

ansa-Titanocene Catalysts for α -Olefin Polymerization. Syntheses, Structures, and Reactions with Methylaluminoxane and Boron-Based Activators

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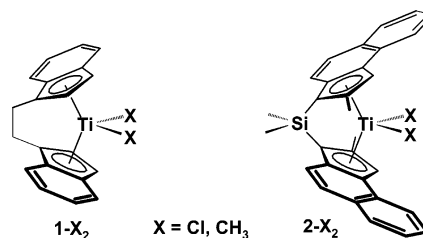
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The racemic isomers of $C_2H_4(1\text{-Ind})_2TiCl_2$ and $Me_2Si(2\text{-Me-Benzind})_2TiMe_2$ were synthesized and structurally characterized. Reactions of these and related *ansa*-titanocene complexes with methylaluminoxane or with the cationizing reagent $[CPh_3]^+[B(C_6F_5)_4]^-/Al_2Me_6$ were monitored by UV/vis, 1H NMR, and EPR methods. Under conditions approaching those typically used in olefin polymerizations, heterobinuclear cations of the type $[DianTi^{IV}(\mu-Me)_2AlMe_2]^+$ (with Dian = bridged ligand dianion) dominate in each of these reaction systems, which catalyze the polymerization of propene at temperatures below ambient. Above 0 °C, these cations are reduced, mainly to neutral heterobinuclear species $DianTi^{III}(\mu-Me)_2AlMe_2$, which appear to be inactive with regard to polymerization catalysis. In the absence of monomer, the main reducing agent appears to be ethyl aluminum admixtures in Al_2Me_6 . Addition of monomer increases the rate of reduction rather drastically, probably via formation of titanium hydrides.

Introduction

A great numbers of *ansa*-metallocene complexes,¹ activated by methylaluminoxane (MAO) or boron-based activators,² have been studied as olefin-polymerization catalysts. Titanocene-based catalyst systems are generally more easily deactivated than their zirconium analogues, especially at higher temperatures. A more facile reduction of their Ti(IV) centers is sometimes invoked in this regard,³ but has apparently not been investigated in any detail so far. The possibility to monitor reactive Ti(IV) intermediates in titanocene/MAO and related reaction systems by 1H NMR methods has recently been demonstrated.⁴ The stability of catalytically relevant intermediates, formed upon activation of *ansa*-titanocene complexes with MAO or boron-based activators, is thus amenable to direct evaluation now.

In this article, we report syntheses and crystal structures for the Ti analogues of two prototypical *ansa*-zirconocene complexes, *rac*- $C_2H_4(1\text{-Ind})_2TiX_2$ (**1**) and *rac*- $Me_2Si(2\text{-Me-Benzind})_2TiX_2$ (**2**), with X = Cl or CH₃, results of UV/vis, 1H NMR, and EPR spectroscopic studies on the formation and decay of reactive species upon reaction of these and related *ansa*-titanocene complexes with MAO and boron-based activators, and preliminary observations on the properties of these catalyst systems with regard to olefin polymerization.



Results and Discussion

1. Complex Syntheses and Structures. Although alternative syntheses of their Zr analogues have been studied in detail,^{5–7} no syntheses have been reported so far for the *rac* isomers of the *ansa*-titanocene complexes **1** and **2**. To prepare the titanocene complex **1-Cl**₂, we had to modify our previously described racemose-

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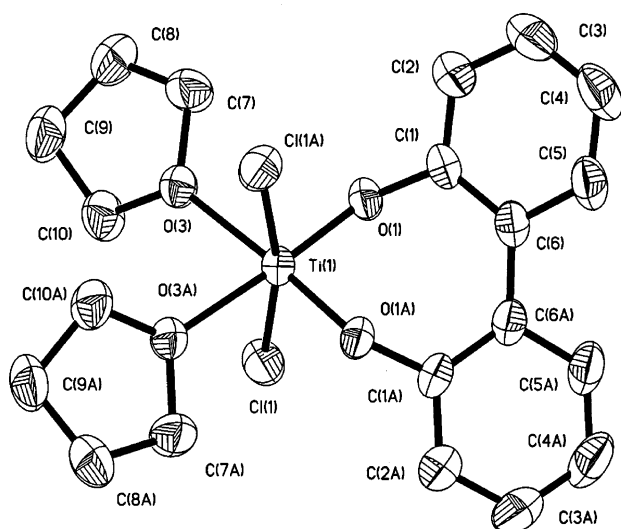
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Table 1. Selected Bond Distances (Å) and Angles (deg) for $\text{TiCl}_2(\text{O}_2\text{biphen}) \cdot 2\text{THF}$, $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(\text{O}_2\text{biphen})$, $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{TiCl}_2$ (1-Cl₂), and $\text{rac-Me}_2\text{Si}(2\text{-Me-Benz}[e]\text{Ind})_2\text{ZrMe}_2$ (2-Me₂)

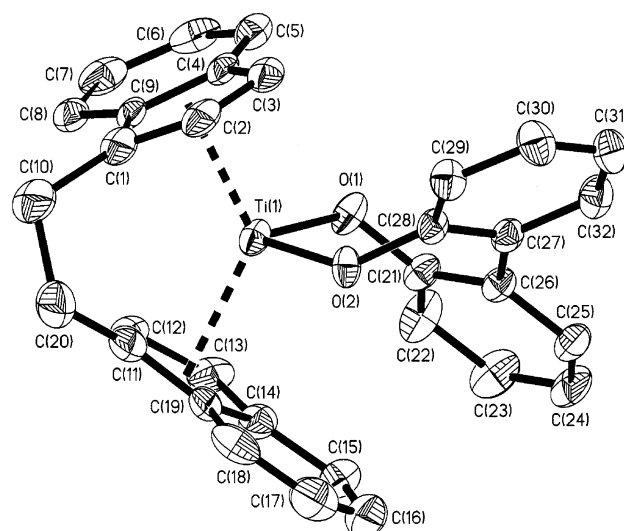
	$\text{TiCl}_2(\text{O}_2\text{biphen}) \cdot 2\text{THF}$	$\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(\text{O}_2\text{biphen})$	$\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{TiCl}_2$ (1-Cl ₂)	$\text{rac-Me}_2\text{Si}(2\text{-Me-Benz}[e]\text{Ind})_2\text{ZrMe}_2$ (2-Me ₂)
Ti–O(1, 2)	1.819(3)	1.902(3), 1.867(3)		
Ti–O(3)	2.163(3)			
Ti–Cl(1)	2.3526(10)		2.3275(8)	
Ti–C(31, 32)				2.136(5), 2.146(5)
Ti–Z(1, 2) ^a		2.117, 2.171	2.127	2.131, 2.138
O(1, 2)–C	1.381(4)	1.359(5), 1.370(5)		
O(1)–Ti–O(1A,2)	92.5(2)	91.28(14)		
Cl(1)–Ti–Cl(1A)	167.76(6)		95.89(4)	
C(31)–Ti–C(32)				90.4(2)
Z(1)–Ti–Z(2) ^a		126.5	129.0	131.7
Ti–O(1, 2)–C	132.7(2)	125.8(3), 129.9(3)		
Ph(1)–Ph(2) ^b	40.0	41.8		

^a Z(1), Z(2): indenyl C₅-ring centroids. ^b Ph(1), Ph(2): mean planes of biphenolate C₆-rings

**Figure 1.** Molecular structure of $\text{TiCl}_2(\text{O}_2\text{biphen}) \cdot 2\text{THF}$ in the crystalline state (thermal ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

lective syntheses of *ansa*-zirconocene complexes.^{7b} For this purpose, the biphenolate precursor $\text{TiCl}_2(\text{O}_2\text{biphen}) \cdot 2\text{THF}$ was prepared in ca. 90% yield by reaction of 1,1'-bi-2-phenol with TiCl_4 in toluene, followed by addition of THF.⁸ Single crystals of $\text{TiCl}_2(\text{O}_2\text{biphen}) \cdot 2\text{THF}$ were obtained by recrystallization from THF/hexane at -80°C . A diffractometric structure determination (Figure 1, Table 1) revealed a monomeric, C_2 -symmetric, distorted octahedral geometry in the crystalline state, with *trans*-positioned Cl ligands, *cis*-positioned THF ligands, and a twisted seven-membered chelate ring.⁹

When $\text{TiCl}_2(\text{O}_2\text{biphen}) \cdot 2\text{THF}$ was reacted with 1 equiv of the ligand salt $\text{C}_2\text{H}_4(1\text{-Ind})_2\text{Li}_2(\text{THF})_2$ in toluene/THF at room temperature, the signals of the reactants

**Figure 2.** Molecular structure of $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(\text{O}_2\text{biphen})$ (thermal ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

were no longer apparent in the ^1H NMR spectrum of the product mixture, while signals assignable to $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(\text{O}_2\text{biphen})$ and further broadened signals appeared in the aromatic region.¹⁰ After workup (see Experimental Section) crude $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(\text{O}_2\text{biphen})$ was isolated in 12% yield as a dark orange powder, which was used to prepare the dichloro complex $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{TiCl}_2$ (1-Cl₂), described below. Analytically and NMR-spectrally pure $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(\text{O}_2\text{biphen})$ was obtained by recrystallization from toluene/pentane. By keeping a toluene solution at 4°C , we obtained crystals suitable for an X-ray diffraction analysis, which revealed a slight deviation from the expected C_2 symmetry, (Figure 2, Table 1) in that the lines from the Ti center to the midpoints of the ethano bridge and the biphenolate fragment are not quite collinear.¹¹ The indenyl rings adopt a forward orientation, as found for other ethylene-bridged metallocenes with bis-indenyl ligands.¹² The *S*-conformer of the twisted biphenolate ligand appears to fit favorably the

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(8) A THF-free, probably polymeric form of $\text{TiCl}_2\text{O}_2\text{biphen}$ and its use for racemoselective preparation of *ansa*-titanocenes has been described: McLaughlin, M. L.; Erickson, M. S.; Fronczek, F. R. *J. Organomet. Chem.* **1991**, *415*, 75.

(9) For a related Zr biphenolate complex, which contains *tert*-butyl groups in 3,3'-positions and methyl groups in 5,5'-positions, a similar crystal structure has been described in ref 7b.

(10) An EPR measurement indicated the presence of some Ti(III) species.

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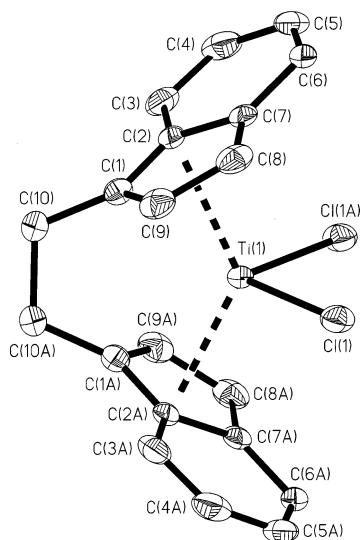


Figure 3. Molecular structure of **1-Cl₂** (thermal ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Different *rac*-C₂H₄(1-Ind)₂MCl₂ Complexes with M = Ti, Zr, and Hf^a

	Ti	Zr ^a	Hf ^b
M–Cl	2.3275	2.3884	2.396
M–Z ^c	2.127	2.219	2.217
Cl–M–Cl	95.89	99.09	96.39
Z–M–Z ^c	129.0	125.3	125.7

^a Ref 12a. ^b Ref 12b. ^c Z: centroids of indenyl C₅-ring.

spatial requirements of the *S,S*-configured bridgehead carbon atoms and the ensuing λ conformation of the Ti–C(1), C(10), C(20), C(11) chelate ring.

Crude *rac*-C₂H₄(1-Ind)₂Ti(O₂biphen) was converted to *rac*-C₂H₄(1-Ind)₂TiCl₂ (**1-Cl₂**) by reaction with MeAlCl₂ in toluene and extraction of the crude reaction product with CH₂Cl₂. As indicated by its ¹H NMR (see Experimental Section), pure **1-Cl₂** was obtained in 42% yield. Recrystallization from toluene afforded red crystals suitable for X-ray analysis.

A structure with crystallographic C₂ symmetry was revealed by X-ray diffraction analysis for complex **1-Cl₂** (Table 1, Figure 3). In the stereoisomer shown in Figure 3, the *ansa*-ligand assumes the λ -1*S*,1'*S* conformation, which was also found for the biphenolate complex *rac*-C₂H₄(1-Ind)₂Ti(O₂biphen) and for the analogous metallocene complexes *rac*-C₂H₄(1-Ind)₂ZrCl₂^{12a} and *rac*-C₂H₄(1-Ind)₂HfCl₂.^{12b} All of these complexes have in common a forward orientation of their indenyl rings. Due to the trend of metal radii, complex **1-Cl₂** has the shortest M–Cl and M–centroid bonds in this series; the Z–Ti–Z angle is the largest and, hence, the Cl–Ti–Cl angle the smallest among these group 4 metallocenes (Table 2).

From the dichloride **1-Cl₂**, the dimethyl derivative **1-Me₂** is obtained, in near-quantitative yield, by reaction with 2 equiv of methyl lithium in diethyl ether solution. The ¹H NMR spectrum of complex **1-Me₂** (see Experi-

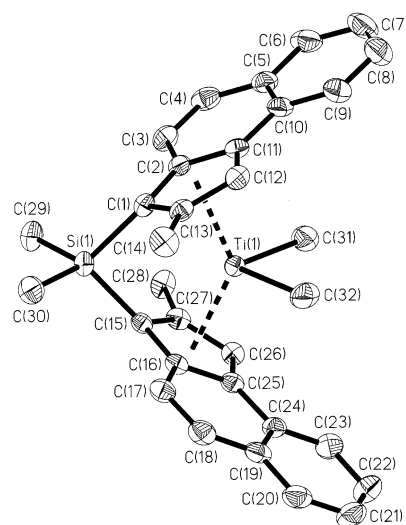


Figure 4. Molecular structure of complex **2-Me₂** (thermal ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

mental Section) is in accord with the expected C₂ symmetry

For complex **2**, we have chosen a preparation that yields, instead of the exceedingly insoluble dichloride complex **2-Cl₂**, directly the more soluble dimethyl derivative **2-Me₂** in a one-pot reaction.¹³ As a convenient synthon, we have used a methylmagnesium salt of the dimethylsilyl-bridged 2-methylbenzindenyl ligand, Me₂-Si(2-Me-benz[e]indMgMe)₂, which was prepared in situ by transmetalating the ligand dilithium salt⁶ with 2 equiv of MeMgBr. Reaction of a suspension of the methylmagnesium ligand salt with TiCl₄(Et₂O)_n in diethyl ether, first at –78 °C, then at ambient temperature, gave, after appropriate workup (see Experimental Section), complex **2-Me₂** in 28% yield. Crystals suitable for X-ray analysis were obtained by slow evaporation from a concentrated diethyl ether solution at room temperature.

A diffractometric structure determination of complex **2-Me₂** revealed an almost perfect C₂ symmetry (Figure 4, Table 1), with the TiMe₂ and Me₂Si fragments aligned in the molecular mid-plane. As with other Me₂Si-bridged bis-indenyl complexes, both 2-Me-benz[e]indenyl ligands are coordinated via their C₅-rings in an η^5 fashion. Some strain is apparent by a deviation of the Si–C(ring) bonds from the C₅-ring planes by 20° and by a rather small (ring)C–Si–C(ring) angle of ca. 94°. The Ti–Cp centroid distances of 2.131 and 2.138 Å as well as the Ti–methyl distances of 2.136 and 2.146 Å are similar to those reported for comparable *ansa*-titanocene structures.¹⁴

The dichloride *rac*-Me₂Si(2-Me-benz[e]ind)₂TiCl₂ (**2-Cl₂**) was obtained in 58% yield by reaction of **2-Me₂** with AlCl₃·THF and appropriate workup (see Experimental Section).

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2. Reactions of Complexes 1 and 2 with MAO and with $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. As was shown for their zirconium analogues,^{15–17} activation reactions of these complexes are conveniently studied by UV/vis and by ^1H NMR spectroscopy.⁴ When a toluene solution of MAO is added to a ca. 1 mM solution of complex **1-Cl₂** in toluene at a ratio of $[\text{Al}]/[\text{Ti}] = 3$ at room temperature, the absorption band of **1-Cl₂** at 652 nm is rapidly diminished in size concomitantly with the appearance of a new band at 533 nm, which is complete within 3–4 min. By its ^1H NMR spectrum the new species is identified as the methyl chloride complex *rac*-C₂H₄(1-Ind)₂Ti(Cl)Me.¹⁸ Upon further addition of MAO to $[\text{Al}]/[\text{Ti}] = 6$, ^1H NMR spectra indicate the presence of *rac*-C₂H₄(1-Ind)₂Ti(Cl)Me, *rac*-C₂H₄(1-Ind)₂TiMe₂ (**1-Me₂**),¹⁸ and another, presumably cationic species, which becomes dominant at $[\text{Al}]/[\text{Ti}] = 9$, where the signals of the two neutral complexes have completely disappeared.¹⁹

Further increase of the $[\text{Al}]/[\text{Ti}]$ ratios causes a bathochromic shift of the lowest-energy band to $\lambda_{\text{max}} \approx 620$ nm. While an isosbestic point at $\lambda = 586$ nm would indicate a single reaction at room temperature; its lack at -20 °C points to the occurrence of a reaction intermediate. When **1-Cl₂** is reacted with MAO at -50 °C, a first bathochromic shift to $\lambda_{\text{max}} = 606$ nm, which requires ca. 2 h for completion, is observed at a ratio of $[\text{Al}]/[\text{Ti}] \approx 16$ –30. A second bathochromic shift to $\lambda_{\text{max}} = 643$ nm occurs upon further addition of MAO to a ratio of $[\text{Al}]/[\text{Ti}] = 100$. An isosbestic point at $\lambda = 631$ nm indicates a clean conversion to the new complex species.

^1H NMR signals of the reaction system *rac*-C₂H₄(1-Ind)₂TiCl₂/MAO, recorded at a ratio of $[\text{Al}]/[\text{Ti}] = 200$ in *d*₈-toluene at 20 °C, indicate the presence of the heterobinuclear ion pair [*rac*-C₂H₄(1-Ind)₂Ti(μ -Me)₂AlMe₂]⁺[Me-MAO][−]. The close similarity of these signals to those of the heterobinuclear ion pair [*rac*-C₂H₄(1-Ind)₂Ti(μ -Me)₂AlMe₂]⁺[B(C₆F₅)₄][−], prepared via reaction of **1-Cl₂** with Al₂Me₆ and [CPh₃]⁺[B(C₆F₅)₄][−] in a 1:20:1 ratio (Figure 6), shows that the cationic AlMe₃ adduct [*rac*-C₂H₄(1-Ind)₂Ti(μ -Me)₂AlMe₂]⁺ dominates in these reaction systems. Nonuniformly broadened signals, typical of contact ion pairs of the type *rac*-C₂H₄(1-Ind)₂TiMe⁺⋯MeMAO[−],⁴ were detected at $[\text{Al}]/[\text{Ti}]$ ratios below 100. While some uncertainty remains especially with regard to the nature of the counteranion MAOX[−],²⁰ the close similarity of the NMR spectra shown in Figure 6

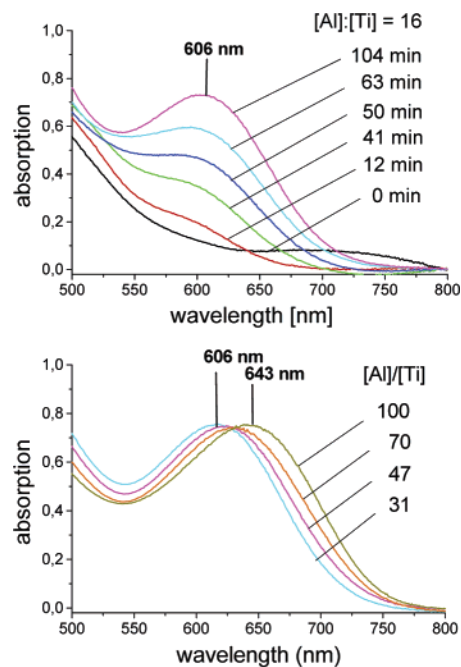


Figure 5. Reaction of *rac*-C₂H₄(1-Ind)₂TiCl₂ (**1-Cl₂**) with MAO at -50 °C: Slow formation of species with $\lambda_{\text{max}} = 606$ nm at $[\text{Al}]/[\text{Ti}] = 16$ (top) and conversion to species with $\lambda_{\text{max}} = 643$ nm at $[\text{Al}]/[\text{Ti}] > 30$ (bottom, spectra taken after 10–15 min).

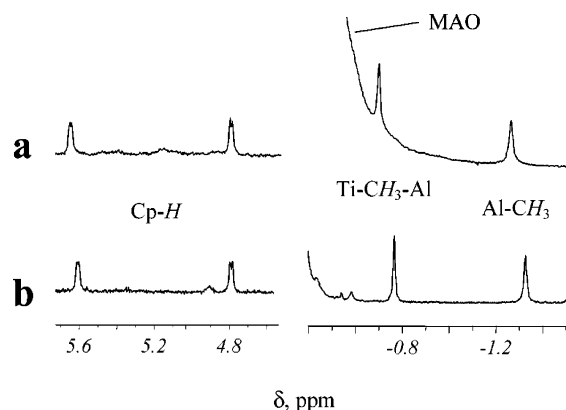


Figure 6. ^1H NMR spectra (toluene-*d*₈, 20 °C) of the systems *rac*-C₂H₄(1-Ind)₂TiCl₂/MAO, with $[\text{Al}]/[\text{Ti}] = 200$ (a, top) and *rac*-C₂H₄(1-Ind)₂TiCl₂/Al₂Me₆/CPh₃⁺[B(C₆F₅)₄][−], with $[\text{Ti}]:[\text{Al}]:[\text{B}] = 1:20:1$ (b, bottom).

indicates that the species with $\lambda_{\text{max}} = 606$ nm observed at $[\text{Al}]/[\text{Ti}] = 16$ –30 is indeed the contact ion pair *rac*-C₂H₄(1-Ind)₂TiMe⁺⋯MAOX[−], while that with $\lambda_{\text{max}} = 643$ nm, formed at higher $[\text{Al}]/[\text{Ti}]$ ratios, represents an outer-sphere ion pair of the cationic AlMe₃ adduct [*rac*-C₂H₄(1-Ind)₂Ti(μ -Me)₂AlMe₂]⁺ with its MAOX[−] counteranion (Scheme 1).¹⁶

While the reaction sequence thus established for the activation of complex **1-Cl₂** with MAO (Scheme 1) is rather similar to activation sequences previously established for related *ansa*-zirconocene/MAO systems,^{15–17} several differences are to be noted: First, much lower

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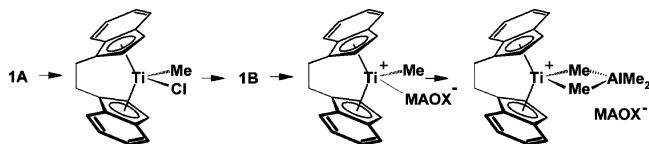
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(18) Identified by spectral comparison with authentic *rac*-C₂H₄(1-Ind)₂Ti(Cl)Me ($\lambda_{\text{max}} = 533$ nm) and *rac*-C₂H₄(1-Ind)₂TiMe₂ ($\lambda_{\text{max}} = 452$ nm), obtained by reaction of complex **1-Cl₂** with 1 and 2 equiv of methylolithium, respectively.

(19) For the system **1-Cl₂**/MAO, no evidence was obtained for the formation of a series of homobinuclear cations of the type [DianTiMe(μ -X)XTiDian]⁺ with X = Cl or Me at 20 °C, which were identified by Bryliakov et al. in the reaction system (C₅H₅)₂TiCl₂/MAO at -15 °C.^{4a}

(20) The MAO-derived anions MAOX[−], assumed to be formed upon activation of a metallocene dichloride with MAO,¹⁶ are not sufficiently characterized yet to warrant an unambiguous identification of the entity X as either Cl or Me;²¹ exchange of the primarily abstracted Cl[−] anion with a neutral Al-Me unit might form a neutral Al-Cl species and a MAOMe[−] anion.

Scheme 1. Reaction Sequence for the Activation of the Dichloride Complex 1-Cl₂ with Increasing MAO Concentrations (X = Cl or Me)²⁰



excess ratios of MAO are required for each reaction step of the *ansa*-titanocene/MAO systems studied here. Independent experiments show that complete formation of the monomethyl complex requires just 1 equiv of AlMe₃, while an excess of AlMe₃ is required to complete the analogous transformation of the Zr congener.²² Formation of the dimethyl complex goes to completion upon addition to 1-Cl₂ of just 2 equiv of AlMe₃, while an analogous reaction has not been reported for reactions of a zirconocene dichloride with MAO. Very modest [Al]:[Zr] ratios are also required for each of the cationization steps represented in Scheme 1. This observation could have its origin in a higher compressibility of a CH₃ than of a Cl ligand, which would favor CH₃ over Cl as a ligand in the more narrow titanocene coordination gap.^{22,23}

Another difference concerns the tendency of the cationic activation products to undergo decomposition: While their zirconocene analogues are stable for about 1 week at room temperature,^{15–17} the cationic complexes formed in the reaction system *rac*-C₂H₄(1-Ind)₂TiCl₂/MAO are unstable at room temperature. Especially the characteristic absorption band at 606 nm associated with the contact ion pair *rac*-C₂H₄(1-Ind)₂TiMe⁺...MeMAO[−] begins to decay within minutes at room temperature; it is stable for extended periods only at temperatures below −20 °C. The AlMe₃-containing outer-sphere ion pair [*rac*-C₂H₄(1-Ind)₂Ti(μ-Me)₂AlMe₂]⁺[Me-MAO][−], on the other hand, is reasonably stable over several hours at room temperature; at this temperature its absorption band at 643 nm decays with a half-life of several days (Figure 7). In the reaction system *rac*-C₂H₄(1-Ind)₂TiCl₂/AlMe₃/CPh₃B(C₆F₅)₄ ([Ti]:[Al]:[B] = 1:20:1), the concentration of [*rac*-C₂H₄(1-Ind)₂Ti(μ-Me)₂AlMe₂]⁺[B(C₆F₅)₄][−] likewise decreases by a factor of 3 during 2 days at room temperature. The products of this decay reaction will be further characterized below.

As a congener to another prototypical *ansa*-zirconocene/MAO system, we have studied reactions of the sterically more encumbered complex Me₂Si(2-Me-Benz[e]Ind)₂TiCl₂ (2-Cl₂) and its dimethyl derivative 2-Me₂ with MAO. Addition of increasing amounts of MAO to a toluene solution of 2-Cl₂ at 20 °C causes a hypsochromic shift of the lowest-energy absorption band, from λ_{max} = 651 nm to λ_{max} ≈ 550 nm. We assign this change, which requires an [Al]/[Ti] ratio of ca. 30, to the formation of *rac*-Me₂Si(2-Me-Benz[e]Ind)₂Ti(Cl)Me by a first Me/Cl exchange with the AlMe₃ contained in MAO. Addition of further amounts of MAO, up to an [Al]/[Ti] ratio of

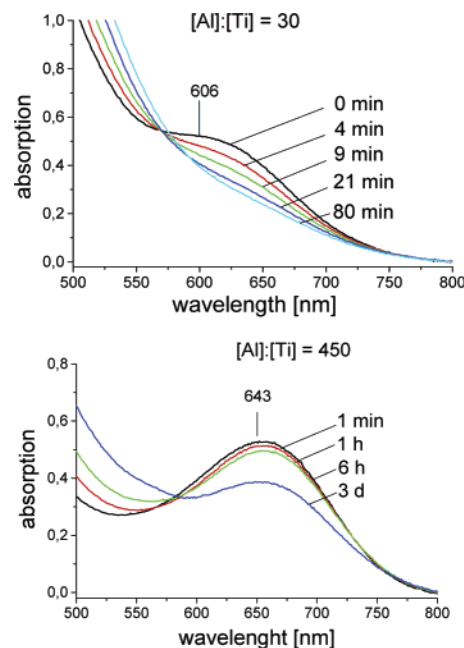


Figure 7. Decay of absorption bands of *rac*-C₂H₄(1-Ind)₂-TiMe⁺...MeMAO[−] at 606 nm (top) and of [*rac*-C₂H₄(1-Ind)₂-Ti(μ-Me)₂AlMe₂]⁺[MeMAO][−] at 643 nm (bottom) in toluene at 20 °C.

ca. 6–8:1, causes a second hypsochromic shift, due to the formation of the dimethyl complex with λ_{max} = 489 nm. As in the system 1-Cl₂/MAO, both chlorides are replaced by methyl groups by exchange with the AlMe₃ content of MAO; here, however, a higher excess of MAO is required for each exchange step than in the case of 1-Cl₂/MAO. Further addition of MAO causes, again, two successive bathochromic shifts of the lowest-energy absorption bands to 654 and then to 667 nm. The same observations pertain, as expected, if a toluene solution of *rac*-Me₂Si(2-Me-Benz[e]Ind)₂TiMe₂ is treated with excess MAO at −50 °C (Figure 8).

In analogy with the previous case, we can safely assume that the ion pairs *rac*-Me₂Si(2-Me-Benz[e]Ind)₂TiMe⁺...Me-MAO[−] and [*rac*-Me₂Si(2-Me-Benz[e]Ind)₂Ti(μ-Me)₂AlMe₂]⁺Me-MAO[−] are formed at [Al]/[Ti] ratios of ca. 140:1 and ca. 400:1, respectively. Isosbestic points found at λ = 516 nm and at λ = 516 and 650 nm for the first and the second step, respectively, document clean reactions without intermediates or side products. While the reaction steps in the system 2-Cl₂/MAO thus appear to follow closely those described in Scheme 1 for 1-Cl₂/MAO, it is remarkable that the formation of each species in this system requires much higher MAO concentrations than in the system 1-Cl₂/MAO (Table 3). We ascribe this observation to an opening of the coordination gap aperture by the shorter Me₂Si bridge,²³ which reduces the pressure on the Ti-bound ligands and, hence, the advantage of a more easily compressible CH₃ over a Cl ligand. No significant differences are to be noted, however, between the systems 2-Cl₂/MAO and 2-Me₂/MAO: Abstraction of Cl[−] and Me[−] units by MAO appears to require practically identical [Al]:[Ti] ratios.

To check on the identity of the species formed from 2-Cl₂ or 2-Me₂ at high [Al]/[Ti] ratios, the heterobinuclear ion pair [*rac*-Me₂Si(2-Me-Benz[e]Ind)₂TiMe₂(μ-Me)₂AlMe₂]⁺(C₆F₅)₄B[−] was generated by reaction of

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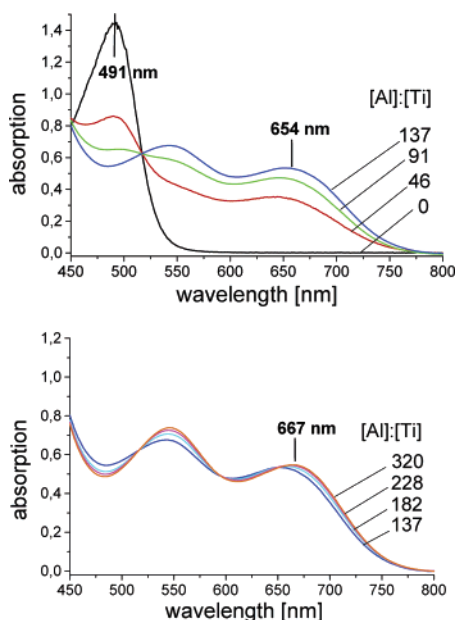


Figure 8. Reaction of *rac*-Me₂Si(2-Me-Benz[e]Ind)₂TiMe₂ (**2-Me₂**) with excess MAO at $-50\text{ }^{\circ}\text{C}$: First bathochromic shift to $\lambda_{\text{max}} = 654\text{ nm}$ at $[\text{Al}]/[\text{Ti}] = 40\text{--}140$ (top) and second bathochromic shift to $\lambda_{\text{max}} = 667\text{ nm}$ at $[\text{Al}]/[\text{Ti}] > 140$ (bottom, spectra taken after ca. 10–15 min).

2-Me₂ with 1.1 equiv of trityl perfluorotetraphenyl borate in the presence of excess Al₂Me₆ in toluene solution at room temperature. The absorption band at 668 nm formed under these conditions closely coincides with that at 667 nm, generated by MAO activation of either **2-Cl₂** or **2-Me₂**. This indicates that the same heterobinuclear cation, [*rac*-Me₂Si(2-Me-Benz[e]Ind)₂Ti-(μ -Me)₂AlMe₂]⁺, is formed in all of these reaction systems.

These assignments are supported by ¹H NMR signals obtained from solutions containing complex **2-Me₂** together with an excess of MAO ($[\text{Al}]/[\text{Ti}] \approx 500$) or with an equivalent amount of (C₆H₅)₃C⁺B(C₆F₅)₄[−] and excess trimethyl aluminum, in C₆D₆ at room temperature (Table 4).

To check on conceivable effects of different lengths of the interannular bridges on the stability of cationic species in these reaction systems, we have included in this series also a congener of complex **1-Cl₂** with only one bridging CH₂ unit, *rac*-CH₂(1-Ind)₂TiCl₂ (**3-Cl₂**).^{14c} As shown in Table 4, the cationic AlMe₃ adduct [*rac*-CH₂(1-Ind)₂Ti(μ -Me)₂AlMe₂]⁺, formed from **3A** with excess MAO, falls in line with the other species of this type derived from complexes **1-Cl₂** and **2-Cl₂**. It can thus be safely assumed that formation of these species at elevated MAO concentrations is a general characteristic for *ansa*-titanocene as for *ansa*-zirconocene complexes.

The UV/vis bands and ¹H NMR signals characteristic for these cationic AlMe₃ adducts, generated in the presence of excess MAO, are completely formed within ca. 5–10 min at room temperature and remain stable for some time. After 20–30 min, some decay of these characteristics becomes noticeable at room temperature; in the course of several days they finally disappear altogether.

3. EPR Studies on the Reductive Decay of Cationic Titanocene Species. To identify the products that arise from the decay of the cationic species de-

scribed above, we have first studied by EPR the interaction of *rac*-C₂H₄(1-Ind)₂TiCl₂ with Al₂Me₆ in toluene ($[\text{Ti}] = 0.001\text{ M}$, $[\text{Al}]/[\text{Ti}] = 20$). EPR spectra recorded 1 day after the onset of the decay reaction at room temperature display a signal at $g_0 = 1.978$ with hyperfine structure (hfs) from Ti ($a_{\text{Ti}} = 12\text{ G}$, Figure 9a) and partially resolved hfs from Al ($a_{\text{Al}} = 2.3\text{ G}$). The intensity of the EPR signal indicates, within an accuracy of 20–30%, essentially complete reduction of Ti(IV) to Ti(III). The hfs due to Al indicates that the signal at $g_0 = 1.978$ belongs to a heterobinuclear complex containing titanium(III) and aluminum atoms, most likely to the species *rac*-C₂H₄(1-Ind)₂Ti^{III}(μ -Me)₂AlMe₂ (type **A**).²⁴

With regard to the nature of the reducing agent in solutions of *rac*-C₂H₄(1-Ind)₂TiCl₂ and Al₂Me₆, we assume that Me₂AlEt admixtures of the latter might generate, by elimination of C₂H₄, a metal hydride species that would be capable of causing reduction of Ti(IV).²⁷ In accord with an estimate that the Al₂Me₆ used in our study contains ca. 2% of ethyl instead of methyl groups,²⁸ only partial conversion of Ti(IV) to Ti(III) was observed at an $[\text{Al}]/[\text{Ti}]$ ratio of 5, whereas at $[\text{Al}]/[\text{Ti}] = 20$, complete reduction occurred. To corroborate our hypothesis, we have used as a reducing agent triisobutylaluminum (TIBA) instead of Al₂Me₆. TIBA always contains some HAL(*i*Bu)₂,²⁹ which should lead to immediate reduction of Ti(IV). Addition of 10 equiv of TIBA to a solution of *rac*-C₂H₄(1-Ind)₂TiCl₂ in toluene caused indeed an immediate and complete reduction of Ti(IV) to Ti(III). The EPR spectrum observed displays an EPR signal at $g_0 = 1.978$ with hfs from Al of 1.8 G and a doublet at $g_0 = 1.986$ from a Ti(III) hydride complex with $a_{\text{H}} = 5.5\text{ G}$ (Figure 9b).²⁶ By analogy with the system *rac*-C₂H₄(1-Ind)₂TiCl₂/Al₂Me₆, the signal at $g_0 = 1.978$ with hfs from Al can be attributed to a heterobinuclear complex of type **A**, containing some isobutyl aluminum fragment, while the hydride signal indicates that a surplus of hydride species remains in this reaction system even after reduction of all Ti^{IV} species.

When 1 equiv of (C₆H₅)₃C⁺B(C₆F₅)₄[−] is added to a mixture of *rac*-C₂H₄(1-Ind)₂TiCl₂ and Al₂Me₆ ($[\text{Al}]/[\text{Ti}] = 20$) in toluene, we observe, besides the signal of complex **A**, a weaker singlet signal at $g_0 = 1.965$. Clues to the nature of this species are apparent from the literature: Four-coordinated complexes of the type Cp₂-Ti^{III}L₂, where L₂ are bidentate ligands such as acetate, 2-hydroxypyridine, or bipyridyl, exhibit EPR signals at

(24) A related complex, (C₅H₅)₂Ti^{III}(μ -Me)₂AlMe₂, has been reported to give an EPR signal at $g_0 = 1.977$ with unresolved hfs from Al in toluene solution at $-40\text{ }^{\circ}\text{C}$ (ref 25), while a similar EPR spectrum with $g_0 = 1.975$ and hfs from Al of 3.7 G has been reported for (C₅H₅)₂-Ti^{III}(μ -Cl)₂AlEtCl (ref 26). That species **A** is *rac*-C₂H₄(1-Ind)₂Ti^{III}(μ -Me)₂AlMe₂, rather than a chloride-containing analogue *rac*-C₂H₄(1-Ind)₂Ti^{III}(μ -Me)₂(μ -Cl)₂-AlMe₂, is indicated by the observation that higher ratios of $[\text{Al}]/[\text{Ti}] = 50$, at which all Ti-bound Cl[−] ions are likely to be replaced by Me[−] units, do not cause any changes in the EPR spectrum.

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(27) Formation of C₂H₄ was always detected by ¹H NMR in 1-Cl₂/Al₂Me₆ reaction mixtures.

(28) Al-Et units in trimethyl aluminum give rise to ¹H NMR signals at 1.05 (t, 3H, CH₃) and 0.02 ppm (q, 2H, CH₂), ³J_{HH} = 8.1 Hz, at 250 MHz in C₆D₆ at 20 $^{\circ}\text{C}$.

(29) Al-H units in tri-isobutyl aluminum give a broad ($\nu_{1/2} \approx 15\text{ Hz}$) singlet at 4.07 ppm in *d*₈-toluene at 20 $^{\circ}\text{C}$; isobutene signals: 4.76 (sept, 2H, CH₂) and 1.61 ppm (t, 6H, CH₃), ⁴J_{HH} = 1.2 Hz.

Table 3. Positions of Lowest-Energy UV/Vis Absorption Bands and [Al]/[Ti] Ratios Required for the Formation of Individual Species in the Reaction Systems 1-Cl₂/MAO, 2-Cl₂/MAO, and 2-Me₂/MAO

species ^a	$\lambda_{\max}/\text{nm}$		[Al]/[Ti]	
	1-Cl ₂ /MAO	2-(Cl ₂ ,Me ₂)/MAO	1-Cl ₂ /MAO	2-(Cl ₂ ,Me ₂)/MAO
DiAnTiCl ₂	652	651		
DiAnTi(Cl)Me	533	550	3	28
DiAnTiMe ₂	452	491	6–8	44
[DiAnTiMe] ⁺ [MeMAO] [−]	606	654	16	100
[DiAnTi(μ -Me) ₂ AlMe ₂] ⁺ [MAOCi] [−]	643	667	100	424

^a DiAn: *rac*-C₂H₄(1-Ind)₂ for 1-Cl₂, *rac*-Me₂Si(2-Me-Benz[e]Ind)₂ for 2-Cl₂ and 2-Me₂.

Table 4. Selected ¹H NMR Signals for Heterobinuclear Methyl Titanocenium Cations (at room temperature, δ in ppm)

species	Cp- <i>H</i>	bridge	Al-CH ₃	Ti-CH ₃ -Al
[<i>rac</i> -C ₂ H ₄ (1-Ind) ₂ Ti(μ -Me) ₂ AlMe ₂] ⁺ [Me-MAO] ^{−a}	5.65, 4.78	3.27 ^f	−0.69	−1.26
[<i>rac</i> -C ₂ H ₄ (1-Ind) ₂ Ti(μ -Me) ₂ AlMe ₂] ⁺ [B(C ₆ F ₅) ₄] ^{−b}	5.57, 4.74	3.24 ^f	−0.76	−1.33
[<i>rac</i> -Me ₂ Si(2-Me-Benzind) ₂ Ti(μ -Me) ₂ AlMe ₂] ⁺ [Me-MAO] ^{−c}	6.42	1.16 ^g	−0.81	−1.72
[<i>rac</i> -Me ₂ Si(2-Me-Benzind) ₂ Ti(μ -Me) ₂ AlMe ₂] ⁺ [B(C ₆ F ₅) ₄] ^{−d}	6.31	0.85 ^g	−0.83	−1.71
[<i>rac</i> -CH ₂ (1-Ind) ₂ Ti(μ -Me) ₂ AlMe ₂] ⁺ [Me-MAO] ^{−e}	5.92, 4.20	4.31 ^h	−0.65	−1.65

^a In toluene-*d*₈, [Al]:[Ti] = 200. ^b In toluene-*d*₈, [B]:[Al]:[Ti] = 1:20:1. ^c In benzene-*d*₆, [Al]:[Ti] = 500. ^d In benzene-*d*₆, [B]:[Al]:[Ti] = 1:20:1. ^e In toluene-*d*₈, [Al]:[Ti] = 200. ^f -C₂H₄-. ^g -Si(CH₃)₂-. ^h -CH₂-.

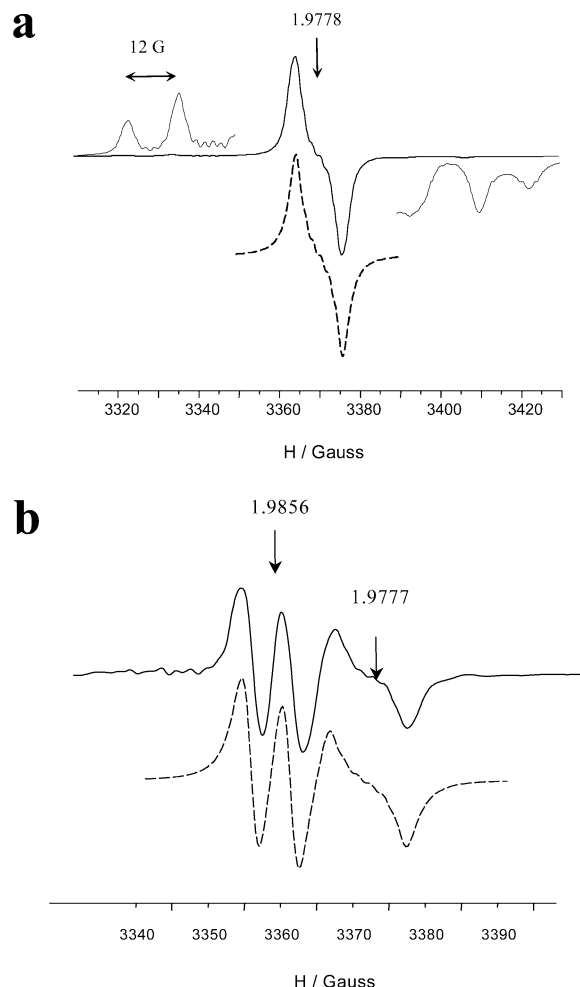


Figure 9. EPR spectra (toluene-*d*₈, 20 °C) of (a) *rac*-C₂H₄(1-Ind)₂TiCl₂/Al₂Me₆, [Al]:[Ti] = 20, 1 day after onset of the reaction and (b) *rac*-C₂H₄(1-Ind)₂TiCl₂/Al(*i*Bu)₃, [Al]:[Ti] = 10, 10 min after onset of the reaction b; dashed lines represent simulations of the experimental spectra.

$g_0 = 1.978\text{--}1.980$,³⁰ whereas EPR signals at $g_0 = 1.950\text{--}1.957$ are associated with three-coordinated complexes such as (C₅Me₅)₂Ti^{III}Me or (C₅H₅)₂Ti^{III}L₁, which contain a monodentate ligand L₁ = Ph or *o*-, *m*-, *p*-CH₃C₆H₄.³¹

For [(C₅H₂Me₃)₂TiCl] in methyltetrahydrofuran (mthf) solution, for example, Mach and Reynor have assigned two well-separated isotropic EPR signals at $g_0 = 1.979$ and at $g_0 = 1.965$ to a complex with a mthf molecule in its fourth coordination site ($g_0 = 1.979$) and a three-coordinated complex without coordinated solvent ($g_0 = 1.965$), respectively.³² By analogy, the singlet at $g_0 = 1.965$ in the reaction system C₂H₄(1-Ind)₂TiCl₂/Al₂Me₆/[CPh₃]⁺[B(C₆F₅)₄][−] might be due to a three-coordinated complex of the type C₂H₄(1-Ind)₂Ti^{III}Me (type B), which has lost from its fourth coordination site the AlMe₃ unit contained in complex A (Scheme 2).³³

EPR signals assignable to complexes of type A and type B were observed also in toluene solutions containing *rac*-Me₂Si(2-Me-Benzind)₂TiMe₂ and Al₂Me₆/[CPh₃]⁺[B(C₆F₅)₄][−] ([Ti] = 10^{−3} M; Ti:Al:B = 1:20:1) 1 day after onset of the reaction.³⁴

When MAO is added to a toluene solution of *rac*-C₂H₄(1-Ind)₂TiCl₂, we observe that pronounced amounts of precipitate settle on the bottom of the EPR tube during 1 day after onset of the reaction at room temperature. By analogy with the corresponding zirconocene reaction systems, we can assume that this precipitate contains some MAO-bound, insoluble Ti(IV) species. At the same time, EPR spectra indicate reduction of ca. 10% of total titanium to Ti(III). EPR spectra of the solution decanted from the upper part of the EPR tube display a superposition of two rhombic anisotropic signals from titanium complexes A' and B' with the

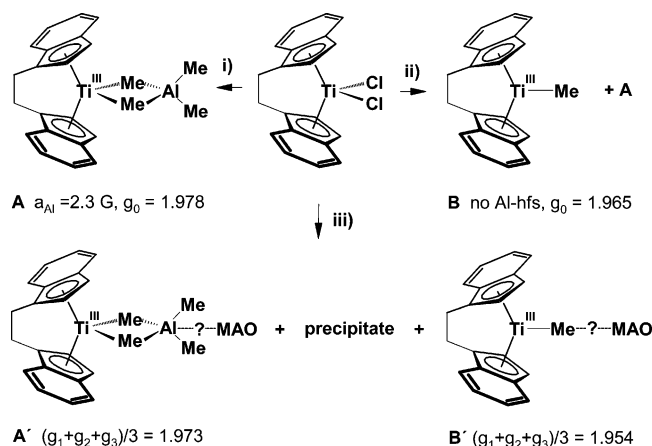
(30) (a) Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059. (b) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 1841. (c) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078.

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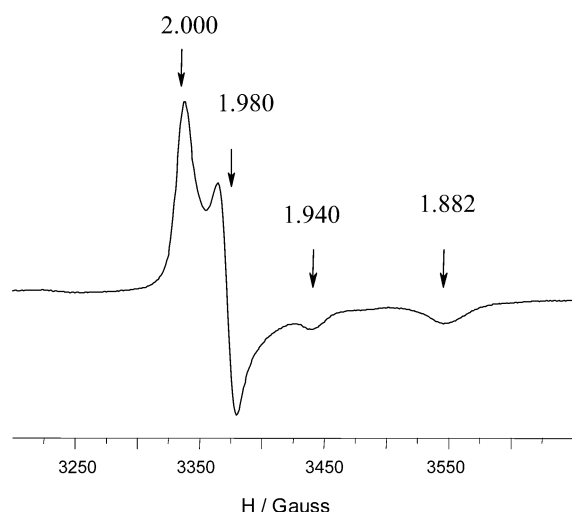
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(33) That B is an ion pair with positively charged titanium(III) center appears less probable, since the zwitterionic complex *rac*-(ebthi)-Ti⁺-η²-Me₃SiC₂B(C₆F₅)₃][−] (ebthi = 1,2-ethylene-1,1'-bis(η⁵-tetrahydroindenyl)) has been reported to give an EPR signal at $g_0 = 1.98$: Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **2003**, *115*, 1455.

(34) In this reaction mixture, we observe also the EPR signal of the trityl radical.³⁵ Possibly, Ti(III) reacts with (C₆H₅)₃C⁺ to afford (C₆H₅)₃C• and Ti(IV).

Scheme 2. Reactions of the Complex 1-Cl₂, in toluene at 20 °C^a

^a (i) 20 equiv of Al₂Me₆; (ii) 20 equiv of Al₂Me₆ and 1 equiv of (C₆H₅)₃C⁺B(C₆F₅)₄⁻; (iii) MAO at [Al]:[Ti] = 200.

**Figure 10.** EPR spectrum (toluene-*d*₈, 20 °C) of the system 1-Cl₂/MAO in toluene ([Ti] = 10⁻³ M, [Al]/[Ti] = 200) 1 day after onset of the reaction.

following parameters: **A'** ($g_1 = 2.000$, $g_2 = 1.980$, $g_3 = 1.940$) and **B'** ($g_1 = 2.000$, $g_2 = 1.980$, $g_3 = 1.882$) (Figure 10). The anisotropy of the spectra indicates that the tumbling of the titanium(III) species is restricted, presumably by coordination to the bulky MAO molecules.²¹ The corresponding isotropic g -values ($g_0 = (g_1 + g_2 + g_3)/3$) for complexes **A'** and **B'** ($g_0 = 1.973$ and $g_0 = 1.954$, respectively) are close to those for complexes **A** and **B**, discussed above.

When solutions of [Ti^{III}(C₅H₂Me₃)₂Cl] in methyltetrahydrofuran (mthf) are frozen, the isotropic EPR signals at $g_0 = 1.979$ and at $g_0 = 1.965$ discussed above are replaced by two rhombic signals similar to those of **B'** and **A'**, assigned to the uncoordinated starting complex ($g_1 = 2.000$, $g_2 = 1.984$, $g_3 = 1.909$) and the same complex coordinated with mthf ($g_1 = 2.000$, $g_2 = 1.984$, $g_3 = 1.954$).³⁴ It is thus tempting to assign complex **A'** to a heterobinuclear complex similar to *rac*-C₂H₄(1-Ind)₂-Ti^{III}(μ-Me)₂AlMe₂, the mobility of which is reduced due to some kind of attachment to MAO. For the assignment of **B'**, we propose that **B'** is a neutral complex C₂H₄(1-Ind)₂Ti^{III}Me somehow attached to a molecule of MAO (Scheme 2).

Table 5. Polymerization of Propene with 1-Cl₂/MAO and with 2-Me₂/MAO^a

catalyst/amount	Al:Ti	temp (°C)	time (h)	g PP	activity ^b
1-Cl ₂ /40 μmol	450:1	-20	1.5	9.7	161
1-Cl ₂ /40 μmol	400:1	20	1	0	0
2-Me ₂ /40 μmol	375:1	-20	3	11.9	100
2-Me ₂ /44 μmol	190:1	30	2.5	5.4	50

^a Propene pressure 1 bar. ^b g PP/(mol Ti·h·bar).

EPR spectra recorded several hours after onset of the reactions of *rac*-Me₂Si(2-Me-Benzind)₂TiMe₂ or of *rac*-CH₂(1-Ind)₂TiCl₂ with MAO ([Ti] = 10⁻³ M, [Al]/[Ti] = 100) likewise display a superposition of anisotropic signals from complexes **A'** and **B'**, as observed in the case of the system *rac*-C₂H₄(1-Ind)₂TiCl₂/MAO.

Preliminary data for propene polymerization with *rac*-C₂H₄(1-Ind)₂TiCl₂/MAO and *rac*-Me₂Si(2-Me-Benzind)₂TiMe₂/MAO show that these catalysts are reasonably active at -20 °C but less so at room temperature. 1-Cl₂/MAO in particular is totally inactive at 20 °C (Table 5). At first glance, this appears to be at variance with the relatively slow reductions of the heterobinuclear ion pairs formed upon reaction with MAO, which require several hours or even days at room temperature. Apparently, catalyst deactivation is accelerated in the presence of monomer.

In agreement with this assumption, addition of propene (200 equiv) to a freshly prepared solution of *rac*-C₂H₄(1-Ind)₂TiCl₂ and MAO in toluene ([Ti] = 10⁻³ M, Al/Ti = 200) gave immediately a 5-fold increase of the Ti(III) concentration as measured by EPR. We propose that hydride species, assumed to arise as side products or reaction intermediates in the course of titanocene-catalyzed polymerization, are responsible for rapid catalyst reduction and deactivation.

No well-defined neutral titanium(III)-based molecular systems with established activity for catalytic olefin polymerization have been reported in the literature so far. Reduction of the predominant Ti(IV) species [Di-AnTi(μ-Me)₂AlR₂]⁺, with R = methyl or polymeryl, to the Ti(III) congener DiAnTi(μ-Me)₂AlR₂ thus appears to be the main, although possibly not the only,³⁶ cause for deactivation of titanocene-based polymerization catalysts. Since all three catalyst systems studied, *rac*-C₂H₄(1-Ind)₂TiCl₂/MAO, *rac*-CH₂(1-Ind)₂TiCl₂/MAO, and *rac*-Me₂Si(2-Me-Benzind)₂TiMe₂/MAO, show closely similar activation and deactivation behavior, useful clues with regard to structural features that might stabilize the catalytically active Ti(IV) state are not available yet. It remains to be elucidated which circumstances are responsible for the stability of some titanium-containing constrained-geometry and titanocene-based olefin polymerization catalysts, which remain highly active for olefin polymerization at elevated temperatures.^{40,41}

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Experimental Section

Toluene- d_8 and benzene- d_6 were dried over molecular sieves (4 Å) prior to use. All operations were carried out under dry nitrogen (99.999%) in a glovebox. MAO was prepared from commercial MAO (Witco) by removal of the solvent in vacuo at 20 °C. The solid product obtained (polymeric MAO with total Al content 40 wt % and Al as residual AlMe_3 ca. 5 wt %) was used for the preparation of the samples. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 250 (250 MHz) or Bruker Avance 600 (600 MHz) instruments.

$\text{C}_2\text{H}_4(1\text{-Ind})_2\text{Li}_2(\text{THF})_2$. $\text{C}_2\text{H}_4(1\text{-Ind})_2\text{Li}_2$ was prepared according to ref 5b. From the resulting reaction mixture, the solvent was removed under vacuum. The precipitate formed by addition of pentane was collected by filtration and dried under reduced pressure. The pure lithium salt contained 2 THF per molecule as indicated by NMR spectroscopy.

(1,1'-Bi-2-phenolate) $\text{TiCl}_2(\text{THF})_2$. To a solution of 13.0 g (70 mmol) of 1,1'-bi-2-phenol in 50 mL of toluene was slowly added 7.6 mL (70 mmol) of TiCl_4 . Excess HCl gas pressure was allowed to escape via a bubbler. After stirring at room temperature for 4 h, the solvent was removed under vacuum. The resulting brown powder was washed with pentane and dried under reduced pressure. THF (100 mL) was added, and the solution was kept at room temperature for 2 days. The solvent was removed under vacuum, and pentane was added. The suspension was filtered, and the precipitate was washed with pentane and dried in vacuo to yield 28.4 g (91%) of a dark orange powder. Single crystals suitable for X-ray analysis were obtained from THF/pentane at -80 °C. ^1H NMR (CD_2Cl_2 , 600 MHz, 25 °C, δ , ppm): 7.49 (2H, d, $J_{\text{HH}} = 7.4$ Hz, 6,6'-biphenolate-*H*); 7.30 (2H, t, $J_{\text{HH}} = 7.2$ Hz, 4,4'-biphenolate-*H*); 7.14 (2H, m, 5,5'-biphenolate-*H*); 6.82 (2H, bs, 3,3'-biphenolate-*H*); 4.26 (8H, bs, THF); 1.97 (8H, bs, THF). ^{13}C NMR (CD_2Cl_2 , 25 °C, δ , ppm): 166.2, 131.6, 128.8, 127.4, 124.3, 115.1 (biphenolate- $\text{C}_{2,2'}$, - $\text{C}_{6,6'}$, - $\text{C}_{4,4'}$, - $\text{C}_{1,1'}$, - $\text{C}_{5,5'}$, - $\text{C}_{3,3'}$); 73.7, 25.9 (THF). EI-MS (70 eV): m/e 302 ($\text{M}^+ - 2\text{THF}$). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{Cl}_2\text{Ti}$ (447.18): C, 53.72; H, 5.41. Found: C, 53.37; H, 5.16.

$\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(1,1'\text{-bi-2-phenolate})$. To a dry mixture of 2.76 g (6.2 mmol) of (1,1'-Bi-2-phenolate) $\text{TiCl}_2(\text{THF})_2$ (**1**) and 2.55 g (6.2 mmol) of $\text{C}_2\text{H}_4(1\text{-Ind})_2\text{Li}_2(\text{THF})_2$ were added 30 mL of toluene and 10 mL of THF. After stirring at room temperature for 1 h 100 mL of pentane was added and the reaction mixture was kept at -80 °C for 1 h. The brown suspension was filtered, and the solvent was removed from the filtrate under vacuum. A crude dark orange powder (0.37 g, 12%) was obtained and was used without further purification for the preparation of complex **3** (see below). An analytically pure sample of **2** was obtained by cooling a solution of crude product in toluene/pentane at 4 °C. The red precipitate was filtered, washed with pentane, and dried in vacuo. Crystals suitable for X-ray diffraction analysis were obtained from a toluene solution at 4 °C. ^1H NMR (600 MHz, CD_2Cl_2 , 25 °C, δ , ppm): 7.73 (2H, d, $J_{\text{HH}} = 8.6$ Hz, 7,7'-Ind-*H*); 7.16 (4H, m, 4,4'-biphenolate-*H* and 6,6'-Ind-*H*); 7.06 (2H, d, $J_{\text{HH}} = 7.5$ Hz, 6,6'-biphenolate-*H*); 6.89 (2H, m, 5,5'-Ind-*H*); 6.84 (2H, m, 5,5'-biphenolate-*H*); 6.47 (4H, m, 3,3'-biphenolate-*H* and 4,4'-Ind-*H*); 6.21 (2H, d, $J_{\text{HH}} = 3.0$ Hz, 2,2'-Ind-*H*); 5.72 (2H, d, $J_{\text{HH}} = 3.0$ Hz, 3,3'-Ind-*H*); 3.79–4.01 (4H, m, C_2H_4). ^{13}C NMR (CD_2Cl_2 , 25 °C, δ , ppm): 165.7, 131.2, 128.4, 126.2, 117.1 (biphenolate- $\text{C}_{2,2'}$, - $\text{C}_{6,6'}$, - $\text{C}_{4,4'}$, - $\text{C}_{5,5'}$, - $\text{C}_{3,3'}$); 131.3, 127.2, 127.0, 125.9 (biphenolate, Ind); 126.4, 124.0, 121.4, 120.3, 114.8, 111.5 (Ind- $\text{C}_{6,6'}$, - $\text{C}_{4,4'}$, - $\text{C}_{7,7'}$, - $\text{C}_{5,5'}$, - $\text{C}_{2,2'}$, - $\text{C}_{3,3'}$); 29.4 (C_2H_4). EI-MS (70 eV): m/e 488 (M^+). Anal. Calcd for $\text{C}_{32}\text{H}_{24}\text{O}_2\text{Ti}$ (488.42): C, 78.69; H, 4.95. Found: C, 78.50; H, 5.00.

$\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{TiCl}_2$. Crude $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{Ti}(1,1'\text{-bi-2-phenolate})$ (0.37 g, 0.76 mmol) was dissolved in 10 mL of

toluene, and 0.76 mL of MeAlCl_2 (1 M in hexane, 0.76 mmol) was added. The solvent was removed under reduced pressure. Diethyl ether was added, and the resulting suspension was filtered. The precipitate was washed with diethyl ether until the filtrate was essentially colorless. The resulting brown residue was extracted with methylene chloride, which gave a dark green solution. The solvent was removed in vacuo to yield 0.12 g (42%) of pure $\text{rac-C}_2\text{H}_4(\text{Ind})_2\text{TiCl}_2$. Recrystallization from toluene at room temperature afforded red crystals suitable for X-ray analysis. ^1H NMR (600 MHz, CD_2Cl_2 , 25 °C, δ , ppm): 7.62 (2H, d, $J_{\text{HH}} = 8.6$ Hz, 7,7'-Ind-*H*); 7.44 (2H, d, $J_{\text{HH}} = 8.5$ Hz, 4,4'-Ind-*H*); 7.36 (2H, m, 5,5'-Ind-*H*); 7.26 (2H, m, 6,6'-Ind-*H*); 6.69 (2H, d, $J_{\text{HH}} = 3.2$ Hz, 3,3'-Ind-*H*); 6.12 (2H, d, $J_{\text{HH}} = 3.2$ Hz, 2,2'-Ind-*H*); 3.70–3.94 (4H, m, C_2H_4). ^{13}C NMR (CD_2Cl_2 , 25 °C, δ , ppm): 131.5, 130.0, 128.7, 128.5, 126.7, 126.1, 122.8, 120.2, 115.7 (Ind- $\text{C}_{3a/3a'}$, - $\text{C}_{7a/7a'}$, - $\text{C}_{6/6'}$, - $\text{C}_{5/5'}$, - $\text{C}_{1/1'}$, - $\text{C}_{4/4'}$, - $\text{C}_{7/7'}$, - $\text{C}_{3/3'}$, - $\text{C}_{2/2'}$); 29.7 (C_2H_4). EI-MS (70 eV): m/e 374 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{Ti}$ (375.11): C, 64.04; H, 4.30. Found: C, 64.88; H, 4.42.

$\text{rac-Me}_2\text{Si}(2\text{-Me-Benzind})_2\text{TiMe}_2$ (2-Me**).** At room temperature, 1.8 g of TiCl_4 (9.49 mmol) was dissolved in 20 mL of pentane. The solution was cooled to -78 °C, and 60 mL of Et_2O was slowly added. The yellow suspension was then warmed to room temperature. $\text{Me}_2\text{Si}(2\text{-Me-Benz[e]indH})_2$ (3.95 g, 9.49 mmol) was dissolved at room temperature in 60 mL of Et_2O , and 12 mL (19 mmol) of MeLi (solution in Et_2O , 1.6 M) was slowly added, yielding a brown solution. After stirring the reaction mixture for 2 h, 6.2 mL (19 mmol) of MeMgBr (3.06 M solution in Et_2O) was added. The solution was stirred for an additional 2 h while a white material, presumably LiBr, precipitated. Both reaction mixtures were then cooled to -78 °C and combined via cannula. The resulting dark suspension was allowed to come to room temperature overnight. ^1H NMR spectra of the crude product mixture showed a *rac-meso* ratio of about 1:1. The dark precipitate was collected by filtration, dried in vacuo, and then extracted with CH_2Cl_2 . Evaporation of the solvent yielded 1.05 g (22.5%) of pure racemic **2-Me**. When the filtrate of the original reaction mixture was concentrated to about the half its volume under reduced pressure, an additional 0.26 g (5.6%) of racemic **2-Me** was obtained after several days by the same procedure. Dissolving this product in CH_2Cl_2 , filtering, removal of solvent in vacuo, and repeating the same procedure in toluene gave analytically pure complex. Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated ether solution at room temperature. ^1H NMR (δ in ppm, CD_2Cl_2 , 298 K, 600 MHz): 8.17 (d, 2H, $^3J_{\text{HH}} = 7.84$ Hz, 4,4'-benzind H_2), 7.77 (d, 2H, $^3J_{\text{HH}} = 7.92$ Hz, 7,7'-benzind H_2), 7.68 (s, 2H, 3,3'-benzind H_2), 7.59 (dd, 2H, $^3J_{\text{HH}} = 7.53$ Hz, $^3J_{\text{HH}} = 7.38$ Hz, 5,5'-benzind H_2), 7.48 (dd, 2H, $^3J_{\text{HH}} = 7.47$ Hz, $^3J_{\text{HH}} = 7.41$ Hz, 6,6'-benzind H_2), 7.39 (d, 2H, $^3J_{\text{HH}} = 9.15$ Hz, 9,9'-benzind H_2), 7.21 (d, 2H, $^3J_{\text{HH}} = 9.14$ Hz, 8,8'-benzind H_2), 1.93 (s, 6H, 2- CH_3), 1.05 (s, 6H, Si- CH_3), -1.18 (s, 6H, Ti- CH_3). ^{13}C NMR (CD_2Cl_2 as internal standard, 298 K, 150 MHz, ppm): 132.7, 132.5, 131.6, 130.3, 128.7, 127.4, 126.8, 126.3, 125.0, 124.6, 124.5, 122.9, 87.1 (benz[e]ind-*C*); 51.0 (Ti- CH_3), 18.5 (2-benz[e]ind- CH_3), 2.2 (-Si- CH_3). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{SiTi}$: C, 78.02; H, 6.54. Found: C, 77.90; H, 6.20. MS: 477 [$\text{M}]^+ - \text{CH}_3$ (40%), 462 [$\text{M}]^+ - 2\text{CH}_3$ (100%).

$\text{rac-Me}_2\text{Si}(2\text{-Me-Benz[e]ind})_2\text{TiCl}_2$ (2-Cl**).** $\text{AlCl}_3(\text{THF})$ was prepared by slowly adding 0.55 mL of THF to a suspension of 0.89 g (6.67 mmol) of AlCl_3 in 30 mL of toluene at -30 °C. The resulting clear solution was allowed to come to room temperature, and the solvent was removed in vacuo. The white powder was used without further purification. At room temperature, 230 mg (0.467 mmol) of solid $\text{Me}_2\text{Si}(2\text{-Me-Benz[e]ind})\text{TiMe}_2$ (**2-Me**) and 200 mg (0.97 mmol) of solid $\text{AlCl}_3(\text{THF})$ were mixed, and 20 mL of CH_2Cl_2 was added. The dark solution was stirred for 2 days while some dark precipitate was formed. The ^1H NMR spectra of the reaction mixture indicated a clean conversion to $\text{Me}_2\text{Si}(2\text{-Me-Benz[e]ind})\text{TiCl}_2$. The solvent was evaporated, and the solid residue was washed

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Table 6. Crystallographic Data for Complexes (1,1'-bi-2-phenolate)TiCl₂(THF)₂, *rac*-C₂H₄(1-Ind)₂Ti(1,1'-bi-2-phenolate), *rac*-C₂H₄(1-Ind)₂TiCl₂ (1-Cl₂), and *rac*-Me₂Si(2-Me-Benzind)₂TiMe₂ (2-Me₂)

	(1,1'-bi-2-phenolate)- TiCl ₂ (THF)	<i>rac</i> -C ₂ H ₄ (1-Ind) ₂ Ti(1,1'- bi-2-phenolate)	<i>rac</i> -C ₂ H ₄ (1-Ind) ₂ TiCl ₂ (1-Cl ₂)	<i>rac</i> -Me ₂ Si(2-Me-Benzind) ₂ TiMe ₂ (2-Me ₂)
formula	C ₁₃ H ₁₂ ClO ₂ Ti _{0.5} ^a	C ₃₂ H ₂₄ O ₂ Ti	C ₂₀ H ₁₆ Cl ₂ Ti	C ₃₂ H ₃₂ SiTi
diffractometer	Siemens P4	Siemens P4	Enraf Nonius CAD 4	Enraf Nonius CAD 4
cryst color and form	red plates	red plates	red rhombohedron	red plates
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P21/n</i>	<i>C2/c</i>	<i>P21/c</i>
<i>a</i> [Å]	12.945(2)	11.055(7)	15.333(5)	8.6895(14)
<i>b</i> [Å]	17.144(3)	13.841(11)	10.4415(18)	23.235(3)
<i>c</i> [Å]	12.512(2)	15.851(17)	11.797(5)	12.4943(19)
α [deg]	90	90	90	90
β [deg]	91.560(10)	108.19(8)	122.49(3)	97.09(2)
γ [deg]	90	90	90	90
<i>Z</i> , <i>V</i> [Å ³]	8, 2775.9(7)	4, 2304(3)	4, 1593.2(9)	4, 2530.4(7)
cryst size [mm]	0.2 × 0.3 × 0.4	0.25 × 0.3 × 0.3	0.3 × 0.3 × 0.6	0.05 × 0.25 × 0.6
<i>T</i> [K], <i>d</i> _{calcd} [g/cm ³]	243, 1.242	193, 1.408	183, 1.564	183, 1.307
μ [mm ⁻¹], <i>F</i> (000)	0.527, 1072	0.401, 1016	0.868, 768	0.868, 768
scan mode, θ range [deg]	ω , 1.97–25.00	ω , 1.99–25.00	ω , 2.51–27.08	ω , 2.36–27.06
no. of reflns collected	2706	4990	1921	5927
no. of ind reflns (<i>R</i> _{int})	2279 (2.22%)	4035 (5.04%)	1749 (6.93%)	5467 (3.17%)
solution	direct	direct	direct	direct
refinement	Shelxl-93 ^b	Shelxl-97 ^b	Shelxl-97 ^b	Shelxl-97 ^b
no. of params, GOF (<i>F</i> ²)	145, 1.090	316, 1.007	137, 1.108	307, 1.008
<i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i> ²) ^c	5.97%, 16.85%	5.63%, 11.62%	4.58%, 11.83%	6.92%, 14.15%
weighting scheme (<i>a</i> , <i>b</i>) ^d	0.1125, 3.1876	0.0600, 0.7858	0.0842, 1.2532	0.0690, 2.4145
largest diff peak [e ⁻ /Å ³]	0.872	0.402	0.646	0.509
abs corr	Ψ-scan	Ψ-scan	Ψ-scan	Ψ-scan

^a One disordered molecule of hexane was found per Ti and refined with geometrical restraints. Due to the high disorder, H atoms were neglected. ^b G. Sheldrick, University of Göttingen, 1993 and 1997. ^c Observed data (*I* > 2σ(*I*)). ^d Weighting scheme: $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$.

twice with small amounts of toluene. The dark powder was dried in vacuo to yield 0.143 g (58%) of Me₂Si(2-Me-Benz[e]-ind)TiCl₂. Resolving of the complex in CH₂Cl₂, filtering the solution, and removing the solvent under vacuo yielded analytically pure complex. Anal. Calcd for C₃₀H₂₆Cl₂SiTi: C, 67.55; H, 4.91. Found: C, 67.54; H, 5.22. MS: 534 [M]⁺ (76%) 497 [M]⁺ – Cl (43%). ¹H NMR (δ in ppm, in CD₂Cl₂ as internal standard, 298 K, 600 MHz): 7.95 (d, 2H, ³*J*_{HH} = 7.70 Hz, 4,4'-benzind-*H*), 7.79 (d, 2H, ³*J*_{HH} = 7.53 Hz, 7,7'-benzind-*H*), 7.57 (m, 6H, 5,5'-, 6,6'-, 9,9'-benzind-*H*), 7.43 (s, 2H, 3,3'-benzind-*H*), 7.32 (d, 2H, ³*J*_{HH} = 9.20 Hz, 8,8'-benzind-*H*), 2.18 (s, 6H, 2-CH₃), 1.38 (s, 6H, Si-CH₃). ¹³C NMR (δ in ppm, in CD₂Cl₂ as internal standard, 298 K, 150 MHz): 137.7, 135.8, 133.6, 131.2, 130.2, 128.7, 128.6, 128.3, 128.1, 127.9, 125.4, 123.7, 88.7 (benz[e]ind-C); 19.8 (2-benz[e]ind-CH₃), 2.0 (–Si-CH₃).

UV/Vis, ¹H NMR, and EPR Measurements of Reaction Systems. UV/vis spectra of the reaction mixtures were recorded on a Cary 50 Varian spectrometer, using an immersion probe with fiber-optical light guide, placed in a specially designed Schlenk vessel. Absorbance values were corrected for dilution by the activator solutions added. ¹H NMR spectra were recorded in standard 5 mm NMR tubes on a Bruker AMX 250 MHz spectrometer. Typical operating conditions for ¹H NMR measurements: spectral width 5 kHz; spectrum accumulation frequency 0.2–0.5 Hz; number of transients 32–64. For calculations of ¹H chemical shifts, the residual solvent peaks were taken as 2.09 ppm (CHD₂ group of deuterated toluene) and 7.15 ppm (deuterated benzene), respectively. Samples for NMR and EPR measurements were prepared in standard 5 mm glass NMR tubes as follows: In a glovebox, the appropriate amount of Ti complex was dissolved in deuterated toluene or benzene, then weighed quantities of MAO or B(C₆F₅)₃ were added as solids. In the experiments with Al₂Me₆/[Ph₃C]⁺–[B(C₆F₅)₄][–], a toluene solution of Al₂Me₆ was added to the solution of the titanocene complex first, followed by solid [Ph₃C][B(C₆F₅)₄]. The samples were capped with rubber stoppers. The following ¹H NMR signals were used to identify and, where applicable, to quantify the cationic titanocene species discussed above.

[*rac*-C₂H₄(1-Ind)₂Ti(μ-Me)₂AlMe₂]⁺[Me-MAO][–]. ¹H NMR (C₆D₆, 20 °C, δ, ppm): 5.65 (2H, *J*_{HH} = 2.7 Hz, 3,3'-ind-*H*), 4.78 (2H, d, *J*_{HH} = 2.7 Hz, 2,2'-ind-*H*), 3.27 (4H, m, C₂H₄), –0.69 (6H, s, Al(CH₃)₂), –1.26 (6H, s, Ti-(μ-CH₃)-Al).

[*rac*-C₂H₄(1-Ind)₂Ti(μ-Me)₂AlMe₂]⁺[B(C₆F₅)₄][–]. ¹H NMR (C₆D₆, 20 °C, δ, ppm): 5.57 (2H, *J*_{HH} = 2.7 Hz, 3,3'-ind-*H*), 4.74 (2H, d, *J*_{HH} = 2.7 Hz, 2,2'-ind-*H*), 3.24 (m, 4H, C₂H₄), –0.76 (6H, s, Al-(CH₃)₂), –1.33 (6H, s, Ti-(μ-CH₃)-Al).

***rac*-Me₂Si(2-Me-Benzind)₂TiMe₂.** ¹H NMR (C₆D₆, 20 °C, δ, ppm): 8.02 (2H, d, 4,4'-benzind-*H*), 7.63 (2H, d, 7,7'-benzind-*H*), 7.54 (2H, s, 3,3'-benzind-*H*), 7.3–7.4 (4H, m, 5,5'- and 6,6'-benzind-*H*), 7.28 (2H, d, 8,8'- or 9,9'-benzind-*H*), 7.09 (2H, d, 8,8'- or 9,9'-benzind-*H*), 1.81 (6H, s, 2-CH₃), 0.68 (6H, s, Si-(CH₃)₂), –0.69 (6H, s, Ti-(CH₃)₂).

***rac*-Me₂Si(2-Me-Benzind)₂TiMe₂···MeB(C₆F₅)₃.** ¹H NMR (C₆D₆, 20 °C, δ, ppm): 7.88 (2H, d, 4,4'-benzind-*H*), 7.18 (2H, d, 7,7'-benzind-*H*), 7.27 (2H, s, 3,3'-benzind-*H*), 7.3–7.4 (4H, m, 5,5'- and 6,6'-benzind-*H*), 6.84 (2H + 2H, AB, 8,8'- and 9,9'-benzind-*H*), 1.46 (6H, s, 2-CH₃), 0.48 (6H, s, Si(CH₃)₂), 0.32 (3H, s, Ti-CH₃), –0.8 (3H, bs, B-(μ-CH₃)-Ti).

***rac*-Me₂Si(2-Me-Benzind)₂TiMe₂⁺B(C₆F₅)₄[–].** ¹H NMR (C₆D₆, 20 °C, δ, ppm): 1.42 (6H, s, 2-CH₃), 0.58 (6H, s, Si(CH₃)₂), 0.46 (3H, s, Ti-CH₃).

[*rac*-Me₂Si(2-Me-Benzind)₂Ti(μ-Me)₂AlMe₂]⁺[Me-MAO][–]. ¹H NMR (C₆D₆, 20 °C, δ, ppm): 7.83 (2H, d, 4,4'-benzind-*H*), 6.42 (2H, s, 3,3'-benzind-*H*), 1.56 (6H, s, 2-CH₃), 1.16 (6H, s, Si(CH₃)₂), –0.81 (6H, s, Al-CH₃), –1.72 (6H, s, Ti-(μ-CH₃)₂-Al).

[*rac*-Me₂Si(2-Me-Benzind)₂Ti(μ-Me)₂AlMe₂]⁺[B(C₆F₅)₄][–]. ¹H NMR (C₆D₆, 20 °C, δ, ppm): 7.74 (2H, d, 4,4'-benzind-*H*), 6.31 (2H, s, 3,3'-benzind-*H*), 6.92 (2H, d, 8,8'- or 9,9'-benzind-*H*), 1.42 (6H, s, 2-CH₃), 0.85 (6H, s, Si(CH₃)₂), –0.83 (6H, s, Al(CH₃)₂), –1.71 (6H, s, Ti-(μ-CH₃)₂-Al).

[*rac*-CH₂(1-Ind)₂Ti(μ-Me)₂AlMe₂]⁺[B(C₆F₅)₄][–]. ¹H NMR (C₆D₆, 20 °C, δ, ppm): 5.92 (2H, *J*_{HH} = 2.5 Hz, 3,3'-ind-*H*), 4.20 (2H, d, *J*_{HH} = 2.5 Hz, 2,2'-ind-*H*), 4.31 (2H, s, CH₂), –0.65 (6H, s, Al-(CH₃)₂), –1.65 (6H, s, Ti-(μ-CH₃)₂-Al).

EPR spectra were recorded at 25 °C on a Bruker ER-300D spectrometer. EPR signals were quantified by double integration using copper chloride as standard.

Crystal Structures. X-ray diffraction analyses were carried out on a Siemens P4 or an Enraf-Nonius CAD 4 diffractometer using Mo K α radiation (71.073 pm) and a graphite monochromator. Crystal decay was monitored by measuring three standard reflections every 100 reflections. Details of the X-ray diffraction analysis are given in Table 6. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre

as supplementary publications CCDC 230670, 230738, 230750, and 230753.

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