Amide functionalized cyclopentadienyl complexes

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AMIDE FUNCTIONALIZED CYCLOPENTADIENYL COMPLEXES

A thesis submitted in part fulfilment of the degree of Master of Science

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Statement of Copyright

Declaration

The work described in this thesis was carried out at the University of Durham, Department of Chemistry, between October 1997 and September 1998.

All the work is my own unless otherwise stated and it has not been submitted previously for a degree at this or any other university.

Acknowledgements

I would like to thank all the members of the inorganic department, especially the occupants of lab 108. In particular, many thanks go to Andrew Johnson and Brian Bridgewater for their help, advice and encouragement.

On the technical side, I would like to thank Alan Kenwright and Ian McKeag for their NMR services, Mike Jones and Lara Turner for their mass spectroscopic analysis and Gordon Haswell and Ray Hart for their glassblowing and for always being cheerful.

Most of all I would like to thank my supervisr Dr. Andrew Hughes for his continued patient support.

Abstract

The work in this thesis is concerned with the synthesis of amide functionalized cyclopentadienyl ligands and their complexation with Group 4 metals.

The synthesis of the ligands $C_5H_5(CH_2)_3N(H)R'$ (R' = C_6H_{11}, $CH_2C_6H_5$, $CH(CH_3)C_6H_5$) was investigated and for the ligands $C_5H_5(CH_2)_3N(H)C_6H_{11}$ and $C_5H_5(CH_2)_3N(H)CH_2C_6H_5$ coordination to a zirconium centre was achieved via homoleptic amide reactions to yield the metal complexes $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NR'](NMe_2)_2$ (R' = C_6H_{11}, $CH_2C_6H_5$). Preparation of the chiral ligand 2-pyrrolidine methylene cyclopentadiene, $C_5H_5CH_2(C_4H_7)NH$, was also attempted.

Chapter 1 provides an introduction to the history, types and applications of functionalized cyclopentadienyl complexes, including a detailed discussion of amide functionalized cyclopentadienyl complexes.

Chapter 2 provides a general discussion of the preparation of trimethylene-bridged amide functionalized cyclopentadienyl complexes and describes the results obtained in this work.

Chapter 3 describes the experimental procedures utilized in this work.

Abbreviations

^{n}Bu	^{n}Butyl group, C_4H_9
^{t}Bu	^{t}Butyl group, $C(CH_3)_3$
^{i}Pr	Isopropyl group, $CH(CH_3)_2$
Ph	Phenyl group, C_6H_5
Me	Methyl group, CH_3
Ts	Tosylate group, 4-$CH_3C_6H_4SO_2$
THF	Tetrahydrofuran, C_4H_8O
TMS	Trimethylsilyl, $(CH_3)_3Si$
L	General two electron ligand
X	General one electron ligand
Z	Carbon or silicon bridge
R	Any hydrocarbon group
CpH	Cyclopentadiene, C_5H_5
MAO	Methyl Aluminoxane, $[AlOMe]_n$
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
MS	Mass Spectroscopy
EI	Electron Ionisation

Abbreviations for NMR spectra

s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
br	broad

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Chapter 2. Preparation Of Trimethylene-Bridged Amide Functionalized Cyclopentadienyl Complexes: Results And Discussion

Chapter 3. Experimental

Chapter 1

Introduction to Amide Functionalized Cyclopentadienyl Complexes

1. Introduction to Amide Functionalized Cyclopentadienyl Complexes

1.1 Metal-Cyclopentadienyl Chemistry

The use of the cyclopentadienyl ligand in organotransition metal chemistry has been an area of continual growth and development since the discovery and structural elucidation of bis(η^5-cyclopentadienyl)iron, or ferrocene, some 46 years ago.[1,2,3] The importance of the ligand does not appear to be subsiding. Recent applications have included the use of bis(cyclopentadienyl) complexes of d- and f-block elements as "metallocene catalysts" in homogeneous olefin polymerisations[4] as well as the employment of chiral cyclopentadienyl complexes as reagents for stereoselective synthesis.[5] In general, transition metal complexes continue to find application in many areas of catalysis and organic synthesis.[6]

1.1.1 Metallocenes

Following the afore-mentioned discovery of ferrocene, a wide range of metallocenes (so called because of their similarity in behaviour to aromatic molecules) has been synthesized. Indeed, cyclopentadienyl derivatives are now known for most of the f-block metals as well as for every main group and transition metal of the periodic table.[7]

Such a rapid growth of interest was inspired by the then novel concept of a five-electron donor (or six-electron donor when considering the metal to be oxidised rather than neutral). Previous metal-ligand interactions considered had included only the covalent bond (e.g. M-CH_3) and the coordinate covalent bond (e.g. M-CO). It was a revolution in bonding theory to propose a metal-ligand bond between a metal and the π orbitals of $[C_5H_5]^-$, although the subsequent intensity of research has now rendered this a well-established and well-known fact.

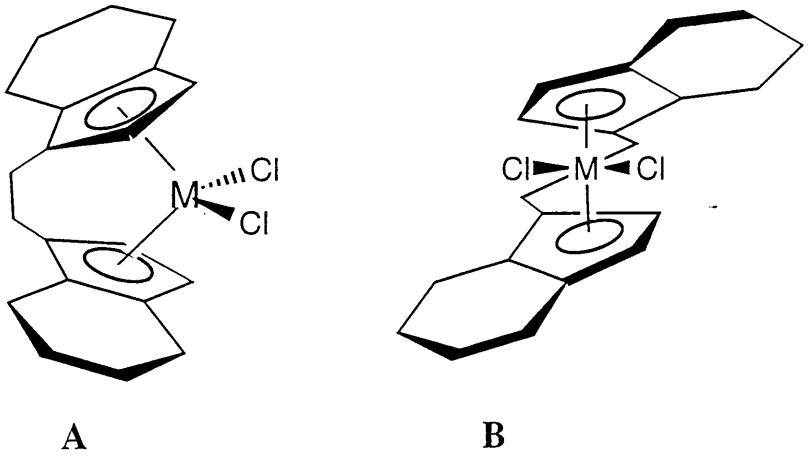
The introduction of group 3 and 4 metallocenes in the early 1980s opened a whole new chapter in the field of Ziegler-Natta catalysis.[4(b),4(c),8] The original heterogeneous Ziegler-Natta catalyst is made by the treatment of titanium tetrachloride with triethylaluminium to form a fibrous material that is partially alkylated and uses Et_2AlCl as a cocatalyst, while the third generation catalysts introduced around 1980 use a $MgCl_2$ supported $TiCl_4$. The titanium centre behaves as a Lewis acid due to its unfilled coordination sphere and thus accepts ethylene or propylene into its vacant coordination site.

Since 1980, a range of homogeneous catalysts based on cyclopentadienyl titanium complexes has been explored. The cyclopentadienyl ligand is known to act predominantly as an inert supporting ligand for the reactive transition metal centre and as such does not actively participate in a given substrate transformation. Such structurally well-defined and, on a molecular level, modifiable metal complexes allowed critical polymerisation parameters such as the activity, molecular weight, polydispersity and microstructure of the resulting

polyolefins to be controlled for the first time in the history of this industrially important process. In addition, the understanding of mechanistic features such as the nature of the active sites and the influence of ligand structure on the regio- and stereo-selectivity has been greatly increased by the use of metallocenes as homogeneous polymerisation catalysts.

1.1.2 Biscyclopentadienyl complexes (ansa-metallocenes)

The highly consistent electronic and steric situation associated with (and generally considered an advantage of) bent metallocenes occasionally turns into a disadvantage as it is recognised to cause substantial steric blocking of the metal-centred reaction site.[9] Catalytic activity is enhanced when the two cyclopentadienyl rings are "tied back" by an alkyl or silyl bridge (Figure1.1).[10] Such complexes, first prepared and pioneered by Brintzinger, have found many applications in various areas of catalysis, with the more recent interest in chiral Brintzinger catalysts such as complex B (Figure 1.1) leading to their employment in a wide range of enantioselective organic reactions, including asymmetric Diels-Alder, asymmetric alkene and imine hydrogenation, asymmetric hydrosilylation and stereoselective alkene insertion, to name but a few.[10(c)]



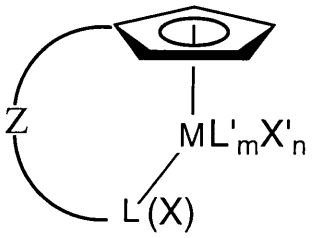
A B

Figure 1.1

However, the problem is alleviated only to a certain extent in such complexes and the "wedge" of the metallocene moiety is still too congested, with each cyclopentadienyl group occupying three coordination sites, to allow, for instance, the efficient polymerisation of α-olefins.[11] Thus, a search for new ligand systems was prompted.

1.2 Functionalized cyclopentadienyl complexes

In response to this problem, functionalized cyclopentadienyl ligands were formulated. These are comprised of a coordinating site X or L tethered to the periphery of a cyclopentadienyl ring via a covalent bridge, Z, of appropriate length (Figure 1.2).



X = one electron ligand
L = two electron ligand
} neutral ligand formalism
Z = covalent (carbon or silicon) bridge

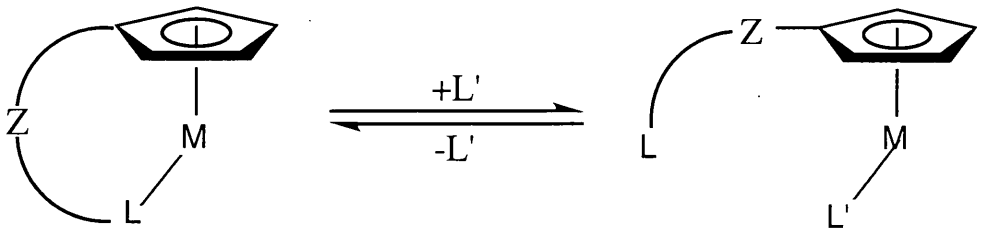
Figure 1.2

These bidentate ligands may give rise to chelate complexes in which the cyclopentadienyl group and the additional donor group X or L are both interacting with the metal centre.[12] Such complexes differ significantly from both *ansa*-metallocenes and the simple half-sandwich complexes without the link Z and offer several advantages:

(1) In some reactions, such as catalytic cycles, the cyclopentadienyl ligand may be involved in irreversible chemical reaction or may even dissociate from the metal.[13] The entire ligand framework could be stabilised by a second donor L or X tethered to the cyclopentadienyl ligand providing additional "anchorage" of the cyclopentadienyl ligand system to the metal, thus preventing exchange or decomposition reactions.

(2) The design of semi-labile ligands is possible if a weakly bonding additional ligand X or L is utilised. In such systems, the pendant ligand X or L could be easily displaced by an incoming substrate molecule, while the cyclopentadienyl moiety would remain firmly bound to the reactive metal centre. At the same time, however, the pendant ligand should be able to protect the metal from deactivating through bimolecular aggregation reactions (Scheme 1).[12] Suitable pendant groups could be derived from solvent molecules, as has been shown by the wide use of phosphine-ether ligands in selective homogeneous catalysis.[14]

(3) Each of the features C_5R_4, X, L and Z in the cyclopentadienyl bifunctional ligand systems can be independantly modified, creating potential for imparting novel properties to the resulting chelate complexes and for controlling the reactivity at the metal centre.[15]



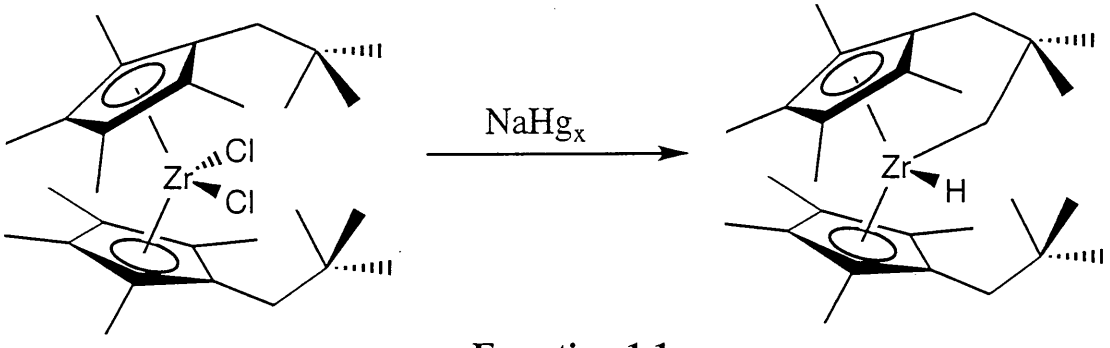
Scheme 1.1

The functionalized cyclopentadienyl ligand systems thus far known can be categorised according to the nature of the pendent group X or L.

1.2.1 Ligands based on a carbon functionality

The special case of *ansa*-metallocenes, in which the ligating group X is another cyclopentadienyl ligand, has been discussed briefly in Section 1.1.2.

The most weakly "bonding" donor L for intramolecular complexation would be represented by an alkyl sidechain. Agostic bonding between the alkyl chain of a cyclopentadienyl ligand and a coordinatively unsaturated metal centre has not, to date, been detected.[16] Distal methyl groups of the pentamethylcyclopentadienyl ligand[14(c),17] are known to undergo a cyclometallation reaction to form so-called "tucked-in" complexes in which the metal centre is coordinated to both the η^5-cyclopentadienyl and the η^1-alkyl groups.[15,18] Bercaw has demonstrated that intramolecular C-H activation through oxidative addition[19(a)] or sigma-bond metathesis[19(b)] occurs preferentially at the γ-position of the alkyl chain (Equation 1.1), leading to the formation of a five-membered metallacycle.[12]



Equation 1.1

The highly active "one-armed bandit" hydrogenation catalysts based on a rhodium complex with the 1-(3-butenyl)-1, 2-dicarbollide ligand designed by Hawthorne (Figure 1.3)[20(a)] triggered research into cyclopentadienyl ligands with a terminal olefin functionality, as the *nido*-carborane dianion $C_2B_9H_{11}^{2-}$ ("dicarbollide") binds to metals via the open B_3C_2 face in an η^5 fashion and is sterically and electronically comparable to the cyclopentadiene dianion. Okuda and co-workers found 3-butenyl and 4-pentenyl substituents to have an appropriate chain length and synthesized ligands such as 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene.[20] Several transition metal derivatives of this ligand, as well as the homologous 4-pentenyl system, have been converted into cobalt, iridium and nickel complexes containing intramolecular C=C bond coordination[21] (Figure 1.4).[12]

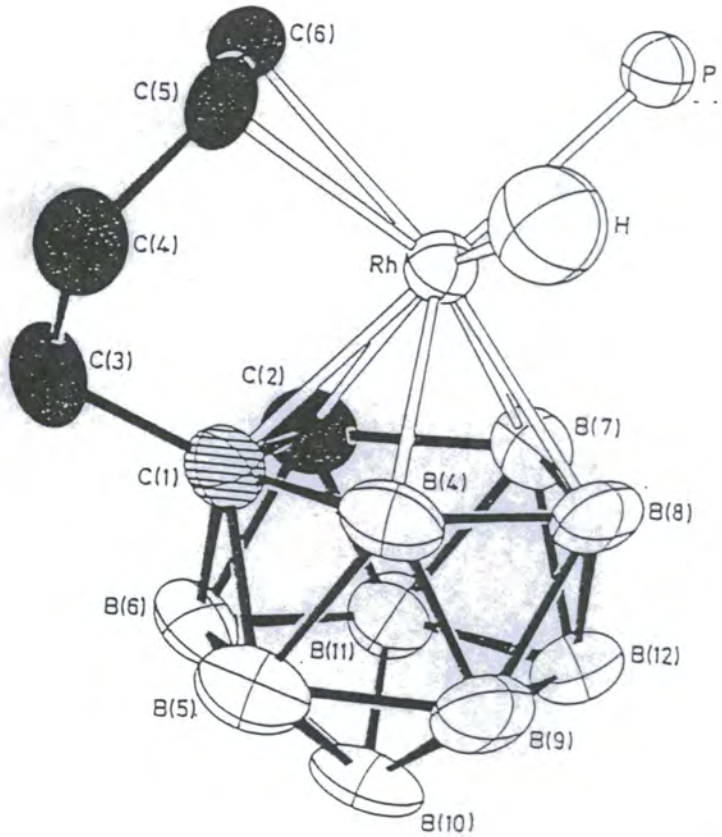


Figure 1.3

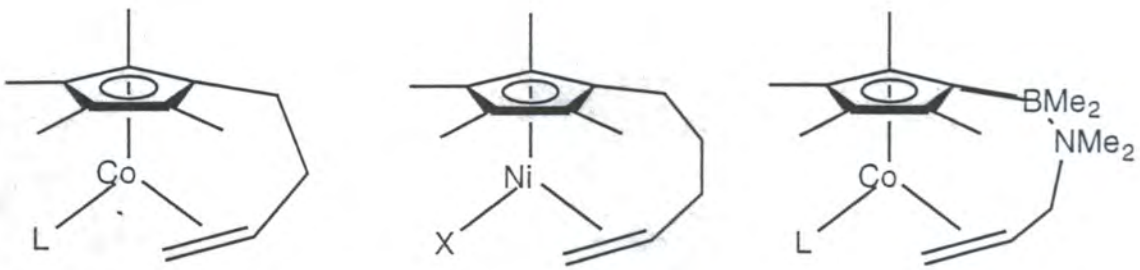


Figure 1.4

1.2.2 Ligands based on a phosphorus functionality

Relatively little work has been done with regard to phosphorus-functionalized cyclopentadienyl systems, which is somewhat surprising when considering the general importance of phosphine ligands in organometallic chemistry and homogeneous catalysis,

along with the fact that cyclopentadienyl ligands with a tethered phosphine group -PR'_2 are the oldest examples of this type of ligand.[22]

The 5 + 2 electron cyclopentadienyl-phosphino ligand appears to form a fairly rigid chelate ring with late transition metal centres. Results suggest that the optimum bridge length is a 2 or 3 carbon chain, creating a five- or six-membered metallacycle, although a certain conformational mobility was reported for $Ru[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2](PPh_3)Cl$[21(a)] as well as for $Co[\eta^5:\eta^2\text{-}C_5H_4CH_2CH_2PR_2](L)$ (L = CO, C_2H_4), (R = Ph, ^tBu, ^iPr).[23 (b)]

The first isolable zirconium alkylidene complex $Zr[\eta^5:\eta^1:\eta^3\text{-}1,3\text{-}C_5H_3(SiMe_2CH_2P^iPr_2)_2(=CHPh)Cl]$ (Figure 1.5), reported by Fryzuk *et al.*, was synthesized using a cyclopentadienyl ligand with two pendent diisopropyl phosphino groups, $1,3\text{-}C_5H_3(SiMe_2CH_2P^iPr_2)_2$.[24] A highly rigid ligand sphere around the zirconium centre allows a benzylidene complex to form by α-hydrogen elimination.

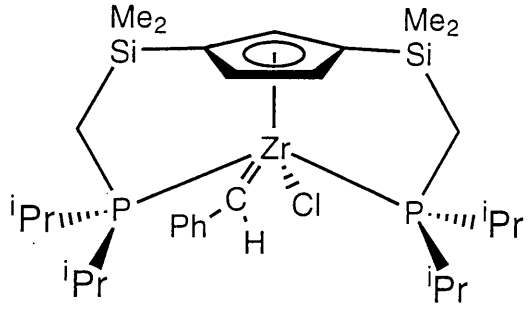
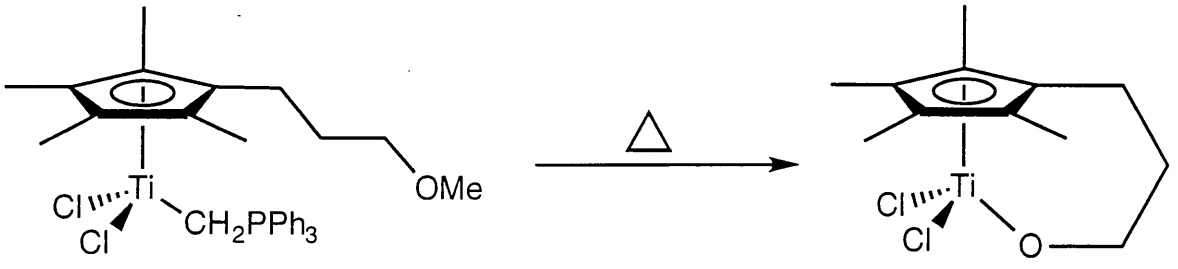


Figure 1.5

1.2.3 Ligands based on an oxygen or a sulphur functionality

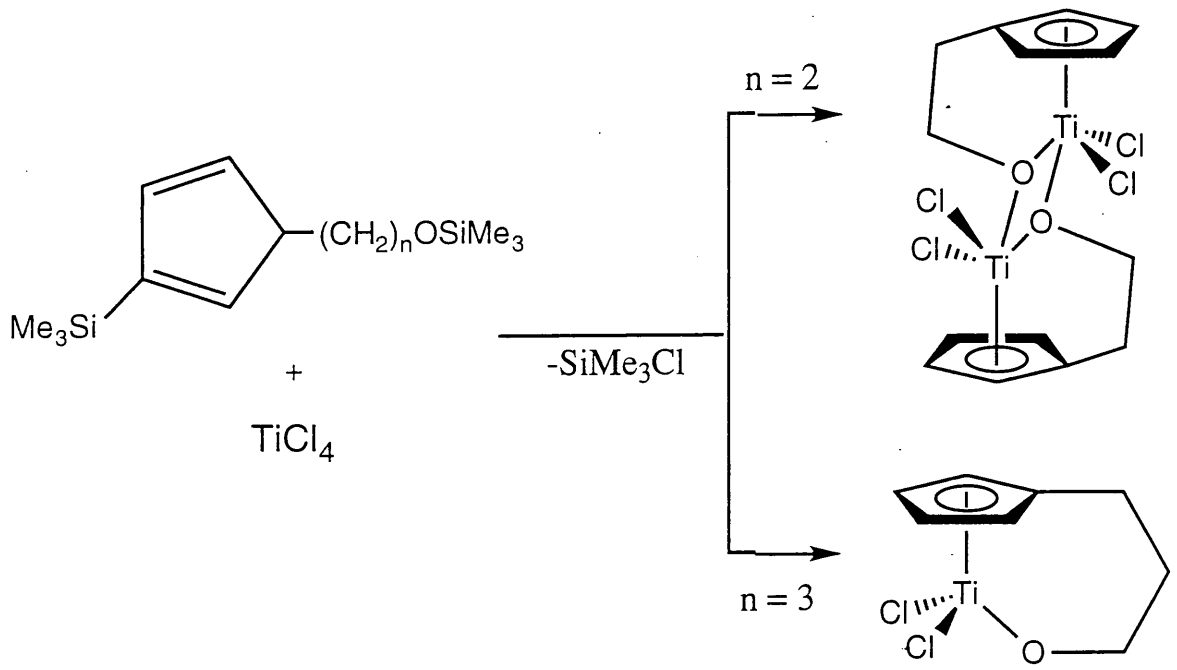
Despite the availability of suitable ligand precursors, relatively few transition metal complexes containing bridged cyclopentadienyl-alkoxo ligands are known, possibly due to their tendency towards dimerization and oligomerization when coordinated to early transition metals.

The first example reported was $Ti[\eta^5:\eta^1\text{-}C_5Me_4(CH_2)_3O]Cl_2$, formed by thermolysis of the titanium ylide $Ti[C_5Me_4(CH_2)_3OMe]Cl_2(CHPPh_3)$ at 150°C (Equation 1.2).[25]



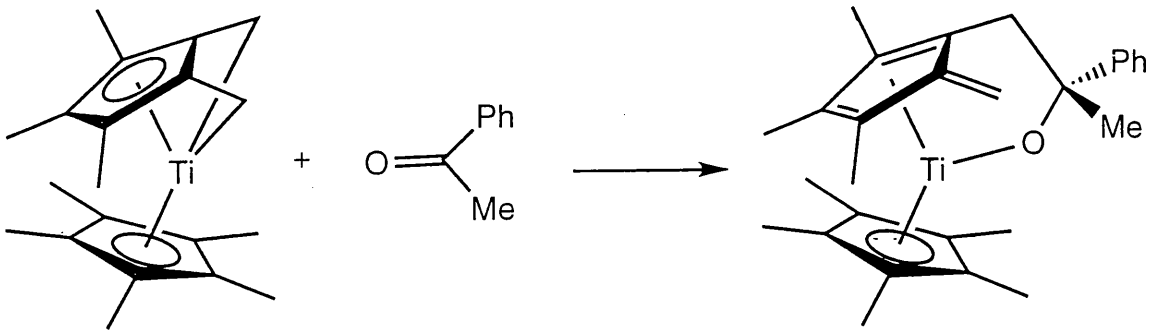
Equation 1.2

An alternative synthetic route to linked alkoxo-cyclopentadienyl titanium complexes involves reacting the ligands as trimethylsilyl ethers, $C_5H_4(SiMe_3)(CH_2)_nOSiMe_3$, with $TiCl_4$, giving $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_nO]Cl_2$ in good yield.[26] The nature of the product obtained appears to be dependent on the length of bridge Z. When Z = $(CH_2)_2$, molecular structure determination shows the product to be dimeric $[Ti\{\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2O\}Cl_2]_2$ with the alkoxide function bridging two titanium centres, whereas the longer bridge length (Z = $(CH_2)_3$) produces a monomeric complex (Scheme 1.2).[26]



Scheme 1.2

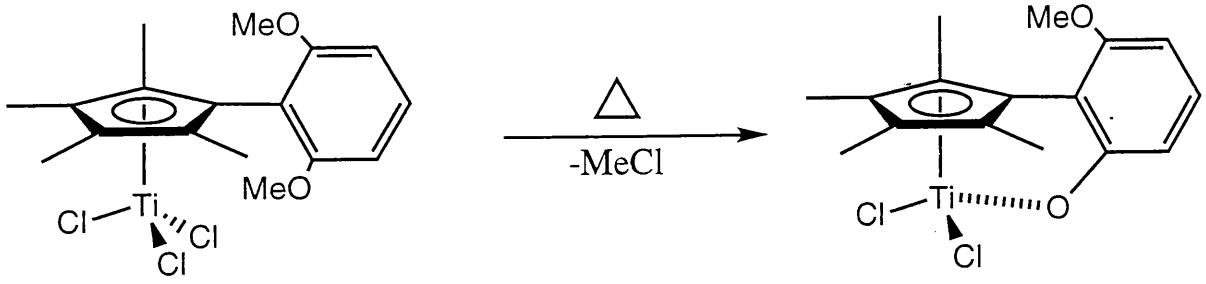
Linked-alkoxo-fluorenyl zirconium complexes of the composition $Zr[\eta^5:\eta^1\text{-}C_{13}H_8ZO]Cl_2(THF)_2$ (Z = $(CH_2)_2$, $(CHR)_2$) have also been reported.[27] Alkoxo-functionalized cyclopentadienyl complexes can also be generated via reaction of the corresponding fulvene complex with aldehydes and ketones. For example, thermolysis of the paramagnetic titanium (III) complex $Ti(\eta^5\text{-}C_5Me_5)R$ (R = Me, Et, Pr) produces the titanium fulvene complex $Ti(\eta^5\text{-}C_5Me_5)[\eta^7\text{-}C_5Me_4(CH_2)_2]$ which can be reacted with acetophenone to give an alkoxo bridging titanium complex (Equation 1.3).[25]



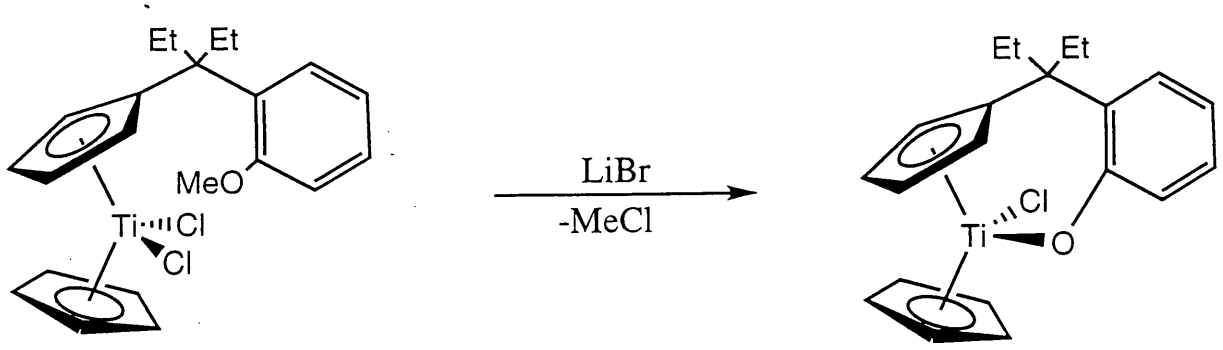
Equation 1.3

Similarly, various aldehydes and ketones can be inserted into the fulvene complex $Ti(C_5H_4Me)(Ph)(\eta^6\text{-}C_5H_4CH_2)$. With acetaldehyde, NOE measurements indicate the formation of one diastereomer (>95%) in which the methyl substituent and the titanium bound phenyl ligand are disposed *cis* at the metallacyclic ring.[28]

An interesting chelate complex is formed during thermolysis of a titanium complex containing a tetramethylcyclopentadienyl ligand with a 2,6-dimethoxyphenyl group (Equation 1.4). Likewise, a benzyloxo bridged complex $Ti(\eta^5:\eta^1\text{-}C_5H_4CEt_2C_6H_4O)(\eta^5\text{-}C_5H_5)Cl$, can be formed from the ortho-methoxybenzyl functionalized titanocene $Ti(\eta^5\text{-}C_5H_4CEt_2C_6H_4OMe)(\eta^5\text{-}C_5H_5)Cl_2$ and LiBr (Equation 1.5).[29]



Equation 1.4



Equation 1.5

The literature contains many examples of cyclopentadienyl ligands containing a pendent ether functionality such as 2-methoxyethyl[30(a)] and α-tetrahydrofurylmethyl[30(b)](Figure 1.6).[30] Much of the interest in these ligands has been directed towards synthesizing lipophilic and volatile mononuclear earth alkaline and lanthanide complexes[31] but transition metal derivatives ought to provide much potential for the design of semi-labile ligands.[32] At present, however, it is not conclusively known how strongly the oxygen atom in compounds such as $Ti(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2OMe)Cl_3$ is bonded, but a similar cationic sulphur system, containing a 2-thienylmethyl group, exhibited semi-labile properties in reacting reversibly with hydrogen and hydrogen sulphide (Equation 1.6).[33]

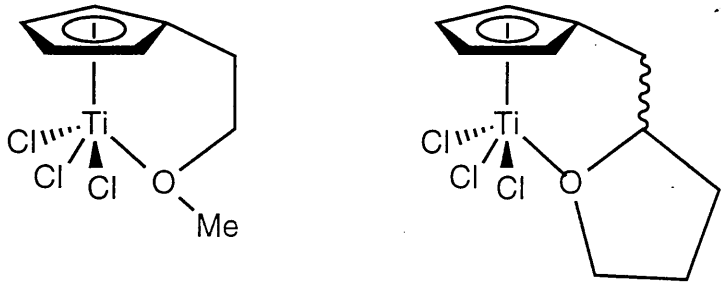
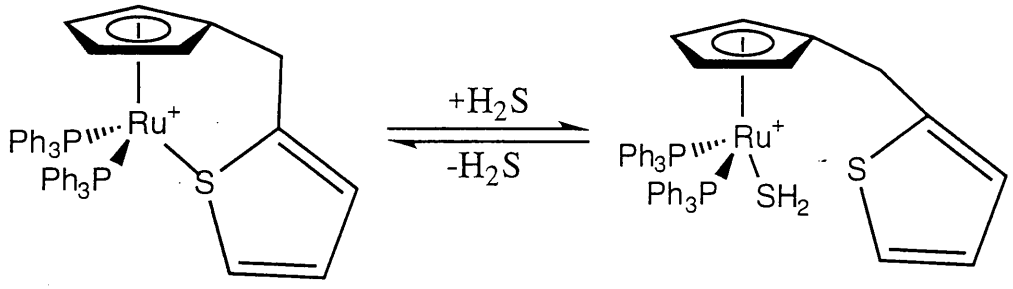


Figure 1.6



Equation 1.6

1.2.4 Ligands based on a nitrogen functionality

By far the most ubiquitous ligands of this type are linked amido-cyclopentadienyl ligands, which will be discussed in detail in Section 1.3.

Linked cyclopentadienyl imido ligands are also known. The organoimido group RN^{2-} (LX_2 type) is of particular interest due to the isolobal analogy between 14-electron $M(NR)_2$ (M = group 6 metal) and $M'(C_5R_5)_2$ (M' = group 4 metal) complexes proposed by Schrock.[34] Early work on such systems included the synthesis by Green and co-workers of the *ansa*-complex $Nb(\eta^5:\sigma\text{–}C_5H_4(CH_2)_3N)Cl_2$ in a one-pot reaction between $(C_5H_4)TMS(CH_2)_3N(TMS)_2$ and $NbCl_5$. Reaction with excess PMe_3 formed the complex $Nb(\eta^5:\sigma\text{-}C_5H_4(CH_2)_3N)(PMe_3)Cl_2$ (Figure 1.7), the molecular structure of which was shown to exhibit a strain-free chelate ring in close analogy to Brintzinger-type *ansa*-zirconocene complexes.[35] It is not yet known whether the olefin polymerisation properties of this niobium imido complex are comparable with those of zirconocene derivatives.

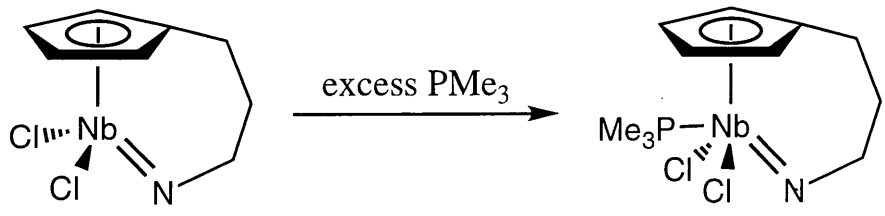


Figure 1.7

In addition, many half-sandwich compounds containing amine functions NR_2 are known. These neutral donors (analogous to ether functions as both are "L-type" ligands) are labile and so can be pendant or bound to the metal centre. As amines are known generally as hard ligands, it is perhaps surprising that alkylamino groups can be coordinated to a soft organotransition metal fragment once it is tethered to the cyclopentadienyl ligand (Figure 1.6).[36] Literature examples of such systems include $Mn[\eta^5:\eta^1\text{-}C_5H_4CH_2CHMeNMe\text{-}(CH_2CH{=}CH_2)](CO)_2$,[36(a)] *cis*-$Mo[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2NMe_2](CO)_2I$,[36(b)] $Co[\eta^5:\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2]I_2$,[36(d)] and $[Ti(\eta^5:\eta^1\text{-}C_5H_4(Me_2C_5H_4N)Cl(\mu\text{-}O)]_2$.[36(e)] Recently, the amino-substituted cyclopentadienyl chromium derivatives $[CH_2C_2H_4CH_2Cr(\eta^5:\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2)]$ and $[CH_2C_4H_8CH_2Cr(\eta^5:\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2)]$ have shown a remarkable activity for the catalytic polymerisation of ethylene.[36(f)]

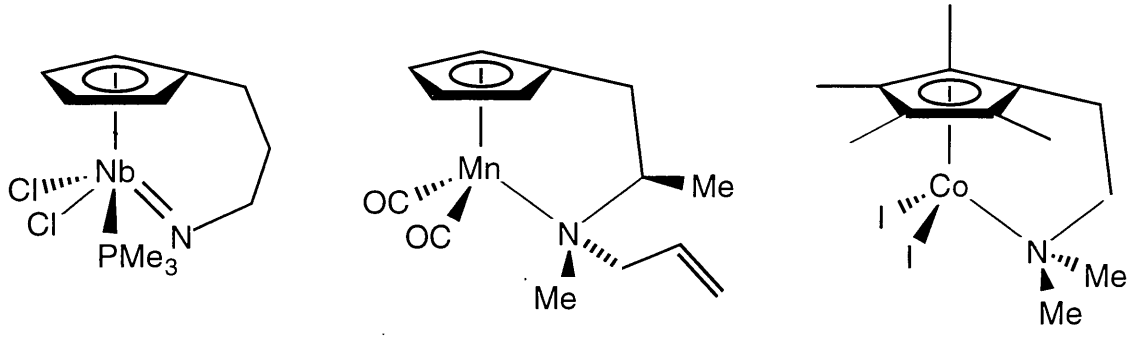


Figure 1.8

1.3 Amide Functionalized Cyclopentadienyl Ligands

In contrast to the five-electron L_2X-type cyclopentadienyl ligand, the amido group is a three-electron ligand of the LX-type (incorporating π-donation from the trigonal planar nitrogen atom).

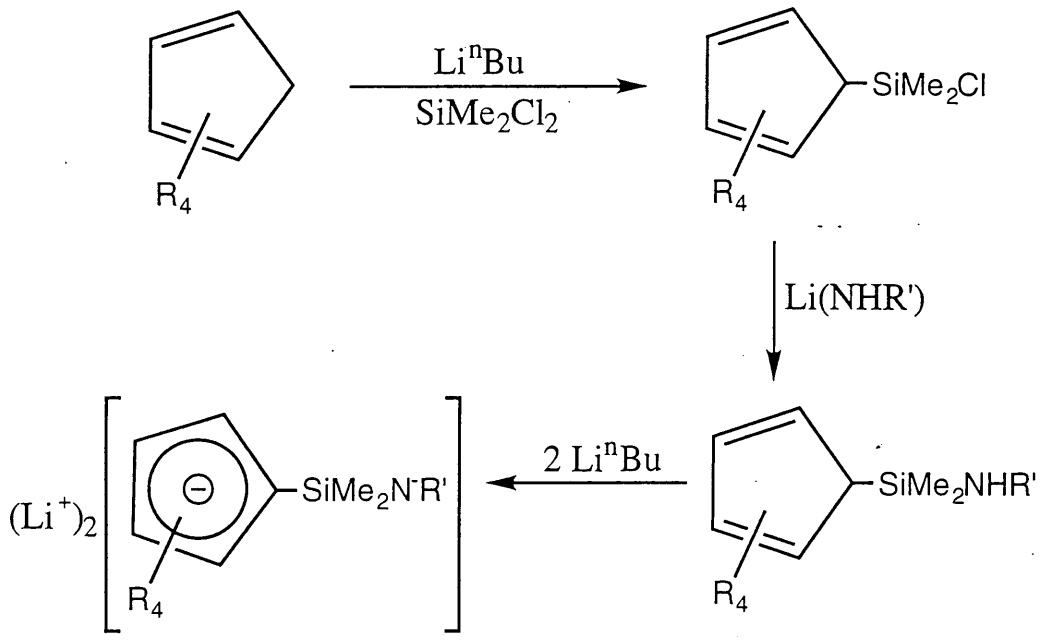
The first complexes containing bridged amido-cyclopentadienyl ligands were introduced by Bercaw and Shapiro in the late eighties.[37] The intention was to synthesize complexes with less steric constraint at the metal centre than Brintzinger-type *ansa*-metallocenes in the hope that they would produce efficient olefin polymerisation catalysts. Complexes such as $[Sc\{\eta^5:\eta^1\text{-}C_5Me_4(SiMe_2N^tBu)\}(PMe_3)(\mu\text{-}H)]_2$ and $[Sc\{\eta^5:\eta^1\text{-}C_5Me_4(SiMe_2N^tBu)\}(\mu\text{-}CH_2CH_2CH_3)]_2$ were in fact found to exhibit much higher reactivity towards α-olefins than the analogous *ansa*-scandocene complexes.[37,38] Iron and titanium complexes containing sterically demanding derivatives of this dianionic ligand, such as $Ti[\eta^5:\eta^1\text{-}C_5H_3(^tBu)SiMe_2N^tBu]X_2$ (X = Cl, alkyl), were synthesized shortly thereafter.[5(a),39] These initial studies were followed by the synthesis of linked amido-cyclopentadienyl ligands incorporating carbon bridges. Complexes of the type $M[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2CH_2NMe](NMe_2)_2$ (M = Zr, Hf) were synthesized by Teuben *et al.* by aminolysis of zirconium and hafnium tetrakis(dimethylamide) and could easily be converted to halo and alkyl derivatives.[40]

Group 4 metal complexes containing an amido-cyclopentadienyl ligand $C_5R_4\text{-}Z\text{-}NR'$ have attracted considerable industrial interest as homogeneous polymerisation catalysts and much of the data on this subject resides in the patent literature.

1.3.1 Synthesis

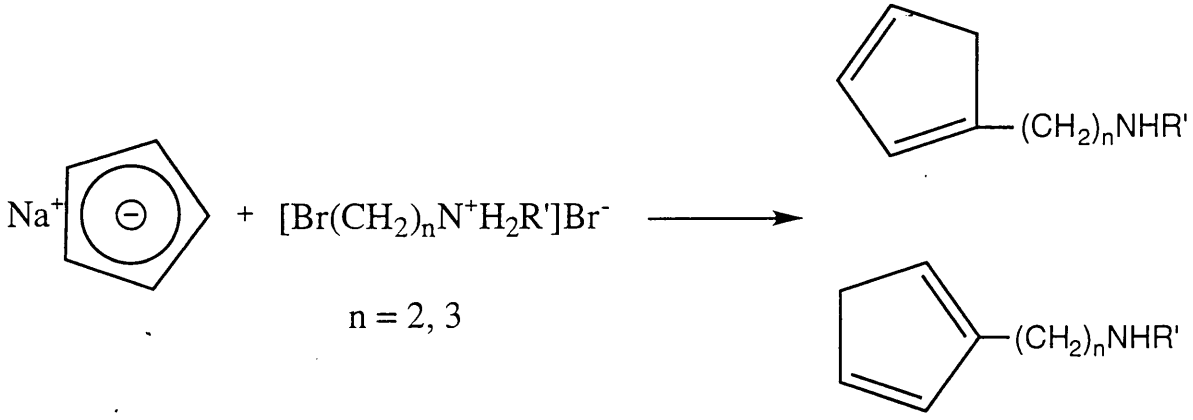
The most widely used synthetic procedures involve coordinating the pre-assembled ligand $(C_5R_4H)Z(NHR')$ to the metal centre by an appropriate method. As was previously mentioned, $SiMe_2$ and carbon chains $(CH_2)_n$ (n = 2,3) are commonly used as the bridging function Z but mixed group bridges, such as $SiMe_2CH_2$, are also known. The range of suitable cyclopentadienyl units C_5R_4 appears very large. Simple C_5H_4 and C_5Me_4 groups are commonly used but annulated ring systems such as indenyl and fluorenyl groups or donor-substituted systems may also be employed.[41]

The procedure frequently used for the introduction of the $SiMe_2$ link involves reaction between metallated cyclopentadiene, usually as its lithium salt $Li(C_5R_4H)$, and dichlorodimethylsilane to give $(C_5R_4H)SiMe_2Cl$ (R = H, Me). This can then be reacted with a variety of lithium amides Li(NHR') or excess amine NH_2R' to produce the ligand precursor $(C_5R_4H)SiMe_2NHR'$ (Scheme 1.3).[15] By this method, the afore-mentioned $(C_5Me_4H)SiMe_2NH^tBu$ ligand, first described by Bercaw and Shapiro, is obtained as a moisture sensitive, distillable oil in overall yield of 76% based on $Li(C_5Me_4H)$.[38]



Scheme 1.3

Di- and trimethylene-linked ligands are usually prepared by adding $[X'(CH_2)_nN^+H_2R']X'^-$ (n = 2,3; R' = Me, ^{i}Pr, ^{t}Bu etc.; X' = Cl, Br) to an excess of $Na(C_5H_5)$ or $Na(C_9H_7)$. The products, $C_5H_5(CH_2)_nNHR'$, exist as several double-bond isomers (Equation 1.7).[40, 42]



Equation 1.7

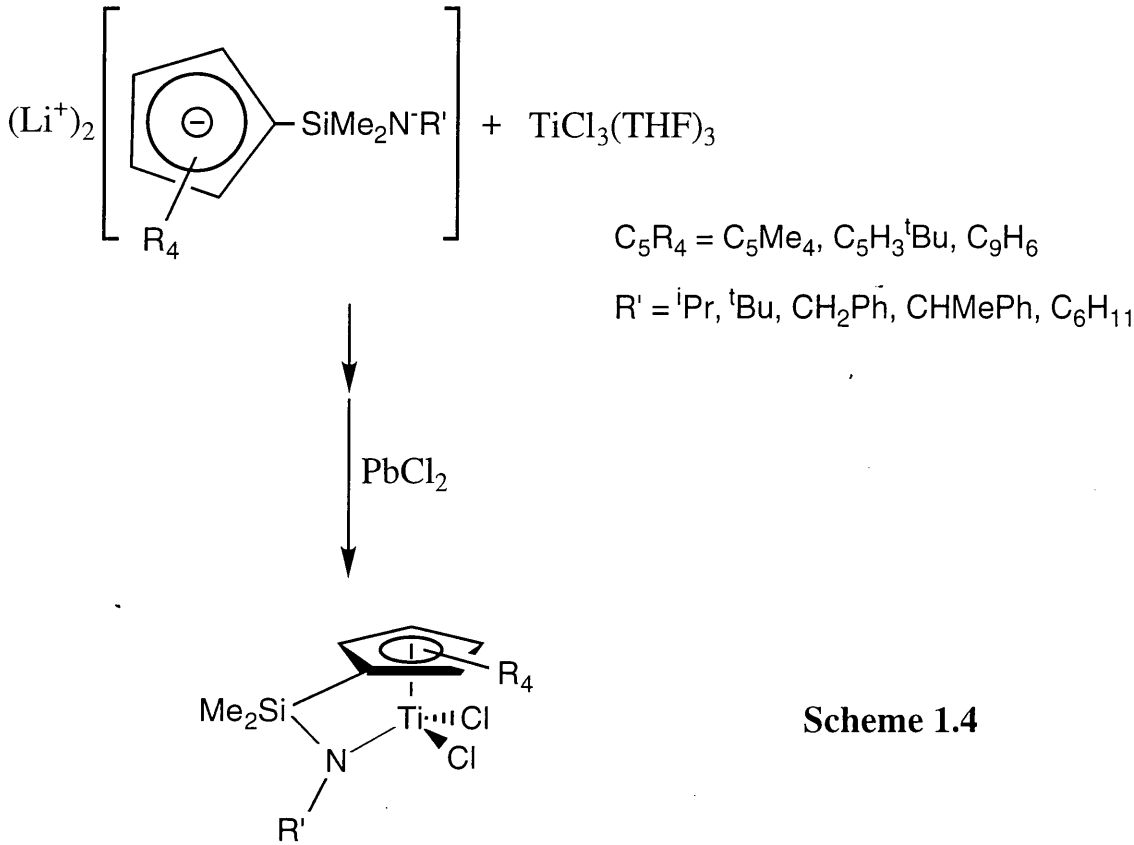
Li^{n}Bu is commonly used to achieve the double metallation of the ligand, the product of which, $Li_2(C_5R_4ZNR')$, is usually used *in situ* without isolation, although isolation may be possible. The use of a magnesium derivative $[MgCl(THF)]_2(C_5Me_4SiMe_2N^tBu)$ as a less reducing ligand transfer agent has been reported.[43]

Several different synthetic procedures have been developed for the complexation of the linked amido-cyclopentadienyl ligand. These are discussed below.

Metathesis Reactions

The metathetical reaction of the doubly metallated ligand precursor $(C_5R_4ZNR')^{2-}$ with appropriate metal halides appears to be the most common complexation procedure, the thermodynamic driving force being the formation of an alkali metal halide such as sodium chloride. The first amido-cyclopentadienyl titanium complex, *racemic* $Ti[\eta^5:\eta^1\text{-}(C_5H_3{}^tBu)SiMe_2N{}^tBu]Cl_2$, was obtained from the reaction of $Li_2[(C_5H_3{}^tBu)SiMe_2N{}^tBu]$ with $TiCl_4(THF)_2$.[39] Higher, more reproducible yields are obtained from the use of $TiCl_3(THF)_3$ (followed by oxidation of the titanium (III) intermediate) rather than the more reduction-sensitive $TiCl_4(THF)_2$.[18(a)]

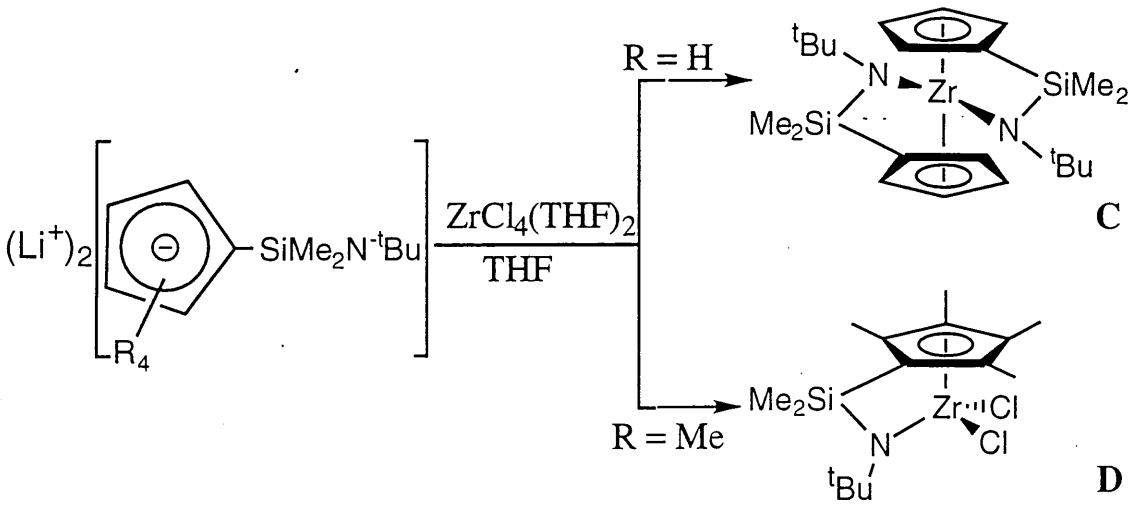
Teuben *et al.* found the best reagent for the oxidation/chlorination of the titanium (III) intermediate to be lead dichloride[44] and this modification of the original methodology provides a route to complexes of the general type $Ti(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')Cl_2$ in which the cyclopentadienyl moieties and amido-substituents can be varied (Scheme 1.4).[41, 45, 46, 47]



Scheme 1.4

A disadvantage of this procedure is that low yields are occasionally encountered, especially when the ligand used contains an unsubstituted cyclopentadienyl ring, as strongly reducing (i.e. more ionic) cyclopentadienyl anions can lead to reduction of the metal centre.[18, 48] Formation of bis(ligand) complexes of the type $Ti(\eta^5:\eta^1\text{-}C_5R_4ZNR')_2$ may account for low yields in some cases. For example, irrespective of molar ratio, the reaction between $(C_5H_4SiMe_2N{}^tBu)Li_2$ and $ZrCl_4$ leads exclusively to the formation of the bis(ligand)

complex, C, whereas reaction of $(C_5Me_4SiMe_2N^tBu)Li_2$ with $ZrCl_4$ or $ZrCl_4(THF)_2$ gives the desired mono(ligand) complex, D (Scheme 1.5).[48]

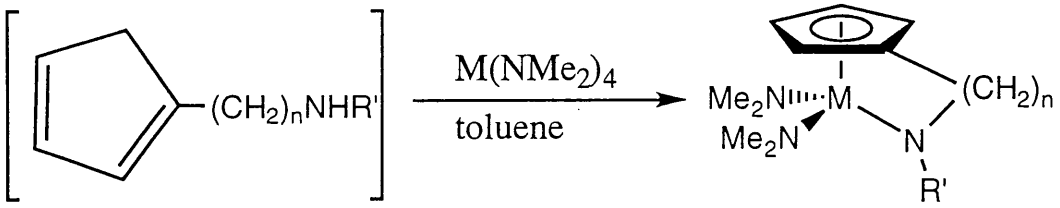


Scheme 1.5

Another potential problem in metathesis complexation methods is the formation of solvent adducts; a result of the expected higher Lewis acidity of the complexes of the linked amido-cyclopentadienyl ligand.[38] Such solvent adducts are not desired as they may interfere in subsequent alkylation reactions or with activation procedures during olefin polymerisation. Zirconium complexes of fluorenyl-based ligands are found to be easily isolable as solvent adducts, forming species such as $Zr(\eta^5:\eta^1\text{-}C_{13}H_8SiMe_2N^tBu)Cl_2(L)$ (L = THF or Et_2O). However, by increasing the length of the bridging group Z from $SiMe_2$ to CH_2SiMe_2, the resulting fluorenyl complexes may be isolated without a solvent molecule and solvent molecules may be irreversibly lost upon heating to give insoluble oligomers.[49]

Homoleptic Amide Reactions

This method, in which cyclopentadienes are reacted with homoleptic metal amides $M(NR''_2)_n$ with amine elimination, was first applied many years ago to the synthesis of amido metallocene complexes of the type $M(C_5R_5)_x(NR'')_y$[50(a)] and was later expanded to the stereoselective synthesis of Brintzinger-type *ansa*-metallocenes.[50(b)] It has more recently been employed for the complexation of amido-functionalized cyclopentadienyl ligands, initially those with a carbon bridge $C_5H_5(CH_2)_nNR'$ (n = 2,3; R' = Me, ^{i}Pr, tBu).[40, 42, 51] Reaction of the free ligand with $M(NMe_2)_4$ (M = Ti, Zr, Hf,) produces the bis amide complexes as distillable oils (Scheme 1.6).[52]



n = 2: R' = Me, ^{t}Bu;
n = 3: R' = Me, ^{t}Bu

M = Zr, Ti

Scheme 1.6

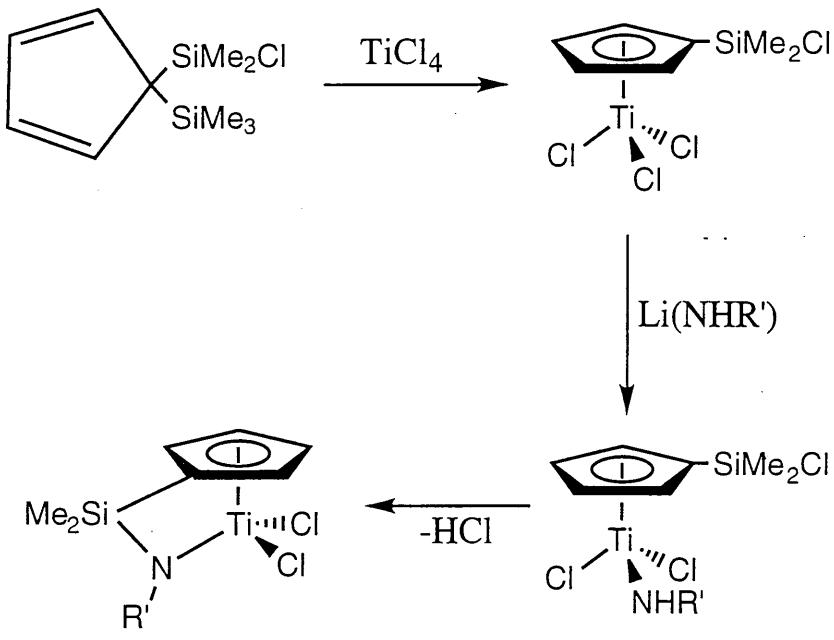
Similarly, dimethylsilanediyl-bridged amido cyclopentadienyl ligands, $C_5H_5SiMe_2NHR'$, may be reacted with homoleptic amides $M(NR''_2)_4$ (M = Ti, Zr, Hf) to give corresponding complexes of the general type $M(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NR')(NR''_2)_2$.[48, 53]

The driving force for these reactions is found in the generation of the highly volatile amines. The reaction is accelerated with more acidic ligands and sterically less demanding cyclic systems and can proceed with nearly quantitative yields.[53] Although the products are often liquids, they can be converted into solid dichloro complexes relatively easily and the zirconium dichloro complexes $Zr[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2NR']Cl_2$ (R' = ^{t}Bu) are accessible from $Zr(NMe_2)_2Cl_2(THF)_2$ and C_5H_5ZNHR'.[54]

Amido linkage from preformed half-sandwich complexes

This alternative approach involves introducing the amido linkage within the preformed half-sandwich complex.[55] $LiC_5H_5(SiMe_3)$ and $SiMe_2Cl_2$ can be reacted to form the functionalized cyclopentadiene $C_5H_4(SiMe_2Cl)SiMe_3$, which is then reacted with $TiCl_4$ to form $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ with selective elimination of chlorotrimethylsilane. Reaction of this trichloro complex with lithium amides LiNHR' (e.g. R' = ^{t}Bu,[55(a)] ^{i}Pr,[47] CH_2Ph[47]) in the presence of a base such as triethylamine gives the desired titanium complexes $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NR')Cl_2$ in good yields. The mechanism is thought to involve initial attack of the amide anion at the titanium centre followed by bridging of the silicon, which is presumably less electrophilic than titanium (Scheme 1.7).[55]

However, this method is, as yet, limited to the unsubstituted cyclopentadienyl system C_5H_4. It cannot be applied to substituted or annulated ring systems such as indenyl, nor to metal centres other than titanium.[41]



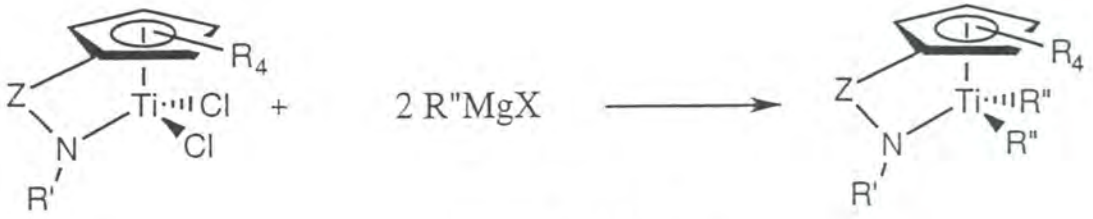
Scheme 1.7

1.3.2 Hydrido and alkyl complexes

The importance of alkyl complexes as precursors for α-olefin polymerisation catalysts has led to much attention being focused on their synthesis from the chloro or amido derivatives. Organolithium or Grignard reagents without β-hydrogens (such as methyl, benzyl, trimethylsilyl, neophyl and neopentyl) serve as suitable alkylating reagents. In general, more thermally and photochemically stable complexes are obtained from bulkier alkyl groups, with complexes such as some dimethyltitanium derivatives being unstable over long periods of time at ambient temperatures.

Surprisingly, only one isolable monomeric scandium alkyl complex, $Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{CH(SiMe_3)_2\}$, is known. This is isolated from the reaction between $Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Cl$ and $LiCH(SiMe_3)_2$, and even the reaction with $LiCH_2SiMe_3$ does not give the desired product.[38]

However, a fairly extensive range of dialkyl complexes of group 4 metals has been reported. They are generally synthesized as described above (Equation 1.8)[47, 49, 55, 56] and in the case of zirconium complexes containing carbon links, the amine adduct $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]Cl_2(NMe_2H)$ can be directly converted to the dialkyl.[40]



Equation 1.8

The steric bulk of the alkyl group appears to have an influence on the retention of coordinated solvent molecules. The chromium complex $Cr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)R''$ retains a THF molecule for R'' = Me and Ph but not when R'' = CH_2SiMe_3.[57] Similarly, zirconium dimethyl derivatives $Zr[\eta^5:\eta^1\text{-}C_{13}H_8SiMe_2N^tBu]Me_2(THF)$ or $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]Me_2(Et_2O)$ tend to retain solvents, whereas the complexes with larger alkyls can be isolated without coordinated solvent.[40, 58]

The electron deficiency in benzyl complexes of early transition metals is relieved by a distorted coordination of the benzyl ligand. The titanium compound $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2Ph](CH_2Ph)_2$, for instance, exhibits an α-agostic bonding interaction of the CH_2-hydrogen atoms of one of the benzyl groups with the titanium (Figure 1.9).[47] These different conformations of the benzyl ligands are related to the various metal-carbon distances and different angles at the benzylic carbon of the two benzyl groups. However, the unsymmetrical distortion cannot be detected by NMR analysis at room temperature. In contrast, NMR spectroscopic data on the zirconium dibenzyl complex $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe](CH_2Ph)_2$ does indicate some η^2-benzyl interaction.[40, 59]

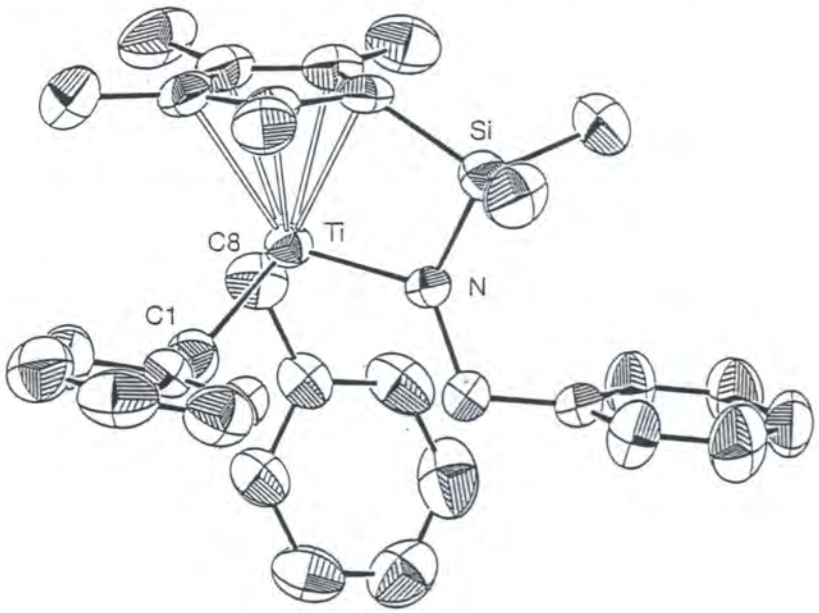
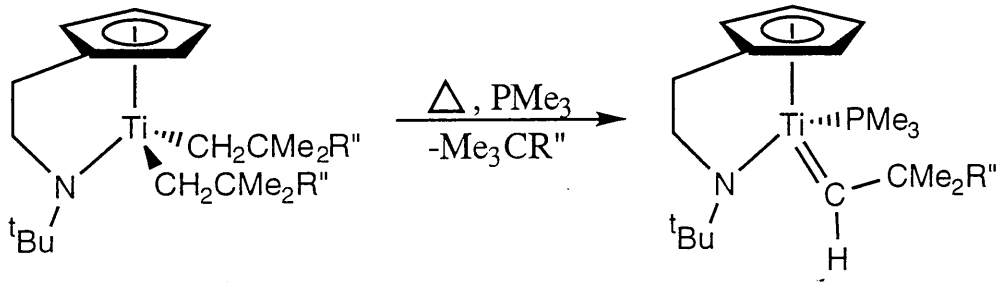


Figure 1.9

The reaction of one equivalent of $C_6H_5CH_2MgCl$ with $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]Cl_2(NMe_2H)$ yields the dimeric mono(benzyl) complex $[Zr(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe)(CH_2Ph)(\mu\text{-}Cl)]_2$, in which the electronic unsaturation is relieved by the formation of chloride bridges rather than a distortion of the benzyl ligands. Two different Zr-Cl distances are seen in the crystal structure due to the *trans* influence of the benzyl ligand.[40] The colourless bis(tetrahydroborate), $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe](\eta^3\text{-}BH_4)_2$, formed by reaction of $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]Cl_2(NMe_2H)$ with excess $LiBH_4$, contains rapidly exchanging terminal and bridging hydrido ligands.

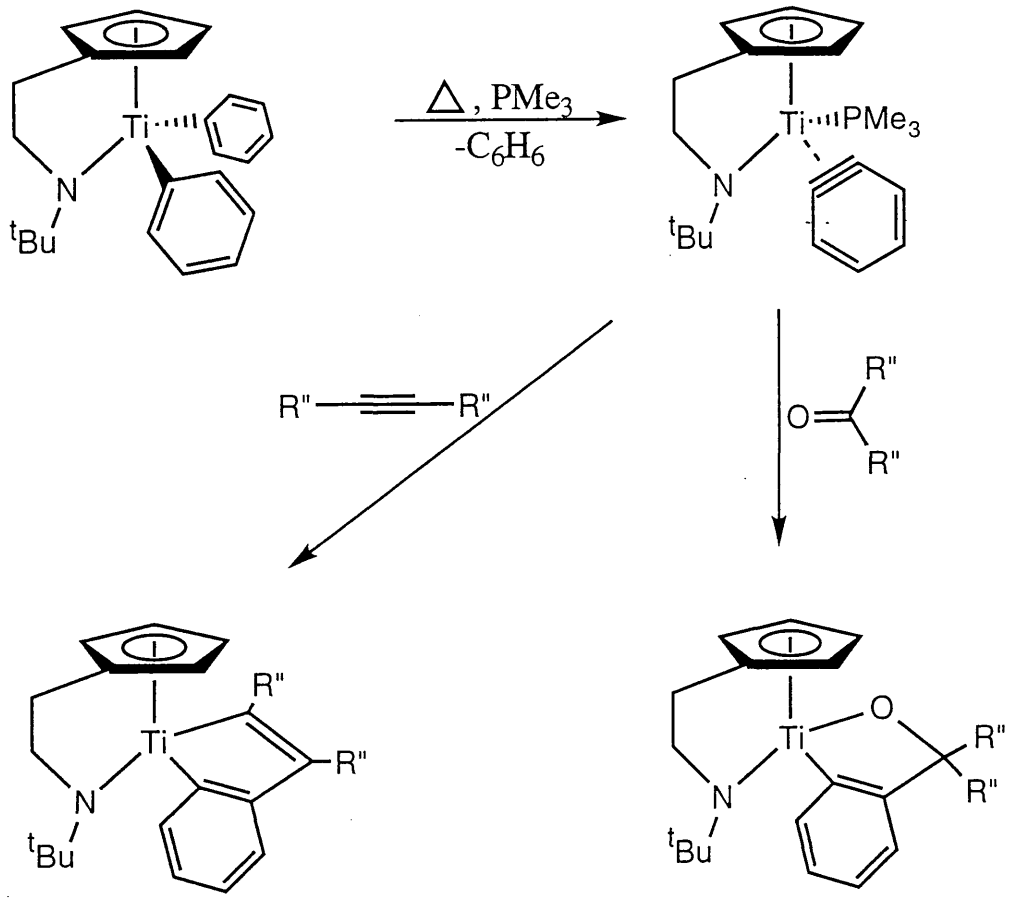
Alkylidene complexes of early transition metals, such as $Ti(\eta^5\text{-}C_5R_5)_2(=CR'_2)$, have played an important part in the development of active initiators for olefin metathesis and ring-opening metathesis polymerisation.[60] The neopentylidene and neophylidene complexes $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^tBu](=CHCMe_2R'')$ can be formed in good yields by thermolysis of $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^tBu](CH_2CMe_2R'')$ (R'' = Me, Ph) and exhibit characteristically low-field ^{13}C signals at δ251 and 246 ppm, respectively (Equation 1.9).[42]



Equation 1.9

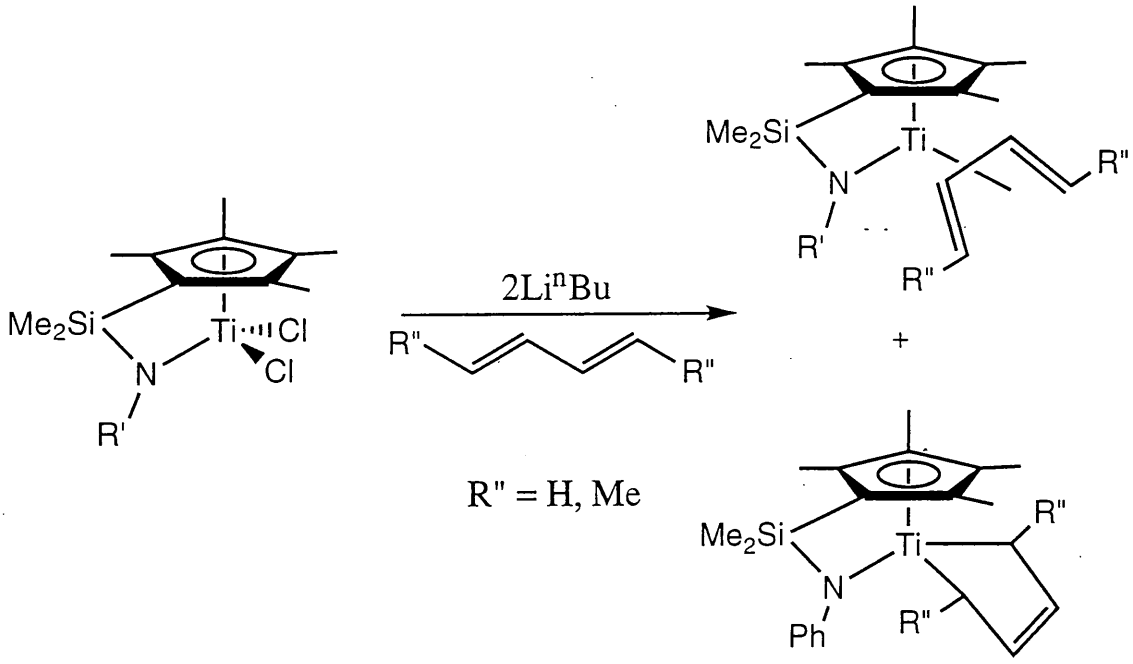
The Ti-C double bonds in the complexes $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^tBu](=CHCMe_2R'')(PMe_3)$ (R'' = Me, Ph) are assumed to be rotationally fixed as two orientations of the alkylidene ligands are observed. This differs from the bis(cyclopentadienyl) metal carbene compounds. Both of the linked amido-cyclopentadienyl complexes were reported to be inactive in ring opening polymerisation of strained cyclic olefins. The thermal decomposition of $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2Ph](CH_2SiMe_3)_2$, however, generates a complex (presumably an alkylidene) that polymerises norbornene with ring opening.[15]

Benzyne complexes are obtained by thermolysis of early transition metal dialkyl complexes containing at least one phenyl group.[61] The elimination of benzene to form benzyne intermediates at the metal fragment allows oxidative coupling with the unsaturated substrates $R'_2C{=}X$ (X = CR''_2, NR'', O, S, P) and $R'C{\equiv}X$ (X = CR', N).[61] Similar behaviour is exhibited by amide-functionalized cyclopentadienyl complexes. For instance, $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^tBu]Ph_2$ is thermolized in the presence of PMe_3 to give a phosphine-stabilised benzyne complex $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^tBu](\eta^2\text{-}C_6H_4)(PMe_3)$ that readily undergoes insertion reactions with alkynes, alkenes, nitriles or ketones (Scheme 1.8).[15, 42]



Scheme 1.8

Diene complexes of the type Ti[η^5:η^1-$C_5Me_4SiMe_2NR'$](1,3-diene) can be formed when dichloro complexes Ti[η^5:η^1-$C_5Me_4SiMe_2NR'$]Cl_2 (R' = Ph, ^{t}Bu) are treated with two equivalents of *n*-butyllithium in the presence of 1,3-dienes such as piperylene and 2,4-hexadiene.[62] The mode of diene coordination is very sensitive to the identity of R'. For R' = ^{t}Bu, the diene coordination mode prone-π at formally titanium (II) is found and proved by the crystal structure of Ti[η^5:η^1-$C_5Me_4SiMe_2N^tBu$](η^4-MeCH=CHCH=CHMe), while for R' = Ph an inseparable mixture of both non-interconvertible isomers (coordination mode prone-π at formally titanium (II) or supine-σ, π at formally titanium (IV), i.e.titanacyclopentene) results (Scheme 1.9).[15]

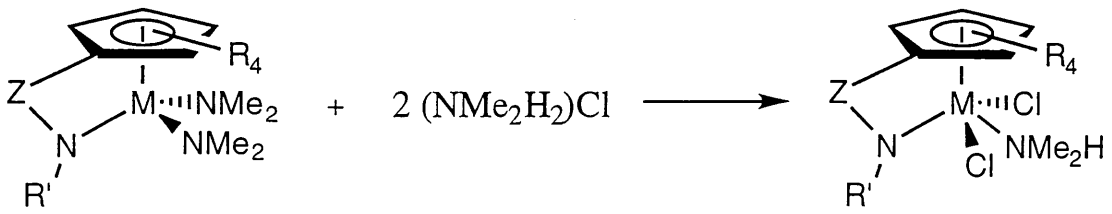


Scheme 1.9

1.3.3 Reactivity

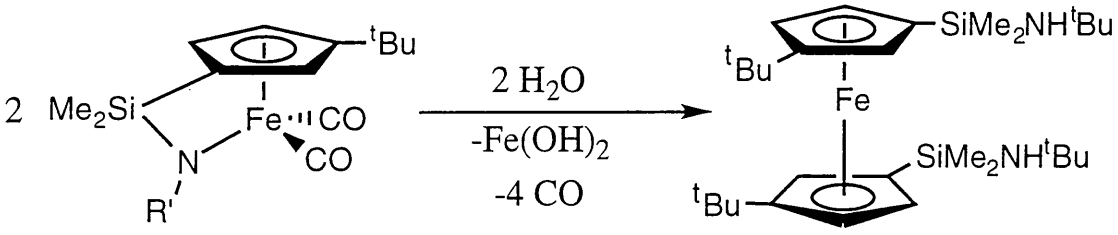
The conversion of the dichloro complexes $M[\eta^5:\eta^1\text{-}C_5R_4ZNR']Cl_2$ (M = Ti, Zr, Hf) to catalyst precursor dialkyl complexes $M[\eta^5:\eta^1\text{-}C_5R_4ZNR']R''_2$ (R" = Me, Ph, CH_2Ph, etc.), discussed in Section 1.3.2, is of obvious importance. Consequently, conversion of the diamido complexes, $M[\eta^5:\eta^1\text{-}C_5R_4ZNR'](NMe_2)_2$, to the corresponding dichloro derivatives is also of considerable relevance.

Treatment of the titanium complexes $Ti[\eta^5:\eta^1\text{-}C_5R_4ZNR'](NMe_2)_2$ with an excess of chlorotrimethylsilane or phosphorus pentachloride can effect complete conversion with good yields, but the corresponding reaction with $Zr[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu](NMe_2)$ (with two equivalents of chlorotrimethylsilane) gives dimeric $[Zr(\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl(\mu\text{-}Cl)]_2$.[48] Treatment of two equivalents of protic reagents such as HCl or $(NEt_3H)Cl$ with $Zr[\eta^5:\eta^1\text{-}C_5H_4ZN^tBu](NMe_2)_2$ produces $Zr[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu]Cl_2(NMe_2H)$, with the NMe_2H ligand coordinated *trans* to the appended amino group. However, the analogous reaction with the titanium complexes $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu](NMe_2)_2$ results in inseparable mixtures of $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu]Cl_2$ and $Ti[\eta^5\text{-}C_5H_4SiMe_2Cl]Cl_2(NMe_2)(NMe_2H)$.[48] The reaction of two equivalents of $(NMe_2H_2)Cl$ or $(NMe_2H_2)I$ with $M[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe](NMe_2)_2$ (M = Zr, Hf) gives high yields of $M[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]X_2(NMe_2H)$ (X = Cl, I).[40] Such results demonstrate the affinity of four-coordinate zirconium complexes for complexing additional L-type ligands (Equation 1.10).[15]



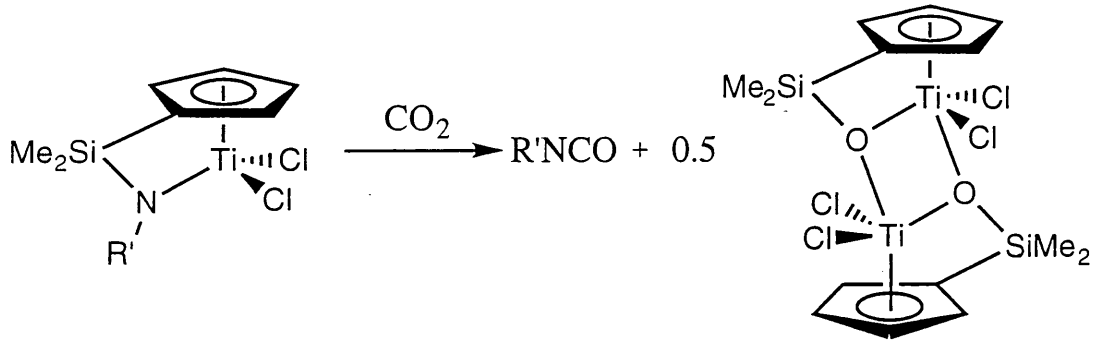
Equation 1.10

The other major consideration concerning such complexes is the reactivity of the bridging Si-N bond, mainly in titanium complexes. The ring strain of the chelate structure enhances the electrophilicity of the silicon atom, making the greater strength of the Si-Cl bond compared to the Si-N bond the driving force.[63] Extreme moisture sensitivity is demonstrated by the electron-rich late metal complex $Fe[\eta^5:\eta^1\text{-}(C_5H_3{}^tBu)SiMe_2N{}^tBu](CO)_2$ that gives the ferrocene derivative $Fe[(\eta^5\text{-}C_5H_3{}^tBu)SiMe_2NH{}^tBu]_2$ upon hydrolysis (Equation 1.11).[39]



Equation 1.11

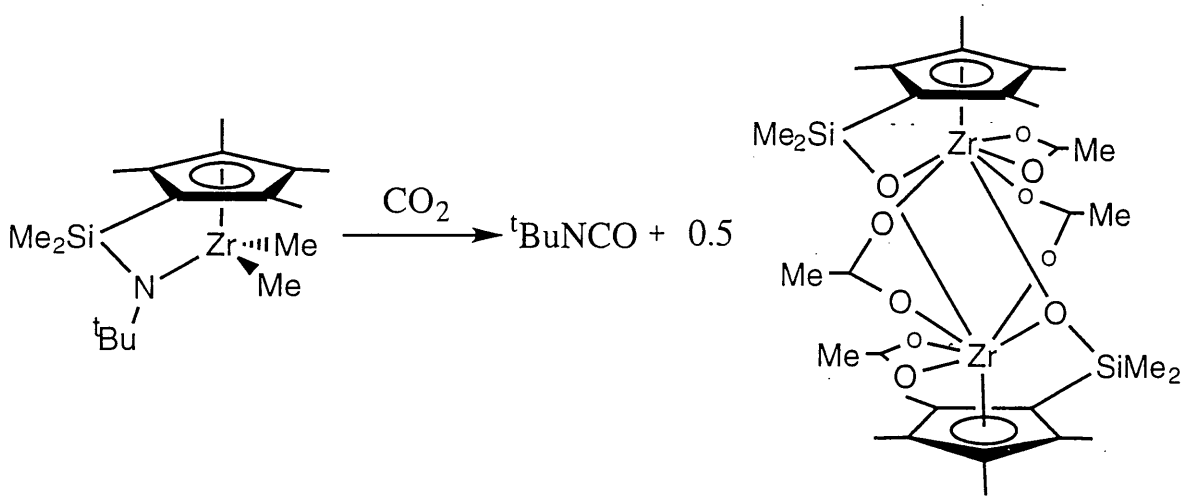
Reaction of carbon dioxide with complexes containing the $C_5R_4SiMe_2NR'$ ligand, such as $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2NR']Cl_2$ (R' = ^{t}Bu, CHMePh), is thought to commence with the insertion of carbon dioxide into the titanium-nitrogen bond to form first a carbamato bridge, followed by the subsequent extrusion of the isocyanate molecule OCNR'. Thus, the Si-N bridge is cleaved and a dimeric siloxide complex with a silicon-oxygen link, $[Ti(\eta^5:\mu:\eta^1\text{-}C_5H_4SiMe_2O)Cl_2]_2$, formed (Equation 1.12).[55(b)]



Equation 1.12

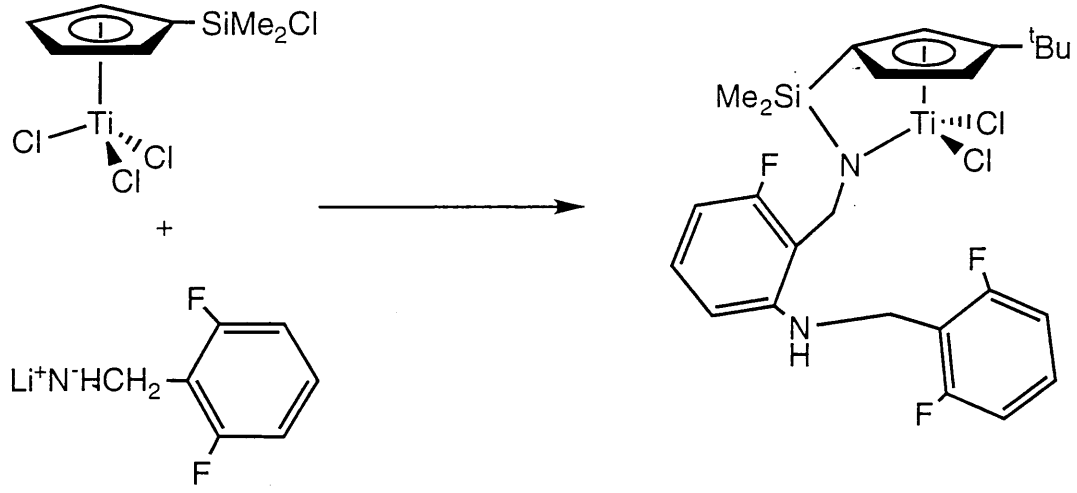
The reaction of two equivalents of CO_2 with $Zr[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N{}^tBu]Me_2$ proceeds with the formation of $[Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N{}^tBu)(\eta^2\text{-}O_2CMe)(\mu:\eta^2\text{-}O_2CMe)]_2$ which reacts

with additional CO_2 to afford the dimeric bridged siloxide $[Zr(\eta^5{:}\mu{:}\eta^1\text{-}C_5Me_4SiMe_2O)(\eta^2\text{-}O_2CMe)(\mu{:}\eta^2\text{-}O_2CMe)]_2$ with the concomitant elimination of OCN^tBu (Equation 1.13).[55, 56]



Equation 1.13

The niobium and tantalum amides $M[\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2N^tBu](NMe_2)_3$ undergo an unprecedented photo-induced rearrangement at room temperature, yielding the *tert*-butylimido complexes $M[\eta^5\text{-}C_5H_4SiMe_2NMe_2](=NR)(NMe_2)_2$ as a result of Si-N bond cleavage.[64]



Equation 1.14

Reaction at the linked-amide substituent has also been occasionally reported. For instance, reaction of $Ti[\eta^5\text{-}C_5H_4SiMe_2Cl]Cl_3$ and $Li(NHCH_2C_6H_3F_2\text{-}2,5)$ gives $Ti[\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5]Cl_2$ but the analogous reaction with the 2,6-difluorobenzyl derivative $Li(NHCH_2C_6H_3F_2\text{-}2,6)$ produces $Ti[\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2\{C_6H_3F\text{-}6\text{-}(NHCH_2C_6H_3F_2\text{-}2,6)\text{-}2\}]Cl_2$ (Equation 1.14).[47] The amido ligand is modified due to

nucleophilic aromatic substitution at one ortho-fluorine atom by another molecule of 2,6-difluorobenzylamide. This substitution may be facilitated by a titanium-fluorine interaction.

1.3.4 Structure

In an attempt to explain the specific polymerisation properties of group 4 metal complexes containing the linked amido-cyclopentadienyl ligand, the single crystal structures of many dichloro complexes of the type $M[\eta^5:\eta^1\text{-}C_5R_4ZNR']Cl_2$ have been elucidated. Some representative examples are compiled in Table 1.[15]

Compound	Cp-M-N, °	M-Cp, Å	M-N, Å
$Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu]Cl_2$	107.0	2.019	1.901(3)
$Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]Cl_2$	107.6	2.030	1.908(6)
$Ti[\eta^5:\eta^1\text{-}C_5Me_4(CH_2)_2N^tBu]Cl_2$	107.9	-	1.909(5)
$Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^iPr]Cl_2$	105.5	2.017	1.878(2)
$Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^iPr]Cl_2$	104.4	2.008	1.864(2)
$Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3N^iPr]Cl_2$	112.6	2.027	1.867(2)
$Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu](NMe_2)_2$	105.5	2.083	1.972(4)
$Zr[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]Cl_2$	102.0	2.163	2.056(6)
$Zr[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu](NMe_2)_2$	100.2	2.233	2.108(4)
$Y[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]\{N(SiMe_3)_2\}$	97.7	2.300	2.184(7)

Table 1

The complex $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^iPr]Cl_2$ (Figure 1.10) has a structure typical of its type.[47] The basic geometry consists of a three-legged piano-stool or pseudo-tetrahedral arrangement of the bifunctional amido-cyclopentadienyl ligand C_5R_4ZNR' and two terminal ligands X. Bonding of the cyclopentadienyl ligand C_5R_4 to the metal centre is in the usual η^5-fashion and the metal-ligand bond lengths are in the expected range. The metal centre is often unsymmetrically bound to the planar cyclopentadienyl ring due to the geometrical constraint of the chelating ligand. When Z = $SiMe_2$ or CH_2CH_2, the bridging atom bound to the cyclopentadienyl periphery is displaced from the plane of the cyclic π-system, while in the case of the longer bridge (Z = $(CH_2)_3$) this carbon atom is displaced away from the metal centre and is located above the cyclopentadienyl ring.[42, 47]

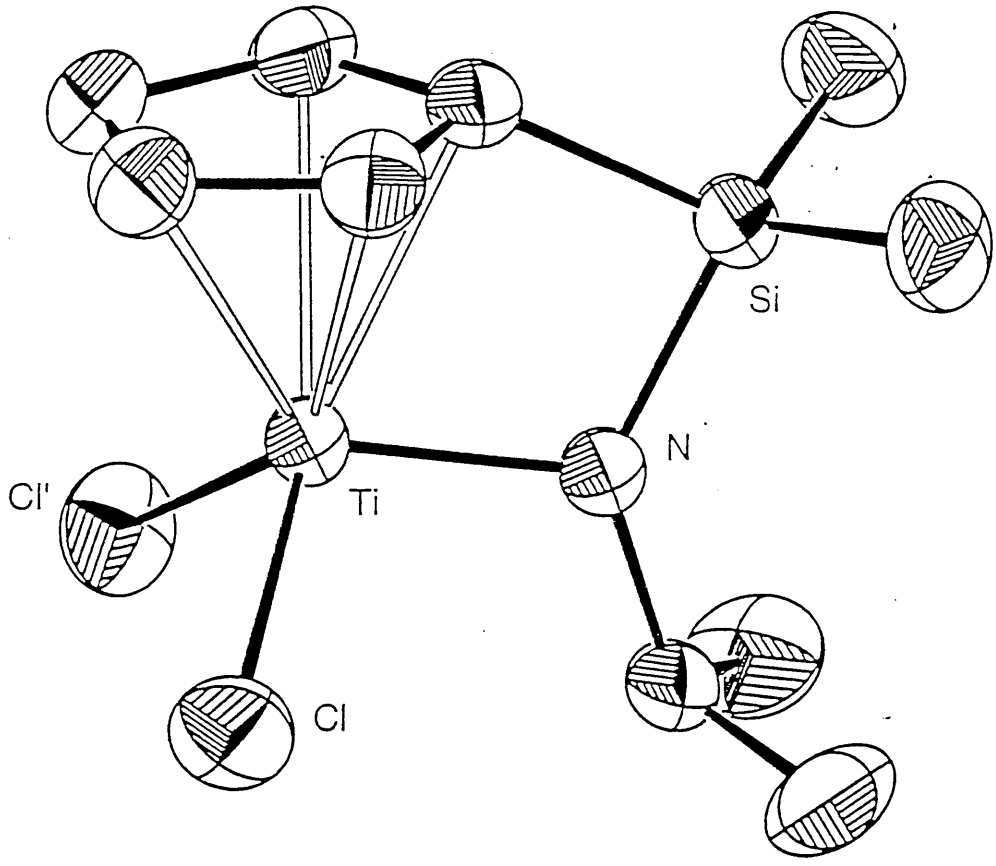


Figure 1.10

The distance between the metal and the amido-nitrogen is fairly sensitive to the nature of the metal fragment but is shorter than a metal-nitrogen single bond. For dichloro titanium (IV) complexes $Ti[\eta^5:\eta^1\text{-}C_5R_4ZNR']Cl_2$, bond lengths around (and sometimes shorter than) 1.9Å are observed whereas the distance varies between 1.96 and 1.97Å in titanium derivatives containing titanium-nitrogen single bonds.[65] These bond lengths are slightly larger than those reported for non-bridged monocyclopentadienyl amido complexes, though. For example, the Ti-N distances in $Ti[\eta^5:\eta^1\text{-}C_5R_4SiMe_2N^tBu]Cl_2$ are 1.901(3)Å (R = H)[48] and 1.908(6)Å (R = Me)[66] compared to 1.865(2)Å (R = H)[67] and 1.865(5)Å (R = Me)[67] in $Ti(\eta^5\text{-}C_5R_5)(N^iPr_2)Cl_2$. Thus, it appears that chelation disturbs an optimal overlap of the amido nitrogen p_π orbital with the titanium d_π orbital. This phenomenon is demonstrated by complexes such as the formally 18-electron diamido complex

$Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu](NMe_2)_2$, in which the value of the metal-nitrogen distance is 1.972(4)Å, indicating a less pronounced double bond character.[48] A notably longer metal-nitrogen bond of 2.007(4)Å is observed in the titanium (II) diene complex $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu](\eta^4\text{-}MeCH{=}CHCH{=}CHMe)$.[62]

The Cp(centroid)-M-N angles in complexes $M[\eta^5:\eta^1\text{-}C_5R_4ZNR']X_2$ typically range from 97-107°, which is 25-35° smaller than the Cp-N-Cp angles of 125-135° found in the corresponding 16-electron metallocene complexes $M(\eta^5\text{-}C_5R_5)X_2$,[9] implying the presence of strain within the ligand system and an openness of the coordination sphere. While there is a positive correlation between Cp-M-N angle and bridge length, too much importance should not be placed upon any relationship between this geometric parameter and reactivity.[54, 66] Chelation also results in a slight reduction of the metal-Cp distance as shown by the comparison of $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu]Cl_2$ (Ti-Cp: 2.019Å)[48] and $Ti(\eta^5\text{-}C_5H_5)(NH^tBu)Cl_2$ (Ti-Cp: 2.032Å).[68]

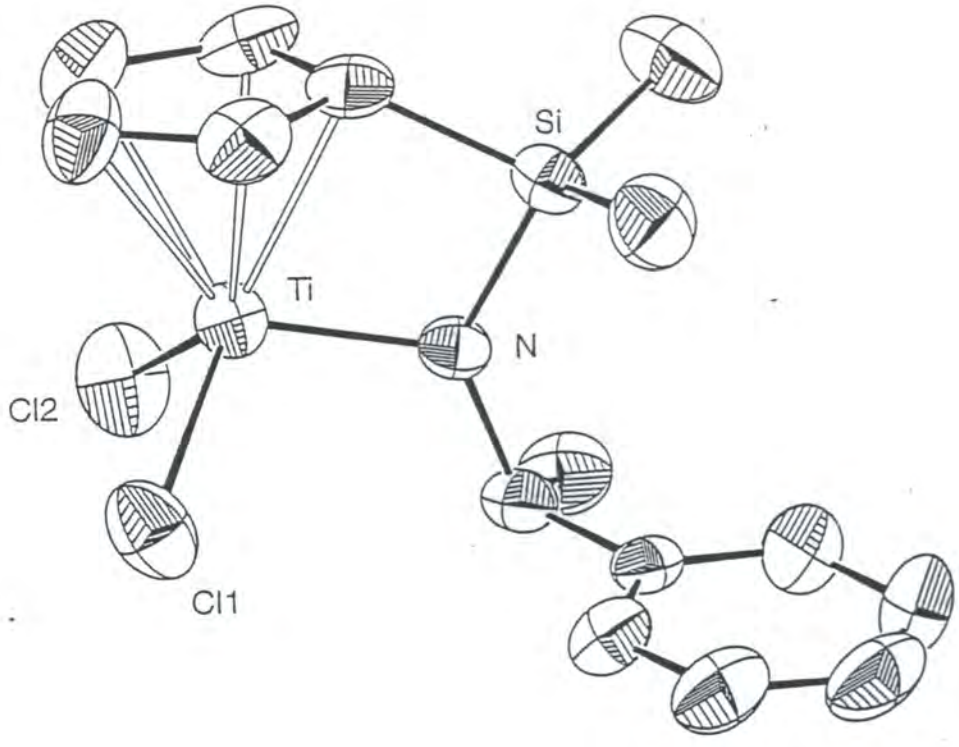


Figure 1.11

The most interesting feature in the X-ray structural analysis of the first optically active titanium complexes containing amido-cyclopentadienyl ligands (-)-(S)-$Ti[\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCHMePh]Cl_2$, is that the phenyl group is arranged coplanarly to the C_5H_4 ring, turned away from the metal centre (Figure 1.11).[46] Similarly, the benzyl group in $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5]Cl_2$ is turned away from the metal centre.[47]

It is a characteristic feature of complexes containing a secondary amido substituent R' for the methine proton to orientate itself towards the metal centre. This phenomenon is frequently demonstrated by *iso*-propyl-amido complexes such as $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^iPr]Cl_2$,[47] $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^iPr]Cl_2$[54] and $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3N^iPr]Cl_2$.[54]

Compound	**M-H$_{Methine}$, Å**	**M-N-C$_{Methine}$, o**	**δ(H$_{Methine}$), ppm**
(-)-(*S*)-$Ti[\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCHMePh]Cl_2$	2.84	120.5(3)	6.54
$Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^iPr]Cl_2$	2.79	117.4(1)	5.69
$Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2N^iPr]Cl_2$	2.67	114.2(2)	5.92
$Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3N^iPr]Cl_2$	2.38	104.5(1)	6.57

Table 2

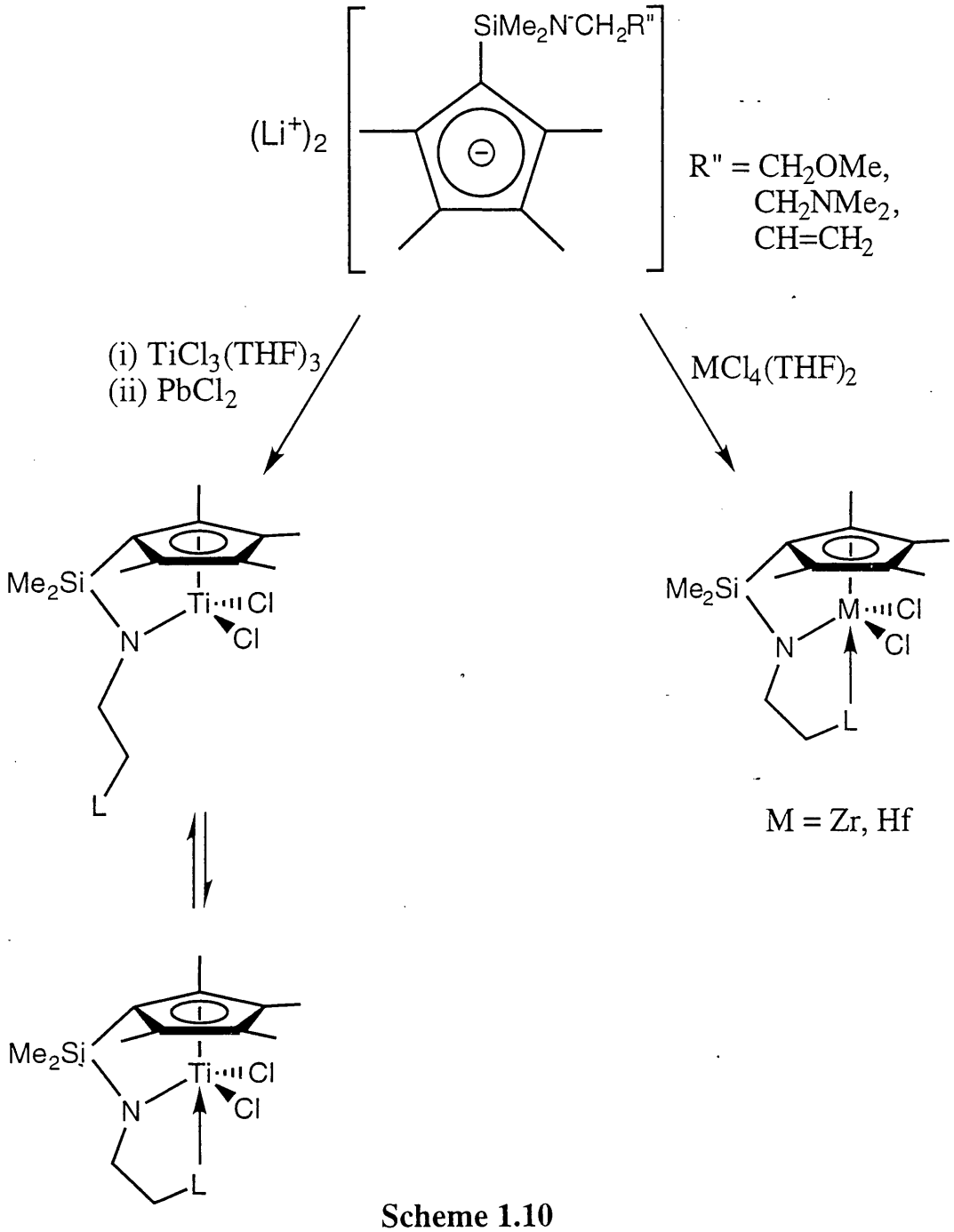
Table 2[15] displays values for M-N-$C_{Methine}$ angles and M-$H_{Methine}$ distances. Complexes with longer bridge lengths (Z = $(CH_2)_3$) show a β-agostic interaction not seen in complexes with Z = $SiMe_2$. Where Z = $(CH_2)_3$, the Ti-N-$C_{methine}$ angle and the Ti-$H_{methine}$ distance for the β-agostic interaction are similar to those found in the non-bridged cyclopentadienyl amido complex $Ti(\eta^5\text{-}C_5H_5)(N^iPr_2)Cl_2$,[67] where one of the *iso*-propyl groups is directed towards the metal centre as a result of a β-agostic interaction of the methine proton, leading to a Ti-$H_{methine}$ distance of 2.25Å and a Ti-N-$C_{methine}$ angle of 101.4(2)°.

The down frequency shifts for the C_{ipso} of the cyclopentadienyl group in the $^{13}C\{^1H\}$ NMR spectra of complexes of the type $Ti(\eta^5:\eta^1\text{-}C_5R_4ZR')Cl_2$ have been found to be characteristic of the presence of a chelating amido group. For instance, the ^{13}C chemical shift for the *ipso* carbon in $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ was reported to be 135.1ppm compared to 110.0ppm in $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2N^tBu)Cl_2$.[55]

1.3.5 Polydentate amido-cyclopentadienyl ligands

A desire to increase the Lewis acidity of early transition metal centres has led to the introduction of a new tridentate ligand system in which an additional weak neutral donor site is incorporated within the chelating amido-cyclopentadienyl ligand framework.[45] The possibility of further modification of the coordination sphere around a reactive transition metal centre is provided by such ligands, with donor groups such as OMe or NMe_2 attached to the amido functionality. The synthetic routes to group 4 metal complexes of these ligands are analogous to those used for simpler amido substituents. The tridentate-linked amido cyclopentadienyl ligands $[C_5Me_4SiMe_2NCH_2X]^{2-}$ (X = CH_2OMe, CH_2NMe, $CH{=}CH_2$) have been synthesized and coordinated at tetravalent titanium, zirconium and hafnium centres, using the metathetical pathway, to produce the hexane-soluble complexes $M[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2X]Cl_2$ (Scheme 1.10).[45, 15] Unsubstituted-cyclopentadienyl bridged

titanium derivatives, $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2X]Cl_2$ (X = CH_2OMe, CH_2NMe) can be prepared from $Ti[\eta^5:\eta^1\text{-}C_5H_4SiMe_2Cl]Cl_3$.[69]



Scheme 1.10

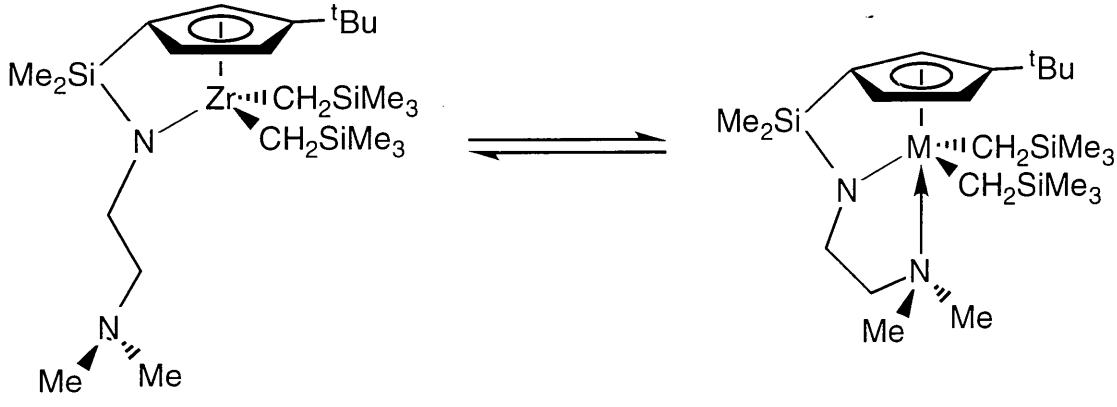
The question of whether the additional donor in such complexes is rigidly bonded or fluxional cannot be determined by ^1H or ^{13}C NMR spectroscopy as the molecules possess a mirror plane regardless of the coordination of the appended donor group.

Analogous dialkyl complexes can also be prepared and the dimethyl derivatives allow NOE measurements to be recorded in order to study the coordination mode. A spatial relationship between the $TiMe_2$ signal and OMe and NMe_2 groups could not be established for titanium complexes $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2X]Me_2$, but homologous zirconium compounds

$Zr[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2X]Me_2$ exhibit an NOE between the proton signals of the $ZrMe_2$ groups and the third donor function, OMe or NMe_2, indicating that the zirconium (and hafnium) complexes retain the intramolecular coordination in solution.[15] This is presumed to be due to the higher Lewis acidity of zirconium and hafnium in comparison to titanium.

Dialkyl complexes of the type $M[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe]R''_2$ (M = Zr, Hf) can be prepared with R'' = Me, Ph, CH_2SiMe_3 and CH_2Ph. Surprisingly, dialkyls with β-hydrogens (R'' = Et, ^{i}Pr, ^{t}Bu) can also be isolated in this series, with the crystal structure of the most thermally stable (dec.>90°C) of these complexes, $Hf(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(^nBu)_2$, showing the two *n*-butyl groups to be undistorted.[15]

The coordination mode of the NMe_2 function in the planar chiral derivatives $M[\eta^5:\eta^1\text{-}(C_5H_3{}^tBu)SiMe_2NCH_2CH_2NMe_2]Cl_2$ (M = Ti, Zr) can be assessed directly from NMR spectra. If the NMe_2 group is bound rigidly, nitrogen inversion is prevented. Consequently, two inequivalent methyl signals are detected, as is the case for the zirconium complex $Zr[\eta^5:\eta^1\text{-}(C_5H_3{}^tBu)SiMe_2NCH_2CH_2NMe_2]Cl_2$. Contrastingly, for the titanium derivative, $Ti[\eta^5:\eta^1\text{-}(C_5H_3{}^tBu)SiMe_2NCH_2CH_2NMe_2]Cl_2$, only one signal for the NMe_2 group is observed in the temperature range -80 to +80°C, suggesting that the coordination does not occur or is fluxional on the NMR time scale.[45] The bulky dialkyl $Zr[\eta^5:\eta^1\text{-}(C_5H_3{}^tBu)SiMe_2NCH_2CH_2NMe_2](CH_2SiMe_3)_2$ exhibits a fluxional bonding mode with an activation energy for N-Me exchange of $\Delta G^{\ddagger}$ (7°C) = 13.1kJ.mol^{-1} (Equation 1.15).[15]

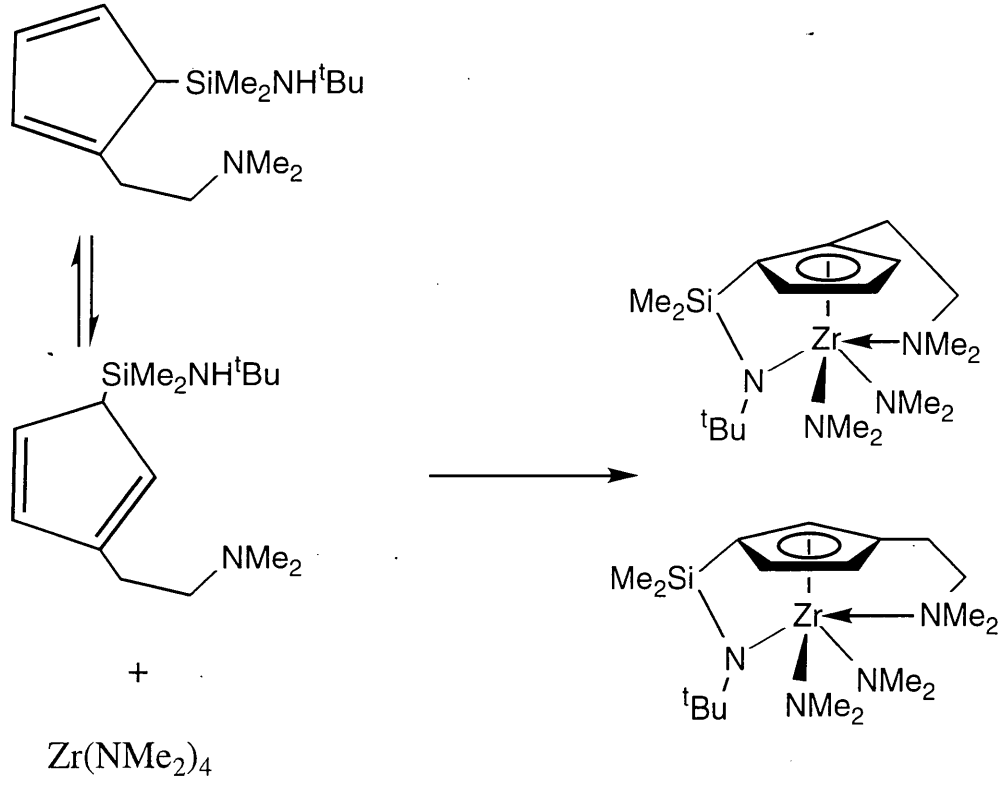


Equation 1.15

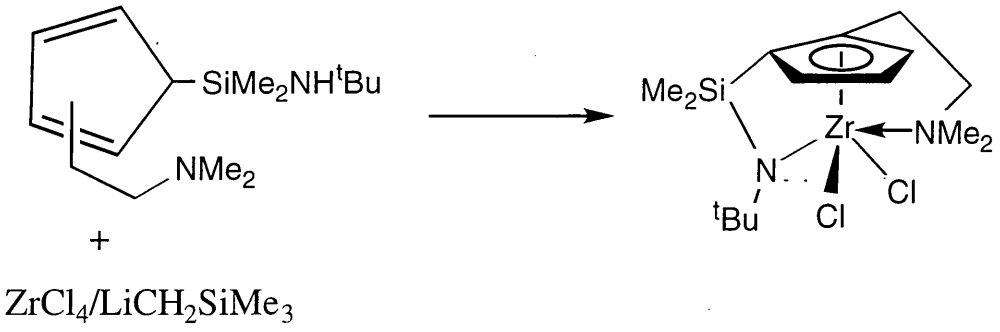
A tridentate ligand system in which the additional donor is attached directly to the cyclopentadienyl ring, $[C_5H_4(CH_2CH_2NMe_2)]SiMe_2NH^tBu$, was prepared in one step from $C_5H_4CH_2CH_2NMe_2$, $SiMe_2Cl_2$ and *tert*-butylamine. The product was obtained in 71% yield as a mixture of 1,3- and 1,2-isomers in a 7:3 ratio. The ligand was initially attached to scandium in an efficient alkane elimination by treatment of *in situ* generated $Sc(CH_2SiMe_3)_3(THF)_2$ with the neutral ligand $[C_5H_4(CH_2CH_2NMe_2)]SiMe_2NH^tBu$, producing the alkyl scandium species

$Sc[\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)SiMe_2N^tBu](CH_2SiMe_3)$.[70] The complex was produced in 52% yield as the 1,3-isomer and the reaction was 100% diastereoselective for the (1S, R_{Sc})/(1R, S_{Sc}) pair of enantiomers. When treated with dihydrogen, the complex gave two of four possible μ-dihydrides $[Sc\{\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)SiMe_2N^tBu\}(\mu\text{-}H)]_2$. Thermolysis of $Sc[\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)SiMe_3N^tBu](CH_2SiMe_3)$ at 70°C for three days results in the loss of $SiMe_4$, producing a mixture of two dimeric compounds with bridging methylene units.[70]

The tridentate ligand was also reacted with $Zr(NMe_2)_4$ to give a mixture of bis-amido complexes in which the ligand was 1,2- and 1,3-substituted (Scheme 1.11).[15, 71] The analogous dichlorides were synthesized from this mixture using $NMe_2H.HCl$ and the 1,3-isomer isolated. This was easily methylated using methyllithium to form $Zr[\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)SiMe_2N^tBu](CH_3)_2$ and the cationic alkyls $[Zr\{\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)SiMe_2N^tBu\}(CH_3)]^+[R'B(C_6F_5)_3]^-$ (R' = CH, CF) were prepared via methide abstraction by Lewis acids ($B(C_6F_5)_3$ and $[(Ph_3C)^+(B(C_6F_5)_4)^-]$). Zirconium complexes of the ligand as its 1,2-isomer were obtained from alkane elimination reactions with zirconium alkyls R_nZrCl_{4-n} (R = CH_3, n = 3; R = CH_2SiMe_3, n = 2) (Equation 1.16).[71] NMR data suggest that coordination of the NMe_2 group is fluxional and the X-ray crystal structure of $Zr[\eta^5:\eta^1:\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)SiMe_2N^tBu]ClMe$ reveals a weak donor bond between the zirconium and the amine ligand.

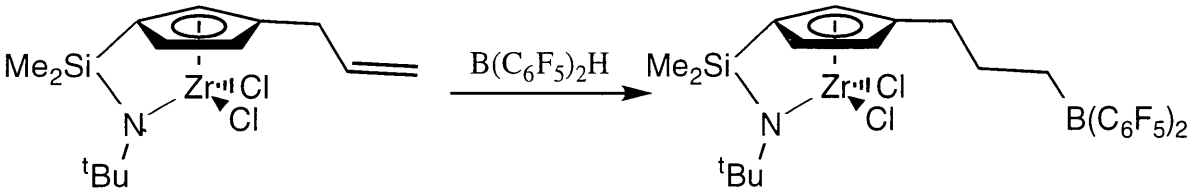


Scheme 1.11

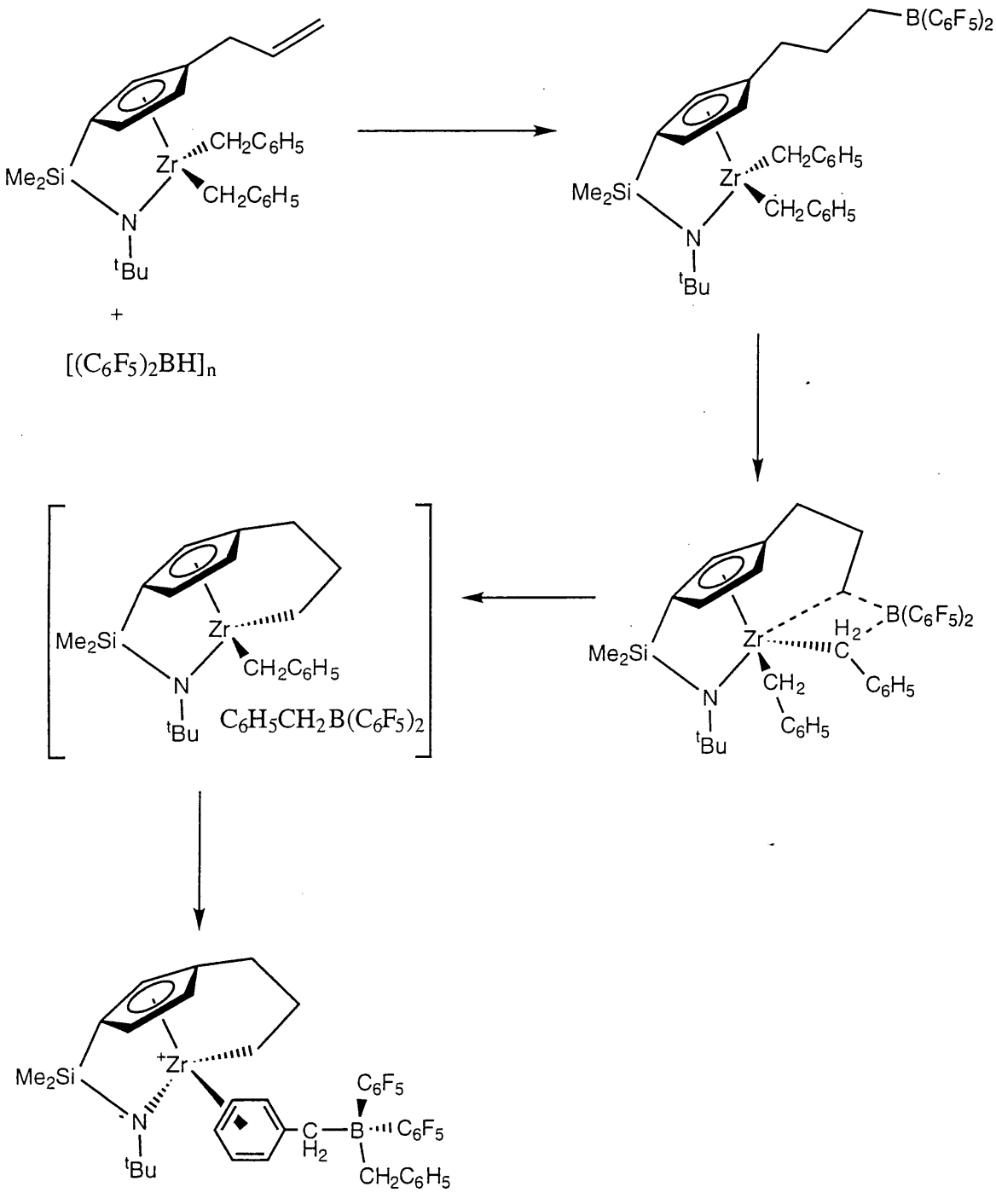


Equation 1.16

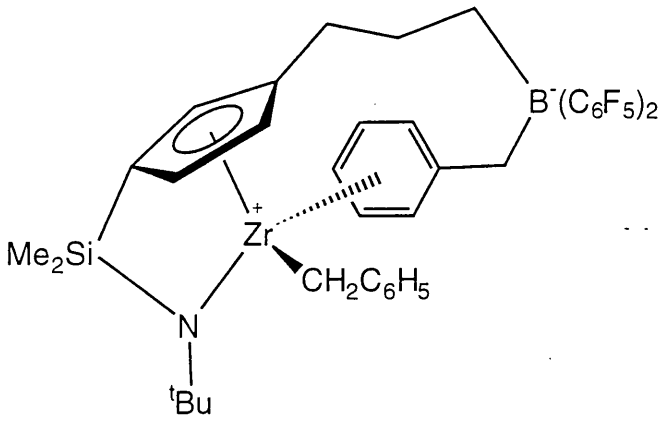
Alternative tridentate ligands in which the additional donor is attached to the cyclopentadienyl ring have also been reported. The reaction of $Zr[\eta^5:\eta^1\text{-}C_5H_3(C_3H_5)SiMe_2N^tBu]Cl_2$ with the electrophilic borane $[(C_6F_5)_2BH]_n$ led to the hydroboration of the pendant double bond, giving $Zr[\eta^5:\eta^1\text{-}C_5H_3(CH_2CH_2CH_2B(C_6F_5)_2)SiMe_2N^tBu]Cl_2$ (Equation 1.17).[72] Attempts to alkylate this compound met with failure and hydroborations of most of the analogous dialkyl derivatives were not clean. However, the bis(benzyl) complex $Zr[\eta^5:\eta^1\text{-}C_5H_3(C_3H_5)SiMe_2N^tBu](CH_2Ph)_2$ reacted cleanly with $[(C_6F_5)_2BH]_n$ to yield a complex, E, whose structure was elucidated using various NMR techniques. In this complex, both benzyl groups on zirconium were observed to transfer to boron, giving the cationic zirconium compound, E, stabilised by a coordinated benzyl group from the counterion $[(C_6H_5CH_2)B(C_6F_5)_2]$ (Scheme 12).[72] It is thought that a three-carbon tether is too long to avoid this exchange, thus leading to the production of E rather than the desired complex F (Figure 1.12).[72]



Equation 1.17


Me2Si
Zr
CH2C6H5
CH2C6H5
N
tBu
+
[(C6F5)2BH]n
B(C6F5)2
C6H5CH2B(C6F5)2
H2
C
CH2
C6H5
+Zr
C6F5
B
H2
E

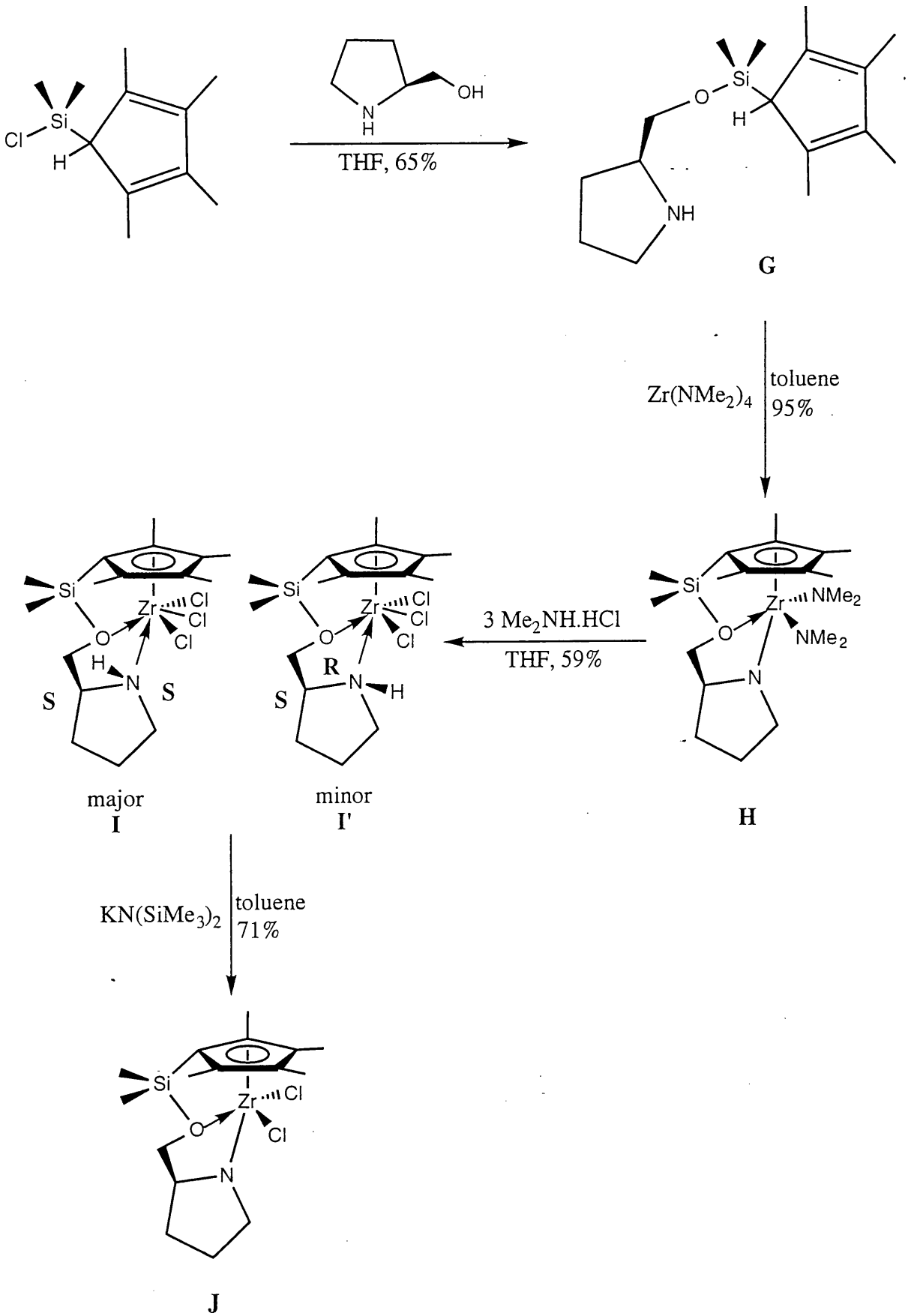
Scheme 1.12



F

Figure 1.12

An interesting tridentate ligand complex of relevance to the work in this thesis is formed from the reaction of dimethyl(tetramethylcyclopentadienyl)chlorosilane with (S)-(-)pyrrolidine methanol (prolinol) (Scheme 13)[73]. The resulting ligand, $(C_5Me_4H)SiMe_2OCH_2[(-)\text{-}(S)\text{-}C_4H_7NH]$, can be reacted with $Zr(NMe_2)_4$ to produce a linked amido complex, H, that upon treatment with $Me_2NH.HCl$, forms a diastereomeric mixture of the N-protonated complexes, I and I'. The dichloro complex, J, can subsequently be prepared and both I and J were shown to exhibit a limited ethylene polymerisation activity.[73]

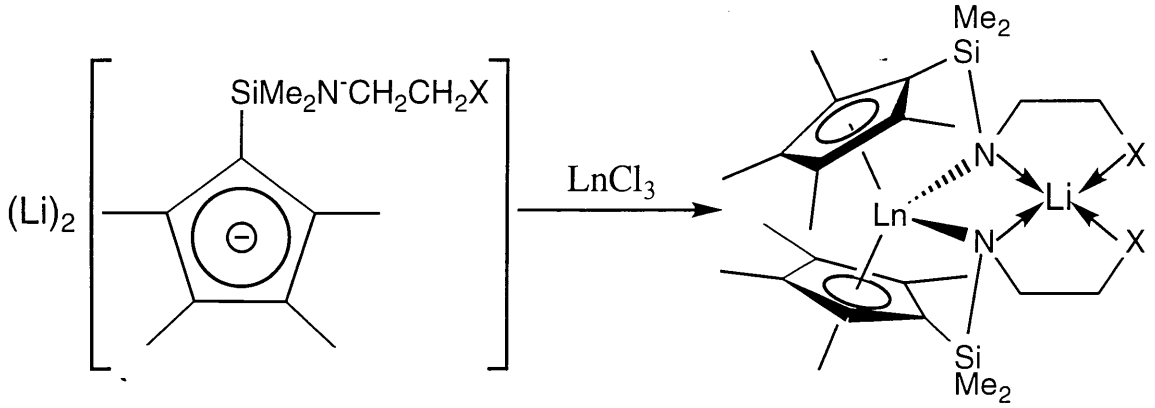

Cl
Si
H
OH
N
H
THF, 65%
O
Si
H
NH
G
Zr(NMe2)4
toluene
95%
Si
Zr
NMe2
NMe2
O
N
H
3 Me2NH.HCl
THF, 59%
Si
Zr
Cl
Cl
Cl
O
H
N
S
S
major
I
R
S
minor
I'
H
KN(SiMe3)2
toluene
71%
J

Scheme 1.13

1.3.6 Complexes with two amido-cyclopentadienyl ligands

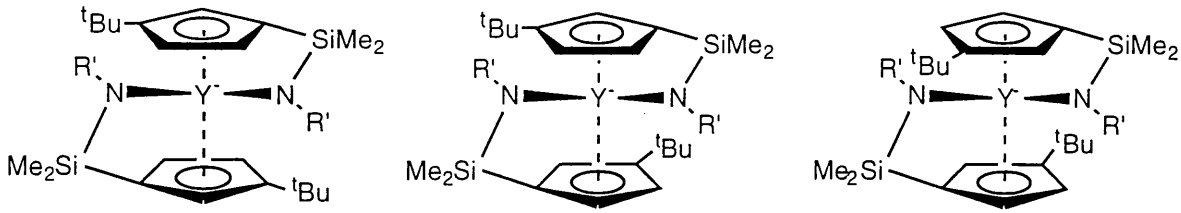
When an excess of the dianionic linked-amido-cyclopentadienyl ligand is used during the synthesis of half-sandwich complexes, it is sometimes possible for double coordination to occur, producing metallocene complexes of the type $[M(\eta^5:\eta^1\text{-}C_5R_4ZNR')_2]$ (where Z is a carbon or silicon bridge).[45, 69, 74] Neutral complexes with a characteristic C_2-symmetric metallocene structure, such as $Zr[\eta^5:\eta^1\text{-}C_5H_4SiMe_2NPh]_2$ are formed with group 4 metals,[53] while group 3 metals produce anionic complexes of the composition $[M(\eta^5:\eta^1\text{-}C_5R_4ZNR')_2]^-$.[15]

Such complexes are easily isolated when tridentate ligands of the type $C_5R_4SiMe_2NCH_2CH_2X$ (X = OMe, NMe_2) are used.[75] The hydrocarbon-soluble, heterobimetallic complexes $Li[M(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$ (M = Y, Lu) are formed in good yields from the reaction of $Li_2(C_5R_4SiMe_2NCH_2CH_2X)$ with anhydrous yttrium or lutetium trichloride (Equation 1.18).[15] The crystal structure of $Li[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)_2]$ reveals the metallocene unit tightly coordinating the lithium ion together with the ligand side chains. The amido nitrogen atom shows a distorted tetrahedral geometry in accordance with a formal 20-electron configuration at the rare earth metal centre and the yttrium-nitrogen bond is significantly longer than in $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)\{N(SiMe_3)_2\}$.[55]



Equation 1.18

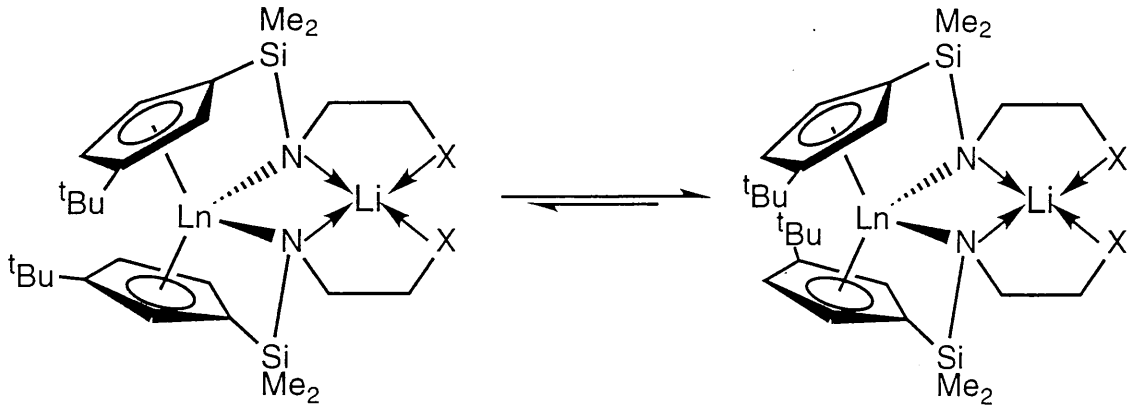
When a *tert*-butyl-cyclopentadienyl ligand is employed, three diastereomeric pairs of enantiomers are expected (Figure 1.13).[15]



(*R*, *R*) (*R*, *S*) (*S*, *S*)

Figure 1.13

The sterically more constrained (*R*, *S*)-isomer is preferentially formed under kinetic control. This is converted into the thermodynamically more stable C_2-symmetric (*R*, *R*)-isomer by donor solvents such as THF (Equation 1.19).[15]



(*R*, *S*) (*R*, *R*)

Equation 1.19

Interestingly, these complexes were shown to be active in the ring-opening polymerisation of ε-caprolactone. The high molecular weight (M_n > 30 000) and moderate polydispersity (M_w/M_n < 2.0) poly(ε-caprolactone)s obtained are produced by the action of the nucleophilic amido-nitrogen atom.[75]

1.4 Application Of Amide Functionalized Cyclopentadienyl Complexes In Catalysis

1.4.1 Polymerisation of ethylene, α-olefins and dienes

Olefin polymerisation is by far the area of overwhelming interest in the applications of linked amido-cyclopentadienyl ligands. As was mentioned earlier, the introduction of group 3 and 4 metallocenes revolutionised the area of Ziegler-Natta catalysis, the process by which vast quantities of polyethylene and polypropylene are made at atmospheric pressure and ambient temperature. However, the problems associated with such complexes prompted a search for even more effective systems, resulting in huge interest in group 4 metal complexes containing linked amido-cyclopentadienyl ligands, sometimes referred to as "constrained geometry catalysts".[66] There has been an almost explosive growth of interest and activity in synthesizing and testing these complexes which have the potential to produce polyolefins with new rheological properties and good processability at temperatures as high as 160°C. Such interest has now spread to the analogous group 3 and 5 complexes.

The aspecific oligomerization of α-olefins propylene, 1-butene and 1-pentene was found to be catalysed by the dimeric scandium hydride complex $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(PMe_3)]_2(\mu\text{-}H)_2$.[38] This gave an advantage over the scandocenes, but the polymerisation was shown to be slow, giving relatively low molecular weights (Mn = 4000 for poly(1-butene), 3000 for poly(1-pentene)), with addition of PMe_3 further reducing the polymerisation rates. More active catalyst precursors were found in the dimeric Lewis-base-free n-alkyl complexes $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)]_2(\mu\text{-}CH_2CH_2R)_2$ (R = Me, Et) which gave higher polymerisation rates and higher molecular weights (Mn = 6000 for poly(1-pentene), 9600 for polypropylene).

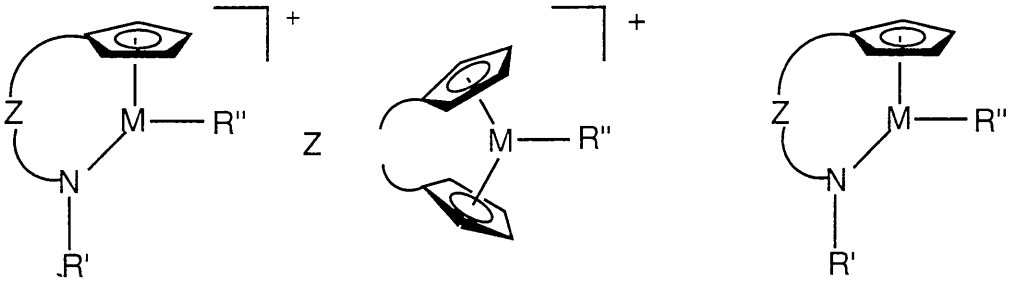
It appears that titanium complexes $Ti[\eta^5:\eta^1\text{-}C_5Me_4ZNR']Cl_2$ (where Z is the bridge backbone) activated with methylaluminoxane, will be the commercially utilised catalysts for olefin polymerisation. These catalysts have been shown to form high molecular weight polyethylene with long-chain branching, resulting from the incorporation of oligoethylene chains formed by β-hydride elimination.[66] In addition, useful properties as copolymerisation catalysts have been observed, allowing efficient and uniform incorporation of higher α-olefins such as 1-octene to produce low-density polyethylene with thermoelastic properties. The ability to incorporate higher olefins is thought to be a result of the coordination sphere being more open in comparison to conventional metallocene systems.[66, 76] It is interesting to note, however, that zirconium systems do not exhibit the same high activity as their titanium analogs,[66, 77] as an open coordination site can sometimes turn into a disadvantage with significant regoirregularity and low selectivity being occasionally observed.

Liang *et al.* recently coordinated amide functionalized cyclopentadienyl ligands to chromium (III) to produce the first constrained geometry chromium alkyls in the hope of generating a

new family of Cr-based copolymerisation catalysts. The polymerisation of ethylene was found to be catalysed by the complex $Cr[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2{}^tBu]CH_2SiMe_3$, but this system is unable to polymerise 1-hexene, which is head-to-tail dimerized with a small amount of internal olefin formed.[57]

Catalytic activity was found to be influenced by the nature of the ligand substituents R in the C_5R_4 ring and the amido substituent R' in NR'. This dependence of activity is proposed to be due to electronic properties imparted by R, R', (and Z), since a peralkylated cyclopentadienyl ring and a *tert*-butyl group as amido-substituent R' seem to be preferable,[66] although, as both of theses groups are bulky, steric factors could also have an influence. The most significant influence on catalytic activity, however, is the length of the bridge Z, with catalyst precursors with the shorter bridge Z = $SiMe_2$ and CH_2CH_2 often giving the best polymerisation characteristics. This observation has been recently contradicted, however, by Sinnema *et al.*, who found the $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_nN^iPr]$ system to be several times more efficient in the homopolymerisation of ethene for n = 3 than for n = 2.[54] They also found that activity was higher for R' = Me in the $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NR']$ system than for R' = ^{i}Pr or ^{t}Bu. It is still thought that the bite angle of the chelating ligand (angle Cp-Ti-N) is a crucial influencing factor on the performance of a catalyst.

The active species in polymerisation reactions is proposed to be the 12-electron alkyl cation of the type $[M(\eta^5:\eta^1\text{-}C_5R_4ZNR')R'']^+$, K (Figure 1.14).[52, 78] This is in contrast to the 14-electron group 4 metallocenium polymerisation catalysts $[M(\eta^5\text{-}C_5R_5)_2R'']^+$, L, but in analogy with the scandium catalysts described earlier, M.

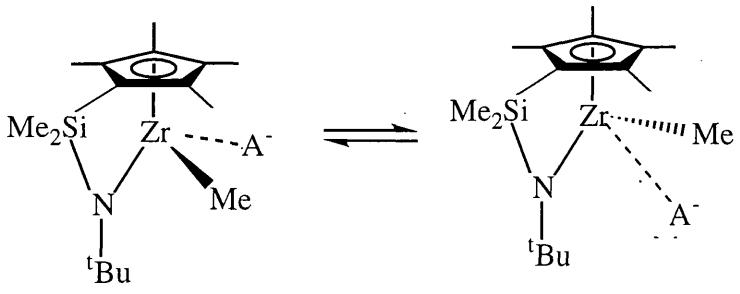


K **L** **M**

Group 4 Group 4 Group 3

Figure 1.14

The catalytic species can be generated either by reaction with methylaluminoxane or by reacting a dialkyl complex with a Lewis acid such as $B(C_6F_5)_3$. Variable temperature NMR studies have revealed an activation barrier of 80.9(2) kJmol^{-1} for the ion pair reorganisation and symmetrization (Equation 1.20)[15] caused by the back-skip of the alkyl group in $[Zr(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Me]^+[MeB(C_6F_5)_3]^-$.[77]



$A^- = MeB^-(C_6F_5)_3$, $B^-(C_6F_4X)_4$, $FAl^-(C_{12}F_9)_3$

Equation 20

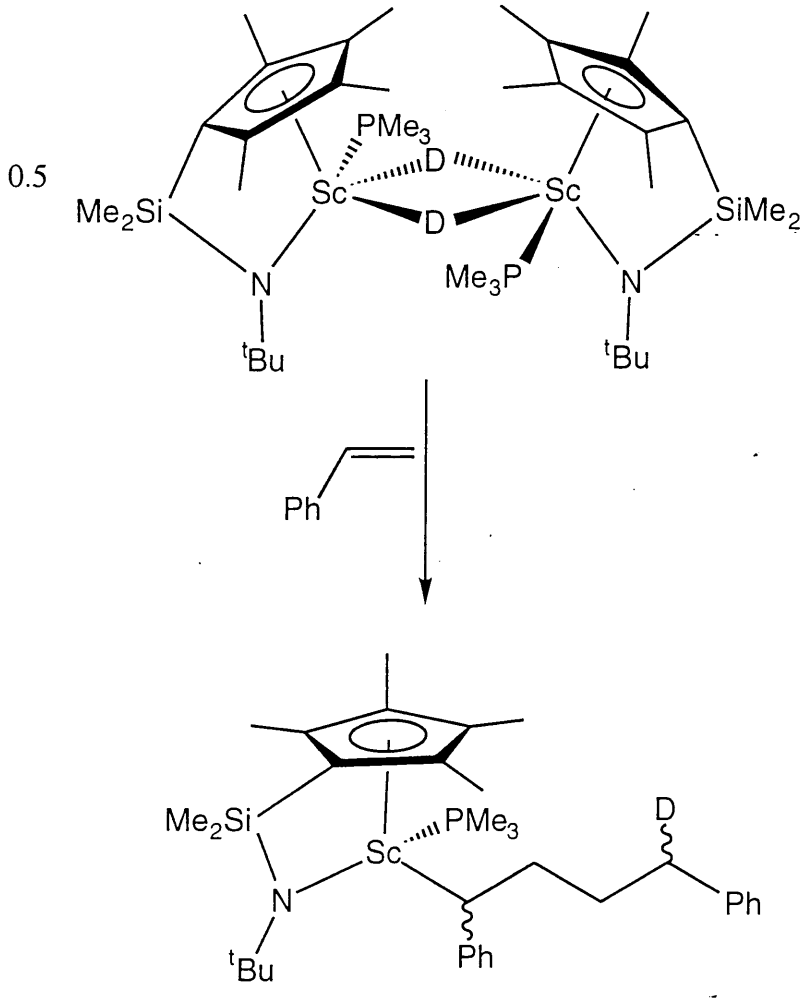
For the complexes $[Zr\{\eta^5:\eta^1\text{-}C_5H_4(CH_2)_nNR'\}(CH_2Ph)]^+[PhCH_2B(C_6F_5)_3]^-$, a strong dependence on the bridge length n and the amido-substituent R' has been found for the position of the equilibrium between solvent- separated ion pair and the contact ion pair in which the anion is η^6-coordinated to the metal centre through the benzyl phenyl group. This can give a reasonable indication of the change in steric requirements of the ligand upon variation in bridge length and/or substitution on the amido functionality. For example, in the reaction products of $(C_5R_5)Zr(CH_2Ph)_3$ with $B(C_6F_5)_3$ the phenyl group of the anion is η^6-bound for R = H, but exists as a solvent separated ion pair for R = Me. However, the observed ligand dependence of the polymerisation efficiency does not clearly correlate with overall ligand steric hindrance as deduced from such studies and the match between the metal centre and bridge length appears to be of prime importance.[54]

Diene complexes such as $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR'](1,3\text{-diene})$ may serve as precursors for cationic species,[62] as addition of $B(C_6F_5)_3$ leads to the formation of a zwitterionic structure, as was also observed in a zirconocene catalyst generated from $Zr(\eta^5\text{-}C_5H_5)(\eta^4\text{-}1,3\text{-diene})$ and $B(C_6F_5)_3$.[79]

The polypropylene resulting from the propylene polymerisation catalysed by methylaluminoxane-activated $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]Cl_2$ is atactic with some slightly syndiotactic preference ([rrrr]) = 20%) and 2-5% regioirregularity caused by 2,1-insertion. Isospecificity is not increased by incorporating a chiral amido substituent R'' in one diastereomer of $Ti[\eta^5:\eta^1\text{-}C_9H_6SiMe_2NCHMePh]Cl_2$, for instance.[80] Curiously, the fluorenyl-based system $Zr[\eta^5:\eta^1\text{-}C_{13}H_8SiMe_2N^tBu]Cl_2$ is thought to function as a syndiospecific catalyst when activated with methylaluminoxane and as an isospecific catalyst when activated with a Lewis acid.[58] It has been proposed that a tight ion pair may force the back-skip of the growing polypropylene chain to take place prior to the next insertion, eventually resulting in isospecificity.[81] In general, the significant regioirregularity and low stereoselectivity of resulting polymers indicates a considerable opening up of the reaction site when one cyclopentadienyl ligand in an *ansa*-metallocene is replaced by an amido group.

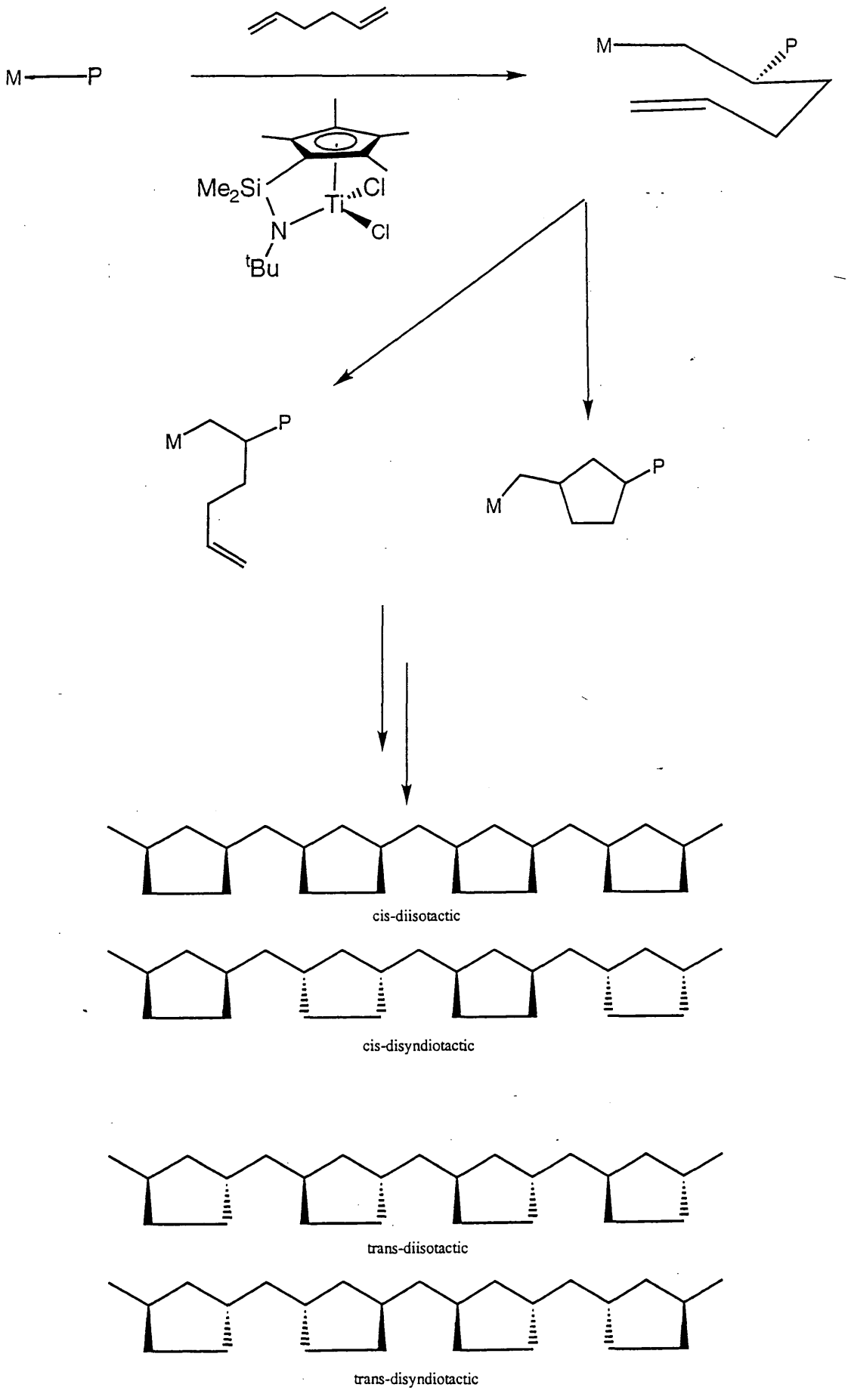
Copolymerisation

Conventional Ziegler catalysts usually tend to induce homopolymerisation of each of the monomers involved and the efficient copolymerisation of ethylene with styrene became possible only with the advent of metallocene catalysts. With such catalysts, poly(ethene-*co*-styrene) could be formed but the incorporation of styrene was still low. Amide-functionalized cyclopentadienyl systems were found to exhibit a considerable improvement on this and it has been recently demonstrated that ethylene-styrene copolymer with up to 30 mol% of styrene can be produced at a reasonable rate using what proved to be one of the best pro-catalysts, $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]Cl_2$.[82] In this recent study, ethene was copolymerised with styrene using five different methylaluminoxane activated complexes of the general composition $M[(Cp)SiMe_2NR']Cl_2$, varying the substituents on the cyclopentadienyl ring, Cp, and the amide, NR'. All complexes produced random poly(ethene-*co*-styrene) without any regioregular or stereoregular microstructure but the reaction characteristics were found to vary with changes in the cyclopentadienyl and amide substituents. The highest catalytic activity was shown by the complex with Cp = tetramethylcyclopentadiene, R' = ^{t}butyl, M = Ti. The fluorenyl-substituted complex (R' = ^{t}butyl, M = Zr) produced the highest molecular weight polymer and the complexes with Cp = 3-trimethylsilyl-1-indenyl, R' = ^{t}butyl, M = Ti and Cp = fluorenyl, R' = benzyl, M = Ti promoted high styrene incorporation.[82] Moreover, ^{13}C NMR spectroscopic microstructure analysis of the copolymer suggests that the maximum amount of styrene incorporated appears to be 66 mol% as no more than two styrene units coupled in a tail-to-tail manner are present in the chain.[83] Once a secondary insertion of styrene has occurred, following the primary insertion of the initial styrene, a further styrene unit cannot be inserted in the polymer chain. This proposal is supported by the isolation of the scandium complex $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(PMe_3)](CHPhCH_2CH_2CHDPh)$ from $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(PMe_3)]_2(\mu\text{-}D)_2$ that cannot insert further styrene (Equation 1.21).[38]



Equation 1.21

Methylaluminoxane-activated $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]Cl_2$ is also known to catalyse cyclopolymerisation of 1,5-hexadiene, producing a polymer containing randomly distributed *cis*- and *trans*-cyclopentane rings (Scheme 1.14).[84]


M
P
Me2Si
Ti
Cl
Cl
N
tBu
cis-diisotactic
cis-disyndiotactic
trans-diisotactic
trans-disyndiotactic

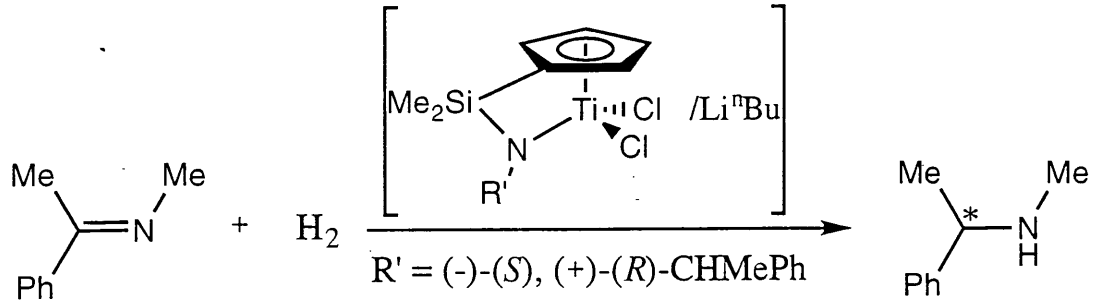
Scheme 1.14

The recent investigation by Mülhaupt and co-workers on ethene/1-octene and ethene/1-butene copolymerisation using various methylaluminoxane-activated metallocene catalysts tested silylene-bridged substituted bis(indenyl) zirconocene systems and half sandwich titanocene. The influence of the ligand substitution on comonomer incorporation, catalyst activity, molar mass, molar mass distribution, degree of polymerisation and copolymerisation parameters was evaluated. In ethene/1-octene copolymerisation, the highest comonomer incorporation was achieved with MAO-activated $Ti[\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N^tBu]Cl_2$ catalyst, although the best performance in terms of comonomer incorporation combined with high catalyst activity and polymer molar mass was found for silylene-bridged bis(indenyl) zirconocenes. The workers concluded that both silylene-bridged bis(indenyl) zirconocenes and half sandwich titanocenes offer attractive synthetic potential to prepare copolymers covering the entire feasible composition range.[85]

1.4.2 Hydrogenation

There are several examples of catalytic hydrogenation reactions being achieved using metallocene (mainly titanocene or zirconocene)[86, 87] and also dicyclopentadienyl lanthanide systems.[88, 89] In addition, the catalytic enantioselective hydrogenation of substituted olefins and, in particular, of imines has been successfully achieved using activated chiral Brintzinger-type titanocene and zirconocene derivatives.[90]

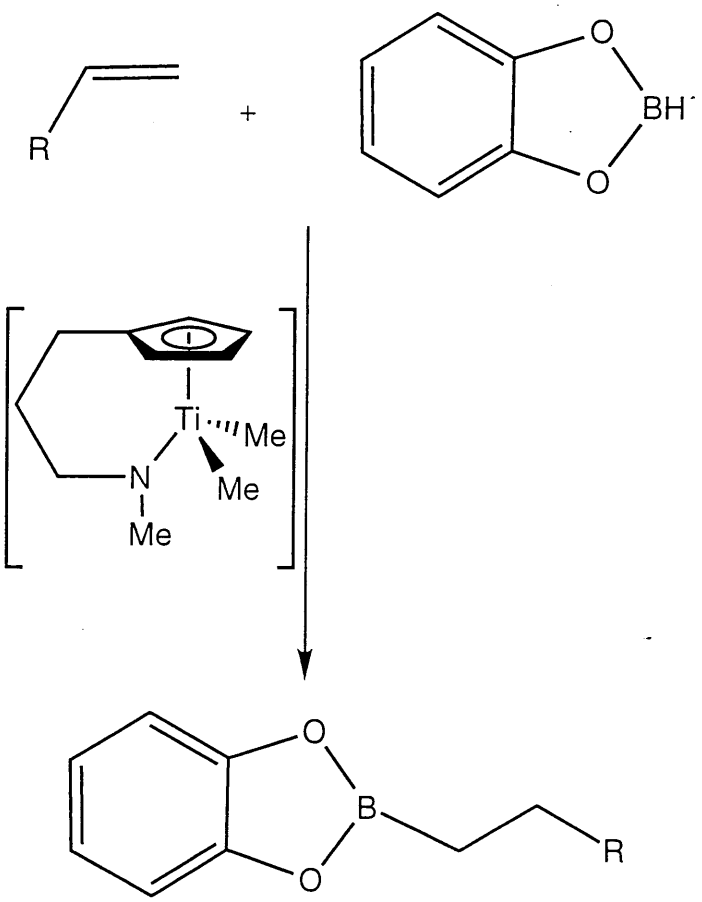
Similarly active hydrogenation catalysts for imines are generated when optically active titanium complexes of the type $Ti[\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR']Cl_2$ (R = H, Me: R' = CHMePh) are treated with Li^nBu.[46] Okuda *et al.* found these complexes to catalyse the hydrogenation of imines such as acetophenone *N*-benzylimine. The catalytic efficiency is comparable to that observed with titanocene derivatives, although enantioselectivity is low. By analogy with the titanocene system, the active species is proposed to be a titanium (III) hydrido species, possibly of the type $Ti[\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR']H$ (Equation 1.22).[46]



Equation 1.22

1.4.3 Hydroboration

Hydroboration of alkenes with catecholborane is known to be catalysed by metallocenes of group 3 metals.[10(c)] Teuben and co-workers found the complexes $Ti[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]Me_2$ and $Zr[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe]X_2$ (X = BH_4, CH_2Ph) to form stable catalysts in the hydroboration of 1-hexene using catecholborane as the boration agent. A moderate catalytic performance was observed, which it was speculated may be improved by using larger metal centres such as lanthanides (Equation 1.23).[91]



Equation 1.23

1.5 Summary

The overwhelming interest in utilising amide-functionalized cyclopentadienyl ligands in olefin polymerisation has dwarfed that concerning any alternative applications. The rapid growth of interest is not so surprising, however, as the introduction of the linked amido-cyclopentadienyl ligand has led to a whole new class of remarkable olefin polymerisation catalysts. Complexes of the type $M[\eta^5:\eta^1\text{-}C_5R_4ZNR']L'_mX'_n$ clearly exhibit some properties intermediate to those of *ansa*-metallocenes and half-sandwich complexes and they may also be considered as a hybrid between *ansa*-metallocenes and the newly emerging complexes containing chelating bis(amido) ligands derived from the diamines R'HN(Z)NHR'. However, there is much to be explored in the chemistry of amide functionalized cyclopentadienyl complexes and the extent of their potential is as yet unrealised.

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Chapter 2

Preparation of Trimethylene-Bridged Amide Functionalized Cyclopentadienyl Complexes: Results and Discussion

2. Preparation Of Trimethylene-Bridged Amide Functionalized Cyclopentadienyl Complexes: Results And Discussion

2.1 Aims

As discussed earlier, the vast potential of linked amido-cyclopentadienyl ligands as replacements for bridged bis(cyclopentadienyl) ligands in *ansa*-metallocenes is widely recognised, but many aspects of the chemistry of such ligands and their resulting complexes have yet to be fully understood.

The aim of this project was to further explore the potential of amide-functionalized cyclopentadienyl complexes via the synthesis of novel trimethylene-bridged ligands (R' = cyclohexyl, C_6H_{11}, and benzyl, $CH_2C_6H_5$) and demonstrate their reactivity by coordination to metal centres. For this purpose, group 4 metal homoleptic amides were used due to their ease of reaction. In addition, it was hoped to discover more about the influence of a chiral amido substituent, R', by the synthesis of the ligands (2-pyrrolidine)methylene cyclopentadiene and 3[(1-phenylethyl)amino]propylene cyclopentadiene.

2.2 Ligand Design

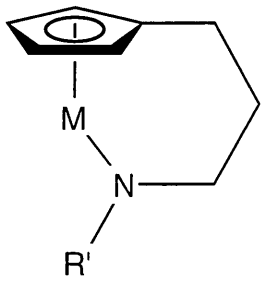


Figure 2.1

The synthesis and coordination chemistry of the above ligand has been quite extensively explored for R' = Me[1, 2] and R' = ^{t}Bu.[3] Such a system was prepared for the following reasons:

Z (the bridge backbone) = A Trimethylene Group

The effect of a short bridging group (Z = SiR_2, CR_2, C_2R_4; R = H or Me) is to open up one side of the complex, producing a highly open and reactive site. Although such a property can be desirable and the reactive site must be open enough to allow, say, the insertion of α-olefins, it does not allow for much steric control of the polymerisation reaction, and the homopoly α-olefins produced are generally atactic. It is thought that a trimethylene backbone would offer a greater degree of steric control.

In addition to this, coordination of such a ligand to metal centres should produce less strained complexes than those with a shorter bridge length. A carbon rather than a

silicon backbone was used due to the reactivity and potential cleavage of the Si-N bonds.

L = Nitrogen: A Secondary Amine

Deprotonation of a secondary amine gives a ligand of the LX type. When coordinated, it forms an amide and is capable of electronically stabilising the metal. It has the advantage of being more versatile than an imido ligand, with the ability to donate either one or three electrons to the metal centre, and forms stronger bonds than the labile amine ligands.

The Nature of R'

Previous work has found that *tert*-butyl groups tend to enhance catalytic activity but the complexes produced from $C_5H_5(CH_2)_3N(H)^tBu$ were mainly oils,[4] making them difficult to handle. Complexes of a more crystalline nature were obtained from ligands with R' = Me.[1, 2] One of the aims of this investigation was to synthesize novel ligands of the above type by varying the R' group.

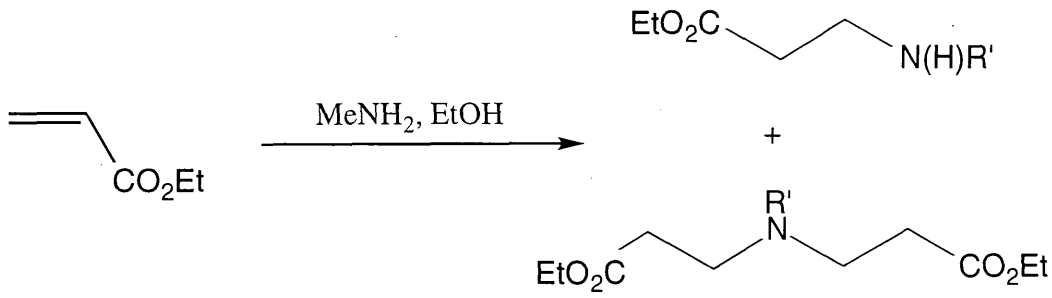
2.3 Synthesis of amine functionalized cyclopentadienyl ligands

In common with the preparation of metallocene complexes, the usual synthetic route to amido-bridged half-sandwich complexes consists of initially assembling the ligand $(C_5R_4H)Z(NHR')$ and then coordinating it to the metal centre. Linked amine cyclopentadienyl ligands are usually synthesized by one of two routes according to the nature of the bridging group Z. When Z = $SiMe_2$, the ligand is commonly prepared by reaction of $Li(C_5R_4H)$ with $SiMe_2Cl_2$ to produce $(C_5R_4H)SiMe_2Cl$ (R = H or Me), which can then be reacted with a range of lithium amides, Li(NHR'), to give the neutral ligand $(C_5R_4H)SiMe_2NHR'$. For di- and tri- methylene linked ligands (Z = $(CH_2)_n$; n = 2, 3) the reaction of excess $Na(C_5H_5)$ with $[X(CH_2)_nN^+H_2R']X^-$ (R' = Me, ^{i}Pr, ^{t}Bu; X = Cl, Br; n = 2, 3) has been employed to produce $C_5H_5(CH_2)_nN(H)R'$ as several bond isomers.[1] A modification of this procedure was used for the synthesis of the ligands $C_5H_5(CH_2)_3N(H)R'$ (R' = C_6H_{11}, $CH_2C_6H_5$, $CH(CH_3)C_6H_5$).

2.4 Synthesis of $C_5H_5(CH_2)_3N(H)R'$ (R' = C_6H_{11}, $CH_2C_6H_5$, $CH(CH_3)C_6H_5$)

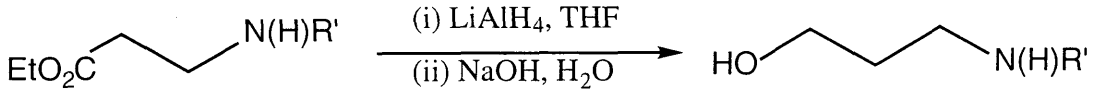
$HO(CH_2)_3N(H)R'$

Previous work with these ligand systems incorporated a two-step synthesis of $HO(CH_2)_3N(H)R'$ from CH_2CHCO_2Et via $EtO_2C(CH_2)_2N(H)R'$.[2] Initially, the conjugate addition of methylamine to ethyl acrylate in ethanol was employed to produce the mono-substituted ester, $EtO_2C(CH_2)_2N(H)R'$.[5] Unfortunately, the di-substituted product is also formed in similar amounts and the desired product must be distilled from the reaction mixture in only 35% yield (Equation 2.1).[2] Higher yields of the appropriate monosubstituted product are obtained with bulkier amines; *tert*-butylamine, for example, gives the mono-substituted ester $EtO_2C(CH_2)_2N(H)^tBu$ in >95% yield.[3]



Equation 2.1

The mono-substituted ester was then reduced to the corresponding alcohol, $HO(CH_2)_3N(H)Me$, using $LiAlH_4$ and the product isolated by an aqueous work-up (Equation 2.2).[2] Early workers achieved only moderate yields of 38%[6] and 48%,[7] but it was found that by adding slowly over three hours at 0°C a solution of the ester, diluted with twice the volume of THF, to the $LiAlH_4$, followed by the slow addition of water that was diluted with five times the volume of THF, a yield of 74% was obtained.[2] It is thought that the low yields are a result of the heat produced at the point of contact of the ester (or water for the aqueous work-up) and reducing agent.

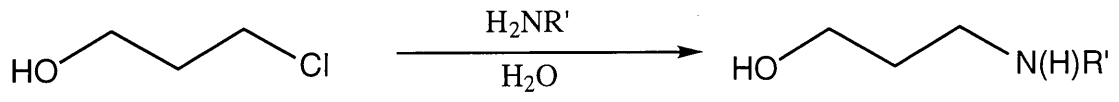


Equation 2.2

Another problem in this methodology was the production of significant amounts of solid $Al_2O_3{:}nH_2O$ during the aqueous work-up, which tended to absorb a large proportion of the product, with the result that only small amounts could be obtained by ether extraction. In response to this problem, a saturated NaOH solution was used in place of water in the aqueous work-up, the high pH causing most of the hydrolysis products to dissolve in the aqueous layer. Subsequent extraction of the aqueous layer

with several portions of THF could then produce the desired alcohol as a reasonably pure colourless oil.

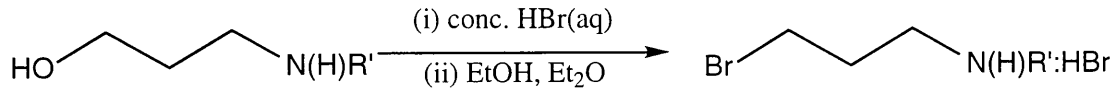
In the present work, an alternative synthetic route was employed and found to be much more suitable. This procedure comprised a one-step reaction between 3-chloropropane, $Cl(CH_2)_3OH$, and the appropriate amine, $R'NH_2$, in the presence of a small amount of water (Equation 2.3).[8] The reaction could be performed at a reasonable rate by simple reflux in air and the product easily isolated (as a solid for R' = C_6H_{11}; as separable oils for R' = $CH_2C_6H_5$, $CH(CH_3)C_6H_5$) in adequate (60 - 90%) yields.



Equation 2.3

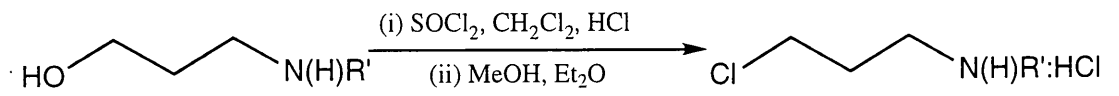
Cl(CH$_2$)$_3$N(H)R'.HCl

Originally, a modification of the experimental procedure described by Cortese was used to convert the alcohol, $HO(CH_2)_3N(H)R'$, into the hydrobromide salt, $Br(CH_2)_3N(H)R'.HBr$.[9] The alcohol was refluxed with an aqueous solution of HBr followed by distillation of a portion of the volatiles. Reflux was resumed and this cycle continued until only an oily residue remained. The product could then be extracted into ethanol or THF and crystallised by the addition of diethyl ether followed by cooling (Equation 2.4). The hydrobromide salt could be obtained in 58% yield, but investigation of the product obtained from $HO(CH_2)_3N(H)^tBu$ found that it was difficult to obtain a sample which was completely dry due to the mildly hygroscopic nature of the compound and the aqueous reaction conditions. Hence, problems arose in the next stage synthesis of the cyclopentadiene.[3]



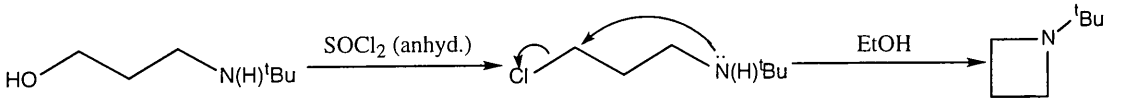
Equation 2.4

As a result, alternative methods were sought and the use of thionyl chloride to convert the alcohol, $HO(CH_2)_3N(H)R'$, into the hydrochloride salt, $Cl(CH_2)_3N(H)R'.HCl$ became the preferred method (Equation 2.5).[2]



Equation 2.5

An important point to note in this methodology, however, is the addition of a small amount of HCl. In previous work it was discovered that the reaction between thionyl chloride and the pure, undiluted alcohol, $HO(CH_2)_3N(H)^tBu$, was significantly exothermic, leading to the vaporisation and escape of the HCl formed. Thus, there was insufficient HCl present in the reaction mixture to protonate the amine, allowing ring closure to occur forming a large quantity of N-*tert*-butylazetidine and a reduced yield (< 30%) of the desired hydrochloride salt (Equation 2.6).[3]



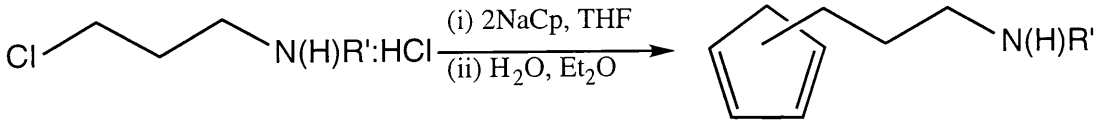
Equation 2.6

To avoid this unwanted side reaction, CH_2Cl_2 is used as the solvent and a few drops of concentrated HCl are added to ensure that protonation of the amine occurs. For R' = Me, ^{t}Bu, the suspension was refluxed with ethanol to destroy the excess $SOCl_2$, but this was found to be unnecessary with R' = C_6H_{11}, $CH_2C_6H_5$, the excess $SOCl_2$ being removed with the solvent under reduced pressure.

By this method, the product was easily isolable in good yields (> 80%) and, where solid (R' = C_6H_{11}, $CH_2C_6H_5$), could be recrystallized from methanol and diethyl ether.

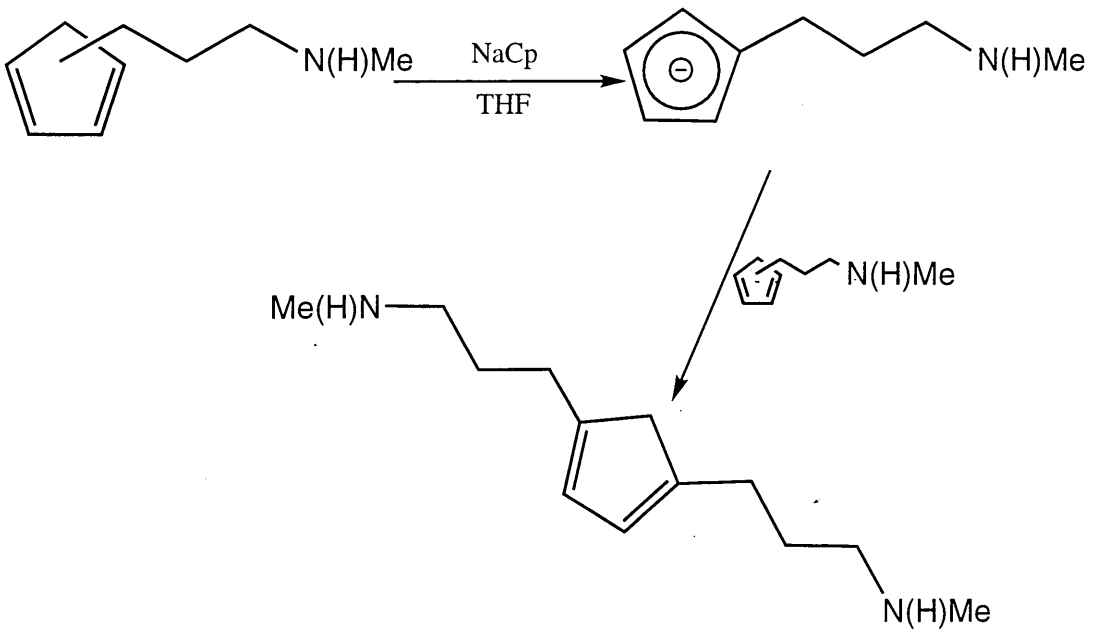
$\underline{C_5H_5(CH_2)_3N(H)R'}$

The amine-functionalized cyclopentadiene ligand is synthesized from the reaction of the hydrochloride salt, $Cl(CH_2)_3N(H)R'.HCl$, with an excess of sodium cyclopentadiene in THF (Equation 2.7).[2]



Equation 2.7

A minimum of two equivalents of NaCp is required as one equivalent is used to convert the amine hydrochloride to the free amine while the second nucleophilic $C_5H_5^-$ couples with the chloride. Where R' = Me, it was found that optimum reaction conditions were achieved when two NaCp equivalents were used. Considerably lower yields (< 25%) were obtained when three rather than two equivalents of NaCp were added[1] and a second product, shown by NMR and mass spectroscopic analysis to be the disubstituted cyclopentadiene, distilled at a slightly higher temperature (Equation 2.8).[2]



Equation 2.8

The experimental procedure employed by previous workers has generally involved a dropwise addition of a THF solution of NaCp to a suspension of the hydrochloride or hydrobromide salt in THF.[1] In this work, however, the reaction was found to proceed more efficiently when the solid hydrochloride salt was added slowly and with stirring to the NaCp solution. Indeed, in many attempts where the method of adding the NaCp solution to the hydrochloride salt was used, the desired product was not detected at all and the reaction products were comprised mainly of dicyclopentadiene. It is thought that the increased effectiveness of the reaction when the addition is "reversed" is due to the fact that, under these circumstances, the NaCp is always in excess. Hence, as each small addition of solid hydrochloride salt enters the reaction vessel, it is surrounded by an excess of nucleophilic $C_5H_5^-$ ions, so there is sufficient NaCp for conversion of the hydrochloride to the corresponding free amine, followed by coupling of a second $C_5H_5^-$ unit, to easily occur. This situation does not occur when the addition is carried out the original way, where presumably the first additions of NaCp generate the free amine which then, in the absence of any further $C_5H_5^-$ ions, undergoes unwanted side reactions such as the ring closure reaction discussed above. Thus, by the time the second equivalent of NaCp has been added there is none of the desired ligand precursor left to react and any reflux or continued stirring of the reaction mixture merely leads to dimerization of the excess cyclopentadiene anions. Care was taken to ensure that each addition of solid hydrochloride salt dissolved before the next addition to ensure that the large excess of NaCp was maintained. When this was not done, (as in the case of the 2-chloromethyl pyrrolidine derivative which was only sparingly soluble in THF) the reaction conditions were effectively a mimic of the traditional order of addition and the desired product was not obtained.

Earlier workers found the products of the addition of NaCp to the hydrochloride salt, $Cl(CH_2)_3N(H)Me.HCl$, to consist of a 5:1 mixture of the desired linked amine cyclopentadiene ligand and dicyclopentadiene.[1] This mixture could not be effectively separated by distillation, so a method of isolating the product was devised which took advantage of the basic nature of the amine. The reaction products are taken up in light petroleum ether and extracted with dilute HCl, the extracts being added directly to a mixture of NaOH, water and diethyl ether. Hence, the product is converted to its chloride salt and as such extracts into the aqueous layer, leaving the dicyclopentadiene behind in the petroleum ether layer. As this aqueous layer is immediately run into a basic mixture, the neutral ligand is formed again before any irreversible reaction occurs with the acid. The product then extracts into the organic layer, from which it can be separated and further purified by distillation in adequate yields (40 - 60%).[1, 2] In this investigation, however, NMR spectra of the initial reaction products indicated the absence of even small amounts of dicyclopentadiene, so that such an acid-base work-up was deemed unnecessary.

The ligands $C_5H_5(CH_2)_3N(H)R'$ are known to exist as a mixture of double bond isomers, usually shown by ^1H and ^{13}C NMR spectroscopy. The compound $C_5H_5(CH_2)_3N(H)Me$ was shown to exist as an almost 1:1 mixture of two of the three possible isomers (Figure 2.2).[2] The ^{13}C NMR spectrum was the more informative, showing two quaternary resonances at δ149.1 and 146.5 ppm and a total of six olefinic CH resonances between δ125 and 135 ppm.[1] Similar results were obtained for $C_5H_5(CH_2)_3N(H)(C_6H_{11})$ and $C_5H_5(CH_2)_3N(H)(CH_2C_6H_5)$. It has not been possible to provide a complete assignment of the C_5H_5 resonances in the ^1H NMR spectra of these compounds because of the heavy overlap of the different isomers.

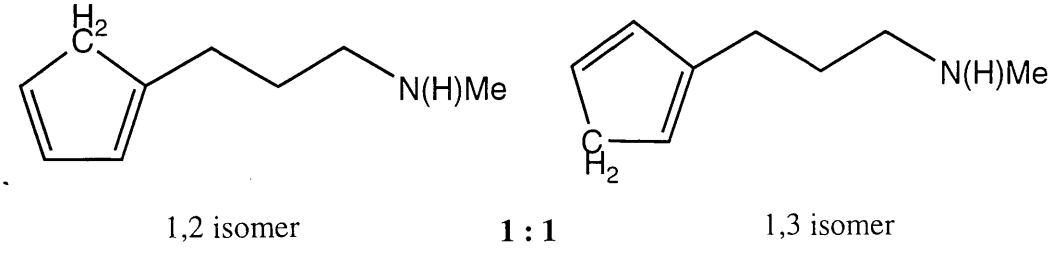


Figure 2.2

2.5 Preparation of chiral ligand systems

The development of catalytic processes that will potentially allow control over enantioselective bond formation is a challenge of obvious importance. The afore-mentioned C_2-symmetric *ansa*-metallocenes have already found considerable application in this area. Chiral titanocenes, for instance, are involved in a wide variety of useful asymmetric reactions, including the enantioselective hydrogenation of olefins and reduction of imines or ketones. Many of the reactions effected with high levels of

enantioselectivity by catalytic amounts of these complexes are of great significance in the preparation of new materials and to the synthesis of therapeutic agents.[11]

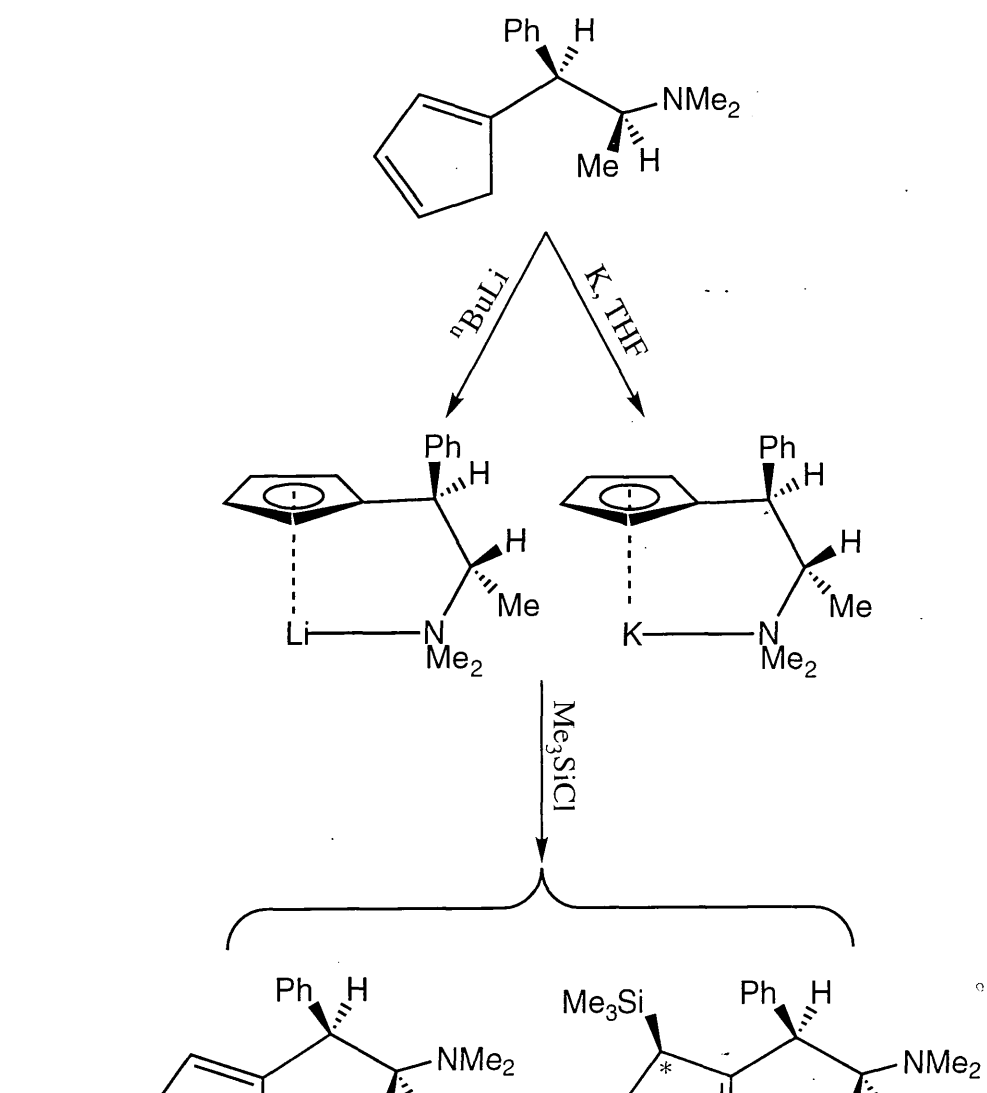
Chirally modified cyclopentadienyl ligands were first applied to metal-mediated organic transformations twenty years ago by Cesarotti *et al* with the synthesis of menthyl-substituted titanocene and zirconocene derivatives.[12] Subsequent "tailoring" was focused mainly on modifying the steric bulk of the chiral substituents.[13]

More recently, there has been some attention focused on chirally modified N-functionalized cyclopentadienyl ligands, in which chirality can be introduced via the nitrogen substituent or into the bridge Z.

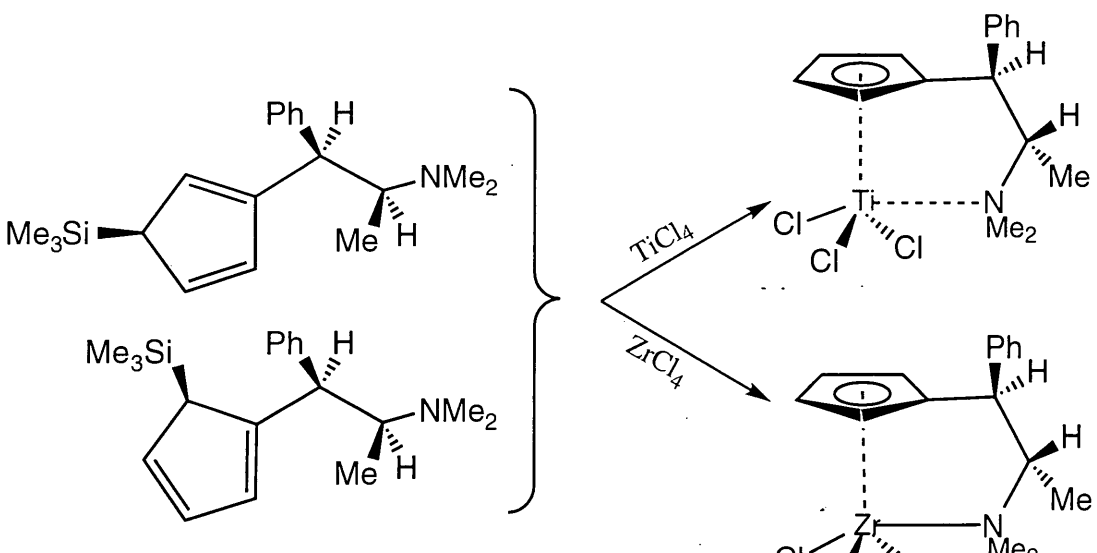
The introduction of chirality into the bridging group Z was applied in the design of the chiral amino-functionalized ligand, $C_5H_4CH(Ph)CH(Me)NMe_2$, from which a series of metal complexes was synthesized.[14] Metallation was accomplished by reaction with ^nBuLi or K (Scheme 2.1)[14] while the complexes $[C_5H_4CH(Ph)CH(Me)NMe_2]MCl_3$ (M = Ti, Zr) were synthesized by the reaction of MCl_4 with the trimethylsilyl derivative of the ligand (Scheme 2.2).[14] In the titanium complex, the nitrogen side-arm is only weakly coordinated to the metal centre, whereas in the zirconium compound it is firmly bound to the metal centre and this complex was shown to catalyse the Diels-Alder reaction between methacroleine and cyclopentadiene, albeit with no measurable enantiomeric excess.[14]

Linked amido-cyclopentadienyl ligands containing a chiral amido substituent have recently been reported by Okuda *et al.*[15]

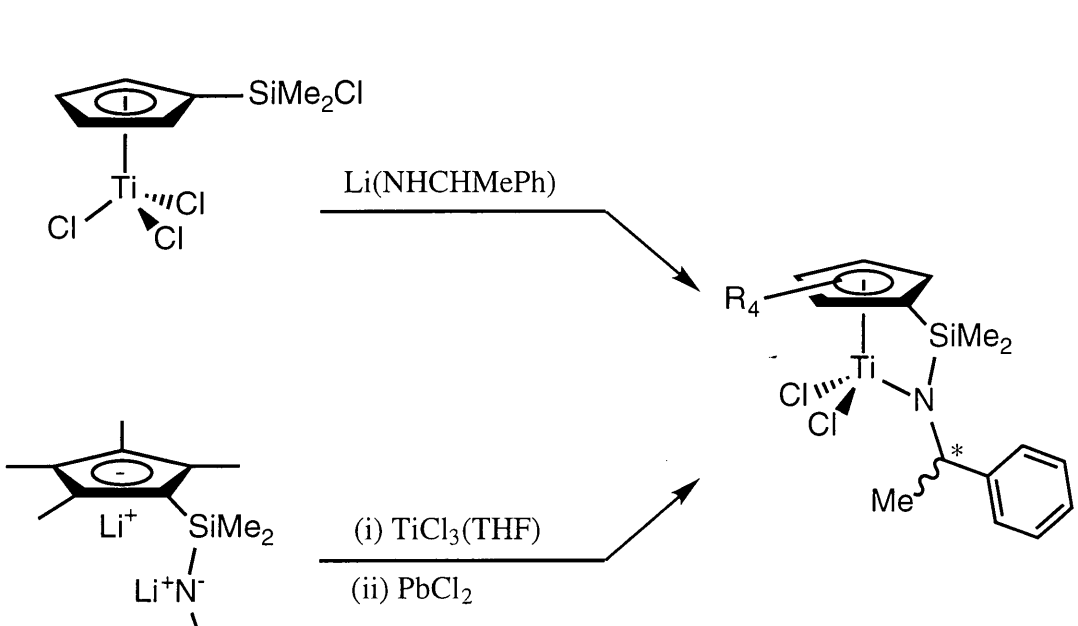
Optically active titanium complexes of the composition $Ti(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCHMePh)Cl$ (R = H, Me) were prepared in both enantiomerically pure forms by the introduction of the appropriate enantiomer of 1-phenylethylamine (Scheme 2.3).[15] Upon activation with *n*-butyl lithium, these complexes were shown to exhibit hydrogenation activity toward imines with slight enantioselectivity.[15] However, reports on such work are, to date, few.


Ph
H
NMe2
Me
H
nBuLi
K, THF
Ph
H
H
Me
Li
N
Me2
Ph
H
H
Me
K
N
Me2
Me3SiCl
Ph
H
NMe2
Me3Si
*
Me
H
Me3Si
Ph
H
NMe2
*
Me
H

Scheme 2.1

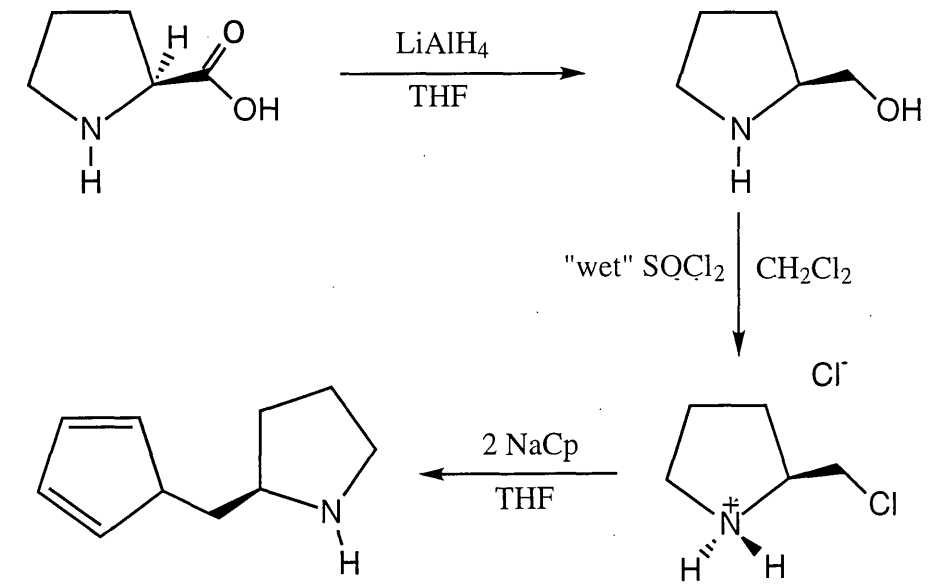


Scheme 2.2



Scheme 2.3

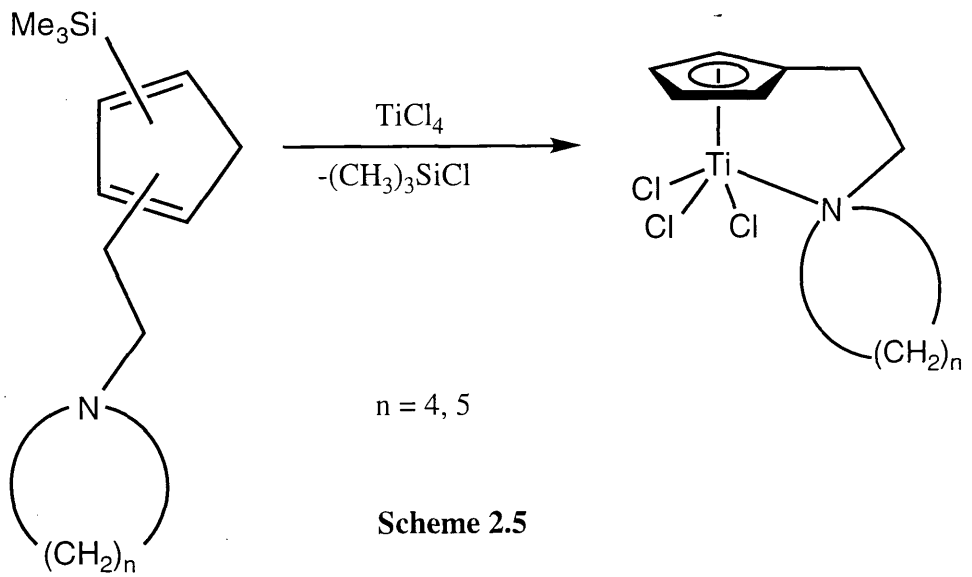
In this project, it was hoped to prepare a chiral linked amido-cyclopentadienyl ligand by utilising the natural amino acid proline. The originally proposed synthetic route is outlined in Scheme 2.4.



and other double bond isomers

Scheme 2.4

The use of proline derivatives or similar compounds in amido-functionalized cyclopentadienyl chemistry has already been reported. Herrmann *et al.* reported the synthesis and characterisation of novel monocyclopentadienyl complexes with linked pyrrolidine (*N*) and piperidine (*N*) functions as σ-donating pendant groups (Scheme 2.5)[16] and the use of prolinol in the synthesis of the tridentate ligand $(C_5Me_4H)SiMe_2OCH_2[(-)\text{-}(S)\text{-}C_4H_7NH]$ has been discussed in section 1.3.5.



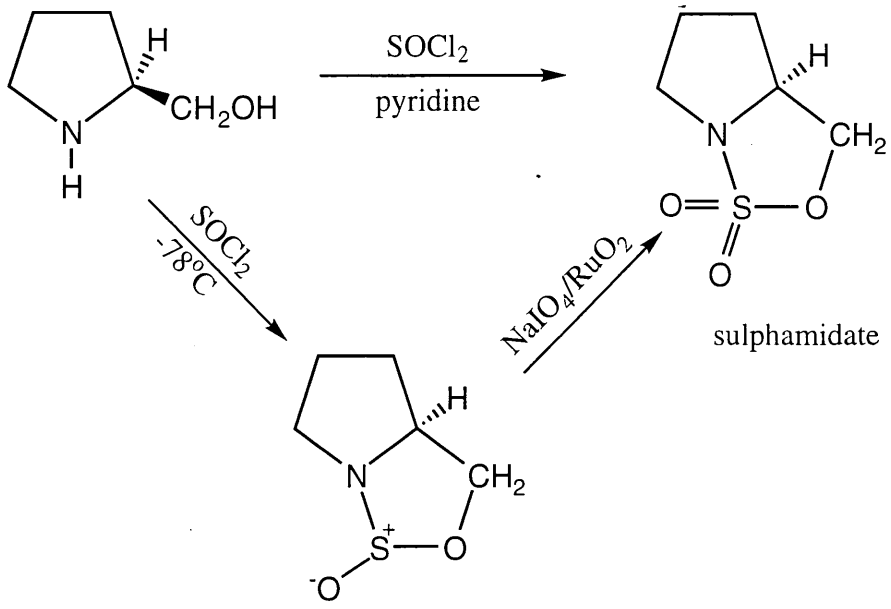
Scheme 2.5

Reduction of the amino acid, proline, to the alcohol 2-pyrrolidine methanol (prolinol) is effected by $LiAlH_4$ and is relatively straightforward. The product is obtained in 72% yield as a pale yellow oil which can be further purified by vacuum distillation, although the crude product is usually of sufficient purity to be used in the next stage.

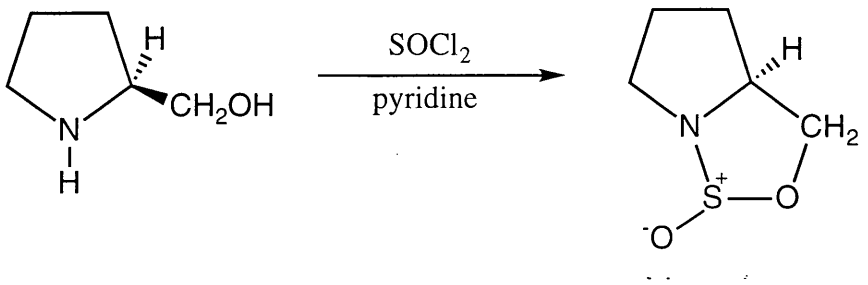
The apparent conversion of prolinol to the corresponding hydrochloride salt, 2-chloromethylpyrrolidine, was performed in the same manner as described above for ligands of the type $C_5H_5(CH_2)_3N(H)R'$ The reaction product was isolated as a cream solid.

Problems were encountered in the coupling of the cyclopentadienyl unit to the hydrochloride salt and the desired ligand, $C_5H_5CH_2(C_4H_7)N(H)$, was never actually synthesized. Both orders of addition (NaCp solution to hydrochloride salt suspension and solid hydrochloride salt to NaCp solution) were attempted with no success, although the hydrochloride salt was seen to be only sparingly soluble in THF and so the act of reversing the order of addition and adding solid hydrochloride salt to NaCp solution may not have been as effective as possible. The reaction products of each attempt consisted of a mixture of unidentifiable products and dicyclopentadiene.

It is not known why this stage of the synthesis should fail with this compound. Several workers report the production of sulphamidite complexes from the reaction of prolinol and $SOCl_2$ (Scheme 2.6 and Scheme 2.7),[17, 18] so it may be that the product obtained from this second stage of the synthetic pathway is not the desired hydrochloride salt of prolinol; hence its failure to react as required with sodium cyclopentadiene. (This could not be confirmed without further characterization data, as the NMR spectra of all the possible products would be expected to be similar.) In addition, the product from the reaction of prolinol with $SOCl_2$ appeared to be very hygroscopic and this may also have had a detrimental effect on its reaction with NaCp.



Scheme 2.6



sulphamidite

Scheme 2.7

The lack of success with the proline system prompted attempts to synthesize an alternative chiral ligand system. For this, the ligand $C_5H_5(CH_2)_3N(H)(CH(CH_3)Ph)$ was chosen as it is of the same type as those ligands already prepared in this work and the corresponding silicon-bridged species is also known. The synthetic methodology for the ligands $C_5H_5(CH_2)_3N(H)R'$ (R' = C_6H_{11}, $CH_2C_6H_5$) was followed. The alcohol was obtained as a yellow oil in 73% yield. The hydrochloride salt was obtained in some attempts as an oil and in others as an oily solid, a phenomenon thought to be dependent on the purity of the product. Again, some problems were encountered in the reaction with NaCp, with some attempts merely dimerizing the cyclopentadiene, but gas chromatography mass spectrometry data on the products of the final attempted reaction show the presence of a small amount of the desired product (too small to be detected by NMR), suggesting that modifications of the experimental technique may be needed to improve the efficiency of the reaction.

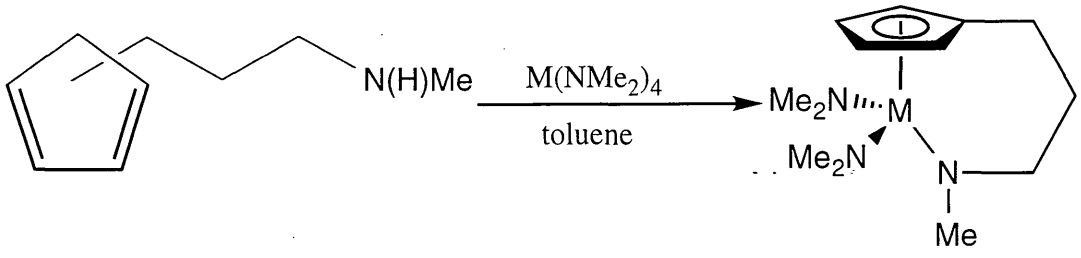
2.6 Complexation of amide functionalized cyclopentadienyl ligands

The most commonly employed reaction for the preparation of ring closed complexes with $C_5H_5(CH_2)_3N(H)R'$ has been that with group 4 homoleptic amides, $M(NMe_2)_4$.[1] Reaction of the neutral ligand with stoichiometric amounts of $Zr(NMe_2)_4$ and $Hf(NMe_2)_4$ is known to give the bis(amide) zirconium and hafnium complexes (e.g. A and B in Figure 2.3)[2] in high yields. This reaction was successfully carried out to demonstrate the coordination of the ligands $C_5H_5(CH_2)_3N(H)(C_6H_{11})$ and $C_5H_5(CH_2)_3N(H)(CH_2C_6H_5)$, yielding the desired products as air sensitive brown oils.

The aminolysis route to metallated cyclopentadienes has several advantages over other metallation procedures. It is a straightforward, one-step procedure and the elimination product (dimethylamine) is easily removed from the reaction mixture due to its high volatility, thus simplifying the purification of the final product. The reaction is fairly versatile and can be used to synthesize a wide range of group 4 metal complexes. The pK_a of secondary amines is in the range 35 - 40 and, as a result, transition metal amides, $M\text{-}NR_2$, will react with a large variety of "acids".

The use of cyclopentadienyl metal amides as starting materials has not been widely explored, but they can be converted relatively easily to metal halide complexes which

can be used to prepare a variety of interesting and useful complexes, particularly metal alkyls.



A; M = Zr

B; M = Hf

Figure 2.3

The dihalide complexes C, D and E (Figure 2.4)[2] are readily formed via the aminolysis of A and B, which can be achieved by the addition of two equivalents of acid (HCl or HI) in the form of dimethylamine hydrohalide,[1] or by reaction with Me_3SiCl (for the complex E).[19] Both routes provide the appropriate dihalide complex as its $NHMe_2$ adduct. This may be used directly in many cases, or the adduct-free complex $Zr(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3NMe)Cl_2$ can be isolated by sublimation under reduced pressure.[19]

The dichloride, C, has been shown to be a superb precursor to a variety of alkyl complexes; the reaction with two equivalents of the alkylating agents MeMgCl or Me_3SiCH_2Li giving the corresponding bis(alkyl) complexes, F and G. When one equivalent of the alkylating agent $C_6H_5CH_2MgCl$ is used, the dimer H is formed, the crystal structure of which shows two different Zr-Cl distances resulting from the *trans* influence of the benzyl ligand. The colourless bis(tetrahydroborate), I, which contains rapidly exchanging terminal and bridging hydrido ligands, is prepared from the reaction of C with excess $LiBH_4$.[2]

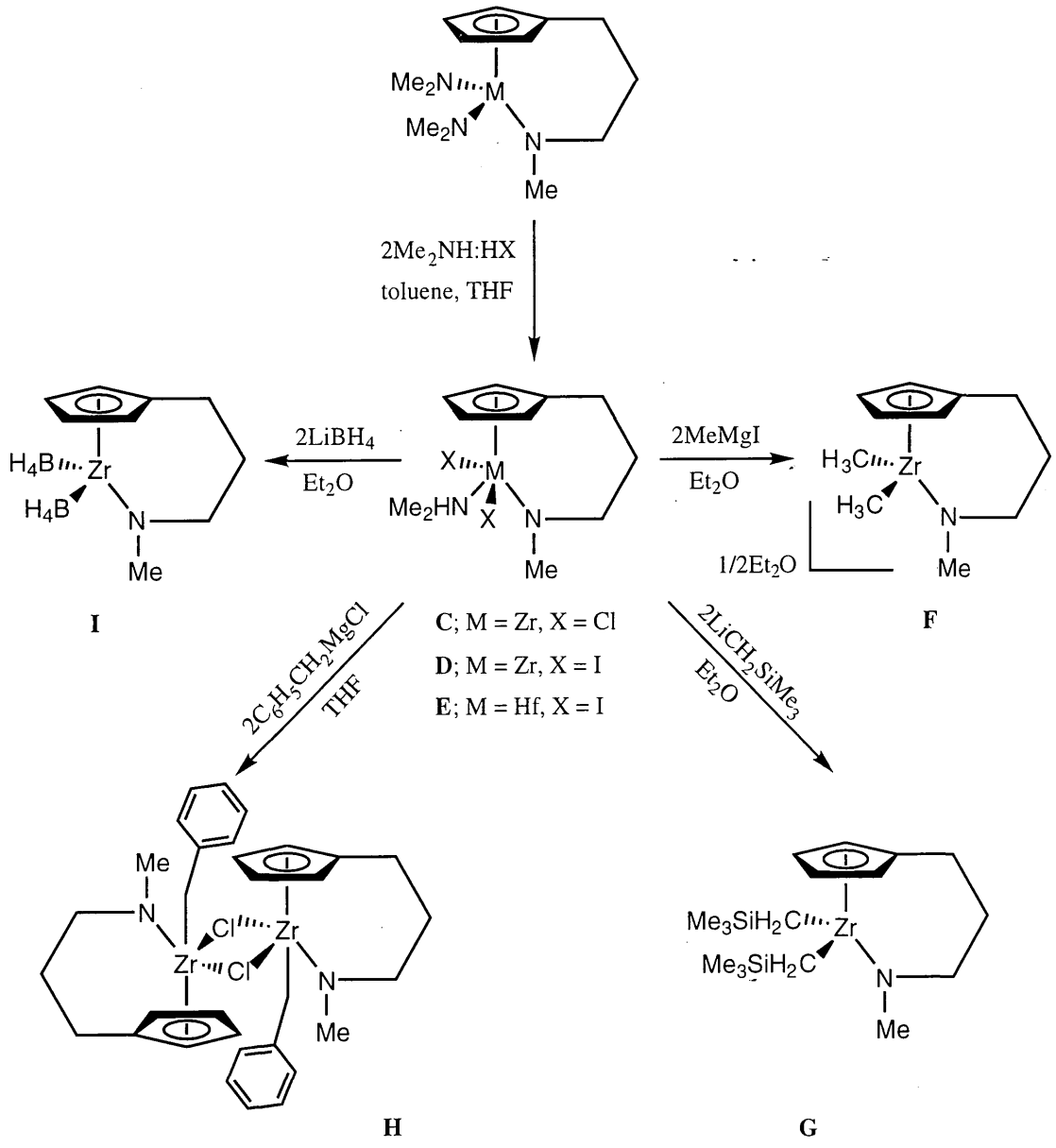


Figure 2.4

Reaction of metal-halide complexes with alkylating agents is by far the most common method for the synthesis of metal-carbon bonds. However, the aminolysis reaction of the metal-amide bonds in the complex A (Figure 2.5) and a suitably acidic hydrocarbon ($pK_a < 35$) also gives metal "alkyl" complexes. The reaction of A with two equivalents of phenylacetylene, for example, gave the corresponding bis(alkyl)complex J, while reaction with an excess of cyclopentadiene gave the chiral mono-substituted complex, K (Figure 2.5).[2]

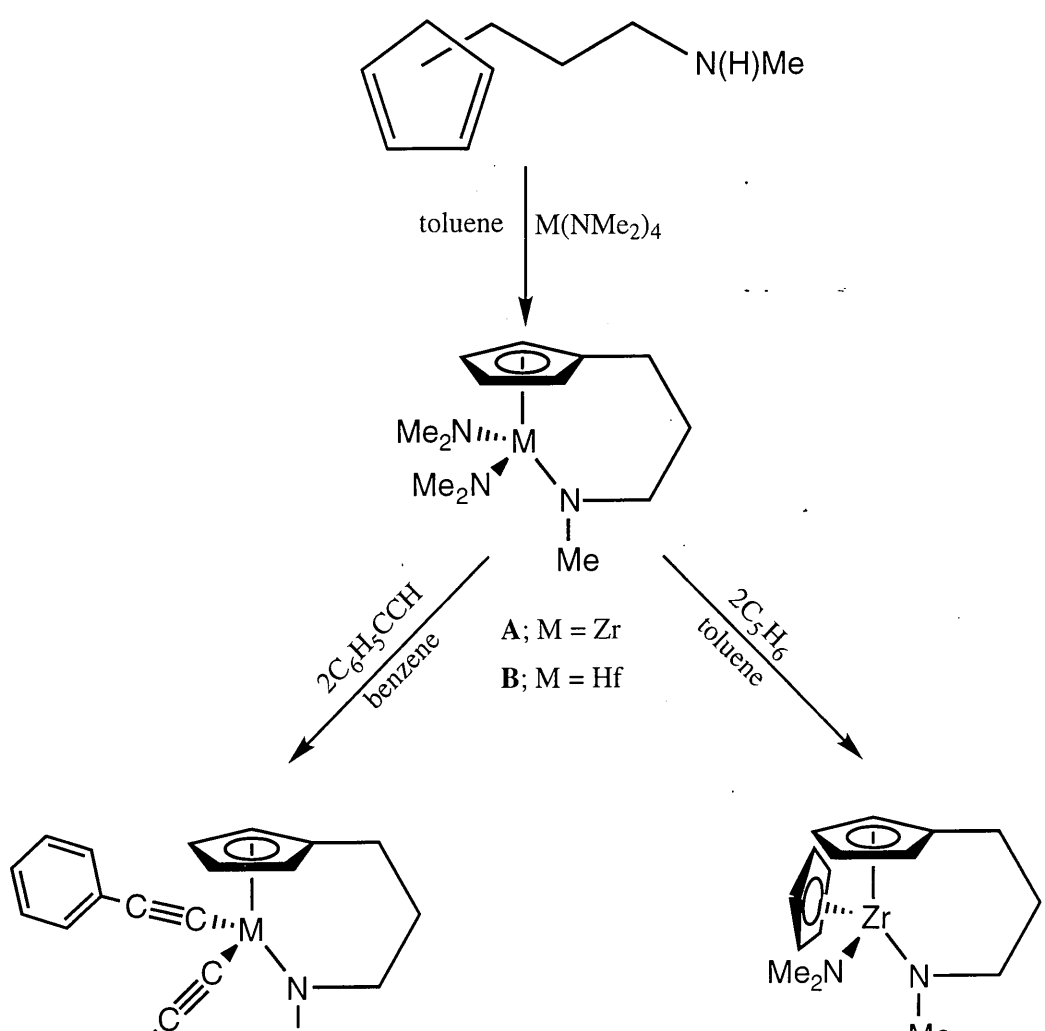


Figure 2.5

It has not to date been possible to prepare group 4 amine substituted metal chlorides directly. Both the dilithiated and disilylated derivatives of $C_5H_5(CH_2)_3N(H)R'$ (R' = Me, ^tBu) give unidentifiable products on work-up following reaction with $TiCl_4$, $TiCl_3(THF)_3$ and $TiCl_4(THF)_2$.[2] The products of these reactions were highly insoluble, indicating perhaps a polymeric structure.[1, 3] However, it has been shown to be possible to directly prepare group 4 metal amido-cyclopentadienyl complexes with alkyl ligands. Teuben and co-workers, for example, recently reported the synthesis of $Zr(\eta^5:\eta^1\text{-}C_5H_4(CH_2)_3N^iPr)(CH_2Ph)_2$ from the one-step reaction between the neutral ligand, $C_5H_5(CH_2)_3N(H)^iPr$, and $Zr(CH_2Ph)_4$.[19]

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Chapter 3

Experimental

3. Experimental

3.1 Experimental Details

All manipulations of air sensitive compounds were performed under an atmosphere of dry nitrogen using standard Schlenk-line and glove-box (Braun Labstar 50) techniques.

Solvents were dried by storing over 3Å molecular sieves (Lancaster) or sodium wire followed by prolonged reflux under nitrogen over an appropriate drying agent (usually sodium or sodium/potassium amalgam). The solvents were collected and stored in Young's ampoules and degassed using the freeze-thaw technique.

NMR solvents ($CDCl_3$ and C_6D_6) were stored in Young's ampoules over molecular sieves and degassed using the freeze-thaw technique. Manipulations were carried out using vacuum distillation. Chemical shifts are quoted as δ in ppm with respect to the following unless otherwise stated: ^1H (C_6D_6, 7.16ppm; $CDCl_3$, 7.26ppm); ^{13}C (C_6D_6, 128.06ppm; $CDCl_3$, 77.16ppm).

3.2 Preparation Of $C_5H_5(CH_2)_3NH(C_6H_{11})$

3-(N-cyclohexylamino)propanol

3-(N-cyclohexylamino)propanol was prepared by a modification of the method used by Wagner *et al.*.[1] 3-chloropropanol (19.5g, 0.206mol) was added dropwise into a 250ml flask containing a stirred mixture of cyclohexylamine (40.86g, 0.412mol) and 6ml of water. The reaction mixture was refluxed for 6 h and the resulting dark orange solution extracted with several portions of toluene. The toluene extracts were combined and the solvent removed under reduced pressure to yield a pale yellow solid. After the solid was rinsed with hexanes, yellow impurities were washed into the mother liquor, leaving white flakes (21.5g, 0.137mol, 63% yield). The solid was used in subsequent reactions or further purified by recrystallization from toluene and hexanes, producing shiny white crystals.

^1H NMR δ/ppm $CDCl_3$; 3.81 (t, 2H, OCH_2), 2.90 (t, 2H, NCH_2), 2.65 (br, 1H, OH), 2.41 (m, 1H, C-1 ring), 1.95, 1.67, 1.19 (m, 13H, ring H (except C-1), CCH_2C, NH);^{13}C NMR δ/ppm $CDCl_3$ (^1H decoupled); 64.9 ($HOCH_2$), 56.8 (CHNH), 47.2 (NCH_2), 33.6 (2xC-ring), 31.3 ($C\underline{C}H_2C$), 26.2 (C-ring), 25.1 (2xC-ring); MS, *m/z*- 157 [EI]

3-(N-cyclohexylamino)chloropropane[2]

Caution: $Cl(CH_2)_3NH(C_6H_{11}).HCl$ is a potential nitrogen mustard and was therefore handled wearing protective clothing in a fume hood.

In a 500ml two-necked flask with reflux condenser and dropping funnel, a slurry of $HO(CH_2)_3NH(C_6H_{11})$ (20.1g, 0.128mol) in dichloromethane (200ml) was cooled to 0°C with stirring and HCl (2ml of a 10M solution, 2mmol) added dropwise. Thionyl

chloride (23ml, 37.7g, 0.317mol) was added dropwise over 30-60 min with the evolution of white fumes. The reaction mixture was refluxed for a minimum of 5 h, cooled and the solvent removed under reduced pressure to yield a "dirty" white solid (23.6g, 0.111mol, 87% yield). The crude product was washed with diethyl ether and used in subsequent reactions or further purified by recrystallization from methanol and diethyl ether to produce a white crystalline solid.

^{1}H NMR δ/ppm $CDCl_3$; 9.41 (br, 2H, NH_2^+), 3.68 (t, 2H, CH_2Cl), 2.46 (m, 2H, NCH_2), 2.21, 1.95, 1.62, 1.25 (m, 13H, ring H, CCH_2C); ^{13}C NMR δ/ppm $CDCl_3$ (^{1}H decoupled); 57.83 (CHNH), 42.35, 41.99 (NCH_2, CH_2Cl), 29.28 (2xC-ring), 28.80 ($C\underline{C}H_2C$), 24.91 (C-ring), 24.69 (2xC-ring);

Chloride analysis confirmed the presence of 32.6%Cl by mass.

3-(N-cyclohexylamino)propylene cyclopentadiene

Under N_2, a 250ml two-necked flask fitted with reflux condenser and nitrogen bubbler was charged with a solution of NaC_5H_5 (170ml, 0.17mol from a 1M solution in THF) and cooled to 0°C. $Cl(CH_2)_3NH(C_6H_{11}).HCl$ (9g, 0.0424mol) was placed in a solid addition apparatus and left under reduced pressure for 30 minutes. With a flow of N_2, the solid addition apparatus was connected to the flask and the solid $Cl(CH_2)_3NH(C_6H_{11}).HCl$ slowly added to the NaC_5H_5 solution. The reaction mixture was stirred and allowed to warm to room temperature, then refluxed for ca. 16 hours. The resulting dark red solution was allowed to cool and the solvent removed under reduced pressure. In air, petroleum ether (ca. 80ml) was added to the solid, then removed under reduced pressure to remove any residual THF. To the remaining dark solid, roughly equal portions of diethyl ether and water were added, with further water being added until all the solid had dissolved. The organic layer was separated and the aqueous layer washed with diethyl ether until the washings were colourless. Similarly, the combined organic layers were washed with water until the washings were colourless. The remaining orange/brown organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to leave a brown oil (5.6g, 0.0273mol, 64% yield). NMR analysis indicated that there was no dicyclopentadiene present. Hence, further purification was deemed unnecessary. The product was obtained as mixture of double bond isomers as discussed in Section 2 for the compound $C_5H_5(CH_2)_3N(H)Me$.

^{1}H NMR δ/ppm $CDCl_3$; 6.43 (overlapped m, 3H, 2 x CH of C_5H_5 of isomer 1, 1 x CH of isomer 2), 6.26 (m, 1H, CH of C_5H_5 of isomer 2), 6.16 (m, 1H, CH of C_5H_5 of isomer 2), 6.01 (m, 1H, CH of C_5H_5 of isomer 1), 2.95 (m, 2H, CH_2 of isomer 1), 2.88 (m, 2H, CH_2 of isomer 2), 2.65 (t, 2H, CH_2N), 2.40, 1.72, 1.21 (overlapped m, 34H, CH_2N, 2 x $CH_2C_5H_5$, 2 x $CH_2C\underline{H_2}CH_2$, 2 x NH, cyclohexyl ring H); ^{13}C NMR δ/ppm $CDCl_3$ (^{1}H decoupled); 134.8 (1C, CH of C_5H_5), 133.9 (1C, CH of C_5H_5), 132.5 (1C,

CH of C_5H_5), 130.7 (1C, CH of C_5H_5), 126.5 (1C, CH of C_5H_5), 126.1 (1C, CH of C_5H_5), 57.0 (1C, NCH_2), 56.9 (1C, NCH_2), 46.9 (1C, C-cyclohexyl ring), 46.8 (1C, C-cyclohexyl ring), 43.4 (1C, $C_5H_5\underline{C}H_2$), 41.4 (1C, $C_5H_5\underline{C}H_2$), 33.8 (4H, 2xC-cyclohexyl ring of each isomer), 30.7 (1C, CH_2), 29.7 (1C, CH_2), 28.8 (1C, CH_2), 27.9 (1C, CH_2), 26.4 (2C, C-cyclohexyl ring of each isomer), 25.3 (4H, 2xC-cyclohexyl ring of each isomer). A peak for each of the *ipso* carbons of the C_5H_5 groups of each isomer should be present in the 145 - 150ppm region but these are too small to be seen.; MS: *m/z*-205 [EI]

3.3 Preparation of $Zr[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2CH_2N(C_6H_{11})](NMe_2)_2$

A solution of $Zr(NMe_2)_4$ (1.70g, 6.34mmol) in toluene (ca. 20ml) was cooled to -10°C. $C_5H_5(CH_2)_3NH(C_6H_{11})$ (1.30g, 6.34mmol) was dissolved in toluene (ca. 20ml) and the resulting solution dried, degassed and added dropwise over 20 minutes to the $Zr(NMe_2)_4$ solution. The reaction mixture was allowed to warm to room temperature with stirring and was then heated to ca. 40°C for 15 minutes. The volatiles were removed under reduced pressure and residual toluene was stripped from the product using a small amount of hexanes. The product was extracted into pentane to produce a clear yellow solution. Removal of the solvent under reduced pressure yielded a dark yellow oil (1.5g, 3.93mmol, 62% yield).

^1H NMR δ/ppm C_6D_6; 5.97 (t, 2H, C_5H_4), 5.70 (t, 2H, C_5H_4), 2.88 (s, 12H, 2xNMe_2), 2.76 (m, 2H, NCH_2), 2.52 (m, 2H, $C_5H_4C\underline{H}_2$), 1.76, 1.49, 1.20 (m, 13H, $CH_2C\underline{H}_2N$, cyclohexyl ring H); ^{13}C NMR δ/ppm C_6D_6(^1H decoupled); 126.6 (C_5H_4 *ipso*), 109.5 (CH of C_5H_4), 109.0 (CH of C_5H_4), 45.6 (2xNMe_2). It is not possible to fully assign the remaining peaks without further analysis and purification of the product.; MS: *m/z*-381 [EI]

3.4 Preparation of $C_5H_5(CH_2)_3NHCH_2(C_6H_5)$

3-(benzylamino)propanol

3-(benzylamino)propanol was prepared as described for 3-(*N*-cyclohexylamino)propanol. Concentration of the organic layer under reduced pressure yielded a thick yellow oil which was used in subsequent reactions without any further purification (81% yield).

^1H NMR δ/ppm $CDCl_3$; approx. 7.26 (m, 5H, aromatic H), 3.79, 3.70 (overlapped m, 4H, OCH_2, aromatic-C-CH_2N), 2.79 (t, 2H, NCH_2), 2.56 (br, 1H, OH), 1.67 (m, 2H, CCH_2C)

3-(benzylamino)chloropropane

3-(benzylamino)chloropropane was synthesized according to the method used for the synthesis of 3-(*N*-cylohexylamino)chloropropane. The product was crystallized as a

white solid from methanol in only 7% yield, but the yield would have increased dramatically with subsequent crystallizations.

^{1}H NMR δ/ppm $CDCl_3$; 9.65 (br, 2H, NH_2), approx. 7.26 (m, 5H, aromatic H), 3.46, 3.33 (overlapped m, 4H, $ClCH_2$, aromatic-C-CH_2N), 2.16 (m, 4H, NCH_2, CCH_2C)

3-(benzylamino)propylene cyclopentadiene

Similarly, 3-(benzylamino)propylene cyclopentadiene was prepared by the same procedure as that used for the synthesis of 3-(*N*-cylohexylamino)propylene cyclopentadiene. The product was isolated as a yellow/brown oil (81% yield) and the absence of any significant amounts of dicyclopentadiene was confirmed by NMR data.

^{1}H NMR δ/ppm $CDCl_3$; approximately 7.26 (m, 10H, 2x aromatic ring H), 6.37 (overlapped m, 3H, 2 x CH of C_5H_5 of isomer 1, 1 x CH of isomer 2), 6.19 (m, 1H, CH of C_5H_5 of isomer 2), 6.10 (m, 1H, CH of C_5H_5 of isomer 2), 5.95 (m, 1H, CH of C_5H_5 of isomer 1), 3.73 (m, 4H, 2 x aromatic-C-CH_2N), 2.89 (m, 2H, CH_2 of C_5H_5 of isomer 1), 2.88 (m, 2H, CH_2 of C_5H_5 of isomer 2), 2.62 (overlapped t, 4H, 2 x CH_2N), 2.38 (overlapped m, 4H, 2 x $C_5H_5CH_2$), 1.72 (overlapped m, 6H, 2 x CH_2CN); ^{13}C NMR δ/ppm $CDCl_3$ (^{1}H decoupled); 134.7 (1C, CH of C_5H_5), 133.9 (1C, CH of C_5H_5), 132.5 (1C, CH of C_5H_5), 130.7 (1C, CH of C_5H_5), 128.7, 128.5, 128.2, 127.2, 127.0, 126.9 (12C, aromatic ring C), 126.6 (1C, CH of C_5H_5), 126.2 (1C, CH of C_5H_5), 54.1 (2C, 2 x NCH_2), 49.3 (1C, aromatic-C-CH_2N), 49.3 (1C, aromatic-C-CH_2N), 43.4 (1C, $C_5H_5CH_2$), 41.4 (1C, $C_5H_5CH_2$), 30.2 (1C, CH_2), 29.3 (1C, CH_2), 28.6 (1C, CH_2), 27.8 (1C, CH_2). A peak for each of the *ipso* carbons of the C_5H_5 groups of each isomer should be present in the 145 - 150ppm region but these are too small to be seen.; MS: *m/z*-213 [EI]

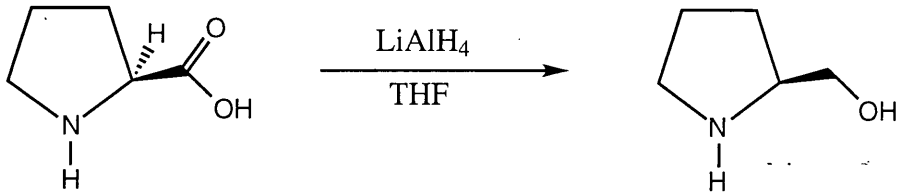
3.5 Preparation of Zr[η^5:η^1-$C_5H_4CH_2CH_2CH_2N(CH_2C_6H_5)$](NMe$_2$)$_2$

Zr[η^5:η^1-$C_5H_4CH_2CH_2CH_2N(CH_2C_6H_5)$](NMe$_2$)$_2$ was prepared and isolated as a "cloudy", pale orange oil according to the method used for the preparation of Zr[η^5:η^1-$C_5H_4CH_2CH_2CH_2N(C_6H_{11})$](NMe$_2$)$_2$.

^{1}H NMR δ/ppm C_6D_6; 7.17, 7.06 (overlapped m, 5H, aromatic ring H), 5.89 (t, 2H, C_5H_4), 5.67 (t, 2H, C_5H_4), 2.87 (m, 2H, aromatic-C-CH_2N), 2.79 (s, 12H, 2xNMe$_2$), 2.60 (m, 2H, NCH_2), 2.29 (m, 2H, $C_5H_4CH_2$), 1.60 (m, 2H, CH_2CH_2N); ^{13}C NMR δ/ppm C_6D_6 (^{1}H decoupled); 109.9 (CH of C_5H_4), 109.3 (CH of C_5H_4), 58.1 (1C, NCH_2), 54.3 (1C, aromatic-C-CH_2), 45.2 (2xNMe$_2$), 33.6 ($C_5H_4CH_2$), 28.5 (CH_2CH_2N). The aromatic peaks and the peak for the *ipso* carbon of C_5H_4 were too small to be seen in this sample.; MS: *m/z*-389 [EI]

3.6 Attempted preparation of $C_5H_5CH_2(C_4H_7)NH$

2-pyrrolidine methanol



proline prolinol

Under a flow of nitrogen, in a 500ml, two-necked flask fitted with reflux condenser, stopper and magnetic stirrer a suspension of approximately 6g $LiAlH_4$ in 250ml THF was made. To the suspension, 10g S-(-)-proline was added in small portions over a period of one hour. The suspension was then refluxed for 1.5 hours. The reaction mixture was allowed to cool and excess $LiAlH_4$ decomposed by the cautious addition of a solution of KOH in water, leading to the formation of a large amount of aluminates as a "sticky" white solid. The mixture was then reheated and the hot solution separated from the solid by-products by suction filtration. The aluminates were then refluxed with a further 200ml of THF, followed by filtration, in an attempt to extract any remaining product. The combined filtrates were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to give crude 2-pyrrolidine methanol (prolinol) as a yellow oil (6.34g, 0.062(77)mol, 72% yield). The yield is reduced by the adherence of the product to the aluminates formed from the decomposition of $LiAlH_4$, but all attempts to overcome this, such as dissolving the aluminates in a more concentrated alkali, failed. The prolinol obtained could be further purified by vacuum distillation but was of sufficient purity to be used directly in the next step.

^1H NMR δ/ppm $CDCl_3$; 3.44, 3.29 (overlapped m, 3H, NCH, $HOCH_2$), 2.81 (t, 2H, NCH_2), 1.67, 1.34 (overlapped m, 4H, $CH_2CH_2CH_2$, CH_2CH_2CH); ^{13}C NMR δ/ppm $CDCl_3$ (^1H decoupled); 64.4 ($HOCH_2$), 59.8 (NCH), 46.1 (NCH_2), 27.3 (CH_2), 25.6 (CH_2)

2-chloromethylpyrrolidine hydrochloride

A procedure analogous to that used for the synthesis of 3-(N-cyclohexylamino)chloropropane was followed. The crude product was obtained as a cream/white solid in 95% yield and could be further purified if necessary by recrystallization from THF or a methanol/diethyl ether mix.

^1H NMR δ/ppm $CDCl_3$; 3.94, 3.69 (overlapped m, 3H, NCH, $ClCH_2$), 3.31 (m, 2H, NCH_2), 2.05, 1.76 (overlapped m, 4H, $CH_2CH_2CH_2$, CH_2CH_2CH); ^{13}C NMR δ/ppm

$CDCl_3$ (^1H decoupled); 65.1 ($ClCH_2$), 57.5 (NCH), 44.5 (NCH_2), 24.4 (CH_2), 21.8 (CH_2)

Preparation of 2-(pyrrolidine)methyl cyclopentadiene

Again, the procedure used for the synthesis of 3-(N-cyclohexylamino)propylene cyclopentadiene was employed with both methods of addition (NaCp to a slurry of the hydrochloride salt or solid hydrochloride salt to NaCp solution) but all attempts met with failure. In all cases, NMR analysis of the brown oil obtained revealed the presence of dicyclopentadiene as the only major product. The possible reasons for this have been discussed in Section 2.

3.7 Preparation of $C_5H_5(CH_2)_3NHCH(CH_3)(C_6H_5)$

3-[(1-phenylethyl)amino]propanol

3-[(1-phenylethyl)amino]propanol was prepared as described for 3-(*N*-cyclohexylamino)propanol. Concentration of the organic layer under reduced pressure yielded a thick yellow oil (73% yield) which was used directly in subsequent reactions but could be further purified by vacuum distillation.

^{1}H NMR δ/ppm $CDCl_3$; 7.28 (m, 5H, aromatic H), 3.71 (m, 3H, OCH_2, aromatic-C-CHN), approximately 3.00 (br, 1H, NH), 2.65 (m, 2H, NCH_2), 1.60 (m, 2H, $C\underline{C}H_2C$), 1.32 (d, 3H, $CH_2C\underline{H}_3$); ^{13}C NMR δ/ppm $CDCl_3$ (^{1}H decoupled); 144.9, 128.5, 127.7, 126.5 (6C, aromatic C), 63.8 ($HOCH_2$), 58.6 (aromatic-C-$\underline{C}$HN), 47.5 (NCH_2), 31.4 ($C\underline{C}H_2C$), 24.2 ($CH_2\underline{C}H_3$)

3-[(1-phenylethyl)amino]chloropropane hydrochloride

3-[(1-phenylethyl)amino]chloropropane was synthesized according to the method used for the synthesis of 3-(*N*-cylohexylamino)chloropropane. The product was obtained as a cream "oily" solid which could, with difficulty, be recrystallized from methanol and diethyl ether in low yields

^{1}H NMR δ/ppm $CDCl_3$; 8.60 (br, NH_2), 7.48, 7.29 (overlapped m, 5H, aromatic H), 3.56 (m, 3H, $ClCH_2$, aromatic-C-CHN), 1.65 (m, 4H, NCH_2, $CC\underline{H}_2C$), 1.11 (t, 3H, $CH_2C\underline{H}_3$); ^{13}C NMR δ/ppm $CDCl_3$ (^{1}H decoupled); 127-138 (6C, aromatic C), 59.3 ($HOCH_2$), 51.9 (aromatic-C-$\underline{C}$HN), 43.8 (NCH_2), 28.4 ($C\underline{C}H_2C$), 20.5 ($CH_2\underline{C}H_3$)

3-[(1-phenylethyl)amino]propylene cyclopentadienyl

Similarly, the procedure used for the synthesis of 3-(*N*-cylohexylamino)propylene cyclopentadiene was used for the preparation of 3-[(1-phenylethyl)amino]propylene cyclopentadiene. The product was not isolated in any significant yields with the absence of dicyclopentadiene but its presence in the product mixture was confirmed by GC mass spectrometry.

MS: *m/z*- 227 [EI]

3.8 References

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