

Review

Monocyclopentadienyl titanium catalysts: ethene polymerisation versus ethene trimerisation

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Abstract

The chemistry of monocyclopentadienyl titanium complexes with pendant arene groups on the cyclopentadienyl ligand is reviewed, with an emphasis on cationic titanium dialkyl derivatives and their performance in catalytic olefin conversion. In these cationic species, the pendant arene group can coordinate in intramolecular fashion to the metal centre. The effect of this arene coordination on catalytic olefin conversion depends strongly on the nature of the bridge between the cyclopentadienyl and arene moieties. Whereas intramolecular arene coordination is generally detrimental to styrene and propene polymerisation performance, it causes a dramatic switch in ethene conversion behaviour, resulting in high activity and selectivity for catalytic trimerisation of ethene to 1-hexene. Possible reasons for this behaviour are discussed.

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Keywords: Catalysis; Ethene; Polymerisation; Titanium; Trimerisation

1. Introduction

In the late 1980s, Ishihara et al. discovered that the combination of $\text{Cp}^{\text{R}}\text{TiX}_3$ (Cp^{R} , substituted or unsubstituted cyclopentadienyl; X, monoanionic ligand) with methyl alumoxane (MAO) cocatalyst was able to catalyse the polymerisation of styrene to *syndiotactic* polystyrene [1–4]. Since then, a range of publications have appeared that address the catalytic properties of $\text{Cp}^{\text{R}}\text{TiX}_3/\text{MAO}$ or $\text{Cp}^{\text{R}}\text{TiR}_3$ (R = hydrocarbyl) in combination with other activators in catalytic olefin conversion (see e.g. [5–14] and references cited therein).

At first glance these precatalyst/cocatalyst combinations look very simple, but it has proven to be difficult to determine precisely what the nature of the catalytically active species for the various processes is. There has been considerable controversy on the oxidation state of the metal centre in the species responsible for the syndiotactic polymerisation of styrene, Ti(III) or Ti(IV) [15–18]. After extensive investigations, it appears that a Ti(III) species is responsible for syndiotactic styrene polymerisation, whereas a Ti(IV) species effects the (co)polymerisation of ethene and various

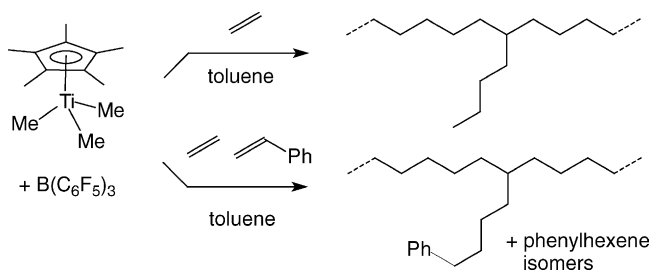
1-alkenes [19]. This was corroborated by recent observations by Mahanthappa and Waymouth, who used well-defined Ti(III) and Ti(IV) hydrocarbyl catalyst precursors [20].

A surprising observation was made by Pellecchia et al., who found that the $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) catalyst system in toluene solvent catalyses the homopolymerisation of ethene to give polyethene with C_4 short-chain branches [21] (Scheme 1). This suggested the presence of a catalytic species that can trimerise ethene to 1-hexene, which is subsequently incorporated into the polymer. Similarly, attempted copolymerisation of ethene and styrene with this catalyst system resulted in formation of phenylhexenes together with polyethene containing 4-phenyl-1-butyl branches [22,23]. The selective trimerisation of ethene to 1-hexene has been observed for several Cr-based catalyst systems [24–32]. As the proposed reaction pathway for this conversion involves metallacyclic intermediates via an oxidative coupling/insertion/H-transfer/reductive elimination sequence [24] (Scheme 2), the observation of ethene trimerisation in the $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{toluene}/\text{ethene}$ system (albeit as a minor side reaction) could imply the involvement of a Ti(II) species.

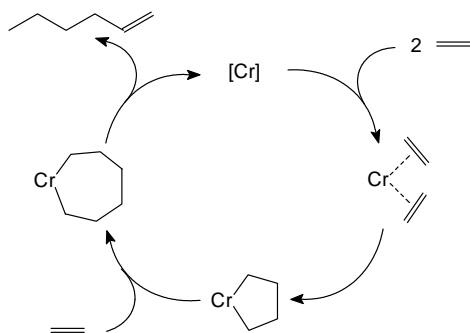
The above observations suggest that interesting information might be gained from a closer study of cationic monocyclopentadienyl titanium hydrocarbyl species. In the

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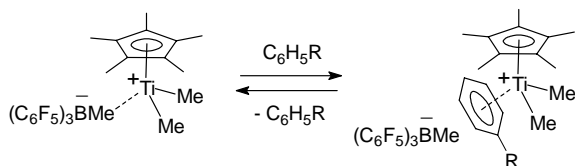
Scheme 1.



Scheme 2.

early 1990s, Gillis et al. observed by NMR spectroscopy that Cp^*MMe_2 -cations ($M = \text{Ti}, \text{Zr}, \text{Hf}$) can be solvated by aromatic solvents such as benzene or toluene to give species $[\text{Cp}^*\text{MMe}_2(\eta^6\text{-arene})]^+$ [33]. Whereas this solvation is an equilibrium for Ti (Scheme 3), the arene appears to be considerably more strongly bound for the 4d/5d congeners Zr and Hf, and the existence of these species was corroborated for two Hf derivatives by single crystal X-ray structure determinations [34,35]. Flores et al. also obtained NMR spectroscopic evidence for *intra*-molecular coordination of the arene moiety in the cation $[(\eta^5, \eta^6\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{Ph})\text{TiMe}_2]^+$ [36].

This prompted us, as well as Sassmannshausen et al., to investigate the structural and reactive properties of cationic monocyclopentadienyl titanium hydrocarbyl species with an intramolecularly coordinated aromatic group. It turns out that, whereas intramolecular arene coordination in these species is generally detrimental to their performance in catalytic styrene and propene polymerisation (lowering the activity of the catalyst and the molecular weight of the polymer produced), it is able to switch the catalyst selectivity in ethene conversion from ethene polymerisation to ethene trimerisation. This phenomenon allowed us to access titanium-based ethene trimerisation catalysts that in catalyst



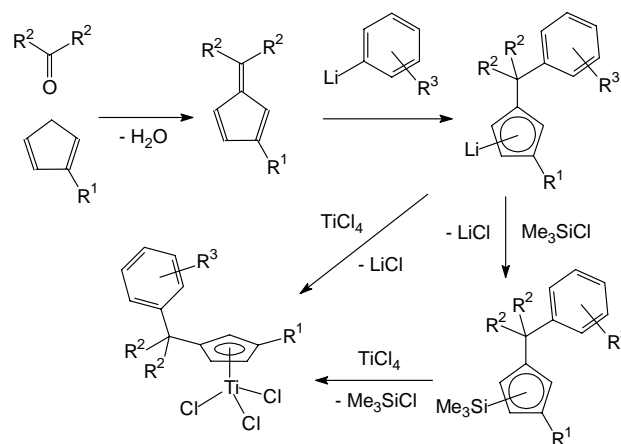
Scheme 3.

activity and overall productivity may be compared with the best chromium based catalysts currently available.

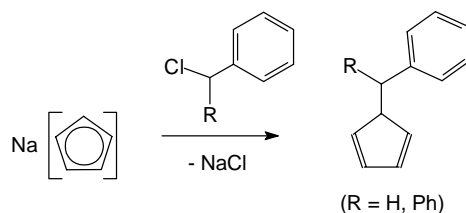
This paper reviews the recent developments in the chemistry of monocyclopentadienyl titanium complexes with pendant arene functionalities, in particular with respect to their catalytic properties. Although some examples of analogous Zr complexes have been reported [37–40], these are not discussed explicitly.

2. Synthesis of linked cyclopentadienyl-arene ligands and their group 4 metal complexes

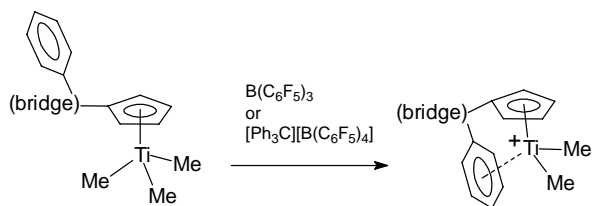
Cyclopentadienyl ligands that are connected to an arene moiety via a covalent link can be synthesised through various routes. A very versatile route to Cp-arene ligands with a one- or two carbon link is the addition of aryl-lithium or benzyl Grignard reagents to fulvenes (Scheme 4) [37,41–44]. As these fulvenes are readily accessible via the reaction of (substituted) cyclopentadienes with ketones [45], the route allows a wide variation in substituents on the cyclopentadienyl group, on the carbon atom of the spacer that is attached to the cyclopentadienyl group, and on the arene moiety. This procedure has also been extended to include benzo-fulvene [39,40]. Benzyl, diphenylmethyl and 2-phenylethyl cyclopentadienes have been prepared from CpNa and the appropriate benzylic halide or (2-bromoethyl)benzene [37,46,47] (Scheme 5), whereas the sterically demanding triphenylmethyl group can be introduced by reaction of trityl halides with cyclopentadienyl tin reagents [48,49]. Lig-



Scheme 4.



Scheme 5.



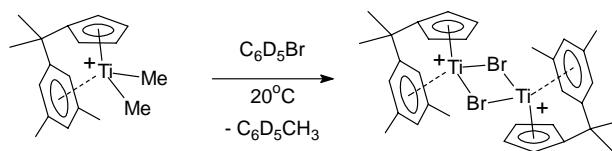
Scheme 6.

ands with a dimethylsilyl bridge can be obtained by reaction of CpNa with aryl-substituted chlorosilanes [37,50]. The substituted tetramethyl cyclopentadiene $HC_5Me_4(CH_2)_2Ph$ was obtained from 2,3,4,5-tetramethylcyclopentenone by reaction with (2-bromomagnesioethyl)benzene followed by protonation and dehydration [36].

Attachment of one cyclopentadienyl-arene ligand to titanium can conveniently be performed by reaction of the corresponding trimethylsilyl-cyclopentadiene reagents with $TiCl_4$ [37,44]. Alternatively, reaction of the cyclopentadienyl anion (as its Li or Na salt) with Ti-halides can be employed. Subsequent trialkylation to give $(\eta^5\text{-cyclopentadienyl-arene})TiR_3$ compounds ($R = Me, CH_2Ph$) proceeds smoothly with Grignard or dialkyl magnesium reagents [36,37,43].

3. Generation and stability of cationic cyclopentadienyl-arene titanium dialkyl cations

The trimethyl complexes $[\eta^5\text{-cyclopentadienyl(bridge)-arene}]TiMe_3$ can be converted into the monocations $\{[\eta^5,\eta^6\text{-cyclopentadienyl(bridge)arene}]TiMe_2\}^+$ by reaction with the Lewis acid $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ (Scheme 6). The coordination of the arene moiety to the metal centre could be established by 1H and ^{13}C NMR spectroscopy. It is observed that the the arene *o*-H resonances are shifted upfield, the *m*- and *p*-H resonances downfield relative to the resonances in the neutral trimethyl complexes [36,37]. In the ^{13}C NMR spectra, the *m*-C resonances are shifted upfield, whereas the other arene C resonances are shifted downfield; these shifts are accompanied by a noticeable increase in the C–H coupling constants [36]. For the complexes with $[C_5H_4(\text{bridge})\text{arene}]$ -ligands, the chemical shift difference between the two sets of cyclopentadienyl proton resonances increases upon coordination of the arene moiety, in response to the chelate strain imposed on the ligand system. This phenomenon is also observed in *ansa*-metallocenes [51]. Thus the observed chemical shift difference is smaller in the C_2 -bridged cation $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2CH_2Ph)TiMe_2]^+$ ($\Delta\delta = 0.97$ ppm) than in the more strained C_1 -bridged cation $[(\eta^5,\eta^6\text{-}C_5H_4CMe_2Ph)TiMe_2]^+$ ($\Delta\delta = 1.46$ ppm) [37]. Although the spectroscopic evidence clearly establishes the coordination of the arene moiety to the metal centre in solution, this interaction is sufficiently weak to be readily disrupted by the addition of hard Lewis basic ligands (e.g. THF) [37,43]. As yet no structural data

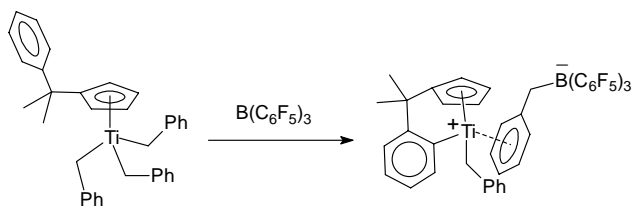


Scheme 7.

based on single crystal X-ray diffraction are available for $(\eta^5,\eta^6\text{-cyclopentadienyl-arene})titanium$ dialkyl cations, although a structure of the dinuclear Ti(III) dication $\{[\eta^5,\eta^6\text{-}C_5H_4CMe_2(3,5\text{-}Me_2C_6H_3)]Ti(\mu\text{-}Br)\}_2^{2+}$ (a decomposition product of the corresponding dimethyl cation, vide infra; Scheme 7) is available [43]. In this structure it can be seen that the C_1 -bridge in the ligand imposes substantial geometrical constraints, as the arene moiety is asymmetrically coordinated, with average Ti–C(arene) distances $Ti\text{-}C_{ipso} = 2.38$ Å, $Ti\text{-}C_o = 2.25$ Å, $Ti\text{-}C_m = 2.69$ Å and $Ti\text{-}C_p = 2.73$ Å.

The $[(\eta^5,\eta^6\text{-cyclopentadienyl-arene})TiMe_2]^+$ species appear to be reasonably stable in solution at or below $0^\circ C$ for the systems with C_1 or C_2 spacers between the cyclopentadienyl and arene moieties. In contrast, Bochmann and coworkers observed that reaction between $(\eta^5\text{-}C_5H_4SiMe_2Ph)TiMe_3$ and $[CPh_3][B(C_6F_5)_4]$ resulted in a very unstable product (decomposition at $-60^\circ C$), suggesting a much less favourable Ti–arene interaction in the $SiMe_2$ -bridged species [37]. The ionic compound $\{[\eta^5,\eta^6\text{-}C_5H_4CMe_2(3,5\text{-}Me_2C_6H_3)]TiMe_2\}[MeB(C_6F_5)_3]$, with a 3,5-dimethylated arene moiety, was found to be quite stable in C_6D_5Br solution and decomposes gradually at ambient temperature over several days to form the Ti(III) dication $\{[\eta^5,\eta^6\text{-}C_5H_4CMe_2(3,5\text{-}Me_2C_6H_3)]Ti(\mu\text{-}Br)\}_2^{2+}$, which was structurally characterised (Scheme 7). This decomposition involves reaction with the solvent, giving toluene-*d*₅ as co-product. In the presence of excess $B(C_6F_5)_3$, this decomposition is preceded by Me/C_6F_5 exchange between the Ti centre and the borane [43,52].

Reactions of the tribenzyl complexes $(\eta^5\text{-}C_5H_4CHPh_2)Ti(CH_2Ph)_3$ and $[\eta^5\text{-}C_5H_4CMe_2(3,5\text{-}Me_2C_6H_3)]Ti(CH_2Ph)_3$ with $[CPh_3][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ produce highly fluxional cationic species, that appear to interconvert between states where either the pendant arene is coordinated to the metal centre, or where the metal centre is stabilised by η^2/η^3 bonding of the benzyl groups [37,53]. Whereas the $[C_5H_4CMe_2(3,5\text{-}Me_2C_6H_3)]Ti(CH_2Ph)_2$ -cation is thermally relatively robust (decomposing gradually in C_6D_5Br to give the same product as described above for the analogous dimethyl cation), the dibenzyl cation with an unsubstituted pendant arene group rapidly degrades (even at $-30^\circ C$) via cyclometallation of the phenyl group to give the $(\eta^5,\eta^1\text{-}C_5H_4CMe_2C_6H_4)Ti(CH_2Ph)$ -cation (Scheme 8). The latter is stabilised by η^2 bonding of the benzyl group (when $[B(C_6F_5)_4]^-$ is the counterion), or by η^6 -coordination of the $[PhCH_2B(C_6F_5)_3]^-$ counterion when $B(C_6F_5)_3$ is employed to generate the ionic species [53].



Scheme 8.

Apparently, the stability of the (cyclopentadienyl-arene) titanium dialkyl cations may be improved by steric protection of the aryl *o*-position, or by a less constrained ligand geometry—Sassmannshausen et al., noticed that the C₂-bridged cation $[(\eta^5, \eta^6\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{TiMe}_2]^+$ appears to be thermally more robust than the more strained C₁-bridged cation $[(\eta^5, \eta^6\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiMe}_2]^+$ [37].

4. Catalytic olefin conversion with cyclopentadienyl-arene titanium catalysts

The properties of (cyclopentadienyl-arene)titanium catalysts in the catalytic conversion of olefins has been studied with styrene, propene and ethene as substrates. In the polymerisation of styrene to syndiotactic polystyrene, Flores et al., observed that the C₂-bridged catalyst $[\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{Ph}]\text{TiCl}_3/\text{MAO}$ exhibits an activity that is two to three times lower than that of $(\text{C}_5\text{Me}_5)\text{TiCl}_3/\text{MAO}$, which they attributed to the blocking of the incoming substrate by the pendant arene group when it is coordinated to the metal centre. They proposed an equilibrium between two states—one inactive (with the arene coordinated), and one active (without intramolecular arene coordination) [36]. The related catalyst without cyclopentadienyl methyl substitution, $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Ph}]\text{TiCl}_3/\text{MAO}$, was found to be three times more active than its C₅Me₄-analogue, prompting the authors to conclude that the arene in this system is essentially non-coordinating [46]. In this case, the cationic species $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Ph}]\text{TiMe}_2^+$ was not studied separately, but it is interesting to note that Sassmannshausen et al., found relatively stable arene coordination in the C₂-bridged cation $[(\eta^5, \eta^6\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{TiMe}_2]^+$ [37]. Schwecke and Kaminsky reported the polymerisation of styrene with the C₁-bridged catalyst $(\text{C}_5\text{H}_4\text{CH}_2\text{Ph})\text{TiCl}_3/\text{MAO}$, and observed that this produces (with moderate activity) *s*-PS with a molecular weight that is three times lower than that produced by $(\text{C}_5\text{H}_5)\text{TiCl}_3/\text{MAO}$. This was attributed to a selective slow-down of the chain growth rate by the coordinating arene group, whereas the chain transfer rate is relatively little affected [54]. The same paper shows one result for the related CMe₂-bridged catalyst, $(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3/\text{MAO}$, that produces *s*-PS with an even lower molecular weight at a much slower rate. This led the authors to conclude that the dimethyl substitu-

tion of the bridge carbon favours intramolecular arene coordination.

Conversion of propene by $(\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{TiMe}_3$, $(\text{C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{TiMe}_3$ and $(\text{C}_5\text{H}_4\text{CHPh}_2)\text{Ti}(\text{CH}_2\text{Ph})_3$, activated by $\text{B}(\text{C}_6\text{F}_5)_3$, was studied by Sassmannshausen et al. All systems produced atactic polypropene with a significantly lower activity and a lower molecular weight than $(\text{C}_5\text{Me}_5)\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ [37]. This too was attributed to intramolecular arene coordination, and it was remarked that the highest activity was found for the SiMe₂-bridged system, for which it was not possible to generate a stable dialkyl cation, presumably due to a relatively unfavourable geometry for intramolecular coordination (*vide supra*). Longo et al. found that $(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3/\text{MAO}$ produced essentially atactic polypropene at 50 °C, but isotactically enriched polypropene at –60 °C (by chain-end control). The latter was not observed for $\text{CpTiCl}_3/\text{MAO}$, suggesting that the Cp-arene system at low temperature behaves more like $\text{Cp}_2\text{TiCl}_2/\text{MAO}$ than as a half-sandwich catalyst, and that intramolecular arene coordination is of less importance at elevated temperatures [39]. In the same paper, attempted ethene/styrene copolymerisation with the same catalyst was reported to yield a mixture of some atactic polystyrene and a less soluble fraction that contained both polystyrene and polyethene homo-sequences as well as ethene-styrene heterosequences.

Remarkably few data were available on catalytic ethene conversion with (cyclopentadienyl-arene)titanium catalysts prior to our work on the C₁-bridged systems. Flores et al., reported the polymerisation of ethene with the $[\text{C}_5\text{R}_4(\text{CH}_2)_2\text{Ph}]\text{TiCl}_3/\text{MAO}$ (R = Me, H) catalyst systems. For R = Me, high density polyethene (Mp 137 °C) with an *M_w* of 3–5 × 10⁴ was obtained, with an appreciable catalyst activity [36]. For R = H, a significantly lower activity was observed [46]. This, combined with their observations in styrene polymerisation (*vide supra*) led to the conclusion of the authors that in this case the pendant arene moiety does not interact significantly with the metal centre.

The C₁-bridged catalyst $(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3/\text{MAO}$ was found to be highly active in the catalytic conversion of ethene. Surprisingly, polyethene is only a minor side product in this reaction (1.8 wt.% at 5 bar ethene and 30 °C, toluene solvent). The main products stem from an olefin trimerisation process: C₆ (83 wt.%, >99% 1-hexene) and C₁₀ (14 wt.%, >75% 5-methyl-non-1-ene), the latter deriving from co-trimerisation of 1-hexene with two molecules of ethene [55]. A comparative experiment with an analogous catalyst without the pendant arene functionality, $(\text{C}_5\text{H}_4\text{CMe}_3)\text{TiCl}_3/\text{MAO}$, showed a much lower activity, and polyethene as main product. Nevertheless, some 1-hexene production was observed in this reaction as well. These observations suggest that the pendant arene functionality is instrumental in “switching” the catalyst from ethene polymerisation to ethene trimerisation activity. In the absence of such an intramolecular interaction, coordination of the toluene solvent may

also induce some trimerisation activity, albeit much less efficiently. This feature may then explain the observation of Pellecchia et al. of the formation of C₄-branched polyethene with the Cp*TiMe₃/B(C₆F₅)₃/toluene catalyst system [21]. That the [(η⁵,η⁶-C₅H₄CMe₂Ph)TiMe₂]-cation is the likely starting point for the trimerisation catalysis by (C₅H₄CMe₂Ph)TiCl₃/MAO is borne out by the observation that good trimerisation selectivity is also observed with the (C₅H₄CMe₂Ph)TiMe₃ species when activated by [PhNMe₂H][B(C₆F₅)₄] or B(C₅F₅)₃ [44].

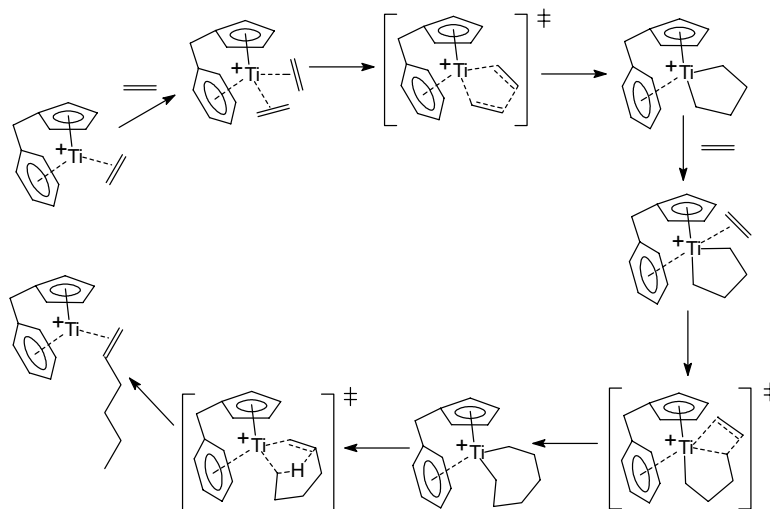
Subsequent experiments [44,52,55] showed that the rate of ethene conversion by this type of catalyst is approximately first order in ethene concentration, and that gradually increasing the π-basicity of the pendant arene (by introducing one or two methyl substituents) progressively decreases the rate of ethene conversion with retention of trimerisation selectivity. This suggests that in the rate-determining step one ethene molecule is being captured and that in this step a loosening of the metal–arene interaction is involved. The importance of the nature of the bridge between the cyclopentadienyl and arene moieties for the catalysis was shown by a comparison of the catalysts [C₅H₄(B)Ph]TiCl₃/MAO with B = CH₂, CMe₂, SiMe₂ and CMe₂CH₂ [44]. Both the CH₂- and SiMe₂-bridged systems showed poor selectivity for trimerisation relative to polymerisation (50 and 42 wt.% trimerisation products, respectively), in line with the observations of Schwecke and Kaminsky [54] and Sassmannshausen et al. [37] of inefficient intramolecular metal–arene interaction in these systems relative to the CMe₂-bridged catalyst. The CMe₂CH₂-bridged catalyst showed good trimerisation selectivity but very poor activity, suggesting a strong metal–arene interaction. Thus it appears that there exists a delicate balance between the favourability of the metal–arene interaction (to reach good selectivity for trimerisation) and ease of dissociation/slippage of the arene ligand moiety (to achieve good reaction rates). The bridge

in the ligand plays a crucial role in this respect, determining the orientation of the arene moiety relative to the metal centre and the degree of strain introduced in the chelating bonding mode.

5. Mechanism of the catalytic ethene trimerisation

If we assume that the basic catalytic cycle for ethene trimerisation for (cyclopentadienyl-arene)titanium catalysts is similar to that proposed for the family of chromium-based trimerisation catalysts (involving metallacyclic intermediates, see Scheme 2) [24], several questions remain—(a) what role does the interaction of the pendant arene moiety with the metal play in the catalytic trimerisation cycle, and (b) how does this moiety induce the switch in the action of cationic monocylopentadienyl titanium dialkyl catalysts from ethene polymerisation to ethene trimerisation.

Blok et al. performed extensive DFT calculations on the system with the C₅H₄CH₂Ph-ligand [56], and obtained viable structures of intermediates and transition states for the trimerisation sequence. This leads from a Ti(II) ethene adduct to a Ti(II) 1-hexene adduct via a sequence involving oxidative coupling of two ethene molecules (to give a titanacyclopentane), insertion of a third ethene molecule (to give a titanacycloheptane) and direct Cβ-to-Cα hydrogen transfer [57,58], leading to the 1-hexene adduct (Scheme 9). Thermochemical analysis led to calculated free energy barriers at 30 °C for these three reaction steps of 15, 20 and 21 kcal/mol, respectively. In comparison, the formation of the 1-butene complex from the metallacyclopentane intermediate would involve a barrier of 41 kcal/mol (due to the poor flexibility of the 5-membered metallacycle). This is consistent with the absence of 1-butene formation in the catalytic ethene trimerisation experiments with catalysts of this type.



Scheme 9.

It was observed in the calculations [56] that the pendant arene moiety is more tightly bound to the metal centre in the Ti(II) olefin complexes than in the Ti(IV) metallacycles. It was also seen that in the transition state of what was proposed to be the rate-determining step in the trimerisation catalysis (insertion of ethene into the titanacyclopentane intermediate), there is a considerable increase in metal–arene separation. This could be consistent with the experimental observation that an increase of the π -basicity of the arene leads to a lower trimerisation rate [44].

Calculations on the diethyl complex $[(C_5H_4CH_2Ph)Ti(CH_2CH_3)_2]^+$ revealed that the formation of the Ti(II) ethene adduct by elimination of ethane is exothermic, and favoured by the stronger Ti–arene interaction in the Ti(II) olefin adduct compared to that in the Ti(IV) dialkyl species. The free energy barrier for C β -to-C α hydrogen transfer to give ethane and the Ti(II) ethene complex (the latter leading to the catalytic trimerisation cycle) is lower than that for ethene insertion into the Ti–ethyl bond (leading to polymerisation), if only by a small amount (1 kcal/mol) [56]. It has to be noted that the CH₂-bridged complex does not represent a system with a very favourable arene coordination (see above), and has only a 50 wt.% selectivity for trimerisation products [44]. It is likely that in the CMe₂-bridged system, with a more favourable metal–arene interaction, the discrimination between the routes leading to the trimerisation sequence or to polymerisation will be more pronounced.¹

6. Conclusions

The pendant arene group in cyclopentadienyl–arene titanium complexes has a profound effect on the performance of half-sandwich titanium catalysts in ethene conversion, leading to ethene trimerisation catalysis. This is likely to occur because coordination of the arene moiety to the metal centre makes alkane elimination from the Ti(IV) (cyclopentadienyl–arene)Ti(*n*-alkyl)₂-cation, to give the Ti(II) olefin complex, exothermic. Similarly, it causes the C β -to-C α hydrogen transfer in the titanacycloheptane intermediate to be favoured over further ethene insertion, leading selectively to 1-hexene. It is presently unclear what the fate of the catalyst is in the homoconversion of 1-alkenes. Thus far it appears that the system is reluctant to catalyse the homotrimerisation of 1-alkenes such as propene or 1-hexene (unlike e.g. the 1,3,5-triazacyclohexane chromium catalysts investigated by Köhn et al. [59–61]), although 1-hexene is readily cotrimerised with two molecules of ethene to produce mainly 5-methyl-1-nonene.

The pendant arene moiety, combined with a bridge to the cyclopentadienyl group that imparts a certain degree of chelate strain to the η^5, η^6 -bonding mode, gives access to a new class of highly active ethene trimerisation catalysts. Ligand modification has allowed us to obtain catalysts that can convert ethene to trimerisation products with ethene turnover frequencies in excess of $1 \times 10^6 \text{ h}^{-1}$. With this, the catalyst activity approaches that of the most active chromium-based catalysts to date [29]. Recently, two other non-chromium catalysts for the trimerisation of ethene were discovered, one based on bis(arene) vanadium species [62], the other based on Cl₃Ta(alkyl)₂ [63], but as yet these display activities that are at least two orders of magnitude lower than Cr- or Ti-based catalysts.

As the way in which the chromium-based catalysts achieve their selectivity for ethene trimerisation versus polymerisation is as yet to a large extent unclear, the discovery of a family of well-defined titanium-based ethene trimerisation catalysts, together with insight into the manner in which their selectivity is achieved, may lead to new possibilities for the discovery of alternative catalyst systems for selective ethene trimerisation.

References

- [1] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2464.
- [2] N. Ishihara, M. Kuramoto, M. Uoi, *Eur. Pat. Appl.* 210615 (1987).
- [3] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356.
- [4] N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, *J. Mol. Catal. A* 128 (1998) 167.
- [5] C. Pellecchia, P. Longo, A. Proto, A. Zambelli, *Makromol. Chem. Rapid Commun.* 12 (1992) 265.
- [6] C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, *Organometallics* 12 (1993) 4473.
- [7] H. Kucht, A. Kucht, J.C.W. Chien, M.D. Rausch, *Appl. Organomet. Chem.* 8 (1994) 393.
- [8] D. Jeremic, Q. Wang, R. Quyoum, M.C. Baird, *J. Organomet. Chem.* 497 (1995) 143.
- [9] C. Pellecchia, D. Pappalardo, M. D'Arco, A. Zambelli, *Macromolecules* 29 (1996) 1158.
- [10] J. Sassmannshausen, M. Bochmann, J. Rösch, D. Lilge, *J. Organomet. Chem.* 548 (1997) 23.
- [11] A. Grassi, S. Saccheo, A. Zambelli, F. Laschi, *Macromolecules* 33 (1998) 5588.
- [12] S.W. Ewart, M.C. Baird, *Top. Catal.* 7 (1999) 1.
- [13] A. Grassi, M. Caprio, A. Zambelli, D.E. Bowen, *Macromolecules* 33 (2000) 8130.
- [14] A. Miyazawa, T. Kase, K. Soga, *Macromolecules* 33 (2000) 2796.
- [15] J.C.W. Chien, Z. Salajka, S. Dong, *Macromolecules* 25 (1992) 3199.
- [16] T.E. Ready, R. Gurge, J.C.W. Chien, M.D. Rausch, *Organometallics* 17 (1998) 5236.
- [17] A. Grassi, C. Pellecchia, L. Oliva, F. Laschi, *Macromol. Chem. Phys.* 196 (1995) 1093.
- [18] A. Grassi, A. Zambelli, F. Laschi, *Organometallics* 15 (1996) 480.
- [19] C. Pellecchia, A. Grassi, *Top. Catal.* 7 (1999) 125, and references cited therein.
- [20] M.K. Mahanthappa, R.M. Waymouth, *J. Am. Chem. Soc.* 123 (2001) 12093.
- [21] C. Pellecchia, D. Pappalardo, G.-J. Gruter, *Macromolecules* 32 (1999) 4491.

¹ After submission of this paper, two additional reports [64,65] were published with DFT calculations on the catalytic ethene trimerisation by cyclopentadienyl–arene titanium catalysts, both dealing with the CMe₂-bridged catalyst system. The results from these studies essentially corroborate the process as described here.

- [22] C. Pellecchia, M. Mazzeo, G.-J. Gruter, *Macromol. Rapid Commun.* 20 (1999) 337.
- [23] C. Pellecchia, D. Pappalardo, L. Oliva, M. Mazzeo, G.-J. Gruter, *Macromolecules* 33 (2000) 2807.
- [24] J.R. Briggs, *J. Chem. Soc. Chem. Commun.* (1989) 674.
- [25] J.R. Briggs, US Pat. 4,668,838 (1987) (to Union Carbide).
- [26] W.K. Reagen, B.K. Conroy, EP 416 403 (1990) (to Phillips Petroleum).
- [27] M. Tamura, K. Uchida, K. Iwanaga, Y. Ito, EP 699 648 (1995) (to Sumitomo Chemical).
- [28] W.K. Reagen, T.M. Pettijohn, J.W. Freeman, US Pat. 5,523,507 (1996) (to Phillips Petroleum).
- [29] A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, *Chem. Commun.* (2002) 858.
- [30] D.F. Wass, PCT Appl. WO 02/04119 (to British Petroleum).
- [31] D.S. McGuinness, P. Wasserscheid, W. Keim, C. Hu, U. Englert, J.T. Dixon, C. Grove, *Chem. Commun.* (2003) 334.
- [32] D.S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J.T. Dixon, A. Bollmann, H. Maumela, F. Hess, U. Englert, *J. Am. Chem. Soc.* 125 (2003) 5272.
- [33] D.J. Gillis, M.-J. Tudoret, M.C. Baird, *J. Am. Chem. Soc.* 115 (1993) 2543.
- [34] S.J. Lancaster, O.B. Robinson, M. Bochmann, S.J. Coles, M.B. Hursthouse, *Organometallics* 14 (1995) 2456.
- [35] D.J. Gillis, R. Quyoum, M.-J. Tudoret, Q. Wang, D. Jeremic, A.W. Roszak, M.C. Baird, *Organometallics* 15 (1996) 3600.
- [36] J.C. Flores, J.S. Wood, J.C.W. Chien, M.D. Rausch, *Organometallics* 15 (1996) 4944.
- [37] J. Sassmannshausen, A.K. Powell, C.E. Anson, S. Wocadlo, M. Bochmann, *J. Organomet. Chem.* 592 (1999) 84.
- [38] J. Sassmannshausen, *Organometallics* 19 (2000) 482.
- [39] P. Longo, A.G. Amendola, E. Fortunato, A.C. Boccia, A. Zambelli, *Macromol. Rapid Commun.* 22 (2001) 339.
- [40] C. De Rosa, F. Auriemma, T. Circelli, P. Longo, A.C. Boccia, *Macromolecules* 36 (2003) 3465.
- [41] P. Renaut, G. Tainturier, B. Gautheron, *J. Organomet. Chem.* 148 (1978) 35.
- [42] Y. Qian, J. Huang, J. Yang, A.S.C. Chan, W. Chen, X. Chen, G. Li, X. Jin, Q. Yang, *J. Organomet. Chem.* 547 (1997) 263.
- [43] P.J.W. Deckers, A.J. van der Linden, A. Meetsma, B. Hessen, *Eur. J. Inorg. Chem.* (2000) 929.
- [44] P.J.W. Deckers, B. Hessen, J.H. Teuben, *Organometallics* 21 (2002) 5122.
- [45] K.J. Stone, R.D. Little, *J. Org. Chem.* 49 (1984) 1849.
- [46] M.S. Blais, J.C.W. Chien, M.D. Rausch, *Organometallics* 17 (1998) 3775.
- [47] E.H. Licht, H.G. Alt, M.M. Karim, *J. Organomet. Chem.* 599 (2000) 275.
- [48] K.A. Rufanov, N.B. Kazennova, A.V. Churakov, D.A. Lemenovskii, L.A. Kuz'mina, *J. Organomet. Chem.* 485 (1995) 173.
- [49] K.A. Rufanov, A.V. Churakov, N.B. Kazennova, G.P. Brusova, D.A. Lemenovskii, L.A. Kuz'mina, *J. Organomet. Chem.* 498 (1995) 37.
- [50] M. Kira, W. Watanabe, H. Sakurai, *J. Am. Chem. Soc.* 99 (1977) 7780.
- [51] H. Köpf, N. Klouras, *Z. Naturforsch. B* 38 (1983) 321.
- [52] P.J.W. Deckers, Dissertation, University of Groningen, 2002.
- [53] P.J.W. Deckers, B. Hessen, *Organometallics* 21 (2002) 5564.
- [54] C. Schwecke, W. Kaminsky, *J. Polym. Sci. A* 39 (2001) 2805.
- [55] P.J.W. Deckers, B. Hessen, J.H. Teuben, *Angew. Chem. Int. Ed.* 40 (2001) 2516.
- [56] A.N.J. Blok, P.H.M. Budzelaar, A.W. Gal, *Organometallics* 22 (2003) 2564.
- [57] E. Derat, J. Bouquant, P. Bertus, J. Szymoniak, S. Humbel, *J. Organomet. Chem.* 664 (2002) 268.
- [58] Z.-X. Yu, K.N. Houk, *Angew. Chem. Int. Ed.* 42 (2003) 808.
- [59] R.D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 4337.
- [60] H. Maas, S. Mihan, R.D. Köhn, G. Seifert, J. Tropsch, PCT Appl. WO 00/58319 (2000) (to BASF).
- [61] P. Wasserscheid, S. Grimm, R.D. Köhn, M. Haufe, *Adv. Synth. Catal.* 343 (2001) 814.
- [62] A.M. Romano, A. Proto, R. Santi, A. Sommazzi, M. Grande, F. Masi, PCT Appl. WO 01/68572 (2001) (to Enichem).
- [63] C. Andes, S.B. Harkins, S. Murtuza, K. Oyler, A. Sen, *J. Am. Chem. Soc.* 123 (2001) 7423.
- [64] T.J.M. de Bruin, L. Magna, P. Rayboud, H. Toulhoat, *Organometallics* 22 (2003) 3404.
- [65] S. Tobisch, T. Ziegler, *Organometallics* 22 (2003) 5392.