Organo-Lewis Acids As Cocatalysts in Cationic Metallocene Polymerization Catalysis. Unusual Characteristics of Sterically Encumbered Tris(perfluorobiphenyl)borane

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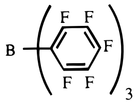
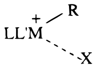
Organo-Lewis acids such as methylalumoxane (MAO)[1] and $B(C_6F_5)_3$[2] (**I**) play pivotal roles as alkide/hydride abstractors/cocatalysts in generating highly active, cationic olefin polymerization catalysts[3] (**II**; L,L′ = anionic ancillary ligands; X^- = weakly coordinating anion). Growing evidence[3,4] argues that catalyst activity, lifetime, high-temperature stability, chain transfer characteristics, and stereoregulation are significantly influenced by the nature of X^-, and that it would be of great interest to investigate the properties of sterically/electronically modified organo-Lewis acid abstractors. We communicate here the unusual cocatalytic characteristics of the new, sterically encumbered fluoroarylborane, tris(2,2′,2″-perfluorobiphenyl)borane (PBB, **III**).[5] Characteristics include substantially different abstractive and ion pair structure/reactivity relationships vis-à-vis **I**.

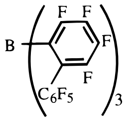
I



II



III



PPB was synthesized as colorless microcrystals in 76% yield from C_6F_5Br.[6] Reaction with group 4 and Th methyls proceeds cleanly to yield cationic complexes (eq 1), which were characterized by standard $^1H/^{13}C/^{19}F$ NMR spectroscopic and analytical techniques.[6] The ^{13}C NMR spectra of **1** and **6−9**

$$\begin{array}{l} LL'MMe_2 \\ L'MMe_3 \end{array} + PBB \xrightarrow[\text{or pentane}]{\text{benzene}}$$

Cp = η^5-C_5H_5

Cp′ = η^5-Me_5C_5

Cp″ = η^5-1,2-$Me_2C_5H_3$

M = Th, Zr_2, Hf

1, $Cp'_2ThMe^+[MePBB]^-$ (1)

2, $Cp_2ZrCl^+[MePBB]^-$

3, $[Cp_2ZrMe(\mu\text{-}Me)MeZrCp_2]^+[MePBB]^-$

4, $[Cp''_2ZrMe(\mu\text{-}Me)MeZrCp''_2]^+[MePBB]^-$

5, $[Cp'_2ZrMe(\mu\text{-}Me)MeZrCp'_2]^+[MePBB]^-$

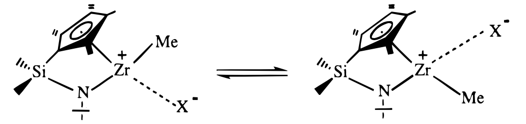
6, $[(Me_4C_5)SiMe_2N^tBu]ZrMe^+[MePBB]^-$

7, $[(Me_4C_5)SiMe_2N^tBu]TiMe^+[MePBB]^-$

8, $Cp'ZrMe_2{}^+[MePBB]^-$

9, $Cp'HfMe_2{}^+[MePBB]^-$

exhibit downfield $M^+{-}^{13}CH_3$ resonances characteristic of cationic complexes,[2,3] while ^{19}F spectra exhibit nine resonances (PBB exhibits seven) indicative of restricted C_6F_5 rotation. Evidence that the $MePBB^-$ anions are *weakly ion-paired* versus the $MeB(C_6F_5)_3{}^-$ counterparts derives from several lines. First, $MePBB^-$ ^1H chemical shifts are essentially invariant to countercation, unlike the $M^+\cdots H_3CB^-(C_6F_5)_3$ analogues.[2c] Second, DNMR studies of ion pair reorganization/symmetrization in **6** (eq 2) yield $\Delta G^\ddagger$ (40 °C) = 16.7(3) kcal/mol versus $\Delta G^\ddagger$ (40 °C) = 19.3(4) kcal/mol for the $MeB(C_6F_5)_3{}^-$ analogue, suggesting looser ion pairing. Third, the three $MePBB^-$ $C_6F_5C_6F_4$ groups are magnetically equivalent in the ^{19}F spectra of **1**, **2**, and **6−9** down to the lowest accessible temperatures (approximately −90 °C), also indicative of loose ion pairing.



(2)

Several other features of PBB abstractive chemistry are distinctive. Whereas the $Cp_2'ThMe_2$ and $Cp_2Zr(Cl)Me$ reaction with $B(C_6F_5)_3$ yields inseparable mixtures of catalytically inactive products,[2c] PBB selectively abstracts a single methyl group to yield cationic/catalytically active ion pairs (eq 1). For group 4 metallocene dimethyls, PBB generates cationic *dimeric*, μ-Me ($^1J_{CH}$ = 134.3 Hz) complexes (**3−5**), even with excess PBB and long reaction times (eq 1). Such cationic species have been detected previously but could not be isolated in a pure state.[7] The crystal structure of complex **4** (Figure 1)[8] reveals unassociated binuclear cation−anion pairs with nearly symmetrical μ-CH_3 (sp^2) bridging and metallocene metrical parameters similar to those in other cationic structures.[2,3] The $MePBB^-$ framework features substantial twisting of the C_6F_5−

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[1] (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.

[2] (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625. (b) Ewen, J. A.; Elder, M. J. *Chem. Abstr.* **1991**, *115*, 136998g. (c) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (d) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1993**, *115*, 2543−2545. (e) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593−6594. (f) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867−5868. (g) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243. (h) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755−1757. (i) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250.

[3] For recent reviews, see: (a) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (b) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (c) Soga, K.; Terano, M., Eds. *Catalyst Design for Tailor-Made Polyolefins*; Elsevier: Tokyo, 1994. (d) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29. (e) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65. (f) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387. (g) Quirk, R. P., Ed. *Transition Metal Catalyzed Polymerizations*; Cambridge University Press: Cambridge, 1988. (h) Kaminsky, W., Sinn, H., Eds. *Transition Metals and Organometallics for Catalysts for Olefin Polymerizations*; Springer: New York, 1988.

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

[5] Communicated in part: Chen, Y. -X.; Marks, T. J. *Abstracts of Papers*, 211th National Meeting of the American Society, New Orleans, LA, March 24−28, 1996; American Chemical Society: Washington, DC, 1996; INOR 591.

[6] Complete synthetic precedures and characterization details are given in the Supporting Information.

[7] Bochmann, M.; Lancaster, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634−1637.

[8] Crystal data: $Zr_2F_{27}BC_{68}H_{48}$; space group $P2_1/c$; a = 11.582(2) Å, b = 20.997(5) Å, c = 26.008(5) Å, β = 90.72(1)° at −120 °C; V = 6324(1) Å^3; Z = 4. Structure was solved by direct methods and refined with weighted and unweighted difference Fourier syntheses and full-matrix least-squares. $R_{(F)}$ and $R_{w(F)}$ = 0.048 and 0.040, respectively, for 5502 absorption-corrected reflections with $I > 2.50\sigma(I)$.

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Table 1. α-Olefin Polymerization Data[a]

entry	catalyst	μmol of cat	cond.[b]	monomer(s)[c]	polym. yield (g)	10^{-5}activity[d]	$10^{-3}M_w$[e]	M_w/M_n	remarks
1	$(Cp_2ZrMe)_2Me^+MePBB^-$ (**3**)	15	100, 40	E	0.80	48.0	559	3.06	
2	$Cp_2ZrMe^+MeB(C_6F_5)_3^-$	15	100, 60	E	1.00	40.0	124	2.03	
3	$(Cp''_2ZrMe)_2Me^+MePBB^-$ (**4**)	15	100, 40	E	1.30	78.0	392	2.72	
4	$Cp''_2ZrMe^+MeB(C_6F_5)_3^-$	15	100, 60	E	1.50	60.0	321	1.42	
5	$(Cp'_2ZrMe)_2Me^+MePBB^-$ (**5**)	15	100, 60	E	1.07	43.0	370	2.28	
6	$Cp'_2ZrMe^+MeB(C_6F_5)_3^-$	15	100, 60	E	0.80	32.0	136	2.54	
7	$Cp'TiMe^+_2MePBB^-$	50	5, 15	S	0.35	16.1	170	2.56	[*rrrr*]>98%
8	$Cp'ZrMe^+_2MePBB^-$ (**8**)	50	5, 10	S	1.45	100	27.6	2.63	atactic
9	$Cp'HfMe^+_2MeB(C_6F_5)_3^-$	50	5, 15	S	0.69	31.7	24.8	2.98	atactic
10	$Cp'HfMe^+_2MePBB^-$ (**9**)	50	5, 15	S	1.16	53.3	22.9	2.78	atactic
11	$Cp'TiMe^+_2MeB(C_6F_5)_3^-$	50	25, 5	E/H	0.70	1.70	848	23.7	39.5% H[f]
12	$Cp'TiMe^+_2MePBB^-$	50	25, 5	E/H	4.51	10.8	151	4.32	43.6% H[f]
13	CGC-$ZrMe^+MeB(C_6F_5)_3^-$	15	100, 20	E	0				
14	CGC-$ZrMe^+MePBB^-$ (**6**)	15	100, 4	E	1.56	15.6	7.69	2.78	
15	CGC-$TiMe^+MeB(C_6F_5)_3^-$	15	100, 10	E	0.21	0.84	1058	9.54	
16	CGC-$TiMe^+MePBB^-$ (**7**)	15	100, 40	E	0.83	49.8	305	2.56	
17	CGC-$ZrMe^+MeB(C_6F_5)_3^-$	50	25, 15	E/H	0				
18	CGC-$ZrMe^+MePBB^-$ (**6**)	50	25, 15	E/H	6.97	5.58	10.0	2.68	33.6% H[f]
19	CGC-$TiMe^+MeB(C_6F_5)_3^-$	25	25, 10	E/H	0.05	0.12			63.2% H[f]
20	CGC-$TiMe^+MePBB^-$ (**7**)	25	25, 10	E/H	1.95	4.68	105	1.86	65.3% H[f]

[a] Polymerization procedures designed to minimize mass transfer effects described in ref 2a,c; all polymerizations carried out on high-vacuum line at 25 °C. [b] Conditions given as milliliters of toluene, time (40 and 60 s, all other values in minutes). [c] Ethylene (E) (1 atm) pressure; 17.4 mmol of styrene (S); 44.5 mmol of 1-hexene (H). [d] gram of polymer/[(mole of cationic metallocene) atm h], except in entries 7−10 (polystyrene/[(mole of catalyst) (mole of monomer) h], (reproducibility between runs ≈ 10−15%). [e] GPC relative to polystyrene standards. [f] 1-Hexene incorporation in E/H copolymer.

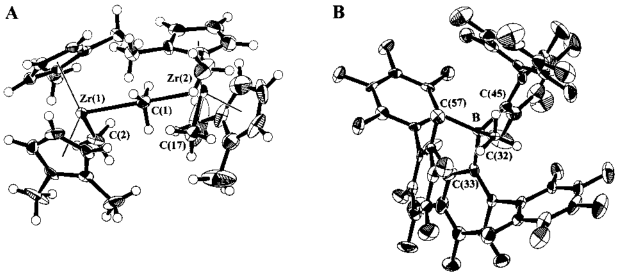

Figure 1. Molecular structure of the cationic (A) and anionic (B) portions of $\{[1,2\text{-}(CH_3)_2\text{-}C_5H_3]_2ZrCH_3(\mu\text{-}CH_3)CH_3Zr[1,2\text{-}(CH_3)_2\text{-}C_5H_3]_2\}^+[CH_3PBB]^-$ (**4**). Important bond distances (Å) and angles (deg) are as follows: Zr(1)−C(1) = 2.439(8), Zr(2)−C(1) = 2.409(9), Zr(1)−C(2) = 2.235(8), Zr(2)−C(17) = 2.247(9), Zr(1)−C(1)−Zr(2) = 170.9(4), B−C(32) = 1.631(9), B−C(33) = 1.672(9), B−C(45) = 1.687(10), B−C(57) = 1.686(10).

C_6F_4 dihedral angles from coplanarity (102°(av)), approximately tetrahedral C−B−C valence angles, and B−C distances comparable to those in $MeB(C_6F_5)_3^-$.[2] The present enhanced stability of μ-Me bonding likely reflects reduced coordinative tendencies of bulky $MePBB^-$ vs $MeB(C_6F_5)_3^-$ and the $LL'ZrMe_2$ precursor ($LL'ZrMe_2$ has a greater affinity for the cation than does $MePBB^-$). Nevertheless, dissociation of **4** can be detected by NMR at high temperatures (eq 3) with $\Delta H = 10.2(2)$ kcal/mol and $\Delta S = 26.3(4)$ eu. Furthermore, 2-D DNMR reveals

$$[Cp_2''ZrMe(\mu\text{-}Me)ZrMeCp_2'']^+[MePBB]^- \rightleftharpoons Cp_2''ZrMe_2 + Cp_2''ZrMe^+(MePBB)^- \quad (3)$$

rapid $ZrMe_{terminal} \rightleftharpoons ZrMe_{bridge}$ exchange above 25 °C in **4** as well rapid exchange with the ZrMe groups of added $Cp_2''ZrMe_2$. In accord with the weak cation−$MePBB^-$ interactions, and in marked contrast to $MeB(C_6F_5)_3^-$ ion pairs,[2c,4a] the present anion MeB groups are NMR exchange *nonlabile*. In regard to ion pair structural energetics, we find[9] that eq 1 for **6** is 20.5 kcal/mol *more exothermic* for PBB than for $B(C_6F_5)_3$ and that complexes **1**, **2**, and **6**−**9** exhibit no NMR evidence of μ-Me complex formation.

Selected polymerization catalytic data comparing PBB and $B(C_6F_5)_3$ are given in Table 1, and several features are noteworthy. First, despite μ-Me ground state geometries, complexes **3**−**5** are *at least as active as* the $B(C_6F_5)_3$ analogues for ethylene polymerization, yielding higher molecular weight polyethylenes (dimer dissociation and slower initiation may be connected with increased polydispersities). The effects of $MePBB^-$ ion pair formation on "constrained geometry" catalysts (CGC) **6** and **7** are dramatic. While the $MeB(C_6F_5)_3^-$ derivatives are essentially inactive (M = Zr) or marginally active (M = Ti) for polymerization at 25 °C (entries 13−16), the $MePBB^-$ analogues are highly active (enhancements of $\gtrsim 10^5$ and ~60, respectively). This trend obtains for ethylene/1-hexene copolymerization, with both PBB catalysts exhibiting comparable or higher comonomer incorporation with narrow polydispersities at higher polymerization rates. For single-ring complexes (entries 7−12),[10] the $MePBB^-$ complexes are again more active for styrene homopolymerization (note the high syndiospecificity in entry 7) and significantly more active for ethylene/1-hexene copolymerization to produce copolymers with much narrower polydispersity.

These results illustrate the substantial and surprising differences in cationic complex ion pair structure and reactivity that can be brought about by modifications in fluoroarylborane cocatalyst architecture. Further exploration of these effects is in progress.

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Supporting Information Available: Details of PBB and catalyst synthesis, characterization and X-ray experimental details, tables of positional and thermal parameters, bond lengths and angles, labeled drawings, and packing diagrams (43 pages). See any current masthead page for ordering and Internet access instructions.

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(9) Luo, L.; Chen, Y.-X.; Marks, T. J. Thermochemical research in progress.

(10) Although $Cp'TiMe_2^+MePBB^-$ could be generated in situ, it was too thermally unstable to isolate.