.47 Hz, 3H, $NCH_2\underline{CH_3}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 145.66 (s, Ph-*ipso*); 129.51 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 126.30 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 122.69 (s, C_5H_4-*ipso*); 121.82 (d, $^1J_{CH}$ = 110.64 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.31 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 50.72 (t, $^1J_{CH}$ = 132.5 Hz, $N\underline{CH_2}CH_3$); 49.61 (t, $^1J_{CH}$ = 127.6 Hz, $Ph\underline{CH_2}$); 39.66 (t, $^1J_{CH}$= 127.6 Hz, NCH_2); 30.11 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4CH_2$); 26.77 (t, $^1J_{CH}$ = 125.7 Hz, $NCH_2\underline{CH_2}$); 14.89 (q, $^1J_{CH}$ = 126.6 Hz, $NCH_2\underline{CH_3}$), IR (cm^{-1}): 3117 (w), 3088 (m),

3079 (m), 3065 (w), 2756 (w), 2712 (w), 2677 (w), 2004 (w), 1930 (vw), 1832 (vw), 1782 (vw), 1753 (vw), 1667 (vw), 1589 (s), 1539 (vw), 1479 (s), 1445 (s), 1422 (w), 1400 (w), 1364 (w), 1350 (m), 1302 (m), 1271 (w), 1231 (m), 1209 (s), 1179 (s), 1163 (m), 1123 (m), 1088 (w), 1072 (w), 1053 (w), 1036 (s), 1007 (s), 980 (s), 939 (m), 907 (s), 893 (w), 864 (s), 841 (m), 795 (vs), 746 (vs), 696 (vs), 662 (m), 606 (m), 571 (m), 552 (m), 542 (m), 523 (s), 433 (s).

Synthesis of [$C_5H_4(CH_2)_3$N-i-Pr]Zr($CH_2Ph)_2$ (88). A cooled suspension (-20 ^oC) of 2.13 g (6.55 mmol) [$C_5H_4(CH_2)_3$N-*i*-Pr]$ZrCl_2$ in 30 mL of ether was treated with 15 mL 0.93 M (13.9 mmol) $PhCH_2MgCl$ in ether. After warming to room temperature the mixture was stirred for 4 h while the colorless mixture turned light yellow. Removal of the solvent yielded a light yellow residue which was stripped with 30 mL of pentane. The solids were extracted with 50 mL of pentane and the resulting light yellow solution was concentrated to 15 mL. Light yellow crystals were obtained on standing overnight at -20 ^oC. 1.92 g of product was isolated. A second crop (0.51 g) was obtained. Total yield: 2.43 g (5.56 mmol. 85%) of [$C_5H_4(CH_2)_3$N-*i*-Pr)Zr($CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.14 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.95 (t, $^3J_{HH}$ = 7.33 Hz, 2H, *p*-Ph); 6.70 (d, $^3J_{HH}$ = 7.32 Hz, 4H, *o*-Ph); 5.59 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.30 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 4.00 (hp, $^3J_{HH}$ = 5.77 Hz, 1H, $\underline{CH}Me_2$); 2.50 (m, 2H, NCH_2); 2.23 (m, 2H, $C_5H_4\underline{CH_2}$); 1.86 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$); 1.58 (m, 2H, $NCH_2\underline{CH_2}$); 1.12 (d, $^3J_{HH}$ = 5.86 Hz, 6H, $CH\underline{Me_2}$); 1.01 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 146.51 (s, Ph-*ipso*); 129.39 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 126.53 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 122.63 (s, C_5H_4-*ipso*); 121.77 (d, $^1J_{CH}$ = 161.1 Hz, *p*-Ph); 111.43 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.75 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 50.98 (t, $^1J_{CH}$ = 125.1 Hz, $Ph\underline{CH_2}$); 43.49 (t, $^1J_{CH}$ = 132.5 Hz, NCH_2); 42.07 (d, $^1J_{CH}$ = 114.8 Hz, $\underline{CH}Me_2$); 30.84 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$); 27.06 (t, $^1J_{CH}$ = 127.0 Hz, $NCH_2\underline{CH_2}$); 21.59 (q, $^1J_{CH}$ = 126.1 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3109 (m), 3063 (w), 3007 (w), 2701 (w), 2679 (w), 2656 (m), 1954 (w), 1941 (w), 1917 (w), 1834 (w), 1790 (w), 1759 (w), 1707 (w), 1661 (w), 1591 (s), 1562 (sh, 1661 cm^{-1}), 1478 (m) 1447 (m), 1362 (s), 1335 (w), 1300 (w), 1275 (w), 1260 (w), 1236 (m), 1213 (s), 1182 m), 1171 (w), 1113w), 1088 (m), 1065 (m), 1051 (w), 1028 (m), 1015 (m), 986 (s), 934 (m), 907 (m), 860 (s), 806 (s), 745 (s), 700 (s), 664 (w), 604 m), 557 (m), 546 (w), 519 (m), 446 w), 420 (s).

Synthesis of [$C_5H_4(CH_2)_3$N-t-Bu]Zr($CH_2Ph)_2$ (89). A cooled (0 ^oC) suspension of 0.40 g (1.18 mmol) of [$C_5H_4(CH_2)_3$N-*t*-Bu]$ZrCl_2$ in 20 mL of ether was treated with 2.7 mL 0.93 M (2.51 mmol) of $PhCH_2MgCl$ in ether and stirred for 3 h at room temperature. The mixture became yellow. The solvent was removed in vacuum and the yellow residue was stripped with 20 mL of pentane. The residue was extracted twice with 40 mL of pentane. The resulting yellow solution was concentrated to 10 mL and transferred into a small vessel. Evaporation of the solvent left an orange oil. Yield: 0.41 g (0.91 mmol, 77%) of [$C_5H_4(CH_2)_3$N-*t*-Bu]Zr($CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.21 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.92 (overlapped resonances: d, $^3J_{HH}$ = 8.42 Hz, 4H, *o*-Ph; 2H, *p*-Ph); 5.79 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.52 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 2.58 (m, 2H, $C_5H_4\underline{CH_2}$); 2.15 (d, $^2J_{HH}$ = 10.62 Hz, 2H, $Ph\underline{CH_2}$); 2.10 (m, 2H, NCH_2); 1.96 (d, $^2J_{HH}$ = 10.62 Hz, 2H, $PhCH_2$); 1.31 (m, 2H, $NCH_2\underline{CH_2}$); 1.20 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 149.04 (s, Ph-*ipso*); 128.74 (d, $^1J_{CH}$ = 156.3 Hz, *o*-Ph);

126.66 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 126.60 (s, C_5H_4-*ipso*); 121.45 (d, $^1J_{CH}$ = 157.5 Hz, *p*-Ph); 114.83 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 112.55 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 63.53 (t, $^1J_{CH}$ = 119.6 Hz, Ph$\underline{CH_2}$); 57.08 (s, $\underline{C}Me_3$); 48.22 (t, $^1J_{CH}$ = 132.5 Hz, NCH_2); 34.14 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$); 29.65 (q, $^1J_{CH}$ = 124.9 Hz, $C\underline{Me_3}$); 28.02 (t, $^1J_{CH}$ = 127.0 Hz, $NCH_2\underline{CH_2}$). IR (cm^{-1}, neat): 3069 (m), 3015 (m), 2963 (s), 2924 (s), 2855 (s), 2774 (w), 1933 (w), 1848 (w), 1792 (w), 1721 (w), 1665 (w), 1593 (vs), 1537 (w), 1483 (s), 1449 (m), 1387 (m), 1358 (s), 1300 (vw), 1277 (w), 1252 (m), 1206 (vs), 1154 (vw), 1096 (m), 1071 (m), 1030 (s), 1011 (m), 988 (s), 937 (m), 885 (m), 862 (m), 808 (vs), 746 (vs), 698 (vs), 610 (w), 559 (m), 519 (m).

5.11 References and Notes.

(1) For recent reviews see (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144. (b) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, 3907. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans*. **1996**, 255. (d) Brintzinger. H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (e) *Catalyst Design for Tailor-Made Polyolefins*: Soga, K.; Terano, M., Eds. Elsevier: Tokyo, 1994. (f) Möhring, P.C.; Coville, N.J. *J. Organomet. Chem.* **1994**, *479*, 1. (g) Marks, T.J. *Acc. Chem. Rev.* **1992**, *25*, 57. (h) Jordan, R.F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(2) (a) Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S. Eur. Patent Appl. EP 416436-A1, 1991 (Dow Chemical Co.). (b) Canich, J.M.; Hlatky, G.G.; Turner, H.W. PCT Appl. WO 92-00333, 1992. Canich J.M. Eur. Patent Appl. EP 420-436-A1, 1991 (Exxon Chemical Co.).

(3) (a) Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1993**, *12*, 1936. (b) Hughes, A.K.; Marsh, S.M.B.; Howard, J.A.K.; Ford, P.S. *J. Organomet. Chem.* **1997**, *528*, 195. (c) Antonelli, D.M.; Green, M.L.H.; Mountford, P. *J. Organomet. Chem.* **1992**, *438*, C4. (d) Fandos, R.; Meetsma, A.; Teuben, J.H. *Organometallics*, **1991**, *10*, 59. (e) Rasika Dias, H.V.; Wang, Z. *J. Organomet. Chem.* **1997**, *539*, 77. (f) Rieger, B. *J. Organomet. Chem.* **1991**, *420*, C17.

(4) Precoordination of the $ZrCl_4$ with various Lewis-bases (Et_3N, pyridine, THF, TMEDA) or using other solvents or reaction temperatures did not show improvement.

(5) Chandra, G.; Lappert, M.F. *J. Chem. Soc.* (A), **1968**, 1940

(6) (a) Herrmann, W.A.; Morawitz, M.J.A.; Priermeier, T. *Angew. Chem. Int. Ed.* **1994**, *33*, 1946. (b) Herrmann, W.A.; Morawitz, M.J.A. *J. Organomet. Chem.* **1994**, *482*, 169. (c) Diamond, G.M.:Rodewald, S.; Jordan, R.F. *Organometallics* **1995**, *14*, 5. (d) Carpenetti, D.W.; Kloppenburg, L.; Kupec, J.T.; Petersen, J.L. *Organometallics* **1996**, *15*, 1572. (e) Christopher, J.N.; Jordan, R.F.; Petersen, J.L.; Young, V.G. *Organometallics* **1997**, *16*, 3044. (f) Herrmann, W.A.; Baratta, W. *J. Organomet. Chem.* **1996**, *506*, 357. (g) Diamond, G.M.; Jordan, R.F.; Petersen, J.L. *Organometallics* **1996**, *15*, 4030. (h) Christopher, J.N.; Diamond,

G.M.; Jordan, R.F.; Petersen, J.L. *Organometallics* **1996**, *15*, 4038. (I) Diamond, G.M.; Jordan, R.F.; Petersen, J.L. *Organometallics* **1996**, *15*, 4045.

(7) Synthesis performed according to Hughes *et al.* see ref. 3a, b.

(8) Carpenetti, D.W.; Kloppenburg, L.; Kupec, J.T.; Peterssen, J.L. *Organometallics* **1996**, *15*, 1572.

(9) Stevens, J.C.; Timmers, F.J.; Wilson, D.R.; Schmidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; Lai, S. *Eur. Pat. Appl.* EP 416815 **1991**.

(10) (a) Van der Linden, A.; Schaverien, C.J.; Meijboom, N.; Ganter, C.; Orpen, A.G.; *J. Am. Chem. Soc.* **1995**, *117*, 3008. (b) Mu, Y.; Piers, W.E.; MacQuarrie, D.C.; Zaworotko, M.J.; Young, V.G. *Organometallics* **1996**, *15*, 2720

(11) Davidson, P.J.; Lappert, M.F.; Pearce, R. *J. Organomet. Chem.* **1973**, *57*, 269.

(12) Collier, M.R.; Lappert, M.F.; Pearce, R. *J. Chem. Soc., Dalton trans.* **1973**, 445.

(13) (a) Zucchini, U.; Giannini, U.; Albizzati, E.; D'Angelo, R. *J. Chem. Soc., Chem Comm.* **1969**, 1174. (b) Giannini, U.; Zucchini, U. *J. Chem. Soc., Chem Comm.* **1968**, 940. (c) Felten, J.J.; Anderson, W.P. *J. Organomet. Chem.* **1972**, *36*, 87.

(14) Bower, B.K.; Tennent, H.G. *J. Am. Chem. Soc.* **1972**, *94*, 2512.

(15) Hughes, A.K.; Kingsley, A.J. *J. Organomet. Chem.* **1997**, *539*, 109.

(16) (a) Chang, B.-H.; Tung, H.-S.; Brubaker, C.H., Jr. *Inorg. Chim. Acta* **1981**, *51*, 143. (b) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D.R.; Negishi, E. *Chem. Lett.* **1989**, 761. (c) Swanson, D.R.; Rousset, C.J.; Negishi, E. *J. Org. Chem.* **1989**, *54*, 3521. (d) Hoveyda, A.H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079.

(17) (a) Davies, G.R.; Jarvis, J.A.J. *J. Chem Soc., Chem Comm.* **1971**, 1511. (b) Davies, G.R.; Jarvis, J.A.J.; Kilbourn, B.T.; Pioli, A.J.P. *J. Chem. Soc., Chem. Comm.* **1971**, 677. (c) Zucchini, U.; Giannini, U.; Albizzati, E.; D'Angelo, R. *J. Chem. Soc., Chem. Comm.* **1969**, 1174.

(18) Latesky, S.L.; McMullen, A.K.; Niccolai, G.P. Rothwell, I.P. *Organometallics*, **1985**, *4, 902.*

(19) At 160 ^{o}C the decomposition of **62** took 5 hours.

(20) For $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(NMe_2)_2$ (200 ^{o}C, 20 h) and $[C_5H_4(CH_2)_3N(H)\text{-}t\text{-}Bu]Ti(NMe_2)_3$ (160 ^{o}C, 10 h) the same behavior was observed.

(21) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659.

(22) Buchwald, S.L.; Watson, B.T.; Huffman J. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(23) Fryzuk, M.D.; Mao, S.S.H.; Zaworotko, M.J.; MacGillivray, L.R. *J. Am. Chem. Soc.* **1993**, *115*, 5336

(24) The activation of the *t*-butyl amido group could also proceed by a six center transition state (see Chapter 3) inwhich the liberation of RH and *iso*-butene is achieved n one step.

(25) Antonelli, D.M.; Green, M.L.H.; Mountford, P. *J. Organomet. Chem.* **1992**, *438*, C4.

(26) (a) Cummins, C.C.; van Duyne, G.D.; Schaller, C.P.; Wolczanski, P.T. *Organometallics* **1991**, *10*, 164. (b) Cummins, C.C.; Schaller, C.P.; van Duyne, G.D.; Wolczanski, P.T.; Chan, A.W.E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.

(27) (a) Bennett, C.R.; Bradley, D.C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. (b) Simpson, S.J.; Turner, H.W.; Andersen, R.A. *Inorg. Chem.* **1981**, *20*, 2991. (c) Simpson, S.J.; Andersen, R.A. *Inorg. Chem.* **1981**, *20*, 3627. (d) Planalp, R.P.; Andersen, R.A.; Zalkin, A. *Organometallics* **1983**, *2*, 16. (e) Berno, P.; Minhas, R.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052.

(28) Cummins, C.C.; Baxter, S.M.; Wolczanski, P.T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

(29) Duchateau, R. Thesis, **1995**, Groningen.

(30) Chem, Y.-X.; Marks, T.J. *Organometallics*, **1997**, *16*, 3649.

(31) Shapiro P.J.; Cotter, WD.; Schaefer, W.P.; Labinger, J.A.; Bercaw, J.E. *J. Am. Chem. Soc.* **1994**, *116*, 4623

(32) (a) Cotton, F.A.; Kibala, P.A. *Polyhedron* **1987**, *6*, 645. (b) Cotton, F.A.; Kibala, P.A. *Inorg. Chem.* **1990**, *29*, 3192. (c) Wengrovius, J.H.; Schrock, R.R.; Day, C.S. *Inorg. Chem.* **1981**, *20*, 1844.

(33) (a) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 629. (b) Kaminsky, W.; Sinn, H. *Liebigs Ann. Chem.* **1975**, *424*, 438

6 Exploration of Catalytic Olefin Polymerization Activity of Cationic Cyclopentadienyl Amido Titanium and Zirconium Alkyl Complexes $\{[C_5H_4(CH_2)_nNR]MR'\}^+$.

6.1 Introduction.

The importance of well defined single-site metallocene catalysts for olefin polymerization has been well established in the last 15 years.[1] A major breakthrough towards industrial application of single site metallocene and related complexes for catalytic olefin polymerization has been the discovery that MAO (methylaluminoxane) is an excellent co-catalyst.[2] A second key step in catalyst development has been the preparation of a wide variety of (*ansa*)-metallocenes. This opened the way to precise stereocontrol of olefin insertion during the polymerization process.[1,3,4] Replacement of the (*ansa*)-metallocene by a linked amido cyclopentadienyl ligand, first introduced by Bercaw *et al*.[5] and now commercially utilized by Exxon and Dow,[6] led to a remarkable difference in performance. Some of the outstanding features of these new catalysts are high and controlled incorporation of α-olefins in ethene co-polymerization[6a,7] and a remarkable stability of the catalyst at high temperatures (up to 160 ^oC).

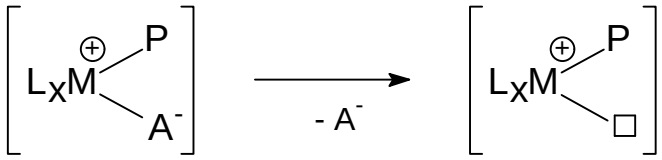
The linked Cp-amido ligand system can easily be modified and ligand features such as bridge length and amide or cyclopentadienyl substitution can be varied over a wide range. Although academic and industrial research groups have extensively explored the chemistry of the $[C_5R_4\text{-}Y\text{-}NR]MCl_2$ system (C_5R_4 = C_5H_4, C_5Me_4, C_9H_6; Y = $SiMe_2$, $(SiMe_2)_2$, $(CH_2)_2$, $(CH_2)_3$; R = Me, *i*-Pr, *t*-Bu, Ph), a clear relation between structure of the catalyst and its performance has not been established yet. For titanium a short bridge ($SiMe_2$) and sterically demanding Cp and amido functionalities (C_5Me_4, N-*t*-Bu) appear to give the highest activity, highest molecular weight and highest incorporation of co-monomer[6a] and these systems have been under intense attention. In contrast, the information available on cyclopentadienyl-amido complexes with longer links (*e.g*. CH_2CH_2, $(CH_2)_3$, $(SiMe_2)_2$) is still limited.[8]

In this chapter an exploration of the catalytic olefin polymerization potential of C_2- and C_3 bridged Cp-amido titanium and zirconium complexes $[C_5H_4(CH_2)_nNR]MR'_2$ is described. The complexes have been reacted with two different cation-generating species, methylaluminoxane (MAO) and tris(pentafluorophenyl)borane $B(C_6F_5)_3$, to give catalytically active cationic species $\{[C_5H_4(CH_2)_nNR]MR'\}^+$ and these have been tested for polymerization

activity toward ethene and propene. A provisional attempt is made to rationalize the relation between the structure of the catalysts and their activity and the molecular weight and microstructure of the polymers obtained.

6.2 Cation-Anion Interactions.

It is now generally accepted that cationic group 4 species resulting from activation with (halo)aluminum alkyls or MAO are the active species in catalytic olefin polymerizations. The question remains whether the catalytic active species can be regarded as an essentially free cation or whether it interacts with the anion. Kinetic and reactivity studies performed by Reichert, Fink and Eisch[9] reveal that contact ion pairs are formed first which reversibly dissociate into separated ion pairs. They regarded contact ion-pairs as the resting or 'dormant' state of the catalyst and the species with a free counter ion as the active species (Scheme 1).



'dormant state' active state

Scheme 1.

For example the group 4 metallocenes activated with alkylaluminum halides are incapable to polymerize propene and higher olefins due to the relative strong cation-anion interactions.[2a,10] With more weakly coordinating anions like Me-$[MAO]_n^-$,[2] $B(C_6F_5)_4^-$ [11] and $MeB(C_6F_5)_3^-$ [12] polymerization does take place as studies by Ewen[13] and Marks[14] demonstrate. They observed that $[ZrMe]^+B(C_6F_5)_4^-$ and $[Zr]Cl_2$-MAO show about the same activity and produce polymers with similar molecular weight, microstructure and melting point which suggests that $[Me(MAO)_n]^-$ and $B(C_6F_5)_4^-$ have comparable, poor, coordinating abilities. However, the $[ZrMe]^+$ cation in combination with the smaller anion $[MeB(C_6F_5)_3]^-$ is considerably less active and this is attributed to stronger coordination of the anion. It is clear that cation-anion interactions are of crucial importance for the catalytic activity of these species.

The strength of the cation-anion interaction is not only determined by the anion itself but also by the steric crowding exerted by the auxillary ligand set and it can be expected that altering the ligands and/or using different metals will cause substantial differences in catalytic performance.

Solid state molecular structures can provide useful information about how the ligands affect the steric crowding around the metal center. For example the molecular structures of $[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]TiCl_2$ (**3**) and $[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]TiCl_2$ (**9**) (Chapter 2) show that in the C_3-bridged complex **9**, the Ti-Cl, Ti-N and Ti-Cg distances and the Cl-Ti-Cl angles are almost the same as in **3** but the Cg-Ti-N, Ti-N-CH_2 and Ti-N-Ci-Pr angles differ considerably from **3** and the amido group is pushed towards the metal center narrowing the reaction space. However, solid state structures have limited value as models for molecules in solution, especially when effects are to be associated with rotation and movement of ligands or substituents.

For cationic benzyl species, generated from bis(benzyl) group 4 complexes and tris(pentafluorophenyl)borane, ^{19}F NMR spectroscopy provides a convenient probe for the presence of anion-cation interaction in solution. The difference in chemical shift between the *meta* and the *para* fluoro substituents of the pentafluorophenyl substituents of the borate anion, $\Delta\delta[(m\text{-}F)\text{-}(p\text{-}F)]$, is about 4 ppm for the η^6-coordinated anion, and 3 ppm for the free anion.[15] For example, the complex $[(\eta^5\text{-}C_5H_5)Zr(CH_2Ph_2)]^+[PhCH_2B(C_6F_5)_3]^-$ exists in solution as a contact ion-pair in which the phenyl group of the anion is η^6-bound to the metal center[16] whereas $[(\eta^5\text{-}C_5Me_5)Zr(CH_2Ph_2)]^+[PhCH_2B(C_6F_5)_3]^-$ is a solvent-separated ion pair[17] (Figure 1).

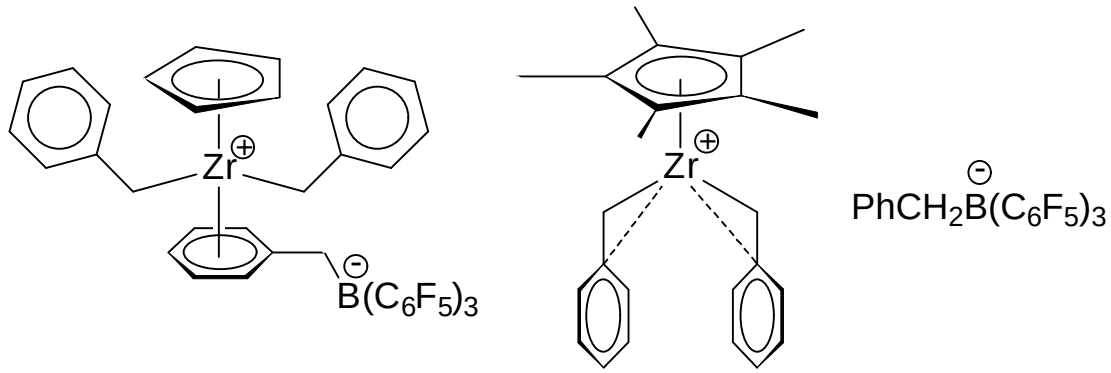
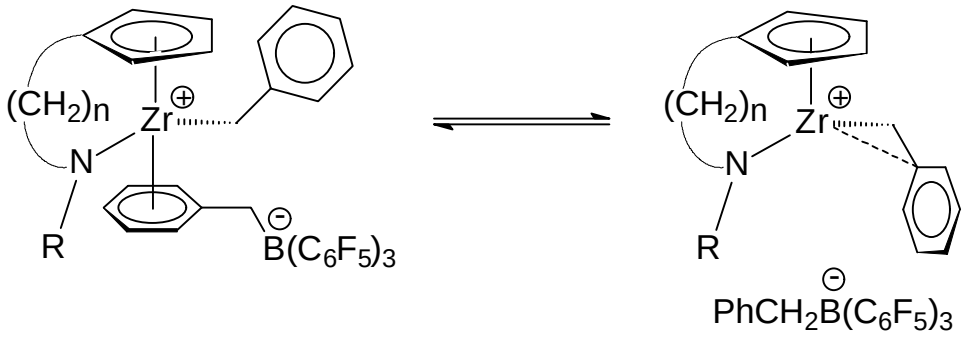


Figure 1. Cation-anion interaction *vs* steric congestion around the metal center.

6.3 Generation of Zirconium Benzyl Complexes $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+$ $[PhCH_2B(C_6F_5)_3]^-$.

All Cp-amido zirconium dibenzyls $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ (Chapter 5) react cleanly and instantaneously in C_6D_5Br with $B(C_6F_5)_3$. One benzyl group is abstracted and ionic species $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ are formed

The cation-anion interaction, as determined by ^{19}F-NMR spectroscopy (-35 ^oC), strongly depends on the nature of the Cp-amido ligand. In C_6D_5Br, the complexes $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ are present as an equilibrium mixture of the contact ion-pair (η^6-coordination of the borate benzyl to the cation) and the solvent-separated ion-pair (Scheme 2)



n = 2; R = *i*-Pr (**92**), *t*-Bu (**93**)

n = 3; R = Me (**94**), Et (**95**), *t*-Bu (**96**)

$[C_5Me_4SiMe_2N$-*t*-Bu] (**97**)

Scheme 2. Equilibrium between contact ion-pair and solvent separated ion-pair in the system $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$.

The *m*-F resonances of the two species are well-separated and the ratio contact ion-pair *vs* solvent separated ion-pair was determined at a specific concentration (0.2 M) for various Cp-amido ligands (Table 1). For a fixed bridge (n = 2), changing the substituent R from *i*-Pr to *t*-Bu shifts the equilibrium from predominantly bound to predominantly free anion. Lengthening the bridge from n = 2 to n = 3, for R = *i*-Pr, has a similar effect. For **95** (n = 3, R = Et) an intermediate situation is found, for which both the contact ion pair and the solvent separated ion pair can be readily observed by ^{1}H NMR and ^{13}C NMR spectroscopy. It thus seems that the position of this equilibrium gives a reasonable indication of the relative steric restrictions imposed by the ligand system.

Table 1. Relative amounts of contact ion-pair (bound) and solvent separated ion-pair (free) for $\{[C_5H_4(CH_2)_nNR]ZrCH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$.[a]

n, R	% bound	% free
2, *i*-Pr	92	8
2, *t*-Bu	13	87
3, Me	85	15
3, Et	31	69
3, i-Pr	5	95
$Me_4C_5SiMe_2NtBu$	2	98

[a]) [Zr] = 0.2 M, T = -35 °C

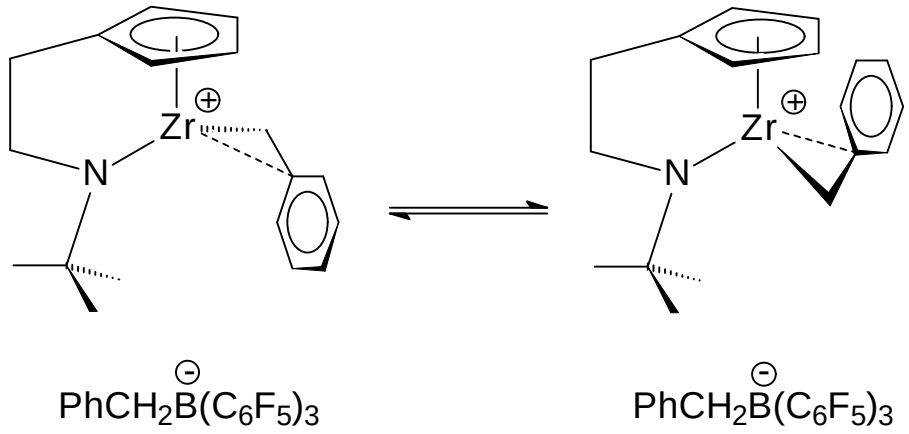
The contact ion-pairs $[C_5H_4(CH_2)_nNR]Zr(\eta^1\text{-}CH_2Ph)[\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ show in their ^{1}H- and ^{13}C NMR spectra diastereotopic B-CH_2 protons and a Zr bound η^1-benzyl group, that freely rotates around the CH_2-Ph bond. An η^1-benzyl group is suggested by the down-field shift of the *ipso* carbon (± 150 ppm), and by the relatively small $^1J_{CH}$ of 120 Hz and the relatively large $^2J_{HH}$ of around 10-11 Hz of the methylene group. For the aromatic protons of the anion five separate resonances are observed, significantly upfield shifted from the positions in the free anion.[17,18] A full listing of ^{1}H- and ^{13}C NMR data of a representative example (n = 3, R = Me) is given in the experimental section. The solvent-separated ion-pair $\{[C_5H_4(CH_2)_nNR]Zr(\eta^2\text{-}CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ adopts, according to the ^{1}H- and ^{13}C NMR spectra, an additional interaction of the Zr bound benzyl group with the metal center. Such an η^2-coordination of the benzyl ligand is characterized by a significant, upfield shift of the *ipso* carbon (± 122 ppm) and a $^1J_{CH}$ larger than 140 Hz together with a small $^2J_{HH}$ of 7-8 Hz for the methylene group.[19,20,21] A full listing of ^{1}H- and ^{13}C NMR data of a representative example (n = 3, R = *i*-Pr) is presented in the experimental section.

Cationic titanium complexes $\{[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ could be generated in the same way as for zirconium. $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2$ (**20**), $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(CH_2Ph)_2$ (**22**) and $[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)_2$ (**23**)[22] react instantaneously with $B(C_6F_5)_3$ to give $\{[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**98**), $\{[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**100**) and $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**101**). In all cases solvent separated ion-pairs are formed (^{19}F NMR: $\Delta\delta$[(*m*-F)-(*p*-F)] = 2.6-2.8 ppm, -35 °C). The ^{1}H NMR spectra of these systems show fluxional behavior. For the sterically least hindered system **98**, the ^{19}F

resonances are rather broad and this indicates that the fluxional behavior (in addition to a fluxional benzyl ligand, *vide infra*) can be ascribed to a rapid equilibrium between solvent separated ion-pair and contact ion-pair.

Variable temperature ^{1}H NMR spectroscopy shows fluxional behavior for the cationic part of $\{[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]ZrCH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$. At -30 ^{o}C the ^{1}H NMR spectrum showed three Cp proton resonances at 5.8 (2H), 5.2 (1H) and 5.1 (1H) ppm. The two *o*-phenyl protons are observed as separate resonances at 6.45 and 6.15 ppm while the diastereotopic benzylic protons appeared as two doublets at 2.90 (d, $^2J_{HH}$ = 7.5 Hz) and 2.25 (d, $^2J_{HH}$ = 7.5 Hz) ppm respectively.

Upon warming, the two resonances of the *o*-phenyl protons of the benzyl ligand coalesce at about -15 ^{o}C to become a sharp doublet at 65 ^{o}C. The three resonances assigned to the Cp-ring protons coalesce at 20 ^{o}C and appear as two resonances at 5.6 and 5.5 ppm respectively on further warming. The two resonances of the benzylic protons coalesced at 15 ^{o}C and form a singlet at 65 ^{o}C. These observations are consistent with fast flipping of the Zr benzyl group (Scheme 3). The free energies of activation ($\Delta G^{\neq}$)[23], calculated from the coalescence of the benzyl *o*-H and $ZrCH_2$ protons respectively, are 52 ± 0.2 kJ/mol (260 K) and 56 ± 0.5 kJ/mol (290 K).



Scheme 3.

The cationic titanium benzyl complexes **98**, **100** and **101** are more fluxional than the zirconium analogues. The systems could not be frozen out at -35 ^{o}C and broad ^{1}H NMR resonances remain. The predominant existence of **98** as solvent separated ion-pair and the higher fluxionality of the cationic titanium benzyl compounds reflect the smaller ionic radius of titanium (0.74 Å, Ti^{4+} vs 0.86 Å, Zr^{4+}).[24]

From NMR studies on the cationic benzyl complexes, it is clear that interactions between cations and anions depend on the size of the bridge, the amido substituents and the metal. For zirconium, compounds with short bridges and small amido substituents exist predominantly as contact ion-pairs while for sterically more demanding Cp-amido ligands the equilibrium is almost fully at the solvent separated ion-pair side. For titanium, the equilibrium lies on the side of solvent separated ion-pairs. The cations $\{[C_5H_4(CH_2)_nNR]Zr(\eta\text{-}CH_2Ph)\}^+$ are thermally quite robust in solution whereas the titanium analogues seem to engage in C-H activation processes as was indicated by slow formation of toluene (25 ^oC, ^1H NMR).

6.4 Catalytic Polymerization of Ethene and Propene.

The compounds presented in previous chapters are expected to have interesting potential as catalysts or catalyst precursors for olefin polymerization. To explore this a range of dichlorides $[C_5H_4(CH_2)_nNR]MCl_2$ has been tested with MAO as cocatalyst in the polymerization of ethene (Table 2 and 4) and propene (Table 3). In addition, cationic complexes $\{[C_5H_4(CH_2)_nNR]M(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (M = Ti, Zr) have been tested as well (Table 3).

6.4.1 Ethene Polymerization with $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO.

Metallocene catalysts are usually premixed with MAO[25] before being passed into the reactor. However, for $[C_5H_4(CH_2)_nNR]TiCl_2$ this procedure did not result in active catalyst systems apparently due to fast reduction of the metal to inactive Ti(III).[26]

Therefore a different test procedure was used in which $[C_5H_4(CH_2)_nNR]TiCl_2$, dissolved in toluene, was injected into an autoclave containing a MAO/toluene mixture which had been saturated with ethene. All $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO systems (n = 2, 3; R = Me, *i*-Pr, *t*-Bu) tested showed polymerization activity (Table 2).

Variation of the length of the backbone and of the amido substituent of the supporting ligand affects both the activity of the catalyst and the molecular weight of the polymers. In the C_2 series the productivity increases with larger amido substituents. $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]TiCl_2$/MAO is twice as active as $[C_5H_4(CH_2)_2NMe]TiCl_2$/MAO. Elongation of the backbone causes considerable decrease in activity of the catalyst. $[C_5H_4(CH_2)_2NMe]TiCl_2$/MAO is more than two times as active as the C_3 analogue. In contrast to the C_2 series, larger amido

substituents in the C_3 series cause a decrease in activity: $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$/MAO is about 6 times less active than $[C_5H_4(CH_2)_3NMe]TiCl_2$/MAO.

Table 2. Ethene polymerization with $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO catalysts.[a]

entry	catalyst R	productivity. (g/mmol h)	Mw	Mn	Mw/Mn
C_2-bridge					
1a	Me	840	777,000	211,000	3.68
1b	Me	840	732,000	191,000	3.83
2a	*i*-Pr	1470	122,700	51,900	2.36
2b	*i*-Pr	1460	113,000	49,300	2.29
3a	*t*-Bu	1850	57,600	31,400	1.83
3b	*t*-Bu	1750	72,900	29,800	2.44
C_3-bridge					
4a	Me	330	848,000	140,600	6.03
4b	Me	370	779,000	130,000	5.99
5a	*i*-Pr	60	212,000	38,300	5.53
5b	*i*-Pr	55	99,200	32,600	3.04

[a]) toluene solvent (300 mL), [Ti] = 7.0 x 10^{-5} M, Al/Ti = 520,
2 bar ethene, T = 50 ^{o}C, 30 min. run time.

The observation that the C_3 catalysts are less active than the C_2 analogues is in line with the fact that $[C_5Me_4(SiMe_2)_2N$-*t*-Bu$]TiCl_2$/MAO is less active than $[C_5Me_4SiMe_2N$-*t*-Bu$]TiCl_2$/MAO and that a short bridge is required for a high activity. In analogy $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$/MAO is two times more active than the sterically less crowded $[C_5H_4(CH_2)_2NMe]TiCl_2$/MAO system but trends are difficult to rationalize (cf section 6.6). It seems that the maximal activity for the systems under study here can be expected for a C_2-bridge and a largest possible substituent on the amido function.

The molecular weight of the polyethene also strongly depends on the catalyst used. In the C_2-series Mw drops one order of magnitude from $[C_5H_4(CH_2)_2NMe]TiCl_2$/MAO (Mw = 750,000) to $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$/MAO (Mw = 65,000). In the C_3 series a similar change is observed, although not as dramatic. The molecular weight distributions differ significantly between the C_2 and C_3 series. The C_2 catalysts produce polyethene with MWD's ranging from 3.8 to 1.8 suggesting more or less single site behaviour, while the polyethene (Mw/Mn

= 5.5 - 6) produced with the C_3 catalysts indicates that more than one species are simultaneously active.

The fact that the molecular weight drops with increasing steric bulk of the amido substituent contrasts however with the observation made for the $[C_5Me_4SiMe_2NR]TiCl_2$/MAO systems.

6.4.2 Propene Polymerization with $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO.

The MAO activated catalysts all are quite active (Table 3). The recorded characteristics (gas uptake, temperature and stirring speed) were for each run very similar. All $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO systems were still active after 30 min. although the rate of monomer uptake had decreased considerably. The $[C_5H_4(CH_2)_3NMe]TiCl_2$/MAO catalyst is an exception since it was completely inactive within 10 min. and therefor shows the lowest productivity. For the complexes within the C_2-series the catalyst with the smallest amido substituent has the highest productivity. Apart from the fast deactivation of the $[C_5H_4(CH_2)_3NMe]TiCl_2$/MAO system there are no marked differences in productivity between the C_2-and C_3-bridged catalysts. The polypropenes produced by the various catalysts show large differences in molecular weight. Whereas for the C_2 catalysts, the one with R = Me produces high molecular weight polypropene (Mw = 720,000), the sterically less accessible (R = *i*-Pr, *t*-Bu) give low molecular weight polymer (Mw = 16,300 and 11,400 resp.). For C_3, R = *i*-Pr, also relatively low molecular weight polypropene was obtained. For $[C_5H_4(CH_2)_2N$-*i*-$Pr]TiCl_2$/MAO and in lesser extent for $[C_5H_4(CH_2)_2N$-*t*-$Bu]TiCl_2$/MAO the molecular weights are considerably lower than compared to the borane activated analogues (*vide infra*). The ^{13}C NMR spectra of the polymers show resonances of *sec*-butyl end groups in the region of 25.5 - 22 ppm,[27] indicating that chain transfer to aluminum[28] is an important termination mechanism.

All MAO activated systems (again with exception of the catalyst with C_3, R = Me) show single site behavior as is indicated by the narrow dispersity (Mw/Mn = 2.84 - 1.58). The polypropenes produced have been characterized by NMR spectroscopy which allows conclusions with respect to the tacticity and the regioselectivity of the polymerization (*i.e.* 2,1 insertions). All samples are atactic polypropene with a substantial number of regio-errors[29] (up to 4.5%).

Table 3. Propene polymerization with $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO and $[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)_2/B(C_6F_5)_3$.[a]

entry	catalyst	[Ti]x10^4 M	productivity g/mmol h	Mw	Mn	Mw/Mn	% 2,1 insert.
MAO							
1	C_2, Me	2.01	295	720,000	344,000	2.09	2.2
2	C_2, *i*-Pr	2.02	114	16,300	8,420	1.94	3.8
3	C_2, *t*-Bu	2.04	224	11,400	6,520	1.75	4.5
4	C_3, Me	2.03	42	50,900	17,900	2.84	3.7
5	C_3, *i*-Pr	2.01	136	44,600	28,300	1.58	1.6
$B(C_6F_5)_3$							
6a	C_2, Me	3.91	782	1,064,000	543,500	1.96	4.6
6b	C_2, Me	3.92	662	1,047,000	411,300	2.55	n.d.
7a	C_2, *i*-Pr	4.00	1110	138,200	62,600	2.21	5.4
7b	C_2, *i*-Pr	4.01	1085	131,700	60,100	2.19	n.d.
7c	C_2, *i*-Pr	2.12	933	115,000	64,300	1.79	n.d.
8a	C_2, *t*-Bu	3.94	492	32,700	10,200	3.21	n.d.
8b	C_2, *t*-Bu	3.92	750	29,900	13.600	2.20	5.7
9a	C_3, Me	2.01	1909	97,000	19,600	4.95	n.d.
9b	C_3, Me	2.01	2328	99,600	20,100	4.96	6.7
10a[b]	C_3, *i*-Pr	3.95	2309	135,200	54,900	2.46	n.d.
10b	C_3, *i*-Pr	2.01	567	329,500	119,500	2.76	n.d.
10c	C_3, *i*-Pr	2.11	1190	234,400	108,100	2.17	2.3

[a]) toluene solvent (200 mL), MAO/Ti = 520, $B(C_6F_5)_3$/Ti = 1.5, 4.7 bar propene, T = 30 ^oC, run 30 min. [b]) 10 min. run, strong exotherm.

6.4.3 Propene Polymerization with $[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)_2/B(C_6F_5)_3$.

The borane activated catalysts $\{[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ were all active but, as expected for single component systems that have to scavenge impurities themselves, the reproducibility of the experiments is moderate.

Some catalysts have clearly different activity *vs* time profiles during the run (Figure 2). $\{[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**98**) showed an induction period (7-8 min). Then propene uptake started, the temperature began to rise gradually and, after some time, the stirring speed dropped due to buildup of high molecular weight polymer and formation of a highly viscous solution. The induction time suggests a slow start of the catalyst, possibly by initial formation of a single insertion product in which the vacant site at titanium is blocked by intramolecular benzyl arene coordination as is also observed for zirconium (*vide infra*).

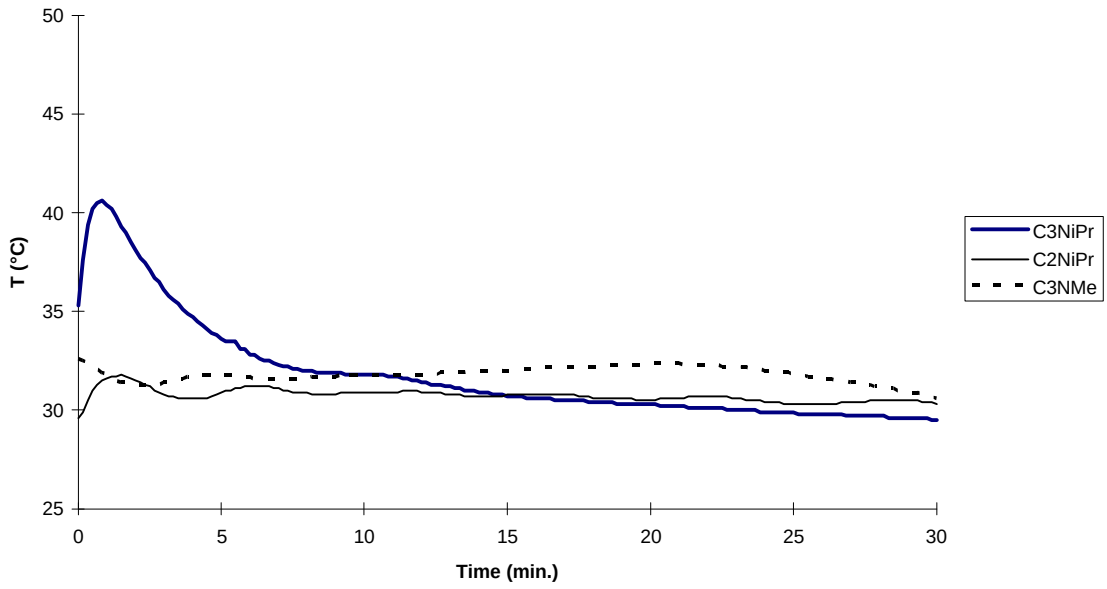


Figure 2. Temperature vs time profile of the catalytic propene polymerization with $\{[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]Ti(CH_2Ph)\}^+[X]^-$ (**99**), $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[X]^-$ (**101**) and $\{[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]Ti(CH_2Ph)\}^+[X]^-$ (**102**). $[X]^- = [PhCH_2B(C_6F_5)_3]^-$

The other borane activated catalysts did not show an induction period but start polymerizing immediately upon catalyst injection. The system $\{[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**102**) gives a very exothermic start, followed by slow decay (Figure 2). The uptake of propene ceased almost completely after 10 min. In contrast,

{[$C_5H_4(CH_2)_2$N-*i*-Pr]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**99**), {[$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**100**) and {[$C_5H_4(CH_2)_3$NMe]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**101**) only give a weak exotherm with almost constant uptake of propene and constant stirring speed during the whole run.[30]

The borane activated catalysts {[$C_5H_4(CH_2)_n$NR]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ have a higher productivity[31] than the [$C_5H_4(CH_2)_n$NR]$TiCl_2$/MAO systems but it is difficult to rationalize the differences. Within the borane activated catalyst series the C_3 bridged {[$C_5H_4(CH_2)_3$NMe]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**101**) is more productive than {[$C_5H_4(CH_2)_2$NMe]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**98**) although the induction time of the latter makes comparison difficult. {[$C_5H_4(CH_2)_2$N-*i*-Pr]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**99**) has a similar productivity as {[$C_5H_4(CH_2)_3$N-*i*-Pr]Ti(CH_2Ph)}$^+$ [Ph$CH_2B(C_6F_5)_3$]$^-$ (**102**), but the exceptional exothermal behavior of the latter again makes it difficult to compare the catalysts. In the C_2-series the differences in overall productivity is not large and a clear trend is not present.

The bis(benzyl)/borane systems give for all Cp-amido ligands higher molecular weight polypropene than the [$C_5H_4(CH_2)_n$NR]$TiCl_2$/MAO catalysts. For the C_2 catalyst the molecular weights decrease with larger substituents R on the amido ligand. Mw drops from over 1,000,000 for {[$C_5H_4(CH_2)_2$NMe]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**98**)[32] to around 30,000 for {[$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**100**). The molecular weights of the polypropene produced with the C_3-bridged catalysts show a different picture. Surpisingly {[$C_5H_4(CH_2)_3$NMe]Ti(CH_2Ph)}$^+$[Ph$CH_2B(C_6F_5)_3$]$^-$ (**101**) gives a bimodal molecular weight distribution (Mw/Mn = 5) with Mw's of around 100,000 and 20,000 which suggest that two different species are active simultaneously. Increasing the size of the nitrogen substituent resulted in higher molecular weights.

Like observed for the MAO activated catalysts, the polypropene produced was identified by ^{13}C NMR spectroscopy as essentially atactic polypropene. All ^{13}C NMR spectra showed regio-irregularities originating from 2,1 insertions but the percentage (2.3 - 6.7%) seems to be substantially higher than for the MAO activated catalysts. Here also the number of 2,1 insertions depends on the amido substituent R and the length of the bridge. For the C_2 catalysts the number of regio-errors increases with the size of the nitrogen substituent whereas for the C_3-bridged catalysts an inverse trend is observed. The number of regioirregular insertions observed for polypropene produced with the Cp-amido catalysts is about the same as reported for [$C_5Me_4SiMe_2$NR]$TiCl_2$ and [$C_9H_6SiMe_2$NR]$TiCl_2$ (R = *t*-Bu, CHMePh).[29]

Triad analysis of the polypropene samples produced with the C_2 bridged titanium catalysts (Table 4). show the samples to be essentially atatic, although in some cases the polymers

are clearly syndiotactically enriched. For the $[C_5H_4(CH_2)_2NMe]Ti$ and the $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti catalysts, the co-catalyst used do not substantially change the relative amounts of the mm-, mr- and rr triads. However in the case of $[C_5H_4(CH_2)_2N$-*i*-Pr]Ti catalysts the relative amounts of the mm-, mr- and rr triads are clearly changed.

Table 4. Triad's of the polypropene samples produced with C_2 bridged Cp-amido titanium catalysts

Cat	%mm	%mr	%rr
C_2NMe/B[a]	14.3	48.8	36.9
C_2NMe/M[b]	17.2	48.4	34.4
C_2NiPr/B	14.8	53.9	35.9
C_2NiPr/M	21.4	54.5	24.2
C_2NtBu/B	24.5	51.8	24.0
C_2NtBu/M	23.8	53.5	22.7

[a]) Borane activated, [b]) MAO activated

^{1}H NMR spectra of the polypropene samples produced with $[C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$/MAO and $\{[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ showed resonances of olefinic end groups, which were assigned to vinylidene (4.65 and 4.73 ppm), 1-alkene (4.9-5.0 and 5.78 ppm) and 2-alkene end groups (5.4-5.5 ppm). The vinylidene and 2-alkene end groups can be addressed to β-H transfer after 1,2 insertion and 2,1 insertion respectively. The presence of an 1-alkene end group could be an indication for β-Me transfer. An other possibilty could be β-H transfer from the methyl substituent after a 2,1-insertion. Although this is thought to be less likely for the traditional metallocene systems it could be a real possibility for the more open Cp-amido systems

6.4.4 Ethene Polymerization with $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO.

The $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO systems were tested for ethene polymerization activity under various conditions and the results are listed in Table 5. Unlike the titanium systems, the zirconium precursors were preactivated with excess MAO (see experimental) as no reduction of the metal occurred. The zirconium systems have a much lower activity than their titanium analogues and in order to get reasonable productivities polymerization runs were performed at higher ethene pressure (5 and 20 bar) and higher temperature (80 ^oC).

At 50 °C and 5 bar of ethene the productivity is essentially independent of the bridge length. The complexes tested (n = 2, 3, R = *i*-Pr) are 6 times more active than the well known dimethylsilyl bridged catalyst $[C_5Me_4SiMe_2N\text{-}t\text{-}Bu]ZrCl_2$.

At 80 °C and 20 bar of ethene the difference between the n = 2 and n = 3 (R = *i*-Pr) catalysts is striking: the C_3 catalyst is approximately 5 times more productive. The steric bulk on the amido function seems to have little effect in the C_2-bridged series as is indicated by the similar productivities for R = *i*-Pr and R = *t*-Bu. In contrast, in the C_3-bridged series the steric bulk on the amido function clearly influences the productivity since $[C_5H_4(CH_2)_3NMe]ZrCl_2$/MAO is about twice as active as $[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]ZrCl_2$/MAO.

The much larger productivity of $[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]ZrCl_2$/MAO compared to $[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]ZrCl_2$/MAO is remarkable because for the titanium compounds an opposite trend is observed. Moreover, a lower productivity is found for C_3-bridged (*ansa*)-bis(indenyl) zirconium complexes compared to the C_2-bridged analogue.[33]

At relatively high catalyst concentration (2.0×10^{-4} M), the catalyst with n = 3, R = Me and $[C_5Me_4(SiMe_2)N\text{-}t\text{-}Bu]ZrCl_2$ both showed a strong reaction exotherm, precluding a good comparision of productivities. At a lower catalyst concentration (3.3×10^{-5} M) the exotherm was not observed and in this case the n = 3, R = Me catalyst is the most productive. The relative differences between the other catalysts at this lower concentration were found to be the same as at higher concentration.

Table 5. Ethene polymerization with $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO catalysts.[a]

entry	catalyst n, R	[Zr]x10^5 M	T (°C)	p(C_2H_4) (bar)	productivity. (g/ mmol h)
1	2, *i*-Pr	20	50	5	60
2	3, *i*-Pr	20	50	5	65
3	Si, *t*-Bu[b]	20	50	5	10
4	2, *i*-Pr	20	80	20	170
5	2, *t*-Bu	22	80	20	155
6	3, *i*-Pr	21	80	20	829
7	3, Me	21	80[c]	20	2367
8	Si, *t*-Bu[b]	20	80[c]	20	2750
9	2, *i*-Pr	3.3	80	20	81
10	3, *i*-Pr	3.3	80	20	606
11	3, Me	3.3	80	20	1617

12	Si, *t*-Bu[b]	3.3	80	20	667

[a]) toluene solvent (300 mL), Al/Zr = 520, 30 min. run time.

[b]) [$C_5Me_4SiMe_2N$-*t*-Bu] [c]) large exotherm

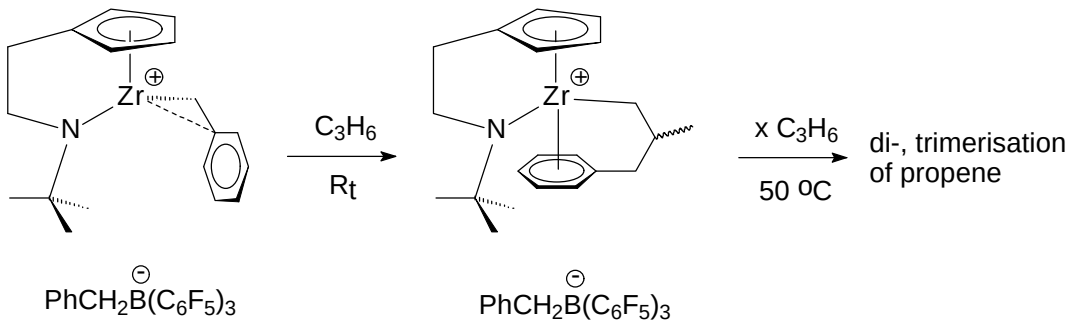
It appears that the activity of the $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO system can exceed under certain conditions the activity of the $[C_5Me_4SiMe_2N$-*t*-Bu$]MCl_2$/MAO, especially for n = 3 and a small substituent R on the amido functionality. Since for $[C_5R_4SiMe_2N$-*t*-Bu$]MCl_2$/MAO (M = Ti, Zr) catalyst systems it was observed that methyl substituents on the Cp-moiety greatly improve catalyst activity,[6a] it would be interesting to study the effect of methyl substituents on the cyclopentadienyl in carbon bridged Cp-amido complexes e.g. in $[C_5Me_4(CH_2)_nNR]ZrCl_2$[34] (n = 2, 3). This should be a future point of attention.

The observation that $[C_5Me_4SiMe_2N$-t-Bu$]ZrCl_2$/MAO under milder polymerization conditions (50 ^oC, 5 bar ethene) is less active than the n = 2, 3 R = *i*-Pr catalysts and the fact that it responds more strongly to an exotherm than $[C_5H_4(CH_2)_3NMe]ZrCl_2$/MAO indicates that the silicon bridged catalyst has a steeper activity *vs* temperature curve than the others. This temperature dependence of catalyst performance should be investigated in more detail to determine the optimum conditions for the various catalysts.

GPC analysis revealed that all samples are high molecular weight (Mw ≈ 1,500,000) polyethene with very broad and polymodal MWD's.

6.4.5 Propene Oligomerization with $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$.

NMR-tube studies of the reaction of $\{[C_5H_4(CH_2)_2NR]ZrCH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$ (R = Me and *t*-Bu) and $\{[C_5Me_4SiMe_2N$-*t*-Bu$]ZrCH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$ with an excess of propene in bromobenzene show that one single propene insertion takes place at room temperature (Scheme 4). $\{[C_5H_4(CH_2)_2NMe]ZrCH_2CH(Me)CH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$ (**103**) was identified by ^1H- and ^{19}F NMR spectroscopy as a solvent separated ion-pair. $\{[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCH_2CH(Me)CH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$ (**104**) and $\{[C_5Me_4SiMe_2N$-*t*-Bu$]ZrCH_2CH(Me)CH_2Ph\}^+[PhCH_2B(C_6F_5)_3]^-$ (**105**) showed the same characteristics in their ^1H spectra.[35]



Scheme 4.

At 50 ^{o}C, the single insertion products undergo slow subsequent insertion of propene yielding low molecular weight oligomers. {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrCH_2CHMeCH_2Ph}$^+$[PhCH_2B(C_6F_5)$_3$]$^-$ produced oligomers with a molecular weight of about 130 mass units (^{1}H NMR) with a turnover frequency of 60 h^{-1} and {[$C_5Me_4SiMe_2$N-*t*-Bu]ZrCH_2CHMeCH_2Ph}$^+$[PhCH_2B(C_6F_5)$_3$]$^-$ gave a molecular weight of about 340 with a rate of 25 h^{-1}. {[$C_5H_4(CH_2)_2$NMe]ZrCH_2CH(Me)CH_2Ph}$^+$ [PhCH_2B(C_6F_5)$_3$]$^-$ was not active at all.

This low tendency of the benzyl zirconium cationic complexes to undergo more than one insertion of propene can be rationalized by assuming stabilization of the first insertion products (**103**, **104** and **105**) most probably by intramolecular η^6-coordination of the phenyl group of the original benzyl ligand (Scheme 4).[36] In this way the vacant coordination site necessary for further propene insertion is blocked. A similar mono insertion of propene has been observed for Zr(CH_2Ph)$_4$/B(C_6F_5)$_3$ and this product was structurally characterized by X-ray diffraction showing an η^6-bonded arene moiety.[37] Once a second insertion had taken place, it is very likely that a strong intermolecular η^6-coordination of the benzyl borate anion inhibits propene insertion. This could explain the low productivity observed.

6.5 Catalyst Productivity, Polymer Molecular Weight and Microstructure as a Function of Steric Aspects of the Supporting Cyclopentadienyl-Amido Ligand System and Catalyst Cation-Anion Interactions.

The series of polymerization experiments described in this chapter represent a only first screening of catalytic activity of a particular series of titanium and zirconium complexes. Despite the fact that the overall picture obtained from these experiments is rather confusing and more detailed investigations need to be done, some clear and remarkable features can be mentioned and discussed.

The observation that the structurally congested system [$C_5H_4(CH_2)_2$N-*t*-Bu]TiCl_2/MAO is twice as productive in polymerization of ethene than the more open system [$C_5H_4(CH_2)_2$NMe]TiCl_2/MAO is in line with the productivities observed for the [$C_5Me_4SiMe_2$NR]TiCl_2/MAO. However, the fact that [$C_5H_4(CH_2)_3$N-*i*-Pr]ZrCl_2/MAO is about 5 times more active than the C_2 analogue is counter-intuitive. The often suggested explanation that the more open metal center, i.e. the one with the smaller bite angle Cp-M-N will have the highest catalytic activity may be too simple.

Cationic group 4 complexes are extremely electron deficient species that will relieve their electronic and coordinative unsaturation in almost every conceivable way and that this will also hold true for the catalytically active cation during polymerization. Theoretical studies[38] suggest that between the monomer insertions, the catalyst acts as a fast, repetitive molecular machine but that under special conditions (e.g. after an insertion error) enters a dormant state. This dormant state can be stabilized by α, β or γ-agostic interactions of the polymer chain with the metal center but also by steric shielding of the active center by substituents on the growing polymer chain close to the metal and by a strong anion-cation interaction. Less strong anion[15-21] and also solvent[39] interaction with the active center have been suggested to be important variables to influence the propagation and termination steps in olefin polymerization. [40,41]

Clear differences in catalyst productivity and molecular weight of the polymers obtained using different anions have been observed for (R)-Me_2SiCp"(-)-menthyl-Cp$ZrMe_2$ and Cp-amido systems. Systems with large, weakly coordinating, cations appeared to be more productive. Recent theoretical studies[42] on sterically less hindered Cp amido titanium system have shown that olefin insertion is possible when the anion interacts with the metal. The calculated energy barrier ($\Delta H^{\neq}$ = 14 kcal/mol) is relatively low. As shown in section 6.3, the strength of cation-anion interaction can be tuned not only by varying the anion but also by adjusting the auxillary ligand set.

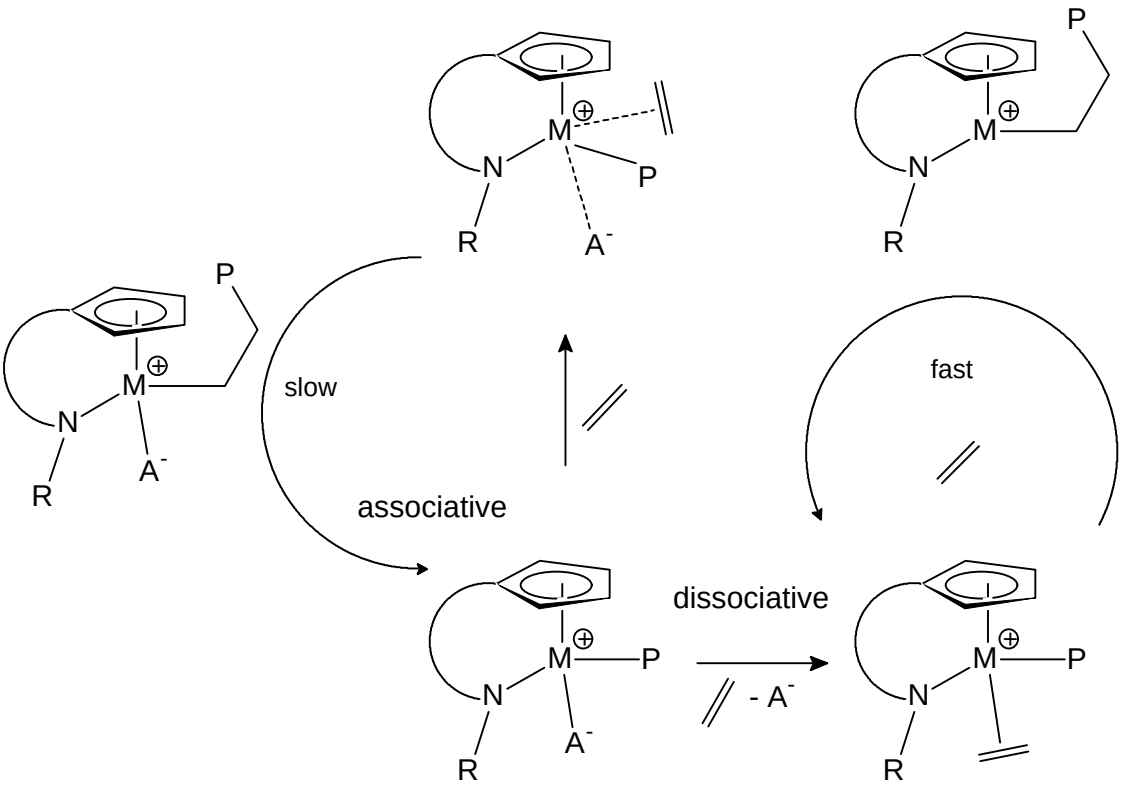
6.5.1 Catalyst Productivity. [43]

The MAO activated Cp-amido titanium and zirconium and $B(C_6F_5)_3$ activated titanium catalysts are in most cases moderately active. The titanium catalysts are much more active than the zirconium analogues. This could be due to the larger ion-radius of zirconium which gives a more open system and allows tighter bonding of the anion. The observation that in the C_2-series of the titanium catalysts the polymerization activity increases slightly when larger amido substituents are used, may be ascribed to repulsion by the amido substituent, loosening anion coordination and favoring insertion of ethene. Similarly, $[C_5H_4(CH_2)_3N$-*i*-Pr$]ZrCl_2$/MAO is (5 times) more active than the C_2 Zr catalyst. This can be explained by stronger anion interaction in the more open $[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrCl_2$/MAO system.

$\{[C_5H_4(CH_2)_3N$-*i*-Pr$]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ is clearly different from the other systems. The extremely high initial activity of this system indicates that this catalyst is operative in a different mode.

It is possible that the ionic Cp amido polymerization catalysts used here, can operate in two modes. In the first (Scheme 5, **A**) the anion remains coordinated throughout the whole process. Olefin insertion takes place via an associative mechanism in which the cation-anion interaction weakens during the coordination of the olefin and strengthens again after completion of the insertion. In the second mode the ions are free (Scheme 5, **B**) and the system shows the intrinsic activity of the cation. In mode **A** the catalysts will show a relatively moderate activity whereas much higher activity is expected for catalysts operating in mode **B**.

For the most of the catalysts presented here an associative mechanism (mode **A**) is likely. However in the case of $\{[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$, the steric hindrance of the $[C_5H_4(CH_2)_3N\text{-}i\text{-}Pr]$ ligand may cause complete dissociation of the counter ion and the system may be operative in mode **B**.



A **B**

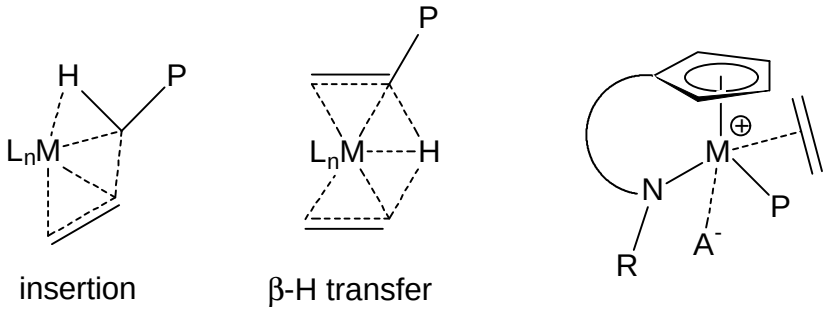
Scheme 5. Two possible modes of operation. **A**: Anion remains coordinated to the metal center during the whole insertion cyclus. **B**: Full dissociation of anion. A^- denotes anion

6.5.2 Molecular Weight and Microstructure of the Polymers

Molecular Weight of the Polymers

In general, the relative rates of propagation and termination determine the molecular weight of the polymer.[44,45,46] Several termination mechanisms have been recognized like β-H elimination, β-H transfer to the incoming monomer, β-Me transfer and chain transfer to the co-catalyst (commonly observed when MAO is used[28]).

A density functional study by Ziegler *et al*. on metallocene catalysts,[47] shows that chain termination by β-H transfer to the incoming monomer is favored over β-H transfer to the metal when monomer is present. The transition state for β-H transfer, either to the metal center or to the incoming olefin, requires more space than the olefin insertion step.[47,**Error! Bookmark not defined.**] This implies that steric congestion around the metal can affect the molecular weight of the polymer (Scheme 6). As has been propsed before (**6.5.1**), cation-anion interactions may also have consequenses for the steric congestion of the metal center.



Scheme 6. Illustration of the transition states of olefin insertion and chain transfer to the olefin, the latter is thought to be sterically more crowded and more sensitive to interaction of the anion with the metal center. A^- denotes anion.

For the titanium based catalysts, variation of the C_n bridge length and steric bulk of the auxiliary Cp-amido ligand system strongly affects the molecular weight of the polymers produced. Remarkable is that the molecular weight of the polyethene produced with $[C_5H_4(CH_2)_2NR]TiCl_2$/MAO decreases when catalysts with larger amido substituents are used while for the $[C_5Me_4SiMe_2NR]TiCl_2$/MAO series an reverse trend is observed.[6a] In the case of the propene polymerizations with $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO and $\{[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)^3]^-$ catalysts about the same trend is observed for the C_2-series: the molecular weight drops dramatically when catalysts with larger amido

substituents are used. The C_3-bridged borane activated catalysts show a different trend: the molecular weight of the polypropene produced increases when catalysts with larger amido subsituents are used. The $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)^3]^-$ system is different in this that it produces polypropene with a clearly bimodal molecular weight distribution.

The trend observed for the C_2-bridged catalyst may be explained by involvement of cation-anion interactions during the olefin insertion.

Assuming an associative insertion mechanism of olefins for most of the Cp-amido catalysts presented here (*vide supra*), it is likely that in the $[C_5H_4(CH_2)_2NMe]TiCl_2$/MAO and $\{[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)\}^+[PhCh_2B(C_6F_5)_3]^-$ systems the relatively strong anion coordination hinders β-H transfer to the incoming olefin much more than olefin insertion. Bulky Cp-amido ligands, like those with a *t*-Bu on nitrogen weaken coordination of the anion and consequently lower the molecular weight of the polymer. A longer carbon bridge (C_3 vs C_2) also weakens the cation-anion interaction. In this case bulky nitrogen substituents (*i*-Pr), in combination with a long bridge (C_3), will obstruct β-H transfer, resulting in polymers with higher molecular weight. This could explain the reversed trend in molecular weight observed for the C_3-series.

The unexpected behavior of the $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ system, producing bimodal polypropene, suggests two active species.[48] It is possible that $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+\{PhCH_2B(C_6F_5)_3]^-$ is simultaneously operative in both modes **A** and **B** (*vide supra*) with for each mode own rates of propagation and chain transfer. In that case, the catalyst does not act as a truly single site catalyst in the sense that all species react identically. One should realize that all catalysts discussed here in principle can operate simultaneously in the two modes under appropriate conditions.

Another explanation has been suggested by Chien *et al*.[49] They observed that the catalytic activity of the 12 electron, cationic species $\{[C_5H_4(CH_2)_2NMe_2]TiMe_2\}^+$ is second order in ethene or propene which implies that in this system two monomer molecules are involved in the olefin coordination/insertion steps.[50] The system operates with one or two olefins coordinated (depending on parameters like steric hindrance of the ligand system, solvent, concentration of the olefin). Therefore, $\{[C_5H_4(CH_2)_2NMe_2]TiMe_2\}^+$ does not perform like a true single site catalyst. Since the cationic Cp-amido complexes discussed here are isoelectronic with $\{[C_5H_4(CH_2)_2NMe_2]TiMe_2\}^+$, the same could count for them. Apparently, in the case of the $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ system the polymerization conditions allow two species to be simultaneously active.

The very broad, polymodal molecular weight distributions observed for the polyethene produced with the $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO catalysts is difficult to rationalize, but may be partly associated with transport limitations in the polymers formed.[51] Another possibility

could be the formation of different catalytic species by reaction of MAO with the Cp-amido ligand.

Microstructure of the Polymers

Regio-irregular (2,1)-insertions require a sterically more congested transition state than regular insertions. The number of regio-irregularities will thus depend on the steric congestion of the metal center. Frequent regio-irregularities can be expected for open systems, like the Cp-amido systems used in this study, in which 2,1 insertion of propene is possible.

Although one would expect $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2/B(C_6F_5)_3$, to be the most open system and thus to give polypropene with the highest amount of 2,1 insertions, the contrary is observed. Polypropene produced with the sterically more congested system $[C_5H_4(CH_2)_2N$-*t*-Bu$]Ti(CH_2Ph)_2/B(C_6F_5)_3$ has a higher number of 2,1 insertions than with $[C_5H_4(CH_2)_2NMe]Ti(CH_2Ph)_2/B(C_6F_5)_3$. $[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)_2/B(C_6F_5)_3$ gives the highest number of regio-irregular insertions while $[C_5H_4(CH_2)_3N$-*i*-Pr$]Ti(CH_2Ph)_2/B(C_6F_5)_3$ gives the lowest number of regio-irregularities. For the MAO activated catalysts the same trends are observed. In this case $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$/MAO produces polypropene with the highest number of regi-irregular insertions.

One could give the same explanation as for the differences in molecular weight, the larger amido substituents in the C_2 series disturb the interactions between the catalyst and counterion and allow 2,1 insertions to occur more frequently. The same could be valid for elongation of the C_3-backbone but in combination with the larger N-*i*-Pr group the system becomes sterically too congested and this leads to less regio-irregular insertions. The lower values found for the MAO activated catalyst could suggest stronger cation-anion interactions than in the borane activated systems. An other argument for a difference in cation-anion interaction between the Mao- and the borane activated species is the clearly different triad ratio found for the $[C_5H_4(CH_2)_2N$-*i*-Pr$]$Ti catalyst. Such a changed triad ratio is a strong indication that the steric congestion of the metal center is changed.

Although the presence of cation-anion interactions, during the olefin coordination/insertion, can be used to rationalize some of the observed differences in activities of the catalytic systems and the molecular weight and microstructure of the polymers produced, one should keep in mind that the study presented here, has its limitations. Illustrative examples are deactivation of the $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO system by reduction, or active site blocking by strong arene coordination after one propene insertion in the cationic Cp-amido zirconium benzyl species $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+$.

6.6 Concluding Remarks and Prospects.

All $[C_5H_4(CH_2)_nNR]MX_2$ (M = Ti, Zr) systems showed to be active olefin polymerization catalysts when activated with MAO (X = Cl) or $B(C_6F_5)_3$ (X = CH_2Ph). Surprisingly, the $[C_5H_4(CH_2)_nNR]TiCl_2$ complexes are rather easily reduced by MAO and polymerization runs have to be performed without preactivation. The runs with $[C_5H_4(CH_2)_nNR]ZrCl_2$ can be performed by preactivation with MAO.

Ethene polymerization tests show that the activity of the titanium catalysts depend on the nature of the Cp-amido ligand. C_2-bridged complexes are more active than the C_3-bridged analogues.

It seems that variation of the ligand set causes an optimum in catalyst activity. It is well possible that C_2-bridged catalysts with nitrogen substituents bigger than *t*-Bu show even higher activities than $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$/MAO. However this optimum appears to be passed upon extension of the backbone with one methylene unit. In this case a clear decrease in activity is observed.

In contrast to the titanium systems, the zirconium catalysts show a different catalyst nature/activity trend in that the C_3-bridged catalysts are more active than the C_2-bridged analogues.

The molecular weight of the polyethene produced with the titanium catalysts strongly depends on the ligands used. Catalyst with sterically less demanding ligand produce polyethene with a high molecular weight (M_w = 800,000), whereas the sterically more crowded catalysts produced low molecular weight polyethene (M_w = 65,000).

The $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO and $[C_5H_4(CH_2)_nNR]Ti(CH2Ph)_2/B(C_6F_5)_3$ systems were also tested in the catalytic polymerization of propene. The borane based titanium catalysts showed higher activities and produced atactic polypropene with higher molecular weights than the MAO based titanium catalysts although the performances of the individual catalysts are influenced by factors like reduction of the catalysts, induction times, limiting monomer diffusion and heat transfer.

The $[C_5H_4(CH_2)_3NR]Ti(CH_2Ph)_2/B(C_6F_5)_3$ catalysts appear to be more active than the C_2-bridged analogues, the $[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)_2/B(C_6F_5)_3$ system being the most active in the series tested. The molecular weights of the polypropene and the number of regio-irregular insertions strongly depend on the amido substituent and the bridge length of the Cp-amido ligand.

Despite the explorative character of this investigation, the results of the polymerization tests suggest that cation-anion interactions strongly influence/determine the catalyst activity and polymer properties. To get a deeper insight in the effect of cation-anion interactions on

olefin polymerization, this investigation should be extended using other anions like, for example, $[MeB(C_6F_5)_3]^-$, $[B(C_6F_5)_4]^-$ or $[B(3,5\text{-}(CF_3)_2C_6H_2)_4]^-$. Polymerization tests with propene or higher α-olefins (including co-polymerization of ethene with higher α-olefins) are in this respect more interesting than tests with ethene since the polymers of the former are easier to characterize and the microstructure of the polymers (tacticity, regio-regularity, comonomer incorporation and chain-branching) can give more information.
Another point of attention could be the determination of the optimum in performance in the $[C_5H_4(CH_2)_2NR]TiCl_2$/MAO system by making the ligand system more bulky with very large substituents R and/or with substituents on the cyclopentadienyl ring.

6.7 Experimental

General Comments on Olefin Polymerization Experiments.

Early transition metal based olefin polymerization catalysts are extremely reactive materials. They react rapidly with oxygen, water and other contaminants in the solvent and monomer feed that contain active hydrogen and also with Lewis basic components of the reaction mixture and olefins. Without proper precautions this reactivity will rapidly lead to catalyst deactivation and in the same cases no catalytic activity could be observed at all as all catalyst may have been consumed before the catalytic process even starts.
Rigorous removal of oxygen, water and other reactive contaminants from the polymerization reactor, solvent and olefins is essential for reproducible experiments. With MAO activated catalyst this condition is realized by using very large excess of MAO which is a very effective impurity scavenger. For single component catalysts e.g. the borane activated complexes $\{[C_5H_4(CH_2)_nNR]M(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ the problem of removing impurities is hard to solve. In these experiments the catalyst itself acts as a scavenger and it is clear that for these systems it will be difficult to obtain reproducible data.
Sometimes the catalyst is extremely active, resulting in a runaway exothermal polymerization. Such an exotherm has to be avoided since due to the oncontrolled raise in temperature the polymerization process becomes too complicated and poorly reproducible. To keep the temperature within close limits ($\pm$ 3 ^oC) the best way to achieve this is to use lower concentrations of catalyst but this is difficult to realize because of the aforementioned reasons.

Equipment.

At Groningen University a center for catalytic olefin polymerization (KOP-center) has been established in 1997. The facility is equipped with specially designed polymerization reactors and advanced catalyst handling techniques.

Polymerization reactions using MAO activated catalysts were carried out in a thermostatted (electrical heating, water cooling) Medimex 1l stainless steel autoclave equiped with temperature, pressure, mass-flow and stirrer control. Various parameters like internal and mantle temperature, pressure, mass-flow and stirring speed were recorded during the runs. Polymerization reactions using borane activated catalysts were carried out in a 500 mL stainless steel autoclave autoclave equiped with the same facilities as used for the 1L autoclave.

The runs with the MAO activated catalysts $[C_5H_4(CH_2)_nNR]MCl_2$/MAO were fairly reproducible (within 10%). To obtain reasonable reproducibility (within 25%) for the single component catalysts $([C_5H_4(CH_2)_nNR]M(CH_2Ph)_2$ rather large amounts of catalyst (80 μmol) has to be used. Using smaller amouts of catalyst (40 μmol) results in large spread of productivities (>50%). With 20 μmol of catalyst it is in general difficult to observe activity.

The productivities listed in tables 2, 3 and 4 are based on the observed productivity over the 30 min run time extrapolated to 1 h. They allow the determination of a relative order of catalyst activity within a series rather than absolute activities. In all experiments decreasing olefin uptake is observed during the run, most probably caused by factors like reaction with contaminants in the feed or diffusion limitations in viscous or heterogeneous mixtures although different mechanisms of losing catalyst activity (e.g. allylic hydrogen transfer from propene to give an inactive η^3-allyl complex) cannot be excluded *a priori*.

Olefin and Solvent Purification Procedures.

The monomers (ethene, propene) were passed over activated copper (RT) and molsieves (4 Å) prior to use. Toluene (Aldrich) was continuously passed over activated copper (R3-11, BASF) and molsieves (4 Å) in a closed cycle including the storage tank.

Experimental Procedures.

Ethene polymerization experiments.

Cp-amido titanium dichloride/MAO: For each run a total of 300 mL of toluene was used as solvent. The reactor was dried at 120 ^oC and vacuum (10^{-1} torr) for 1 h. Then the reactor was filled with toluene (250 mL), thermostated at a desired temperature and pressurized with 2 bar ethene. 500 eq. of MAO was injected and the injector was flushed with 10 mL of toluene. The appropriate Cp-amido titanium dichlorides (20-22 μmol) were dissolved in 10 mL of toluene and injected after which the injector was flushed twice with 10 mL of toluene.

Cp-amido zirconium dichloride/MAO: For each run a total of 200 mL of toluene (300 mL for the last five entries in Table 3) was used as solvent. The appropriate Cp-amido zirconium dichlorides were stirred for 15 min. in 10 mL of toluene with 175 eq. of MAO (33% of the total amount of MAO used, Al/Zr = 520) before use. The remaining MAO was transferred directly into the reactor with the solvent. At the desired reaction temperature the catalyst solution was injected into the reactor.

After 30 min. the runs were terminated by injecting 10 mL of methanol and cooling and venting the reactor. The polymers were slurried in methanol (acidified with 5-8% HCl) for several hours,

repeatedly rinsed with ethanol and petroleum ether and dried in vacuo at 70°C. The data in Tables 2 and 3 represent single runs, performed as a series using the same batch of MAO/toluene activator and solvent for internal consistency. Duplo runs performed for several experiments showed a variance in catalyst activity of about 5-10% for the titanum catalysts and 15-20% for the zirconium catalysts.

Propene polymerization experiments.

$[C_5H_4(CH_2)_nNR]TiCl_2/MAO$: The autoclave was set at the desired temperature and filled with 150 mL of toluene. 13.5 mL 1.5 M (20.3 mmol) of MAO was injected and the injector was flushed with 10 mL of toluene. The solution was saturated with propene at 4.7 bar for 15 min. Approximately 40 μmol of the dichloride was dissolved in 10 mL of toluene and injected. The injector was flushed twice with 10 mL of toluene. After 30 min. the reaction was terminated by injection of 10 mL of methanol. After venting excess propene, the toluene was removed and the polymer was dried in vacuum at 100 °C for 1 hour. The resulting polymer was dissolved in chloroform and filtered. The solvent was removed in vacuum and the polymers were dried in vacuum at 100 °C for 1 hour.

$[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)_2/B(C_6F_5)_3$: After drying, the autoclave was filled with N_2 (1.0 bar over-pressure) and 150 mL of toluene. A toluene solution (10 mL) of $B(C_6F_5)_3$ (50% excess) was injected according to procedure described (vide supra) and the autoclave was saturated with propene (4.7 bar) for 10 min. Afterwards a toluene solution (10 mL) of $[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)_2$ was injected. The reaction was terminated after 30 min. by injecting 10 mL of methanol. Workup of the polymers was performed as described (vide supra).

Molecular Weight Determinations.

The molecular weight of the polyethene samples was determined by high temperature GPC (150 °C) using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standard samples as references. The measurements were performed on a PL-GPC210 (Polymer Laboratories) equiped with 4 PL-Gel mixed-A columns, 210 differential viscometer (Viscotek), refractive index meter and DM400 data manager (Viscotek).

The molecular weight of the polypropene samples was determined by GPC at ambient temperatures (30 °C) using $CHCL_3$ as solvent and narrow MWD polystyrene standard samples as references. The measurements were performed on a LC-1000 system (Spectra Physics) equiped with 2 PL-Gel mixed-C columns, RALLS light scattering detector, H502 viscometer (Viscotek), refractive index detector and DM400 data manager (Viscotek).

Generation of Cationic Complexes $\{[C_5H_4(CH_2)_nNR]M(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$.

For considerations with respect to synthetic aspects see Chapter 2.

Reactions of $[C_5H_4(CH_2)_nNR]Ti/Zr(CH_2Ph)_2$ with $B(C_6F_5)_3$ in C_6D_5Br. In these experiments equimolar amounts (0.08 mmol) of a Ti/Zr dibenzyl complex and $B(C_6F_5)_3$ were dissolved in 0.4 mL of

C_6D_5Br, giving 0.2 M solutions of the various ionic complexes without noticeable byproducts (determined by NMR). Low temperature (-35 °C) ^{1}H- and ^{13}C NMR data of two representative zirconium species (one contact ion pair, n = 3, R = Me (**94**), and one solvent-separated ion pair, n = 3, R = *i*-Pr (**96**)) are given below. ^{1}H-NMR assignments were supported by ^{1}H,^{1}H-COSY spectra.

[C$_5$H$_4$(CH$_2$)$_3$NMe]Zr(h^1-CH$_2$Ph)[h^6-PhCH$_2$B(C6F$_5$)$_3$]: ^{1}H NMR (500 MHz, C_6D_5Br, -35 °C): δ 7.20 (2H, ZrBz *m*-H); 7.10, 6.92, 6.80, 6.60, 6.57 (BBz ArH); 6.95 (ZrBz *p*-H); 6.52 (d, 7.3 Hz, 2H, ZrBz *o*-H); 5.48, 5.34, 5.20, 4.58 (C_5H_4); 3.26, 3.12 (br, BCH_2); 2.42-2.40 (2H, NCH_2); 2.35, 2.22 (m, $C_5H_4\underline{CH_2}$); 1.68, 1.63 (d, 10.8 Hz, $ZrCH_2$); 1.63, 1.17 (m, -CH_2-). ^{13}C NMR (125.7 MHz, C_6D_5Br, -35 °C): δ 155.95 (BBz C-*ipso*); 149.05 (ZrBz C-*ipso*); 148.1 (d, $^1J_{CF}$ = 242 Hz, *o*- C_6F_5); 138.2 (d, $^1J_{CF}$ = 247 Hz, *p*-C_6F_5); 136.7 (d, $^1J_{CF}$ = 247 Hz, *m*-C_6F_5); 133.35 (s, C_5H_4-*ipso*); 129 (overlap, BBz CH); 128.79 (d, part overlap, BBz CH); 128.42 (d, 156.6 Hz, ZrBz *o*-CH); 128.16 (d, 162.4 Hz, BBz CH); 127.11 (d, part overlap, BBz CH); 125.13 (d, 153.0 Hz, ZrBz *m*-CH); 124 (v.br., *ipso*-C_6F_5); 123.11 (d, 167.5, BBz *p*-CH); 122.40 (d, 159.4 Hz, ZrBz *p*-CH); 117.07 (d, 180.9 Hz, C_5H_4); 116.37 (d, 173.5 Hz, C_5H_4); 109.21 (d, 169.7 Hz, C_5H_4); 105.56 (d, 166.0 Hz, C_5H_4); 54.41 (t, 120.3 Hz, $ZrCH_2$); 43.98 (q, 132.4 Hz, NMe); 34.6 (br, BCH_2); 32.40 (t, 128.7 Hz, $C_5H_4\underline{CH_2}$); 26.65 (t, 128.7 Hz, $NCH_2\underline{CH_2}$). ^{19}F NMR (282 MHz, C_6D_5Br, -35 °C): δ -132.9 (*o*-F), -162.0 (*p*-F), -166.0 (*m*-F), Δδ(*p*-*m*) = 4.0.

{[C$_5$H$_4$(CH$_2$)$_3$N-i-Pr]Zr(h^2-CH$_2$Ph)}[PhCH$_2$B(C$_6$F$_5$)$_3$]: ^{1}H NMR (500 MHz, C_6D_5Br, -35 °C): δ 7.31 (ZrBz *m*-H); 7.28 (ZrBz *p*-H); 7.26 (BBz *o*-H); 7.24 (ZrBz *m*-H); 7.07 (m, BBz *m*-H); 6.91 (t, 7.1 Hz, BBz p-H); 6.77 (d, 7.3 Hz, ZrBz *o*-H); 6.26 (d, 6.4 Hz, ZrBz *o*-H); 5.97, 5.62, 5.25, 4.50 (C_5H_4); 3.45 (br, 2H, BCH_2); 3.22 (m, i-Pr CH); 2.75 (d, 7.8 Hz, $ZrCH_2$); 2.4 (m, 2H, NCH_2); 2.20-15 (m, $C_5H_4\underline{CH_2}$); 1.64 (d, 7.8 Hz, $ZrCH_2$); 1.62, 1.47 (m, $NCH_2\underline{CH_2}$); 1.03 (d, 4.9 Hz, i-Pr Me); 0.92 (d, 5.4 Hz, *i*-Pr Me). ^{13}C NMR (125.7 MHz, C_6D_5Br, -35 °C): δ 148.60 (BBz C-*ipso*); 133.29 (d, 164.1 Hz, ZrBz CH); 132.74 (d, 164.1 Hz, ZrBz CH); 132.25 (C_5H_4-*ipso*); 131.82 (d, 160.4 Hz, ZrBz CH); 128.82 (d, part. overlap, BBz m-CH); 128.11 (d, 164.1 Hz, ZrBz CH); 127.18 (d, 156.7 Hz, BBz *m*-CH); 124.04 (d, 160.4 Hz, ZrBz CH); 122.93 (d, 160.4 Hz, BBz *p*-CH); 121.82 (ZrBz C-*ipso*); 115.16 (d, 172.0 Hz, C_5H_4); 109.41, 109.30 (d, about 174 Hz, C_5H_4); 108.57 (d, 171.6 Hz, C_5H_4); 53.43 (t, 144.5 Hz, $ZrCH_2$); 44.48 (t, 135.5 Hz, NCH_2); 39.81 (d, 108.1 Hz, *i*-Pr CH); 31.8 (v.br. BCH_2); 28.38 (t, 129.7 Hz, $C_5H_4\underline{CH_2}$); 25.44 (t, 129.5 Hz, -CH_2-); 22.05, 20.77 (q, 127.7 Hz, *i*-Pr Me). ^{19}F NMR (282 MHz, C_6D_5Br, -35 °C): δ -132.5 (*o*-F); -164.8 (*p*-F); -167.8 (*m*-F); Δδ(*p*-*m*) = 3.0.

Reaction of {[C$_5$H$_4$(CH$_2$)$_2$NMe]Zr(CH$_2$Ph)}$^+$[PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ with propene. To a solution of 20.4 mg (0.051 mmol) of $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ and 27.0 mg (0.052 mmol) of $B(C_6F_5)_3$ in 0.5 mL of bromobenzene-d_5, 0.062 mmol of propene was added. The yellow solution turned red-orange. A ^{1}H NMR spectrum showed the two isomers of $\{[C_5H_4(CH_2)_2NMe]Zr(CH_2CH(Me)CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**101**) being present. Full assignment was given from a COESY NMR experiment. ^{1}H NMR (500 MHz, C_6D_5Br) δ 7.2-6.7 (multiplets, 9H, $BCH_2\underline{Ph}$ + $CH_2CH(Me)CH_2\underline{Ph}$); 6.42 (d, J_{HH} = 7.69 Hz, 1H, *o*-H $CH_2CH(Me)CH_2\underline{Ph}$, isomer A); 6.30

(d, J_{HH} = 7.32 Hz, 1H, *o*-H $CH_2CH(Me)CH_2\underline{Ph}$, isomer B); 5.66, 5.50, 5.43, 4.91 (m, 4H, C_5H_4, isomers A and B); 3.81 (M, 1H, NCH_2, isomer A); 3.58 (m, 1H, NCH_2, isomer B); 3.34 (m, 1H, NCH_2, isomer B); 3.30 (s, 2H, BCH_2); 3.14 (m, 1H, NCH_2, isomer A); 2.72 (m, 1H, $CH_2CH(Me)C\underline{H_2}Ph$, isomer B); 2.64 (m, 1H, $CH_2CH(Me)C\underline{H_2}Ph$, isomer A); 2.53 (s, 3H, NMe, isomer A); 2.52 (s, 3H, NMe, isomer B); 2.44 (m, 1H, $CH_2C\underline{H}(Me)CH_2Ph$, isomer B); 2.42-2.32 (m, 2H, $C_5H_4CH_2$, isomers A and B); 1.88 (t, J_{HH} = 11.35 Hz, 1H, $CH_2CH(Me)C\underline{H_2}Ph$, isomer A); 1.75 (t, J_{HH} = 11.72 Hz, 1H, $CH_2CH(Me)C\underline{H_2}Ph$, isomer B); 1.73 (m, 1H, $CH_2C\underline{H}(Me)CH_2Ph$, isomer A); 1.38 (m, 1H, $C\underline{H_2}CH(Me)CH_2Ph$, isomer A); 0.96 (d, $^3J_{HH}$ = 7.7 Hz, 3H, $CH_2CH(\underline{Me})CH_2Ph$, isomer B); 0.94 (d, $^3J_{HH}$ = 6.2 Hz, 3H, $CH_2CH(\underline{Me})CH_2Ph$, isomer A); 0.72 (m, 1H, $C\underline{H_2}CH(Me)CH_2Ph$, isomer B); 0.08 (m, $^3J_{HH}$ = 13.74 Hz, 1H, $C\underline{H_2}CH(Me)CH_2Ph$, isomer B); -0.19 (m, $^3J_{HH}$ = 12.45 Hz, 1H, $C\underline{H_2}CH(Me)CH_2Ph$, isomer A). ^{19}F NMR (282 MHz, C_6D_5Br, -35 ^oC): δ -132.6 (*o*-F); -164.3 (*p*-F); 167.4 (*m*-F), Δδ(*p*-*m*) = 3.1.

Reaction of {[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Zr(CH$_2$Ph)}$^+$[PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ with propene. To a solution of 56.0 mg (0.128 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(CH_2Ph)_2$ and 67 mg (0.13 mmol) of $B(C_6F_5)_3$ in 0.6 mL of bromobenzene-d_5, 0.13 mmol of propene was added. The color changed immediately from yellow to red-orange. ^{1}H NMR (300 MHz, C_6D_5Br, 50 ^oC): δ 7.2-6.7 (10H, $BCH_2\underline{Ph}$ + $CH_2CH(Me)CH_2\underline{Ph}$); 5.50 (m, 2H, C_5H_4); 5.42 (m,2H, C_5H_4); 3.28 (s, 2H, BCH_2); 2.76 (m, 2H, NCH_2); 2.0 (br m, 2H, $CH_2CH(Me)C\underline{H_2}Ph$); 1.86 (m, 2H, $C_5H_4C\underline{H_2}$), 1.82 (m, 1H, $CH_2C\underline{H}(Me)CH_2Ph$); 0.89 (d, $^3J_{HH}$ = 5.13 Hz, 3H, $CH_2CH(\underline{Me})CH_2Ph$); 0.81 (s, 9H, *t*-Bu); 0.47 (m, 2H, $C\underline{H_2}CH(Me)CH_2Ph$). ^{19}F NMR (282 MHz, C_6D_5Br, -35 ^oC): δ -132.8 (*o*-F); -164.2 (*p*-F); -167.2 (*m*-F), Δδ(*p*-*m*) = 3.0.

NMR-tube reaction of {[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Zr(CH$_2$Ph)}$^+$[PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ *with excess of propene.* A mixture of 8.7 mg (0.02 mmol) of $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(CH_2Ph)_2$ and 12 mg (0.023 mmol) of $B(C_6F_5)_3$ in 0.5 mL of bromobenzene-d_5 was treated with 25 eq. of propene. A ^{1}H NMR spectrum revealed the presence of $\{[C_5H_4(CH_2)_2N$-t-Bu$]Zr(CH_2CH(Me)CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**102**). The NMR-tube was kept at room temperature for 30 min but a ^{1}H NMR spectrum showed virtually no change. Heating the tube at 50 ^oC for 1 h resulted in slow oligomerization of propene. GC-MS revealed the presence of dimers, trimers and tetramers.

NMR-tube reaction of {[C$_5$Me$_4$SiMe$_2$N-t-Bu]Zr(CH$_2$Ph)}$^+$[PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ *with excess of propene.* A mixture of 10.5 mg (0.02 mmol) of $[C_5Me_4SiMe_2N$-t-Bu$]Zr(CH_2Ph)_2$ and 13 mg (0.025 mmol) of $B(C_6F_5)_3$ in 0.5 mL of bromobenzene-d_5 was treated with 25 eq. of propene. Formation of $\{[C_5Me_4SiMe_2N$-t-Bu$]Zr(CH_2CH(Me)CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ (**103**) was indicated by the presence a doublet ($^3J_{HH}$ = 5.4 Hz, $CH_2CH(\underline{Me})CH_2Ph$). Standing for 2 h at room temperature no change was observed. Heating of the tube resulted in slow oligomerization of propene. CG-MS showed a mixture of C_6-C_{48} olefins and alkanes.

Synthesis of [C$_5$Me$_4$SiMe$_2$N-t-Bu]Zr(CH$_2$Ph)$_2$ (91). A cooled (0 ^oC) solution of 1.71 g (4.15 mmol) $[C_5Me_4SiMe_2N$-*t*-Bu$]ZrCl_2$ in 20 mL of ether was treated with 9.6 mL 0.93 M (8.9 mmol) of $PhCH_2MgCl$ in ether. After stirring for 1.5 h at room temperature the solvent was removed in vacuum leaving a

light yellow residue. The residue was stripped with 20 mL of pentane and extracting with 50 mL of pentane gave a clear light yellow solution. The solution was concentrated at reflux to 10 mL and cooling overnight to -20 ^{o}C resulted in 1.23 g of light yellow crystals. A second crop (0.40 g) was obtained by concentration and cooling of the mother liquor. In total, 1.63 g (3.12 mmol, 75%) of [$C_5Me_4SiMe_2N$-*t*-Bu]Zr($CH_2Ph)_2$ (**91**) was isolated. ^{1}H NMR (300 MHz, C_6D_6): δ 7.12 (t, $^3J_{HH}$ = 7.51 Hz, 4H, *m*-Ph); 6.90 (t, $^3J_{HH}$ = 7.33 Hz, 2H, *p*-Ph); 6.78 (d, $^3J_{HH}$ = 7.33 Hz, 4H, *o*-Ph); 1.91 (s, 6H, $C_5\underline{Me_4}$); 1.87 (d, $^2J_{HH}$ = 10.99 Hz, 2H, $\underline{CH_2}$Ph); 1.78 (s, 6H, $C_5\underline{Me_4}$); 1.61 (d, $^2J_{HH}$ = 10.99 Hz, 2H, $\underline{CH_2}$Ph); 1.14 (s, 9H, *t*-Bu); 0.42 (s, 6H, $SiMe_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 147.10 (s, *ipso*- Ph); 130.01 (s, C_5Me_4); 129.08 (d, $^1J_{CH}$ = 156.3 Hz, *o*-Ph); 127.26 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 126.22 (s, C_5Me_4); 122..08 (d, $^1J_{CH}$ = 161.1 Hz, *p*-Ph); 97.87 (s, C_5Me_4-*ipso*); 61.02 (t, $^1J_{CH}$ = 122.1 Hz, $\underline{C}H_2$Ph); 56.63 (s, $\underline{C}Me_3$); 33.80 (q, $^1J_{CH}$ = 124.5 Hz, $C\underline{Me_3}$); 14.44 (q, $^1J_{CH}$ = 127.0 Hz, $C_5\underline{Me_4}$); 11.46 (q, $^1J_{CH}$ = 126.6 Hz, $C_5\underline{Me_4}$); 6.69 (q, $^1J_{CH}$ = 119.2 Hz, $SiMe_2$). IR (cm^{-1}): 3136 (w), 3123 (w), 3069 (m), 3013 (w), 2729 (w), 1935 (w), 1858 (m), 1723 (w), 1645 (w), 1589 (s), 1562 (w), 1532 (w), 1478 (m), 1447 (m), 1398 (w), 1383 (m), 1356 (m), 1321 (m), 1248 (s), 1229 (w), 1202 (s), 1152 (w), 1126 (w), 1111 (w), 1084 w), 1015 (s), 991 (m), 945 (w), 909 (m), 889 (w), 868 (m), 843 (s), 814 (s), 795 (m), 760 (s), 745 (m), 696 (s), 675 (w), 627 (w), 569 (m), 559 (m), 536 (m), 515(m), 484 (s), 421 (s). Anal. Calcd for $C_{29}H_{41}NSiZr$: C, 66.60; H, 7.90; Zr, 17.44. Found: C, 66.51; H, 7.89; 17.41.

6.8 References and Notes

(1) (a) Horton, A.D. *Trends in Polymer Science* **1994**, *2*, 158. (b) Brintzinger, H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1143. (c) Bochmann, M. *J. Chem.Soc., Dalton trans.* **1996**, 255.

(2) (a) Sinn, H.; Kaminsky, W.; Volmer, H.J.; Woldt, R. *Angew. Chem.* **1980**, *92*, 396. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(3) Wild, F.R.W.P.; Zsolnai, L.; Huttner, G.; Brintzinger, H.H. *J. Organomet. Chem.* **1982**, *232*, 233.

(4) (a) Ewen, J.A.; Elder, M. *J. Makromol. Chem., Macromol. Symp*. **1993**, *66*, 179. (b) Kaminsky, W.; Külper, K.; Wild, F.R.W.P.; Brintzinger, H.H. *Angew. Chem. Int. Ed. Engl*. **1985**, *24*, 507. (c) Mallin, D.T.; Rausch, M.D.; Chien, J.C.W.; Rieger, B.; Mu, X. *Macromolecules* **1990**, *23*, 3559. (d) Spaleck, W.; Küber, F.; Bachmann, B.; Antberg, M.; Dolle, V.; Rohrmann, J.; Winter, A.; Paulus, E.F. *Organometallics* **1994**, *13*, 954. (e) Ewen, J.A.; Jones, R.L.; Razavi, A.; Ferrara, J.D. *J. Am. Chem. Soc*. **1988**, *110*, 6256. (f) Ewen, J.A.; Elder, M.J.; Jones, R.L.; Curtis, S.; Cheng, H.N. In *Catalytic Olefin Polymerization: Proceedings of the International Symposium on Recent Developments in Olefin Polymerization Catalysts*, Keii, T.; Soga, K. Eds., Elsevier, Amsterdam, 1989, 439. (g) Ewen, J.A.; Elder, M.J. *Eur. Pat. Appl.* EP-A 0537130, 1993. (h) Coates, G.W.; Waymouth, R.M. *Science*, **1995**, *267*, 217.

(5) (a) Shapiro, P.J.; Bunel, E.; Schaefer, W.P.; Bercaw, J.E. *Organometallics* **1990**, *9*, 867. (b) Piers, W.E.; Shapiro, P.J.; Bunel, E.; Bercaw, J.E. *Synlett*. **1990**, *2*, 74.

(6) (a) Stevens, J.C.; Timmers, F.J.; Rosen, G.W.; Knight, G.W.; Lai, S.Y. (Dow Chemical Co.), *Eur. Pat. Appl*. EP 0416815 A2, 1991. (b) Canich, J.A.M. (Exxon Chemical Co.), *U.S. Patent* 5,026,780, 1991.

(7) (a) Sernetz, F.G.; Mülhaupt, R.; Waymouth, R.M. *Macromol. Chem. Phys*. **1996**, *197*, 1071. (b) Pannel, R.B.; Canich, J.A.M.; Hlatky, G.G. (Exxon Chemical Co.) *PCT Int. Appl*. WO 94/00500, 1994.

(8) (a) Hughes, A.K.; Meetsma, A.; Teuben, J.H. *Organometallics* **1993**, *12*, 1936. (b) Hughes, A.K.; Marsh, S.M.B.; Howard, J.A.K.; Ford, P.S. *J. Organomet. Chem*. **1997**, *528*, 195. (c) Antonelli, D.M.; Green, M.L.H.; Mountford, P. *J. Organomet. Chem*. **1992**, *438*, C4. (d) Fandos, R.; Meetsma, A.; Teuben, J.H. *Organometallics* **1991**, *10*, 59. (e) Rasika Dias, H.V.; Wang, Z. *J. Organomet. Chem*. **1997**, *539*, 77. (f) Rieger, B. *J. Organomet. Chem*. **1991**, *420*, C17.

(9) (a) Reichert, K.H.; Scubert, E. *Makromol. Chem*. **1969**, *123*, 58. (b) Reichert, K.H.; Berthold, J. *Makromol. Chem*. **1969**, *121*, 258. (c) Schnell, D.; Fink, G. *Angew. Makromol. Chem.* **1974**, *39*, 131. (d) Fink, G.; Rottler, R. *Angew. Makromol. Chem*. **1981**, *94*, 25. (e) Fink, G.; Rottler, R.; Kreiter, C.G. *Angew. Makromol. Chem*. **1982**, *105*, 15, 31, 39. (f) Fink, G.; Zoller, W. *Makromol Chem*. **1981**, *182*, 3265. (g) Fink, G.; Fenzl, W.; Mynott, R. *Z. Naturforsch. B*, **1985**, *40*, 158. (h) Mynott, R.; Fink, G.; Fenzl, W. *Angew. Makromol. Chem*. **1987**, *154*, 1. (i) Eisch, J.J.; Piotrowski, A.M.; Brownstein, S.K.; Gabe, E.J.; Lee, F.L. *J. Am. Chem. Soc*. **1985**, *107*, 7219. (j) Eisch, J.J.; Caldwell, K.R.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417. (k) Eisch, J.J.; Pombrik, S.I.; Zheng, G.X. *Organometallics* **1993**, *12*, 3826.

(10) Pino, P.; Mülhaupt, R. *Angew. Chem*. **1980**, *92*, 869.

(11) (a) Yang, X.; Stern, C.L.; Marks, T.J. *Organometallics* **1991**, *10*, 840. (b) Hlatky, G.G.; Upton, D.J.; Turner, H.W. *U.S. Pat. Appl*. 459921, 1990. (c) Hlatky, G.G.; Upton, D.J.; Turner, H.W. *Chem. Abstr*. **1991**, *115*, 256897v.

(12) (a) Ewen, J.A.; Elder, M.J. *U.S. Pat. Appl*. 419017, 1989. (b) Ewen, J.A.; Elder, M.J. *Chem. Abstr*. **1991**, *115*, 136998g. (c) Yang, X.; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc*. **1991**, *113*, 3623. (d) Yang, X.; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc*. 1994, *116*, 10015.

(13) Ewen, J.A.; Elder, M.J. *Markomo. Chem., Macromol. Symp.* **1993**, *66*, 179.

(14) Giardello, M.A.; Eisen, M.S.; Stern, C.L.; Marks, T.J. *J. Am. Chem. Soc.* **1993**, *113*, 3326.

(15) Horton, A.D.; de With, J.; van der Linden, A.J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(16) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(17) Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773.

(18) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(19) Tjaden, E.B.; Swenson, D.C.; Jordan, R.G.; Petersen, J.L. *Organometallics* **1995**, *14*, 371.

(20) (a) Jordan, R.F., LaPointe, R.E.; Bajgur, C.S.; Echolls, S.F.; Willet, R. *J. Am. Chem. Soc*. **1987**, *109*, 4111. (b) Jordan, R.F.; LaPointe, R.E.; Baenziger, N.C.; Hinch, G.D. *Organometallics* **1990**, *9*, 1539.

(21) (a) Bochmann, M.; Lancaster, S.J. *Organometallics* **1993**, *12*, 633. (b) Bochmann, M.; Lancaster, S.J.; Hursthouse, M.B.; Malik, K.M.A. *Organometallics* **1994**, *13*, 2235.

(22) The ionic species $\{[C_5H_4(CH_2)_nNR]Ti(CH_2Ph)\}^+[PhCH_2B(CF_5)_3]^-$ were prepared as 0.2 M solutions.

(23) See Chapter 4, ref 12.

(24) Shannon, R.D. *Acta Cryst*. **1976**, *A32*, 751.

(25) To generate catalytically active species, the precatalysts are usually stirred with an excess of MAO for a certain period of time at room temperature. See for example: Kaminsky, W. *Macromol. Chem. Phys.*, **1996**, *197*, 3907.

(26) Treating toluene solutions of $[C_5H_4(CH_2)_nNR]TiCl_2$ (n = 2, 3; R = Me, *i*-Pr) with excess MAO (ca 200 eq.) resulted within one minute in a color change from yellow to blue-green, and finally to brown. In a separate experiment, in which 6 mg of $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**) was mixed at room temperature with 200 eq. of MAO in 10 mL of toluene an ESR resonance at g = 1.975 characteristic of Ti(III) developed together with the color change. This clearly indicates that Cp-amido titanium dichloride complexes $[C_5H_4(CH_2)_nNR]TiCl_2$ are reduced by reaction with MAO.

(27) (a) Cheng, H.N.; Smith, D.A. *Macromolecules* **1986**, *19*, 2065. (b) Longo, P.; Grassi, A.; Pellechia, C.; Zambelli, A. *Macromolecules*, **1987**, *20*, 1015. (c) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428.

(28) (a) Chien, J.C.W.; Wang, B.-P. *J. Polym. Sci., Chem. Ed.* **1990**, *28*, 15. (b) Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489. (c) Mogstad, A.-L.; Waymouth, R.M. *Macromolecules* **1992**, *25*, 2282.

(29) ^{13}C NMR spectra of the samples showed besides the main resonances of the methyl carbons (22-19 ppm) additional resonances at 17-16 and 15-14 ppm. The spectra have the same overall appearance as reported by : McKnight, A.L.; Masood, Md.A.; Waymouth, R.M.; Straus, D.A. *Organometallics* **1997**, *16*, 287. For further information about characterization of polypropene with ^{13}C NMR spectroscopy see ref 27 and: (a) Doi, Y. *Macromolecules* **1979**, *12*, 248. b Cheng, H.N. *Polymer Bull.* **1985**, *14*, 347. (c) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617. (d) Tsutsui, T.; Ishimaru, N.; Mizuno, A.; Toyota, A.; Kashiwa, N. *Polymer* **1989**, *30*, 1350. (e) Cheng, H.N.; Ewen, J.A. *Markomol. Chem.* **1989**, *190*, 1931. (f) Mizuno, A.; Tsutsui, T.; Kashiwa, N. *Polymer* **1992**, *33*, 254. (g) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667.

(30) The temperature remains nearly constant ($\pm$ 1 ^oC) during the whole run.

(31) The large difference in productivity between $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ and $[C_5H_4(CH_2)_3NMe]TiCl_2$/MAO is most probably due to deactivation by reduction of the latter.

(32) The molecular weight distribution shows tailing to lower molecular weight. This may be due to the mixture becoming very viscous rendering stirring and monomer diffusion problems.

(33) Herrmann, H.F.; Böhm, L. (Hoechst A.G.) *Eur. Pat. Appl.* EP 0459320 A2, 1991.

(34) The synthesis of the $[C_5Me_4(CH_2)_2N$-*t*-Bu] ligand is described in the Dow patent (ref 6a) (together with the synthesis and structural characterization of the titanium dichloride complex). The zirconium complex was not mentioned in this patent. However in our hands, the synthesis of this ligand and of the sterically less demanding $[C_5Me_4(CH_2)_2N$-i-Pr] could not be reproduced and low yields were obtained. The coupling of the backbone with tetramethylcyclopentadiene proceeded also adjacent to the CH_2 carbon of the ring. These by-products were formed in up to 40% of the total yield and could no be separated from the desired products $C_5Me_4H(CH_2)_2N(H)R$ (R = *i*-Pr, *t*-Bu).

(35) Complex **103** is observed as two isomeric forms at room temperature indicating a tight intramolecular coordination of the arene moiety, whereas **104** and **105** are more fluxional.

(36) The NMR reveals that the metal-bound arene moiety has a fixed orientation. It is thus assumed that the arene has a strong interaction with metal centre

(37) (a) Pellecchia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (b) Pellecchia, C.; Immirzi, A.; Zambelli, A. *J. Organomet. Chem*. **1994**, *479*, C9

(38) (a) Woo, T.K.; Margl, P.M.; Lohrenz, J.C.W.; Blöchl, P.E.; Ziegler, T. *J. Am. Chem. Soc*. **1996**, *118*, 13021. (b) Fan, L.; Harrison, D.; Woo, T.K.; Ziegler, T. *Organometallics* **1995**, *14*, 2018 (c) Woo, T.K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 432. (d) Meier, R.J.; van Doremaele, G.H.J.; Iarlori, S.; Buda, F. *J. Am. Chem. Soc*. **1994**, *116*, 7274 (e) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc*. **1992**, *114*, 8687. (f) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *Chem Rev*. **1991**, *91*, 823. (g) Hart, J.R.; Rappé, A.K. *J. Am. Chem. Soc*. **1993**, *115*, 6159.

(39) For example, arenes are known to interact with cationic d^o group 4 metals. See: (a) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem Soc., Chem. Commun*. **1989**, 1747. (b) Floriani, C.; Berno, P.; Solari, E. *Chem. Scr*. **1989**, *29*, 423. (c) Bochmann, M.; Karger, G.; Jaggar, A.J. *J. Chem. Soc., Chem. Commun*. **1990**, 1038. (d) Gillis, D.J.; Tudoret, M.-J.; Baird, M.C. *J. Am. Chem*. *Soc*. **1993**, *115*, 2543. (e) Gillis, D.J.; Quyoum, R.; Tudoret, M.-J.; Wang, Q.; Jeremic, D.; Roszak, A.W.; Baird, M.C. *Organometallics* **1996**, *15*, 3600.

(40) Giardello, M.A.; Eisen, M.S.; Stern, C.L. Marks, T.J. *J. Am. Chem. Soc.* **1995**, *117*, 12114.

(41) Chen, Y.-Y.; Stern, C.L.; Yang, S.; Marks, T.J. *J. Am. Chem. Soc.* **1996**, *118*, 12451.

(42) Lanza, G.; Fragalà, I.L.; Marks, T.J. *J. Am. Chem. Soc.* **1998**, *120*, 8257.

(43) When discussing the activity of a catalyst, distinction should be made between activity and productivity. Activity is an intrinsic property of the metal center and is determined by the

shape and energy of the metal frontier orbitals and the electronic and steric characteristics of the ligand set. The productivity is the amount of polymer produced over a certain period of time in a particular catalytic run, extrapolated to standard experimental conditions. The productivity of a catalyst includes parameters like catalyst activation and deactivation, diffusion processes and interactions of the catalyst with other species (i.e. solvent molecules and counterions).

During a polymerization experiment the medium and the catalyst may undergo dramatic changes with respect to the initial situation. When the polymer is soluble the medium viscosity can increase enormously, thus influencing the transport of the monomer to the active site. When the polymer is insoluble, other changes may occur. For instance, the catalyst could be absorbed on the polymer, thus generating a heterogeneous system with polymerization characteristics different from those of the homogeneous catalyst system.

Therefore one has to be very careful when comparing activities of different catalysts especially when the available data stem from different sources. The best way to get a reliable activity comparison is to test catalysts under identical experimental conditions in standardized equipment.

(44) Flory, P.J. Principles of Polymer Chemistry; Cornell University Press, Ithaca, 1986, 317.

(45) Several chain termination mechanisms have been recognized, like β-H or β-alkyl transfer to metal, allylic hydrogen activation, direct β-H transfer to the coordinated olefin or, in the case of MAO, chain transfer to the co-catalyst. For examples of β-H or β-alkyl transfer to metal, see: (a) Jordan, R.F. *Adv. Organomet. Chem.* **1991**, *32*, 325 (b) Ewen, J.A. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253. For allylic hydrogen, see: (c) Eshuis, J.J.W. Thesis, University of Groningen, 1991. (d) Watson, P.L.; Roe, D.C.; *J. Am. Chem. Soc.* **1982**, *104*, 6471. (e) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (f) Jeske, G.; Schock, L.E.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. For direct β-H transfer to the coordinated olefin see: (g) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer*, **1989**, *30*, 428. For β-Me transfer see ref 43c and: (h) Eshuis, J.J.W.; Tan, Y.Y.; Teuben, J.H.; Renkema, J. *J. Mol. Cat.* **1990**, *62*, 277.

(46) Calculations and measurements for Ziegler-Natta and metallocene catalysts have shown that initiation and propagation are in general extremely fast. Often the process seems diffusion controlled and there are indications that polyethene chains up to Mw = 620,000 are formed in tenth of seconds.[1d] This means that even if a small amount of polymer is formed by a catalytic system it will have the essential characteristics (molecular weight, molecular weight distribution and microstructure) of polymer formed by this particular catalyst.

(47) Lohrenz, J.C.W.; Woo, T.K.; Fan, L.; Ziegler, T. *J. Organomet. Chem.* **1995**, *497*, 91.

(48) ^{19}F NMR spectra (C_6D_5Br, -35 ^oC) showed the system to be a single solvent separated species, although the fluxionality of this system (cf. 6.3) still leave the possibility that $\{[C_5H_4(CH_2)_3NMe]Ti(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$ partly exist as a contact ion-pair

(49) Chien, J.C.W.; Yu, Z.; Marques, M.M.; Flores, J.C.; Rausch, M.D. *J. Polymer Science, Part A: Polymer Chemistry* **1998**, *36*, 319.

(50) Ystenes proposed a mechanism of coordination of a second olefin (propene) to explain the high stereoregularity of polypropene produced with heterogeneous Ziegler-Natta systems. Ystenes, M. *J. Catal.* **1991**, *129*, 383.

(51) A similar explanation is given for the broad and polymodal molecular weight distribution found for polyethene produced with the bis imido-pyridine iron dichloro complexes upon activation with MAO. Gibson, V. on the 18th international conference on crganometallic chemistry (XVIII ICOMC), Munich, Germany, 16-21 August 1998.

Samenvatting.

De organometaalchemie en vooral die van overgangsmetalen en lanthaniden heeft zich in 40-50 jaar buitengewoon sterk ontwikkeld. Niet alleen werd een breed gebied van synthese en karakterisatie van nieuwe verbindingen en uitgebreid reactiviteitsonderzoek ontsloten maar ook werd de ontwikkeling van nieuwe methoden en inzichten in meer toepassingsgerichte gebieden zoals de organische synthese maar vooral de (homogene en heterogene) katalyse door de organometaalchemie sterk gestimuleerd.

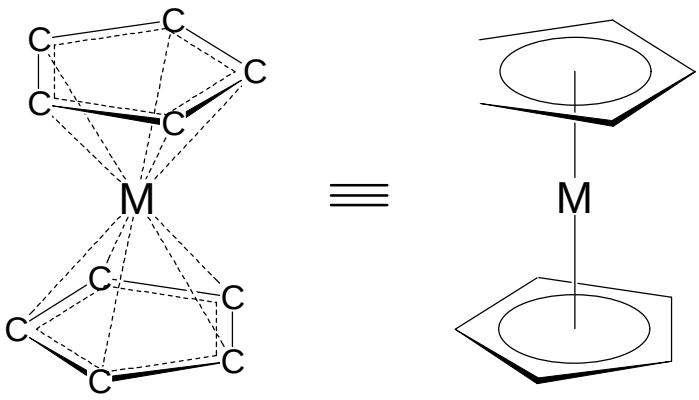
De motor van deze ontwikkeling is de unieke reactiviteit van de metaal-koolstofbinding die gekarakteriseerd is door een polaire, $M^{\delta+}$-$C^{\delta-}$, binding. De polariteit van de M-C binding is tegengesteld maar, hoewel in waarde variërend, doorgaans groter dan bijvoorbeeld die van een C-Cl binding, een binding die naar organische begrippen behoorlijk polair is. De hoge reactiviteit van de C-Cl binding wordt in de regel toegeschreven aan die hoge polariteit.

De polariteit en daarmee de reactiviteit van de metaal-koolstofbinding wordt niet alleen beïnvloed door de aard van het metaal en de valentietoestand maar vooral door wat er aan het metaal gebonden is: het ligandsysteem. Door electronische en sterische eigenschappen van het ligandsysteem te variëren (afstemmen) kan men in belangrijke mate de stabiliteit van het metaalcomplex en de reactiviteit van het metaalcentrum beïnvloeden. Een aspect van de reactiviteit dat voor organisch chemische en katalytische toepassingen uitermate belangrijk is is de door het metaalcentrum veroorzaakte activering van bepaalde bindingen in substraat-moleculen. In wezen is dit de essentiële eigenschap die een metaalverbinding tot katalysator van een bepaalde chemische omzetting kan maken.

Beheersing van de activering van moleculen door een organometaalverbinding opent de mogelijkheid om een scala aan bindingen (C-C, C=C, C≡C, C-H C-O, C-N of, meer algemeen, C-X) te activeren en deze gericht te gebruiken voor de vorming van nieuwe bindingen. Dit kan zowel in stoichiometrische als katalytische reacties. Zo kunnen, met name voor de organische synthese, vaak heel selectief, ingewikkelde nieuwe verbindingen worden gemaakt. Een wetenschappelijk maar meer nog vanuit industrieel oogpunt bijzonder belangrijke, katalytische toepassing is de polymerisatie van olefinen met behulp van overgangsmetaalcomplexen. Het meest sprekende voorbeeld is het maken van polymeren (plastics) met hoge toegevoegde waarde uit eenvoudige grondstoffen zoals etheen en propeen met katalysatoren, gevormd door activering van een verbinding van een groep 4 metaal met een aluminiumalkyl .

Zoals al gezegd is is het ligandsysteem erg belangrijk voor de reactiviteit en stabiliteit van een organometaalcomplex. Een ligandsysteem dat met name voor de vroege

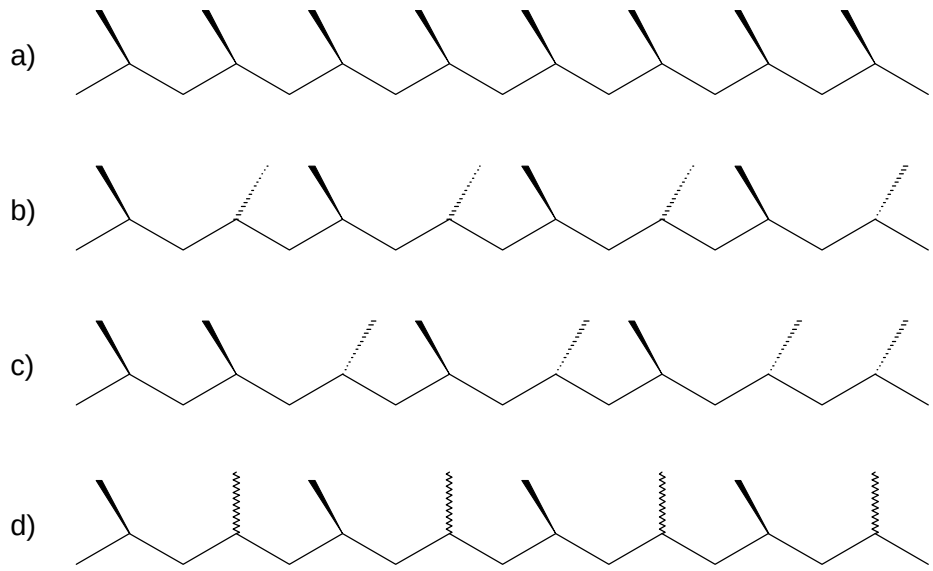
overgangsmetalen veel wordt toegepast is het bis-cyclopentadiënyl-ligandsysteem (Cp_2), twee anionische, aromatische C_5-ringen. Iedere cyclopentadiënyl is met alle koolstofatomen gebonden aan het metaalcentrum (figuur 1).



Figuur 1. **B**asis structuur van een metalloceen verbinding. In bovenstaande figuur zijn de C_5 ringen parallel zoals dat in ferroceen het geval is. In veel andere gevallen, zoals de groep 4 metalen (Ti, Zr, Hf), is de hoek Cp-M-Cp kleiner dan 180^o.

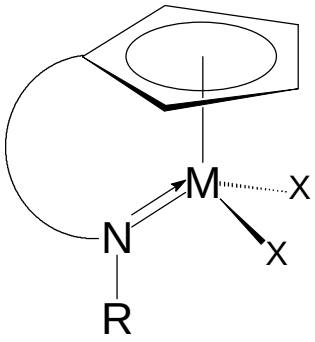
De cyclopentadiënylliganden kunnen samen het metaalcentrum stabiliseren met in totaal 12 electronen. Metaalverbindingen met een bis(cyclopentadiënyl) ligandconfiguratie worden "metallocenen" genoemd (hoewel in feite de naam verwijst naar homologen van het prototype metalloceen, ferroceen, Cp_2Fe).

Voor de groep 4 metalen (titanium, zirkonium en in mindere mate hafnium) is veel onderzoek gedaan naar de effecten van substitutie van de cyclopentadiënylliganden op de reactiviteit en katalytische activiteit in de polymerisatie van olefines. Met name twee ontdekkingen hebben er toe geleid dat de groep 4 metalloceenverbindingen een significante rol zijn gaan spelen in katalytische olefinepolymerisaties op industriële schaal. Allereerst de ontdekking dat Cp_2MCl_2 komplexen (M = Ti, Zr) in combinatie met methylaluminoxaan (MAO) uiterst actieve katalysatoren voor de polymerisatie van etheen en propeen zijn die onder milde experimentele omstandigheden hun werk kunnen doen (lage olefineconcentratie en kamertemperatuur). De andere belangrijke ontwikkeling was het aan elkaar koppelen van de cyclopentadiënylliganden en het gericht plaatsen van extra subsituenten op deze C_5-ringen. Hierdoor kon een grote selectiviteit op het katalysatorsysteem overgebracht worden waardoor naar keuze atactisch, isotactisch, syndiotactisch of hemiisotactisch polypropeen gemaakt kan worden (figuur 2).



Figuur 2. In de polypropeenketen kunnen de propeen-eenheden verschillend georiënteerd zijn. Wanneer de methylgroepen allen aan de zelfde kant van de keten liggen spreekt men van *isotactisch* polypropeen. In *syndiotactisch* polypropeen liggen de methylgroepen om en om aan de ene en aan de ander kant van de. Bij *atactisch* en *hemiisotactisch* polypropeen zijn de methylgroepen van alle, respectievelijk de even propeen-eenheden, willekeurig georiënteerd.

Variatie van substituenten op het cyclopentadiënylligand kan slechts in beperkte mate en men heeft het dan ook niet nagelaten om andere ligandsystemen te onderzoeken.
In dit proefschrift wordt de organometaalchemie van titanium en zirkonium beschreven. Hier wordt een variant van het welbekende *bis*-cyclopentadienyl-ligandsysteem gebruikt en wel het gebrugde cyclopentadiënyl-amidoligand (figuur 3) waarbij een van de cyclopentadiënylliganden is vervangen door een amidogroep. Toen dit onderzoek werd gestart waren een aantal groep 4 metaalcomplexen met dit type ligand al goed beschreven, echter deze onderzoeken richten zich voornamelijk op het dimethylsilyl gebrugde tetramethylcyclopentadiënyl-*tert*-butylamido ligand systeem en de katalytische (co-)polymerisatie van α-olefines met deze verbindingen.
Het hier gepresenteerde onderzoek is breder van opzet. Niet alleen de katalyse maar ook andere aspekten worden belicht: hoe worden de complexen gemaakt, was is hun stabiliteit en reactiviteit en hoe veranderen deze wanneer het ligand wordt gemodificeerd. Bij aanvang van dit project was in de literatuur over de laatst genoemde aspekten weinig bekend.



Figuur 3. Het cyclopentadiënyl-amidoligand en de coördinatie ervan op een groep 4 metaalcentrum. De lone-pair van het stikstofatoom geeft een sterke $N(p_\pi) \rightarrow M(d\pi)$ interactie en het, formeel, anionische stikstofatoom kan het metaalcentrum stabilizeren met maximaal 4 electronen. Men kan dus spreken van een dubbele binding.

In *hoofdstuk 1* passeren na een algemene inleiding een aantal van deze alternatieve liganden de revue. Van deze liganden zijn er maar een paar echt interessant wat betreft de katalytische eigenschappen van de corresponderende organometaalcomplexen. Een veelbelovend ligandsysteem is het dianionische cyclopentadiënyl-amido ligand (Cp-amido). Dit bifunctionele ligand bestaat uit een cyclopentadiënyl dat door middel van een organische brug gekoppeld is aan een amido (figuur 2). De valentie van het metaalcentrum blijft gelijk, echter in vergelijking met het bis-cyclopentadiënylsysteem kan het ligand het metaalcentrum met slechts 10 electronen stabiliseren. Een systeem dat bestaat uit een tetramethylcyclopentadiënylligand is gecombineerd via een dimethylsilyl-brug met een amidofunctie heeft in diverse industriële en universitaire laboratoria grote aandacht gekregen. Als katalysatoren voor olefinepolymerisatie onderscheiden de groep-4 metaalcomplexen van dit ligand zich doordat ze thermisch zeer stabiel zijn en in staat zijn at random hogere α-olefines in te bouwen bij de co-polymerisatie met etheen.

Dit proefschrift beschrijft het onderzoek naar Cp-amido groep 4 metaalcomplexen $[C_5H_4(CH_2)_nNR]MCl_2$ (M = Ti, Zr, n = 2, 3). Met name werd nagegaan wat de consequenties (geometretische structuur, stabiliteit, reactiviteit en katalytische activiteit van de complexen) zijn van het veranderen van bruglengte en variatie van de amido-substituent. In *hoofdstuk 2* wordt de synthese en karakterisatie van een aantal Cp-amido titaniumdichloride komplexen $[C_5H_4(CH_2)_nNR]TiCl_2$ (n = 2, 3; R = Me, Et, *i*-Pr, *t*-Bu, Ad (adamantyl), Ph) beschreven. De komplexen konden via een relatief eenvoudige methode gesynthetiseerd worden door reactie van $TiCl_4$ met de geprotoneerde vorm van het Cp-amido ligand ($C_5H_5(CH_2)_nN(H)R$), en afvanging van het gevormde HCl met een organische base. Het verlengen van de brug heeft duidelijk geometrische consequenties. De bite-angle, de hoek tussen het

stikstofatoom, het metaalcentrum en het zwaartepunt van de cyclopentadiënylgroep, wordt groter en de amido substituent wordt dichter naar het metaal toe geduwd. Hierdoor wordt de vrije ruimte rondom de chlooratomen, de plaats waar het katalytisch proces plaats vindt, verkleind. Cyclovoltammetrie wees uit dat in vergelijking met titanoceendichloride, het metaal in de Cp-amido titaniumdichlorides minder gemakkelijk te reduceren is.

Dat dit een significant gegeven is blijkt in *hoofdstuk 3*. Hierin de komen de carbyl verbindingen $[C_5H_4(CH_2)_nNR]Ti(Cl)R$ en $[C_5H_4(CH_2)_nNR]TiR'_2$ (R' = Me, *i*-Pr, CH_2CMe_3, Ph, CH_2Ph, CH_2CMe_2Ph, C_3H_5) aan bod. De Cp-amidotitanium dichlorides kunnen in het algemeen zonder problemen worden omgezet in een breed scala van mono- en biscarbylverbindingen. De resistentie tegen reductie blijkt uit het feit dat de reactie van Cp-amidotitaniumdichloride met allyl- of iso-propyl-Grignard reagentia de corresponderende titanium(IV)allyl en -iso-propylverbindingen geeft terwijl titannoceendichloride, Cp_2TiCl_2, door deze reagentia gereduceerd wordt tot titaan(III). Met uitzondering van de bis-fenylverbindingen zijn de Cp-amidotitaniumcarbylen thermisch stabieler dan hun titanoceen-analoga. Vaak zijn liganden op het metaalatoom geactiveerd en kunnen bijvoorbeeld door het afsplitsen van (organische) fragmenten andere, vanuit, synthese- en katalyse-oogpunt, zeer interessante organometaalverbindingen geven. Groep 4 metaal carbylcomplexen kunnen onder meer intramoleculaire C-H activering ondergaan waarbij al naar gelang de aard van het carbylfragment, metaal- olefine, metaal-alkyn of metaal-carbeen complexen gevormd worden. Meestal zijn de gevormde producten niet stabiel en moeten ze worden gestabiliseerd door een Lewis base zoals trimethylfosfine, PMe_3. Zo konden respectievelijk de trimethylfosfine gestabiliseerde (Cp-amido)titaan-etheen, -benzyn en -carbeen complexen gesynthetiseerd worden. De thermisch stabielere bis-methyl en bis-benzyl verbindingen konden niet in de corresponderende carbeenverbindingen worden omgezet. Bij temperaturen van ca. 100 ^oC concurreert activering van het Cp-amidoligand met de activering van de overige liganden. De organometaalverbindingen die hierbij ontstonden kon echter niet worden geïdentificeerd.

In *hoofdstuk 4* wordt het trimethylfosfine gestabiliseerde (Cp-amido)titaanbenzyn complex $[C_5H_4(CH_2)_2N$-*t*-$Bu]Ti(C_6H_4)PMe_3$ nader bekeken. Het complex blijkt twee fluxionele processen te ondergaan, een snelle rotatie van het benzynligand, d.w.z. het draaien om een denkbeeldige as die, getrokken vanuit het metaalcentrum, het benzynligand in tweeën deelt, en een langzamer proces van dissociatie en coördinatie van het trimethylfosfine, welke met NMR-spectroscopie aangetoond konden worden. Van het complex werd ook een moleculaire structuur vastgesteld m.b.v. Röntgen-diffractie. Een studie van de reactiviteit van het benzyncomplex t.a.v. onverzadigde substraten zoals olefines, alkynen, nitrillen en ketonen gaf als resultaat dat $[C_5H_4(CH_2)_2N$-*t*-$Bu]Ti(C_6H_4)PMe_3$ in grote lijnen reageert als de

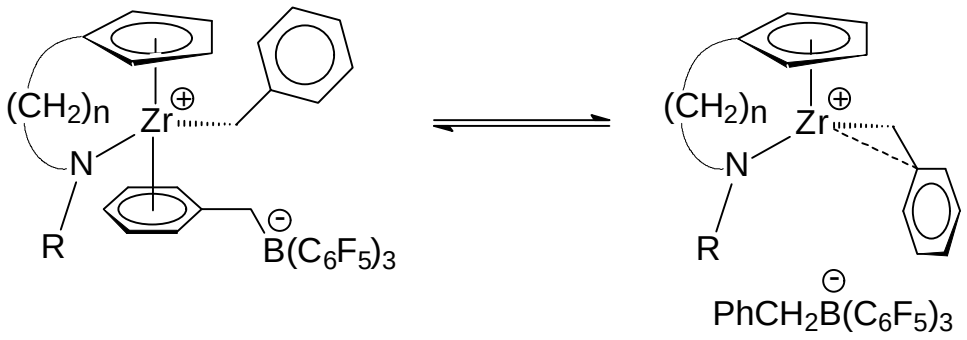
titanoceen analoog $Cp_2Ti(C_6H_4)PMe_3$. Dat de Cp-amidosystemen sterisch minder gehinderd (en ook electronisch minder verzadigd) zijn dan de corresponderende metalloceenverbindingen blijkt uit de reactie van $[C_5H_4(CH_2)_2N$-*t*-Bu]$Ti(C_6H_4)PMe_3$ met benzofenon die in eerste instantie het trimethylfosfine complex van het insertieproduct $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(-*o*-$C_6H_4C(Ph_2)O)PMe_3$ oplevert. Door verwarmen in vacuum kan het fosfine vrije complex $[C_5H_4(CH_2)_2N$-*t*-Bu]Ti(-*o*-$C_6H_4C(Ph_2)O)$ verkregen worden. Van beide complexen is de moleculaire structuur bepaald.

Hoofdstuk 5 behandelt de Cp-amidozirconiumchemie. Een reeks Cp-amidozirconium verbindingen, $[C_5H_4(CH_2)_nNR]ZrCl_2$, werd gemaakt door het geprotoneerde Cp-amine ligand eerst te laten reageren met tetra(dimethylamide)zirconium en daarna het gevormde Cp-amidobis(dimethylamide)zirconium te behandelen met trimethylsilylchloride. De Cp-amidozirconiumdichlorides bleken goede uitgangstoffen te zijn voor de bis(carbyl) verbindingen en $[C_5H_4(CH_2)_nNR]ZrR_2$ waarvan een groot aantal kon worden gesynthetiseerd.

In tegenstelling tot de titaniumcarbylverbindingen reageren de Cp-amidozirconium-bis(carbylen) thermisch vrijwel uitsluitend via Cp-amidoligand activering. Alleen in het geval van Cp-amidobis(ethyl)zirconium leverde thermolyse een identificeerbaar produkt op in de vorm van de etheengebrugde, dinucleaire verbinding $\{[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrEt\}_2(\mu{:}\eta^2,\eta^2$-$C_2H_4)$.

In *hoofdstuk 6* worden de synthese en karakterisatie van de kationische Cp-amido titanium- en -zirconiumcomplexen $\{[C_5H_4(CH_2)_nNR]MR'\}^+$ (M = Ti, Zr) besproken. De complexen zijn getest op hun katalytische activiteit t.a.v. etheen- en propeenpolymerisatie en gekeken is naar de consequenties van ligandvariatie op de activiteit van de katalysator, het molecuulgewicht van het polymeer en de microstructuur van het polymeer.

Om de sterische afscherming van het metaalcentrum door het Cp-amidoligand van complexen in oplossing te bepalen, wordt de interactie tussen het Cp-amidozirconiumbenzylkation $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+$ en het benzyl-trispentafluorofenylboraatanion $[PhCH_2B(C_6F_5)_3]^-$ met behulp van lage temperatuur ^{19}F NMR-spectroscopie bekeken. Het blijkt dat er evenwicht is tussen het '*contact*' ion-paar, waarbij de aromaatring van het boraat interactie vertoont met het metaalcentrum, en een '*solvent separated*' ionpaar waarbij het kation en anion volledig gescheiden zijn (figuur 4). De ligging van dit evenwicht wordt onder andere bepaald door de ligandparameters.



Figuur 4. Het evenwicht tussen het 'contact' ionpaar (links) en 'solvent separated' ionpaar (rechts) bij het ionisch complex $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}^+[PhCH_2B(C_6F_5)_3]^-$.

De $[C_5H_4(CH_2)_nNR]MCl_2$ (m = Ti, Zr) complexen werden in combinatie met methylaluminoxaan (MAO) getest in de katalytische polymerisatie van etheen. Propeen polymerisaties werden uitgevoerd met $[C_5H_4(CH_2)_nNR]TiCl_2$/MAO en $\{[C_5H_4(CH_2)_nNR]Ti(CH_2PH)\}^+[PhCH_2B(C_6F_5)_3]^-$. Het blijkt dat de titaancomplexen een hogere activiteit vertonen dan de zirconiumcomplexen. In de titaancomplexen is het verband tussen ligandparameters en katalysatoractiviteit moeilijk te leggen. Het $\{[C_5H_4(CH_2)_3N$-*i*-$Pr]Ti(CH_2PH)\}^+[PhCH_2B(C_6F_5)_3]^-$ systeem vertoont afwijkend gedrag. In vergelijking met de andere boraangeactiveerde titaancomplexen heeft het een veel hogere initiële activiteit, echter na korte tijd treedt deactivatie van de katalysator op. Verrassend is dat een langere brug (met dezelfde amidosubstituent) in de zirconium complexen resulteert in een 5-maal hogere activiteit. In de patentliteratuur wordt juist een lagere activiteit waargenomen wanneer liganden met een langere silyl brug worden gebruikt.

De molecuulgewichten van de polymeren verkregen met de titaancomplexen zijn in sterke mate afhankelijk van de Cp-amidoliganden. De complexen met het kleinste Cp-ligand ($[C_5H_4(CH_2)_2NMe]$) geven het hoogste molecuulgewicht. De molecuulgewichten dalen met een factor 10 voor polyetheen en een factor 30 voor polypropeen wanneer het sterisch meer gehinderde $[C_5H_4(CH_2)_2N$-*t*-Bu] ligand wordt gebruikt. Daarentegen stijgt het aantal regio-irregulaire propeen inserties wanneer sterisch meer gehinderde C_2-gebrugde Cp-amidoliganden worden gebruikt. Voor de C_3-gebrugde liganden wordt een omgekeerde trend waargenomen. Ook de aard van de activator blijkt van invloed te zijn op de activiteit van de katalysator, het molecuulgewicht en micro-structuur van het polymeer. Een verklaring voor deze waarnemingen wordt gezocht in een complex samenspel tussen kation en anion.

Summary.

This thesis describe a study of organotitanium and -zirconium complexes bearing a cyclopentadienyl ligand with a linked amido functionality, [$C_5H_4(CH_2)_nNR$] (Cp-amido). In particular, the relation between the ligand parameters (bridge length n and the organic fragment R on the nitrogen atom) on the one side and molecular structure, stability and performance in catalytic olefin polymerization on the other side, has been investigated.

In *Chapter 1*, the general introduction, attention is paid to the unique character of the metal carbon bond and its ability to activate a wide range of chemical bonds. Such organometallic compounds have to be stabilized by means of organic fragments bound to the metal center: the ligand set. The reactivity and selectivity of the organometallic compound strongly depends on the electronic and steric properties of the ligand set and can be altered almost on demand by tuning the ligands. A type of ligand that has dominated in particular the early transition metal chemistry, is the cyclopentadienyl group and its derivatives. In the last 10-15 years other types of ligands have been investigated and a brief overview of these is given in this chapter.

In *Chapter 2* an efficient method is presented for the introduction of the Cp-amido ligands to titanium. With the base induced dehydrochlorination of titanium(IV) chloride using the neutral ligand $C_5H_5(CH_2)_nN(H)R$, multigram scale syntheses of the starting materials [η^5,η^1-$C_5H_4(CH_2)_nNR$]$TiCl_2$ can be easily performed. The molecular structures of [η^5,η^1-$C_5H_4(CH_2)_2N$-*i*-Pr]$TiCl_2$, [η^5,η^1-$C_5H_4(CH_2)_2N$-*t*-Bu]$TiCl_2$ and [η^5,η^1-$C_5H_4(CH_2)_3N$-*i*-Pr]$TiCl_2$ are presented and discussed. Changing the CH_2CH_2 bridge for a $CH_2CH_2CH_2$ bridge and using bulkier nitrogen substituents causes distinct structural changes. A longer backbone pushes the nitrogen substituent towards the metal leaving less space in the gap between the Cp-amido ligand core whereas changing the *i*-Pr group for the more bulky *t*-Bu group causes a lenghtening of the nitrogen-titanium bond. These structural changes have also consequences for the NMR spectra of the compounds. Cyclovoltammetry reveals that the dichloro complexes [η^5,η^1-$C_5H_4(CH_2)_nNR$]$TiCl_2$ are considerably more stable against reduction to Ti(III) than for example $CpTiCl_3$ and Cp_2TiCl_2.

In *Chapter 3* the synthesis of a wide range of mono- and bis(carbyl) complexes [η^5,η^1-$C_5H_4(CH_2)_nNR$]Ti(R')Cl and [η^5,η^1-$C_5H_4(CH_2)_nNR$]TiR'_2 is described. The thermal stability is examined and compared with the Cp_2TiR_2 analogues and the Cp-amido titanium complexes appear to be in most cases more stable than their Cp_2Ti analogues. Two types of C-H activation processes are recognized. Below 100 ^oC selective C-H activation of the carbyl groups R' is observed and in combination with PMe_3 stable aryne, olefin and alkylidene

complexes were obtained. Above 100 °C activation of the amido substituent R competes with low temperature C-H activation. An unprecedented Lewis base free benzyne complex [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4) can be obtained upon thermolysis of [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]$TiPh_2$ without PMe_3. A more detailed study indicates an equilibrium between [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]$TiPh_2$ and [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4) and benzene. As a consequence of the better stability against reduction of the Cp-amido titanium dichlorides, the mono- and bis-allyl and the mono chloro-isopropyl complexes can be isolated whereas the titanocene analogues are unknown.

Chapter 4 describes the synthesis, characterization, molecular structure and reactivity of the benzyne complex [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4)PMe_3. The reactivity of [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]Ti(C_6H_4)PMe_3 towards unsaturated substrates like olefins, alkynes, nitrils and ketones has been tested. In general similar products are obtained as for Cp_2Ti-benzyne complexes. A special case in the reaction with ketones is that with benzophenone. First, the phosphine adduct [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]Ti($C_6H_4C(Ph_2)O$).PMe_3 is formed which easily looses PMe_3 giving [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]Ti($C_6H_4C(Ph_2)O$).

In *Chapter 5*, the chemistry of the Cp-amido zirconium complexes [η^5,η^1-$C_5H_4(CH_2)_n$NR]$ZrCl_2$ and [η^5,η^1-$C_5H_4(CH_2)_n$NR]ZrR'_2 is discussed. For the preparation of the dichlorides [η^5,η^1-$C_5H_4(CH_2)_n$NR]$ZrCl_2$ the amine elimination method is used. Besides $Zr(NMe_2)_4$, also $Zr(NMe_2)_2Cl_2(THF)_2$ is a suitable starting material and a range of zirconium dichlorides is prepared. The dichlorides are good precursors for the bis(carbyl) complexes [η^5,η^1-$C_5H_4(CH_2)_n$NR]ZrR'_2. Another way to prepare bis(carbyl) complexes is the reaction of homoleptic zirconium alkys ZrR_4 with the protonated, neutral form of the ligand $C_5H_5(CH_2)_n$N(H)R. Studies of the thermal stability of the [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]ZrR_2 compounds show that they are more stable than the titanium analogues [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]TiR_2. Similar to the bis(carbyl) titanium compounds two different C-H activation processes are observed for [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]ZrR_2. Activation of the R ligand in [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ at room temperature leads to the ethene bridged {[η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4) under liberation of ethene. All other [η^5,η^1-$C_5H_4(CH_2)_2$N-*t*-Bu]ZrR_2 complexes are much more stable and start to decompose above 100 °C. Under these circumstances direct activation of the amido *tert*-butyl group rather than H-abstraction from the carbyl ligand is observed.

Chapter 6 discusses the generation of cationic {[η^5,η^1-$C_5H_4(CH_2)_n$NR]MR}$^+$ species (M = Ti, Zr; R = alkyl) and their activity as catalysts in olefin polymerisation. With the combination of bis(benzyl) complexes [$C_5H_4(CH_2)_n$NR]$Zr(CH_2Ph)_2$ and $B(C_6F_5)_3$, ^{19}F NMR spectroscopy provides an elegant way to quantify the cation-anion interactions. A distinct correlation is

found between the ratio of contact ion-pair/solvent separated ion pair and the ligand and/or metal used. In this way clear information can be gained about the relative steric congestion around the metal center of complexes in solution. The ethene and propene polymerization activity of the complexes are tested using the dichlorides in combination with MAO or the bis-benzyl compounds with tris-pentafluorophenyl borane. The productivity of the catalyst strongly depends on the catalyst used. The titanium catalyst are much more active than the zirconium species. Surprisingly the C_3-bridged zirconium complexes showed to be more productive than the C_2-bridged analogues whereas the titanium analoques showed a reverse order of productivity. The molecular weight and, in the case of polypropene, the microstructure of the polymers produced also strongly depend on the catalyst used. For example, the molecular weight of polyethene drops by over one order of magnitude when $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiCl_2$/MAO is used instead of $[C_5H_4(CH_2)_2NMe]TiCl_2$/MAO. Additional, the number of regioirregular insertions of propene (2,1-insertions) increases when catalysts with more bulky ligands are used. These observations might be explained by a complex coorperation between cation and anion during the polymerization.

Dankwoord.

Hier ligt het dan, het resultaat van 5 jaar kokkerellen en een jaar schrijven. Rest mij nog de dankbare taak om iedereen, die op wat voor wijze dan ook heeft bijgedragen aan het tot stand komen van dit proefschrift, te bedanken. Een aantal mensen wil ik hierbij nog met name noemen.

Allereerst mijn promotor, Jan Teuben. Jou wil ik bedanken voor de kans die je me geboden hebt om mijn promotie onderzoek te kunnen doen, voor de vele leerzame onderhouden, voor het vertrouwen, de kritiek en het geduld wat je met deze 'weerbarstige' Fries hebt gehad. Ook jouw adviezen en ondersteuning betreffende het schrijven van dit proefschrift zijn van grote waarde geweest.
Bart Hessen mijn co-promotor wil ik bedanken voor zijn belangstelling in mijn onderzoek, de vele leerzame en vruchtbare discussies en zijn enthousiasme die hebben geleid tot de totstandkoming van hoofdstuk 6.
De leden van de beoordelingscommissie, Prof. Dr. B.L. Feringa, Prof. Dr. P.W.N.M. van Leeuwen en Prof. Dr. J. Okuda worden bedankt voor hun uitermate snelle beoordeling van het manuscript.
Ook op de 'werkvloer' hebben een aantal mensen bijgedragen aan de gereedkoming van dit proefschrift. Auke Meetsma, Ton Spek, Sergei Troyanov en Nora Veldman voor het oplossen van de in dit proefschrift beschreven kristalstructuren. Hans Roedelof, ook al ben je niet meer in ons midden, jou wil ik bedanken voor de cyclovoltammetrische metingen en voor het corrigeren van de vele manuscripten. Oetze Staal voor het runnen van de autoclaven en de vele genoegelijke uurtjes sleutelen aan het 'expresso apparaat' (metselen is toch moeilijker dan ik dacht). Jan Helmantel voor de vele technische zaken en voor het levendig houden van de Fries-Groningse betrekkingen (alles nuver?). Wolter Beukema voor de computertechnische beslommeringen. Harm Draaier, Jan Ebels en Jannes Hommes voor de element analyses. Henk Knol voor de talloze vaten, buizen, filters en kranen en bovendien het stante pede aansmelten van NMR-buizen. Het NMR-service team bestaande uit Wim Kruisinga, Jan Herrema, Henk Druiven en Ron Hulst voor NMR-problemen (ook in het weekend). Albert Kiewiet en Andries Jekel voor de MS en GC-MS metingen. Joop Vorenkamp voor de GPC metingen (zelfs na 5 uur).
Speciale dank gaat uit naar de studenten Loes van der Veen (Tram 13), Koert Liekelema (er zijn dingen die moeten en er zijn dingen die eerst moeten), Alex (Leggy) Arnold en Marco Bouwkamp (ja, wat nou!) die grotere en kleinere bijdragen hebben geleverd. Zonder jullie inzet zou dit proefschrift een stuk dunner en zeker minder compleet zijn geweest!

Mijn (ex-)collega's: Martin Booij, Bart Hessen, Hans Pattiasina, Klaas den Haan, Eric Heeres, Ytsen Wielstra, Jilles Edema, Johan Eshuis, Gerrit Luinstra, Berth-Jan Deelman, Jan-Karel Buijink, Rob Duchateau, Helena Ribeiro da Costa, Esther Gielens, Stéphanie Ringelberg, Jeannette de Wolf, Peter Witte, Edward Brussee, Erik Bijpost, Patrick Deckers, Nathalie Peper, Cindy Visser, Dirk Beetstra, Timo Sciarone, Guillaume Pool, Sandro Gambarotta, Rosa Fandos, Gwenaëlle Trouvé, David Dawson, Joop Knol, Kees Hummelen, Minze Rispens, Isabel del Hierro, Daan van Leusen, Stephan Albus, Winfried Kretschmer, Sergio Bambirra, Susanna Lieber, Giansiro Prini, Jayne Jubb, Karen Duplooy, Pietro Berno, Mark Butcher, Hector Knight Castro, Anneke Jonkman, Andrew Hughes, Tiffany, Joëlle, Stéphanie en alle hoofd- en bijvakkers, stagiairs en stagiaires voor de steun, gezelligheid, slap geouwehoer, de vele stap- en filmavonden en het tolereren van mijn bemoeizucht.

Rob Duchateau en Hendrik Luttikhedde wil ik in het bijzonder bedanken voor het functioneren als de 'Schaduwcommissie'. Jullie waren een grote steun bij het begin en het einde van het schrijven van het manuscript. Rob, jou wil ik persoonlijk bedanken voor de vele wetenschappelijke en niet wetenschappelijjke discussies en de vele drinksessies in binnen- en buitenland (al had ik er de volgende morgen soms spijt van...).

Ook mijn vrienden van buiten de chemie wil ik bedanken voor de vriendschap en de warme belangstelling julliezijds in mijn wederwaardigheden. Het blijft moeilijk om uit te leggen wat ik nu precies gedaan heb.

Als laatste maar zeker niet als minste wil ik mijn ouders bedanken voor de vrije opvoeding, Jullie steunden en stimuleerden me in alle dingen die ik gedaan heb. Jullie waren een thuis als dat nodig was.

Piet-Jan Sinnema

Stellingen

behorende bij het proefschrift van Piet-Jan Sinnema

1. Het mechanisme dat Cámpora en Buchwald voorstellen voor de reversibele isomerisatie van *syn*-$Cp_2Ti(2\text{-}MeOC_6H_3)(PMe_3)$ naar *anti*-$Cp_2Ti(2\text{-}MeOC_6H_3)(PMe_3)$ is niet het enig denkbare en op grond van de geschatte activeringsenergie ook niet het juiste mechanisme.
   J. Cámpora, S.L. Buchwald *Organometallics* **1993**, *12*, 4182.

2. Wetenschappelijk is het niet acceptabel om van $[Cp^*Zr(CH_2Ph)_2]^+[PhCH_2B(C_6F_5)_3]^-$ wel een kristalstructuur maar geen NMR data te rapporteren.
   C. Pellecchia, A. Immirzi, D. Pappalardo, A. Peluso *Organometallics* **1994**, *13*, 3773.

3. In de discussie over mogelijke ligand-interacties van het kation van $\{[1,3\text{-}(t\text{-}Bu)_2C_5H_3]Zr(CH_2Ph)_2\}^+[PhCH_2B(C_6F_5)_3]^-$ wordt voorbijgegaan aan die tussen het kationisch metaalcentrum en het oplosmiddel.
   J.I. Amor, T. Cuenca, M. Galakhov, P. Royo *J. Organomet. Chem.* **1995**, *497*, 127.

4. Het plan voor de bouw van een parkeergarage onder de Grote Markt valt niet te rijmen met het beleid van de gemeente Groningen om de auto uit de binnenstad te weren.

5. Het is niet mogelijk om uit NMR-data alleen te concluderen dat in het 'constrained geometry' complex $[C_5Me_4(CH_2)_2NMe]TiCl_2$ het titaniumatoom een negatieve lading en het stikstofatoom een positieve lading heeft.
   M. Galakhov, P. Gómez-Sal, A. Martin, M. Mena, C. Yélamos *Eur. J. Inorg. Chem.* **1998**, 1319

6. Bij een opbrengst van 10% als zuivere verbinding wordt het begrip "efficiënte synthesemethode" door Chen en Marks wel heel ruim genomen.
   Y.-X. Chen, T.J. Marks *Organometallics* **1997**, *16*, 3649

7. Als de Viagra-pil door het ziekenfonds vergoed zal worden, kan men rekenen op een nieuwe geboortegolf. Dat staat als een paal boven water.

8. Zuurkasten dienen te worden ontworpen door gebruikers.

9. Ondanks de kwalificatie 'plug and play' geldt voor veel computers, accessoires en software nog altijd 'plug and pray'

10. Het feit dat aanpassingen aan (gemotoriseerde) rolstoelen voor gehandicapten onder het lage BTW-tarief vallen en de even noodzakelijke aanpassingen aan auto's onder het hoge BTW-tarief, is meten met twee maten.

11. Handicapvermelding in het rijbewijs dient ook bril en contactlenzen te omvatten.

12. Ten aanzien van de groei van Schiphol, bedrijven de betrokken partijen (overheid, Schiphol, omwonenden en de milieu-beweging) struisvogelpolitiek.

13. In het belang van het algemeen dient de overheid, in navolging van de Keuringsdienst van Waren, Kema-keur en het Stoomwezen, een instantie in het leven te roepen die toeziet op de kwaliteit van software (*NICS*, Nationaal Instituut voor Controle van Software).

14. Onkruid blijft onuitroeibaar want in tegenstelling tot de bestrijders heeft onkruid geen vakantie of atv.

15. Ter bevordering van de verkeersveiligheid dienen de handy's zodanig (onhandig) ontworpen te zijn dat ze alleen met *twee* handen te bedienen zijn.

16. Ofschoon het vergelijken van de productiviteit van verschillende katalysatoren al moeilijk genoeg is, hebben de auteurs van onderstaand artikel dit voor de lezers onnodig verzwaard door te goochelen met katalysator- en substraatconcentraties.
A.L. McKnight, Md.A. Masood, R.M. Waymouth, D.A. Straus *Organometallics* **1997**, *16*, 2879.

17. Het besluit van het College van Decanen om het gebruik van moderne visualisatiemiddelen tijdens de toelichting op het proefschrift voorafgaande aan de promotieplechtigheid, niet toe te staan is onzinnig en draagt niet bij aan de popularisering van de (exacte) wetenschap.

Groningen, 23 april 1999