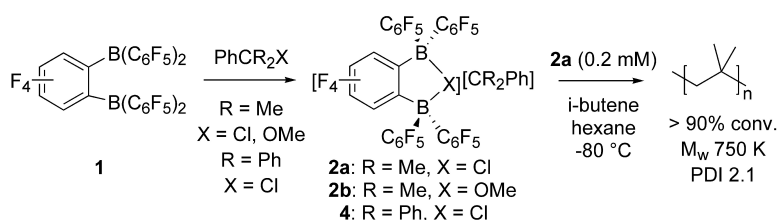


Isobutene Polymerization Using a Chelating Diborane Co-Initiator

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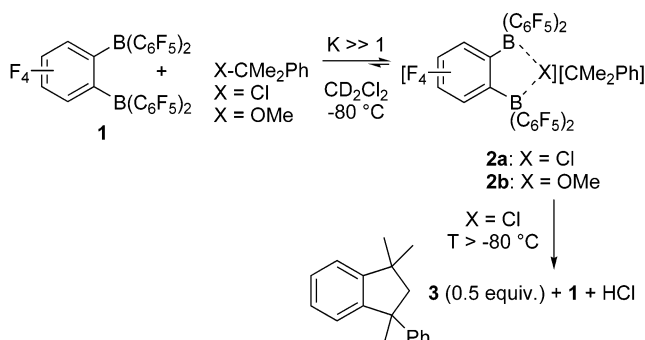
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There is considerable interest in counteranion design and synthesis in the context of olefin polymerization using single-site metallocene catalysts.¹ The counteranion influences catalyst activity/stability, polymer MW, and tacticity in a manner that is reasonably well understood. Less attention has been devoted to systematic modification of the counteranion, despite its importance in chain transfer processes,² in cationic polymerization of isobutene (IB). Previous work, which involved the use of weakly coordinating counteranions (WCA)³ to hinder chain transfer in IB homo-/copolymerization, has focused on various transition metal and main group initiators paired with a WCA.⁴ The use of chelating diborane **1** (see Scheme 1) or related compounds⁵ as activators in olefin polymerization has been explored,⁶ and chelated WCA derived from such compounds {e.g., [Ph₃C][1-(μ-X)] (X = OMe, OC₆F₅ etc.)} present advantages in ethylene polymerization over trityl activators partnered with mononuclear WCA.^{6a} We expected chelating diborane **1** might be effective in cationic polymerization of IB, and this communication presents preliminary results to this effect.

Scheme 1



We investigated the reaction of diborane **1** with cumyl chloride (CumCl) and cumyl methyl ether (CumOMe) by variable-temperature ¹H and ¹⁹F NMR spectroscopy. As shown in Scheme 1, ionization is observed at low *T* with either of these initiators and diborane **1** to form ion-pairs **2a–b** in which the cumyl cation⁷ (Figure 1a) is partnered with symmetrical, counteranions as is evident from the ¹⁹F NMR spectra (Figure 1b).

In the case of ion-pair **2b**, the known [1-(μ-OMe)] counteranion is formed (see Supporting Information).^{6a} By analogy, reaction with CumCl forms ion pair **2a**, featuring the unknown [1-(μ-Cl)] anion partnered with the cumyl cation. On the basis of the extent of ionization, the Lewis acidity of **1** toward CumCl exceeds that of BCl₃ and is comparable to that of SbF₅ where ionization is essentially irreversible.⁸

Ion-pair **2a** is stable at -80 °C, but on warming, decomposition to the known indan **3**⁸ occurs while diborane **1** and HCl are the

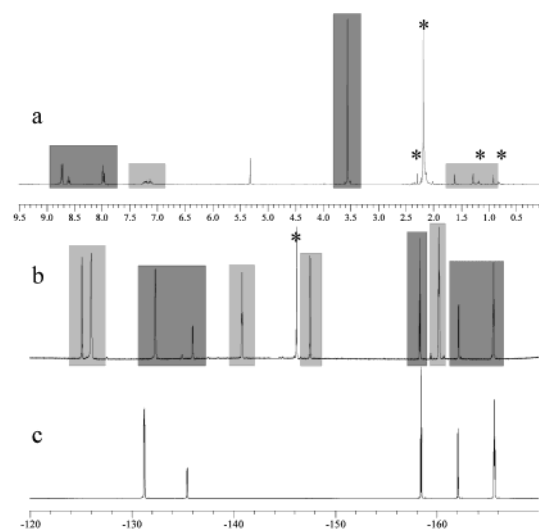
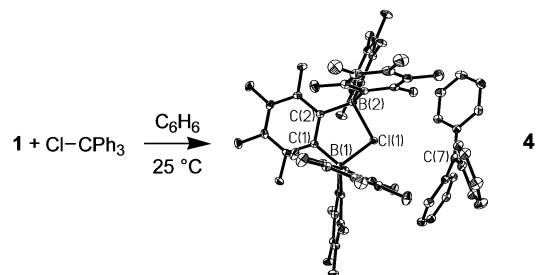


Figure 1. (a) ¹H NMR spectrum (400 MHz, CD₂Cl₂, -40 °C) and (b) ¹⁹F NMR spectrum (376 MHz, CD₂Cl₂, -20 °C) of a mixture of diborane **1** (2.0 equiv) and CumCl (1.0 equiv). (c) ¹⁹F NMR spectrum (282 MHz, CD₂Cl₂, 25 °C) of ion-pair **4**. Signals due to ion-pair **2a** are highlighted in dark gray, while those due to **1** and indan **3** are in light gray. The peaks marked with an asterisk are due to 2,3,5,6-tetrafluoro-*p*-xylene, *n*-hexane, and toluene.

Scheme 2



other major byproducts of this decomposition (Scheme 1). A similar process also ensues for **2b** although competitive degradation of the counteranion is observed as will be described in detail elsewhere.

As a model for ion-pair **2a** we investigated the reaction of Ph₃C-Cl with diborane **1**; the expected ion-pair **4** is quantitatively formed in either benzene-*d*₆ or CD₂Cl₂ solution at room temperature (Scheme 2, ¹⁹F NMR spectrum in Figure 1c).⁹

The X-ray structure of this compound appears in Scheme 2.¹⁰ Notable features include a puckered, five-membered ring for the chelated counteranion with marginally dissimilar B(1)-Cl(1) and B(2)-Cl(1) bond lengths of 2.0329(16) and 2.0399(15) Å, respectively. The B(1)-Cl(1)-B(2) angle is acute at 94.34(6)° so as to accommodate the bridging Cl between the two B atoms. Even with this feature and concomitant puckering of the ring, there is evidence

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Table 1. Polymerization of IB Initiated Using Diborane **1**^a

entry	[CumCl] (mM)	[DTBMP] (mM)	[IB] (M)	conv. (%)	\bar{M}_n (K)	PDI	<i>f</i> (%) ^b
1 ^c	—	0	2.76	100	172	2.60	—
2	—	0	2.76	100	285	2.40	—
3	—	2.0	2.76	5.8	302	2.48	—
4	—	5.0	2.76	1.4	552	3.60	—
5	—	15.0	2.76	0.47	753	4.60	—
6 ^d	—	0	2.76	0.10	98	1.80	—
7	0.20	20.0	2.76	42	361	1.72	156
8	0.30	20.0	2.35	21	255	1.92	68
9	0.55	20.0	2.76	40	146	1.75	134
10	0.20	2.0	2.35	93	779	2.11	166
11 ^d	0.20	20.0	2.76	0	—	—	—

^a Diborane **1** dissolved in toluene (0.3 mL) was added to a solution of IB in hexane (total volume 24.5 mL) at -78°C containing DTBMP, and then a solution of CumCl in CH_2Cl_2 (0.2 mL) was added. Final concentration of **1** = 2.0 mM. ^b Initiator efficiency $f = 100(X_n^o/X_n)$ where $X_n^o = ([\text{IB}]_0/[\text{CumCl}]_0)(\text{conv.}/100)$. ^c Diborane **1** in hexane solution added to monomer in hexane at -78°C . Final **1** = 0.5 mM. ^d $\text{B}(\text{C}_6\text{F}_5)_3$ (4.0 mM) was substituted for diborane **1**.

of angle strain as exemplified in the acute C(1)–B(1)–Cl(1) and C(2)–B(2)–Cl(1) angles of $98.03(9)$ and $98.98(9)^\circ$, respectively. Evidently, the “bite” angle of diborane **1** is not optimal for chloride binding as judged by comparison to the structure of $[\text{PPN}][1,8\text{-(Cl}_2\text{B)}_2\text{C}_{10}\text{H}_6(\mu\text{-Cl})]$ in which both the B–Cl bond lengths are shorter [av $1.92(1)$ Å] and the angles within the six-membered ring less distorted from tetrahedral values.¹¹

The triphenylmethyl cation has a propeller arrangement of the phenyl rings about the central carbon which features sp^2 hybridization [$\Sigma\angle\text{C}(7) = 359.99(13)^\circ$]. While this atom is oriented toward the bridging Cl of the counteranion, this interaction may be electrostatic in nature; the C(7)–Cl(1) distance of $3.899(15)$ Å is significantly longer than the sum of the van der Waals radii of Cl and sp^2 -hybridized C (3.65 Å).

Diborane **1** is an effective initiator for IB polymerization even in apolar media such as hexane (Table 1, entries 1 and 2). Despite the use of a vacuum line, silanized glassware, and final purification of both monomer and solvent by vacuum transfer from tri-*n*-octylaluminum, it proved impossible to prevent protic initiation by diborane **1** except through the addition of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP). As shown in the Table 1, entries 3–5, about a 5–10-fold excess of DTBMP with respect to **1** was required to inhibit protic initiation. Evidently under these conditions (1.5–2.0 ppm H_2O) protic initiation of IB polymerization is highly effective. The MW in the absence of DTBMP appears limited by these low levels of H_2O as seen from the increase in MW with [DTBMP] (Table 1, entries 3–5).¹²

Controlled polymerization of IB, initiated by CumCl and excess diborane **1**, was possible in the presence of a **large** excess of DTBMP in hexane solution (Table 1, entries 7–9) where MW correlates with CumCl concentration. Under more typical conditions (entry 10 vs 7),¹³ polyIB of high-molecular weight is obtained at high conversion. Calculated initiator efficiencies (*f*) routinely approach or exceed 100%, consistent with effective initiation and chain transfer. The initiator efficiency of diborane **1** in concert with CumCl is superior compared to that in some other initiator systems which feature WCA under similar conditions.^{4i–k}

That the chelated nature of the counteranion is important for effective initiation was revealed by comparative experiments using $\text{B}(\text{C}_6\text{F}_5)_3$. As shown in Table 1, this borane was ineffective for IB polymerization using either CumCl (entry 11) or protic initiation (entry 6) even at equivalent concentrations with respect to boron.¹⁴ Future work will explore the utility of diborane **1** as co-initiator

for the controlled polymerization of IB and other susceptible monomers.

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Supporting Information Available: Experimental procedures, selected NMR spectra and tables of crystallographic and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters for compound **4** (PDF). This material is available free of charge on the Internet at <http://pubs.acs.org>.

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- Compound **4**: ^1H NMR (CDCl_3 , 300 MHz): δ 8.23 (tt, 3H, *p*- C_6H_5), 7.83 (m, 6H, *m*- C_6H_5), 7.61 (dd, 6H, *o*- C_6H_5). ^{19}F NMR (CDCl_3 , 282 MHz) δ –132.0 (d, 8F, *o*- C_6F_5), –136.1 (d, 2F, *o*- C_6F_4), –158.6 (t, 4F, *p*- C_6F_5), –162.1 (d, 2F, *m*- C_6F_4), –165.6 (m, 8F, *m*- C_6F_5). ^{13}C [^1H] (CDCl_3 , 75 MHz): δ 210.8 (s, CPh_3), 147.9 (d, $^1J_{\text{C-F}} = 245$ Hz, *o*- C_6F_5), 146.9 (d, $^1J_{\text{C-F}} = 242$ Hz, *o*- C_6F_4), 143.7 (s, *p*- C_6H_5), 142.4 (s, *o*- C_6H_5), 139.8 (s, *ipso*- C_6H_5), 139.8 (d, $^1J_{\text{C-F}} = 251$ Hz, *p*- C_6F_5), 138.4 (d, $^1J_{\text{C-F}} = 240$ Hz, *m*- C_6F_4), 136.7 (d, $^1J_{\text{C-F}} = 249$ Hz, *m*- C_6F_5), 133.7 (br s, *ipso*- C_6F_4), 130.6 (s, *m*- C_6H_5), 118.1 (br s, *ipso*- C_6F_5). Anal. Calcd for $\text{C}_{49}\text{H}_{15}\text{B}_2\text{F}_{24}\text{Cl}$: C, 52.70; H, 1.35. Found C, 52.36; H, 1.40.
- Molecular structure of compound **4** with 30% thermal ellipsoids depicted: Triclinic, *P*1, *a* = 11.2135(4) Å, *b* = 11.7384(5) Å, *c* = 19.3086(8) Å, α = 72.610(1)°, β = 89.354(1)°, γ = 62.433(1)°, *V* = 2125.66(15) Å³, *Z* = 2, *R* = 0.0468, *wR* = 0.0744 based on 12, 469 independent reflections with *I* > 2 σ (*I*).
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- For use of $[(\text{Cp}^*_2\text{Zr})_2\text{H}_3][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-X})\text{B}(\text{C}_6\text{F}_5)_3]$ (X = CN, NH_2) in IB polymerization see ref 12.

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