Catalytic Trimerization of Ethene with Highly Active Cyclopentadienyl–Arene Titanium Catalysts

Patrick J. W. Deckers, Bart Hessen,* and Jan H. Teuben
Dutch Polymer Institute/Center for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands
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The mono(cyclopentadienyl–arene)titanium complexes \([\eta^5-C_5H_5R-(\text{bridge})-\text{Ar}]\text{TiCl}_3\), activated by methylalumoxane (MAO) cocatalyst, form a family of highly active catalysts for the trimerization of ethene, giving 1-hexene as the main product. Concomitant cotrimORIZATION of ethene and 1-hexene, to give mainly 5-methyl-1-non-1-ene, is also observed. The selectivity for trimerization depends on the presence of a pendant arene group on the cyclopentadienyl ligand and the nature of the bridge between these two ligand moieties. In the absence of a pendant arene, polyethene is the main product. The highest activity and selectivity for trimerization was observed for catalysts with a disubstituted C3 bridge between the cyclopentadienyl and arene ligand moieties. A SiMe3 substituent on the cyclopentadienyl ligand improves catalyst activity and selectivity, whereas methyl substitution of the arene decreases activity. Nevertheless, combining cyclopentadienyl SiMe3 substitution with arene Me substitution gives rise to a catalyst with the highest activity and selectivity, evidence of the strongly nonlinear additivity of ligand substituent effects in this system. The cyclopentadienyl–arene ligand is likely to exhibit hemilabile behavior during catalysis, stabilizing intermediates by \(\eta^5\) coordination and dissociating or slipping to make room for the incoming substrate. The presence of two pendant arene groups on the cyclopentadienyl ligand diminishes the activity of the catalyst but greatly enhances its stability.

Introduction

Linear 1-alkenes are important chemical intermediates that are used in the production of detergent alcohols (C6–C16) and synthetic lubricants, and as comonomers in the production of linear low-density polyethene (LLDPE, C6 and C8). They are largely synthesized by catalytic oligomerization of ethene, polyethene (LLDPE, C6 and C8). They are largely synthesized by catalytic oligomerization of ethene, yielding a Flory–Schultz distribution of chain lengths.2 The selective synthesis of one specific linear alkene from ethene would be very attractive but (apart from the trivial dimerization of ethene to 1-butene)3 is difficult to perform catalytically. The selective trimerization of ethene to give 1-hexene as the main product can be achieved with chromium Ziegler-type catalysts, consisting of a combination of Cr(III) salts (usually carboxylates) with aluminum alkyls in conjunction with some Lewis basic donor (especially pyrroles or 1,2-diethoxyethane).4 The precise nature of the active species in these catalysts is as yet unknown, and it is difficult to control catalyst performance by well-directed catalyst modifications, although a recent report on diphosphine/CrCl3/MAO catalysts showed strong ligand effects on catalyst activity and selectivity.5 Two catalyst systems for the trimerization of ethene based on group 5 metals (V, Ta)7 have been reported, but the activities of these catalysts are orders of magnitude lower than those of the Cr-based Ziegler-type catalysts.
Catalytic Trimerization of Ethene

in Scheme 2. Cyclopentadienyl ligands with \( -\text{CR}_2\text{Ar} \) (R = alkyl, Ar = aryl) substituents are readily accessible from the reaction of 6,6-dialkylfulvenes with the appropriate aryllithium salts.\(^{12}\) The resulting lithium cyclopentadienides, \([\text{C}_6\text{H}_5\text{CR}_2\text{Ar}]\text{Li}\), can be optionally quenched with trimethylsilyl chloride to afford the corresponding \([\text{C}_6\text{H}_5\text{CR}_2\text{Ar}]\text{SiMe}_3\) reagents.\(^{9a}\) Introduction of a \(-\text{SiMe}_2\text{Ph}\) or \(-\text{CH}_2\text{Ph}\) moiety on the cyclopentadienyl ligand can be achieved by reaction of CpLi with dimethylphenylsilyl chloride (PhMe_2SiCl)\(^{9a}\) or benzyl chloride,\(^{11}\) respectively, to give \([\text{C}_6\text{H}_5\text{SiMe}_2\text{Ph}\) or \([\text{C}_6\text{H}_5\text{CH}_2\text{Ph}]\) complexes. Subsequent lithiation with n-BuLi affords the corresponding lithium salts. Reaction of 6-phenyl-6-methylenefulvene with LDA (lithium disopropylamide) gives \([\text{C}_6\text{H}_5\text{C}(-\text{CH}_2\text{Ph})\text{Li}]\).\(^{13}\) All lithium compounds were characterized by \(^1\)H and \(^13\)C NMR spectroscopy and microanalysis.

**Ethenr Trimerization with \([\eta^5-\text{C}_5\text{H}_5\text{CMe}_2\text{Ph}]\)TiCl\(_3\)(1)/MAO.** The results of catalytic ethylene conversion experiments with the catalyst system \([\eta^5-\text{C}_5\text{H}_5\text{CMe}_2\text{Ph}]\)TiCl\(_3\)(1)/MAO (toluene solvent, Ti:Al ratio of 1:1000) under various conditions 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: \(\text{C}_6\) (trimers of ethene) and \(\text{C}_{10}\) (cotrimers of ethene and 1-hexene, vide infra). In addition to the trimerization products, smaller amounts of \(\text{C}_8\) (1 wt %) and polyethene (PE, 1–3 wt %) are produced.

The rate of production of 1-hexene increases with increasing ethene pressure. The \(\text{C}_6\) productivity is around 550–600 kg/(mol of Ti) 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 \(\text{C}_6\) product formed over the fixed run time of 30 min and the ethene pressure suggests that the rate of the trimerization process has a first-order dependence on the ethene concentration.

The \(\text{C}_6\) 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 \(\text{C}_6\) fraction was isolated by evaporation of the low-boiling (bp < 80 °C at 180 Torr) volatile components of the reaction mixture and analyzed separately by NMR and GC/MS.\(^{15}\) \(^1\)H NMR analysis of the olefinic residues in this mixture indicates the presence of 90% RCH=CH\(_2\) end groups, 5% RCH=CHR’, and 5% RR’C=CH\(_2\).

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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 gave melting points higher than 128 °C, indicative of HDPE (high-density polyethene), suggesting that very little of the 1-hexene formed is incorporated into the polymer.

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
In the presence of 15 g of 1-octene added to the direct pentamerization of ethene. In separate experiments, the 1-hexene rather than by without a pendant arene, (1)

In mol of olefinic bonds trimerized/(mmol of Ti) h.

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In mol of olefinic bonds trimerized/(mmol of Ti) h.

In mol of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. b In g of C6 product/(mmol of Ti bar h). c In mol of olefinic bonds trimerized/(mmol of Ti) h.

In mol of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. b In g of C6 product/(mmol of Ti bar h). c In mol of olefinic bonds trimerized/(mmol of Ti) h.

In mol of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. b In g of C6 product/(mmol of Ti bar h). c In mol of olefinic bonds trimerized/(mmol of Ti) h.

In mol of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. b In g of C6 product/(mmol of Ti bar h). c In mol of olefinic bonds trimerized/(mmol of Ti) 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 polyethylene, 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 the catalytic reaction.

It may be noted that even for the tert-butylcyclopentadienyl system 4/MAO a certain amount of ethene trimerization product is observed in addition to the main product, polyethylene. A related observation was made recently by Pelliccia and co-workers in ethene polymerization with the [(η^5-C5Me5)TiMe2][MeB(C6F5)3] catalyst in toluene solvent, where the PE obtained contains a noticeable amount of n-butyl side groups. It was suggested that the catalyst is partly converted to a species that trimerizes ethene to 1-hexene, which is then

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 of reaction time, whereas at 30 °C ethene is consumed over the whole run period, although the uptake rate does slow gradually over the course of the run.

The C10 product fraction is likely to be produced by co-trimerization 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 C6 and C10 product fractions mentioned above, a considerable amount of C12 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 co-trimerization, and these results indicate that the C10 product fraction in the catalytic ethene oligomerization by 1/MAO is indeed formed via co-trimerization of ethene and 1-hexene.

**Effect of the Pendant Arene Group on Ethene Trimerization Catalysis.** The effect of the pendant arene group on ethene trimerization by the (η^5-C5H4CMe2-Ar)TiCl3/MAO catalysts was probed by studying the catalysts with Ar = Ph (1), 4-MeC6H4 (2), 3,5-Me2C6H3 (3) and comparing them with an analogous system without a pendant arene, (η^5-C5H4CMe2)TiCl3 (4). The results are listed in Table 4.
incorporated into the polymer. Our observations indicate that transient coordination of the toluene solvent to the metal center may be instrumental in this, albeit less efficient than the pendant arene group in the \((\eta^5\text{C}_5\text{H}_4\text{CM}_2\text{Ar})\text{TiCl}_3/\text{MAO}\) systems, as the interaction is intermolecular rather than intramolecular.

To estimate the possible role of solvent interactions on the selective ethene trimerization by the (cyclopentadienyl–arene)tinanium catalysts, we investigated the catalyst system \(1/\text{MAO}\) in an 80:20 \((\text{v/v})\) 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 rate is identical with 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 beneficial for the catalyst stability.

**Proposed Catalytic Cycle for Ethene Trimerization.** It has been proposed that the only family of catalysts known thus far to perform efficient and selective ethene trimerization (Ziegler-type catalysts based on the combination of chromium salts with aluminum alkyls and added Lewis bases) acts through a mechanism involving metallaacyclic intermediates. 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 \(\beta\)-H abstraction and reductive elimination can then lead to the formation of 1-hexene and the regeneration of the low-valent chromium species.

This sequence explains the lack of 1-butene formation, as the chromacyclopentane is expected to be much more stable toward \(\beta\)-H abstraction than the more flexible chromacycloheptane. For the very recently reported selective ethene trimerization by TaMe_2Cl_3, a similar catalytic cycle via metallaacycles has been proposed.

It is likely that a similar mechanism is operative in the selective trimerization performed by the (cyclopentadienyl–arene)tinanium catalysts presented here, involving cationic Ti(II) metallaacyclic intermediates and the Ti(II)/Ti(IV) couple for oxidative coupling/reductive elimination. Several catalytic C–C coupling reactions have been reported in neutral titanium systems that involve metallaacyclic intermediates and a Ti(II)/Ti(IV) couple. It is less obvious how the required (cationic) low-valent Ti(II) species would be generated from a mono(cyclopentadienyl)tinanium(IV) trichloride complex and MAO.

One possibility is that the cationic \([(\text{Cp–arene})\text{Ti}-(\text{CH}_2\text{CH}_2\text{R})_2]^+\) species, likely to be generated initially by alkylation of the (Cp–arene)TiCl_3 by MAO followed by alkyl anion abstraction and sequential ethene insertions into the Ti-Me bonds, is in equilibrium with its hydride-olefin isomer \([(\text{Cp–arene})\text{Ti}(\text{H})(\eta^2\text{CH}_2=\text{CHR})-(\text{CH}_2\text{CH}_2\text{R})]^+\). This may be followed either by dissociation of the alkene (to yield a cationic hydrido alkyl Ti(IV) intermediate that is likely to undergo subsequent reductive elimination of the alkane to give a cationic Ti(II) species) or by reductive elimination of the alkane (to yield a cationic Ti(II) olefin complex). In both pathways, the coordination of the arene moiety can provide additional stabilization to the Ti(II) state. Presently it is impossible for us to distinguish between the two pathways (although the latter appears to be the more likely, as it avoids the formation of a “naked” cationic (Cp–arene)Ti(II) species). A theoretical study of the process using DFT calculations is presently in progress. The catalytic cycle as proposed on the basis of the information available at this moment is summarized in Scheme 3.

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 tinacyclopentane intermediate is the rate-determining step. This reaction will require the displacement or slippage of the \(\eta^6\)-coordinated arene ligand to yield a less electron-rich metal center that can capture and insert the third ethene molecule. It is thus possible that the process of arene dissociation or ring slippage from a cationic Ti(IV) species is involved in the rate-determining step, which would be consistent with 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 rate dependence on ethene concentration, 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. However, the selective trimerization of 1-hexene with triazacyclohexane–chromium catalysts was recently reported to have as a rate-

<table>
<thead>
<tr>
<th>Solvent, vol %</th>
<th>C_6 products, g (wt %)</th>
<th>C_{10} products, g (wt %)</th>
<th>PE, g (wt %)</th>
<th>productivity of C_6 products</th>
<th>trimerization products, wt %</th>
<th>trimerization productivity (mol of Ti·h^{-1})</th>
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</thead>
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<tr>
<td>toluene</td>
<td>100</td>
<td>20.9 (83)</td>
<td>3.5 (14)</td>
<td>0.5 (1.8)</td>
<td>555</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>8.1 (87)</td>
<td>0.8 (9)</td>
<td>0.4 (4.3)</td>
<td>215</td>
<td>96</td>
</tr>
<tr>
<td>n-octane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Reaction conditions: 5 bar of ethene pressure, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. \(b\) In mol of C_6 product/(mol of Ti·h).
determining step is the insertion of the third monomer molecule.\(^{23}\)

Zhu and co-workers reported recently that the catalyst system \((\eta^3-C_5Me_5)Ti(OCH_2Ph)_3/MAO\) in heptane produces short chain (ethyl and butyl) branched polyethylene in the homopolymerization of ethene, and they proposed a reduced titanium species as being responsible for in situ dimerization and trimerization of ethene.\(^{24}\) They suggest that free AlMe\(_3\) is not instrumental in the generation of the species that produces 1-hexene. MAO/SiO\(_2\) and [PhNMe\(_2\)H][B(C\(_6\)F\(_5\))\(_4\)] proved to be efficient cocatalysts, affording active and highly selective (> 97 wt %) trimerization catalysts. The selectivity of the \(5/B(C_6F_5)_3\) 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 \([MeB(C_6F_5)_3]^+\) anion.\(^{25}\) It may be taken into account that the experiments with the \(B(C_6F_5)_3\) and [PhNMe\(_2\)H][B(C\(_6\)F\(_5\))\(_3\)] activated systems are conducted in the absence of impurity scavenger, which might partially explain the lower activities, compared to 1/MAO.

### Effect of the Bridge between the Cyclopentadienyl and Arene Groups

To probe structure–performance relationships in the \(Cp\text{-arene})Ti\)-based ethene trimerization catalyst system, the effect of the bridge between the cyclopentadienyl ligand and the arene group on catalytic ethene conversion was investigated. The precatalysts \((\eta^5-C_5H_4(CH_2Ph)TiCl_3\ (6), (\eta^5-C_5H_4SiMe_2Ph)TiCl_3\ (7), and \((\eta^5-C_5H_4CMe_2CH_2Ph)TiCl_3\ (8)\) were tested in ethene conversions with MAO activator and compared with the reference catalyst \((\eta^5-C_5H_4CMMe_2Ph)TiCl_3\ (1)/MAO\ (Table 7).

Table 6. Catalytic Ethene Conversion with 5/Cocatalyst Systems Compared with 1/MAO\(^{a}\)

| Cocatalyst                  | \(C_6\) products, g (wt %) | \(C_{10}\) products, g (wt %) | PE, g (wt %) | Productivity, mol of olefinic bonds trimerized/((mmol of Ti) h) | Trimerization products, wt % | Trimerization productivity
|-----------------------------|-----------------------------|-------------------------------|--------------|---------------------------------------------------------------|-------------------------------|-------------------------------
| \([\text{PhNMe_2H}][\text{B(C_6F_5)_3}]\)\(^{\text{f}}\) | 14.6 (90)                   | 1.2 (7)                       | 0.3 (2.0)    | 390                                                          | 97                            | 73                            |
| \(\text{B(C_6F_5)_3}\)\(^{\text{a}}\) | 5.8 (88)                    | 0.3 (5)                       | 0.4 (6)      | 155                                                          | 93                            | 29                            |
| \(\text{MAO/SiO}_2\)\(^{\text{e}}\) | 13.8 (95)                   | 0.6 (4)                       | n.d.         | 365                                                          | 99f                           | 68                            |
| \(1/\text{MAO}\)\(^{\text{g}}\) | 20.9 (83)                   | 3.5 (14)                      | 0.5 (1.8)    | 555                                                          | 97                            | 110                           |

\(^{\text{a}}\) Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, 30 min reaction time.\(^{\text{b}}\) In mol of olefinic bonds trimerized/(mmol of Ti) h).\(^{\text{c}}\) B:Ti ratio = 1.1. \(^{\text{d}}\) 5 wt % MAO on silica, Al:Ti ratio = 250. \(^{\text{e}}\) Product distribution is based on liquid fraction only (remaining 1 wt % is \(C_8\) and \(C_{12}\) fractions). \(^{\text{f}}\) Al:Ti ratio = 1000.

To evaluate the effect of the cocatalyst on the trimerization catalysts, we performed catalytic ethene conversion studies using \((\eta^5-C_5H_4CH_2Ph)\text{TiMe}_3/B(C_6F_5)_3/toluene\) catalyst \(17\) nor with the \((\text{Cp} \text{-arene})\text{TiMe}_3/MAO\) catalyst. The precatalysts \((\eta^5-C_5H_4(CH_2Ph)\text{TiMe}_3\) (6), \((\eta^5-C_5H_4SiMe_2Ph)\text{TiMe}_3\) (7), and \((\eta^5-C_5H_4CMMe_2Ph)\text{TiMe}_3\) (8) were tested in ethene conversions with MAO activator and compared with the reference catalyst \((\eta^5-C_5H_4CMMe_2Ph)\text{TiCl}_3\) (1)/MAO (Table 7).

The catalysts with the CH\(_2\) and SiMe\(_2\) bridges (6 and 7, respectively) both produce 1-hexene and polyethylene in comparable amounts, together with a Flory–Schulz

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Table 7. Catalytic Ethene Conversion with the \([\eta^5-C_5H_4- \text{(B)}- \text{Ph}]\text{TiCl}_3/\text{MAO} \) Catalyst Systems

<table>
<thead>
<tr>
<th>Catalyst (B)</th>
<th>C_6 products, g (wt %)</th>
<th>C_8 products, g (wt %)</th>
<th>C_10 products, g (wt %)</th>
<th>C_12–24 products, g (wt %)</th>
<th>PE, g (wt %)</th>
<th>Trimerization products, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (CMe_2)</td>
<td>20.9 (83)</td>
<td>0.3 (1)</td>
<td>3.5 (14)</td>
<td>0.1 (0.5)</td>
<td>0.5 (2)</td>
<td>97</td>
</tr>
<tr>
<td>6 (CH_3)</td>
<td>2.7 (42)</td>
<td>0.4 (6)</td>
<td>0.6 (9)</td>
<td>0.6 (9)</td>
<td>2.2 (34)</td>
<td>51</td>
</tr>
<tr>
<td>7 (SiMe_2)</td>
<td>2.1 (36)</td>
<td>0.3 (5)</td>
<td>0.4 (7)</td>
<td>0.5 (8)</td>
<td>2.6 (44)</td>
<td>43</td>
</tr>
<tr>
<td>8 (CMe_2CH_2)</td>
<td>1.2 (83)</td>
<td>0.1 (7)</td>
<td>0.05 (3)</td>
<td>0.01 (0.7)</td>
<td>0.1 (7)</td>
<td>86</td>
</tr>
</tbody>
</table>

*a Reaction conditions: toluene solvent, 5 bar of ethene, \(30^\circ C\), \(15 \mu\text{mol of Ti, Al:Ti} = 1000\), 30 min reaction time.

Table 8. Catalytic Ethene Conversion with the \([\eta^5-C_5H_4, \text{CR_2PH}]\text{TiCl}_3/\text{MAO} \) Catalyst Systems

<table>
<thead>
<tr>
<th>Catalyst (R_2)</th>
<th>C_6 products, g (wt %)</th>
<th>C_10 products, g (wt %)</th>
<th>PE, g (wt %)</th>
<th>Productivity C_6 products</th>
<th>Trimerization products, wt %</th>
<th>Trimerization productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Me_2)</td>
<td>20.9 (83)</td>
<td>3.5 (14)</td>
<td>0.5 (1.8)</td>
<td>555</td>
<td>97</td>
<td>110</td>
</tr>
<tr>
<td>9 (Et_2)</td>
<td>18.5 (88)</td>
<td>1.4 (7)</td>
<td>1.0 (4.6)</td>
<td>495</td>
<td>95</td>
<td>92</td>
</tr>
<tr>
<td>10 (CH_2=CH_2)</td>
<td>24.4 (87)</td>
<td>2.9 (10)</td>
<td>0.6 (2.0)</td>
<td>650</td>
<td>97</td>
<td>125</td>
</tr>
<tr>
<td>11 (CH_2=C=CH_2)</td>
<td>17.3 (88)</td>
<td>1.4 (7)</td>
<td>0.9 (4.7)</td>
<td>460</td>
<td>95</td>
<td>87</td>
</tr>
</tbody>
</table>

*a Reaction conditions: toluene solvent, 5 bar of ethene, \(30^\circ C\), \(15 \mu\text{mol of Ti, Al:Ti} = 1000\), 30 min reaction time. *b In g of C_6 product/((mmol of Ti) bar h). *c In mol of olefinic bonds trimerized/(mmol of Ti) h.

From the above experiments it is clear that a disubstituted C_2 bridge between the cyclopentadienyl and arene moieties gives the best selectivity and activity in catalytic ethene trimerization. To refine this point further, we prepared three more precatalysts of the type \([\eta^5-C_5H_4, \text{arene}]\text{Ti(II)} \) that satisfy this requirement: 9 (B = CMe_2), 10 (B = C(CH_2=CH_2)), and 11 (B = C=CH_2). The data in Table 8 show that, upon activation with MAO, all these catalysts are indeed active and selective in ethene trimerization. The performance of 10/MAO, with the bridging carbon forming part of a 1,1-disubstituted cyclohexane moiety, even exceeds that of the reference catalyst 1/MAO, whereas the catalyst with the C=C bridge is slightly inferior to its CMe_2 analogue in both activity and selectivity. Interestingly, the catalyst 11/MAO, with an sp^2 bridging carbon, also performs reasonably well, with trimerization behavior comparable to that of the catalyst with the C=C bridge.

From the data in Table 7, it can be seen that the bridging unit plays a crucial role in the selective ethene trimerization performance of these catalyst systems. The transformation of the catalyst from a species active in polymerization into one that is active in trimerization, as put forward in the in the proposed mechanism, involves the coordination of the arene moiety to the electron-deficient titanium center to generate the ansa-Cp–arene Ti(II) species (Scheme 3). Apparently, both the CH_2 (6) and SiMe_2 (7) bridged compounds are less effective in this respect than the CMe_2-bridged parent (1). It is as yet unclear whether this is the result of a slow switch from the polymerization catalyst (Ti(IV)–dialkyl) to the trimerization catalyst (Ti(III)/Ti(IV)–metallacycle), promoted by (intramolecular) arene coordination, or if the trimerization catalyst, once formed, can readily be transformed back into a species active in polymerization.
The clean formation of ansa-cyclopentadienyl–arene Ti(II) cations, the prerequisite for selective ethene trimerization activity, is likely to be facile for the CMe$_2$-bridged species, which could explain the differences in ethene conversion for 1/MAO and 6/MAO.$^{27}$

The catalyst performance of the SiMe$_2$-bridged species 7 is most likely related to the poor accessibility of the ansa-Cp–arene coordination mode of the ancillary ligand. Due to the larger ionic radius of silicon (0.26 Å) versus carbon (0.15 Å),$^{28}$ the ligand will have to adopt a much more acute Cp–Si–arene bond angle to accommodate ansa coordination.$^{29}$ Bochmann and co-workers reported that the reaction of (η$^5$-C$_5$H$_5$SiMe$_2$)TiMe$_3$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$]$_2$ affords highly thermally labile species (even at −60 °C), in contrast to the much more stable complex [(η$^5$-C$_5$H$_5$CMe$_2$Ph)TiMe$_2$][B(C$_6$F$_5$)$_4$], tentatively suggesting the absence of the crucial arene coordination in the former cationic species.$^{30}$ These observations may indicate that in 7/MAO the conversion from an ethene polymerization catalyst to an ethene trimerization catalyst is slow compared to that for 1/MAO.

The clean formation of ansa-cyclopentadienyl–arene cationic titanium species for the reaction of the trimethyl derivative of 8, (η$^5$-C$_3$H$_5$CMe$_2$CH$_2$Ph)TiMe$_2$, with B(C$_6$F$_5$)$_3$ $^{30}$ and (for the reaction of (η$^5$-C$_5$Me$_2$CH$_2$CH$_2$-Ph)TiMe$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$])$^{30}$ suggests that the ansa coordination, crucial for trimerization selectivity, is readily accessible for bridges with a C$_2$ backbone. Accordingly, a relatively good trimerization selectivity of 86% is obtained for 8/MAO, albeit at a slow rate. The longer, more flexible CMe$_2$CH$_2$ bridge probably allows for a stronger η$^6$-arene coordination in 8 than for 1 with the CMe$_2$ bridge.$^{30}$ The “constrained geometry” of the C$_1$-bridged ansa-(η$^5$:η$^5$-C$_5$-arene)Ti species might facilitate the slippage or dissociation of the arene ring, proposed for the rate-determining insertion of the third ethene molecule into the titanacyclopentane, resulting in a higher trimerization activity of 1/MAO relative to 8/MAO.

The differences in trimerization activity between the 1/MAO, 9/MAO, and 10/MAO systems are relatively small (maximum 25%) and can be the result of the different steric properties of the backbone substituents$^{31}$ or other effects that influence the propensity for arene “ring slippage” in the proposed rate-determining step. Since ansa-cyclopentadienyl–arene coordination of the ancillary ligand is crucial to ethene trimerization reactivity (vide supra), the behavior of the [C$_5$H$_4$C(=CH$_2$)-Ph] ligand (11) is somewhat puzzling. To adopt the required conformation, the Cp–C–arene bond angle in this ligand has to be reduced even more from its unstrained value (around 120°) than for the nonelective SiMe$_2$-bridged species 7. One possibility is that the unsaturated moiety in the bridge of 11 gets alkylated in the process, which would effectively turn it into a CRR'-bridged species. Further study of the cationic dialkyl derivative of 11 would be required to investigate this issue.

**Effect of Substituents on the Cyclopentadienyl Group.** The effect of the attachment of substituents on the cyclopentadienyl moiety of the cyclopentadienyl–arene catalysts was probed by the synthesis of three precatalysts of the type (η$^5$-C$_3$H$_5$CMe$_2$Ph)TiCl$_3$: 12 (R = SiMe$_3$), 13 (R = CMe$_2$), and 14 (R = CMe$_2$Ph). The results of catalytic ethene conversion with these cata-

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**Table 9. Catalytic Ethene Conversion with the [η$^5$-(3-R)C$_3$H$_5$CMe$_2$Ph]TiCl$_3$/MAO Catalyst Systems**

<table>
<thead>
<tr>
<th>Catalyst (R)</th>
<th>time, min</th>
<th>C$_8$ products, g (wt %)</th>
<th>C$_{10}$ products, g (wt %)</th>
<th>PE, g (wt %)</th>
<th>productivity</th>
<th>trimerization products, wt %</th>
<th>trimerization productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (H)</td>
<td>30</td>
<td>20.9 (83)</td>
<td>3.5 (14)</td>
<td>0.5 (1.8)</td>
<td>555</td>
<td>97</td>
<td>110</td>
</tr>
<tr>
<td>1 (K)</td>
<td>30</td>
<td>22.9 (78)</td>
<td>3.3 (11)</td>
<td>0.4 (1.2)</td>
<td>670</td>
<td>96</td>
<td>130</td>
</tr>
<tr>
<td>12 (SiMe$_3$)</td>
<td>30</td>
<td>25.2 (85)</td>
<td>3.3 (11)</td>
<td>0.4 (1.2)</td>
<td>670</td>
<td>96</td>
<td>130</td>
</tr>
<tr>
<td>13 (CMe$_3$)</td>
<td>30</td>
<td>14.7 (89)</td>
<td>0.9 (5)</td>
<td>0.3 (2.3)</td>
<td>335</td>
<td>96</td>
<td>59</td>
</tr>
<tr>
<td>14 (CMe$_2$Ph)</td>
<td>30</td>
<td>11.9 (91)</td>
<td>0.6 (5)</td>
<td>0.3 (2.3)</td>
<td>315</td>
<td>96</td>
<td>59</td>
</tr>
</tbody>
</table>

$a$ Reaction conditions: toluene solvent, 5 bar of ethene, 30 °C, 15 μmol of Ti, Al:Ti = 1000. $^b$ g of C$_8$ product/(mmol of Ti) bar h. $^c$ g of C$_8$ product/(mmol of Ti) h.

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(27) Metal–arene interactions were proposed to explain the observation that in ethene polymerization with (η$^5$-C$_5$H$_5$-(B–Ph))ZrCl$_2$/MAO systems (B = CH$_2$, CMe$_2$), SiMe$_3$), the CH$_2$, and SiMe$_2$-bridged species are about 20 times as active as the CMe$_2$-bridged species. See: Alt, H. G.; Köppl, A. Chem. Rev. 2000, 100, 1205.


(29) For example, in the X-ray structures of Me$_2$X((η$^5$-C$_5$H$_5$)TiMe$_3$, with [Ph$_3$C][B(C$_6$F$_5$)$_4$])$_2$ suggests that the arene moiety does not coordinate arene coordination in the former cationic species. $^{30}$ These observations may indicate that in 7/MAO the conversion from an ethene polymerization catalyst to an ethene trimerization catalyst is slow compared to that for 1/MAO.


ysts using MAO activator, and comparative data for the reference catalyst \(1/\text{MAO}\), are listed in Table 9.

As expected, all three systems show good selectivity for trimerization. The SiMe_3-substituted catalyst \(12/\text{MAO}\) shows a somewhat improved activity over \(1/\text{MAO}\), but the CMe_2-substituted catalyst \(13/\text{MAO}\) exhibits a lower productivity and selectivity over the 30 min run period. This appears to be due to a catalyst degradation process in the latter system. Its initial ethene uptake rate is comparable to that of \(12/\text{MAO}\) but decreases much more rapidly over time, the catalyst being fully deactivated after 15 min. The catalyst \(14/\text{MAO}\), which has two CMe_2Ph substituents on the cyclopentadienyl ring that, in principle, can both (alternately) coordinate to the metal center, is selective but rather slow compared to \(1/\text{MAO}\). Nevertheless, the catalyst \(14/\text{MAO}\) does have a very interesting feature. As mentioned before, the thermal stability of \(1/\text{MAO}\) is only modest, and even at 30 °C catalyst degradation is taking place noticeably. The top two entries of Table 9 describe the behavior of \(1/\text{MAO}\) at run times of 30 and 120 min, respectively. It is clear that catalyst deactivation limits the total production attainable by this catalyst to around 48 kg of trimerization product (g of Ti). In contrast, \(14/\text{MAO}\) displays a comparable productivity (around 310 kg of \(C_6/\text{mol h bar}\)) over both the 30 and 120 min runs, affording a production of 71 kg of trimerization product (g of Ti) after 120 min, at which stage the catalyst is still active. Thus, the presence of two CMe_2Ph substituents slows down the catalysis but greatly improves catalyst stability. The increased stability may be related to our earlier observation that \(1/\text{MAO}\) degrades less rapidly in neat toluene solvent than in an \(n\)-octane/toluene (80/20 v/v) mixture, possibly indicating catalyst stabilization by transient toluene coordination. The lower activity may be caused by competition between the loose pendant arene substituent and incoming ethene on the titanacyclopentane intermediate.

The stabilities of the catalysts \(12 (R = \text{SiMe}_3)/\text{MAO}\) and \(13 (R = \text{CMe}_2)/\text{MAO}\) differ significantly. The actual deactivation mechanism is not known presently, but various possible pathways can be suggested. For instance, it is possible that electronic effects play a role in the stabilization of the catalytic species. As suggested earlier, (transient) arene coordination improves the catalyst stability. The electron-donating tert-butyl group of \(13\) increases the electron density on the titanium center, making it less prone to arene coordination and thus possibly more amenable to catalyst deactivation. A second possible deactivation pathway involves cyclo-metallation of the EMe_2 substituent (E = Si, \(12; E = C, 13\)). Marks and co-workers reported that for caticonic zirconocene species \([\eta^5-C_5H_4R]([\eta^5-C_5H_4CMe_2]ZrR')\) this process occurs more easily for \(E = C\) than for \(E = Si\). A similar trend in our systems could explain the greater stability of \(12/\text{MAO}\) relative to \(13/\text{MAO}\) in selective ethene trimerization.

The addition of a substituent on the cyclopentadienyl ring also affects the composition of the trimerization products formed. For the SiMe_3-substituted catalyst \(12/\text{MAO}\) the 1-hexene content of the \(C_6\) fraction rises to 99.9% (99.7% for \(1/\text{MAO}\)) and the 5-methyl-1-nonene content of the \(C_{10}\) fraction to 92% (85% for \(1/\text{MAO}\)). For the tert-butyl-substituted catalyst \(13/\text{MAO}\) these trends are similar (99.8% and 91%, respectively).

Considering all the possibilities to form \(C_{10}\) products from ethene and 1-hexene via the proposed trimerization mechanism, it appears that one pathway is by far the most favorable. This is illustrated in Scheme 4 and proceeds through selective oxidative coupling of ethene with 1-hexene to give a titanacyclopentane with the n-butyl substituent on the \(\beta\)-carbon. This is followed by an insertion of ethene into the Ti–C bond at the unsubstituted side of the metallacycle, giving a \(\beta\)-n-butyl-substituted titanacyclopentane, which then affords 5-methyl-1-ene via \(\beta\)-H transfer from the unsubstituted side of the metallacycle and reductive elimination.

The similar product distribution within the \(C_{10}\) fractions observed for the SiMe_3 (12) and CMe_2 (13) substituted catalysts suggests that the selectivity of the cotrimerization is mainly controlled by the steric properties of the substituted cyclopentadienyl ligand rather than by its electronic properties.

**Combining Ligand Effects.** The investigation of the effect of single ligand variations on the catalytic ethene conversion with (cyclopentadienyl–arene) titanium species (variation in bridging group, substituents on the cyclopentadienyl moiety, and substituents on the arenyl moiety) has resulted in the identification of specific features that appear to be advantageous to catalyst efficiency. In comparison under standard conditions to the reference catalyst \(1/\text{MAO}\), the catalyst with the \(C[(\text{CH}_2)_3]_{\text{SiMe}_3}\) bridging group (10) shows a 17% increase in \(C_6\) productivity, and the catalyst with the SiMe_3-substituted cyclopentadienyl group (12) shows a 20% increase. Combining these features in the catalyst \(\eta^5-(3\text{SiMe}_3)\text{C}_3\text{H}_2\text{C}(\text{CH}_3)_2\text{Ph})\text{TiCl}_3\) (15)/MAO leads to a 57% increase in \(C_6\) productivity relative to \(1/\text{MAO}\) (Table 10). This suggests that the effects of variations in bridging group and cyclopentadienyl substituent are roughly additive, with a slightly positive nonlinearity.

In contrast to the positive effect on \(C_6\) productivity of substitution on the cyclopentadienyl group, the attach-

\(^{32}\) A similar pathway has been proposed for the cotrimerization of ethene with styrene with \([\text{Cp}^\text{Me}_2]^+\) cations. See: Pellecchia, C.; Pappalardo, D.; Oliva, L.; Mazzeo, M.; Gruter, G. J. Macromolecules 2000, 33, 2807.
ment of methyl substituents on the aryl group was seen to lead to a decrease in C₆ productivity relative to 1/MAO (for the catalyst with the 3,5-Me₂C₆H₃ group (3) a reduction by 62%). Remarkably, the catalyst [η⁵-C₅H₅CMe₂-X-Ar]TiCl₃/MAO, combining Cp substitution with aryl substitution, turned out to be the most active catalyst of all (Table 10), with an increase in the rate of C₆ production by 92% relative to 1/MAO and a very high selectivity for the combined trimerization products (99%). Aryl substitution in the tert-butyl cyclopentadienyl derivatives [η⁵-C₅Me₂C₆H₅CMe₂-3,5-Me₂C₆H₃]TiCl₃ (16)/MAO, combining Cp substitution with aryl substitution, has no effect on initial ethene uptake rate but significantly improves catalyst stability, as can be seen from the ethene uptake profile, affording a catalyst with comparable productivity to 1/MAO over a 30 min run period. A judicious combination of substituents on the key positions (backbone, cyclopentadienyl, and arene) can thus improve the three major parameters in the catalytic trimerization process: activity, selectivity, and stability. The precise interplay of steric and electronic effects is as yet unclear and warrants further investigation.

**Conclusions**

We have identified a catalyst system, [η⁵-C₅H₅CMe₂R]-TiCl₃/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. The intrinsic selectivity for ethene trimerization of the catalytic species is essentially independent of solvent and cocatalyst, and hameliable behavior of the cyclopentadienyl-arene ancillary ligand appears to be essential for obtaining this high selectivity for trimerization.

We have shown that a wide range of titanium precatalysts of the type [η⁵-C₅H₅R-(B)-Ar]TiCl₃ can be activated with MAO to effect catalytic ethene trimerization (summarized in Table 11). The nature of the bridging moiety (B) between the cyclopentadienyl and the arene group is crucial for obtaining a good selectivity in 1-hexene production. Thus far, only disubstituted C₁ bridges have afforded highly selective and active ethene trimerization catalysts. Apparently, the conformational constraints imposed by the bridging unit are of major importance to catalyst performance. The introduction of additional substituents on the cyclopentadienyl moiety can influence both catalyst activity and stability. The introduction of a trimethylsilyl substituent is highly favorable for catalyst activity, whereas the addition of a second CMe₂Ph substituent greatly increases catalyst stability (albeit at the cost of a lower activity). Combining two ligand variations at a time shows in some cases a significant positive nonlinear additivity of the substituent effects on catalyst activity. In addition, steric effects can be employed to improve the selectivity for formation of a single monomethyl-branched α-olefin product in the trimerization of ethene with 1-alkenes. Although some ethene oligomerization processes that produce 1-hexene in excess of the amount expected from Schulz–Flory product distributions and ethene polymerization catalysts that produce branched polyethylenes are known (e.g., for certain Ziegler-type catalyst sys-

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**Table 10. Catalytic Ethene Conversion with the [η⁵-(3-R)C₅H₅CMe₂Ar]TiCl₃/MAO Catalyst Systems**

<table>
<thead>
<tr>
<th>catalyst (R, X, Ar)</th>
<th>C₆ products, g (wt %)</th>
<th>C₁₀ products, g (wt %)</th>
<th>PE, productivity C₆ products</th>
<th>trimerizn products, wt %</th>
<th>trimerizn productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (H, Me, Ph)</td>
<td>20.9 (83)</td>
<td>3.5 (14)</td>
<td>0.5 (1.8)</td>
<td>555</td>
<td>97</td>
</tr>
<tr>
<td>10</td>
<td>24.4 (87)</td>
<td>2.9 (10)</td>
<td>0.6 (2.0)</td>
<td>650</td>
<td>97</td>
</tr>
<tr>
<td>15</td>
<td>33.9 (84)</td>
<td>5.2 (13)</td>
<td>1.2 (3.0)</td>
<td>905</td>
<td>97</td>
</tr>
<tr>
<td>3 (H, Me, 3,5-Me₃C₆H₃)</td>
<td>7.9 (93)</td>
<td>0.1 (4)</td>
<td>0.1 (1.3)</td>
<td>210</td>
<td>97</td>
</tr>
<tr>
<td>16</td>
<td>40.1 (84)</td>
<td>7.0 (15)</td>
<td>0.3 (0.6)</td>
<td>1070</td>
<td>99</td>
</tr>
<tr>
<td>17</td>
<td>24.4 (91)</td>
<td>1.6 (6)</td>
<td>0.7 (2.8)</td>
<td>650</td>
<td>97</td>
</tr>
</tbody>
</table>

* Reaction conditions: toluene solvent, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. *b* In g of C₆ product/((mmol of Ti) h). *c* In mol of olefinic bonds trimerized/((mmol of Ti) h).

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**Table 11. Overview of Trimerization Activity and Selectivity with [η⁵-(3-R)C₅H₅-(B)-Ar]TiCl₃/MAO Catalyst Systems**

<table>
<thead>
<tr>
<th>precatalyst</th>
<th>R</th>
<th>B</th>
<th>Ar</th>
<th>trimerizn products, wt %</th>
<th>trimerizn productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>CMe₂</td>
<td>Ph</td>
<td>97</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>CMe₂</td>
<td>4-Me</td>
<td>98</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>CMe₂</td>
<td>3,5-Me₂C₆H₅</td>
<td>97</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>C₂H₅</td>
<td>Ph</td>
<td>&lt;51</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>SiMe₂</td>
<td>Ph</td>
<td>&lt;43</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H</td>
<td>CMe₂CH₂</td>
<td></td>
<td>86</td>
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<td>Ph</td>
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<td>H</td>
<td>C[(CH₂)₅]</td>
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<td>125</td>
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<tr>
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<td>Ph</td>
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<td>87</td>
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<td>CMe₂</td>
<td>Ph</td>
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<td>130</td>
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<tr>
<td>13</td>
<td>SiMe₂</td>
<td>CMe₂</td>
<td>Ph</td>
<td>94</td>
<td>73</td>
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<tr>
<td>14</td>
<td>SiMe₂</td>
<td>CMe₂</td>
<td>Ph</td>
<td>96</td>
<td>59</td>
</tr>
<tr>
<td>15</td>
<td>SiMe₂</td>
<td>C[(CH₂)₅]</td>
<td>Ph</td>
<td>97</td>
<td>177</td>
</tr>
<tr>
<td>16</td>
<td>SiMe₂</td>
<td>CMe₂</td>
<td>3,5-Me₂C₆H₅</td>
<td>99</td>
<td>211</td>
</tr>
<tr>
<td>17</td>
<td>SiMe₂</td>
<td>CMe₂</td>
<td>3,5-Me₂C₆H₅</td>
<td>97</td>
<td>121</td>
</tr>
</tbody>
</table>

* Reaction conditions: toluene solvent, 30 °C, 15 μmol of Ti, Al:Ti = 1000, 30 min reaction time. *b* In mol of olefinic bonds trimerized/((mmol of Ti) h).

(34) Sassmannshausen, J.; Organometallics 2000, 19, 482.


Experimental Section

Materials and Methods. All experiments were carried out under a purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (CDCl₃) or dried over Na/K alloy and vacuum-transferred before use (CD₂Cl₂, THF). Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF). All experiments were carried out in a nitrogen atmosphere prior to use. Diethyl ether and THF (Aldrich, anhydrous, 99.8%) was passed over BASF R3-11 supported Cu oxygen scavenger and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆). Toluene (Aldrich, anhydrous, 99.8%) was passed over BASF R3-11 supported Cu oxygen scavenger and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF).

The titanium complexes (over columns of Al₂O₃ (Fluka), BASF R3-11 supported Cu prior to use. Toluene (Aldrich, anhydrous, 99.8%) was passed over BASF R3-11 supported Cu oxygen scavenger and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF).

To our knowledge the present system is the first highly active ethene trimerization catalyst that is not based on chromium. Very recently catalyst systems for ethene trimerization based on TaMe₂Cl₃ and (arene)₂(C₂H₅)₂TiCl₃ (Fluka), prior to use. Toluene (Aldrich, anhydrous, 99.8%) was passed over BASF R3-11 supported Cu oxygen scavenger and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF). Systems), to our knowledge the present system is the first highly active ethene trimerization catalyst that is not based on chromium. Very recently catalyst systems for ethene trimerization based on TaMe₂Cl₃ and (arene)₂(C₂H₅)₂TiCl₃ (Fluka), prior to use. Toluene (Aldrich, anhydrous, 99.8%) was passed over BASF R3-11 supported Cu oxygen scavenger and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF).

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The titanium complexes (over columns of Al₂O₃ (Fluka), BASF R3-11 supported Cu prior to use. Toluene (Aldrich, anhydrous, 99.8%) was passed over BASF R3-11 supported Cu oxygen scavenger and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF).

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Experimental Section

Materials and Methods. All experiments were carried out under a purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (CDCl₃) or dried over Na/K alloy and vacuum-transferred before use (CD₂Cl₂, THF). Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF). All experiments were carried out under a purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (CDCl₃) or dried over Na/K alloy and vacuum-transferred before use (CD₂Cl₂, THF). Deuterated solvents (Aldrich, Acros) were dried over Al₂O₃ (Fluka), and vacuum-transferred before use (C₆D₆, THF).
Preparation of \( \text{[C}_{5}\text{H}_{3}-1,3-(\text{CMe}_{2}\text{Ph})_{2}]\text{Li} \) (13). To a solution of 1.47 g (6.0 mmol) of \( \text{[C}_{5}\text{H}_{3}(\text{SiMe}_{3})_{2}\text{CMe}_{2}\text{Ph}]\text{Li} \) in 30 mL of methylene chloride, cooled to \(-20^\circ\text{C}\), was added dropwise 0.70 mL (1.2 g, 6.3 mmol) of TiCl\(_{4}\). The red-brown solution was warmed to room temperature and was stirred overnight. The residual was removed in vacuo, and the residue was stirred with 20 mL of pentane, which was subsequently pumped off. Extraction with toluene afforded a brown oil that could not be crystallized from pentane, hexane, toluene, or methylene chloride. The oil was diluted with cold pentane to 1.98 g (5.0 mmol, 83%) of product (about 95% purity as indicated by NMR spectroscopy). \(^{1}H\) NMR (300 MHz, CD\(_{2}D_{2}CF_{2}D_{2}CF_{2}CF_{3})\): \( \delta \) 7.1-7.0 (m, 3H, Ph \& Cp H), 6.87 (d, \( j_{HH} = 7.0 \), 2H, Ph \& Cp H), 6.60 (ps t, \( j_{HH} = 4.4 \), 1H, Ph H), 6.40 (ps t, \( j_{HH} = 3.3 \), 1H, Ph H), 6.29 (ps t, \( j_{HH} = 2.9 \), 1H, Ph H), 1.64 (s, 3H, C(CH\(_{3}\))\(_{3}\)), 1.04 (s, 5H, C(CH\(_{3}\))\(_{2}\)). \(^{13}C\) NMR (75.4 MHz, CD\(_{2}D_{2}CF_{2}D_{2}CF_{2}CF_{3})\): \( \delta \) 128.5, 126.6, 126.1, 121.7, 121.0, 119.6 (Ph), 41.6 (C(CH\(_{3}\))\(_{3}\)), 34.7 (C(CH\(_{3}\))\(_{2}\)), 30.4 (C(CH\(_{3}\))\(_{2}\)), 28.9, 28.7 (C(CH\(_{3}\))\(_{2}\)).

Preparation of \( \text{[C}_{5}\text{H}_{13}-1,3-(\text{CMe}_{3}\text{Ph})_{2}]\text{Li} \) to a suspension of 2.28 g (27.1 mmol) of PhLi in 50 mL of n-hexane was added 6.14 g (27.4 mmol) of \( \text{[Fc}_{2}\text{C}_{6}\text{H}_{4}\text{SiMe}_{3}]_{2}\text{Ph} \). The mixture was refluxed for 5 h. The precipitate was washed on a glass and rinsed with 2 \( \times 20 \) mL of pentane. Drying in vacuo yielded 4.18 g (13.6 mmol, 50%) of an off-white solid. \(^{1}H\) NMR (300 MHz, CD\(_{2}D_{2}CF_{2}D_{2}CF_{2}CF_{3})\): \( \delta \) 7.55 (d, \( j_{HH} = 8.2 \), 4H, Ph \& H), 7.16 (m, 4H, Ph \& m-H), 7.01 (m, 2H, Ph \& p-H), 5.87 (m, 1H, Ph H), 5.83 (m, 2H, Ph H), 1.79 (s, 12H, C(CH\(_{3}\))\(_{3}\)). \(^{13}C\) NMR (75.4 MHz, CD\(_{2}D_{2}CF_{2}D_{2}CF_{2}CF_{3})\): \( \delta \) 157.5, 156.1, 148.8 (Ph and Cp Cipso), 128.6, 128.6, 126.1, 121.7, 121.6, 120.5, 119.6 (Ph), 41.6 (C(CH\(_{3}\))\(_{3}\)), 34.7 (C(CH\(_{3}\))\(_{2}\)), 30.4 (C(CH\(_{3}\))\(_{2}\)), 28.9, 28.7 (C(CH\(_{3}\))\(_{2}\))

Preparation of \( \text{[C}_{5}\text{H}_{3}-1,3-(\text{CMe}_{2}\text{Ph})_{2}]\text{TiCl}_{3} \) (14). To a solution of \( \text{[C}_{5}\text{H}_{3}-1,3-(\text{CMe}_{2}\text{Ph})_{2}]\text{Li} \) in 30 mL of methylene chloride, cooled to \(-40^\circ\text{C}\), was added dropwise 0.47 mL (0.8 g, 4.2 mmol) of TiCl\(_{4}\). The dark brown solution was warmed to room temperature and was stirred overnight. The solution was removed in vacuo, and the residue was stirred with 40 mL of pentane, which was subsequently pumped off. The residue was extracted with 50 mL of toluene, which was replaced by a 1:1 (v/v) mixture of methylene chloride and pentane (30 mL in total). Cooling to \(-40^\circ\text{C}\) afforded 0.22 g (0.5 mmol, 12%) of the title compound. \(^{1}H\) NMR (300 MHz, CD\(_{2}D_{2}CF_{2}D_{2}CF_{2}CF_{3})\): \( \delta \) 6.98 (m, 2H, Ph \& p-H), 6.96 (m, 4H, Ph m- or o-H),
Preparation of \( C_2H_3(SiMe_3)_2C[(CH_2)_5]Ph \). To a solution of 1.67 g (7.3 mmol) of \( C_2H_3(C(CH_3)_2)_2Ph \) in 70 mL of diethyl ether, cooled with ice–water, was added dropwise 0.8 mL (0.7 g, 6.4 mmol) of trimethylsilyl chloride. The reaction mixture was warmed to room temperature and was stirred overnight. The white suspension was cooled to 40 °C, was added dropwise 1.20 g (3.3 mmol) of \( C_5H_3-(CH_2)_3 \) (1H NMR spectroscopy showed that the sample contained 72% of light brown crystals. 1H NMR (300 MHz, C_6D_6/THF-d_8): \( \delta \) 6.7 (m, 1H, Ar C ipso), 6.55 (s, 2H, Ar C ipso), 6.60 (s, 1H, Ph C), 6.30 (m, 1H, Ph C), 2.54 (m, 2H, \( \alpha \text{-CH}_2 \)), 2.07, 1.86 (m, 1H each, \( \alpha \text{-CH}_2 \)), 1.4 (br, 3H, \( \alpha \text{-CH}_3 \)), 1.15 (br, 3H, \( \beta \text{-CH}_3 \)) and \( \gamma \text{-CH}_2 \)), 0.13 (s, 9H, Si(CH_3)_3). 13C NMR (75.4 MHz, C_6D_6): \( \delta \) 156.2, 148.8 (Ph and Cp C ipso), 128.4, 126.5, 126.0 (Ph CH), 121.5, 120.5 (Cp CH), 41.7 (C(CH_3)_2), 28.5, 28.4 (C(CH_3)_2). Anal. Calcd for \( C_{29}H_{51}SiTiCl_3 \): C, 60.62; H, 5.53. Found: C, 60.16; H, 5.56.

Preparation of \( \eta^5-(3-SiMe_3)C_5H_3CMe_2-(3,5-Me_2C_6H_3) \) Li. A solution of 1.88 g (17 mmol) of \( (3,5\text{-dimethylphenyl})\text{li}thium \) in 40 mL of diethyl ether was cooled to –40 °C. An equimolar amount of 3-tert-butyl-6,6-dimethylfulvene (2.7 g) was added. The reaction mixture was warmed to room temperature and was stirred overnight. Removing the solvent in vacuo gave a yellow oil which solidified in refluxing hexane. The solid was repeatedly rinsed with pentane to yield 2.35 g (8.6 mmol, 51%) of the title compound. 1H NMR (300 MHz, C_6D_6): \( \delta \) 7.17 (2H, Ar o-H), 6.63 (3H, Ar p-H), 5.81, 5.77, 5.71 (1H each, Cp H), 2.13 (s, 6H, ArCH_3), 1.77 (6H, C(CH_3)_2), 1.40 (s, 9H, Si(CH_3)_3).

Preparation of \( [\eta^5-(3-SiMe_3)C_5H_3CMe_2-3,5-Me_2C_6H_3] \) TiCl_3 (17). A solution of 1.54 g (5.6 mmol) of \( (C_5H_3CMe_2-3,5-Me_2C_6H_3)Li \) in 30 mL of methylene chloride, cooled to –20 °C, was added dropwise 0.65 mL (1.1 g, 5.8 mmol) of titanium tetrachloride. The mixture was warmed to room temperature and was stirred overnight. Removing the volatiles, stripping with pentane, and extracting with toluene afforded a brown oil. Repeated rinsing with cold pentane afforded 0.06 g (4.9 mmol, 88%) of the oil, which was 95% pure, as seen by NMR spectroscopy. 1H NMR (300 MHz, C_6D_6): \( \delta \) 6.7–6.5 (2H, Ar p-H and Cp H), 6.63 (3H, Ar o-H), 6.43 (t, \( \frac{1}{2} J = 2.9, 1.9 \) Hz, Cp H), 6.29 (t, \( \frac{1}{2} J = 2.9, 1.9 \) Hz, Cp H), 2.09 (3H, ArCH_3), 1.70 (s, 3H, C(CH_3)_2), 1.69 (3H, C(CH_3)_2), 1.05 (s, 9H, Si(CH_3)_3). 13C NMR (75.4 MHz, C_6D_6): \( \delta \) 157.3, 156.5, 149.0 (Ar and Cp C ipso), 137.8 (Ar m-Cipso), 124.6 (Ar p-Ch), 124.1 (Ar o-Ch), 120.6, 120.1, 119.5 (Cp Ph), 41.7 (C(CH_3)_2), 34.7 (C(CH_3)_2), 30.4 (C(CH_3)_2), 29.0, 28.9 (C(CH_3)_2), 21.5 (Ar CH).
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 equilibration 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 of 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 the 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 (η⁵-C₅H₄CMe₂Ph)TiMe₃ (5) with MAO/SiO₂ as Cocatalyst. A stainless steel 1 L 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 equilibration 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 of 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 amount of 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.

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