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Non Flory-Schulz ethene oligomerization with titanium-based catalysts

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Switching a catalyst system from ethene polymerization to ethene trimerization with hemilabile [C$_5$H$_4$CMe$_2$Ar]$^-$ ancillary ligands[*]

4.1 Introduction

The chemistry of transition metal complexes with chelating ligands containing mixed functionalities is enjoying an increasing popularity. Particularly interesting are ligands which contain both tightly bound and substitutionally labile groups, e.g. via combination of 'soft' and 'hard' donor atoms[1], to give systems in which the effective electron donation to the metal center depends on the coordination mode of the labile group[2]. These ligands, termed hemilabile ligands[3] (more exactly formulated, ligands that exhibit hemilabile behavior), have one or more functionalities that are tightly bound to the metal center, as well as one or more weakly chelating groups that are capable of temporarily occupying coordination sites at reactive metal centers in the absence of small molecule substrates.

T = Tightly bound group
L = Labile group
S = Substrate, solvent or ligand
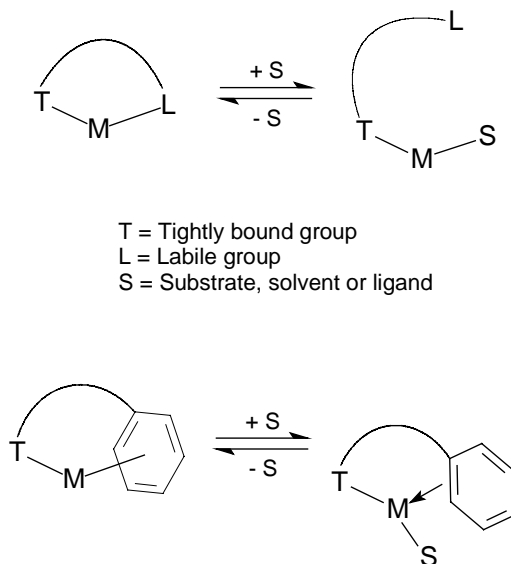
Scheme 1: Characteristics of hemilabile ligands

However, in the presence of such substrates, the labile portion of the ligand dissociates to allow formation of a metal-small molecule complex, while the tightly bound moiety keeps the ligand anchored to the metal center (Scheme 1, top). For multihapto labile moieties, e.g. arenes, dissociation of the labile group can also take place via a (reversible) change in hapticity, e.g. from η^6 to η^2, to lower the ligand electron donation to the metal, and allow substrate coordination (Scheme 1, bottom).

The hemilabile nature of this type of ligands can be observed in several ways. On the most fundamental level, the hemilability of a chelate can be observed via fluxional processes that involve the dissociation and recoordination of the weakly bonding moiety via intramolecular ligand exchange processes. For transition metal species with two or more hemilabile ligands[4], or with hemilabile ligands with two or more weakly coordinating groups per ligand[5], the different labile groups compete for coordination to the metal center, and dynamic exchange processes can be observed. Similarly, exchange processes and/or coordination equilibria between labile groups of hemilabile ligands and other species, such as coordinating counterions[6] or excess ligand[7], can occur. In dimeric transition metal complexes, labile functionalities can alternately coordinate to each metal center[8]. In addition, the hemilabile character of bifunctional ligands can be manifested by replacement of the substitutionally labile group by small molecules such as cyanides[9], alkenes[10] and CO[11,12].

In the previous chapter, we showed that the ancillary $[C_5H_4CMe_2Ar]^-$ ligand (Ar = Ph or $3,5\text{-}Me_2C_6H_3$) displays hemilabile behavior in cationic titanium dialkyl species. Reaction of the neutral $(\eta^5\text{-}C_5H_4CMe_2Ar)TiR_3$ compounds with the Lewis acid $B(C_6F_5)_3$ affords the cationic $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)TiR_2]^+$ species, in which the arene moiety coordinates to the titanium center.
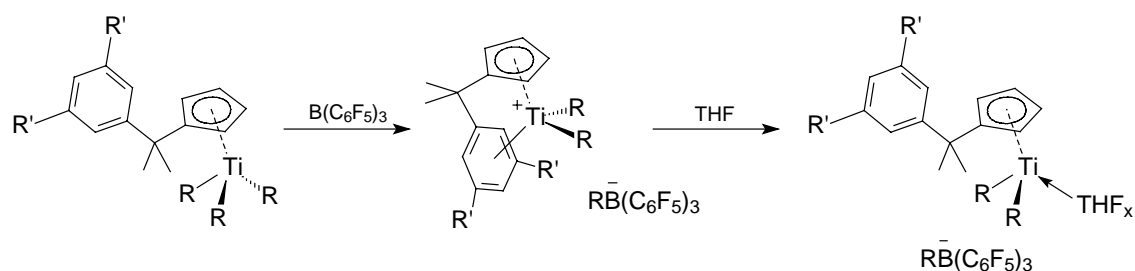
Scheme 2:   Hemilabile behavior of $[C_5H_4CMe_2Ar]^-$ ligands in cationic titanium species

In the presence of the Lewis base THF, the arene moiety is displaced to give a $[(\eta^5\text{-}C_5H_4CMe_2Ar)TiR_2(THF)_x]^+$ cationic species, thus behaving as a substitutionally labile group. The hemilabile properties of $[C_5H_4CMe_2Ar]^-$ ligand systems are expected to affect the stability and reactive properties of monocyclopentadienyl titanium catalysts, and may allow the study of intermediate species.

4.2 Examples of hemilabile ligands in catalysis

The flexible coordination mode of hemilabile ligands has previously been exploited to maximize the stability of metal complexes while retaining their reactive possibilities, and has been implicated in a number of catalytic reactions[13]. For example, combinations of [(allyl)NiBr]$_2$, AgOTf and a tertiary phosphine (e.g. PPh$_3$) were shown to be good catalysts for the quantitative hydrovinylation of vinylarenes with ethene (Scheme 3)[14]. Efforts to find an asymmetric version of this reaction led to the development of catalyst systems with chiral binaphtyl-based [P,O] ligands (instead of PPh$_3$, Scheme 3, ligand A), in which the alkoxy group acts as a substitutionally labile moiety, to afford highly active (>95% conversion) and enantioselective (80% ee) catalysts[15]. The role of oxygen chelation and the importance of its hemilabile behavior became apparent from experiments using ligand B and C (Scheme 3), respectively[16]. Ligand B (no oxygen moiety) was active in hydrovinylation, but with complete loss of enantioselectivity (<3% ee), indicating that (transient) oxygen coordination is crucial to attain stereocontrol. On the other hand, ligand C (with the acetoxy group) was completely inactive in the hydrovinylation of vinylarenes due to the inability of ethene to displace the stronger coordinating ester group.
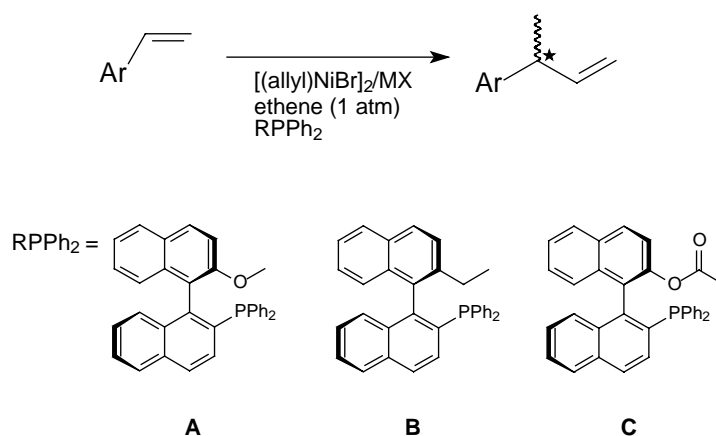
Scheme 3: Hemilabile ligand effects in hydrovinylation reactions

Similar hemilabile ligand effects on catalyst selectivity have been observed for hydrogenation of olefins[17], hydroformylation of epoxides[18], alkyne dimerization[19], CO$_2$/butadiene coupling reactions[20], and catalytic isomerization of allyl to vinyl ethers[21]. For the latter conversion, Rh(I) complexes with redox-switchable hemilabile ligands were used, such as the [P,O] ligand (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$-C$_6$H$_4$-OCH$_2$CH$_2$PPh$_2$). In these systems, the bonding affinity of the hemilabile [P,O] ligand can be controlled by adjusting the oxidation state of the ferrocene group, which is covalently attached via an aryl π-system to the labile oxygen group.

Hemilabile ligands can also be used to characterize putative catalytic intermediates that are too reactive to observe for analogous species without hemilabile ligands. Cationic palladium allyl complexes with bidentate [P,O] chelates have been applied in the oligomerization of ethene[22] and cooligomerization of ethene with styrene and CO[23]. Insertion of ethene in the palladium-allyl is the key step of these reactions. Evidence for mono-insertion of strained olefins (e.g. norbornene) in related palladium-allyl species had been observed[24], but not for ethene. By judicious choice of hemilabile [P,O] ligands the ethene insertion product could be trapped and observed by NMR spectroscopy (Scheme 4)[25].
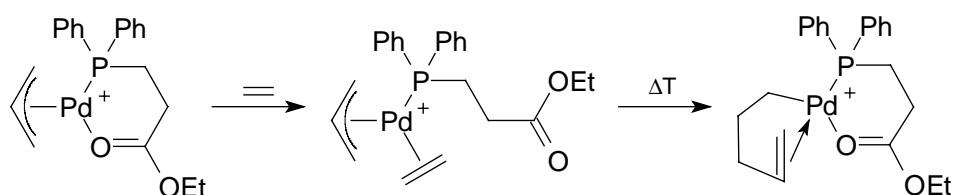
Scheme 4: Trapping the ethene mono-insertion product

Stabilization of catalytic species[26] otherwise prone to decomposition is another virtue of hemilabile ligands. In this way, catalyst deactivation can be circumvented. The in situ generated species $[(1\text{-MeInd})\text{Ni}(\text{PPh}_3)]^+$ was found to catalyze a number of olefin C-C coupling reactions[27]. However, redistribution of the phosphine ligands afforded the inactive species $[(1\text{-MeInd})\text{Ni}(\text{PPh}_3)_2]^+$ (Scheme 5). By introducing a labile amine moiety the reactive intermediate is stabilized with respect to ligand redistribution[28]. The amine can be replaced by olefins to allow catalytic C-C bond formation (though with some loss of activity)[29].
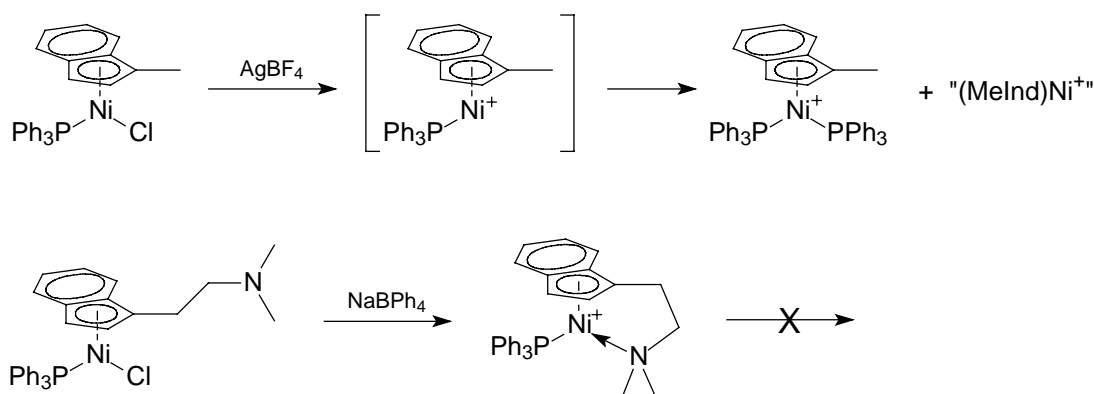
Scheme 5: Stability of $[(1\text{-RInd})\text{Ni}(\text{PPh}_3)]^+$ cationic species

4.3 Monocyclopentadienyl titanium complexes with hemilabile groups

The last example demonstrates the successful use of cyclopentadienyl-based hemilabile ligands in catalysis[30]. The chemistry of cyclopentadienyl complexes containing a neutral donor-functionalized side chain (e.g. Cp-N[31], Cp-O[32], Cp-P, Cp-As and Cp-S[33]) and their potential applications as catalysts presents a rapidly growing area of research. The presence of the donor atom in the coordination sphere of the metal center is expected to affect the stability and/or selectivity of the resulting catalytic species. Yanlong and coworkers reported the first example of a chelating hemilabile cyclopentadienyl ligand on a titanium half-sandwich complex, $[\eta^5,\eta^1-C_5H_4(CH_2)_2OMe]TiCl_3$[34] (**A**, Scheme 6), shortly followed by reports on $[\eta^5,\eta^1-C_5R_4(CH_2)_nNMe_2]TiCl_3$ (R = H, Me; n = 2, 3) (**B**)[35] and related chelating aminoalkylcyclopentadienyl systems[36]. Jutzi and Kleimeier described the preparation of the first half-sandwich titanium trichloride compound containing a pendant aminoalkyl side chain (**C**)[37]. The presence of the tethered amino groups has significant effects on olefin polymerization reactivity of these complexes compared to CpTiCl$_3$. The $[(Cp-N)TiR_2]^+$ catalysts display lower activity and stereoselectivity for styrene polymerization, but higher activity in ethene and propene polymerization than $[CpTiR_2]^+$ species.
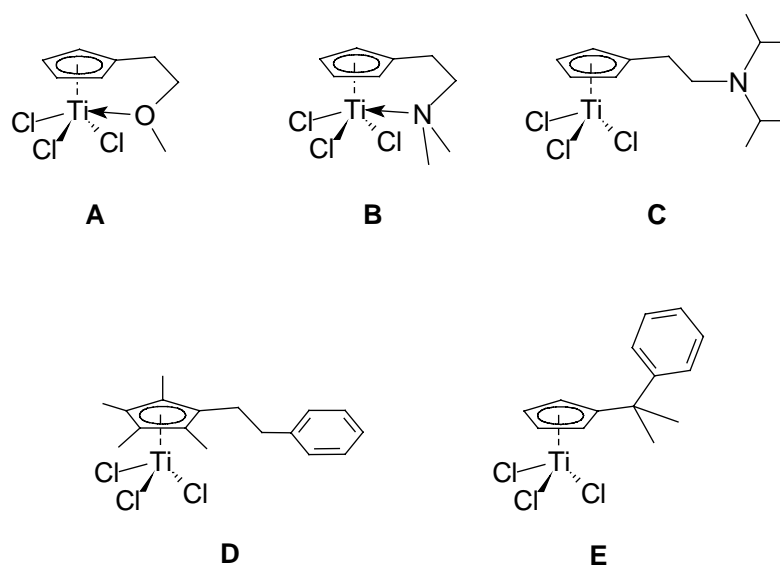
Scheme 6: Half-sandwich titanium complexes with hemilabile ligands

In contrast with hemilabile coordination in aminoalkylcyclopentadienyl ligands occurring between the lone pair of electrons on nitrogen and LUMO orbitals of the titanium center[38], the $[C_5Me_4CH_2CH_2Ph]^-$ ligand (**D**) uses π-electrons[39] to establish substitutionally labile interactions[40]. The styrene polymerization activity of the catalyst system $(\eta^5-C_5Me_4CH_2CH_2Ph)TiCl_3$/MAO is about 2-3 times smaller than

that for Cp*TiCl$_3$/MAO, but with comparable syndiospecificity. The system shows modest ethene polymerization activity.

As mentioned before, the [C$_5$H$_4$CMe$_2$Ar]$^-$ ligand (**E**) shows hemilabile behavior in cationic titanium dialkyl species (Scheme 2). In this chapter the catalytic olefin conversion properties of the [(η^5-C$_5$H$_4$CMe$_2$Ar)TiMe$_2$]$^+$ cationic species and the role of the hemilabile pendant arene group will be discussed together with the effect of solvent and activators on catalyst activity and selectivity. It was observed that the pendant arene group has a dramatic effect on the product selectivity in catalytic ethene conversion. While this study was in progress, several groups reported the preparation and catalytic propene and styrene polymerization properties of this and related [(Cp-Ar)TiR$_2$]$^+$ cationic species[41].

4.4 Catalytic olefin conversion with [(η^5,η^6-C$_5$H$_4$CMe$_2$Ar)TiMe$_2$]$^+$ cationic species

Reaction of (η^5-C$_5$H$_4$CMe$_2$Ar)TiMe$_3$ (Ar = Ph, **3**, or 3,5-Me$_2$C$_6$H$_3$, **4**) with the Lewis acid B(C$_6$F$_5$)$_3$ in C$_6$D$_5$Br affords the cationic species [(η^5,η^6-C$_5$H$_4$CMe$_2$Ar)TiMe$_2$]$^+$ (Ar = Ph, **15**, or 3,5-Me$_2$C$_6$H$_3$, **16**), the generation of which is described in Chapter 3. For Ar = 3,5-Me$_2$C$_6$H$_3$ (**16**) this yields a relatively stable 16-electron complex that was found not to polymerize propene or styrene at ambient temperature and pressure in C$_6$D$_5$Br solvent (studies performed in an NMR tube). For **15** the coordination of the arene moiety is noticeably weaker, but (under the conditions described above) again no polymerization of propene and styrene was observed, although modest activity in propene and styrene polymerization was reported later for the cation **15** in toluene solvent, generated by activation with either [Ph$_3$C][B(C$_6$F$_5$)$_4$]^{41a} or MAO^{41b,c}.
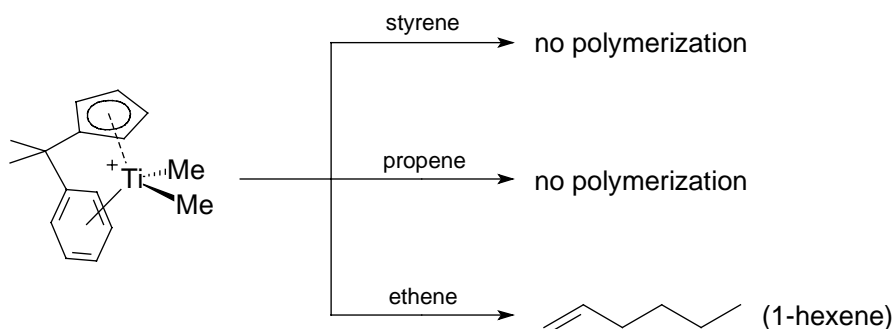
Scheme 7: Reactivity of **15** towards olefins at ambient temperature and pressure in C$_6$D$_5$Br solvent (NMR tube experiments)

Addition of ethene to an NMR tube containing a solution of **15** in C$_6$D$_5$Br at ambient temperature resulted in the formation of a trace of polyethene and,

unexpectedly and much more interestingly, substantial amounts of *1-hexene*, as observed by ^{1}H NMR and confirmed by GC/MS. For the cationic species **16** only trace amounts of polyethene and 1-hexene were observed under similar conditions. These preliminary experiments suggested that, apparently, the labile arene group can transform the $[Cp^RTiMe_2]^+$ catalyst system, at least partially, from an ethene polymerization catalyst into an ethene trimerization catalyst, producing 1-hexene.

4.5 Ethene trimerization with (η^5-C$_5$H$_4$CMe$_2$Ph)TiCl$_3$ (1)/MAO

To elaborate on the unexpected ethene trimerization activity observed for cation **15**, the catalyst system (η^5-C$_5$H$_4$CMe$_2$Ph)TiCl$_3$ (**1**)/MAO was investigated under various conditions. This combination of reagents is also expected to generate the cationic species **15**. The results of catalytic ethene conversion experiments with the catalyst system **1**/MAO (toluene solvent, Ti:Al ratio of 1:1000) are listed in Table 1. Analysis of the liquid fraction by GC (using cyclooctane as internal standard), GC/MS and NMR techniques revealed that, under these conditions, the catalyst produces olefin trimerization products with high selectivity (>95 wt% overall). These trimerization products consist of two fractions: C_6 (trimers of ethene) and C_{10} (cotrimers of ethene and 1-hexene, *vide infra*). In addition to the trimerization products, smaller amounts of C_8 product (1 wt%) and polyethene (PE, 1-3 wt%) are produced.

Table 1: Catalytic ethene conversions with the **1**/MAO catalyst system as function of ethene pressure (toluene solvent, 30 °C, 15 µmol Ti, Al:Ti = 1000, 30 min reaction time)

P(ethene) [bar]	C$_6$ products [g] (wt%)	C$_{10}$ products [g] (wt%)	PE [g] (wt%)	Productivity C$_6$ products[a]	Trimerization products [wt%]	Trimerization productivity[b]
2	8.0 (87)	1.0 (11)	0.2 (1.6)	535	98	41.0
5	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
10	47.2 (86)	5.1 (9)	1.4 (2.6)	630	95	239

[a] in g C$_6$ product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h

The rate of production of 1-hexene increases with increasing ethene pressure. The C_6 productivity is around 550-600 kg per mole Ti, bar and h, over a range of 2-10 bar of ethene pressure. Although no true kinetic studies were undertaken, the roughly linear dependence between the amount of C_6 products formed and the ethene pressure suggests that the trimerization process follows first-order kinetics in ethene.

The C_6 product fraction consists predominantly of 1-hexene (99.5%) with the remaining 0.5% being a mixture of 2- and 3-hexenes. For entry 2 in Table 1, the C_{10}

fraction was isolated, by evaporation of the low-boiling (<125 °C) volatile components of the reaction mixture, and analyzed separately by NMR and GC/MS[42]. NMR analysis of the olefinic residues in this mixture indicates the presence of 90% $RCH_2CH=CH_2$ end-groups, 5% RCH=CHR' and 5% $RR'C=CH_2$. GC/MS indicates that the C_{10} fraction mainly consists of 5-methylnon-1-ene (83%). The only detectable product in the C_8 fraction (by GC) is 1-octene. DSC analyses of the polyethene samples give melting points higher than 128 °C, indicative of HDPE[43] (High Density Polyethene), suggesting that very little of the 1-hexene formed is incorporated into the polymer.

Table 2: Catalytic ethene conversions with the **1**/MAO catalyst system as function of temperature (toluene solvent, 5 bar ethene pressure, 15 μmol Ti, Al:Ti = 1000, 30 min reaction time)

T [°C]	C_6 products [g] (wt%)	C_{10} products [g] (wt%)	PE [g] (wt%)	Productivity C_6 products[a]	Trimerization products [wt%]	Trimerization productivity[b]
30	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
50	12.4 (83)	1.6 (11)	0.7 (4.6)	330	94	63.5
80	3.3 (76)	0.2 (4)	0.8 (19)	90	80	16.5

[a] in g C_6 product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h

The thermal stability of the catalyst system **1**/MAO is modest (Table 2): increasing the reaction temperature decreases the overall catalyst productivity over the 30 min run period, and increases the relative amount of PE produced. This is likely to be associated with catalyst degradation, as suggested by the more rapid decrease in ethene uptake rate during the runs at elevated temperature. At 80 °C, ethene uptake stops completely after about 10 min reaction time, whereas at 30 °C ethene is consumed over the whole run period, although the uptake rate clearly slows down in the course of the run.

The product C_{10} fraction is likely to be produced by cotrimerization of ethene and 1-hexene rather than by direct pentamerization of ethene. In separate experiments, ethene was converted by the catalyst **1**/MAO at 30 °C in the presence of 15 g of 1-octene added to the reaction mixture (Table 3). In addition to the C_6 and C_{10} product fractions mentioned above, a considerable amount of C_{12} products (cotrimers of ethene and 1-octene, obtained in 2-3 g quantities, depending on the ethene pressure) is now observed as well. This is likely to stem from ethene/1-octene cotrimerization, and these results indicate that the C_{10} product fraction in the catalytic ethene oligomerization by **1**/MAO is indeed formed via cotrimerization of ethene and 1-hexene.

Table 3: Catalytic ethene conversions with the **1**/MAO catalyst system in the presence of added 1-octene (toluene solvent, 30 °C, 15 μmol Ti, Al:Ti = 1000, 30 min reaction time)

P(eth.)	1-octene	C_6 products	C_{10} products	C_{12} products	PE	Productivity	Trimerization	TP[b]
[bar]	[g]	[g] (wt%)	[g] (wt%)	[g] (wt%)	[g] (wt%)	C_6 products[a]	products [wt%]	
2	0	8.0 (87)	1.0 (11)	0.03 (0.4)	0.2 (1.6)	535	98	41.0
2	15	6.3 (69)	0.7 (8)	2.0 (22)	0.1 (1.1)	425	99[c]	37.0
5	0	20.9 (83)	3.5 (14)	0.1 (0.4)	0.5 (1.8)	555	97	109.5
5	15	16.6 (75)	2.2 (10)	2.7 (12)	0.5 (2.3)	445	97[c]	92.0

[a] in g C_6 product per mmole Ti, bar and h; [b] Trimerization Productivity (in mole olefinic bonds trimerized per mmole Ti and h); [c] C_8 fraction not determined due to overlap with added 1-octene

4.6 Effect of the pendant arene group on ethene trimerization reactivity

The effect of the pendant arene group on ethene conversion by the $(\eta^5\text{-}C_5H_4CMe_2Ar)TiCl_3$/MAO catalysts was probed by studying the catalysts with Ar = Ph (**1**), $4\text{-}MeC_6H_4$ (**24**), $3,5\text{-}Me_2C_6H_3$ (**2**), and comparing them with an analogous system without a pendant arene, $(\eta^5\text{-}C_5H_4CMe_3)TiCl_3$ (**25**). The results are listed in Table 4.

Table 4: Catalytic ethene conversions with the $(\eta^5\text{-}C_5H_4CMe_2R)TiCl_3$/MAO catalyst systems (toluene solvent, 5 bar ethene, 30 °C, 15 μmol Ti, Al:Ti = 1000, 30 min reaction time)

Catalyst (R)	C_6 products	C_{10} products	PE	Productivity	Trimerization	Trimerization
	[g] (wt%)	[g] (wt%)	[g] (wt%)	C_6 products[a]	products [wt%]	productivity[b]
1 (Ph)	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
24 ($4\text{-}MeC_6H_4$)	14.7 (88)	1.6 (10)	0.3 (1.6)	395	98	74.5
2 ($3,5\text{-}Me_2C_6H_3$)	7.9 (93)	0.1 (4)	0.1 (1.3)	210	97	38.0
25 (Me)	0.5 (17)	0.1 (4)	2.4 (76)	13	21	2.5

[a] in g C_6 product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h

It can be seen that making the pendant phenyl group more electron-rich, by adding one or two methyl substituents respectively, significantly diminishes the productivity of the catalyst with each methyl group added, whereas the selectivity for trimerization is retained. This reduction of catalyst productivity upon methyl substitution of the pendant group reflects a slowing down of the catalytic cycle, as no

evidence was found for a more rapid catalyst deactivation in these systems. The absence of the pendant arene group leads to the predominant formation of polyethene, indicating that the pendant arene group is essential to obtaining selective trimerization. These observations suggest that the cyclopentadienyl-arene ligand is likely to display hemilabile character in the course of the catalysis: it has to be present for coordination, apparently helping to generate the species responsible for the selective trimerization, but if it binds too strongly it can slow down the catalytic reaction.

It may be noted that even for the *tert*-butylcyclopentadienyl system **25**/MAO a certain amount of ethene trimerization product is observed in addition to the main product, polyethene. A related observation was made recently by Pellecchia and coworkers in ethene polymerization with the [Cp*TiMe$_2$][MeB(C$_6$F$_5$)$_3$] catalyst in toluene solvent, where the PE obtained contains a noticeable amount of *n*-butyl side groups[44]. It was suggested that the catalyst is partly converted to a species that trimerizes ethene to 1-hexene, which is then incorporated into the polymer. Our observations indicate that transient coordination of the toluene solvent to the metal center may be instrumental in this[45], albeit less efficient than the pendant arene group in the (η^5-C$_5$H$_4$CMe$_2$Ar)TiCl$_3$/MAO systems as the interaction is intermolecular rather than intramolecular.

Table 5: Catalytic ethene conversions with the **1**/MAO catalyst system (5 bar ethene pressure, 30 °C, 15 μmol Ti, Al:Ti = 1000, 30 min reaction time) in two different solvents

Toluene [vol%]	*n*-octane [vol%]	C$_6$ products [g] (wt%)	C$_{10}$ products [g] (wt%)	PE [g] (wt%)	Productivity C$_6$ products[a]	Trimerization products [wt%]	Trimerization productivity[b]
100	0	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
20	80	8.1 (87)	0.8 (9)	0.4 (4.3)	215	96[c]	41.0

[a] in g C$_6$ product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h; [c] C$_8$ fraction not determined due to overlap with *n*-octane

In order to estimate the possible role of solvent interactions on the selective ethene trimerization by the cyclopentadienyl-arene titanium catalysts, we investigated the catalyst system **1**/MAO in an 80:20 vol% mixture of *n*-octane and toluene (Table 5). The ethene conversion results showed that the selectivity for trimerization is largely retained, but that the catalyst productivity over the 30 min run is lower than in neat toluene. The initial ethene uptake profile is identical to that of the corresponding run in neat toluene, but the catalyst appears to deactivate more rapidly in the *n*-octane/toluene mixture. These findings indicate that the intrinsic trimerization process and its selectivity do not depend on the aromatic solvent, but that having an aromatic solvent may be benificial for the catalyst stability.

4.7 Proposed catalytic cycle for ethene trimerization

It has been proposed that the only family of catalysts known thus far to affect selective ethene trimerization (Ziegler-type catalysts based on the combination of chromium salts with aluminum alkyls and added Lewis bases[46]) acts through a mechanism involving metallacyclic intermediates (Scheme 8). This may proceed through initial oxidative coupling of two ethene molecules by a low-valent chromium species, generated in situ, to produce a chromacyclopentane compound. Insertion of an additional ethene molecule into one of the Cr-C bonds then affords a chromacycloheptane species. Subsequent β-H abstraction followed by reductive elimination can then lead to the formation of 1-hexene and the regeneration of the low-valent chromium species[47].
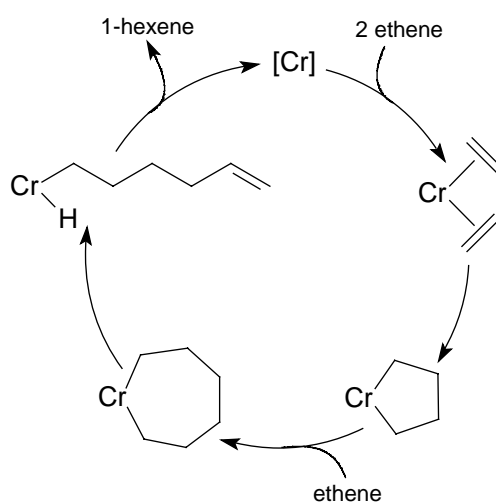

Scheme 8: Proposed catalytic cycle for selective ethene trimerization by Cr-based catalysts

This sequence would explain the high selectivity for 1-hexene (and the lack of 1-butene formation) as the chromacyclopentane is expected to be much more stable towards β-H abstraction than the more flexible chromacycloheptane[48]. For the very recently reported selective ethene trimerization by TaMe$_2$Cl$_3$ a similar catalytic cycle via metallacycles has been proposed[49].

It is likely that a similar mechanism is operative in the selective trimerization performed by the cyclopentadienyl-arene titanium catalysts presented here. Several catalytic C-C coupling reactions have been reported in neutral titanium systems that involve metallacyclic intermediates and a Ti(IV)/Ti(II) couple[50]. It is less obvious how such a low-valent Ti(II) species would be generated from a monocyclopentadienyl titanium(IV) trichloride complex and MAO. Based on the information available so far, a tentative reaction sequence is proposed, which is outlined in Scheme 9.

The reaction of $(\eta^5\text{-}C_5H_4CMe_2Ar)TiCl_3$ with MAO will generate the 16 electron cationic species $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)TiMe_2]^+$ initially. It is likely that these cations will undergo multiple ethene insertions into the Ti-Me bonds to produce bis(n-alkyl) compounds $[(C_5H_4CMe_2Ar)Ti(CH_2CH_2R)_2]^+$ (**A**). These are in equilibrium with hydride-olefin species (**B**) through (reversible) β-H elimination. Normally, dissociation of the olefin is energetically unfavorable unless it is driven out by another incoming ligand[51].
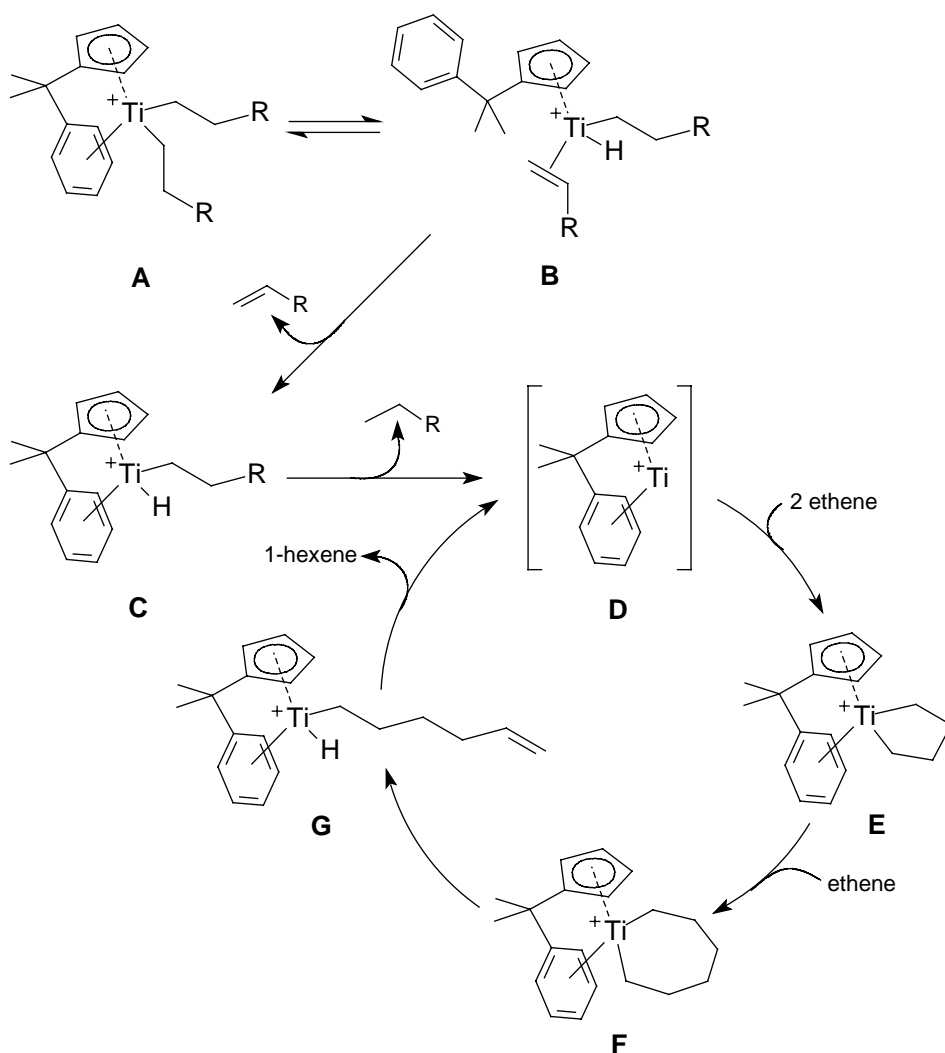
Scheme 9: Proposed reaction pathway for catalyst transformation and catalytic ethene trimerization for present systems

In a regular ethene polymerization catalyst, a molecule of ethene can drive out the polymer chain as an alkene, and then rapidly insert into the M-H bond to start the growth of a new chain (this thus represents a normal chain-transfer process in catalytic ethene polymerization, see Chapter 1). In our systems, with the pendant arene group, it is possible that the alkene is driven out by the incoming arene, which

will lead to the 16-electron hydride-alkyl species, $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ar)$ $Ti(H)CH_2CH_2R]^+$ (**C**). Such a species is expected to be unstable with respect to reductive elimination[52], which will release the second polymer chain as the alkane RCH_2CH_3 and form a cationic Ti(II) intermediate (**D**). This can capture two ethene molecules to give a cationic titanacyclopentane (**E**), and subsequently perform the catalytic ethene trimerization following the pathway involving ethene insertion, β-H abstraction and reductive elimination (e.g. via intermediates **F** and **G**) as described for the chromium-based systems.

If the rate of 1-hexene formation is indeed first order in ethene (*vide supra*), it is very likely that the insertion of the third ethene molecule into one of the metal-carbon bonds of the proposed 16-electron cationic titanacyclopentane intermediate (**E**) is the rate-determining step. This reaction step will probably involve displacement or slippage of the η^6-coordinated arene ligand to yield a less electron-rich metal center that will more readily capture and insert the third ethene molecule. It is well possible that the process of arene dissociation or ring slippage makes the last insertion step rate-determining, thus resulting in the observed decrease in catalyst activity upon increasing the donor ability of the pendant arene group.

Kinetic studies of chromium-based ethene trimerization catalysts have revealed a second order dependence on ethene, indicating that in these systems the formation of the chromacyclopentane (or a bis(ethene) adduct leading to this species) is likely to be rate-determining[53]. However, the selective trimerization of 1-hexene with triazacyclohexane-chromium catalysts was recently reported to have as rate-determining step the insertion of the third monomer molecule[54].

Recent calculations performed on the model system $[(\eta^5,\eta^6\text{-}C_5H_4CH_2Ph)Ti]^+$ confirm our proposed pathway[55]. However, the calculations indicate a direct α,β'-proton shift as the termination step from intermediate **F** rather than via β-H elimination to give **G**, followed by reductive elimination. The same pathway in the titanacyclopentane **E** is energetically unfavorable explaining the preference for trimerization over dimerization in this system. The authors suggest similar proton transfer from one alkyl chain to the other in the polymerization type catalyst **A** to generate directly the trimerization active species **D**. During the trimerization the hapticity of the arene group changes along the cycle.

Zhu and coworkers reported recently that the catalyst system $Cp^*Ti(OCH_2Ph)_3/MAO$ in heptane produces short chain (ethyl and butyl) branched polyethene, and they proposed a reduced titanium species as being responsible for in situ dimerization and trimerization of ethene[56]. They suggest that free $AlMe_3$, present in MAO, is essential in the reduction of titanium(IV) and the subsequent oligomerization of ethene. Decreasing the $AlMe_3$ amount in the cocatalyst does indeed diminish the degree of branching in the PE obtained with this catalyst system. The presence of ethyl branches (in addition to butyl branches) in the polyethene generated by this catalyst suggests that another oligomerization mechanism is at work in this particular system, as neither with the $Cp^*TiMe_3/B(C_6F_5)_3$/toluene

catalyst[44], nor with the present systems, indications for the formation of significant amounts of 1-butene have been found.

Table 6: Catalytic ethene conversions with $(\eta^5\text{-}C_5H_4CMe_2Ph)TiMe_3$/cocatalyst systems compared with **1**/MAO (toluene solvent, 5 bar ethene, 30 °C, 15 μmol Ti, 30 min reaction time)

Cocatalyst	C_6 products [g] (wt%)	C_{10} products [g] (wt%)	PE [g] (wt%)	Productivity C_6 products[a]	Trimerization products [wt%]	Trimerization productivity[b]
$[PhNMe_2H][B(C_6F_5)_4]^c$	14.6 (90)	1.2 (7)	0.3 (2.0)	390	97	73.0
$B(C_6F_5)_3^c$	5.8 (88)	0.3 (5)	0.4 (6)	155	93	28.5
MAO/SiO_2^d	13.8 (95)	0.6 (4)	n.d.	365	99[e]	67.5
1/MAO[f]	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5

[a] in g C_6 product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h; [c] B:Ti ratio = 1.1; [d] 5 wt% MAO on silica, Al:Ti ratio = 250; [e] Product distribution is based on liquid fraction only (remaining 1 wt% is C_8 and C_{12+} fractions); [f] Al:Ti ratio = 1000

To evaluate the effect of the cocatalyst on the trimerization catalysis, we performed catalytic ethene conversion studies using $(\eta^5\text{-}C_5H_4CMe_2Ph)TiMe_3$ (**3**), with the cocatalysts $[PhNMe_2H][B(C_6F_5)_4]$, $B(C_6F_5)_3$ and MAO/SiO_2 (Table 6). All catalyst systems show predominant formation of trimerization products, indicating that free $AlMe_3$ is not instrumental in the generation of the species that produces 1-hexene. MAO/SiO_2 and $[PhNMe_2H][B(C_6F_5)_4]$ prove to be good cocatalysts to afford active and highly selective (>97 wt%) trimerization catalysts. The selectivity of the **3**/$B(C_6F_5)_3$ catalyst system is slightly worse (about 93 wt% of trimerization products) and its activity is rather low. This may be associated with the relatively strong coordinative ability of the $[MeB(C_6F_5)_5]^-$ anion[57]. It may be taken into account that the experiments with the $B(C_6F_5)_3$ and $[PhNMe_2H][B(C_6F_5)_4]$ activated systems are conducted in the absence of impurity scavenger, which might partially explain the lower activities, compared to **1**/MAO.

4.8 Conclusions

We have identified a catalyst system, $(\eta^5\text{-}C_5H_4CMe_2R)TiCl_3$/MAO, that by attachment of a pendant arene group to the cyclopentadienyl ancillary ligand (R = aryl) can be transformed from an ethene polymerization catalyst into a selective ethene trimerization catalyst. We have shown that the intrinsic selectivity for ethene trimerization of the catalytic species, derived from the initially formed $[(\eta^5\text{-}C_5H_4CMe_2Ar)TiMe_2]^+$ cations, is essentially independent of solvent and cocatalyst,

and that hemilabile behavior of the cyclopentadienyl-arene ancillary ligand is essential for obtaining this high selectivity for trimerization.

Although some ethene oligomerization processes that produce 1-hexene in excess of the amount expected from Flory-Schulz product distributions, and ethene polymerization catalysts that produce branched polyethenes, are known (e.g. for certain Ziegler-type catalyst systems)[58], to our knowledge the present system is the first highly selective ethene trimerization catalyst that is not based on chromium. Very recently a catalyst system for ethene trimerization based on $TaMe_2Cl_3$ was reported that shows good selectivity for 1-hexene, but its activity is at least two orders of magnitude smaller than the titanium catalyst systems described here. The principle that a hemilabile ligand functionality can divert the metal species from one catalytic cycle into another may be applicable to other types of catalysis.

4.9   Experimental Section

General considerations - All experiments were carried out under purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over molecular sieves (Aldrich, 4Å) prior to use (C_6D_5Br), or dried over Na/K alloy and vacuum transferred (C_6D_6). Cyclooctane (Aldrich, used as internal standard) and *n*-octane (Aldrich) were distilled from sodium, and 1-octene (Aldrich) was distilled from CaH_2 prior to use. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å) under nitrogen atmosphere prior to use. Methylene chloride (Aldrich) was dried over molecular sieves (Aldrich, 4Å) under nitrogen atmosphere before use. Ethene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å). - NMR spectra were recorded on a Varian Gemini 300 spectrometer. The ^{1}H NMR spectra were referenced to resonances of residual protons in the deuterated solvent (δ = 7.15 ppm for C_6D_6). The ^{13}C NMR spectra were referenced to the carbon resonances of the deuterated solvent (δ = 128 ppm for C_6D_6). Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive). GC analyses were performed on a HP 6890 instrument equipped with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC/MS analyses were conducted using a HP 5973 mass-selective detector attached to a HP 6890 GC instrument. DSC analyses were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter. The elemental analysis was performed at the Microanalytical Department of the University of Groningen. Given values are the average of at least two independent determinations. - The compounds (η^5-$C_5H_4CMe_3$)$TiCl_3$ (**25**)[59], $C_5H_4(SiMe_3)CMe_2$-4-MeC_6H_4[60] and $B(C_6F_5)_3$[61] were prepared according to published procedures. A toluene solution of MAO (9.8 wt% Al, Akzo Nobel Chemicals), MAO supported on silica (5 wt%, Witco) and [$PhNMe_2H$][$B(C_6F_5)_4$] (Akzo Nobel Chemicals) were used as received.

Preparation of (η^5-$C_5H_4CMe_2$-4-MeC_6H_4)$TiCl_3$ (24) - To a solution of 2.60 g (9.6 mmol) of $C_5H_4(SiMe_3)CMe_2$-4-MeC_6H_4 in 40 ml of methylene chloride at -30 °C, 1.06 ml (1.8 g, 10 mmol) of titanium tetrachloride was added dropwise. The brown-red suspension was

allowed to warm to room temperature and was stirred overnight. The solvent was removed in vacuo, and the residue was stirred with 20 ml of pentane, which was subsequently pumped off. Extraction with methylene chloride and concentration and cooling of the extract to -40 °C afforded 2.32 g (6.6 mmol, 69%) of **24** as brown crystals. - ^{1}H NMR (300 MHz, C_6D_6): δ 6.88 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar CH), 6.80 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar CH), 6.31 (ps. t, $^3J_{HH}$ = 2.4 Hz, 2H, Cp), 6.00 (ps. t, $^3J_{HH}$ = 2.4 Hz, 2H, Cp), 2.07 (s, 3H, ArMe), 1.56 (s, 6H, CMe_2) - $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 154.6 (Ar C *ipso*), 145.2 (Cp C *ipso*), 136.1 (Ar *p*-C *ipso*), 129.3, 126.1 (Ar *o*- and *m*-CH), 123.3, 121.7 (Cp CH), 40.6 (CMe_2 C *ipso*), 28.8 (CMe_2), 20.7 (ArMe) - Anal. Calcd. for $C_{15}H_{17}TiCl_3$: C, 51.25; H, 4.87; Ti, 13.62. Found: C, 51.49; H, 4.89; Ti, 13.54.

Qualitative olefin conversion experiments with [(η^5,η^6-C$_5$H$_4$CMe$_2$Ar)TiMe$_2$] [MeB(C$_6$F$_5$)$_3$] (15, 16) - Bromobenzene-d_5 solutions of **15** and **16** were prepared as described in Chapter 3. For the styrene polymerization experiments 50 µl of styrene was added via a microsyringe. For the propene and ethene experiments, the solutions were transferred into NMR tubes equipped with a rubber septum. The monomer was injected via a gas-tight glass syringe. The progress of the olefin conversion was monitored with ^{1}H NMR spectroscopy. No yields (polymer nor 1-hexene) have been determined in these experiments. No significant conversion of styrene or propene was observed. With ethene, rapid conversion was observed, accompanied by formation of 1-hexene and traces of polyethene as white fluffy materials.

General procedure for the catalytic ethene conversions - A stainless steel 1L autoclave (Medimex), fully temperature and pressure controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C prior to use. The reactor was cooled to the desired temperature, charged with 200 ml of toluene, and pressurized with ethene. After equilibrating for 15 min, the appropriate amount of MAO/toluene was injected, together with 25 ml of toluene. Subsequently, a mixture of 2.50 g cyclooctane (internal standard) and 1.0 ml of a 15 mM stock solution of the titanium halide complex in toluene was injected, together with 25 ml of toluene, to start the reaction. During the reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by adding an aliquot of ethanol, and the reactor was vented. Remaining residual MAO was destroyed by adding further ethanol, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer was stirred for 1 h in acidified ethanol, repeatedly rinsed with ethanol on a glass frit, and dried in vacuo at 70 °C overnight. For entry 2 in Table 1, the volatiles of the liquid fraction of the reaction mixture were removed on a rotary evaporator operating at 80 °C and 180 mm Hg to give 3.8 g of a fraction, predominantly containing the C_{10} isomers (some residual amounts of toluene and cyclooctane were observed by ^{1}H NMR spectroscopy).

Procedure for the catalytic ethene conversions using (η^5-C$_5$H$_4$CMe$_2$Ph)TiMe$_3$ (3) with B(C$_6$F$_5$)$_3$ or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] as cocatalyst - A stainless steel 500 ml autoclave (Medimex), fully temperature and pressure controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C. The reactor was cooled to the desired temperature, charged with 150 ml of toluene and pressurized with

ethene. After equilibrating for 15 min, the appropriate amount of boron-based cocatalyst in 5 ml of toluene was injected, together with 25 ml of toluene. Subsequently, a mixture of 2.50 g cyclooctane (internal standard) and 1.0 ml of a 15 mM stock solution of the titanium trimethyl complex in toluene was injected, together with 25 ml of toluene, to start the reaction. During the reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by venting the reactor, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer was repeatedly rinsed with ethanol on a glass frit, and was dried in vacuo at 70 °C overnight.

Procedure for the catalytic ethene conversions using (η^5-C$_5$H$_4$CMe$_2$Ph)TiMe$_3$ (3) with MAO/SiO$_2$ as cocatalyst - A stainless steel 1L autoclave (Medimex), fully temperature and pressure controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C. The reactor was cooled to the desired temperature, charged with 200 ml of toluene, and pressurized with ethene. After equilibrating for 15 min, a slurry of 2.05 g of silica with 5 wt% MAO in 10 ml of toluene was injected together with 30 ml of toluene. Subsequently, a mixture of 2.50 g cyclooctane (internal standard) and 1.0 ml of a 15 mM stock solution of the titanium trimethyl complex in toluene was injected, together with 25 ml of toluene, to start the reaction. During reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by adding an aliquot of ethanol, and the reactor was vented. Remaining residual MAO was destroyed by adding further ethanol, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer, precipitated on the silica support, could not be quantified, since the suspended fine polymer/support particles could not be separated quantitatively from the liquid fraction.

4.10   References and notes

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