Nine-Membered Titanacyclic Complexes Based on an Ethylene-Bridged Bis(phenolato) Ligand: Synthesis, Structure, and Olefin Polymerization Activity

Stefan Fokken, Thomas P. Spaniol, and Jun Okuda*

Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität Mainz, J.-J.-Becher-Weg 24, D-55099 Mainz, Germany

Fritz G. Sernetz and Rolf Mülhaupt

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Received May 19, 1997[⊗]

Summary: Tetravalent titanium complexes containing the ethylene-linked bis(phenolato) ligand ebmp exhibit a C_2-symmetric conformation according to single-crystal X-ray structural analyses. In solution, a fluxional process equivalent to an enantiomerization is detected. Upon activation with methylaluminoxane, these complexes copolymerize ethylene and styrene with remarkably high incorporation of styrene.

Chiral *ansa*-metallocenes of early transition metals and lanthanides based on linked bis(cyclopentadienyl) ligands such as Brintzinger's ethylenebis(tetrahydroindenyl)[1] have gained enormous importance as homogeneous catalyst precursors for stereospecific α-olefin polymerizations.[2] More recently, chelating bis(amido)[3] and bis(phenoxo)[4] ligands have attracted much attention as ancillary ligand frameworks for group 4 metal centers. Such ligands not only are more easily accessible than cyclopentadienyl ligands but the complexes derived therefrom also allow novel types of α-olefin polymerizations: McConville et al., for example, reported the first example of a room-temperature living α-olefin polymerization using Ti(RNCH$_2$CH$_2$CH$_2$NR)X$_2$ (R = 2,6-diisopropylphenyl).[3c] According to Kakugo et al., alternating copolymerization of ethylene with styrene became possible when methylaluminoxane-activated Ti(tbmp)Cl$_2$ (tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato)) was employed.[4] Related complexes of the type Ti(mbmp)X$_2$ (mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)), on the other hand, were known to show only low activity, at least partially due to the peculiar rigid ligand structure that blocks one segment of the coordination sphere.[5] We report here that the ethylene-linked bis(phenolato) ligand ebmp derived from 2,2′-ethylenebis(6-*tert*-butyl-4-methylphenol) (ebmpH$_2$) constitutes a new supporting ligand system for monomeric tetravalent titanium centers and present preliminary results concerning the synthesis and structure of the ebmp complexes of titanium in the context of their polymerization properties.

The ethylene-linked bis(phenol) ebmpH$_2$ is prepared by the coupling reaction of the acetyl-protected α-bromo-*o*-cresol with magnesium/cuprous chloride in diethyl ether and isolated as colorless crystals in 15% yield.[6] In analogy with related bulky linked bis(phenols) mbmpH$_2$[5] and tbmpH$_2$,[4] ebmpH$_2$ undergoes smooth reaction with a variety of simple titanium precursors. Thus, titanium tetrachloride gives orange Ti(ebmp)Cl$_2$ and titanium tetraisopropoxide gives pale yellow Ti(ebmp)(O*i*Pr)$_2$, respectively, both in excellent yields (Scheme 1).[6] Both compounds are assumed to be monomeric in solution.[7]

When Ti(ebmp)(O*i*Pr)$_2$ is treated with SiMe$_3$X (X = Br, I), the dark brown dibromo and diiodo derivatives Ti(ebmp)X$_2$ are obtained in 91 and 85% yields, respectively. The single-crystal X-ray structural analysis of the dibromo complex Ti(ebmp)Br$_2$ confirms the monomeric structure (Figure 1).[8] A C_2-symmetric nine-membered metallacyclic system with almost coplanar phenyl rings linked by a skewed ethylene bridge is observed. The formally eight-electron titanium center is tetrahedrally coordinated. The comparatively short titanium−oxygen bond distances of 1.754(4) and 1.747(4) Å and the large angles of 163.5(3) and 161.0(3)° at the oxygen atoms suggest the presence of a pronounced pπ−dπ interaction.[9]

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

(1) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

(2) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem.* **1995**, *107*, 1255. (b) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (c) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, 1995.

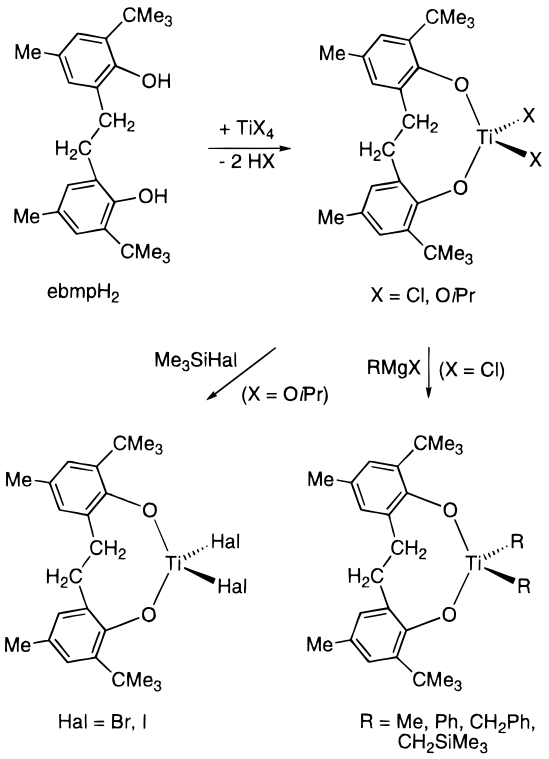
(3) (a) Canich, J. M.; Turner, H. W. PCT Int. Appl. WO 92/12612. (b) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343. Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333. (c) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478. Guerin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154. (d) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, 118, 10008. (e) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. Horton, A. D.; de With, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1375. (f) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562. Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, 119, 3830.

(4) (a) Kakugo, M.; Miyatake, T.; Mizunuma, K. *Chem. Express* **1987**, *2*, 445. (b) Miyatake, T.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 349. (c) Miyatake, T.; Mizunuma, K.; Kakugo, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203. (d) Schaverien, C. J.; van der Linden, A. J.; Orpen, A. G. *Am. Chem. Soc., Polym. Div., Polymer Prepr.* **1994**, *35*, 672. Schaverien, C. J.; van der Linden, A. J.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (e) Fokken, S.; Spaniol, T. P.; Kang, H. C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069. Porri, L.; Ripa, A.; Colombo, P., Moano, E.; Capelli, S.; Meille, S. V. *J. Organomet. Chem.* **1996**, *514*, 213.

(5) (a) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem.* **1989**, *101*, 93; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 146. (c) Okuda, J.; Fokken, S.; Kang., H.-C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221. (d) Schermerhorn, E. J. Master's Thesis, State University of New York at Albany, 1993. (e) Fokken, S. Ph.D. Thesis, University of Marburg, 1997.

S0276-7333(97)00410-X CCC: $14.00

Scheme 1



Analytical and ^{1}H and ^{13}C NMR spectroscopic as well as mass spectral data are consistent with a monomeric structure for Ti(ebmp)X_2 that possesses equivalent halves of the bis(phenolato) ligands. However, the four protons of the ethylene bridge are either a broad signal or two AB spin systems, depending on the ligand X as well as on the temperature. The variable-temperature NMR spectra for the dibromo complex, for example, reveal a fluxional process that can be described as an inversion of the nine-membered ring. While at 60 °C only one singlet at δ 2.71 is observed for all four protons of the C_2H_4 bridge, lowering the temperature results in the decoalescence (T_c = 30 °C) and in an AB spin multiplet signal set below 0 °C. The activation barrier for this process was found to be $\Delta G^{\ddagger} = 60.4(2)$ kJ mol^{-1}. Although somewhat dependent on the nature of the ligand X, the $\Delta G^{\ddagger}$ values for the ring inversion are in the range of 60 kJ mol^{-1}. Such a process, which is equivalent to an enantiomerization of the chiral complex, is well-known in simple organic heterocyclic compounds.[10] Evidently, the nine-membered ring of Ti(ebmp)X_2 is not conformationally rigid at ambient temperatures (eq 1).

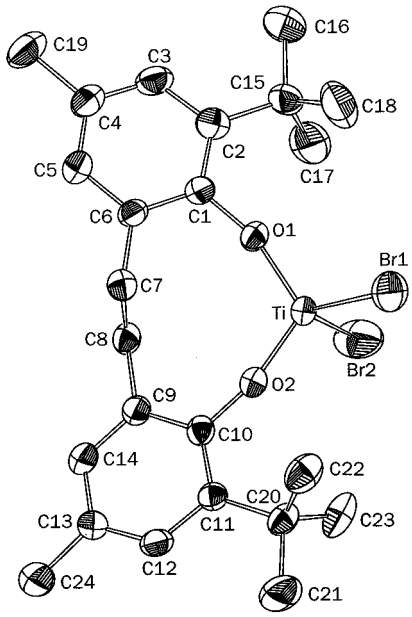


Figure 1. ORTEP diagram of the molecular structure of Ti(ebmp)Br_2. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (pm) and bond angles (deg): Ti−O1, 175.4(4); Ti−O2, 174.7(4); Ti−Br1, 237.2(2); Ti−Br2, 236.3(2); O1−Ti−O2, 114.3(2); Br1−Ti−Br2, 109.80; C1−O2−Ti, 163.5(3); Ti−O2−C10, 161.0(3).

Alkyl groups such as Me, CH_2SiMe_3, CH_2Ph, and Ph can be straightforwardly introduced by the reaction of the dichloro complex with Grignard reagents. Analytical and NMR spectroscopic data of the crystalline complexes are consistent with a mononuclear structure of the composition Ti(ebmp)R_2.[11a] The fluxional behavior due to the ring inversion is also detectable. A single-

(6) (a) ebmpH_2: ^{1}H NMR ($CDCl_3$, 25 °C) δ 1.43 (s, 18 H, 6-C(CH_3)$_3$), 2.26 (s, 6 H, 4-CH_3), 2.78 (s, 4 H, 2-CH_2), 5.60 (s, 2 H, OH), 6,85 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 3-H), 6.97 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 5-H); ^{13}C NMR ($CDCl_3$, 25 °C) δ 20.8 (4-CH_3), 30.1 (6-C(CH_3)$_3$), 32.3 (2-CH_2), 34.2 (6-*C*(CH_3)$_3$), 125.9 (C-5), 128.2 (C-2), 128.5 (C-3), 129.2 (C-4), 135.5 (C-6), 150.3 (C-1); EI MS *m*/*z* 354 (22%, M^+), 177 (100%, $[M/2]^+$). Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.17; H, 9.64. (b) Ti(ebmp)Cl_2: titanium tetrachloride (3.0 mL, 27.4 mmol) was added to a stirred solution of ebmpH_2 (9.70 g, 27.4 mmol) in 20 mL of hexane. Within 3 min precipitation of the orange product started and was completed by stirring for 3 h, followed by cooling to −18 °C overnight; 94% yield. ^{1}H NMR ($CDCl_3$, 25 °C) δ 1.59 (s, 18 H, 6-C(CH_3)$_3$), 2.34 (s, 6 H, 4-CH_3), 2.78 (s, 4 H, 2-CH_2), 6.99 (d, $^4J_{HH}$ = 1.7 Hz, 2 H, 3-H), 7.03 (d, $^4J_{HH}$ = 1.7 Hz, 2 H, 5-H); ^{13}C NMR ($CDCl_3$, 25 °C): δ 21.3 (q, $^1J_{CH}$ = 126.4 Hz, 4-CH_3), 30.7 (q, $^1J_{CH}$ = 126.1 Hz, 6-C(*C*H_3)$_3$), 33.3 (s, 6-*C*(CH_3)$_3$), 35.1 (t, $^1J_{CH}$ = 135.5 Hz, 2-CH_2), 125.5 (d, $^1J_{CH}$ = 156.5 Hz, C-3), 128.4 (d, $^1J_{CH}$ = 154.5 Hz, C-5), 134.4 (s, C-2), 134.6 (s, C-4), 137.6 (s, C-6), 167.2 (s, C-1); EI MS *m*/*z* 470 (68%, M^+), 455 (60%, $[M - CH_3]^+$), 419 (34%, $[M - CH_4 - Cl]^+$), 220 (17%, $[M - 2\ CH_3]^{2+}$), 207 (11%), 192 (11%), 57 (100%, $[C_4H_9]^+$). Anal. Calcd for $C_{24}H_{32}Cl_2O_2Ti$: C, 61.16; H, 6.84. Found: C, 61.06; H, 6.88. (c) Ti(tbmp)(O*i*Pr)$_2$: 98% yield; ^{1}H NMR ($CDCl_3$, 25 °C) δ 1.28 (d, $^3J_{HH}$ = 6.1 Hz, 12 H, OCH(*CH*$_3$)$_2$, 1.51 (s, 18 H, 6-C(*CH*$_3$)$_3$), 2.30 (s, 6 H, 4-CH_3), 2.77 (s, broad, 4 H, 2-CH_2), 4.71 (septet, $^3J_{HH}$ = 6.1 Hz, 2 H, O*CH*(CH_3)$_2$, 6.91 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 5-H), 6.98 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 3-H); ^{13}C NMR ($CDCl_3$, 25 °C) δ 21.0 (q, $^1J_{HH}$ = 126.1 Hz, 4-CH_3), 26.4 (q, $^1J_{HH}$ = 126.1 Hz, OCH(*CH*$_3$)$_2$), 30.2 (q, $^1J_{HH}$ = 125.7 Hz, 6-C(*CH*$_3$)$_3$), 33.9 (t, $^1J_{HH}$ = 124.7 Hz, 2-CH_2), 34.8 (s, 6-*C*(CH_3)$_3$), 80.0 (d, $^1J_{HH}$ = 144.6 Hz, O*CH*(CH_3)$_2$), 125.3 (d, $^1J_{HH}$ = 155.0 Hz, C-3), 128.1 (d, $^1J_{HH}$ = 157.2 Hz, C-5), 129.4 (s, C-2), 132.0 (s, C-4), 136.7 (s, C-6), 160.7 (s, C-1); EIMS *m*/*z* 518 (100%, M^+), 503 (2%, $[M - CH_3]^+$), 461 (1%, $[M - C_4H_9]^+$), 458 (4%, $[M - HOC_3H_7]^+$), 443 (8%, $[M - HOC_3H_7 - CH_3]^+$), 202 (18%, $[M - 2\ C_4H_9]^{2+}$), 187 (36%, $[M - 2\ C_4H_9 - 2\ CH_3]^{2+}$). Anal. Calcd for $C_{30}H_{46}O_4Ti$: C, 69.48; H, 8.94. Found: C, 69.43; H, 8.91.

(7) In contrast to Ti(tbmp)(O*i*Pr)$_2$ and Ti(mbmp)(O*i*Pr)$_2$ as well as other related complexes, Ti(ebmp)(O*i*Pr)$_2$ is monomeric in the crystal according to an X-ray structural analysis.[5e]

(8) Crystal data for Ti(ebmp)Br_2: $C_{24}H_{32}Br_2O_2Ti$, M_r = 560.2, 0.50 × 0.30 × 0.10 mm, triclinic, *P*1 (No. 2), *a* = 928.8(3) pm, *b* = 1151.2(4) pm, *c* = 1311.8(8) pm, α = 101.61(4)°, β = 104.77(4)°, γ = 102.80(3)°, *V* = 1.272(1) nm^3, *Z* = 2, ρ_{calcd} = 1.462 Mg m^{-3}, Mo Kα (λ = 71.070 pm), empirical absorption correction, *T* = 296(2) K, ω-scans, 3° < θ < 30°, *F*(000) = 568, μ(Mo Kα) = 3.49 mm^{-1}, number of reflections measured 7795, 7372 independent reflections. The structure was solved (direct methods) and refined against all F^2 data, resulting in R = 0.0687 and wR2 = 0.1152 for 3524 observed reflections with $I > 2\sigma(I)$.

(9) (a) Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1966**, *5*, 1782. (b) Svetich, G. W.; Voge, A. A. *J. Chem. Soc. D* **1971**, 676. (c) Toth, R.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 172. (d) Boyle, T. J.; Eilerts, N. W.; Heppert, J. A.; Takusagawa, F. *Organometallics* **1994**, *13*, 2218. (e) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F. *Organometallics* **1992**, *11*, 1112. (f) Yasuda, H.; Nakayama, Y.; Takei, K.; Nakamura, A.; Kai, Y.; Kanehisa, N. *J. Organomet. Chem.* **1994**, *473*, 105. (g) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

(10) Dunitz, J. D. *Pure Appl. Chem.* **1971**, *25*, 495. *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: New York, 1988.

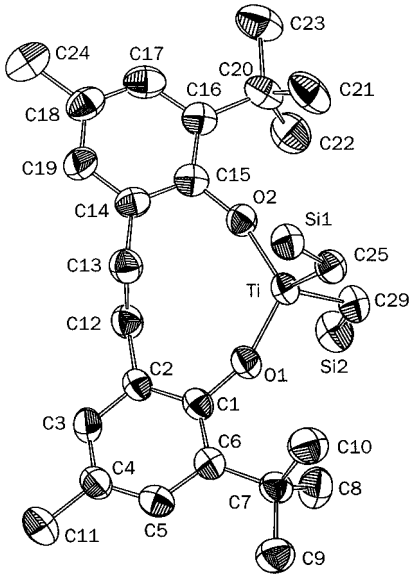
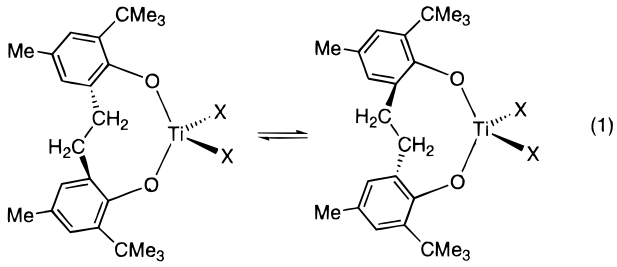


Figure 2. ORTEP diagram of the molecular structure of Ti(ebmp)(CH_2SiMe_3)$_2$. Thermal ellipsoids are drawn at the 50% probability level. Methyl groups at the silicon atoms and hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (pm) and bond angles (deg): Ti−O1, 178.4(3); Ti−O2, 178.6(3); Ti−C25, 207.3(4); Ti−C29, 206.7(4); C25−Si1, 186.3(4); C29−Si2, 186.3(5); O1−Ti−O2, 120.8(1); C25−Ti−C29, 106.7(2); Ti−O1−C1, 158.9(3); Ti−O2−C15, 158.9(3); Ti−C25−Si1, 122.1(2); Ti−C29−Si2, 121.7(2).



crystal X-ray structural analysis of Ti(ebmp)(CH_2SiMe_3)$_2$ confirmed the structure to have a tetrahedral titanium center (Figure 2).[11b] The C_2-symmetric complex reveals a quite remarkable conformation in which the bulky $SiMe_3$ groups of the two alkyl ligands are strongly bent *toward* the ethylene bridge. If crystal-packing effects can be neglected, we can ascribe this conformation to the steric constraint caused by the two *tert*-butyl groups of the ebmp ligand.[12]

Table 1. Comparison of Various Titanium Bis(phenolato) Complexes in the Copolymerization of Ethylene with Styrene[a]

catalyst	activity, g of polymer/((mol of Ti) h (mol/L))	styrene content, mol %
Ti(tbmp)Cl_2	82000	6.0
Ti(tbmp)(O*i*Pr)$_2$	109000	5.5
Ti(mbmp)Cl_2	1000	*b*
Ti(sibmp)(O*i*Pr)$_2$[c]	10000	10.0
Ti(ebmp)Cl_2	1000	36.4
Ti(ebmp)(O*i*Pr)$_2$	1000	35.2

[a] Polymerization conditions: reaction in 200 mL of dry toluene, $c_{styrene}$ = 1.1 mol/L, $p_{ethylene}$ = 2.56 bar, $c_{ethylene}$ = 0.22 mol/L, 100 μmol of catalyst, reaction temperature 60 °C, reaction time 1 h.[13] [b] No copolymer, mixture of polyethylene and polystyrene. [c] sibmp = 2,2′-sulfinylbis(6-*tert*-butyl-4-methylphenolato).[5e,15]

Our preliminary studies showed that complexes of the type Ti(ebmp)X_2 are active toward ethylene and syndiospecific styrene polymerization upon treatment with excess methylaluminoxane.[13] The productivity values for these polymerizations are comparable to those using Ti(mbmp) complexes.[4c,d] However, we found that in the copolymerization of ethylene with styrene, Ti(ebmp)X_2 species show unusually high incorporation of styrene when compared with related linked bis(phenolato) complexes of titanium (Table 1).[13] The significantly more open coordination sphere around the titanium center containing the ebmp ligand apparently results in a higher incorporation of styrene monomer. During the copolymerization of ethylene with styrene, the bulky monomer styrene is notoriously difficult to incorporate.[13,14] We believe that there is further opportunity to rationally design polymerization catalysts based on linked metal bis(phenolato) complexes.

Acknowledgment. Generous financial support by the Volkswagen-Foundation, the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Grant No. SFB 260), the German Ministry for Science and Technology (Project No. 03M40719), and BASF AG (Kunststofflaboratorium) is gratefully acknowledged. F.G.S. thanks the Studienstiftung des Deutschen Volkes for a predoctoral fellowship.

Supporting Information Available: Listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for Ti(ebmp)Br_2 and Ti(ebmp)(CH_2SiMe_3)$_2$ (12 pages). Ordering information is given on any current masthead page.

OM9704105

(11) (a) Ti(ebmp)(CH_2SiMe_3)$_2$: A solution of ((trimethylsilyl)methyl)-magnesium chloride in diethyl ether (1.22 mL of a 1 M solution) was added to a stirred solution of (ebmp)$TiCl_2$ (576 mg, 1.22 mmol) in 15 mL of diethyl ether at −78 °C. After it was warmed to room temperature and stirred for an additional 4 h, the bright yellow reaction mixture was evaporated to dryness and extracted with 2 × 10 mL of pentane. When the extracts were cooled, light yellow crystals were obtained in two crops in 72% yield: ^{1}H NMR ($CDCl_3$, 25 °C) δ −0.19 (s, 18 H, Si(CH_3)$_3$), 1.80 (s, 18 H, 6-C(CH_3)$_3$), 2.10 (m, 4 H, 2-CH_2, TiCH_2), 2.31 (s, 6 H, 4-CH_3), 2.43 (m, 4 H, 2-CH_2, TiCH_2), 6.93 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 3-H), 7.08 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 5-H); ^{13}C NMR ($CDCl_3$, 25 °C) δ 2.1 (q, $^1J_{CH}$ = 118.2 Hz, Si(CH_3)$_3$), 21.1 (q, $^1J_{CH}$ = 126.4 Hz, 4-CH_3), 31.0 (q, $^1J_{CH}$ = 125.9 Hz, 6-C(CH_3)$_3$), 33.1 (t, $^1J_{CH}$ = 125.7 Hz, 2-CH_2), 35.3 (s, 6-*C*(CH_3)$_3$), 85.1 (t, $^1J_{CH}$ = 111.2 Hz, Ti-CH_2), 125.7 (d, $^1J_{CH}$ = 155.5 Hz, C-5), 128.5 (d, $^1J_{CH}$ = 155.5 Hz, C-3), 130.8 (s, C-4), 132.9 (s, C-2), 136.6 (s, C-6), 161.4 (s, C-1); EIMS *m*/*z* 574 (16%, M^+), 559 (5%, $[M - CH_3]^+$), 487 (20%, $[M - CH_2SiMe_3]^+$), 399 (100%, $[M - CH_2SiMe_3 - SiMe_4]^+$), 73 (92%, $[CH_2SiMe_3]^+$). Anal. Calcd for $C_{32}H_{54}Si_2O_2Ti$: C, 66.86; H, 9.47. Found: C, 65.41; H, 9.91. (b) Crystal data for Ti(ebmp)(CH_2SiMe_3)$_2$: $C_{32}H_{54}O_2Si_2Ti$, M_r = 574.8, 0.60 × 0.60 × 0.90 mm, orthorhombic, *Pbca* (No. 61), *a* = 2470.8(9) pm, *b* = 2470.8(5) pm, *c* = 1152.8(2) pm, *V* = 7.038(3) nm^3, *Z* = 8, ρ_{calcd} = 1,085 Mg m^{-3}, Mo Kα (λ = 71.070 pm), *T* = 296(2) K, ω-scans, 3° < θ < 30°, *F*(000) = 2496, μ(Mo Kα) = 0.335 mm^{-1}, number of reflections measured 13 511, 10 244 independent reflections. The structure was solved (direct methods) and refined against all F^2 data, resulting in *R* = 0.0772 and wR2 = 0.0947 for 3934 observed reflections with $I > 2\sigma(I)$.

(12) A similar conformation of two CH_2SiMe_3 ligands is observed in the *ansa*-titanocene derivative: Gomez, R., Cuenca, T.; Royo, P.; Herrmann, W. A.; Herdtweck, E. *J. Organomet. Chem.* **1990**, *382*, 103.

(13) Sernetz, F. G.; Mülhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562. Sernetz, F. G. Ph.D. Thesis, University of Freiburg, 1996.

(14) Only with the use of cyclopentadienylmetal complexes did an efficient copolymerization of ethylene with styrene become feasible: Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, *29*, 1158. Amor, F.; Eberle, T.; Okuda, J. *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 1571. Xu, G.; Lin, S. *Macromolecules* **1997**, *30*, 685.

(15) Okuda, J.; Fokken, S.; Kang., H.-C.; Massa, W. *Polyhedron*, in press.