"Constrained Geometry" Dialkyl Catalysts. Efficient Syntheses, C−H Bond Activation Chemistry, Monomer−Dimer Equilibration, and α-Olefin Polymerization Catalysis

You-Xian Chen and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received April 7, 1997[⊗]

This contribution reports an efficient synthesis of the "constrained geometry" group 4 dibenzyl complexes $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)MR_2$ ($CGCMR_2$, where R = CH_2Ph; M = Ti (**1**), Zr (**2**)), as well as the substantially different reaction patterns in the cocatalytic activation of the R = CH_2Ph and Me complexes with $B(C_6F_5)_3$, PBB (tris(2,2′,2″-perfluorobiphenyl)-borane), and $Ph_3C^+B(C_6F_5)_4^-$. The resulting cationic complexes are highly but not equivalently active for α-olefin polymerization and copolymerization catalysis. The reaction of the neutral free ligand $CGCH_2$ with $Ti(CH_2Ph)_4$ in aromatic or saturated hydrocarbon solvents at 60 °C cleanly affords **1** in 90% yield, while the corresponding reaction with $Zr(CH_2Ph)_4$ produces **2** in lower yield. When activated with $Ph_3C^+B(C_6F_5)_4^-$ at low temperatures, **2** generates cationic $CGCZrCH_2Ph^+$ $B(C_6F_5)_4^-$ (**4**). However, unlike the corresponding metallocene dibenzyl, the cationic derivative of which ($Cp_2ZrCH_2Ph^+B(C_6F_5)_4^-$ (**3**)) can be isolated in quantitative yield, the reaction of **1** with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ affords intramolecular C−H metalation products $Me_2Si(\eta^5,\eta^1\text{-}C_5Me_3CH_2)(^tBuN)Ti^+[\eta^n\text{-}PhCH_2B(C_6F_5)_3]^-$ (**5**) and $Me_2Si(\eta^5,\eta^1\text{-}C_5Me_3CH_2)(^tBuN)Ti^+B(C_6F_5)_4^-$ (**6**), respectively. In contrast, the reaction of $CGCTiMe_2$ with $B(C_6F_5)_3$ cleanly generates $CGCTiCH_3^+CH_3B(C_6F_5)_3^-$ (**8**) without C−H bond activation as well as dinuclear $[CGCTiMe(\mu\text{-}Me)MeTiCGC]^+MeB(C_6F_5)_3^-$ (**11**), which is in equilibrium with **8** and $CGCTiMe_2$ ($\Delta G_{298K} = 1.3(2)$ kcal/mol in favor of **8**). The reaction of $CGCTiMe_2$ with sterically encumbered PBB and $Ph_3C^+B(C_6F_5)_4^-$ yields predominantly cationic dinuclear species, and analytically pure $[CGCTiMe(\mu\text{-}Me)MeTiCGC]^+[MePBB]^-$ (**9**) can be isolated in quantitative yield. Complexes **5** and **6** are highly active homogeneous catalysts for ethylene and propylene polymerization, producing ultra-high molecular weight ($M_w > 10^6$) polyethylenes with high melting transition temperatures ($T_m = 142$ °C), as well as syndiotactic-enriched atactic polypropylenes having appreciable molecular weights. Although C−H bond-activated complexes **5** and **6** are ineffective for ethylene and 1-hexene copolymerization, the $CGCTi(CH_2Ph)_2$/MAO system is highly active at 60 °C to incorporate 1-hexene in large quantities (69.9%). Finally, comparisons of polymerization catalysts bearing different counteranions at various temperatures demonstrate the substantial influence of anion identity on α-olefin polymerization activity, catalyst stability, and product polymer microstructure.

Introduction

Constrained geometry catalysts having the formula $R_2Si(C_5R'_4)(R''N)MX_2$ ($CGCMX_2$; M = Ti, Zr, Hf; X = Cl, Me) are currently of great scientific and technological interest[1] as a new generation of highly active and selective Ziegler−Natta-type catalysts[2] for the copolymerization of ethylene and α-olefins. The R = Me, R′ = Me, R″ = ^{t}Bu synthetic approach initially developed by Bercaw and co-workers[3] for scandium complexes, and later detailed in patents[1d,e] for the synthesis of group 4 analogues, involves reaction of the CGC ligand dilithio salt with the appropriate metal halide, followed by oxidation for M = Ti (Scheme 1). The corresponding dimethyl catalyst precursors can then be synthesized by subsequent alkylation of the dichlorides with MeLi at low temperature.[4]

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

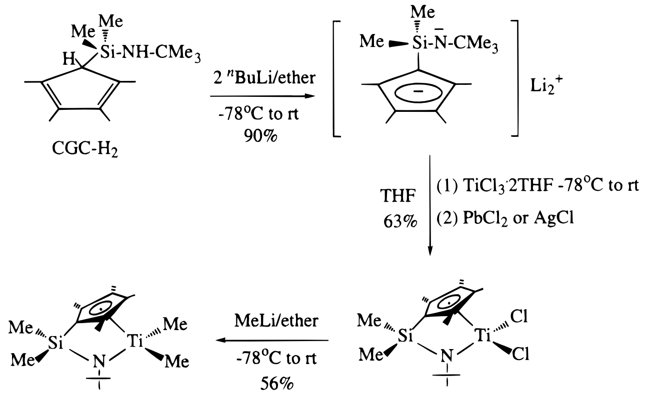
[1] (a) Woo, T. K.; Margl, P. M.; Lohrenz, J. C. W.; Blochl, P. E.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 13021−13030. (b) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451−12452. (c) Stevens, J. C. In *Studies in Surface Science and Catalysis*; Hightower, J. W., Delglass, W. N., Iglesia, E., Bell, A. T., Eds.; Elsevier: Amsterdam, 1996; Vol. 101, pp 11−20 and references therein. (d) 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.). (e) 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.).

[2] 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.

[3] (a) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (b) Piers, W. E.; Shapiro, P. J.; Bunnel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74. (c) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

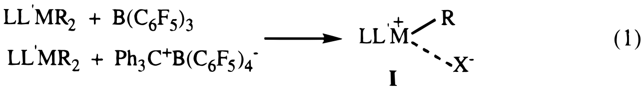
[4] Fu, P.-F.; Wilson, D. J.; Rudolph, P. R.; Stern, C. L.; Marks, T. J. Submitted for publication.

Scheme 1



In regard to alternative group 4 metallocene synthetic strategies, the $M(NR_2)_4$ precursor amine elimination approach originally developed by Lappert[5] for nonbridged metallocenes, later exploited by Teuben,[6] Herrmann,[7] and Collins[8] for *ansa*cyclopentadienyl or indenyl complexes, and recently elegantly utilized by Jordan[9] for stereoselective syntheses of chiral *ansa*-metallocenes, generally provides a more efficient preparation than conventional salt elimination synthetic routes. However, it is reported to be unsuitable for $CGCTi(NMe_2)_2$ and leads instead to a myriad of undesired products.[10] Furthermore, although the amine elimination route provides an efficient preparation of Cp-unsubstitued $Me_2Si(C_5H_4)(^tBuN)M(NMe_2)_2$ (M = Ti, Zr) analogues, the amido complexes cannot be protonolytically converted to the corresponding dichloride derivatives without the formation of dimethylamine adducts.[10] For subsequent catalysis, it is critical that the amido complexes be converted to dichoride or ideally to dialkyl polymerization catalyst precursors, because amide-derived catalysts are significantly less active than chloride-derived catalysts.[11]

Metallocene dialkyls are also ideal for studying the molecular basis of polymerization catalysis, since the reaction of group 4 metallocene dialkyls with perfluoroaryl boranes[12] and borates[13] can afford isolable *and* characterizable catalysts (e.g., **I**; L, L′ = anionic ancillary ligands; M = Th, Ti, Zr, Hf; X^- = weakly coordinating anion) rather than the complicated and intractable species produced in the case of metallocene dichlorides activated with MAO,[14] eq 1. Studying stoichiometrically-precise, isolated ion pairs (**I**) has provided much insight into catalyst molecular structure, activity, lifetime, high-temperature stability, chain transfer characteristics, and stereoregulation, all of which are intimately connected with the nature of the relatively strong cation−anion ion pairing.[1b,15]



$$\left.\begin{array}{l} LL'MR_2 + B(C_6F_5)_3 \\ LL'MR_2 + Ph_3C^+B(C_6F_5)_4^- \end{array}\right\} \longrightarrow \underset{\mathbf{I}}{LL'\overset{+}{M}(R)\cdots X^-} \qquad (1)$$

In view of the technological importance of CGC complexes and the great scientific interest in the corresponding dialkyls as catalyst precursors, we report here a highly efficient synthetic approach from the neutral $CGCH_2$ ligand directly to the $CGCMR_2$ catalyst precursors via toluene elimination.[16] Some attractive features of this approach to the Ti complex include a one-step sythesis (to the dibenzyl catalyst precursor), high isolated yields, a convenient synthetic temperature (60 °C), and a simple work-up procedure (extraction and filtration). We also report here the isolation, characterization, and implementation of several cationic CGC complexes in homogeneous α-olefin polymerization and copolymerization experiments, as well as the characterization of intramolecular C−H bond activation and monomer−(*μ*-methyl) dimer equilibration processes.

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 of 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

---

[5] Chandra, G.; Lappert, M. F. *J. Chem. Soc.* A **1968**, 1940.

[6] Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936−1945.

[7] (a) Herrmann, W. A.; Morawietz, M. J. A. *J. Organomet. Chem.* **1994,** *482*, 169−181. (b) Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1946.

[8] Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 377.

[9] (a) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024−8033. (b) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030−4037, 4038−4044, 4045−4053. (c) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5−7.

[10] Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572−1581.

[11] Kim, Il.; Jordan, R. F. *Macromolecules* **1996**, *29*, 489−491.

[12] (a) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867−5868. (b) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593−6594. (c) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755−1757. (d) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (e) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243. (f) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543−2545. (g) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625. (h) Ewen, J. A.; Elder, M. J. *Chem. Abstr.* **1991**, *115*, 136998g.

[13] (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.

[14] (a) Kaminsky, W.; Kulper, K.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507−509. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99−149.

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

[16] (a) After this study was completed, we became aware of a European patent application briefly describing a variant of this reaction, see: Nickias, P. N.; Devore, D. D.; Wilson, D. R. PCT Appl. WO 08199, **1993**. We thank Dr. D. D. Devore of Dow Chemical Co. for bringing this to our attention. (b) The use of alkane elimination in the one-step synthesis of organoscandium complexes containing a multidentate Cp ligand has been recently reported, see: Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720−2726. (c) For the synthesis of bis(phenolate) dibenzyls of Ti and Zr, see: van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008−3021.

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 nonhalogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from P_2O_5 and stored over activated Davison 4A molecular sieves. BrC_6F_5 (Aldrich) was vacuum distilled from P_2O_5. 1-Hexene (Aldrich) was dried over CaH_2 and vacuum-transferred into a storage tube containing activated 4A molecular sieves. $TiCl_3$, $ZrCl_4$, $TiCl_4$, $PhCH_2MgCl$ (1.0 M in diethyl ether), MeLi (1.0 M in diethyl ether), and ^{n}BuLi (1.6 M in hexanes) were purchased from Aldrich. $Cp_2Zr(CH_2Ph)_2$,[17] $Ti(CH_2Ph)_4$,[18] $Zr(CH_2Ph)_4$,[18] $B(C_6F_5)_3$,[19] $Ph_3C^+B(C_6F_5)_4^-$,[13a] tris(2,2′,2″-perfluorobiphenyl)borane ($B(C_{12}F_9)_3$, PBB),[1b] $Me_2Si(C_5Me_4H)(^tBuNH)$[3] ($CGCH_2$), $Me_2Si(C_5Me_4)(^tBuN)TiMe_2$[1d,e,4] ($CGCTiMe_2$), $CGCZrMe_2$,[1d,e,4] and $CGCMMe^+MeB(C_6F_5)_3^-$ (M = Ti, Zr)[4] were prepared according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either Varian VXR 300 (FT 300 MHz, ^{1}H; 75 MHz, ^{13}C) or Varian Gemini-300 (FT 300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) instruments. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced using 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. The ^{13}C NMR assay of the polymer microstructure was conducted in $C_2D_2Cl_4$ at 120 °C. The melting temperatures of the polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. The GPC analysis of the polymer samples was performed at L. J. Broutman & Associates, Ltd., Chicago, IL, on a Waters 150 °C GPC relative to polystyrene standards.

One-Step Synthesis of $CGCTi(CH_2Ph)_2$ (1). $Ti(CH_2Ph)_4$ (2.14 g, 5.2 mmol), $CGCH_2$ ligand (1.01 g, 4.0 mmol), and 50 mL of benzene were heated while stirring at 60 °C for 12 h in the absence of light. The solvent was then removed *in vacuo*, and the black residue was extracted with 50 mL of pentane. The pentane extract was then filtered, and the filtrate solvent was removed *in vacuo* to yield 1.73 g of the title complex. Yield: 90.2%. A small amount of bibenzyl was also detected in the NMR tube reactions. Alternatively, toluene or heptane can be used in place of benzene as the reaction solvent. ^{1}H NMR (C_6D_6, 23 °C): δ 7.16 (d, J_{H-H} = 11.2 Hz, 4 H, Ph), 6.95 (t, J_{H-H} = 7.5 Hz, 4 H, Ph), 6.90 (t, J_{H-H} = 7.5 Hz, 2 H, Ph), 2.58 (d, J_{H-H} = 10.2 Hz, 2 H, CH_2Ph), 2.25 (d, J_{H-H} = 10.2 Hz, 2 H, CH_2Ph), 1.81 (s, 6 H, C_5Me_4), 1.63 (s, 6 H, C_5Me_4), 1.43 (s, 9 H, N^{t}Bu), 0.41 (s, 6 H, $SiMe_2$). ^{13}C NMR (C_6D_6, 23 °C): δ 150.36 (*ipso*-C, Ph), 134.47, 131.57, 126.32 (C_5Me_4), 128.38 (d, J_{C-H} = 164.8 Hz, Ph), 126.17 (d, J_{C-H} = 159.6 Hz, Ph), 122.25 (d, J_{C-H} = 158.8 Hz, Ph), 82.23 (t, J_{C-H} = 120.6 Hz, CH_2Ph), 60.34 (NCMe$_3$), 34.29 (q, J_{C-H} = 126.8 Hz, NCMe_3), 14.56 (q, J_{C-H} = 126.0 Hz, C_5Me_4), 11.65 (q, J_{C-H} = 126.0 Hz, C_5Me_4), 6.23 (q, J_{C-H} = 118.7 Hz, $SiMe_2$). Anal. Calcd for $C_{29}H_{41}NSiTi$: C, 72.62; H, 8.62; N, 2.92. Found: C, 72.39; H, 8.75; N, 2.57.

NMR Experiments and Scale-up Reaction for the Synthesis of $CGCZr(CH_2Ph)_2$ (2). In Teflon-valved NMR tubes, $Zr(CH_2Ph)_4$ and the $CGCH_2$ ligand in the proper mole ratios (1:1 unless otherwise indicated) were dissolved in toluene-d_8 and then heated to various temperatures for measured periods of time: (a) At 110 °C for 12 h, all the $Zr(CH_2Ph)_4$ was consumed (decomposed), but $CGCH_2$ remained unreacted; (b) At 80 °C for 15 h, negligible reaction was observed; (c) At 60−65 °C for 1 week, 30% of the ligand was converted to product; (d) At 90 °C for 48 h and with a $Zr(CH_2Ph)_4/CGCH_2$ ratio of 1.7/1.0, all ligand was converted to the desired product. Therefore, using the conditions of (d) and the procedure described above for the synthesis of $CGCTi(CH_2Ph)_2$, the crude product $CGCZr(CH_2Ph)_2$ (~90% purity by NMR), which probably contains an additional unknown Zr−benzyl species, was isolated in 60% yield. Further purification by fractional recrystallization from pentane at −78 °C resulted in a low yield (10%) due to the high solubility. ^{1}H NMR (C_6D_6, 23 °C): δ 7.17 (t, J_{H-H} = 7.2 Hz, 4 H, Ph), 6.92 (t, J_{H-H} = 7.2 Hz, 2 H, Ph), 6.81 (d, J_{H-H} = 7.5 Hz, 4 H, Ph), 1.92 (s, 6 H, C_5Me_4), 1.89 (d, J_{H-H} = 10.8 Hz, 2 H, CH_2Ph), 1.78 (s, 6 H, C_5Me_4), 1.67 (d, J_{H-H} = 10.8 Hz, 2 H, CH_2Ph), 1.16 (s, 9 H, N^{t}Bu), 0.45 (s, 6 H, $SiMe_2$). ^{13}C NMR (C_6D_6, 23 °C): δ 147.12 (*ipso*-C, Ph), 130.73, 130.21, 126.85 (C_5Me_4), 128.29 (d, J_{C-H} = 158.1 Hz, Ph), 126.07 (d, J_{C-H} = 159.6 Hz, Ph), 122.11 (d, J_{C-H} = 168.7 Hz, Ph), 61.01 (t, J_{C-H} = 120.3 Hz, CH_2Ph), 56.75 (NCMe$_3$), 33.13 (q, J_{C-H} = 128.1 Hz, NCMe_3), 14.41 (q, J_{C-H} = 126.7 Hz, C_5Me_4), 11.43 (q, J_{C-H} = 126.7 Hz, C_5Me_4), 6.65 (q, J_{C-H} = 119.0 Hz, $SiMe_2$). Anal. Calcd for $C_{29}H_{41}NSiZr$: C, 66.61; H, 7.90; N, 2.68. Found: C, 66.73; H, 7.83; N, 2.35.

Synthesis of $Cp_2ZrCH_2Ph^+B(C_6F_5)_4)^-$ (3). $Cp_2Zr(CH_2Ph)_2$ (0.081 g, 0.20 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (0.185 g, 0.20 mmol) were loaded into a flamed 50 mL reaction flask having a filter frit in the glovebox, and next the flask was attached to the high-vacuum line. Toluene (20 mL) was then vacuum-transferred into the flask at −78 °C. The mixture was slowly allowed to warm to room temperature and stirred for 2 h. The large quantities of solid which precipitated from the solution were collected by filtration, washed with toluene and then with pentane, and dried *in vacuo* to yield 0.18 g of the title cationic complex as a purple crystalline solid. Yield: 90.8%. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.50 (t, J_{H-H} = 7.5 Hz, 1 H, *p*-Ph), 7.40 (t, J_{H-H} = 7.8 Hz, 2 H, *m*-Ph), 6.99 (d, J_{H-H} = 7.2 Hz, 2 H, *o*-Ph), 6.19 (s, 10 H, Cp), 3.06 (s, 2 H, Zr−CH_2Ph). ^{19}F NMR (CD_2Cl_2, −60 °C): δ −131.54 (d, $^3J_{F-F}$ = 18.5 Hz, 8 F, *o*-F), −160.87 (s br, 4 F, *p*-F), −164.87 (s br, 8 F, *m*-F). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 147.54 (d, J_{C-F} = 240.7 Hz, *m*-C_6F_5), 137.79 (d, J_{C-F} = 250.3 Hz, *p*-C_6F_5), 137.47 (*ipso*-C, C_6F_5), 135.85 (d, J_{C-F} = 244.2 Hz, *m*-C_6F_5), 134.02 (d, J_{C-H} = 159.5 Hz, Ph), 130.62 (d, J_{C-H} = 162.6 Hz, Ph), 130.52 (d, J_{C-H} = 163.1 Hz, Ph), 120.96 (*ipso*-C, Ph), 110.18 (d, J_{C-H} = 176.3 Hz, Cp), 47.34 (t, J_{C-H} = 148.0 Hz, Zr−CH_2Ph). Anal. Calcd for $C_{41}H_{17}BF_{20}Zr$: C, 49.66; H, 1.73. Found: C, 49.42; H, 2.04.

In Situ Generation of $CGCZrCH_2Ph^+B(C_6F_5)_4^-$ (4). $CGCZr(CH_2Ph)_2$ (5.2 mg, 0.010 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (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_2Cl_2 (0.7−1 mL) was then vacuum-transferred into this tube at −78 °C. The NMR measurement was carried out at −60 °C. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.60 (t, J_{H-H} = 8.1 Hz, 1 H, *p*-Ph), 7.42 (t, J_{H-H} = 7.5 Hz, 2 H, *m*-Ph), 6.99 (t, J_{H-H} = 7.8 Hz, 2 H, *o*-Ph), 2.81 (d, J_{H-H} = 9.0 Hz, 1 H, Zr−CH_2Ph), 2.47 (d, J_{H-H} = 9.0 Hz, 1 H, Zr−CH_2Ph), 2.26 (s, 3 H, C_5Me_4), 2.22 (s, 3 H, C_5Me_4), 2.19 (s, 3 H, C_5Me_4), 1.94 (s, 3 H, C_5Me_4), 1.15 (s, 9 H, N^{t}Bu), 0.63 (s, 3 H, $SiMe_2$), 0.62 (s, 3 H, $SiMe_2$). ^{19}F NMR (CD_2Cl_2, −60 °C): δ −131.86 (s br, 8 F, *o*-F), −161.08 (t, $^3J_{F-F}$ = 21.2 Hz, 4 F, *p*-F), −165.03 (s br, 8 F, *m*-F).

Synthesis of $Me_2Si(\eta^5,\eta^1\text{-}C_5Me_3CH_2)(^tBuN)Ti^+[\eta^n\text{-}PhCH_2B(C_6F_5)_3]^-$ ($CGC^{-H}\ Ti^+PhCH_2B(C_6F_5)_3^-$; 5). $CGCTi(CH_2Ph)_2$ (0.63 g, 1.3 mmol) and $B(C_6F_5)_3$ (0.67 g, 1.3 mmol) were charged in the glovebox into a 50 mL reaction flask having a filter frit, and the flask was attached to the high-vacuum line. Pentane (30 mL) was then vacuum-transferred into the flask at −78 °C. The mixture was slowly allowed to warm to room temperature and stirred for 2 h. Large quantities of solid precipitated from the solution, which were collected by filtration, washed twice with 5 mL of pentane, and dried *in vacuo* to produce 0.95 g of the title cationic complex as a brown solid. Yield: 80.6%. ^{1}H NMR (C_7D_8, 23 °C): δ 6.50 (s br, 2 H,

---

(17) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946−1950.

(18) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971,** *26*, 357−372.

(19) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250.

o-BCH$_2$*Ph*), 5.75 (s br, 1 H, *m*-BCH$_2$*Ph*), 5.54 (t, $J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, *p*-BCH$_2$*Ph*), 5.35 (s br, 1 H, *m*-BCH$_2$*Ph*), 3.40 (s br, 1 H, B*CH*$_2$Ph), 3.14 (s br, 1 H, B*CH*$_2$Ph), 2.69 (d, $J_{\mathrm{H-H}} = 3.3$ Hz, 1 H, TiCH$_2$), 2.52 (d, $J_{\mathrm{H-H}} = 3.3$ Hz, 1 H, TiCH$_2$), 1.84 (s, 3 H, C$_5$Me$_3$), 1.33 (s, 3 H, C$_5$Me$_3$), 1.02 (s, 3 H, C$_5$Me$_3$), 0.93 (s, 9 H, N^{t}Bu), 0.09 (s, 3 H, SiMe$_2$), −0.08 (s, 3 H, SiMe$_2$). ^{13}C NMR (C$_7$D$_8$, 23 °C): δ 153.53 (*ipso*-C of BCH$_2$*Ph*), 148.83 (d, $J_{\mathrm{C-F}} = 243.7$ Hz, C$_6$F$_5$), 145.33 (*ipso*-C of C$_6$F$_5$), 137.41 (d, $J_{\mathrm{C-F}} = 243.7$ Hz, C$_6$F$_5$), 136.01 (d, $J_{\mathrm{C-F}} = 242.9$ Hz, C$_6$F$_5$), 132.99, 130.99, 129.53, 127.23, 126.92, 126.60, 125.74, 124.37, 123.75, 113.31 (BCH$_2$*Ph*, *C*$_5$Me$_3$), 73.03 (t, $J_{\mathrm{C-H}} = 155.6$ Hz, TiCH$_2$), 63.75 (N*C*Me$_3$), 35.18 (NC*Me*$_3$), 34.53 (B*CH*$_2$Ph), 14.23 (C$_5$*Me*$_3$), 14.10 (C$_5$*Me*$_3$), 11.36 (C$_5$*Me*$_3$), 6.95 (SiMe$_2$), 1.41 (SiMe$_2$). ^{19}F NMR (C$_7$D$_8$, 23 °C): δ −131.04 (d, $^3J_{\mathrm{F-F}} = 21.4$ Hz, 6 F, *o*-F), −161.13 (t, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 3 F, *p*-F), −165.22 (s br, 6 F, *m*-F). ^{1}H NMR (C$_7$D$_8$, −29 °C): δ 6.58 (d, $J_{\mathrm{H-H}} = 6.6$ Hz, 1 H, *o*-BCH$_2$*Ph*), 6.46 (d, $J_{\mathrm{H-H}} = 6.5$ Hz, 1 H, *o*-BCH$_2$*Ph*), 5.55 (t, $J_{\mathrm{H-H}} = 6.9$ Hz, 1 H, *m*-BCH$_2$*Ph*), 5.37 (t, $J_{\mathrm{H-H}} = 7.2$ Hz, 1 H, *p*-BCH$_2$*Ph*), 5.29 (t, $J_{\mathrm{H-H}} = 6.3$ Hz, 1 H, *m*-BCH$_2$*Ph*), 3.57 (s br, 1 H, B*CH*$_2$Ph), 3.20 (s br, 1 H, B*CH*$_2$Ph), 2.70 (d, $J_{\mathrm{H-H}} = 3.3$ Hz, 1 H, TiCH$_2$), 2.53 (d, $J_{\mathrm{H-H}} = 3.3$ Hz, 1 H, TiCH$_2$), 1.80 (s, 3 H, C$_5$Me$_3$), 1.23 (s, 3 H, C$_5$Me$_3$), 0.93 (s, 3 H, C$_5$Me$_3$), 0.90 (s, 9 H, N^{t}Bu), 0.06 (s, 3 H, SiMe$_2$), −0.07 (s, 3 H, SiMe$_2$). ^{19}F NMR (C$_7$D$_8$, −29 °C): δ −131.18 (d, $^3J_{\mathrm{F-F}} = 18.5$ Hz, 6 F, *o*-F), −160.73 (s br, 3 F, *p*-F), −164.87 (s br, 3 F, *m*-F). Anal. Calcd for C$_{40}$H$_{33}$BF$_{15}$NSiTi: C, 53.41; H, 3.70; N, 1.56. Found: C, 53.07; H, 3.58; N, 1.28.

Synthesis of Me$_2$Si(η^5,η^1-C$_5$Me$_3$CH$_2$)(^{t}BuN)Ti$^+$B(C$_6$F$_5$)$_4^-$ (CGC$^{-\mathrm{H}}$Ti$^+$B(C$_6$F$_5$)$_4^-$] 6). CGCTi(CH$_2$Ph)$_2$ (0.37 g, 0.77 mmol) and Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (0.71 g, 0.77 mmol) were charged in the glovebox into a 50 mL reaction flask having a filter frit, and the flask was attached to the high-vacuum line. Toluene (30 mL) was then vacuum-transferred into the flask at −78 °C. The mixture was slowly allowed to warm to room temperature and stirred for 2 h. A black oil immediately precipitated from the solution, and the volume of toluene was reduced to one-half under reduced pressure. Pentane (10 mL) was condensed into the flask, and the mixture was filtered after stirring for 1 h. The dark red solid which was collected was washed with 5 mL of pentane and dried *in vacuo* to produce 0.72 g of **6**·C$_7$H$_8$. Yield: 87.6%. ^{1}H NMR (C$_7$D$_8$, 23 °C): δ 2.58 (d, $J_{\mathrm{H-H}} = 3.0$ Hz, 1 H, TiCH$_2$), 2.36 (d, $J_{\mathrm{H-H}} = 3.0$ Hz, 1 H, TiCH$_2$), 1.73 (s, 3 H, C$_5$Me$_3$), 1.43 (s, 3 H, C$_5$Me$_3$), 1.25 (s, 3 H, C$_5$Me$_3$), 0.91 (s, 9 H, N^{t}Bu), 0.10 (s, 3 H, SiMe$_2$), −0.09 (s, 3 H, SiMe$_2$). ^{13}C NMR (C$_7$D$_8$, GHMQC, 23 °C): δ 72.40 (TiCH$_2$), 34.30 (NC*Me*$_3$), 13.64 (C$_5$*Me*$_3$), 13.23 (C$_5$*Me*$_3$), 10.34 (C$_5$*Me*$_3$), 6.20 (SiMe$_2$), 0.01 (SiMe$_2$). ^{1}H NMR (CD$_2$Cl$_2$, −50 °C): δ 7.24−7.09 (m, 5 H, CH$_3$*Ph*), 2.93 (d, $J_{\mathrm{H-H}} = 3.0$ Hz, 1 H, TiCH$_2$), 2.84 (d, $J_{\mathrm{H-H}} = 3.0$ Hz, 1 H, TiCH$_2$), 2.67 (s, 3 H, Ph*CH*$_3$), 2.08 (s, 3 H, C$_5$Me$_3$), 2.02 (s, 3 H, C$_5$Me$_3$), 1.61 (s, 3 H, C$_5$Me$_3$), 1.26 (s, 9 H, N^{t}Bu), 0.39 (s, 3 H, SiMe$_2$), 0.15 (s, 3 H, SiMe$_2$). ^{19}F NMR (CD$_2$Cl$_2$, −50 °C): δ −131.88 (s br, 8 F, *o*-F), −161.05 (t, $^3J_{\mathrm{F-F}} = 21.4$ Hz, 4 F, *p*-F), −164.99 (s br, 8 F, *m*-F). Anal. Calcd for C$_{39}$H$_{26}$BF$_{20}$NSiTi·C$_7$H$_8$: C, 51.75; H, 3.21; N, 1.31. Found: C, 51.24; H, 2.99; N, 1.07.

In Situ Generation of CGCTiH$^+$HB(C$_6$F$_5$)$_3^-$ (7). Complex **5** (10 mg) was dissolved in toluene-*d*$_8$ in a J. Young NMR tube. The tube was then evacuated and backfilled with 1 atm of H$_2$ on the high-vacuum line at −78 °C. The mixture was warmed to room temperature and allowed to react for 30 min before recording the NMR spectrum. ^{1}H NMR (C$_7$D$_8$, 23 °C): δ 4.25 (s br, 1 H, B−H), 1.53 (s, 6 H, C$_5$Me$_4$), 1.42 (s, 6 H, C$_5$Me$_4$), 0.60 (s, 9 H, N^{t}Bu), 0.46 (s, 6 H, SiMe$_2$). The Ti−H signal was not detected, presumably because of rapid C−D/Ti−H exchange with C$_6$D$_6$.[12d,25] ^{19}F NMR (C$_7$D$_8$, 23 °C): δ −116.95 (t, $^3J_{\mathrm{F-F}} = 21.5$ Hz, 1 F), −126.16 (t, $^3J_{\mathrm{F-F}} = 20.9$ Hz, 1 F), −127.00 (t, $^3J_{\mathrm{F-F}} = 20.0$ Hz, 1 F), −129.76 (s br, 1 F), −132.46 (s br, 1 F), −133.30 (s br, 1 F), −153.51 (t, $^3J_{\mathrm{F-F}} = 17.2$ Hz, 1 F), −154.81 (t, $^3J_{\mathrm{F-F}} = 19.5$ Hz, 1 F), −155.29 (t, $^3J_{\mathrm{F-F}} = 18.3$ Hz, 1 F), −156.26 (t, $^3J_{\mathrm{F-F}} = 16.6$ Hz, 1 F), −156.40 (t, $^3J_{\mathrm{F-F}} = 21.3$ Hz, 1 F), −157.57 (d, $^3J_{\mathrm{F-F}} = 20.6$ Hz, 1 F), −162.43 (t, $^3J_{\mathrm{F-F}} = 19.7$ Hz, 1 F), −162.56 (t, $^3J_{\mathrm{F-F}} = 22.4$ Hz, 1 F), −164.61 (s br, 1 F).

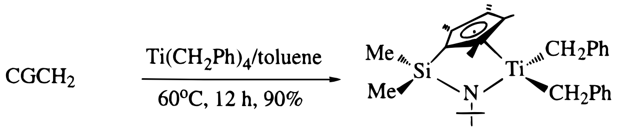
In Situ Generation of CGCTiMe$^+$MeB(C$_6$F$_5$)$_3^-$ (8). CGCTiMe$_2$ (3.3 mg, 0.010 mmol) and B(C$_6$F$_5$)$_3$ (5.1 mg, 0.010 mmol) were loaded into a J. Young NMR tube, and toluene-*d*$_8$ was condensed in. The mixture was allowed to react at room temperature for 1 h before the NMR spectrum was recorded. ^{1}H NMR (C$_7$D$_8$, 23 °C): δ 1.75 (s, 3 H, C$_5$Me$_4$), 1.51 (s, 3 H, C$_5$Me$_4$), 1.44 (s, 3 H, C$_5$Me$_4$), 1.42 (s, 3 H, C$_5$Me$_4$), 0.99 (s, 9 H, N^{t}Bu), 0.93 (s, 3 H, Ti−Me), 0.62 (s br, 3 H, B−Me), 0.26 (s, 3 H, SiMe$_2$), 0.16 (s, 3 H, SiMe$_2$). ^{19}F NMR (C$_7$D$_8$, 23 °C): δ −133.68 (d, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 6 F, *o*-F), −159.49 (t, $^3J_{\mathrm{F-F}} = 21.0$ Hz, 3 F, *p*-F), −164.62 (t, $^3J_{\mathrm{F-F}} = 19.0$ Hz, 6 F, *m*-F).

Synthesis of [CGCTiMe(μ-Me)MeTiCGC]$^+$[MePBB]$^-$ (9). In the glovebox, CGCTiMe$_2$ (65.5 mg, 0.200 mmol) and PBB (96.0 mg, 0.100 mmol) were loaded into a flamed 25 mL reaction flask having a filter frit, which was next attached to the high-vacuum line. Benzene (20 mL) was then vacuum-transferred into the flask at −78 °C. The mixture was slowly allowed to warm to room temperature and stirred for an additional 2 h. The solvent was removed *in vacuo*, and pentane (20 mL) was condensed into the flask. The resulting suspension was filtered, and the collected solid was washed with 5 mL of pentane and dried under vacuum to afford 0.15 g of the title complex as a green-yellow solid. Yield: 93.1%. One of the two possible diastereomers is formed selectively (90%), and spectroscopic data are listed for the major isomer. ^{1}H NMR (C$_7$D$_8$, 23 °C): δ 1.96 (s, 6 H, C$_5$Me$_4$), 1.69 (s, 6 H, C$_5$Me$_4$), 1.63 (s, 6 H, C$_5$Me$_4$), 1.60 (s, 6 H, C$_5$Me$_4$), 1.20 (s, 18 H, N^{t}Bu), 0.56 (s, 6 H, Ti−Me), 0.36 (s, 6 H, SiMe$_2$), 0.34 (s, 6 H, SiMe$_2$), −0.72 (s, 3 H, Ti−Me−Ti), −0.94 (s br, 3 H, B−Me). ^{13}C NMR (C$_7$D$_8$, 23 °C): δ 128.86 (*C*$_5$Me$_4$), 127.68 (*C*$_5$Me$_4$), 127.27 (*C*$_5$Me$_4$), 126.95 (*C*$_5$Me$_4$), 126.64 (*C*$_5$Me$_4$), 65.01 (Ti−Me), 61.64 (N*C*Me$_3$), 33.75 (NC*Me*$_3$), 33.20 (B−Me), 22.68 (Ti−Me−Ti), 15.74 (C$_5$*Me*$_4$), 14.64 (C$_5$*Me*$_4$), 11.91 (C$_5$*Me*$_4$), 11.67 (C$_5$*Me*$_4$), 5.45 (SiMe$_2$), 4.34 (SiMe$_2$). ^{19}F NMR (C$_7$D$_8$, 23 °C): δ −122.74 (s br, 3 F), −139.20 (d, $^3J_{\mathrm{F-F}} = 22.0$ Hz, 3 F), −139.41 (d, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 3 F), −140.28 (d, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 3 F), −156.11 (t, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 3 F), −158.71 (s br, 3 F), −163.59 (t, $^3J_{\mathrm{F-F}} = 22.1$ Hz, 3 F), −163.86 (t, $^3J_{\mathrm{F-F}} = 22.2$ Hz, 3 F), −164.52 (t, $^3J_{\mathrm{F-F}} = 22.6$ Hz, 3 F). Anal. Calcd for C$_{70}$H$_{66}$BF$_{27}$N$_2$Si$_2$Ti$_2$: C, 52.18; H, 4.13; N, 1.74. Found: C, 51.75; H, 3.80; N, 1.34.

In Situ Generation of [CGCTiMe(μ-Me)MeTiCGC]$^+$B(C$_6$F$_5$)$_4^-$ (10). CGCTiMe$_2$ (6.6 mg, 0.020 mmol) and Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ (9.2 mg, 0.010 mmol) were loaded into a J. Young NMR tube, and toluene-*d*$_8$ was condensed in. The NMR spectrum was recorded immediately after the solution was prepared. One of the two possible diastereomers is formed selectively (90%), and spectroscopic data are listed for the major isomer. ^{1}H NMR (C$_7$D$_8$, 23 °C): δ 1.95 (s, 6 H, C$_5$Me$_4$), 1.70 (s, 6 H, C$_5$Me$_4$), 1.64 (s, 6 H, C$_5$Me$_4$), 1.61 (s, 6 H, C$_5$Me$_4$), 1.22 (s, 18 H, N^{t}Bu), 0.53 (s, 6 H, Ti−Me), 0.40 (s, 6 H, SiMe$_2$), 0.35 (s, 6 H, SiMe$_2$), −0.73 (s, 3 H, Ti−Me−Ti). ^{19}F NMR (C$_7$D$_8$, 23 °C): δ −131.90 (s br, 8 F, *o*-F), −162.95 (t, $^3J_{\mathrm{F-F}} = 20.3$ Hz, 4 F, *p*-F), −166.74 (s br, 8 F, *m*-F).

In Situ Generation of [CGCTiMe(μ-Me)MeTiCGC]$^+$-MeB(C$_6$F$_5$)$_3^-$ (11). Stock solutions containing 0.01 mol/L of CGCTiMe$^+$MeB(C$_6$F$_5$)$_3^-$ (**8**) and CGCTiMe$_2$ in C$_7$D$_8$ were used for the preparation of a 1:1 CGCTiMe$^+$MeB(C$_6$F$_5$)$_3^-$:CGCTiMe$_2$ solution. An equilibrium was observed in favor of monomeric species **8**. The spectroscopic data for dinuclear species **11** (one of the two possible diastereomers is formed selectively (90%), and spectroscopic data are listed for the major isomer) are as follows. ^{1}H NMR (C$_7$D$_8$, 23 °C): δ 1.97 (s, 6 H, C$_5$Me$_4$), 1.68 (s, 6 H, C$_5$Me$_4$), 1.64 (s, 6 H, C$_5$Me$_4$), 1.60 (s, 6 H, C$_5$Me$_4$), 1.17 (s, 18 H, N^{t}Bu), 0.53 (s, 6 H, Ti−Me), 0.39 (s br, 3 H, B−Me), 0.34 (s, 6 H, SiMe$_2$), 0.32 (s, 6 H, SiMe$_2$), −0.75 (s, 3 H, Ti−Me−Ti). ^{19}F NMR (C$_7$D$_8$, 23 °C): δ −131.82 (d, $^3J_{\mathrm{F-F}} = 21.2$ Hz, 6 F, *o*-F), −165.16 (t, $^3J_{\mathrm{F-F}} = 21.0$ Hz, 3 F, *p*-F), −167.38 (t, $^3J_{\mathrm{F-F}} = 19.2$ Hz, 6 F, *m*-F).

Scheme 2



1

Ethylene and Propylene Polymerization Experiments. Ethylene and propylene 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 solution of a cationic complex or a 1:1 ratio of metallocene:cocatalyst in 2 mL of toluene or 1,2-difluorobenzene (for those catalysts activated with $Ph_3C^+B(C_6F_5)_4^-$) freshly prepared in the glovebox was quickly injected (using a gas-tight syringe equipped with a spraying needle) into a rapidly stirring flask containing a measured quantity of dry toluene (50 mL for this study) which was presaturated under 1.0 atm of rigorously purified ethylene or propylene. After a measured time interval, the polymerization was quenched by the addition of 2% acidified methanol. The polymer was collected by filtration, washed with methanol, and dried on the high-vacuum line overnight to a constant weight.

Ethylene and 1-Hexene Copolymerization Experiments. On the high-vacuum line, toluene (23 mL) was condensed into a flamed, 100 mL reaction flask equipped with a magnetic stirring bar and a septum-covered sidearm flask. The solvent was then saturated with 1.0 atm of ethylene, 5.5 mL of 1-hexene was added by syringe, and the mixture equilibrated at the desired temperature using an external temperature bath. In the glovebox, 6 mL sample vials equipped with septum caps were loaded with the cationic complexes (25 μmol) or titanocene and MAO (solid after removing toluene and trimethylaluminum *in vacuo*) with an Al_{MAO}:Ti ratio of 50:1. A measured amount of toluene (2 mL) was then syringed into the vials containing the above solutions with a dry, Ar-purged gas-tight syringe. The vials were removed from the glovebox immediatedly prior to the copolymerization studies. Each catalyst solution was then syringed into a reaction flask attached on the high-vacuum line through the septum-sealed sidearm flask. After a measured time interval with rapid stirring, the copolymerization was quenched by the addition of 2% acidified methanol. For MAO-activated copolymerizations, the quenched reaction mixtures were treated with 30 mL of 10% acidifed methanol and stirred for at least 4 h. The precipitated polymer was then collected by decantation, washed three times with methanol, and dried on the high-vacuum line overnight.

Results and Discussion

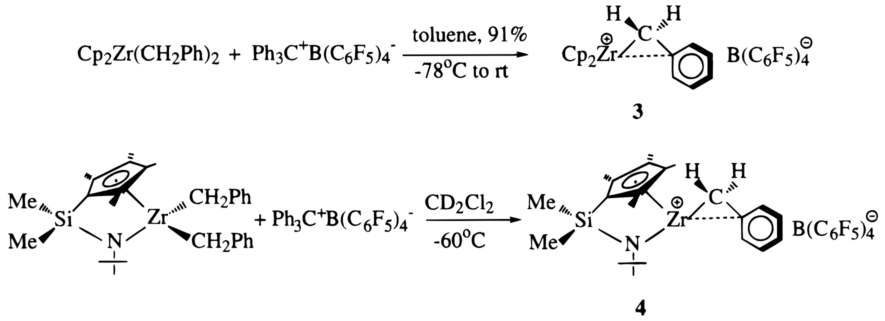
Expedient Synthesis of $CGCM(CH_2Ph)_2$ Complexes (M = Ti(1), Zr (2)). The conventional synthetic route to $CGCTiMe_2$ is depicted in Scheme 1. In our hands, this three-step synthesis affords only a 32% overall yield of the final dimethyl complex and requires 3−4 days. In contrast, the reaction of the neutral $CGCH_2$ ligand with $Ti(CH_2Ph)_4$ (1:1.3) in benzene or toluene at 60 °C for 12 h in the absence of light yields the desired $CGCTi(CH_2Ph)_2$ complex quantitatively (by NMR) and in a 90% isolated yield (Scheme 2). A small amount of bibenzyl byproduct is also detected in the NMR-scale reactions. The product work-up and purification involve only routine extraction and filtration to produce the spectroscopically and analytically pure precatalyst. Alternatively, heptane can be used in place of the aromatic solvent to achieve the same isolated yield. The ^1H NMR spectrum of **1** shows two diastereotopic benzylic protons at δ 2.58 and 2.25 ppm (J_{H-H} = 10.2 Hz), and the possible formation of significant η^n-benzyl bonding ($n > 1$) is excluded by the observation of a normal *ipso*-^{13}C Ph chemical shift at δ 150.36 ppm and a CH_2 $^1J_{C-H}$ value of 120.6 Hz.[20] The corresponding reaction of $CGCH_2$ with $Zr(CH_2Ph)_4$ is less clean and results in a lower conversion of the neutral ligand under a variety of conditions, along with the decomposition of $Zr(CH_2Ph)_4$, especially at higher reaction temperatures (see Experimental Section). Nevertheless, under the conditions of $Zr(CH_2Ph)_4$:$CGCH_2$ = 1.7:1 at 90 °C for 48 h, the crude product $CGCZr(CH_2Ph)_2$ (~90% purity by NMR) can be isolated in 60% yield. Further purification by fractional recrystallization from pentane at −78 °C results in a low yield (10%) due to the high solubility. The NMR spectroscopic data for **2** also indicate two equivalent benzyl groups which engage in normal η^1-CH_2Ph bonding with the expected *ipso*-^{13}C (Ph) chemical shift of δ 147.12 ppm and a CH_2 $^1J_{C-H}$ value of 120.3 Hz.[20]

Reaction of $CGCM(CH_2Ph)_2$ Complexes 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 benzyl group to the electrophilic metal center.[12e,20a,b] Guided by the NMR-scale reaction of $Cp_2Zr(CH_2Ph)_2$ with $Ph_3C^+B(C_6F_5)_4^-$ in $C_2D_2Cl_4$,[20a] a scale-up reaction was carried out, and cationic complex **3** was isolated as a crystalline solid in over 90% yield (Scheme 3). This observation is noteworthy since the corresponding reaction of metallocene dimethyls with $Ph_3C^+B(C_6F_5)_4^-$ often results in the formation of insoluble, oily residues which are difficult to purify and characterize.[15a,d] This enhanced thermal stability and crystallizability of the benzyl complex is reasonably attributable to stabilization by multihapto benzyl coordination. Several lines of evidence for an η^2 bonding mode in **3** include a high-field *ipso*-^{13}C resonance (δ 120.96 ppm, Ph), a high-field Zr−$^{13}CH_2$Ph signal (δ 47.34 ppm), and a large CH_2 $^1J_{C-H}$ value (148.0 Hz). In contrast, the reaction of the $CGCM(CH_2Ph)_2$ complexes with $B(C_6F_5)_3$ and $Ph_3C^+B(C_6F_5)_4^-$ is substantially different. Although the low-temperature NMR-scale reaction of $CGCZr(CH_2Ph)_2$ with $Ph_3C^+B(C_6F_5)_4^-$ in CD_2Cl_2 indicates the formation of cationic species **4** (Scheme 3), preparative-scale reactions at higher temperatures are accompanied by extensive decomposition. In contrast, preparative-scale reactions with the Ti complex are clean and afford C−H activation products, i.e., intramolecularly metalated fulvene-type complexes formulated as **5** and **6** (Scheme 4). Although a number of group 4 metal fulvene-type complexes have been reported,[21] cationic complexes of this type are rare.[22] ^1H NMR spectroscopic characteristics of the cationic portion of complex **5** include three singlets for Cp methyls, one singlet for the ^{t}Bu group, and two singlets for the diastereotopic $SiMe_2$ methyl

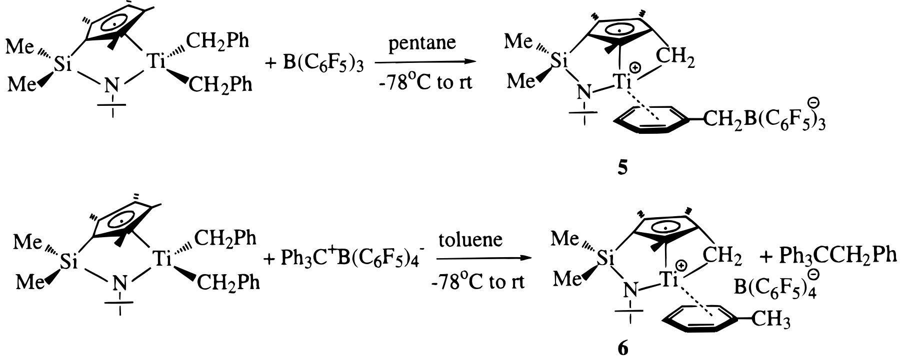
---

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

Scheme 3



Scheme 4



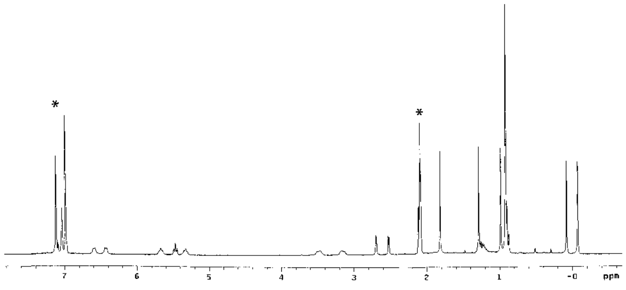


Figure 1. ^{1}H NMR spectrum of complex **5** in toluene-d_8 at 5 °C. The asterisk denotes NMR solvent signals.

groups (Figure 1). The fulvene methylene ^{13}C resonance appears at low field (δ 73.03 ppm) with a large CH$_2$ $^1J_{C-H}$ value (155.6 Hz) reflecting the constricted C−C−M angle and significant sp^2 character at the fulvene carbon. These spectroscopic data are in the range observed for other early transition metal fulvene complexes.[21]

Coordination of the $PhCH_2B(C_6F_5)_3^-$ anion to the highly electrophilic, unsymmetrical Ti center in **5** leads to two broad diastereotopic B*CH*$_2$Ph resonances and five nonequivalent phenyl protons (Figure 1).[23] NMR spectrocopic evidence for η^n-$PhCH_2B(C_6F_5)_3^-$ coordination includes dramatically upfield-shifted[24] *para*- and *meta*-BCH$_2$*Ph* resonances (above δ 6 ppm), a downfield-shifted BCH$_2$*Ph* *ipso*-^{13}C resonance at δ 153.53 ppm,[12e,23] and a large ^{19}F NMR C$_6$F$_5$ $\Delta\delta$ ($\delta_m - \delta_p$) value of 4.09 ppm.[23] The cationic portion of **6** (**6** is isolated as a complex of toluene which, from the NMR, appears to be weakly bound; see Experimental Section for spectroscopic data) exhibits similar NMR parameters; however, the ^{19}F NMR spectrum indicates an essentially unperturbed $B(C_6F_5)_4^-$ anion with no indication of static fluorine coordination. This arene coordination and $B(C_6F_5)_4^-$ noncoordination behavior is reminiscent of $CGCZrMe(toluene)^+B(C_6F_5)_4^-$.[15a]

Hydrogenolytic and Variable-Temperature NMR Studies of Complex 5. Cationic methyl complexes $L_2ZrMe^+MeB(C_6F_5)_3^-$ are known to undergo rapid, stepwise hydrogenolysis to yield mono- or dihydrido complexes, depending on the reaction conditions (e.g., eq 2).[12d,25] However, the present CGC catalysts *do not undergo significant hydrogenolysis* under similar reaction conditions. Thus, the room-temperature NMR-scale reactions of the $CGCMMe^+MeB(C_6F_5)_3^-$ complexes with H$_2$ in C$_6$D$_6$ exhibit no spectroscopic changes and no indication of hydride formation over the course of 4 h. The similar reaction of CGCMMe$_2$, $Ph_3C^+B(C_6F_5)_4^-$,

$$(C_5Me_5)_2ZrMe^+MeB(C_6F_5)_3^- \xrightarrow[-CH_4]{H_2/pentane} (C_5Me_5)_2ZrH^+MeB(C_6F_5)_3^- \xrightarrow[-CH_4]{H_2/C_6H_6} (C_5Me_5)_2ZrH^+HB(C_6F_5)_3^- \quad (2)$$

---

[21] (a) Kreuden, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (b) Sinnema, P. J.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 184. (c) Luinstra, G. A.; Teuben, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 3361. (d) Vondrak, T.; Mach, K.; Varga, V.; Terpstra, A. *J. Organomet. Chem.* **1992**, *425*, 27. (e) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (f) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (g) Bandy, J. A.; Mtetwa, V. S. B.; Prout, K.; Green, J. C.; Davies, C. E.; Green, M. C. H.; Hazel, N. J.; Izguierdo, A.; Martin-polo, J. J. *J. Chem. Soc., Dalton Trans* **1985**, 2037. (h) Pattiasina, J. W.; Hissink, C. E.; de Boer, J. C.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7758. (I) Mcdade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (j) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

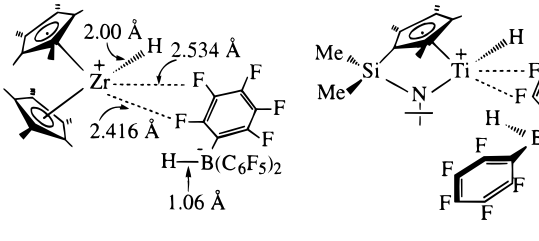
[22] The cationic complex (1,3-^{t}BuCp)$_2$ZrMe$^+$ undergoes intramolecular C−H activation at the ^{t}Bu group to form an η^5,η^1-"tuck-in" cation.[12d]

[23] Similar NMR spectroscopic behavior is noted when $PhCH_2B(C_6F_5)_3^-$ is coordinated to an asymmetric Zr$^+$ center, see: Horton, A. D.; de With, J. *J. Chem. Soc. Chem. Commun.* **1996**, 1375−1376.

[24] Pellecchia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160−1162.

[25] Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.

Scheme 5



7

and H_2 in toluene-d_8 likewise indicates no formation of hydrido complexes. In contrast, exposure of "tuck-in"complex **5** to dihydrogen leads to rapid NMR changes and spectroscopic features indicative of the cationic, ion-paired hydrido species $Me_2Si(C_5Me_4)(^{t}BuN)TiH^{+}HB(C_6F_5)_3^{-}$ (**7**; see Experimental Section for spectroscopic data). The ^{19}F NMR of the $HB(C_6F_5)_3^{-}$ anion is interesting and unprecedented. The appearance of a total of 15 F resonances for the total of 15 aryl F nuclei at room temperature suggests that tight anion coordination restricts rotation of the B$-C_6F_5$ rings in solution, even at 25 °C. A possibly analogous bonding description is the coordination of $HB(C_6F_5)_3^{-}$ to $(C_5Me_5)_2ZrH^{+}$ through two Zr···F bridges (Scheme 5) rather than *via* a the Zr···H···B bridge (presumably for steric reasons).[25] However, unlike **7** which exhibits a static ^{19}F NMR spectrum even at room temperature, the ^{19}F NMR spectrum of $(C_5Me_5)_2ZrH^{+}HB(C_6F_5)_3^{-}$ is dynamic at room temperature, and a limiting spectrum consistent with the solid state symmetry is only observed at low temperatures.[25] Unfortunately, despite the clean NMR-scale reaction, attempted scale-up syntheses of **7** result in black decomposition products exhibiting poor solubility in common NMR solvents and precluding further characterization.

Variable-temperature ^{1}H NMR studies of complex **5** over a broad temperature range (-60 to 100 °C) indicate no spectroscopic changes in the cationic portion; however, the anion ^{1}H NMR spectrum exhibits significant changes (Figure 2). At low temperatures (below -30 °C), five nonequivalent phenyl proton signals are observed at δ 6.58, 6.46 (d, $J_{H-H} = 6.5$ Hz) for the two *ortho*-Ph protons, at 5.37 (t, $J_{H-H} = 7.2$ Hz) for the single *para*-Ph proton, and at 5.55, 5.29 (t, $J_{H-H} = 6.3$ Hz) for two *meta*-Ph protons, as well as signals for the two diastereotopic CH_2B protons. The dramatically high-field-shifted *meta* and *para* proton signals strongly suggest η^{n}-coordination. On warming, the signals for the pairs of magnetically nonequivalent *meta* and *ortho* aryl protons as well as the diastereotopic CH_2B protons broaden, collapse, and eventually coalesce. These spectral changes can be explained by the phenyl ring facial permutation process illustrated in Scheme 6.[26]

Monomer$-$(μ-Methyl)-Dimer Equilibration. The reaction of $CGCTiMe_2$ (or $CGCZrMe_2$) with $B(C_6F_5)_3$ in pentane cleanly generates the corresponding monomeric cationic species $CGCTiMe^{+}MeB(C_6F_5)_3^{-}$ (**8**; Scheme 7).[4] Solution NMR data for **8** indicate coordination of the $MeB(C_6F_5)_3^{-}$ anion to the cationic Ti center, consistent with the solid state structure ($TiCH_3^{+}\cdots B(C_6F_5)_3^{-}$ = 1.675(5) Å) and variable-temperature dynamic NMR solution studies.[1b,4] Interestingly, although the analogous reaction with the sterically encumbered borane PBB yields the same type of monomeric cationic species for $CGCZrMe_2$, the cation$-$anion ion-pairing is significantly "looser", as indicated by DNMR studies of ion pair reorganization/molecular symmetrization.[1b] In the case of $CGCTiMe_2$, PBB generates predominantly a dinuclear μ-methyl complex, even using a 1:1 $CGCTiMe_2$:PBB ratio. Such cationic dinuclear complexes were isolated previously from the reaction of L_2ZrMe_2 with PBB, of which $[1,2\text{-}Me_2C_5H_3)_2Zr(Me)(\mu\text{-}Me)(Me)Zr(1,2\text{-}Me_2C_5H_3)_2]^{+}(MePBB)^{-}$ (**12**) has been crystallographically characterized[1b] (Scheme 8). NMR spectroscopic characteristics of **12** include a high-field μ-Me ^{1}H signal at δ -1.50 ppm and Me$-$B ^{1}H resonance at δ -0.92 ppm, a large μ-Me $^{1}J_{C-H} = 134.3$ Hz, and nine $(MePBB)^{-}$ ^{19}F resonances indicative of restricted C_6F_5 rotation.

Likewise, analytically pure dinuclear cationic **9** can be isolated when a 2:1 $CGCTiMe_2$:PBB ratio is employed (Scheme 9) and exhibits analogous NMR spectroscopic parameters. The course of the reaction of $CGCTiMe_2$ with $Ph_3C^{+}B(C_6F_5)_4^{-}$ is similar to that with PBB. Only a dimeric μ-methyl form can be detected by NMR in toluene-d_8 when using a 1:1 reactant ratio (if a monomeric species is formed, it apparently decomposes and/or precipitates immediately). The spectroscopically clean dinuclear cation $[CGCTiMe(\mu\text{-}Me)MeTiCGC]^{+}B(C_6F_5)_4^{-}$ (**10**) can be detected by NMR in reactions involving a 2:1 CGC$-TiMe_2$:$Ph_3C^{+}B(C_6F_5)_4^{-}$ ratio (see Experimental Section for data). Remarkably, one of the two possible diastereomers of the dinuclear cationic complexes **9**$-$**11** is formed selectively (90%).

In contrast to $CGCTiMe_2$ chemistry with PBB and $Ph_3C^{+}B(C_6F_5)_4^{-}$, the reaction of $CGCTiMe_2$ and $B(C_6F_5)_3$ does not yield ^{1}H NMR-detectable dinuclear species using a 1:1 reactant ratio. However, with a 2:1 $CGCTiMe_2$:$B(C_6F_5)_3$ ratio in toluene-d_8, an equilibrium is established with $\Delta G_{298K} = 1.3(2)$ kcal/mol in favor of monomeric species **8** (eq 3). These results can be

$$\underset{\mathbf{8}}{CGCTiMe^{+}MeB(C_6F_5)_3^{-}} + CGCTiMe_2 \rightleftharpoons \underset{\mathbf{11}}{[CGCTiMe(\mu\text{-}Me)MeTiCGC]^{+}MeB(C_6F_5)_3^{-}} \qquad (3)$$

explained in terms of competition between the fluoroarylborate anion and the neutral metallocene dimethyl for the highly electrophilic metallocene cations which,

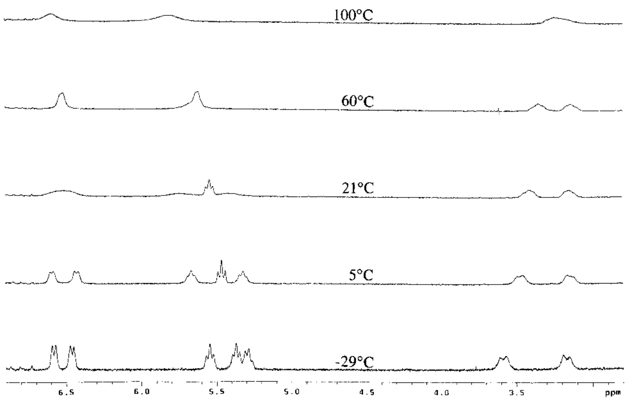
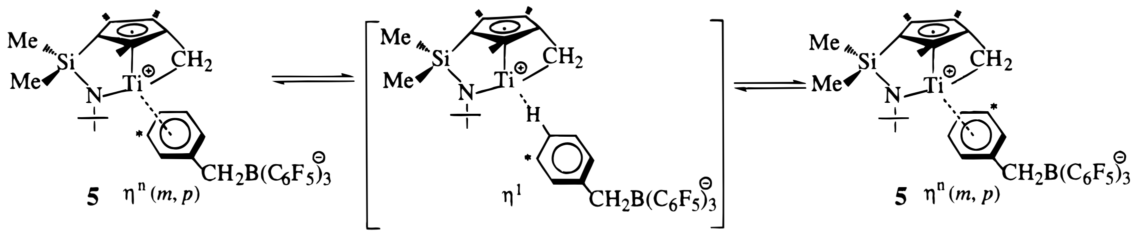


Figure 2. Variable-temperature ^{1}H NMR spectra of the anionic portion of complex **5** in toluene-d_8.

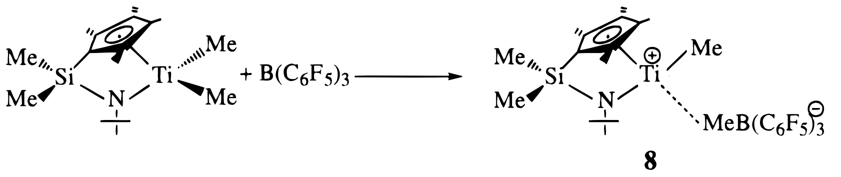
---

[26] Similar fluxional behavior of the coordinated anion BPh_4^{-} has been reported, see: Horton, A. D.; Frijins, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1152.

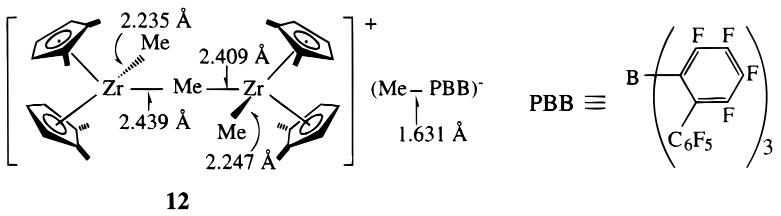
Scheme 6



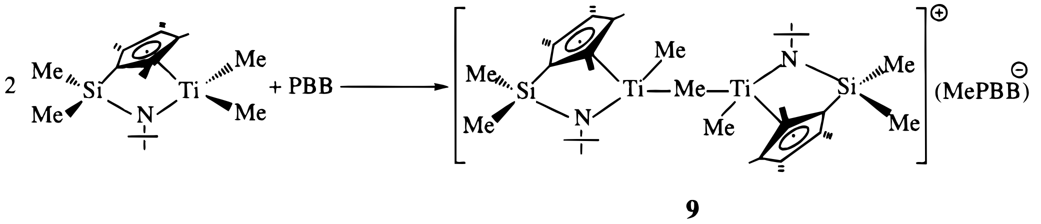
Scheme 7



Scheme 8



Scheme 9



thus, demonstrate that the relative coordinative tendency of the anions/neutrals with respect to the CGC-TiMe$^+$ cation follows the order $MeB(C_6F_5)_3^-$ > CGC-TiMe$_2$ > $MePBB^-$, $B(C_6F_5)_4^-$. As expected, the cationic portions of the aforementioned dinuclear species **9**−**11** are NMR spectroscopically almost identical, regardless of the counteranion. Noteworthy also are *identical* ^{19}F chemical-shift patterns exhibited by counteranions $MePBB^-$ and $B(C_6F_5)_4^-$ in monomeric *versus* dinuclear cationic species (noncoordinating) and the significantly *different* ^{19}F chemical shift patterns of the $MeB(C_6F_5)_3^-$ anion in the corresponding monomeric and dinuclear ion-paired structures (high-field shifted by $\Delta\delta = 5.67$ ppm for the *p*-F and $\Delta\delta = 2.76$ for the *m*-F on proceeding from monomer to dimer). Also noteworthy in the ^{19}F NMR is the large $MeB(C_6F_5)_3^-$ $\Delta\delta$ (δ_m - δ_p) = 5.13 ppm (*partially coordinated*) for mononuclear **8** and the small $\Delta\delta$ (δ_m - δ_p) = 2.22 ppm for dinuclear **11** (*free anion*). These observations illustrate again the aforementioned rather different relative coordinating tendencies of the various fluoroaryl borate counteranions with respect to the CGC cations.

α-Olefin Polymerization and Copolymerization Studies. Table 1 summarizes ethylene and propylene polymerization activities of the various CGCTi-derived catalysts as well as the properties of the resulting polymers. Polymerization procedures were designed to minimize mass transfer effects.[12d] Surprisingly, the "tuck-in" cations **5** and **6** are highly active catalysts for both ethylene and propylene polymerizations, producing ultra-high molecular weight (>10^6) polyethylenes with high melting transition temperatures (T_m = 142 °C) and syndiotactically-enriched atactic polypropylenes with appreciable molecular weights. Again, the substantial activity differences of identical cations having different counteranions (entries 1 vs 3; 2 vs 4; 5 vs 6) demonstrate the significant influence of the nature of the anion on catalytic activity. Although two parallel runs (entries 1 vs 2; 3 vs 4) indicate that catalysts **5** and **6** derived from the CGCM(CH$_2$Ph)$_2$ complexes are somewhat more active than those derived from CGCMMe$_2$ complexes for ethylene polymerization, **5** and **6** are suprisingly ineffective toward ethylene and 1-hexene copolymerization (Table 2, runs 3 and 4), whereas the CGCMMe$_2$-derived catalysts are excellent agents for copolymerization with large quantities of 1-hexene comonomer incorporation (>60%). The fact that tuck-in cations **5** and **6** produce significantly higher molecular weight and melting transition temperature polyethylenes than the CGCMMe$_2$-derived catalysts (presumably a result of significantly suppressed β-H elimination) and the inactivity of **5** and **6** for ethylene and 1-hexene copolymerization may reflect the steric encumberance of what would be a *polymeric ring substituent* produced in the first chain-forming catalytic cycle (Scheme 10). However, the relative inactivity of the CGCM(CH$_2$Ph)$_2$ catalysts for

Table 1. Summary of α-Olefin Polymerization Activities Catalyzed by CGCTi Polymerization Catalysts and Polymer Properties[a]

entry	catalyst	monomer	reaction time (min)	polymer yield (g)	activity[b]	M_w[c]	M_w/M_n	remarks
1	$CGCTiMe^+MeB(C_6F_5)_3^-$ (**8**)	ethylene	7.0	0.20	1.14×10^5	1.06×10^6	9.54	$T_m = 136.8$ °C
2	$CGC^{-H}Ti^+PhCH_2B(C_6F_5)_3^-$ (**5**)	ethylene	7.0	0.23	1.31×10^5	2.00×10^6	6.77	$T_m = 142.1$ °C
3	$CGCTiMe^{+\,d}\ B(C_6F_5)_4^-$	ethylene	1.0	0.31	1.24×10^6	1.22×10^5	2.70	$T_m = 135.5$ °C
4	$CGC^{-H}Ti^+B(C_6F_5)_4^-$ (**6**)	ethylene	1.0	0.39	1.56×10^6	2.45×10^6	7.85	$T_m = 142.6$ °C
5	$CGC^{-H}Ti^+PhCH_2B(C_6F_5)_3^-$ (**5**)	propylene	15	0.65	1.73×10^5	1.69×10^5	2.81	$[mm] = 0.0992$, $[mr] = 0.4905$, $[rr] = 0.4103$
6	$CGC^{-H}Ti^+B(C_6F_5)_4^-$ (**6**)	propylene	5.0	2.65	2.12×10^6	1.42×10^5	3.80	$[mm] = 0.1557$,$[mm] = 0.1557$, $[mr] = 0.4914$, $[rr] = 0.3529$

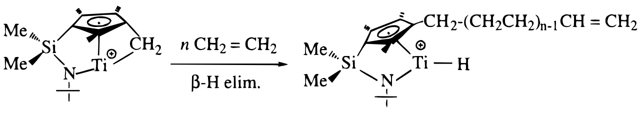
[a] Carried out at 25 °C, 1 atm of monomer, 15 μmol of catalyst, and 50 mL of toluene on a high-vacuum line. [b] In units of g of polymer/mol of Ti·atm·h; reproducibility between runs = ±10−15%. [c] GPC relative to polystyrene standards. [d] Catalyst generated by in situ reaction of $CGCTiMe_2$ and $Ph_3C^+B(C_6F_5)_4^-$ in 2 mL of toluene for 5 min.

Table 2. Summary of Ethylene and 1-Hexene Copolymerization Data for CGCTi Catalysts[a]

entry	catalyst	μmol of cat	conditions	polymer yield (g)	polymerization activity[b]	1-hexene incorporation
1	$CGCTiMe^+MeB(C_6F_5)_3^-$ (**8**)	25	25 °C, 10 min	0.05	1.20×10^4	63.2%
2	$CGCTiMe^+MeB(C_6F_5)_3^-$ (**8**)	25	60 °C, 10 min	2.44	5.86×10^5	69.8%
3	$CGC^{-H}Ti^+PhCH_2B(C_6F_5)_3^-$ (**5**)	25	25 °C, 30 min	trace		
4	$CGC^{-H}Ti^+PhCH_2B(C_6F_5)_3^-$ (**5**)	25	60 °C, 10 min	2.80	6.72×10^5	trace[c]
5	**1**/MAO[d]	20	25 °C, 10 min	0.03	9.00×10^3	65.7%
6	**1**/MAO[d]	20	60 °C, 10 min	1.40	4.20×10^5	69.9%

[a] All polymerization carried out on high-vacuum line at 1.0 atm of ethylene pressure and 44.5 mmol of 1-hexene in 25 mL of toluene. [b] In units of g of polymer/mol of Ti·atm·h; reproducibility between runs = ±10−15%. [c] Mixture of two homopolymers. [d] Mol ratio Al_{MAO}:Ti = 50:1.

Scheme 10



5, **6**

ethylene and 1-hexene copolymerization can be readily overcome using MAO as the activator to generate the catalytically active species *in situ*.[14,27] Thus, under this activation scenario, the $CGCTi(CH_2Ph)_2$/MAO system is highly efficient for ethylene and 1-hexene copolymerization at 60 °C in terms of activity and comonomer incorporation (entries 5 and 6 in Table 2). The fact that $CGCTiR^+X^-$ catalyst polymerization activities are markedly temperature-dependent (1 vs 2; 3 vs 4; 5 vs 6, Table 2) also appears to be consistent with tight cation−anion ion-pairing.

Conclusions

An efficient, one-step synthetic approach to group 4 $CGCM(CH_2Ph)_2$ polymerization catalysts has been developed. The reaction of $CGCM(CH_2Ph)_2$ and $CGCMMe_2$ complexes with $B(C_6F_5)_3$, PBB, and $Ph_3C^+B(C_6F_5)_4^-$ has been investigated in detail, and various cationic complexes, including monomeric species, dinuclear species, and C−H bond activation products, have been isolated and characterized. The formation of various cationic structural variants in the above reactions can be attributed to an interplay of metal alkyl cation stability and the relative coordinating ability of the counteranion. This basic information on cation−anion ion pairing obtained is directly connectable to the polymerization catalysis studied in this work in terms of activity, bulky comonomer incorporation, and product polymer properties.

Acknowledgment. This research was supported by the U.S. Department of Energy (Grant No. DE-FG 02-86 ER 13511). Y.X.C. thanks Akzo-Nobel Chemicals for a postdoctoral fellowship.

OM970288+

---

(27) For a recent review article on the properties of MAO, see: Reddy, S. S.; Sivaram, S. *Prog. Polym. Sci.* **1995**, *20*, 309−367.