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# $[H_2N\{B(C_6F_5)_3\}_2]^-$: A New, Remarkably Stable Diborate Anion for Metallocene Polymerization Catalysts

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*Summary: The reaction between $NaNH_2$ and $B(C_6F_5)_3$ affords the amidodiborate anion $[H_2N\{B(C_6F_5)_3\}_2]^-$, the structure of which shows multiple intramolecular NH···F hydrogen bonding. Reaction with HCl affords $[H(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$, while treatment of zirconocene dimethyls with $[CPh_3][H_2N\{B(C_6F_5)_3\}_2]$ gives highly active alkene polymerization catalysts.*

The importance of the counteranion in olefin polymerization systems based on electrophilic cationic metal complexes is well-documented.[1−4] Significant synthetic effort continues to be invested in devising very weakly coordinating anions or activators leading to such anions. Apart from the widely used activators $B(C_6F_5)_3$ and $A^+[B(C_6F_5)_4]^-$ ($A = CPh_3$, $HNR_3$),[5−9] examples include chelating diboranes,[10] dendrimer-supported anions,[11] alkoxymetalates,[12] and halogenated carboranyl anions,[13] although some perfluorinated compounds proved to be unstable or prone to ligand transfer.[12c,d,14] We have reported recently the very facile synthesis of anions of reduced nucleophilicity by complexation of $B(C_6F_5)_3$ with $CN^-$ or cyanometalates, to give compounds of the type $[CN\{B(C_6F_5)_3\}_2]^-$ and $[M\{CNB(C_6F_5)_3\}_4]^{2-}$, where the negative charge is delocalized over two or more boron centers.[15,16] Although activation of metallocene dialkyls with $[CPh_3][CN\{B(C_6F_5)_3\}_2]$ has given rise to some of the most active alkene polymerization catalysts reported to date,[15] solutions of the metallocene salts $[L_2ZrMe]^+$-$[CN\{B(C_6F_5)_3\}_2]^-$ tend to decompose slowly, due to anion dissociation. We were therefore interested in the preparation of diborate anions of enhanced stability and report here the synthesis and structure of the remarkably stable $[H_2N\{B(C_6F_5)_3\}_2]^-$ anion.

A suspension of sodium amide in diethyl ether reacts with 2 equiv of $B(C_6F_5)_3$ to give $[Na(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$ (**1**) as colorless crystals in high yield (Scheme 1).[17] Surprisingly, the analogous reactions of $B(C_6F_5)_3$ with $LiNMe_2$, $LiPMe_2$, and $LiPCy_2$ or the deprotonation of $B(C_6F_5)_3$·$NHMe_2$ or $B(C_6F_5)_3$·$PHCy_2$ followed by treatment with excess $B(C_6F_5)_3$ did not give

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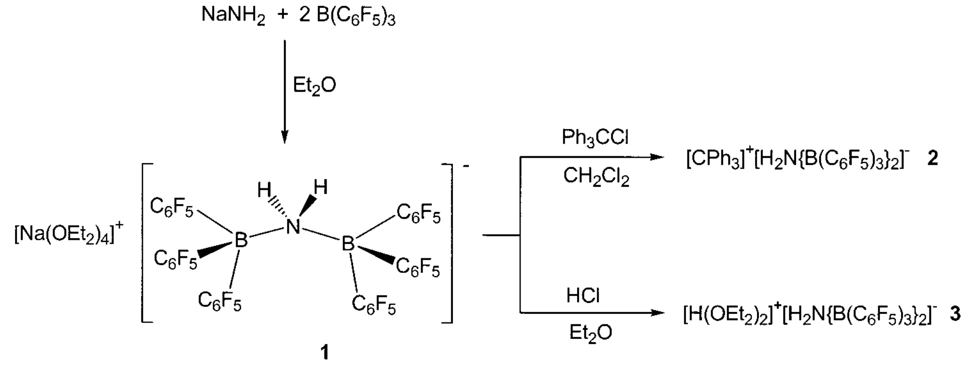
**Scheme 1**



clean products. Mononuclear anions of the type $[XB(C_6F_5)_3]^-$ for use in polymerization systems have previously been obtained by deprotonation of complexes of $B(C_6F_5)_3$ with alcohols, thiols, and oximes.[12a,b]

The structure of **1** was confirmed by X-ray diffraction (Figure 1).[18] The anion in **1** possesses a bent B−N−B core (angle B(5)−N(5)−B(8) = 134.3(2)°). The polarity of the $B-NH_2-B$ moiety has structural consequences and leads to significant intramolecular N−H····F hydrogen bonding, with one N−H hydrogen atom showing close contacts to two and the other to three F atoms. One distance of the former, H(52)···F(82), is particularly short (1.90(2) Å) and correlates with the N−H···F arrangement approaching linearity (155(2)°). The other H···F distances range from 2.18(2) to 2.42(2) Å (compared to the sum of van der Waals radii ~2.5 Å), with very much smaller N−H···F angles of 115−127°. Hydrogen bonding to covalently bonded organic fluorine is rare and has been the subject of detailed studies.[19] The observation of multiple NH···F−C interactions in the present case, some of which are comparatively short, is presumably a reflection of significant bond polarity within the amidodiborate anion. Cooling $CD_2Cl_2$ solutions of **1** to −90 °C leads to a splitting of the *o*-F signal ($\delta$ −135.4 at 25 °C) into five components (ratio 1:2:1:1:1), indicative of hindered rotation. One of these signals is high-field shifted, to $\delta$ −141.8. Although not conclusive by themselves, the complexity of the low-temperature spectra support the notion that H bonding persists in solution.

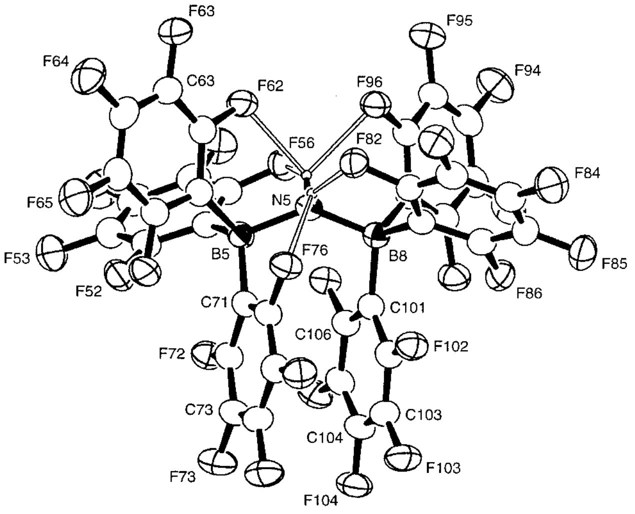


**Figure 1.** Structure of the $[H_2N\{B(C_6F_5)_3\}_2]^-$ anion in **1**, showing the atomic numbering scheme. Open lines indicate H···F hydrogen bonding.

Treatment of **1** with $Ph_3CCl$ in dichloromethane affords $[CPh_3][H_2N\{B(C_6F_5)_3\}_2]$ (**2**) as a bright yellow powder. The resistance of the diborate anion toward protolysis is illustrated by reacting **1** with HCl in diethyl ether to give microcrystalline $[H(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$ (**3**).[20] Formation of this strong Brønsted acid is favored over protolytic anion decomposition: e.g., to give $H_3N{\cdot}B(C_6F_5)_3 + Et_2O{\cdot}B(C_6F_5)_3$.

The suitability of **2** as a catalyst activator was compared with that of $[CPh_3][B(C_6F_5)_4]$ and $[CPh_3][CN\{B(C_6F_5)_3\}_2]$, following our established protocol.[15b] Propene polymerizations were conducted in 100 mL of toluene containing 0.1 mmol of $AlBu^i_3$ under 1 bar of

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(17) Preparation of **1**: a mixture of 9.9 g of $B(C_6F_5)_3$ and 0.38 g (9.6 mmol) of $NaNH_2$ in 50 mL of diethyl ether was stirred for 2 h, concentrated to ca. 10 mL, and cooled to −25 °C. Colorless cubic crystals formed (8 g, 6.2 mmol, 65%). The bulk material had the composition $Na[H_2N\{B(C_6F_5)_3\}_2]{\cdot}3Et_2O$. Anal. Calcd for $C_{48}H_{32}B_2F_{30}NaNO_3$: C, 44.85; H, 2.51; N, 1.09. Found: C, 44.31; H, 2.31; N, 1.08. $^1H$ NMR ($CDCl_3$, 20 °C, 300.13 MHz): $\delta$ 5.6 (br s, 2H, $NH_2$), 3.57 (q, 12H, $J = 7.1$ Hz, $OCH_2CH_3$), 1.21 (t, 18H, $J = 7.1$ Hz, $OCH_2CH_3$). $^{11}B$ NMR ($CDCl_3$, 20 °C, 96.29 MHz): $\delta$ −5.5. $^{19}F$ NMR ($CD_2Cl_2$, 25 °C, 282.4 MHz): $\delta$ −133.4 (d, 12F, $J_{F-F} = 20$ Hz, *o*-F, $C_6F_5$), −160.3 (t, 6F, $J_{F-F} = 20$ Hz, *p*-F, $C_6F_5$), −166.1 (t, 12F, $J_{F-F} = 20$ Hz, *m*-F, $C_6F_5$). $^{19}F$ NMR ($CD_2Cl_2$, −90 °C): *o*-F, $\delta$ −130.1 (1F), −131.2 (2F), −133.3 (1F), −136.0 (1F), −141.8 (1F); *p*-F, −159.5 (3F); *m*-F, −163.8, −164.2, −165.8; all signals are broad.

(18) Crystal data of **1**: $C_{52}H_{42}B_2F_{30}NNaO_4$, fw 1359.5; triclinic; $P\bar{1}$; $a = 11.922(1)$ Å, $b = 14.594(2)$ Å, $c = 16.754(1)$ Å; $\alpha = 86.75(1)°$, $\beta = 74.75(1)°$, $\gamma = 85.47(1)°$; $V = 2801.6(5)$ Å$^3$; $Z = 2$; $D_{calcd} = 1.612$ g/cm$^3$; $\mu = 0.175$ mm$^{-1}$; $F(000) = 1368$; $2.2 \leq \theta \leq 25.5°$; $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$; 19 096 reflections collected, of which 9616 were independent ($R_{int} = 0.0454$) and 7767 observed ($I > 2\sigma(I)$); no. of data/restraints/parameters 9616/0/834; goodness of fit $S = 1.034$.

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(20) **2**: from **1** (3.13 g, 2.4 mmol) and $Ph_3CCl$ (0.67 g, 2.4 mmol) in 20 mL of dichloromethane. Removal of the solvent left an orange-yellow foam, which was dissolved in 30 mL of dichloromethane and filtered. Solvent removal and washing with 2 × 20 mL of light petroleum ether produced a bright yellow powder which was recrystallized from dichloromethane at −25 °C (1.5 g, 1.2 mmol, 50%). Anal. Calcd for $C_{55}H_{17}B_2F_{30}N$: C, 51.48; H, 1.34; N, 1.09. Found: C, 51.07; H, 1.27; N, 1.09. $^1H$ NMR ($CD_2Cl_2$, 20 °C, 300.13 MHz): $\delta$ 8.29 (t, 3H, $J = 6.4$ Hz, *p*-H, $CPh_3$), 7.89 (tr, 6H, $J = 7.6$ Hz, *m*-H, $CPh_3$), 7.67 (d, 6H, $J = 6.8$ Hz, *o*-H, $CPh_3$), 5.67 (br s, 2H, $NH_2$). $^{13}C$ NMR ($CD_2Cl_2$, 20 °C, 75.47 MHz): $\delta$ 211.2 ($CPh_3$), 144.0 (*p*-C, $CPh_3$), 143.0 (*m*-C, $CPh_3$), 140.3 (*i*-C, $CPh_3$), 131.0 (*o*-C, $CPh_3$). $^{11}B$ NMR ($CD_2Cl_2$, 20 °C, 96.29 MHz): $\delta$ −5.3. $^{19}F$ NMR ($CD_2Cl_2$, 20 °C, 282.4 MHz): $\delta$ −133.4 (d, 12F, $J_{F-F} =$ 20 Hz, *o*-F, $C_6F_5$), −160.6 (tr, 6F, $J_{F-F} = 20$ Hz, *p*-F, $C_6F_5$), −166.1 (tr, 12F, $J_{F-F} = 20$ Hz, *m*-F, $C_6F_5$). **3**: HCl gas was bubbled through a solution of **1** (7.7 mmol) in $Et_2O$ at room temperature until gas consumption was complete, as indicated by a paraffin bubbler. Removal of the solvent from the filtrate and rapid stirring with light petroleum gave a white powder (6.0 g, 4.75 mmol, 62%). Anal. Calcd for $C_{44}H_{23}B_2F_{30}NO$: C, 44.44; H, 1.95; N, 1.18. Found: C, 44.47; H, 1.98; N, 1.12. $^1H$ NMR ($CD_2Cl_2$, 25 °C, 300.13 MHz): $\delta$ 16.60 (s, 1H, $H^+$), 5.70 (br s, 2H, $NH_2$), 4.06 (m, br, 8H, $OCH_2$), 1.43 (m, br, 12H, $OCH_2CH_3$). $^{11}B$ NMR ($CD_2Cl_2$, 25 °C, 96.29 MHz): $\delta$ −5.26. $^{19}F$ NMR ($CD_2Cl_2$, 20 °C, 282.4 MHz): $\delta$ −133.5 (d, 12F, $J_{F-F} = 20$ Hz, *o*-F, $C_6F_5$), −160.6 (tr, 6F, $J_{F-F} = 20$ Hz, *p*-F, $C_6F_5$), −166.1 (tr, 12F, $J_{F-F} = 20$ Hz, *m*-F, $C_6F_5$).

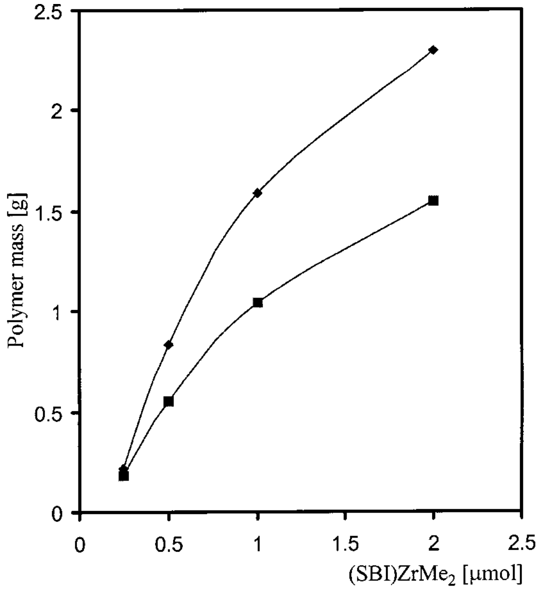

**Figure 2.** Plot of polymer mass versus catalyst concentration, demonstrating the absence of mass transport limitation for [Zr] = 2 × $10^{-5}$ M: (◆) $[CN\{B(C_6F_5)_3\}_2]^-$; (■) $[H_2N\{B(C_6F_5)_3\}_2]^-$.

monomer pressure, using (SBI)ZrMe$_2$ as the standard test catalyst precursor (SBI = *rac*-Me$_2$Si(Ind)$_2$). Plotting polymer yield versus [Zr] established that under the conditions chosen, i.e., [Zr] = ca. 2.5 × $10^{-5}$ mol $L^{-1}$, reactions are not subject to mass transport limitations (Figure 2). The graph also confirms the high activity of the (SBI)ZrMe$_2$/**2** catalyst. Figure 3 shows catalyst productivity as a function of catalyst concentration, for three anions: $[CN\{B(C_6F_5)_3\}_2]^-$, $[H_2N\{B(C_6F_5)_3\}_2]^-$, and $[B(C_6F_5)_4]^-$. Although the two diborate anions should, in principle, show similar charge delocalization and hence similarly low nucleophilicities, the productivity of the system (SBI)ZrMe$_2$/**2** is slightly less than that of (SBI)ZrMe$_2$/$[CPh_3][CN\{B(C_6F_5)_3\}_2]$ but essentially identical with that of (SBI)ZrMe$_2$/$[CPh_3][B(C_6F_5)_4]$. We ascribe the differences between the two diborate anions to differences in polarity between linear $[CN\{B(C_6F_5)_3\}_2]^-$ and bent $[H_2N\{B(C_6F_5)_3\}_2]^-$. The similarity in polymerization activities of catalysts based on $[B(C_6F_5)_4]^-$ and $[H_2N\{B(C_6F_5)_3\}_2]^-$, respectively, and the previously established anion dependence of the activation energies for propene polymerizations[15b] suggests that this polarity of $[H_2N\{B(C_6F_5)_3\}_2]^-$ favors ion pairing by ~1 kJ mol$^{-1}$, relative to $[CN\{B(C_6F_5)_3\}_2]^-$.

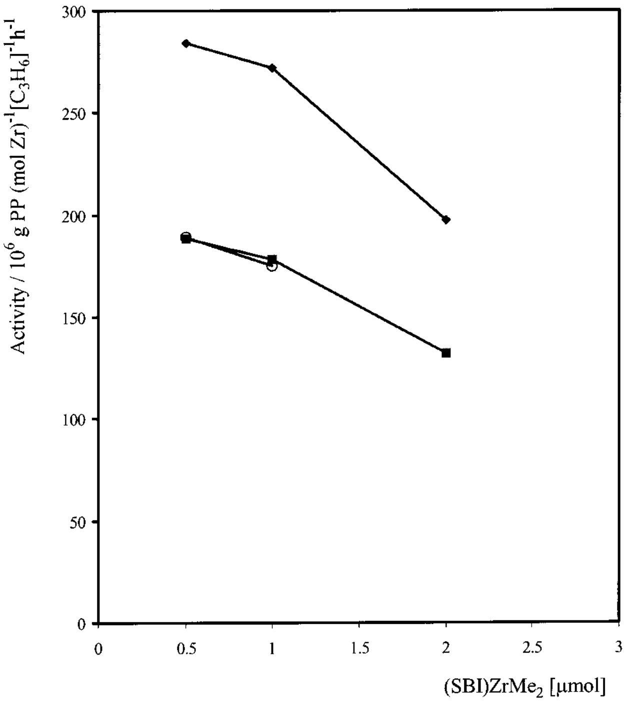

**Figure 3.** Anion dependence of propene polymerization activity of *rac*-(SBI)ZrMe$_2$/[CPh$_3$]X (toluene, 1 bar propene): $X^-$ = $[CN\{B(C_6F_5)_3\}_2]^-$ (◆), $[B(C_6F_5)_4]^-$ (○), $[H_2N\{B(C_6F_5)_3\}_2]^-$ (■).

Monitoring the reaction between (SBI)ZrMe$_2$ and **2** by NMR ($C_6D_6$/1,2-$C_6H_4F_2$ 10/1) demonstrated the formation of $[\{(SBI)ZrMe\}_2(\mu\text{-}Me)][H_2N\{B(C_6F_5)_3\}_2]$ (**4**) as a mixture of two diastereomers.[21,22] Whereas zirconocenium salts of the $[CN\{B(C_6F_5)_3\}_2]^-$ anion have been shown to be prone to slow dissociative decomposition to give cyanoborate complexes $L_2Zr(Me)NCB(C_6F_5)_3$,[15b] solutions of **4** at room temperature showed no formation of (SBI)ZrMe($\mu$-Me)B(C$_6$F$_5$)$_3$ which might arise from dissociation of the anion into $[H_2NB(C_6F_5)_3]^-$ and $B(C_6F_5)_3$. Similarly, the reactions of (Me$_2$SiL$_2$)ZrMe$_2$ with **2** in the presence of AlMe$_3$ in toluene/1,2-$C_6H_4F_2$ gave $[(Me_2SiL_2)Zr(\mu\text{-}Me)_2AlMe_2][H_2N\{B(C_6F_5)_3\}_2]$ (**5**, L = 1-indenyl; **6**, L = C$_5$H$_4$; **7**, L = C$_5$Me$_4$). The compounds were obtained as orange-red amorphous powders which could not be crystallized. Solutions of **4**−**7** in nonchlorinated solvents gave no sign of anion decomposition, even after several days at room temperature.

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**Supporting Information Available:** Preparative and spectroscopic details for **4**−**7**, tables of X-ray data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) For preparative and spectroscopic details of **4**−**7** see Supporting Information.