

The Extraordinary Cocatalytic Action of Polymethylaluminoxane (MAO) in the Polymerization of Terminal Olefins by Metallocenes: Chemical Change in the Group 4 Metallocene Dimethyl Derivatives Induced by MAO^[‡]

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In the polymerization of olefins with Group 4 metallocene dichlorides or dimethyl derivatives as procatalysts the use of polymethylaluminoxane (MAO) as the cocatalyst, especially in extreme excess (10^2 – 10^3 times the metallocene equivalent), has been shown to have an extraordinary accelerating effect on the rate of olefin polymerization, when compared with the cocatalytic action of alkylaluminum halides. In attempts at explaining the greatly superior catalytic activity of MAO in olefin polymerization (the MAO conundrum), hypotheses have generally paralleled the steps involved in the cocatalytic action of R_nAlCl_{3-n} , namely the alkylation of $Cp_2M_tCl_2$, ionization of $Cp_2M_t(R)Cl$ into the metallocenium cation, $[Cp_2M_t-R]^+$, and anion, $[R_{n-1}AlCl_{4-n}]^-$ and subsequent ion-pair separation. In order to understand any differences in catalytic action between such cocatalysts, we have studied the individual action of MAO (100 equiv.) and of $MeAlCl_2$ (1–2 equiv.) on each of the Group 4 metallocene derivatives, Cp_2TiCl_2 , Cp_2ZrCl_2 , $Cp_2Ti(CH_3)_2$ and $Cp_2Zr(CH_3)_2$. With $MeAlCl_2$ each of the metallocene derivatives appeared to form the cation, $[Cp_2M_t-CH_3]^+$, with greater (Ti) or lesser (Zr) ease, because an alkyne such as diphenylacetylene was then found to insert into the M_t-CH_3 bond stereoselectively. In striking contrast, treatment of each metallocene with MAO gave two reactions very different from $MeAlCl_2$, namely a steady evolution of methane gas upon mixing and a finding upon hydrolytic workup that the diphenylacetylene present had undergone *no insertion* into the M_t-CH_3 bond but instead had been reductively dimerized completely to (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene. To account for this astonishing difference in chemical behavior between MAO and $MeAlCl_2$ in their cocatalytic activation of Group 4 metallocenes to olefin polymerization, it is

necessary to postulate a novel, unique sequence of reaction steps occurring between MAO and the metallocene. If one starts with the metallocene dichloride, then the free TMA present in the MAO would generate the $Cp_2M_t(CH_3)_2$. This metallocene dimethyl derivative, complexed with an oligomeric MAO unit, would undergo a transfer-epimetallation with added olefin or acetylene to form a metallacyclop propane or metallacyclop propene, respectively. With added diphenylacetylene the resulting 2,3-diphenylmetallacyclop propene would be expected rapidly to insert a second alkyne to form the 2,3,4,5-tetraphenyl-1-metallacyclop pentadiene. Simple hydrolysis of the latter intermediate would generate (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene while alternative workup with D_2O would give the 1,4-dideuterio derivative of this butadiene. Both such expectations were confirmed by experiment. In the case of added olefin, similar metallacyclop propane and metallacyclop pentane intermediates should be produced until ring opening of the latter five-membered ring leads to an open-chain zwitterion, a process having ample precedent in the research of Gerhard Erker. The solution to the MAO conundrum then, namely the extraordinary cocatalytic activity of MAO in olefin polymerization by metallocenes, lies in the unique catalytic activation of the Group 4 metallocene dimethyl derivative, which occurs by transfer-epimetallation of the olefin monomer by the $Cp_2M_t(CH_3)_2$ –MAO complex. The most advantageous Lewis acidic sites in the MAO–oligomeric mixture for such metallocene–MAO complexation are suggested to be terminal $Me_2Al-O-AlMe$ segments of an open-chain oligomer.

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Introduction

The unexpected efficacy of polymethylaluminoxane (MAO) as a cocatalyst in the polymerization of olefins by Group 4 metallocene procatalysts has been widely recog-

nized since the 1970s. Initially the clue to such cocatalysis was the puzzling observation that small amounts of water markedly increase the polymerization activity of titanocene dichloride/alkylaluminum chloride systems.^[2,3] Subsequent research by Sinn and Kaminsky with halogen-free catalysts typified by zirconocene dimethyl^[4a] combined with trimethylaluminum (TMA) also identified water as a powerful polymerization accelerant.^[4b] As an explanation, Sinn and Kaminsky then proposed that partial hydrolysis of TMA causes the in situ formation of MAO, which consists of a mixture of linear and cyclic oligomers of $[-AlMe-O-]$ units

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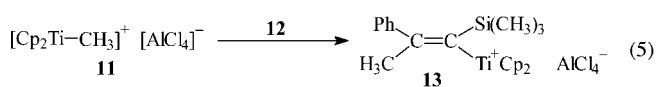
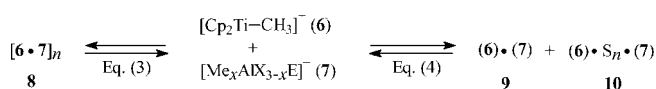
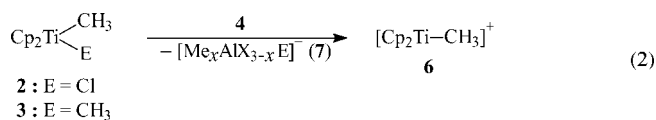
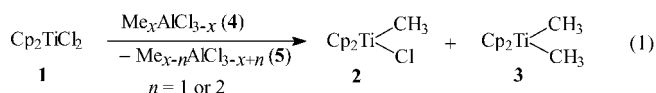
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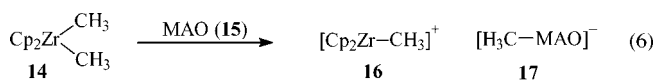
and functions as the superior cocatalyst because of the heightened Lewis acidity of an Al center with two O ligands.^[5] Thereupon, they found that MAO preformed from the partial hydrolysis of TMA does in fact exhibit unusually high polymerization activity when added to a Group 4 metallocene procatalyst. Such catalyst systems were extraordinarily effective both in the polymerization of ethylene into high-density polyethylene and of propylene into atactic polypropylene.^[6,7] Striking in this cocatalysis, however, is the necessity of employing an extreme excess of MAO (10^2 – 10^3 times the metallocene equivalent) to attain such enhanced activity. It is this aspect of its cocatalytic activity that may be termed the MAO conundrum.^[8]

Initial attempts to solve the MAO conundrum have run parallel to studies directed to studying the roles of the alkyl-aluminum halide cocatalyst in the activation of titanocene dichloride (**1**), the titanocene methyl(chloro) derivative (**2**) or titanocene dimethyl (**3**) for polymerization.^[9–16] Starting with titanocene dichloride (**1**) the first role of cocatalyst $\text{Me}_x\text{AlCl}_{3-x}$ (**4**, $x = 1, 2$ or 3) is proposed to be the methylation of **1** with the formation of **2** and/or **3** [Equation (1)]. The second proposed role exerted by the by-product Lewis acid **5**, either with **2** or **3**, is the generation of titanocenium cation **6** as the active site for polymerization initiation [Equation (2)] by the Lewis-acidic extraction of anionic E by **5**.^[10–12] Finally, in the third reaction, which is dependent upon solvent polarity and concentration, the resulting ion pair, **6** and **7**, can be involved in equilibria leading to clustering (**8**) [Equation (3)] or providing tight (**9**) and solvent-separated (**S**, **10**) ion pairs [Equation (4)]. Multinuclear NMR and solvent-polarity evidence support the conclusion that solvent-separated ion pairs (**10**) are the most active initiator of polymerization in the $\text{Cp}_2\text{TiCl}_2/\text{MeAlCl}_2$ catalyst system.^[13,14] The generation of the ion pair, $[\text{Cp}_2\text{Ti}-\text{CH}_3]^+ [\text{AlCl}_4]^-$ (**11**), in this system has been corroborated by its chemical capture with trimethyl(phenylethynyl)silane (**12**) as adduct **13**, whose 3-D structure has been verified by single-crystal X-ray determination [Equation (5)].^[9]



Related studies concerned with generating the zirconocenium cation, $[\text{Cp}_2\text{Zr}-\text{CH}_3]^+$, from $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ or $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ by abstraction of anionic Cl or CH₃ by silver ion have likewise viewed such zirconium cations as active sites for olefin polymerization.^[17,18] In such experiments, however, the $[\text{Cp}_2\text{Zr}-\text{CH}_3]^+$ generated was solvated by acetonitrile and was thus incapable of initiating olefin polymerization.

Accordingly, most explanations for the activation of Group 4 metallocene dialkyl derivatives, such as $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ (**14**), by MAO (**15**), have begun by proposing the generation of the zirconocenium cation **16** at an Al center in **15** having an enhanced Lewis acidity, such as the $[-\text{O}-\text{AlMe}-\text{O}-]$ unit mentioned above [Equation (6)].^[8] Thereupon, complex ion-pairing equilibria would be created because of the diverse linear and cyclic oligomers present in MAO and would give rise to a wide variety of anions **17** of different molecular mass and structure. Copious and careful studies of the global structures present in MAO samples, as well as partial structures found in subunits,^[19] have furnished much useful detail but no overall structural elucidation useful in understanding MAO catalysis.^[8] But particularly pertinent to the action of MAO on Group 4 metallocenes have been two meticulous NMR studies of catalyst systems, the first involving $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ (**14**) with MAO (**15**)^[20] and the second with the procatalysts, Cp_2TiCl_2 (**1**) and the constrained-geometry system, $(\text{Me}_4\text{C}_5)\text{SiMe}_2\text{NBuTiCl}_2$, in their individual reactions with MAO (**15**).^[21] In the first study the types and sizes of the ion pairs formed at various Zr/MAO ratios were examined and the sizes of the MAO counteranions **17** were estimated by pulsed field-gradient NMR spectroscopy. In the second investigation focus was on identifying the most abundant titanium cation present at different Ti/MAO ratios. Such studies have indeed identified several cationic intermediates present, as well as having estimated the size of MAO anion **17** in the zirconocene system. But the pertinence of such information to MAO catalysis remains unclear. Both studies make the unproven assumptions that: 1) The prevalent ion pairs abundant at $M_t/\text{MAO} = 1:100\text{--}300$ are the most active polymerization sites; and 2) the active site generated in MAO cocatalysis of metallocenes exactly parallels the active site generated in $\text{Me}_x\text{AlCl}_{3-x}$ cocatalysis, namely a cation like **6**. Thus, the explanation of MAO cocatalysis arising from the foregoing NMR studies must be viewed as plausible and consistent rather than convincing and decisive.

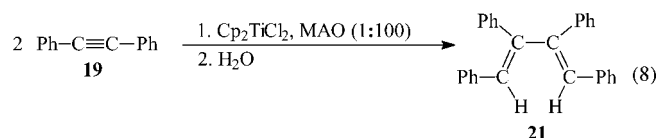
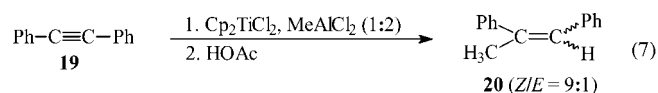


In furthering our ongoing studies of Group 13 organometallic Lewis acids,^[15,22,23] we have undertaken a comparative study of the activation of the Group 4 metallocene derivatives, $\text{Cp}_2\text{M}_t\text{E}_2$, where $M_t = \text{Ti}$ or Zr and $E = \text{Cl}$ or

Me, by the individual reactions with MAO (**15**) and with MeAlCl_2 (**18**), respectively. A comparison of the alkylating and Lewis-acidic reactions of **15** and of **18** on the metallocenes, $\text{Cp}_2\text{M}_t\text{E}_2$, seemed to be reasonable [cf. Equations (1) and (2)], since both have as their principal structural subunit an Al center bonded in turn to a methyl group and to two identical electronegative atoms, **15a** and **18**.



But reaction mixtures of any one of the four $\text{Cp}_2\text{M}_t\text{E}_2$ derivatives with 100 equiv. of MAO in toluene gave a clear sign of an unexpected reaction, not immediately observable with solutions of the $\text{Cp}_2\text{M}_t\text{E}_2$ derivatives with an excess of MeAlCl_2 in CH_2Cl_2 or in toluene: *A steady to vigorous evolution of methane gas*. Furthermore, when the resulting solutions were then treated individually with diphenylacetylene (**19**), in order to capture the methylmetallocenium ion [cf. Equation (5)], a second arresting difference in chemical behavior between **15** and **18** became apparent. When a 1:2 mixture of Cp_2TiCl_2 and MeAlCl_2 was allowed to react with **19** at 25 °C (in toluene or CH_2Cl_2), hydrolytic workup led to almost a quantitative yield of 1,2-diphenyl-1-propene (**20**) as a 9:1 mixture of *Z/E* isomers [Equation (7)].^[24] This product is the hydrocarbon expected to result from the insertion of **19** into the $\text{CH}_3\text{-Ti}$ bond of **6** and subsequent hydrolysis. By sharp contrast in the present study, however, we have now found that when a 1:1 mixture of diphenylacetylene and Cp_2TiCl_2 were allowed to react with 10–100 equiv. of MAO in toluene at 25 °C, hydrolytic workup showed that the diphenylacetylene had been completely consumed *but no 1,2-diphenyl-1-propene (20) whatsoever had been formed*. Instead, the diphenylacetylene had been completely converted into (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**21**) [Equation (8)]!

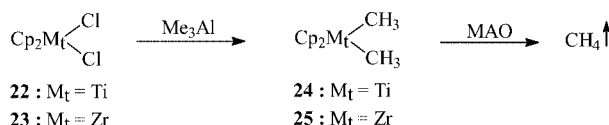


These two surprising differences in chemical behavior between mixtures of Cp_2TiCl_2 and MAO and mixtures of Cp_2TiCl_2 and MeAlCl_2 clearly shows that different chemical reactions may be involved in their individual cocatalytic action in olefin polymerization. The present study has sought to elucidate these reaction differences between MAO and MeAlCl_2 as cocatalysts.

Results and Discussion

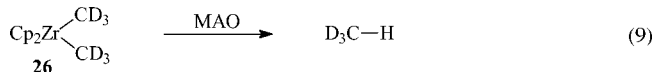
Methane Gas Evolution from Solutions of $\text{Cp}_2\text{M}_t\text{E}_2$ Derivatives **22–25** and MAO (**15**) in Toluene or Dichloromethane

Individual solutions of metallocene derivatives **22–25** reacted promptly with methane evolution, as determined by mass spectrometry, when treated at 25 °C with 100 equiv. of MAO (**15**) in toluene. It is noteworthy that the dichlorides **22** and **23** gave a moderate but steady methane evolution while the dimethyl compounds **24** and **25** exhibited an initially more vigorous and gradually subsiding gas evolution. A likely explanation is that **22** and **23** are converted into **24** and **25**, respectively, by the free Me_3Al present in the MAO and reaction of **24** and **25** with the MAO is the actual source of the methane (Scheme 1).



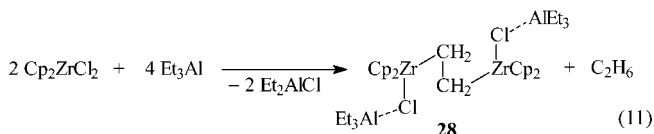
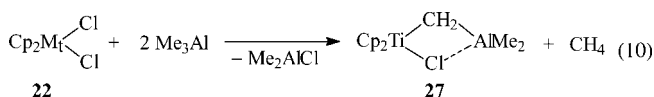
Scheme 1.

A search of the literature then uncovered a pertinent prior study by Kaminsky and Steiger in which zirconocene derivatives **23** and **25** were found consistently to give methane gas evolution when combined with MAO in toluene.^[25] Indeed, in a comprehensive doctoral investigation Steiger has investigated the activation of **23** or **25** by MAO as an olefin polymerization catalyst system and has correlated that polymerization activity with methane evolution. Methane evolution was observed to progress with the ageing or loss of catalyst activity.^[26] The source of the methyl group in such methane evolution has been shown to be zirconocene dimethyl (**25**), by means of a study of the reaction of **26** with MAO (**15**), which latter reagent had been produced from Me_3Al and H_2O [Equation (9)].^[27]



The methane evolved proved to be >99% CD_3H . In the case of individual mixtures of Cp_2TiCl_2 (**22**) or Cp_2ZrCl_2 (**23**) with MeAlCl_2 in CH_2Cl_2 or toluene, on the other hand, no significant gas evolution could be detected at 25 °C over a period of 24 h. In fact, 1 equiv. of an alkyne, such as **12** or **19**, could be carbaluminated in over 90% yield (**13** and **20**) by 1 equiv. of CpTiCl_2 with 2 equiv. of MeAlCl_2 . This finding shows that the Me group of MeAlCl_2 is not significantly diminished through loss of methane. Many similar alkylations of alkynylsilanes by combinations of CpTiCl_2 with Me_2AlCl , EtAlCl_2 or Et_2AlCl likewise show no noticeable loss of alkane.^[28] As discussed in the next section, however, the reaction of alkynes with $[\text{Cp}_2\text{ZrCl}_2]/\text{CH}_3\text{AlCl}_2$ mixtures was surprisingly slow.

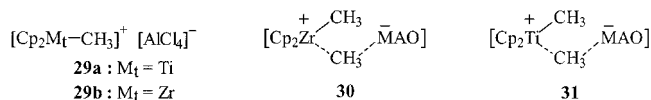
With Me_3Al or Et_3Al itself, however, the loss of alkane can be significant over time. The well-known Tebbe reagent (**27**) results from the reaction of Cp_2TiCl_2 (**22**) with an excess of Me_3Al in toluene at room temperature over 60 h [Equation (10)].^[29] Similarly, the reaction of Cp_2ZrCl_2 (**23**) with Et_3Al can lead to the 1,2-dizirconio compound **28** with ethane evolution [Equation (11)].^[30]



In light of the foregoing observations made both in our group and in that of Kaminsky, it is uncomprehensible that no mention is made of methane gas evolution or NMR spectral instability in either of the foregoing NMR spectroscopic studies of the catalyst systems, $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ with MAO^[20] or Cp_2TiCl_2 with MAO.^[21] For methane gas evolution not to have been a significant factor in altering such systems, NMR sample preparation and spectral measurements would had to have been carried out quickly and at lower temperatures. But the limited experimental descriptions provided^[20,21] make further speculation on this point futile.

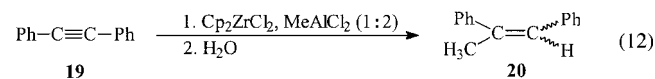
Attempted Capture of Postulated Methylmetallocenium Cations in the $\text{MeAlCl}_2/\text{Cp}_2\text{M}_t\text{E}_2$ and the MAO/ $\text{Cp}_2\text{M}_t\text{E}_2$ Catalyst Systems

From the interaction of a 1:2 mixture of Cp_2TiCl_2 (**22**) or Cp_2ZrCl_2 (**23**) with MeAlCl_2 (**18**), the polymerization-initiating ion pair **29** has been postulated to be generated. Likewise, from the two foregoing cited NMR studies of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ or Cp_2TiCl_2 , each with 200 equiv. of MAO, the principal ion pairs concluded to be present are **30** and **31**.



In order to capture such ions, an alkyne such as alkynylsilane **12** or diphenylacetylene (**19**) has been introduced into each of the four individual catalyst systems. The success of both alkyne insertions with 1:2 mixtures of Cp_2TiCl_2 and CH_3AlCl_2 , as depicted in Equations (5) and (7), therefore represents strong corroboration for the presence (or availability) of ion pair **29a**. Contrary to expectations, however, the reaction of 1:2 mixtures of Cp_2ZrCl_2 and CH_3AlCl_2 was

attempted under similar conditions (18 h, 25 °C, CH_2Cl_2) but no addition whatsoever was observed. Only with protracted reaction times or with use of $(\text{CH}_3)_2\text{AlCl}$ as cocatalyst could low yields of **20** (<10%) be attained [Equation (12)].

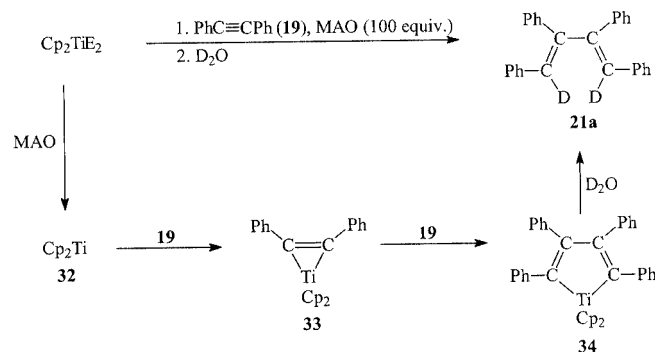


From these observations one can conclude that ion pair **29b** is not as readily generated from **23** by CH_3AlCl_2 (**18**) as is ion pair **29a** from **22** and CH_3AlCl_2 (**18**). This observation may explain why **18** and other alkylaluminum chlorides are relatively poor cocatalysts in olefin polymerizations with zirconocene precatalysts.^[8]

But what has been most disconcerting is the failure of diphenylacetylene (**19**) to undergo any such alkyne insertion whatsoever when **19** is added individually to systems supposedly containing **30** or **31**, respectively. Such an observation could indicate either that such ion pairs are not present or that they react in an entirely different manner in the presence of an extreme excess of MAO.

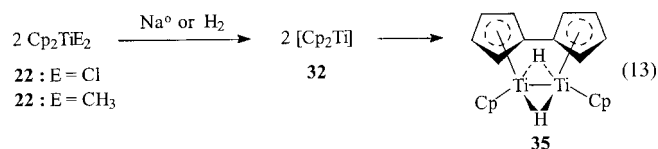
Synergetic Interaction of Group 4 Metallocene Dialkyl Derivatives and MAO with Alkynes: Catalyzed Transfer-Epimetalation

That the latter possibility obtains is clear from Equation (8), which shows that diphenylacetylene undergoes exclusively reductive dimerization, rather than insertion into an $\text{M}_t\text{-CH}_3$ bond. Further insight has come from the four individual reactions of Cp_2TiCl_2 , Cp_2ZrCl_2 , $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ or $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ with one equiv. of **19** and 100 equiv. of MAO, followed by workup with D_2O . The organic product was in each case exclusively (*E,E*)-1,4-dideuterio-1,2,3,4-tetraphenyl-1,3-butadiene (**21a**). The latter dideuteriated derivative presupposes the presence of the titanocycle **34**, in the case of Cp_2TiE_2 , which could have arisen from the generation of titanocene (**32**), the rapid addition of **32** to alkyne **19** to yield **33** and the further insertion of **19** into **33** (Scheme 2).^[31] However, from what else is known about the stability of titanocene (**32**), such a divalent carbene-like in-



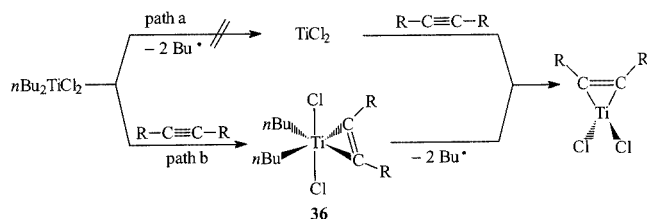
Scheme 2.

intermediate would not be expected to persist at room temperature. For example, the reduction of Cp_2TiCl_2 by sodium^[32] or by sodium naphthalenide^[33] or the reduction of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ by dihydrogen^[34] at 20 °C, each of which reactions was intended to generate **32**, led instead to the isomeric titanocene(III) hydride dimer **35** [Equation (13)].^[35]



As corroborating experiments for the model reaction pathway proposed in Scheme 2 for titanocene dimethyl (**24**), the following reactions were carried out: 1) The reaction between **24** and 1 equiv. of **19** was attempted in refluxing toluene but neither **21** nor any other product was detected; 2) stirring a toluene solution of 1 equiv. of **19** with 100 equiv. of MAO at 25 °C led to the complete recovery of **19**; and 3) as expected by the model, reaction of **24** with **19** in a 1:2 molar ratio, in the presence of 100 equiv. of MAO, led to the complete consumption of **19** and the quantitative formation of diene **21**.

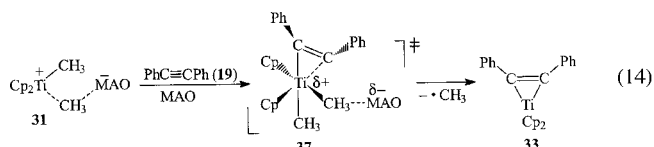
By reason of the instability of Cp_2Ti at 25 °C, therefore, we conclude that the formation of the titanacyclopropene **33** is highly unlikely to arise by the direct epititanation of diphenylacetylene (**19**) by **32**,^[36] as shown in Scheme 2. The instability of **32** can be circumvented, however, if the recently observed process of transfer-epititanation is instead involved, as exemplified in Scheme 3.^[37] In this process TiCl_2 is not liberated from $n\text{Bu}_2\text{TiCl}_2$ by prior elimination of the two butyl radicals (path a) but rather the loss of butyl groups occurs by way of the octahedral complex **36**, in which the TiCl_2 group is simultaneously transferred to the alkyne. In the latter process of transfer-epititanation, no free TiCl_2 need ever be formed.



Scheme 3.

Our first attempt to test for the occurrence of such transfer-epimetallation was disappointing: Neither $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ nor $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ reacted with diphenylacetylene even in refluxing toluene. But these attempted transfer-epimetallation reactions omit the obvious catalytic role of MAO in the reactions of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ (**24**) or of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ (**25**), as well as the demonstrated fact that **24** and **25** exist principally as zwitterion-like intermediates, **30** and **31**, respectively, in the presence of more than 100-fold excess of MAO.^[20,21] We therefore propose that the source of titanacyclopropene **33** is the transfer-epititanation reaction of di-

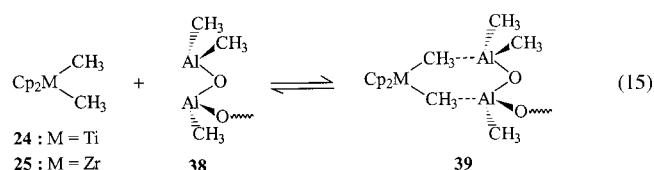
phenylacetylene (**19**) with complexed ion pair **31** via transition state **37** [Equation (14)].



The methyl radicals thereby liberated would attack MAO or the toluene solvent and thus lead to the evolution of methane. A similar transfer-epizirconation involving **30** and **19** would lead to the zirconacyclopropene analogue of **33** and, similar to the sequence, **33** → **34** → **21** in Scheme 2, would explain the isolation of **21** from the reaction of **25** and **19**.

Nature of the Interaction of Group 4 Metallocene Dimethyl Derivatives with MAO

Introduction of diphenylacetylene (**19**) into a mixture of $\text{Cp}_2\text{M}(\text{CH}_3)_2$ (M = Ti, **24**; M = Zr, **25**) and MAO (**15**) in a 1:100 equiv. ratio gives no detectable evidence for the generation of **30** or **31** nor of their capture by **19** to give the hydrocarbon **20** on hydrolysis. Accordingly, some chemical reaction between $\text{Cp}_2\text{M}(\text{CH}_3)_2$ and MAO must be sought other than a simple M–CH₃ heterolysis. If this interaction of MAO would also depend on the Lewis acidity of specific MAO subunits, we would propose as the specifically strong Lewis-acidic site, the bidentate grouping at the ends of open-chain aluminoxane subunits, namely $(\text{CH}_3)_2\text{Al}-\text{O}-\text{Al}(\text{CH}_3)_2$ (**38**). Both on steric and electronic grounds, **38** should best be able to form a Lewis complex (**39**) with both CH₃ groups of **24** and **25** simultaneously. By drawing electron density from the transition metal toward the methyl groups, compound **38** should lower the bond-homolysis energy required to attain transition state **37** and its zirconium analogue [Equation (15)].

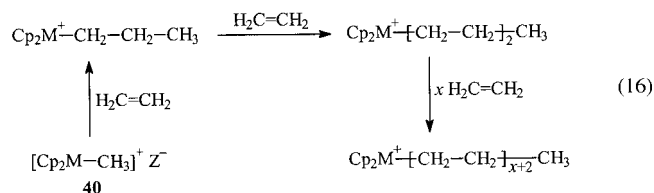


In his kinetic analysis of propene polymerization with the $\text{Cp}_2\text{ZrE}_2/\text{MAO}$ system (E = Cl, CH₃) it is interesting to note that Steiger also assigns a special importance to the proportion of end units like **38** in MAO. Their importance in his view is their superior methylating action on Cp_2ZrCl_2 and $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ precursors. However, both Steiger and our group assign the same reason for the necessity of employing extreme excesses of MAO for the extraordinary catalytic action: Only such an excess will furnish a sufficient proportion of the truly catalytically active end groups **38**.

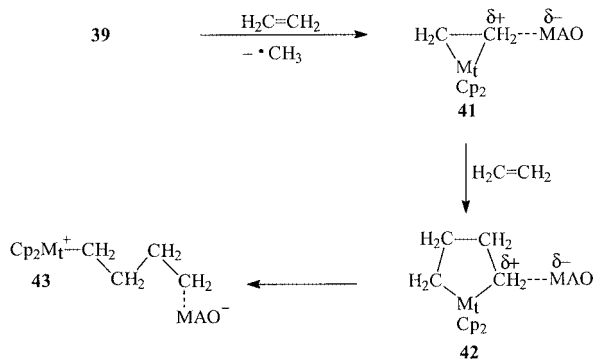
Relevance of Transfer–Epimetallation to the Cocatalytic Action of MAO in Olefin Polymerization by Titanocene and Zirconocene Derivatives

The present study has demonstrated that distinctly different, irreversible reactions take place between titanocene or zirconocene precatalysts **22–25** and the respective cocatalysts, MeAlCl₂ (**18**) or MAO (**15**). While MeAlCl₂ activates these metallocenes (at least Cp₂TiCl₂) by the straightforward reactions of alkyl transfer from Al to M₁, followed by catalyst ion-pair formation [cf. Equations (2)–(5)], activation of these same metallocenes by MAO is accompanied by considerable evolution of methane and the formation of ion pairs **30** and **31** that do *not* insert alkynes in the expected polar manner shown in Equations (3) and (7). Instead, these intermediates apparently undergo transfer-epimetallation with alkyne **19**, for only via this route can the isolation of the reductive dimer of **19**, namely **21**, be explained.

Because of differences shown in the activation of metallocenes for polymerization by MeAlCl₂ or by MAO, we now suggest that the two cocatalysts follow different initiating steps. With MeAlCl₂ the initiation would involve the well-established electrophilic attack of the methylmetallocenium cation of ion pair **40** on ethylene followed by many repetitive insertions [Equation (16)].



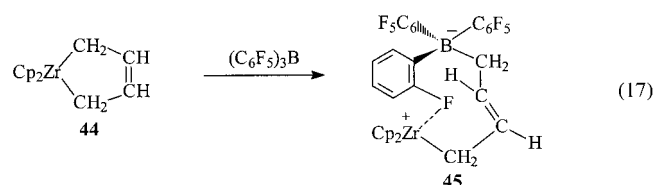
With MAO, on the other hand, zwitterionic-like complex **39** would undergo a transfer-epimetallation with ethylene (accompanied by methane evolution) to form zwitterionic metallacyclopropane **41**. Ring strain should favor rapid insertion of a second ethylene monomer to form zwitterionic metallacyclopentane **42** (Scheme 4).



Scheme 4.

At the point the active site for further polymer growth will likely arise from the ring-opening isomerization of **42**, into open-chain zwitterion **43**. For the feasibility of the step

from **42** to **43** there is excellent precedent in the work of Erker's research group. For example, a mixture of (*s-cis*-η⁴-butadiene)zirconocene (shown as **44**) and (*s-trans*-η⁴-butadiene)zirconocene (not shown) react with the Lewis acid, (C₆F₅)₃B, to form zwitterionic **45** [Equation (17)], whose structure has been established by X-ray crystal structure analysis.^[38] In keeping with our suggestion above for **43**, compound **45** immediately initiates polymerization when exposed to ethylene or propylene gas.



In summary, the explanation for the extraordinary cocatalytic activity of MAO in olefin polymerization with metallocenes, known as the MAO conundrum, lies in realizing that MAO activates metallocenes not for the usual insertions of olefins into polar transition metal–carbon bonds [such as that in Equations (5) and (7)] but rather for homopolar transfer-epimetallations of olefins, starting from **30** or **31** and leading successively to the metallacyclopropanes **41**, the metallacyclopentanes **42** and ultimately to the open-chain zwitterionic initiator **43** (Scheme 4).

Experimental Section

Instrumentation, Analysis and Starting Reagents: All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal/benzophenone ketyl mixture prior to use.^[39] The IR spectra were recorded with a Perkin–Elmer instrument (model 457) and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (¹H and ¹³C) were recorded with a Bruker spectrometer (model EM-360) and tetramethylsilane (Me₄Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in ppm from the Me₄Si reference signal. The GC/MS measurements and analyses were performed with a Hewlett–Packard GC 5890/Hewlett–Packard 5970 mass-selective-detector instrument. The gas chromatographic analyses were carried out with a Hewlett–Packard instrument (model 5880) provided with a 2-m OV-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30-m SE-30 capillary column. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. In all of the foregoing spectral or physical measurements any air- or moisture-sensitive samples were handled in glass tubes filled and sealed under dry argon.

Reactions of Group 4 Metallocene Dichlorides/Methylaluminum Dichloride Mixtures with Diphenylacetylene (19). (a) **Titanocene Dichloride (1):** According to a previously published general procedure,^[24] which is here modified and specified, a solution of 996 mg (4.0 mmol) of titanocene dichloride (**1**) and 712 mg (4.0 mmol) of diphenylacetylene in 100 mL of anhydrous dichloromethane was cooled in an ice bath and then treated with 8 mmol of methylaluminum dichloride (**18**) in hexane. After 18 h of stirring

at room temp., the reaction mixture was quenched with 1.0 mL of water. Basic alumina was added to the CH_2Cl_2 solution, volatiles were removed under vacuum and the solid residue packed on top of an alumina column prepared with hexane. Elution with hexane gave 500 mg of a mixture of 81% of (*Z*)-1,2-diphenyl-1-propene (**20a**) and 19% of (*E*)-1,2-diphenyl-1-propene (**20b**) with no recovered **19**. When the foregoing procedure was repeated and worked up with D_2O , **20a** and **20b** were largely (>90%) deuteriated at their respective vinylic positions. It should be noted that the precise conditions of hydrolysis or deuterolysis can influence both the ratio of **20a/20b** and the extent of vinylic deuteriation. Addition of a mixture of D_2O and triethylamine for such a hydrolytic workup gives a 42:58 mixture of **20a/20b** with only a modest incorporation of deuterium (**20a**: 28%). These results indicate that hydrolysis of the C–Ti bond involves a competition between heterolytic and homolytic cleavages. This important finding will be addressed in a subsequent publication. When the foregoing procedure was carried out as described, but using only 4.0 mmol of MeAlCl_2 (**18**), then 50% of **19** remained and 50% of a 24:1 mixture of **20a/20b** was formed. **(b) Zirconocene Dichloride (23):** In an experiment identical with the titanocene dichloride procedure, 4.0 mmol each of **23** and **19** were allowed to react with 8 mmol of **18** in CH_2Cl_2 solution at room temp. for 18 h. Usual workup revealed that no 1,2-diphenyl-1-propenes (**20a** and **20b**) whatsoever were formed and **19** was recovered unchanged. Repetition of the reaction attempt with $(\text{CH}_3)_2\text{AlCl}$ and prolongation of the reaction time (>24 h) did eventually lead to small amounts of **20a** (ca. 10%).

Attempted Thermal Reactions of Group 4 Metallocene Dimethyl Derivatives with Diphenylacetylene (19): Published procedures were applied for the preparation of titanocene dimethyl (**24**)^[34] and zirconocene dimethyl (**25**)^[40,41] respectively. Then, under argon 840 mg of **24** or 1.00 g of **25** (4.0 mmol) in 40 mL of toluene was added to a solution of 1.43 g (8.0 mmol) of **19** in 20 mL of toluene at 25 °C. The resulting solution was heated at reflux for 8 h and then hydrolyzed with 6 N aqueous HCl. Usual ether extraction and workup led to the quantitative recovery of **19** and no sign of **20a**. Even when the reaction vessel was covered with Al foil to exclude light, there was no sign of reaction.

Reactions of Group 4 Metallocene Derivatives/MAO Mixtures with Diphenylacetylene (19). **(a) General Procedure:** A solution of titanocene dichloride (**22**), titanocene dimethyl (**24**), zirconocene dichloride (**23**) or zirconocene dimethyl (**25**) (0.57 mmol) in 40 mL of toluene was treated under argon at $25 \pm 5^\circ\text{C}$ with 57 mmol of MAO (**15**) in 12.2 mL of toluene (source of MAO: Sigma–Aldrich, used as freshly purchased and containing $5 \pm 1\%$ of free Me_3Al as determined by ^1H NMR spectroscopy). The vigor and extent of gas evolution (CH_4 in each case) was noted. After 5 min, a solution of **19** (100 mg, 0.57 mmol) in 20 mL of toluene was added to the reaction mixture. After 24 h of stirring at room temperature, usual hydrolytic workup with 6 N aqueous HCl, the reaction mixtures of **19** individually with **22**, **24**, **23** or **25** led in each case to the quantitative isolation of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**21**) with no trace of **19** or of the (*Z*)- and (*E*)-1,2-diphenyl-1-propenes (**20a**, **20b**). The (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**21**) was further purified by recrystallization from glacial acetic acid to give white crystals, m.p. 183–184 °C. The melting point of a mixture with authentic **21** was undepressed and the NMR spectroscopic data of the sample isolated from each of the four foregoing reactions were identical with those of authentic **21**. ^1H NMR (CDCl_3): δ = 42–7.30 (m, 10 H), 7.03–6.99 (m, 6 H), 6.75–6.72 (m, 4 H), 6.30 (s, 2 H) ppm. ^{13}C NMR (CDCl_3): δ = 145.60, 139.76, 137.25, 131.64, 130.38, 129.47, 128.77, 127.76, 127.31, 126.58 ppm. When the foregoing reaction between **19** and **24** was repeated as described above,

except with 200 mg (1.54 mmol) of **19**, again upon hydrolytic workup only diene **21** was quantitatively formed with <1% of remaining **19**. **(b) Temperature:** When any of the foregoing reactions were conducted at -78°C by mixing and stirring the components in a reaction flask cooled by an acetone/solid CO_2 mixture, in a Dewar bath protolysis at -78°C after 24 h with methanol led to the complete recovery of **19** with no sign of **21**, **20a** or **20b**. **(c) Deuteriation:** When either **22** or **23** was allowed to react with 100 equiv. of MAO in the presence of 1 equiv. of **19** in toluene at $\pm 5^\circ\text{C}$ for 24 h, according to section (a), workup first with *O*-deuterioacetic acid (>99%) and then with ordinary 6 N aqueous HCl, the (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene was completely 1,4-dideuteriated (**21a**), as shown by ^1H and ^2H NMR spectroscopy. **(d) Control Experiment:** In order to substantiate the necessary presence of all three reactants, **22**, **23**, **24** or **25** together with MAO (**15**) and diphenylacetylene (**19**), one further control experiment was carried out. Stirring of a toluene solution of 1 equiv. of **19** with 100 equiv. of MAO (**15**) at room temperature for 24 h led to the complete recovery of unchanged **19**. **(e) Methane Evolution:** With the metallocene dichlorides **22** and **23**, admixture with MAO and alkyne **19** gave an initially slow but steady and prolonged methane evolution. On the other hand, with the metallocene dimethyls **24** and **25**, admixture with MAO and alkyne **19** produced initially a very vigorous gas evolution that gradually became slow over the first hour. The identification of the gas evolved as >99% methane, and not ethane or dihydrogen, was achieved by withdrawing samples of the evolved gas by a gastight syringe through a septum covering one neck of the reaction vessel and by injecting the sample into the aforementioned Hewlett–Packard GC/MS instrument.

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