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A Novel Phenolate "Constrained Geometry" Catalyst System. Efficient Synthesis, Structural Characterization, and α-Olefin Polymerization Catalysis

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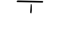
This paper reports the convenient "one-pot" synthesis of a bifunctional $^{-}\mathrm{Me_4Cp}\frown\mathrm{phenolate}^{-}$ ligand and the efficient "one-step" synthesis of the corresponding $\mathrm{Ti^{IV}}$ and $\mathrm{Zr^{IV}}$ complexes. The reaction of 2-bromo-4-methylphenol with 2 equiv of ^{n}BuLi followed by addition of 2,3,4,5-tetramethyl-2-cyclopentenone produces the bifunctional mono-Cp phenol ligand precursor 2-(tetramethylcyclopentadienyl)-4-methylphenol ((TCP)H_2, **1**). Reaction of **1** with $Ti(CH_2Ph)_4$ at 60 °C in toluene cleanly generates (TCP)$Ti(CH_2Ph)_2$ (**2**), while the corresponding reaction with $Zr(CH_2Ph)_4$ at higher temperatures affords the chelated C_2-symmetric zirconocene $(TCP)_2Zr$ (**3**). In solution at room temperature, the two benzyl groups of **2** are magnetically equivalent, however, in the solid state, X-ray diffraction reveals that one benzyl group is coordinated in a normal η^1-fashion and the other in an η^2-mode. The small Cp-(centroid)−Ti−O angle of 107.7(2)° in **2** indicates sterically open features in common with amido-based "constrained geometry" polymerization catalysts. Low-temperature NMR-scale reactions of **2** with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ indicate the formation of the corresponding cationic complexes $(TCP)TiCH_2Ph^+\ PhCH_2B(C_6F_5)_3^-$ (**4**) and $(TCP)TiCH_2Ph^+B(C_6F_5)_4^-$ (**5**). Upon activation with $Ph_3C^+B(C_6F_5)_4^-$, complex **2** is highly active for ethylene, propylene, and styrene polymerization.

Introduction

Ligand modifications have played a key role in developing new "single-site" group 4 metallocene catalyst precursors for optimizing polymerization activity as well as polymer properties such as stereoregularity, molecular weight, thermal/rheological characteristics, bulky and polar comonomer incorporation, and microstructure.[1] In particular, complexes of bifunctional monocyclopentadienyl ligands having an appended heteroatom donor have attracted considerable attention,[2] as exemplified by "constrained geometry" catalysts having the formula $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)MX_2$ (**CGCMX$_2$**; M = Ti, Zr, Hf; X = Cl, Me, CH_2Ph).[3] These catalysts have a convalently attached amide donor ligand which stablizes the electrophilic metal center electronically, while the short $Me_2Si<$ bridging group considerably opens the metal coordination sphere vis-à-vis a conventional metallocene. The result upon activation with a variety of cocatalysts is a new generation of catalysts which, among other features, efficiently produce ultra-low-density elastomeric ethylene−octene copolymers.[3c]



CGCMX$_2$; M = Ti, Zr, Hf; X = Cl, Me, CH_2Ph

Given the impact of the Cp-appended heteroatom donor groups on the catalytic performance of such complexes, ligand design remains a very active and challenging area of olefin polymerization research, and much attention has been focused on the design of new N-[2,4] and O-containing ligands.[2,5] In addition, developing more efficient syntheses of useful ligands as well as of the corresponding metal complexes has attracted

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[1] For recent reviews, see: (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144−187. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (c) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (d) *Catalyst Design for Tailor-Made Polyolefins*; Soga, K., Terano, M., Eds.; Elsevier: Tokyo, 1994. (e) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29. (f) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65. (g) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387.

[2] For reviews, see: (a) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175. (b) Okuda, J. *Comm. Inorg. Chem.* **1994**, *16*, 185−205.

[3] (a) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649−3657. (b) Fu, P.-F.; DiBella, S.; Wilson, D. J.; Rudolph, P. R.; Fragala, I. L.; Stern, C. L.; Marks, T. J. Submitted for publication. (c) Stevens, J. C. In *Studies in Surface Science and Catalysis*; Hightower, J. W., Delglass, W. N., Iglesia, E., Bell, A. T., Eds.; Elsevier: Amsterdam, 1996; Vol. 101, pp 11−20 and references therein. (d) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623 (e) Canich, J. M.; Hlatky, G. G.; Turner, H. W. PCT Appl. WO 92-00333, 1992. Canich, J. M. Eur. Patent Appl. EP 420 436-A1, 1991 (Exxon Chemical Co.). (f) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Patent Appl. EP 416 815-A2, 1991 (Dow Chemical Co.).

[4] For recent examples, see: (a) Amor, F.; Okuda, J. *J. Organomet. Chem.* **1996**, *520*, 245−248. (b) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789−795. (c) Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287. (d) Flores, J.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140. (e) Herrmann, W. A.; Morawietz, M. J. A. *J. Organomet. Chem.* **1994**, *482*, 169. (f) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (g) Piers, W. E.; Shapiro, P. J.; Bunnel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74. (h) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

[5] For recent examples, see: (a) van der Zeijden, A. A. H.; Matteis, C. *Organometallics* **1997**, *16*, 2651. (b) Trouve, G.; Laske, D. A.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.* **1996**, *511*, 255. (c) Christoffers, J.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2266. (d) Huan, Q.; Qian, Y.; Li, G.; Tang, Y. *Transition Met. Chem.* **1990**, *15*, 483.

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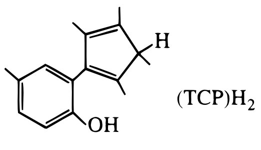
both scientific and technological interest.[3a,6] In view of the importance of the aforementioned issues, we report here a convenient "one-pot" synthesis of a new bifunctional mono-Cp ligand containing an appended phenolate group (ligand **1**; $(TCP)H_2$) as well as efficient one-step syntheses of the corresponding C_s-symmetric Ti and chiral C_2-symmetric Zr complexes.[7] Attractive features of the new ligand system include a simple synthetic procedure as well as great intrinsic steric and electronic flexibility introducible via modification of the aryl fragment. We also report the solution and solid state structure, cocatalyst abstraction/activation chemistry, and the performance in olefin polymerization of the Ti dibenzyl complex.



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Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum line (10^{-6} Torr) or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (<1 ppm O_2). Argon, hydrogen (Matheson, prepurified), ethylene, and propylene (Matheson, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Ether solvents were purified by distillation from Na/K alloy/benzophenone ketyl. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from Na/K alloy. All solvents for high-vacuum line manipulations were stored *in vacuo* over Na/K alloy in Teflon-valved bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all ≥99 atom %D), freeze−pump−thaw degassed, dried over Na/K alloy, and stored in resealable flasks. Other non-halogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from P_2O_5 and stored over activated Davison 4A molecular sieves. C_6F_5Br (Aldrich) was vacuum distilled from P_2O_5. Styrene (Aldrich) was dried over CaH_2 and vacuum-transferred into a storage tube containing activated 4A molecular sieves. $TiCl_4$, $ZrCl_4$, $PhCH_2MgCl$ (1.0 M in diethyl ether), ^nBuLi (1.6 M in hexanes), 2-bromo-4-methylphenol, and 2,3,4,5-tetramethyl-2-cyclopentenone were purchased from Aldrich. $Ti(CH_2Ph)_4$,[8] $Zr(CH_2Ph)_4$,[8] $B(C_6F_5)_3$,[9] and $Ph_3C^+B(C_6F_5)_4^-$ [10a] were prepared and purified according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either Varian VXR 300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C) or Germini-300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) instruments. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances and are reported relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external $CFCl_3$. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J. Young). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. ^{13}C NMR assays of polymer microstructure were conducted in $C_2D_2Cl_4$ at 120 °C. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. GPC analyses of polymer samples were performed at L. J. Broutman & Associates Ltd., Chicago, on a Waters 150C GPC relative to polystyrene standards.

One-Pot Synthesis of 2-(Tetramethylcyclopentadienyl)-4-methylphenol, $(TCP)H_2$ (1). Into a 1 L Schlenk flask were charged 50.0 g (267 mmol) of 2-bromo-4-methylphenol and 250 mL of THF, and then 350 mL of ^nBuLi (560 mmol, 1.6 M in hexanes) was added dropwise with stirring at 0 °C. A white precipitate formed, and the resulting mixture was allowed to warm to room temperature and stirred for another 2 h. The solution was next cooled to −78 °C, and 2,3,4,5-tetramethyl-2-cyclopentenone (40.2 mL, 36.9 g, 267 mmol) was added dropwise over 30 min. The resulting solution was then allowed to warm to room temperature and stirred overnight. The reaction mixture was next treated with 20 mL of water followed by 120 mL of concentrated HCl. The organic layer was separated and treated 3 times with 40 mL of concentrated HCl. Volatiles were removed by rotary evaporation, and the oily residue was distilled under vacuum at 150 °C/15 Torr to yield 28.5 g of the title ligand as a dark brown crystalline solid. Yield: 46.8%. ^1H NMR (C_6D_6, 23 °C): δ 6.88 (s, 1 H, Ar), 6.78 (m, 2 H, Ar), 3.00 (s, 1 H, OH), 2.50 (q, $J_{H-H} = 6.6$ Hz, 1 H, Cp−H), 2.18 (s, 3 H, $Ar-CH_3$), 1.63 (s, 3 H, $Cp-CH_3$), 1.48 (s, 3 H, $Cp-CH_3$), 1.28 (s, 3 H, $Cp-CH_3$), 1.00 (d, $J_{H-H} = 7.2$ Hz, 3 H, $Cp-CH_3$). ^{13}C NMR (C_6D_6, 23 °C): δ 157.11, 138.57, 132,-63, 129.18, 129.00, 125.40 (Ar), 109.88, 101.36, 58.37, 51.40 (Cp), 24.86 ($Ar-CH_3$), 21.00, 20.45, 12.27, 9.63 ($Cp-CH_3$). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.37; H, 8.94.

One-Step Synthesis of $(TCP)Ti(CH_2Ph)_2$ (2). $Ti(CH_2Ph)_4$ (1.01 g, 2.40 mmol), $(TCP)H_2$ (0.46 g, 2.0 mmol), and 50 mL of toluene were heated with stirring at 60−65 °C for 30 h in the absence of light. The solvent was removed *in vacuo*, and the black residue was extracted with 50 mL of pentane. The pentane extracts were then filtered, and the solvent was removed from the filtrate under vacuum. The resulting crude product was washed with 5 mL of cold pentane and dried to produce 0.46 g of the pure product as a brown solid. Yield: 50.4%. The product is very soluble in pentane. ^1H NMR (C_6D_6, 23 °C): δ 7.13 (d, $J_{H-H} = 7.5$ Hz, 4 H, Ph), 7.04 (d, $J_{H-H} = 7.5$ Hz, 4 H, Ph), 6.89 (d, $J_{H-H} = 8.1$ Hz, 2 H, Ar), 6.83 (t, $J_{H-H} = 7.5$ Hz, 2 H, Ph), 6.59 (d, $J_{H-H} = 7.5$ Hz, 1 H, Ar), 2.50 (d, $J_{H-H} = 10.2$ Hz, 2 H, CH_2Ph), 2.32 (d, $J_{H-H} = 10.2$ Hz, 2 H, CH_2Ph), 2.11 (s, 3 H, $Ar-CH_3$), 1.90 (s, 6 H, C_5Me_4), 1.44 (s, 6 H, C_5Me_4). ^{13}C NMR (C_6D_6, 23 °C): δ 170.71, 147.87, 136.73, 130.50, 130.00, 129.76, 128.70 (Ar, Ph), 123.07, 121.18, 114.00 (Cp), 83.85 (t, $J_{C-H} = 127.5$ Hz, CH_2Ph), 20.73 ($Ar-CH_3$), 11.49 (C_5Me_4), 11.25 (C_5Me_4). Anal. Calcd for $C_{30}H_{32}OTi$: C, 78.93; H, 7.09. Found: C, 78.67; H, 6.83.

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[6] (a) Tsuie, B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1997**, *16*, 1392−1400. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720−2726. (c) Diamond, G. M.; Jordan; R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024−8033. (d) Diamond, G. M.; Jordan; R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030−4037; *Ibid.* 4038−4044; *Ibid.* 4045−4053. (e) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572−1581. (f) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 377. (g) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008−3021. (h) Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1946. (i) Nickias, P. N.; Devore, D. D.; Wilson, D. R. PCT Appl. WO 08199, 1993.

[7] Communicated in part previously, see: Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Abstracts of Papers*, 213th National Meeting of the American Society, San Francisco, CA, April 13−17, 1997; American Chemical Society: Washington, DC, 1997; INOR 676.

[8] Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357−372.

[9] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250.

[10] (a) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571. (b) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840−842. (c) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. 426637, 1991; *Chem. Abstr.* **1991**, *115*, 136987c, 136988d. (d) Hlatky, G. G.; Upton, D. J.; Turner, H. W. U.S.Pat. Appl. 459921, 1990; *Chem. Abstr.* **1991**, *115*, 256897v.

One-Step Synthesis of (TCP)$_2$Zr (3). Zr(CH$_2$Ph)$_4$ (2.10 g, 4.60 mmol), (TCP)H$_2$ (0.840 g, 3.68 mmol), and 50 mL of toluene were heated with stirring at 110 °C for 12 h in the absence of light. Using the same work-up procedure as in the synthesis of (TCP)Ti(CH$_2$Ph)$_2$ above, 0.35 g of the title complex was isolated as a colorless crystalline solid. Yield: 35.0%. ^{1}H NMR (C$_6$D$_6$, 23 °C): δ 7.07 (d, $J_{\mathrm{H-H}} = 2.1$ Hz, 2 H, Ar), 7.01 (dd, $J_{\mathrm{H-H}} = 7.8$ Hz, $J_{\mathrm{H-H}} = 2.1$ Hz, 2 H, Ar), 6.73 (d, $J_{\mathrm{H-H}} = 8.4$ Hz, 2 H, Ar), 2.25 (s, 6 H, Ar−CH$_3$), 2.08 (s, 6 H, C$_5$Me$_4$), 1.78 (s, 6 H, C$_5$Me$_4$), 1.72 (s, 12 H, C$_5$Me$_4$). ^{13}C NMR (C$_6$D$_6$, 23 °C): δ 173.89, 138.84, 129.91, 129.24, 129.18, 126.47 (Ar), 120.14, 118.42, 117.09, 115.83 (Cp), 20.83 (Ar−CH$_3$), 11.07, 10.56, 10.00, 9.52 (C$_5$*Me*$_4$). Anal. Calcd for $C_{32}H_{36}O_2Zr$: C, 70.67; H, 6.67. Found: C, 70.49; H, 6.73.

In Situ Generation of (TCP)TiCH$_2$Ph$^+$PhCH$_2$B(C$_6$F$_5$)$_3^-$ (4). (TCP)Ti(CH$_2$Ph)$_2$ (4.6 mg, 0.010 mmol) and B(C$_6$F$_5$)$_3$ (5.1 mg, 0.010 mmol) were loaded in the glovebox into a J. Young NMR tube, which was then attached to the high-vacuum line. CD$_2$Cl$_2$ (0.7−1 mL) was then vacuum-transferred into this tube at −78 °C. The NMR spectroscopy was carried out at −40 °C. ^{1}H NMR (CD$_2$Cl$_2$, −40 °C): δ 7.81 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.65 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.41 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.35 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.23 (d, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.07 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 2 H), 6.85 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 2 H), 6.79 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 6.64 (d, $J_{\mathrm{H-H}} = 6.9$ Hz, 2 H), 6.10 (d, $J_{\mathrm{H-H}} = 6.9$ Hz, 1 H), 3.84 (d, $J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, Ti-*CH*$_2$Ph), 2.96 (d, $J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, Ti−*CH*$_2$Ph), 2.71 (s, br, 2 H, B−*CH*$_2$Ph), 2.44 (s, 3 H, Ar−CH$_3$), 2.33 (s, 3 H, C$_5$Me$_4$), 2.13 (s, 3 H, C$_5$Me$_4$), 2.04 (s, 3 H, C$_5$Me$_4$), 1.57 (s, 3 H, C$_5$Me$_4$). A small amount of dibenzyl (δ 2.84 ppm) was also detected in the NMR reaction. ^{19}F NMR (CD$_2$Cl$_2$, −40 °C): δ −130.00 (s, br, 6 F, *o*-F), −162.30 (t, $^3J_{\mathrm{F-F}} = 21.4$ Hz, 3 F, *p*-F), −165.30 (s, br, 6 F, *m*-F).

In Situ Generation of (TCP)TiCH$_2$Ph$^+$B(C$_6$F$_5$)$_4^-$ (5). (TCP)Ti(CH$_2$Ph)$_2$ (4.6 mg, 0.010 mmol) and Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (9.2 mg, 0.010 mmol) were loaded in the glovebox into a J. Young NMR tube, which was then attached to the high-vacuum line. CD$_2$Cl$_2$ (0.7−1 mL) was then vacuum-transferred into this tube at −78 °C. The NMR spectroscopy was carried out at −60 °C. ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 7.81 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.65 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.43 (t, $J_{\mathrm{H-H}} = 7.5$ Hz, 1 H), 7.40−6.90 (m, obscured by superimposed signals of Ph$_3$CCH$_2$Ph), 6.09 (d, $J_{\mathrm{H-H}} = 8.1$ Hz, 1 H), 3.84 (d, $J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, Ti−*CH*$_2$Ph), 2.96 (d, $J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, Ti−*CH*$_2$Ph), 2.44 (s, 3 H, Ar−CH$_3$), 2.31 (s, 3 H, C$_5$Me$_4$), 2.13 (s, 3 H, C$_5$Me$_4$), 2.03 (s, 3 H, C$_5$Me$_4$), 1.59 (s, 3 H, C$_5$Me$_4$). A small amount of dibenzyl (δ 2.83 ppm) was also detected in the NMR reaction. ^{13}C NMR (CD$_2$Cl$_2$, −60 °C): δ 82.56 (t, $J_{\mathrm{C-H}} = 150.8$ Hz, Ti−*CH*$_2$Ph). ^{19}F NMR (CD$_2$Cl$_2$, −60 °C): δ −131.86 (s, br, 8 F, *o*-F), −161.08 (t, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 4 F, *p*-F), −165.03 (s, br, 8 F, *m*-F).

Ethylene, Propylene, and Styrene Polymerization Experiments. Ethylene, propylene, and styrene polymerizations were carried out at room temperature in 250-mL flamed, round-bottomed flasks equipped with magnetic stirring bars and attached to the high-vacuum line. In a typical experiment, a 1:1 ratio of (TCP)Ti(CH$_2$Ph)$_2$:cocatalyst in 2 mL of toluene or 1,2-difluorobenzene (for those catalysts activated with Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$), freshly prepared in the glovebox, was quickly injected (using a gas-tight syringe equipped with a spraying needle) into a rapidly stirred flask containing a measured quantity of dry toluene, which was presaturated under 1.0 atm of rigorously purified ethylene or propylene. The solution was equilibrated at the desired reaction temperature using an external constant-temperature bath. For styrene polymerization, the toluene solution contained 2.0 mL of freshly distilled styrene under 1.0 atm of Ar. After a measured time interval, the polymerization was quenched by the addition of 2% acidified methanol. The polymer was then collected by filtration, washed with methanol, and dried on the high-vacuum line overnight to a constant weight.

X-ray Crystallographic Studies of (TCP)Ti(CH$_2$Ph)$_2$. Orange crystals of (TCP)Ti(CH$_2$Ph)$_2$ were grown by slow cooling of a saturated pentane solution to −20 °C over several days. The solvent was decanted in the glovebox, and the crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10^{-6} Torr for 24 h). The crystals were then mounted on thin glass fibers and transferred into the cold-steam (−120 °C) of the Enraf-Nonius CAD4 diffractometer. Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Intensity data were all corrected for absorption, anomalous dispersion, and Lorentz and polarization effects. The space group was determined by statistical analysis of intensity distribution and sucessful refinement of the proposed structure. Crystallographic data are summarized in Table 1.

Table 1. Summary of the Crystal Structure Data for (TCP)Ti(CH$_2$Ph)$_2$ (2)

formula	$C_{30}H_{32}TiO$
fw	456.48
cryst color, habit	orange, platey
cryst dimens mm	0.24 × 0.15 × 0.01
cryst syst	triclinic
a, Å	8.324(3)
b, Å	10.432(4)
c, Å	14.634(4)
α, deg	85.67(3)
β, deg	79.23(3)
γ, deg	76.64(4)
V, Å^3	1213.9(8)
space group	$P\bar{1}$ (No. 2)
Z	2
d(calcd), g/cm^3	1.249
μ, cm^{-1}	3.72
diffractometer	Enraf-Nonius, CAD4
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å), graphite monochromated
temperature, °C	−120 °C
scan type	$\omega-\theta$
2θ range, deg	2.0−45.9
intensities (unique, R_i)	3634 (3358, 0.114)
transmission factor range	0.9543−0.9970
secondary extinction	coefficient: 6.29514e-08
intensities > $3\sigma(I)$	1335
no. of params	220
R	0.066
R_w	0.054
max density in ΔF map, e$^-$/Å^3	0.37

The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] Owing to the paucity of data, atoms C17−C30 (the benzyl groups) were refined isotropically while the remaining non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealized positions. The final cycle of full-matrix least-squares refinement was based on 1335 observed reflections ($I > 3.00\sigma(I)$) and 220 variable parameters. All calculations were performed using the TeXsan crystallographic software package of Molecular Structure Corp.

Results and Discussion

Synthesis of (TCP)H$_2$ (1), (TCP)Ti(CH$_2$Ph)$_2$ (2), and (TCP)$_2$Zr (3). The one-pot synthesis of the 2-(tetramethylcyclopentadienyl)-4-methylphenol ligand (TCP)H$_2$ is depicted in Scheme 1. The reaction of commerically available 2-bromo-4-methylphenol with 2 equiv of ^{n}BuLi yields a dilithio salt, which is not isolated and is next reacted with 2,3,4,5-tetramethyl-2-cyclopentenone to produce ligand **1** (obtained as a single isomer judging from the NMR) as a brown crystalline solid after hydrolysis and subsequent vacuum distillation. This

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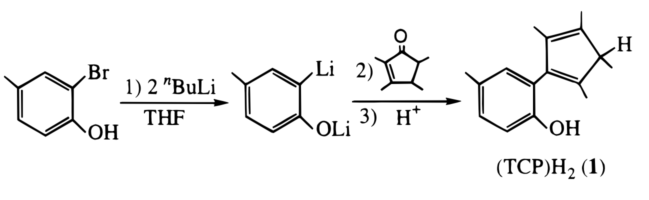
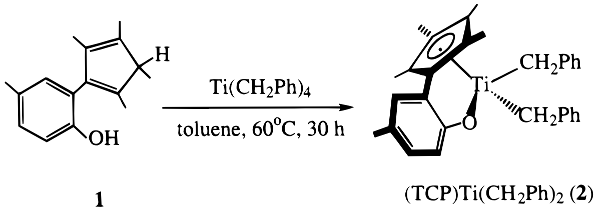
[11] Sheldrick, G. M. SHELXS-86. In *Crystallographic Computing*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175−189.

[12] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. DIRDIF 94. The DIRDIF-94 program system. Technical Report of the Crystallography Laboratory: University of Nijmegen, Nijmegen, The Netherlands, 1994.

Scheme 1



Scheme 2



approach can be compared to the conventional three-step synthesis of $Me_2Si(C_5Me_4H)(^tBuNH)$,[4g,h] with the attraction of the present system being the efficient synthetic procedure as well as the great potential steric and electronic flexibility introducible via modification of the aryl fragment.

Interestingly, in attempts to synthesize the corresponding group 4 metal complexes from **1**, both the conventional metalation/salt elimination (double deprotonation with ^{n}BuLi followed by metalation with MCl_4) and amine elimination approaches[6c–h] (**1** + $M(NMe_2)_4$ at 110 °C for 3 days) gave complex mixtures of unidentified products. On the other hand, the alkane elimination approach reported[3a] earlier for the efficient synthesis of group 4 constrained geometry catalysts afforded the desired complex **2** (Scheme 2) in 50% yield. In solution at room temperature, the ^{1}H NMR spectrum of **2** reveals two magnetically equivalent benzyl groups, each having diastereotopic benzylic protons at δ 2.50 and 2.32 ppm (J_{H-H} = 10.2 Hz). Although the observation of a normal Ph *ipso*-^{13}C chemical shift at δ 147.87 ppm, a CH_2 $^2J_{HH}$ value of 10.2 Hz, and a CH_2 $^1J_{CH}$ value of 127.5 Hz can be taken as evidence against significant η^n-benzyl bonding,[4f,13] the solid state structural results (see below) suggest rapid interconversion[4f] of one η^1 and one η^n group in solution at room temperature. The corresponding reaction of **1** with $Zr(CH_2Ph)_4$ under the same conditions yields a mixture of products. However, at higher reaction temperatures (110 °C for 12 h), the reaction yields a new, chiral chelated C_2-symmetric zirconocene[14] $(TCP)_2Zr$ (**3**; Scheme 3) which has been characterized spectroscopically and analytically. This salt-free synthetic/ligational approach which by design yields only the *rac* isomer may offer attractive features in the stereoselective synthesis of other precursors for *rac*-metallocene catalysts.

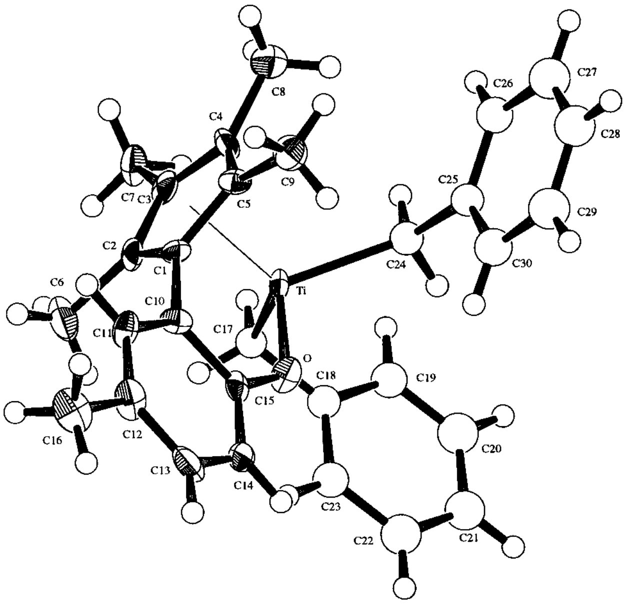


Figure 1. Perspective ORTEP drawing of the molecular structure of the complex (TCP)Ti(CH$_2$Ph)$_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 3

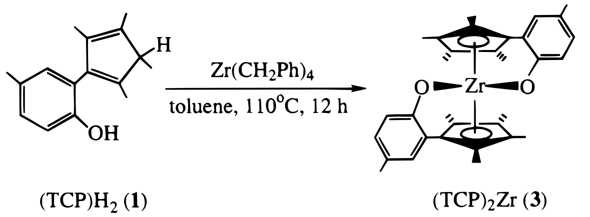


Table 2. Selected Bond Distances (Å) and Angles (deg) for (TCP)Ti(CH$_2$Ph)$_2$ (2)

Bond Distances			
Ti−O	1.851(7)	Ti−Cl	2.33(1)
Ti−C2	2.36(1)	Ti−C3	2.39(1)
Ti−C4	2.37(1)	Ti−C5	2.35(1)
Ti−C17	2.121(10)	Ti−C24	2.13(1)
Ti−C18	2.92(1)	C24−C25	1.50(1)
O−C15	1.36(1)	C17−C18	1.49(1)
Bond Angles			
O−Ti−C17	104.5(4)	O−Ti−C24	108.0(4)
Ti−O−C15	126.6(6)	Ti−C17−C18	106.7(7)
Ti−C24−C25	127.2(7)	O−C15−C10	116.6(10)
O−C15−C14	124(1)	C1−C10−C15	112.6(10)
C1−C10−C11	128(1)	C17−Ti−C24	101.1(4)
Cp(centroid)−Ti−O	107.7(2)		

Crystal Structure of (TCP)Ti(CH$_2$Ph)$_2$ (2). The solid state structure of **2** as derived from single-crystal X-ray diffraction is shown in Figure 1, and important bond distances and angles are summarized in Table 2. The geometry around Ti is slightly distorted tetrahedral, with a Cp(centroid)−Ti−O angle of 107.7(2)° and a C17−Ti−C24 angle of 101.1(4)°. This acute Cp(centroid)−Ti−O angle is nearly identical to that of the Cp−Ti−N angle in $Me_2Si(Me_4C_5)(^tBuN)TiCl_2$ (107.6),[3f] indicating similar sterically open features for both complexes as catalyst precursors. The Ti−C$_{ring}$(av) distance of 2.36(1) Å is probably slightly longer than the corresponding distance in $Me_2Si(Me_4C_5)(^tBuN)TiCl_2$ (2.340(5) Å).[3f] The (phenyl)C10−C1(ring) vector in **2** is bent 15(1)° from the Me$_4$Cp ring mean-square plane, and the phenyl plane−Me$_4$Cp plane dihedral angle is 81(1)°. The Ti−O bond length in **2** (1.851(7) Å) is comparable to those reported for bent metallocene Ti^{IV} and Ti^{III} alkoxide complexes, such as $Cp_2Ti(OCH{=}CH_2)_2$

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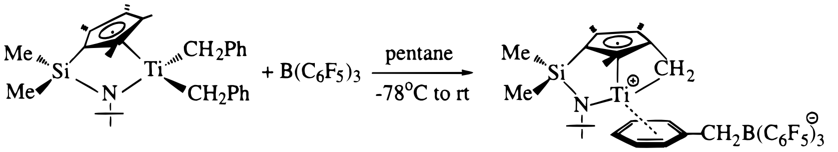
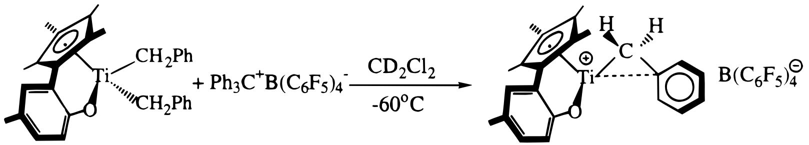
(13) (a) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633−640. (c) Jordan, R. F.; LaPointe, R. E.; Baenziger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. (d) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (e) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (f) Mintz, E. A.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4692. (g) Davis, G. R.; Jarvis, J. A.; Kilburn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 15111.

(14) For related chelated complexes having different ligand frameworks and prepared by different synthetic approaches, see refs 5c and 6h.

Scheme 4



Scheme 5



2 **5**

Table 3. Summary of α-Olefin Polymerization Catalyzed by (TCP)Ti(CH_2Ph)$_2$

entry	cocatalyst	conditions	monomer[a]	polymer yield (g)	activity[b]	M_w[c]	M_w/M_n	remarks
1	$B(C_6F_5)_3$	15 μmol of catalyst 100 mL of toluene, 30 min	ethylene	0.11	1.47×10^4	1.27×10^6	>10	$T_m = 142.5$ °C
2	$Ph_3C^+B(C_6F_5)_4^-$	15 μmol of catalyst 100 mL of toluene, 1 min	ethylene	0.52	2.10×10^6	1.14×10^6	>10	$T_m = 142.4$ °C
3	$Ph_3C^+B(C_6F_5)_4^-$	20 μmol of catalyst 50 mL of toluene, 5 min	propylene	6.37	3.82×10^6	2.36×10^4	1.85	$[mm] = 0.224$ $[mr] = 0.512$ $[rr] = 0.264$
4	$Ph_3C^+B(C_6F_5)_4^-$	25 μmol of catalyst 5 mL of toluene, 5 min	styrene	1.57	4.33×10^7	8.00×10^3	3.32	atactic

[a] Carried out at 25 °C, 1 atm of ethylene, 1 atm of propylene, and 17.4 mmol of styrene. [b] Activities in units of g of polymer/(mole of catalyst·atm·h), except entry 4 in units of g of polystyrene/(mole of catalyst·mole styrene·h). [c] GPC relative to polystyrene standards.

(1.903(2) Å),[15a] $Cp_2Ti(OC_2H_5)Cl$ (1.855(2) Å),[15b] Cp_2TiO-(2,6-$Me_2C_6H_3$) (1.892(2) Å),[15c] $[C_5H_4(CH_2)_3O]TiCl_2$ (1.762(2) Å),[5b] and $[C_5Me_4(CH_2)_3O]TiCl_2$ (1.767(1) Å),[15d] where a partial Ti–O double-bond character involving oxygen π-donation to the metal in addition to the σ-interaction is associated with short Ti–O bond lengths. On the other hand, the present Ti–O–C15 angle (126.6(6)°) is somewhat smaller than typical Ti–O–C angles, as in the above examples (~140°)[15] where Ti–O multiple bonding is assumed operative, reflecting the great steric strain in **2**, also evidenced by the 15° bend of the (phenyl)C10–C1(ring) vector from the Me_4Cp ring mean-square plane.

The two benzyl ligands in complex **2** are inequivalent in the solid state, with one engaging in normal η^1-bonding (Ti–C24 = 2.13(1) Å; ∠Ti–C24–C25 = 127.2(7)°) and the other in partial η^2-bonding, with Ti–C17 and Ti–C_{ipso}(C18) distances of 2.121(10) and 2.92(1) Å, respectively, and a Ti–C17–C18 angle of 106.7(7)° (Figure 1).

Reaction Chemistry of (TCP)Ti(CH_2Ph)$_2$ with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$. The reaction of bis-Cp-type metallocene dibenzyls with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ often generates the corresponding cationic complexes with η^2-bonding of the remaining benzyl group to the electrophilic metal center.[3a,13a–c] In contrast, we previously found that the reaction of the $Me_2Si(Me_4C_5)(^tBuN)M(CH_2Ph)_2$ complexes with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ follows a different course.[3a] While low-temperature NMR-scale reactions of $Me_2Si(Me_4C_5)(^tBuN)M(CH_2Ph)_2$ complexes with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ in CD_2Cl_2 indicate the formation of cationic monobenzyl species, preparative-scale reactions at higher temperature afford C–H activation products, i.e., intramolecularly ring-metallated η^1,η^6-fulvene-type complexes (e.g., Scheme 4).[3a] Likewise, the low-temperature NMR-scale reactions of (TCP)Ti(CH_2Ph)$_2$ with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ in CD_2Cl_2 clearly indicate the formation of the corresponding cationic monobenzyl species $(TCP)TiCH_2Ph^+PhCH_2B(C_6F_5)_3^-$ (**4**) and $(TCP)TiCH_2Ph^+B(C_6F_5)_4^-$ (**5**), respectively, with identical cation structures based upon the NMR analyses (the formation of **5** is depicted in Scheme 5). The Ti–CH_2-Ph ^1H NMR signals of **5** are observed at δ 3.84 (d, J_{H-H} = 6.3 Hz) and 2.96 (d, J_{H-H} = 6.3 Hz) (CD_2Cl_2, −60 °C), which is 1.34 and 0.64 ppm down-field-shifted, respectively, from the benzyl resonances of neutral precursor **2** (δ 2.50 (d, J_{H-H} = 10.2 Hz) and 2.32 (d, J_{H-H} = 10.2 Hz) (C_6D_6, 23 °C)) as a consequence of cation formation. η^2-Coordination of the benzyl ligand in the cationic complex is evidenced by a reduction of the value of $^2J_{H-H}$ for the diastereotopic CH_2Ph protons from 10.2 to 6.3 Hz, a high-field-shifted Ti–$^{13}CH_2$Ph signal (δ 82.56 ppm in **5** vs 83.85 ppm in **2**), and a large CH_2 $^1J_{CH}$ value (150.8 Hz in **5** vs 127.5 Hz in **2**).[13] However, despite the clean NMR-scale reactions at low temperatures, and unlike the case of the constrained geometry monobenzyls,[3a] preparative-scale reactions at higher temperatures are accompanied by extensive decomposition and isolation of the cationic complexs could not be achieved in this case.

α-Olefin Polymerization Studies. Table 3 summarizes ethylene, propylene, and styrene polymerization activities of (TCP)Ti(CH_2Ph)$_2$ upon activation with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ as well as the properties of the resulting polymers. (TCP)Ti(CH_2Ph)$_2$ when activated with $Ph_3C^+B(C_6F_5)_4^-$ is a highly active cata-

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[15] (a) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855. (b) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009. (c) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Torroni, S.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Organomet. Chem.* **1980**, *188*, C31. (d) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59.

lyst for ethylene, propylene, and styrene polymerization, producing high molecular weight (>10^6) polyethylenes with high melting transition temperatures ($T_m = 142$ °C), as well as atactic polypropylene and polystyrene. The open nature of the catalytic site can be associated with the low degree of polymerization stereocontrol, and the homopoly α-olefin products are generally atactic, similar to the performance of group 4 amido-based constrained geometry catalysts.[3c] The broad polydispersities of the polyethylene products may be associated with the rapid decomposition of the cationic species at room temperature (possibly with the formation of η^1,η^6 "tuck-in" cations[3a]) or slow initiation with respect to the fast propagation and significant inhomogenity during the course of the catalytic reaction under the present ethylene polymerization conditions. In contrast, propylene polymerization mediated by **2** activated with $Ph_3C^+B(C_6F_5)_4^-$ is both very rapid and produces a polymer having narrow polydispersity, which can be attributed to the structurally open nature of the cationic metal coordination sphere (catalytic activity is not affected by the steric encumberence of monomer) and apparently greater stabilization of the catalytic sites in the presence of propylene. The substantial activity difference of identical cations having different counteranions (entry 1 vs 2) further demonstrates the significant influence of the anion identity on catalytic activity, as previously shown in detail by us and others.[16]

In summary, a novel phenolic bifunctional mono-Cp constrained geometry ligand framework and the Ti and Zr complexes thereof have been designed and synthesized by one-pot/one-step syntheses. The solid state structure, cocatalyst activation chemistry, and performance for olefin polymerization of the titanium complex has been investigated in detail. The results considerably expand what is known about constrained geometry catalyst design and the consequent olefin polymerization performance.

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Supporting Information Available: Text giving complete X-ray experimental details and tables of crystal data, intensity measurements, structure solution and refinement, atomic coordinates, torsion angles, and bond lengths and angles, and ORTEP diagram of **2** (26 pages). Ordering information is given on any current masthead page.

OM9707376

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[16] (a) Chen, Y.-X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582−2583. (b) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842−857. (c) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451−12452. (d) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128−6129. (e) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114−12129. (f) Jia, L.; Yang, X.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135−3137. (g) Chien, J. C. W.; Song, W.; Rausch, M. D. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2387−2393. (h) Eisch, J.; Pombrik, S. I.; Zheng, G.-X. *Organometallics* **1993**, *12*, 3856−3863. (i) Siedle, A. R.; Lamanna, W. M.; Newmark, R. A.; Stevens, J.; Richardson, D. E.; Ryan, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 215−224.