

New Family of Weakly Coordinating Anions

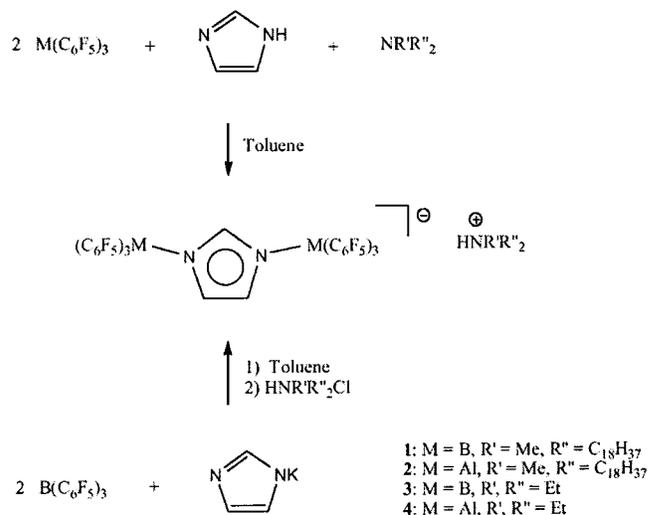
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Weakly coordinating anions have been a subject of intensive research in the past decade due to their increasing importance both in organic and inorganic chemistry.¹ Some of the most extensively used anions in olefin polymerization reactions are based on perfluorophenyl borates such as $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$.^{1c–d,2} Weak nucleophilicity of fluorine atoms and the strong electron-withdrawing nature of C_6F_5 groups are the major contributors to the inertness of these anions. Catalytic activities are highly dependent on the type of anion used and increase as the anion becomes less coordinating. One approach to make borate anions even less coordinating was to increase their size as was demonstrated by Marks and co-workers in the synthesis of perfluoro biphenyl³ and naphthyl⁴ borates. Another strategy to further reduce the coordinating nature of perfluorophenyl anions was to delocalize their negative charge over two borate fragments.⁵ With this approach in mind we successfully prepared⁶ a variety of mono anions having the general formula $[(\text{C}_6\text{F}_5)_3\text{M}-\text{LN}-\text{M}(\text{C}_6\text{F}_5)_3]^-$, where $\text{M} = \text{B}$ and Al and the linking group LN was cyanide,⁷ azide, dicyanamide, and imidazolide. In this communication we wish to report the detailed synthesis and analysis of the anions having an imidazole fragment as a linking group, as these particular species have been found to be the most stable and effective as activators for olefin polymerization reactions.

The reaction of 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Al}(\text{C}_6\text{F}_5)_3$ ⁸ with 1 equiv each of imidazole and dioctadecylmethylamine in toluene gives salts **1** and **2** respectively in high yields as colorless oils (Scheme 1). Alternatively, **1** can be prepared by reacting 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ with potassium imidazolite followed by metathesis of the resulting potassium salts with ammonium chloride derivatives. To gain insight into structural features of these novel anions triethylammonium salt derivatives **3'** and **4** have also been

Scheme 1. Synthesis of Expanded Anions



synthesized which appear as white solids at room temperature (*vide infra*). The anions **1–4** exhibit effective C_{2v} symmetry in solution at room temperature as shown by multinuclear NMR. For example, the ¹⁹F NMR of **1–4** shows three sharp resonances whereas ¹H NMR exhibits only two peaks in the range between 6.8 and 7.60 ppm in a 1:2 ratio corresponding to the imidazolite fragment. Additionally, only one resonance is observed in the ¹¹B NMR spectrum of **1** and **3** at -8.33 and -8.67 ppm, respectively. The chemical shifts of the meta and para fluorines of C_6F_5 groups are very sensitive to the charge density on the boron atom and move downfield with decreasing negative charge. Consistent with this general observation is the fact that the chemical shifts of meta and para fluorines, for example, in **3** (-165.97 , -160.68 ppm), are found downfield from that of model salt $[(\text{C}_6\text{F}_5)_3\text{B-pyrrole}][\text{HNET}_3]^{10}$ (-168.11 , -164.52 ppm), indicating larger charge delocalization in anions **1–4** as compared to their mononuclear analogues. Thermal stability of these new salts is very high. For example, a $t_{1/2}$ of 2 days was observed when **2** was heated to 150°C in C_6D_6 solution. In contrast to **1**, salt **2** is extremely sensitive to hydrolysis which produces $\text{C}_6\text{F}_5\text{H}$

(9) Preparation of **3**: Tris(pentafluorophenyl)borane (3.008 g, 5.88 mmol) and 0.2 g of imidazole (2.94 mmol) were partly dissolved in 50 mL of toluene. To this mixture was added 0.297 mg (2.94 mmol) of triethylamine in 10 mL of toluene. During addition of the amine, an oily solid appeared. After the reaction mixture was stirred overnight at room temperature the solvent volume was reduced to 35 mL and 30 mL of hexane was added to the solution. White solid was collected on the frit, washed with hexane, and dried under reduced pressure to give 3.22 g of product. Yield 91.9%. ¹H NMR (THF-*d*₆): δ 1.35 (t, 9H, ³J_{H-H} = 7.2 Hz, $(\text{CH}_3\text{CH}_2)_3\text{NH}$), 3.29 (q, 6H, ³J_{H-H} = 7.2 Hz, $(\text{CH}_3\text{CH}_2)_3\text{NH}$), 6.92 (s, 2H, H2), 7.60 (s, 1H, H1), 8.01 (br. s, 1H, $\text{CH}_3\text{-CH}_2\text{NH}$). ¹³C{¹H} NMR (THF-*d*₆): δ 9.09 ($\text{CH}_3\text{CH}_2\text{NH}$), 47.83 ($\text{CH}_3\text{CH}_2\text{NH}$), 121.70 (br. s), 124.66 (C2), 137.80 (dm, ²J_{C-F} = 246.2 Hz), 140.39 (dm, ²J_{C-F} = 251.9 Hz), 142.06 (C1), 148.88 (dm, ²J_{C-F} = 242.1 Hz). ¹⁹F NMR (THF-*d*₆): δ -165.97 (t, 12F, ³J_{F-F} = 19.9 Hz, *m*-F), -160.68 (t, 6F, ³J_{F-F} = 21.3 Hz, *p*-F), -132.30 (d, 12F, ³J_{F-F} = 21.5 Hz, *o*-F). ¹¹B NMR (THF-*d*₆): δ -8.67 ($\Delta\nu_{1/2} = 119.9$ Hz). HRMS (LSIMS, negative mode): calcd for $\text{C}_{39}\text{H}_{37}\text{B}_2\text{F}_{30}\text{N}_2$ 1091.0003, found 1091.0047. Anal. Calcd for $\text{C}_{45}\text{H}_{19}\text{-B}_2\text{F}_{30}\text{N}_3$: C, 45.30; H, 1.60; N, 3.52. Found: C, 45.23; H, 1.48; N, 3.47.}}}}}}}}

(10) See Supporting Information for synthetic details.

(11) Crystallographic data for **3**: $\text{C}_{49}\text{H}_{37}\text{B}_2\text{F}_{30}\text{N}_3\text{O}$, two independent molecules in unit cell, $M_w = 1265.36$, triclinic, space group $P\bar{1}$, $a = 13.4968$ (8) Å, $b = 17.822(1)$ Å, $c = 21.321(1)$ Å, $\alpha = 78.194(1)^\circ$, $\beta = 79.992(1)^\circ$, $\gamma = 87.845(1)^\circ$, $V = 4943.6(5)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.700$ Mg/m³, absorption coefficient = 0.180 mm⁻¹, $F(000) = 2520$, number of reflections collected = 35435, number of independent reflections = 22196, GOF = 0.912, $R_1 = 0.0430$ ($I > 2\sigma(I)$), $wR_2 = 0.1021$ (all data). Crystallographic data for **4**: $\text{C}_{49}\text{H}_{37}\text{Al}_2\text{F}_{30}\text{N}_3\text{O}$, $M_w = 1297.70$, monoclinic, space group $P2(1)$, $a = 10.2640$ (5) Å, $b = 22.276(1)$ Å, $c = 12.4462(6)$ Å, $\beta = 112.857(1)^\circ$, $V = 2622.3(2)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.644$ Mg/m³, absorption coefficient = 0.204 mm⁻¹, $F(000) = 1292$, number of reflections collected = 18837, number of independent reflections = 6122, GOF = 1.028, $R_1 = 0.0444$ ($I > 2\sigma(I)$), $wR_2 = 0.1292$ (all data).

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Table 1. Ethylene and 1-Octene Copolymerizations Catalyzed by $\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)(t\text{-BuN})\text{TiMe}_2^a$

entry	activator (μmol)	μmol of catalyst	exotherm ($^\circ\text{C}$)	eff (g polymer/g Ti)	density (g/mL)	MMI (micro melt index)	M_w	M_w/M_n
1	$\text{B}(\text{C}_6\text{F}_5)_3$ (1)	1	2.6	1 480 000	0.900	4.5	78 200	2.01
2	1 (0.5)	0.5	3.1	4 530 000	0.900	6.2	72 600	2.34
3	2 (0.5)	0.5	5.8	6 500 000	0.900	3.0	87 900	2.19
4	5 (0.5)	0.5	2.6	3 750 000	0.902	4.5	77 500	2.20

^a Carried out at 140 $^\circ\text{C}$ in a 2-L Parr reactor. See Supporting Information for detailed polymerization procedures.

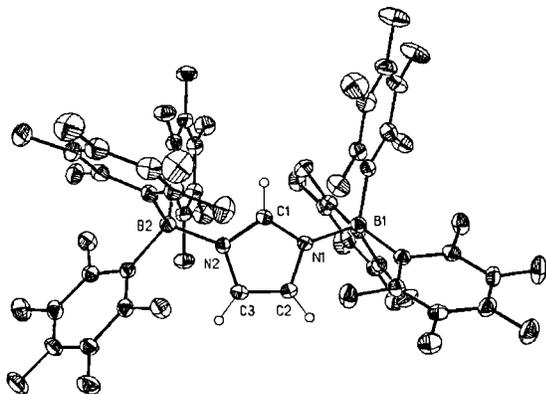


Figure 1. Thermal ellipsoid drawing of **3** shown at the 40% probability level. Ammonium cation has been omitted for clarity. Selected bond lengths (\AA): $\text{B}(1)\text{--N}(1) = 1.583(3)$; $\text{B}(2)\text{--N}(2) = 1.587(3)$; $\text{N}(1)\text{--C}(1) = 1.322(3)$; $\text{N}(1)\text{--C}(2) = 1.386(3)$; $\text{C}(2)\text{--C}(3) = 1.343(3)$; $\text{C}(3)\text{--N}(2) = 1.386(3)$; $\text{C}(1)\text{--N}(2) = 1.340(3)$.

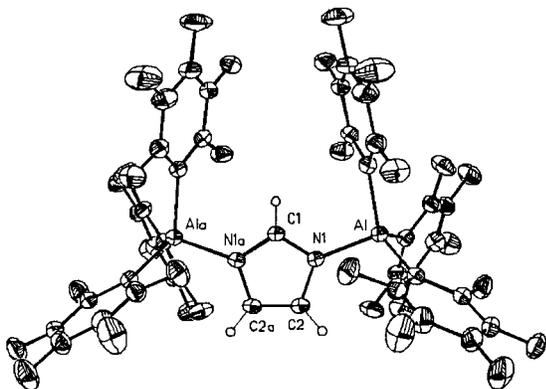


Figure 2. Thermal ellipsoid drawing of **4** shown at the 40% probability level. Ammonium cation has been omitted for clarity. Selected bond lengths (\AA): $\text{Al}\text{--N}(1) = 1.911(2)$; $\text{N}(1)\text{--C}(1) = 1.332(2)$; $\text{N}(1)\text{--C}(2) = 1.384(2)$; $\text{C}(2)\text{--C}(2a) = 1.345(4)$.

as the only product observed in ^{19}F NMR. Cooling a THF/ether/hexane solution of **3** and **4** to -25 $^\circ\text{C}$ gave colorless crystals suitable for X-ray single-crystal analysis. Molecular structures of **3** and **4** are presented in Figures 1 and 2, respectively.¹¹ Both structures contain a molecule of THF that is hydrogen bonded to the triethylammonium cation. The nitrogen atoms of the imidazole

fragment are bonded to two boron (**3**) and two aluminum (**4**) atoms in the expected η^1 fashion. The geometry at B and Al is slightly distorted tetrahedral with the sum of C--B(Al)--C angles of 334.4° and 333.4° for **3** and 339.3° for **4**. The imidazole rings are planar with short internal ring bond distances indicating uninterrupted aromaticity. These bond distances are the same, within experimental error, as those in imidazole and substituted imidazoles.¹²

The utility of these new salts was demonstrated in ethylene-1-octene copolymerization reactions conducted at 140 $^\circ\text{C}$ and catalyzed by $\text{Me}_2\text{Si}(\eta^5\text{-Me}_4\text{C}_5)(t\text{-BuN})\text{TiMe}_2$. As can be seen from Table 1 salt **1** is a very effective activator giving efficiencies noticeably higher than that of $\text{B}(\text{C}_6\text{F}_5)_3$. Curiously, the activator based on aluminum (**2**) is considerably more effective than both $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**).¹³ This is an interesting and somewhat unexpected result in view of the literature reports suggesting superiority of borate over aluminate based activators in olefin polymerization reactions.¹⁴ These polymerization results demonstrate that salts **1** and **2** are among the very best known activators for olefin polymerization reactions. The stability and effectiveness of these new salts as activators seems to correlate with the electron-donating ability of the linking group (LN) and acidity of the Lewis acid.

A major advantage of delocalized anions described here over those prepared by Marks and Piers⁵ is synthetic simplicity. These anions are very easy to prepare from readily available reagents often within a few hours. The synthesis of these salts is quite general and can be applied to the preparation of a wide range of mono- and polynuclear boron and aluminum based anions.

The high weakly coordinating nature of these anions coupled with their preparation ease makes them very good alternative anions that might be of interest to both inorganic and organic chemists.

Supporting Information Available: Experimental procedures, stereoviews of thermal ellipsoid drawings, tables of atomic positions, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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