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Isobutene Polymerization Using a Chelating Diborane Co-Initiator

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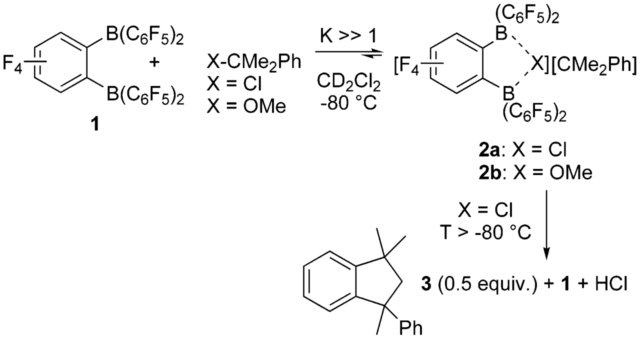
There is considerable interest in counteranion design and synthesis in the context of olefin polymerization using single-site metallocene catalysts.[1] The counteranion influences catalyst activity/stability, polymer MW, and tacticity in a manner that is reasonably well understood. Less attention has 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 compounds[5] as activators in olefin polymerization has been explored,[6] and chelated WCA derived from such compounds {e.g., $[Ph_3C][\mathbf{1}\text{-}(\mu\text{-X})]$ (X = OMe, OC_6F_5 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 ^{1}H and ^{19}F 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 cation[7] (Figure 1a) is partnered with symmetrical, counteranions as is evident from the ^{19}F 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 BCl_3 and is comparable to that of SbF_5 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 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.

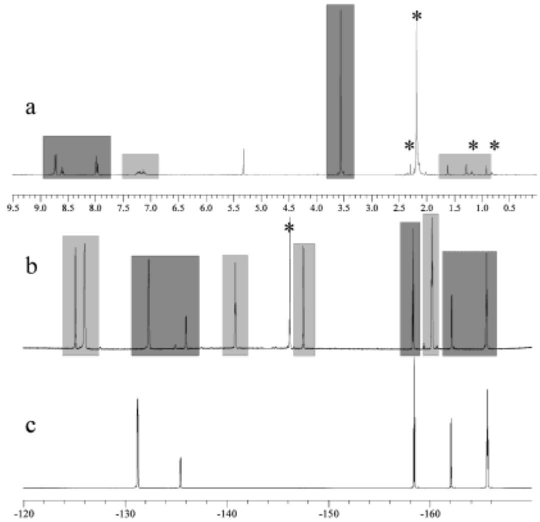
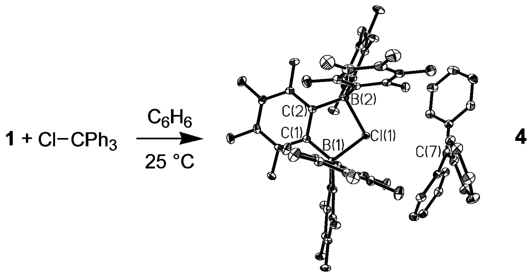


Figure 1. (a) ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, −40 °C) and (b) ^{19}F NMR spectrum (376 MHz, CD_2Cl_2, −20 °C) of a mixture of diborane **1** (2.0 equiv) and CumCl (1.0 equiv). (c) ^{19}F NMR spectrum (282 MHz, CD_2Cl_2, 25 °C) of ion-pair **4**. Signals due to ion-pair **2a** are highlighted in 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



As a model for ion-pair **2a** we investigated the reaction of Ph_3C-Cl with diborane **1**; the expected ion-pair **4** is quantitatively formed in either benzene-d_6 or CD_2Cl_2 solution at room temperature (Scheme 2, ^{19}F 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. (%)	$\bar{M}_w$ (K)	PDI	f (%)[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 $X_n^o = ([IB]_o/[CumCl]_o)(conv./100)$. [c] Diborane **1** in hexane solution added to monomer in hexane at −78 °C. Final [**1**] = 0.5 mM. [d] $B(C_6F_5)_3$ (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)°, respectively. Evidently, the "bite" angle of diborane **1** is not optimal for chloride binding as judged by comparison to the structure of [PPN][1,8-$(Cl_2B)_2C_{10}H_6(\mu\text{-}Cl)$] 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 [$\Sigma\angle C(7) = 359.99(13)°$]. 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 $B(C_6F_5)_3$. 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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(9) Compound **4:** ^1H NMR ($CDCl_3$, 300 MHz): δ 8.23 (tt, 3H, *p*-C_6H_5), 7.83 (m, 6 H, *m*-C_6H_5), 7.61 (dd, 6 H, *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, $^1J_{C-F}$ = 245 Hz, *o*-C_6F_5), 146.9 (d, $^1J_{C-F}$ = 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, $^1J_{C-F}$ = 251 Hz, *p*-C_6F_5), 138.4 (d, $^1J_{C-F}$ = 240 Hz, *m*-C_6F_4), 136.7 (d, $^1J_{C-F}$ = 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 $C_{49}H_{15}B_2F_{24}Cl$: C, 52.70; H, 1.35. Found C, 52.36, H, 1.40.

(10) Molecular structure of compound **4** with 30% thermal ellipsoids depicted: Triclinic, $P\bar{1}$, 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) Å^3, Z = 2, R = 0.0468, wR = 0.0744 based on 12, 469 independent reflections with $I > 2\sigma(I)$.

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(14) For use of $[(Cp'_2Zr)_2H_3][(C_6F_5)_3B-(\mu\text{-}X)\text{-}B(C_6F_5)_3]$ (X = CN, NH_2) in IB polymerization see ref 12.

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