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Novel Trityl Activators with New Weakly Coordinating Anions Derived from C_6F_4-1,2-$[B(C_6F_5)_2]_2$: Synthesis, Structures, and Olefin Polymerization Behavior

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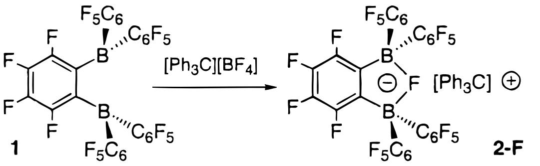
Summary: The weakly coordinating anions $\{C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2(\mu\text{-}OR)\}^-$ *(*$R = CH_3$, C_6F_5*) were prepared as their trityl salts (**2-OR**) and fully characterized. Stoichiometric reactions with* Cp_2ZrMe_2 *yield dimeric (**3-OR**) or monomeric (**4-OR**) metallocenium ions; the latter are highly effective cocatalysts for ethylene polymerization.*

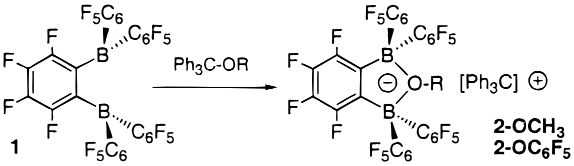
Trityl salts of weakly coordinating borate[1] and aluminate[2] counteranions are highly effective stoichiometric activators for olefin polymerization reactions. Unlike the isoelectronic, but neutral, borane family of initiators,[2,3] alkide abstraction using trityl-based activators is irreverisible, and ion−ion interactions are generally weaker for metallocenium complexes with $[B(Ar_F)_4]^-$ type counteranions as opposed to $[RB(C_6F_5)_3]^-$.[4] To the extent that ion−ion interactions affect the catalyst's activity, stability, and, to a lesser extent, ability to stereoregulate,[2] anion engineering is an important endeavor for catalyst improvements.

Recently we reported the synthesis and characterization of the perfluorinated *o*-phenylene diborane C_6F_4-1,2-$[B(C_6F_5)_2]_2$ (**1**).[5] Although this compound is an effective activator without modification,[6] the character of the methide ion produced leads to cation−anion interactions which attenuate catalyst activity in comparison to $B(C_6F_5)_3$. Essentially, this arises because the methide anion is not chelated by the two borane centers and the resultant anion is comprised of a equilibrium mixture of two exchanging species. One of these contains a neutral $B{-}CH_3$ moiety which is capable of complexing to cationic zirconocenes in the same way "$Al(CH_3)_3$" binds these species.[7] Accordingly, we sought to incorporate anions which can be bound by the diborane in a chelating fashion, leading to more delocalization of the negative charge[8] and weaker ion pairing.

Tritryl salts of F^- and OR^- ($R = CH_3$, C_6F_5) were prepared straightforwardly via the reactions shown in eqs 1 and 2. Diborane **1** abstracts F^- from $[Ph_3C]^+[BF_4]^-$,



(1)



(2)

to give **2-F** as an orange solid in 95% yield with BF_3 as the only byproduct. In an even more atom-economical reaction,[9] **1** reacts directly with trityl ethers in CH_2Cl_2 to afford **2-OCH$_3$** and **2-OC$_6$F$_5$** in >90% yield.

Compounds **2** were characterized by NMR spectroscopy and elemental analysis; in addition, the solid-state structures of **2-OCH$_3$** and **2-OC$_6$F$_5$** were determined crystallographically. Full details can be found in the Supporting Information. The primary tool for determining solution structure for these compounds is ^{19}F NMR spectroscopy. For **2-F** and **2-OCH$_3$**, the spectra are simple and consistent with C_{2v} symmetry for the anion, suggesting **1** is indeed chelating the anion. The ^{11}B NMR data corroborates this assignment, since only one reso-

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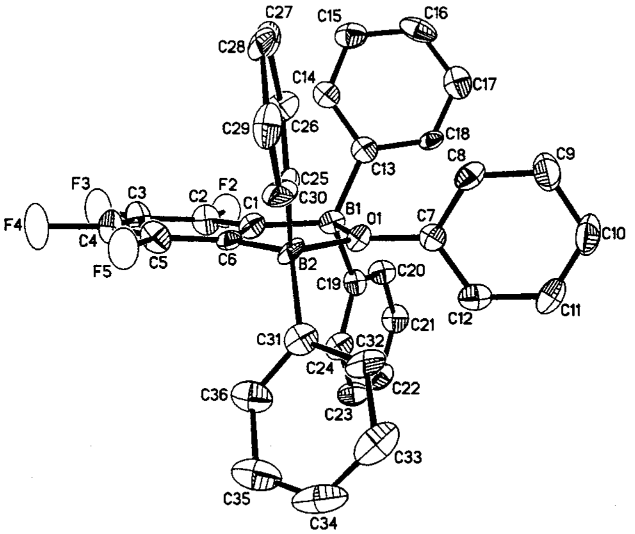
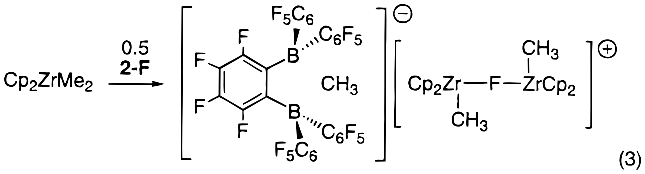


Figure 1. ORTEP diagram for the anionic portion of **2-OC$_6$F$_5$**. The F atoms on the B−C$_6$F$_5$ rings and the OC$_6$F$_5$ ring have been removed for clarity. Selected bond distances (in Å; values in brackets are the analogous values for **2-OCH$_3$**): B(1)−C(1), 1.600(10) [1.614(2)]; B(2)−C(6), 1.572(10) [1.622(2)]; B(1)−O(1), 1.693(8) [1.568(2)]; B(2)−O(1), 1.644(9) [1.562(2)]; O(1)−C(7), 1.386(8) [1.4485(19)]. Selected bond angles (in deg): B(1)−O(1)−B(2), 115.4(5) [117.72(12)]; B(1)−O(1)−C(7), 120.8(5) [121.27(13)]; B(2)−O(1)−C(7), 123.8(5) [120.93(13)]; B(1)−C(1)−C(6), 115.4(6) [113.27(14)]; B(2)−C(6)−C(1), 116.8(6) [112.77(14)].

nance is observed between 0 and 9 ppm, the region expected for four-coordinate boron centers with a formal −0.5 charge. For **2-OC$_6$F$_5$**, evidence for fluxionality is apparent in the room-temperature ^{19}F spectrum. Variable-temperature experiments show that this process is associated with restricted rotation of the boron C$_6$F$_5$ rings, since the patterns present for the backbone fluorines and those associated with the OC$_6$F$_5$ group indicate that the C_{2v} symmetry of the anion is maintained at all temperatures. Presumably, the hindered rotation of the −C$_6$F$_5$ substituents on boron is due to the bulkier character of the pentafluorophenoxide group in comparison to F$^-$ or OCH$_3$$^-$.

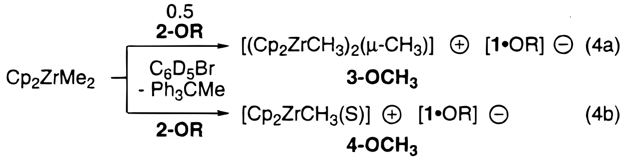
The molecular structure of the anion in **2-OC$_6$F$_5$** is shown in Figure 1 along with selected metrical parameters; in brackets, the analogous data for **2-OCH$_3$** are given for comparison.[10] Confirming the solution structural assignments, in both of these compounds, OR is bound to both borane centers in a symmetrical fashion. Unlike the free diborane, in which the B−C−C−B dihedral angle is 19.9(2)°,[5] these atoms are essentially coplanar (along with O) in anions **2**. Notably, the geometry about oxygen is trigonal planar (the sums of the angles are 360.0 and 359.9° for **2-OC$_6$F$_5$** and **2-OCH$_3$**, respectively) in contrast to the trigonal-pyramidal ground-state structures found for the related alkyloxonium salts [R$_3$O]$^+$[A]$^-$. The energy surface connecting these two geometries is soft;[11] presumably, bulky groups about O will favor planar geometries.[12] Alternatively, the bite angle of **1** may require that O assumes an sp^2 hybridization in order to form strong σ bonds to the two boron atoms.

The stoichiometric reactivity of compounds **2** with 1 or 2 equiv of Cp$_2$ZrMe$_2$ was investigated to assay the stability of the resulting ion pairs. Clean reactions were observed in each case, although in the case of **2-F**, it is clear that F$^-$ transfer to zirconium is facile (eq 3). This is particularly indicated by the highly characteristic ^{19}F NMR spectral fingerprint for the [**1**·Me]$^-$ anion,[6] which forms when free diborane **1** is liberated after the F$^-$ transfer event. The presence of the dimeric μ-F cation[2,13] is evidenced by a signal in the ^{19}F NMR spectrum at −90.4 ppm.



(3)

In contrast, the μ-OR anions are stable in the presence of both [(Cp$_2$ZrMe)$_2$(μ-Me)]$^{+}$ [14] (eq 4a) and [Cp$_2$Zr(S)Me]$^+$ (eq 4b) in C$_6$D$_5$Br, with no OR$^-$ transfer to Zr[15] observable over time periods on the order of days in each case.



This stability appears to be thermodynamic in nature. Gentle heating (60 °C) of solutions of the ion pair **3-OCH$_3$** resulted in decomposition of the dimeric cation through loss of methane,[16] but ^{19}F NMR spectroscopy showed that the anion remained intact throughout. Similarly, heating solutions of the monomeric ion pair **4-OCH$_3$** gives no evidence for decomposition at 40 °C.

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[10] Crystal data for **2-OC$_6$F$_5$**: C$_{57}$H$_{19}$B$_2$Cl$_3$F$_{29}$O, 0.20 × 0.19 × 0.06 mm, triclinic, $P\bar{1}$, a = 12.2241(15) Å, b = 12.8975(16) Å, c = 18.801(2) Å, α = 80.166(2)°, β = 72.091(2)°, γ = 70.812(2)°, V = 2655.9(6) Å^3, Z = 2, FW = 1398.69, D_{calcd} = 1.749 g cm^{-3}, θ range for data collection 1.68−25.00°, Mo Kα radiation, λ = 0.710 73 Å, T = 160(2) K, 15 208 measured reflections, 8865 unique, 3565 reflections with $I_{net} > 2.0\sigma(I_{net})$, μ = 0.319 mm^{-1}, min/max transmission 0.939 and 0.981, final R indices R1 = 0.0812 and wR2 = 0.2135, GOF = 0.969, 36 restraints, 848 parameters. Crystal data for **2-OCH$_3$**: C$_{51}$H$_{20}$B$_2$Cl$_2$F$_{24}$O, 0.60 × 0.35 × 0.35 mm, monoclinic, $P2_1/n$, a = 13.5900(2) Å, b = 19.3540(2) Å, c = 18.5439(2) Å, β = 101.517(2)°, V = 4779.23(10) Å^3, Z = 4, FW = 1197.19, D_{calcd} = 1.664 g cm^{-3}, θ range for data collection 2.00−29.11°, Mo Kα radiation, λ = 0.710 73 Å, T = 160(2) K, 39 886 measured reflections, 11 847 unique, 8912 reflections with $I_{net} > 2.0\sigma(I_{net})$, μ = 0.271 mm^{-1}, final R indices R1 = 0.0446 and wR2 = 0.1158, GOF = 1.061, 15 restraints, 733 parameters. The restraints were applied to geometry and anisotropic displacement parameters of atoms in disordered solvent molecules, to aid their refinement. There were no restraints on the cations and anions.

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[12] A related compound with less bulky groups at boron, [(μ-CH$_3$CO$_2$)(BF$_2$)$_2$(μ-OCH$_3$)], crystallizes with two molecules in the unit cell, one of which is planar at the μ-OCH$_3$ oxygen and the other pyramidal: Binder, H.; Matheis, W.; Deiseroth, H.-J.; Fu-Son, H. *Z. Naturforsch., B* **1983**, *38*, 554.

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Table 1. Polymerization of Ethylene with Cp_2ZrMe_2 and Various Cocatalysts[a]

entry	cocatalyst	scrubbing agent[b]	t (min)	tield (g)	activity[c]	M_n	M_w/M_n
1	$B(C_6F_5)_3$	MAD	20	3.39	10.6	272	2.18
2	$[Ph_3C][B(C_6F_5)_4]$	MAD	20	6.49	20.2	344	2.02
3[d]	$[Ph_3C][B(C_6F_5)_4]$	MAD	30	24.42	24.4	244	2.06
4[d]	$[Ph_3C][B(C_6F_5)_4]$	MAD	30	24.51	24.5		
5[d]	$[Ph_3C][B(C_6F_5)_4]$	MAD	10	8.85	26.6	249	1.92
6	**1**	MAD	30	2.02	4.18	250	2.04
7	**2-F**	MAD	30	0.00	nil		
8	**2-OMe**	MAD	30	3.07	6.36	200	1.92
9	**2-OC$_6$F$_5$**	MAD	30	20.83	43.15	240	1.72
10[e]	PMAO	PMAO	30	4.20	8.40		

[a] For a typical procedure consult ref 21. Conditions: toluene 500 mL, 1000 rpm, 30 °C, 14 psi of C_2H_4 with $[Cp_2ZrMe_2] = [\text{cocatalyst}] = 2\ \mu M$ unless otherwise noted. [b] MAD = $MeAl(BHT)_2$ with [MAD] = 300 μM. [c] Activity in 10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1}. [d] Polymerizations conducted at 29 psi of C_2H_4. [e] Polymerization conducted at 25 °C and 14 psi of C_2H_4 and with [PMAO] = 2.0 mM (Al:Zr = 1000:1).

At 60 °C, decomposition begins, but the primary path involves transfer of a $-C_6F_5$ ring to zirconium,[17] rather than OCH_3^-. This contrasts with the observation of a highly complex product mixture formed upon reaction of $(C_6F_5)_2BOCH_3$[18] with Cp_2ZrMe_2, generated from initial products arising from rapid CH_3/OCH_3 exchange between zirconium and the monomeric borinic ester.[15] Finally, diborane **1** rapidly abstracts OCH_3^- from $Cp_2Zr(OCH_3)_2$;[19] although the cation in the resulting species is not very stable,[20] the ^{19}F and ^{11}B NMR spectra show clean formation of the μ-OCH_3 anion.

The efficacy of these trityl salts as ethylene polymerization initiators using Cp_2ZrMe_2 was examined with a view to comparison with standard borane- and borate-based activators. The results of these experiments, performed using a scrubbing agent which does not interact chemically with the initiators,[6] are given in Table 1.[21] As predicted on the basis of the activation chemistry in the absence of monomer, **2-F** is ineffectual as an activator. Alkoxide derivatives **2-OCH$_3$** and **2-OC$_6$F$_5$**, however, are active; the latter compound gives activities which are more than double those found for $[Ph_3C]^+[B(C_6F_5)_4]^-$, generally the most effective stoichiometric activator found to date. The combination of steric protection of the alkoxide oxygen lone pair and extensive delocalization of the anion's negative charge accounts for its superior performance as a weakly coordinating anion.

In summary, we have prepared a series of trityl salts containing new weakly coordinating anions and examined their behavior as ethylene polymerization cocatalysts in a preliminary fashion. We are currently attempting to more accurately define the nature of the ion−ion interactions in these ion pairs, preparing next-generation derivatives of **1**, and carrying out more advanced olefin polymerization screening experiments.

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Supporting Information Available: Experimental and spectroscopic details for **2-F**, **2-OCH$_3$**, **2-OC$_6$F$_5$**, **3-OR**, and **4-OR**, as well as tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **2-OCH$_3$** and **2-OC$_6$F$_5$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) As evidenced by the production of $Cp_2Zr(CH_3)C_6F_5$.[14d]

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(21) A typical experimental procedure is as follows. A 1 L autoclave was dried under vacuum (10^{-2} mmHg) at 100 °C for several hours and refilled with dry N_2 after cooling to 30 °C. The vessel was charged with 450 mL of dry and deoxygenated toluene under positive pressure of N_2 and then saturated with ethylene monomer at the required pressure. A solution of MAD in toluene (10 mL) was introduced using a small sampling vessel, overpressurized with N_2, to give a final concentration of 300 μM. After the mixture was stirred for 1 h, solutions of the cocatalyst and Cp_2ZrMe_2 in toluene (20 mL each) were sequentially introduced in the same manner so as to give a final concentration of 2 μM for each. Ethylene uptake was monitored using a calibrated mass flow meter; constant monomer flow was observed typically within 5 min after catalyst introduction. The temperature was controlled (to ca. ± 2 °C) using an external cooling jacket connected to a recirculating heating/cooling bath and was monitored by an RTD sensor placed in a thermocouple well in contact with the reactor contents. Polymerizations were conducted for a time period corresponding to 20−30 min, following attainment of steady-state conditions (i.e., constant T and ethylene flow) in the reactor, and polymerizations were quenched by the addition of MeOH through an overpressurized sample vessel. Polymer samples were isolated by filtration, washed with MeOH, and dried in vacuo at 80 °C for 24 h prior to weighing.