Organometallics **2007,** *26,* 5667−5679 5667

Formation of Chelated Counteranions Using Lewis Acidic Diboranes: Relevance to Isobutene Polymerization

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Received July 4, 2007

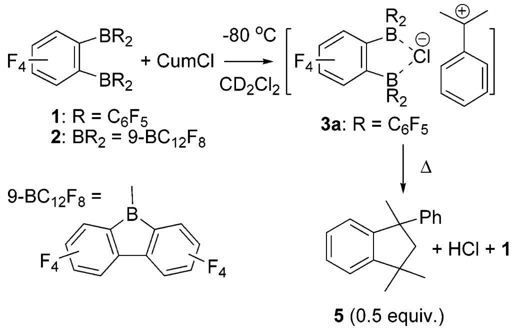
The reactions of chelating diboranes with $PhCMe_2Cl$ and related initiators were studied by variable-temperature NMR spectroscopy. Although thermally stable ion-pairs featuring weakly coodinating anions (WCA) are formed, isobutene polymerization is complicated by the tendency of these WCA to act as hindered bases toward Brønsted acidic chain ends.

Introduction

Protic or electrophilic initiators that give rise to weakly coordinating anions (WCA),[1] partnered with propagating carbocations in isobutene polymerization,[2] is a topic of significant interest in the context of butyl rubber manufacture at elevated temperature.[3] A variety of initiator systems are effective in neat monomer, hydrocarbon, or more polar media,[4] and generally a rather weak temperature dependence is observed for the MW of poly(isobutene) or butyl rubber formed. These polymerizations are uncontrolled and with MW values in several cases comparable to those that can be achieved using γ-ray initiation involving "free" carbocations.[5]

Several years ago we communicated that chelating diborane **1** (Scheme 1)[6] was an effective co-initiator of isobutene polymerization, initiated by cumyl chloride (CumCl) in the presence of the sterically hindered pyridine 2,6-di-*tert*-butyl-4-methylpyridine (DtBMP).[7] Variable-temperature NMR spectroscopic experiments established that CumCl and diborane **1** formed an unstable ion-pair, **3a**, in CD_2Cl_2 solution at low temperature whose structure was inferred from spectroscopic data on the stable ion-pair **4a** formed from triphenylmethyl chloride and diborane **1** (eq 1)[6,7] as well as literature data reported for the cumyl cation.[8]

Scheme 1



The polymerization experiments were conducted on a vacuum line using monomer and solvents purified by vacuum transfer

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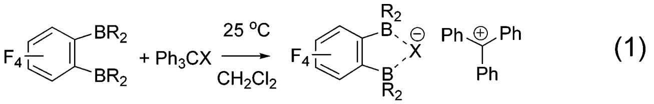

1: R = C_6F_5
2: BR_2 = 9-$BC_{12}F_8$

4a: R = C_6F_5; X = Cl
4b: BR_2 = 9-$BC_{12}F_8$; X = Cl
4c: R = C_6F_5; X = OMe
4d: BR_2 = 9-$BC_{12}F_8$; X = OMe
4e: R = C_6F_5; X = N_3
4f: BR_2 = 9-$BC_{12}F_8$; X = N_3

from tri-*n*-octylaluminum where background impurity levels were ~1 ppm expressed as H_2O.[9] Despite these precautions, a large excess of DtBMP (ca. 1−10 equiv with respect to diborane **1**) had to be used to suppress competing protic initiation in the absence of CumCl, while polymerizations conducted in the presence of CumCl and excess DtBMP were characterized by low conversions (20−40%) but with initiator efficiencies (I_{eff}) consistent with chain transfer (i.e., $I_{\mathrm{eff}} \approx 100-300\%$). A reduction in the amount of DtBMP led to increases in conversion (to as high as 95%) and an increase in I_{eff} (>300%), consistent with more effective chain transfer. In the absence of CumCl and DtBMP, polymerizations were quantitative and characterized by $I_{\mathrm{eff}} > 1000\%$.[9]

These polymerization reactions are uncontrolled, given the weakly coordinating nature of the counteranions present. As will be reported in detail elsewhere, the chain transfer processes involved in these polymerizations do not involve chain transfer to monomer on the basis of the shallow temperature dependence of MW.[10]

With a view to developing initiator systems that would allow controlled isobutene polymerizations, we considered the use of diborane **1** or its more Lewis acidic analogue diborole **2** (Scheme 1)[11] with either cumyl methyl ether (CumOMe) or cumyl azide (CumN_3), which would generate more coordinating counteranions and thus initiator systems that might feature reversible termination as required for a living polymerization.[12]

In this paper we describe the reactions of diboranes **1** and **2** with these initiators to form *inter alia* unstable ion-pairs **3a**−**f**, the characterization of stable ion-pairs **4a**−**f** formed from these compounds and the corresponding Ph_3C-X (eq 1), the X-ray crystal structures of stable μ-N_3 ion-pairs **4e** and **4f**, and oligomerization studies using the model monomer 2,4,4-trimethyl-1-pentene (TMP) and the various initiators in conjunction with diborane **1**.

Results and Discussion

Characterization of Stable Ion-Pairs 4a−f. Thermally stable, and thus isolable, ion-pairs **4a**−**f** are cleanly formed by reaction of these diboranes with the corresponding trityl chloride, methyl ether, or azide (eq 1).[6d] The μ-Cl ion-pair **4a**[7] and μ-OMe ion-pair **4c**[6a] have already been reported in the literature and have been fully characterized by X-ray crystallography. Here we compare and contrast the structures of ion-pairs **4e** and **4f**, both featuring the μ-N_3 anion. Spectroscopic and analytical data for μ-Cl ion-pair **4b** and ion-pairs **4d**−**f** are included in the Experimental Section. In particular, the ^{19}F NMR spectroscopic data are diagnostic for these counteranions (Table 1) and assisted with the characterization of unstable ion-pairs **3a**−**f** to be described later.

The structures of compounds **4e** and **4f** are depicted in Figure 1, while selected crystallographic and refinement data and selected bond lengths and angles appear in Tables 2 and 3, respectively. In contrast to the structure of ion-pair **4a**, which features a weak, electrostatic interaction between the trityl carbocation and the μ-Cl anion,[7] there is limited interaction of this cation with the μ-azido counteranion in these structures. In particular, the closest contact between the central trityl atom C31 and the anion in the structure of ion-pair **4f** is in excess of 4 Å and involves F29, while for ion-pair **4e** an analogous contact with F30 is 3.428(6) Å; this is still well outside the sum of the van der Waals radii for C and F. In both structures the trityl cation has, as expected, a planar configuration for the central C atom (rms displacement 0.001 Å in each case for the four C atoms), which has short C−C bonds (1.436−1.450 Å), and a propeller conformation, the dihedral angles between the phenyl groups and the central C_4 plane being in the range 26.7−41.6°.

In the structure of ion-pair **4f** the five-membered ring, containing the two B atoms, one N atom of the N_3 anion, and C1 and C7 of the perfluorophenylene backbone, is slightly puckered with a dihedral angle between the mean planes defined by B1−C1−C6−B2 (rms displacement 0.007 Å) and B1−N1−B2 of 5.5(1)°. A similar distortion in the case of ion-pair **4e** is observed where the analogous angle is 3.2(1)°. However, in the latter case the B1−C1−C6−B2 unit is not planar (rms displacement 0.037 Å), with B1 and B2 located significantly above and below the mean plane, in contrast to the situation in ion-pair **4f**.

In the structure of ion-pair **4e**, the B−N bond lengths of 1.630(3) and 1.627(3) Å are essentially equivalent, while those observed in the structure of ion-pair **4f** are different at 1.643(3) and 1.681(3) Å and significantly longer on average [1.662(3) Å] than those observed in ion-pair **4e**. In addition, the endocyclic angle at N1 is significantly more acute in ion-pair **4f** [115.0(2)°] than in ion-pair **4e** [117.5(2)°], largely as a result of the longer B−N distances in the former structure.

The C7−B1−C18 and C19−B2−C30 angles in ion-pair **4f** are small, with values of 97.9(2)° and 98.0(2)°, as a consequence of the strained borole ring, while the angles N1−B1−C1 and N1−B2−C6 are 96.8(1)° and 96.6(1)°, respectively. In contrast, in the structure of ion-pair **4e**, the corresponding angles within the central five-membered ring are similar at 95.9(2)° and 95.9(2)°, while the exocyclic C19−B2−C25 and C7−B1−C13 angles are much more obtuse at 111.5(2)° and 113.2(2)°, respectively. In essence, the B atoms in ion-pair **4e** can easily rehybridize so as to allow closer approach of the azide ion in contrast to the structurally less responsive framework present in ion-pair **4f**.

The metrical parameters associated with the bridging azide ion in both structures are fairly similar. As expected N1−N2 is significantly longer than N2−N3 in both structures, although the difference is much more pronounced in ion-pair **4e** [1.251(2) vs 1.120(2) Å] than in ion-pair **4f** [1.199(2) vs 1.130(2) Å]. The central N atom in both structures is essentially sp-hybridized

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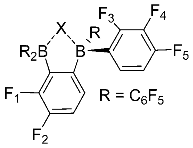
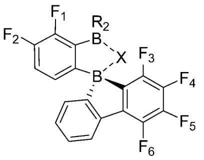
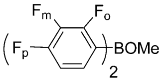
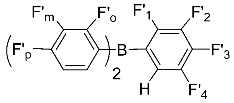
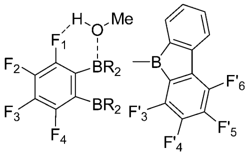
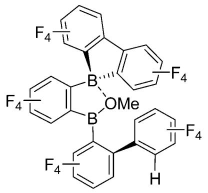
Table 1. ^{19}F Chemical Shifts and Assignments for Chelated Counteranions and Their Degradation Products[a]

Ion-pair **4a** (X = Cl)[b] 	−132.0 (d, 8F, F_3), −136.1 (AA'BB' spin system, 2F, F_1), −158.6 (t, 4F, F_5), −162.1 (AA'BB' spin system, 2F, F_2), −165.6 (m, 8F, F_4)
Ion-pair **4b** (X = Cl) 	−131.9 (s, br, 4F, F_3), −136.0 (s, br, 4F, F_6), −137.0 (AA\`BB\` spin system, 2F, F_1), −156.5 (dt, J = 18 Hz, 9 Hz, 4F, F_5), −157.7 (m, 4F, F_4), -161.3 (AA'BB' spin system, 2F, F_2)
Ion-pair **4c** (X = OMe)	−132.3 (br d, 8F, F_3), −137.6 (AA'BB' spin system, 2F, F_1), −160.1 (t, 4F, F_5), −163.6 (AA'BB' spin system, 2F, F_2), −166.0 (m, 8F, F_4).
Ion-pair **4d**(X = OMe)	−131.9 (s, br, 4F, F_3), −136.5 (s, br, 4F, F_6), −139.5 (AA\`BB\` spin system, 2F, F_1), −157.8 (dt, J = 18.1, 9.1 Hz, 4F, F_5), −158.5 (m, 4F, F_4), −162.5 (AA\`BB\` spin system, 2F, F_2).
Ion-pair **4e** (X = N_3)	−133.9 (m, 8F, F_3), −137.8 (m, 2F, F_1), −159.1 (t, 4F, F_5), −162.8 (d, 2F, F_2), −165.5 (m, 8F, F_4).
Ion-pair **4f** (X = N_3)	−132.2 (s, br, 4F, F_3), −135.9 (s, br, 4F, F_6), −138.4 (AA\`BB\` spin system, 2F, F_1), −157.0 (dt, 4F, J = 18.1, 9.1 Hz, F_5), −157.9 (m, 4F, F_4), −161.6 (AA\`BB\` spin system, 2F, F_2)
Borinic Ester **7** 	−132.2 (br d, 4F, F_o), −150.0 (br t, 2F, F_p), −161.7 (br m, 4F, F_m)
Borane **8** 	−125.5 (br m, 1F, F'_1), −127.5 (br d, 4F, F'_o), −138.2 (m, 1F, F_4), −143.3 (m, 1F, F'_3), −144.7 (tt, 2F, F'_p), −154.6 (m, 1F, F'_2), −160.5 (m, 4F, F'_m)
MeOH adduct **9** 	-124.5 (br d, J = 22 Hz, F'_3 in BR_2, 2F), -130.4 (dd, J_{HF} = 19, J_{FF} = 23 Hz, F_1), -130.6 (br m, F'_3 in BR_2•MeOH, 2F), -131.1 (br s, F_6 in BR_2, 2F), -132.6 (br s, F'_6 in BR_2•MeOH, 2F), -133.4 (br m, F_4, 1F), -141.0 (m, F_5 in BR_2, 2F), -151.4 (m, F'_5 in BR_2•MeOH, 2F), -152.6 (t, J_{FF} = 21 Hz, F_4 in BR_2, 2F), -153.6 (t, J_{FF} = 21 Hz, F'_4 in BR_2•MeOH, 2F), -153.8 (t, J_{FF} = 22 Hz, F_2), -155.9 (t, J_{FF} = 22 Hz, F_3)
Borinic Ester **10** 	-127.4 (m, 1F), -130.1 (br m, 1F), -133.2 (br s, 2F), -133.9 (td, J = 19.8, 3.3 Hz, 1F), -135.5 (br m, 1F), -136.2 (br m, 1F), -136.9 (m, 1F), -141.3 (v br, 1F), -141.7 (8-line multiplet, 1F), -147.3 (td, J = 20.3, 6.6 Hz, 1F), -151.3 (tdd, J = 20.1, 7.9, 4.6 Hz, 1F), -151.6 (8 line multiplet, 1F), -152.0 (br complex m, 1F), -152.3 (br complex m, 1F), -152.8 (br q, J = 19.0 Hz, 1F), -155.4 (br overlapping m, total 2F), -155.7 (br t, J = 19.8 Hz, 1F)

[a] Recorded in CD_2Cl_2 solution at 282 MHz and 25 °C unless otherwise noted. [b] ^{19}F NMR (CDCl3, 300 K, 282 MHz).

with bond angles of 179.3(2)° and 175.8(2)° in ion-pairs **4e** and **4f**, respectively.

The most significant difference between these two structures lies in the more exposed nature of the azide ion in ion-pair **4f** versus **4e**. Space-filling models show that both N2 and N3 are clearly exposed in ion-pair **4f**, while only the latter atom is somewhat unprotected by the $B(C_6F_5)_2$ rings in ion-pair **4e**. In particular, the twisting of these rings with respect to one another in ion-pair **4e** provides additional steric protection for the azide ion that is not possible for diborole **2**.

Isobutene Polymerization Using Cumyl Initiators and Diborane 1 or 2. In comparison to results previously obtained using CumCl and diborane **1** (e.g., Table 4, entries 1 and 2)[7] isobutene polymerization using diborole **2** and this initiator featured comparable conversions that are dependent on the amount of the hindered pyridine, DtBMP, present (entries 3−5). On the other hand, the MW of the polymer formed was uniformly lower and the initiator efficiencies (I_{eff}) higher, consistent with more effective chain transfer and/or increased initiation efficiency. As I_{eff} is greater than 100% (which is expected if chain transfer is effective), the actual efficiency of initiation cannot be directly discerned from these data.

Polymerizations initiated by $CumN_3$ and diborane **1**, in the presence of excess or even reduced quantities of DtBMP, were characterized by lower conversions in hydrocarbon media compared to CumCl (Table 4, entries 6−8). Initiator efficiencies were considerably reduced from those seen using CumCl, suggesting reduced rates of chain transfer (which seems unlikely) or less efficient initiation. Even in more polar media such as CH_2Cl_2 or mixtures with hexane, conversions were low

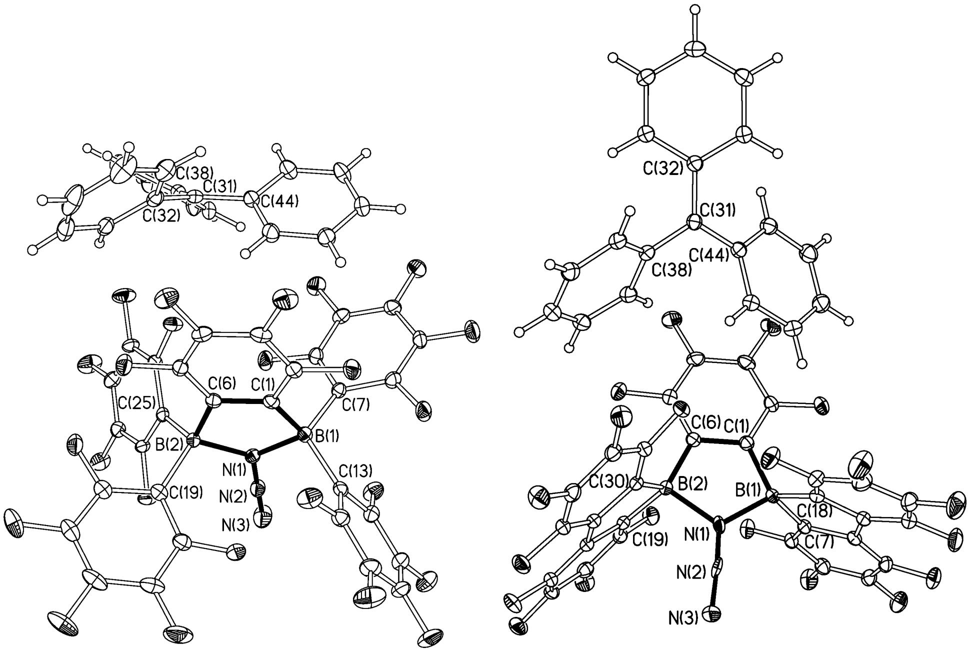


Figure 1. Structures of the ion-pairs **4e** (left) and **4f** (right), with 30% probability displacement ellipsoids and selected atomic labels depicted. The solvent molecules have been omitted.

Table 2. Selected Crystallographic and Refinement Data for Ion-Pairs 4e and 4f

	4e	**4f**
chem form	$[C_{19}H_{15}][C_{30}B_2F_{24}N_3]\cdot CH_2Cl_2$	$[C_{19}H_{15}][C_{30}B_2F_{20}N_3]\cdot CH_2Cl_2$
fw	1208.2	1132.2
T	160 K	160 K
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a (Å)	9.5052(8)	37.975(4)
b (Å)	24.039(2)	10.9235(11)
c (Å)	20.8556(17)	21.671(2)
β (deg)	99.004(2)	91.987(2)
V (Å^3)	4706.6(7)	8984.5(15)
Z	4	8
no. of data collected	34 796	37 471
no. of unique data, R_{int}	9233, 0.0312	10 539, 0.0380
no. of refined params	768	694
R (F, $F^2 > 2\sigma$)	0.0401	0.0417
R_w (F^2, all data)	0.1126	0.1097
GOF (F^2)	1.030	1.006
max., min. electron density (e Å^{-3})	0.65, −0.33	0.61, −0.55

(entries 9 and 10 vs 6), and surprisingly, addition of a solution of μ-N_3 ion pair **3e** (*vide infra*) prepared in CH_2Cl_2 at low temperature to a mixture of DtBMP and isobutene in hexane resulted in the lowest conversion (entries 11, 12).

Finally, even though CumOMe reacts with diborane **1** to form the expected μ-OMe ion-pair **3c** in polar media (*vide infra*), no polymer is formed from these two compounds in hexane and only small quantities form in CH_2Cl_2 using preformed ion-pair **3c** (entries 13−15). In view of the low conversions encountered using diborane **1** and the variable-temperature NMR studies involving either **1** or **2** and these cumyl initiators (to be described next), isobutene polymerization using diborole **2** and either CumOMe or $CumN_3$ was not investigated.

Reaction of Cumyl Chloride (CumCl) with Diborane 1 or 2. We examined the reactions of these initiators, as well as CumCl, with each diborane by variable-temperature ^1H and ^{19}F NMR spectroscopy in CD_2Cl_2 solution. In the case of CumCl and either diborane, formation of μ-Cl ion-pairs **3a** and **3b** occurs cleanly at low temperature. The structure of ion-pair **3a** was confirmed by comparison to that of stable trityl salt **4a** (*vide supra*), while the structure of ion-pair **3b** was inferred by the simple six-line pattern observed in the ^{19}F NMR spectrum of this mixture (Figure 2b, Table 1) along with the characteristic resonances of the cumyl cation (Figure 2a).

As reported elsewhere, ion-pair **3a** is unstable above −40 °C and decomposes cleanly to form indan **5**, diborane **1**, and HCl (Scheme 2). In the case of ion-pair **3b**, decomposition does not rapidly occur until ∼0 °C (Figure 2). However, in addition to indan **5** and diborole **2**, the stable indanyl ion-pair **6** is produced; this carbocation has been reported to form on ionization of CumCl using SbF_5 at sufficiently high temperature.[13] Since benzene was also produced during the formation of **6**, the more Lewis acidic diborole **2** is capable of activating HCl for *ipso*-substitution on indan **5** (or that the more thermally stable ion-pair **3b** is also effective for this process). The amount of benzene formed (Figure 2) corresponds to only one-third of the total amount of indanyl cation **6** generated. Electrophilic

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(13) Matyjaszewski, K.; Sigwalt, P. *Macromolecules* **1987**, *20*, 2679−2689.

Table 3. Selected Bond Lengths and Angles for Ion-Pairs 4e and 4f

compound **4e**		compound **4f**	
Bond Lengths (Å)			
B1−N1	1.630(3)	B1−N1	1.643(3)
B1−C1	1.611(3)	B1−C1	1.614(3)
B1−C7	1.643(3)	B1−C7	1.630(3)
B1−C13	1.639(3)	B1−C18	1.637(3)
B2−N1	1.627(3)	B2−N1	1.680(3)
B2−C6	1.617(3)	B2−C6	1.595(3)
B2−C19	1.654(3)	B2−C19	1.629(3)
B2−C25	1.634(3)	B2−C30	1.624(3)
N1−N2	1.251(2)	N1−N2	1.130(2)
N2−N3	1.120(2)	N2−N3	1.199(2)
Bond Angles (deg)			
N1−B1−C1	95.86(15)	N1−B1−C1	96.76(14)
N1−B1−C7	113.27(16)	N1−B1−C7	114.28(16)
N1−B1−C13	106.00(16)	N1−B1−C18	111.77(16)
C1−B1−C7	107.48(16)	C1−B1−C7	116.97(17)
C1−B1−C13	119.92(17)	C1−B1−C18	120.14(16)
C7−B1−C13	113.17(17)	C7−B1−C18	97.90(15)
N1−B2−C6	95.91(15)	N1−B2−C6	96.63(14)
N1−B2−C19	113.28(16)	N1−B2−C19	106.41(14)
N1−B2−C25	107.25(16)	N1−B2−C30	109.71(15)
C6−B2−C19	108.53(16)	C6−B2−C19	124.36(17)
C6−B2−C25	119.56(16)	C6−B2−C30	120.88(16)
C19−B2−C25	111.48(16)	C19−B2−C30	97.96(15)
B1−N1−B2	117.49(15)	B1−N1−B2	115.01(15)
B1−N1−N2	120.81(16)	B1−N1−N2	123.31(16)
B2−N1−N2	120.90(16)	B2−N1−N2	121.61(15)
N1−N2−N3	179.3(2)	N1−N2−N3	175.82(19)

Table 4. Polymerization of Isobutene Using CumX Initiators and Diborane 1 or 2[a]

entry	diborane	CumX	[DtBMP] (mM)	$\bar{M}_w$ (kg/mol))	PDI	yield (%)	I_{eff} (%)
1	**1**	Cl	20.0	361	1.72	42	156
2	**1**	Cl	2.0	236	1.74	67	384
3	**2**	Cl	20.0	80	1.55	37	552
4	**2**	Cl	10.0	69	1.63	60	1091
5	**2**	Cl	2.0	156	1.72	87	739
6	**1**	N_3	20.0	158	1.58	11	82
7	**1**	N_3	10.0	206	1.82	22	152
8	**1**	N_3	2.0	667	2.20	51	129
9[b]	**1**	N_3	20.0	275	1.50	17	70
10[c]	**1**	N_3	20.0	339	1.86	15	63
11[d]	**1**	N_3	20.0	261	2.30	8	53
12[d]	**1**	N_3	20.0	185	2.08	7	63
13	**1**	OMe	20.0			*e*	
14[f]	**1**	OMe	20.0	75	1.52	3	52
15[f]	**1**	OMe	20.0	139	3.82	5	110

[a] Stock solutions of DtBMP, diborane **1** or **2** (final concentration = 2.0 mM), and CumX (final concentration = 0.2 mM) in toluene were added in that order to an isobutene solution (2.75 M in hexane) at −78 °C unless otherwise noted. Reactions were quenched with MeOH after 1 h. [b] Polymerization in 60:40 v/v hexane/CH_2Cl_2 solution. [c] Polymerization in CH_2Cl_2 solution. [d] A solution of diborane **1** and $CumN_3$ in CH_2Cl_2 was prepared at −78 °C and then added to DtBMP, and isobutene in hexane at that temperature. [e] No polymer formed. [f] A solution of diborane **1** and CumOMe in CH_2Cl_2 was prepared at −78 °C and then added to DtBMP, and isobutene in CH_2Cl_2 at that temperature.

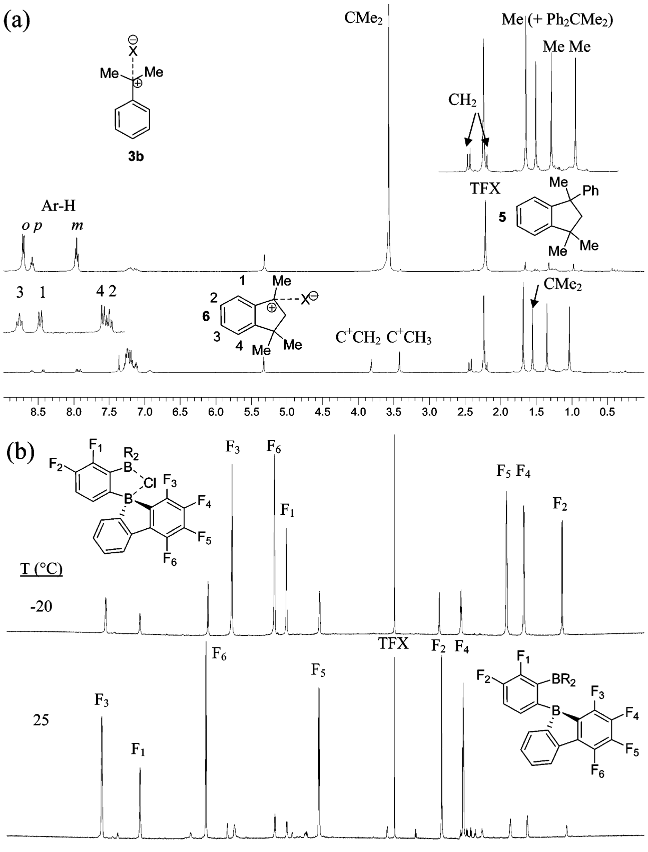
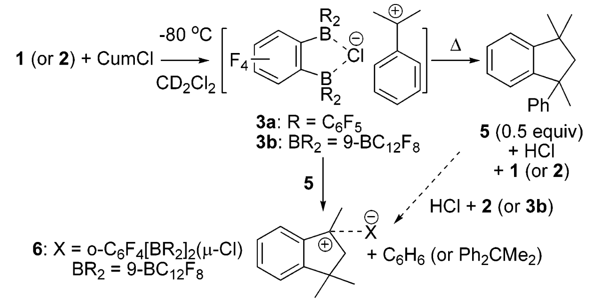


Figure 2. (a) ^1H NMR spectra of ion-pair **3b** formed from diborole **2** and CumCl in CD_2Cl_2 at −20 °C (top spectrum). Signals due to the cumyl cation of ion-pair **3b** are labeled in the top spectrum, while those due to indan **5** are labeled in the top inset and those of indanyl cation **6** are labeled in the bottom spectrum, recorded at 25 °C. TFX = tetrafluoro-*p*-xylene added as an internal standard. (b) ^{19}F NMR spectra of ion-pair **3b** formed from diborole **2** and CumCl in CD_2Cl_2 at −20 °C (top spectrum). Signals due to ion-pair **3b** are labeled (see Table 1 for labeling scheme), while those due to diborole **2** are labeled analogously in the bottom spectrum recorded at 25 °C. TFX = tetrafluoro-*p*-xylene added as an internal standard.

Scheme 2

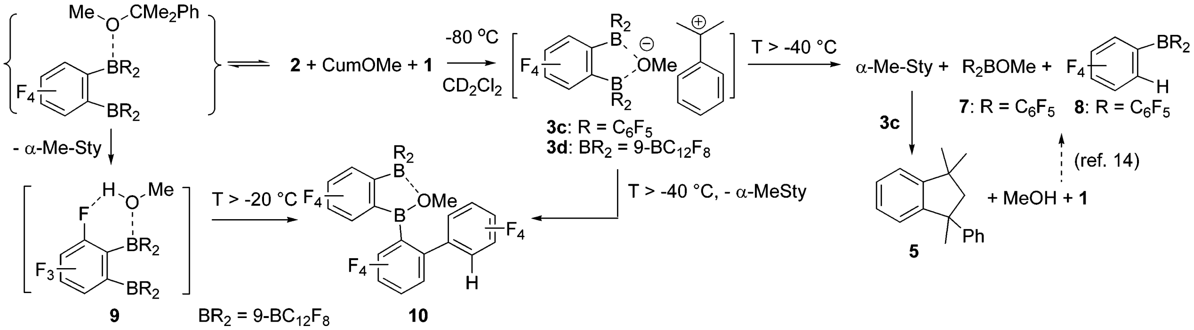


aromatic substitution on indan **5** by ion-pair **3b** would also provide ion-pair **6** and 2,2-diphenylpropane. An extra Me signal is seen at 1.67 ppm (nearly co-incident with one of the Me signals due to indan **5**), which is in agreement with the chemical shift reported for this material, and the total amount formed corresponds to roughly the remaining two-thirds of ion-pair **6** produced.

Given the higher thermal stability of ion-pair **3b**, it seems likely that the reduced MW seen using diborole **2** and CumCl in isobutene polymerization is partly a consequence of more efficient ionization and thus initiation. On the other hand, chelated ion-pairs derived from **2** feature bridging anions that are much more exposed (*vide supra*), and so the chelated counteranion can function more effectively in chain transfer processes. Alternately, since indanyl cation **6** is produced *only* using diborole **2**, it is possible that the combination of HCl and diborole **2** is much more competent for reinitiation of new chains in apolar media compared with diborane **1**.

Reactions with Cumyl Methyl Ether (CumOMe). In the case of CumOMe and excess diborane **1**, ionization is observed to form the expected *μ*-OMe ion-pair **3c**. The structure of this ion-pair is inferred from the spectroscopic data of the corresponding stable trityl ion-pair **4c** (*vide supra*). As with *μ*-Cl

Scheme 3



ion-pair **3a**, μ-OMe ion-pair **3c** is unstable in solution, and some decomposition is evident even at −60 °C. The ion-pair decomposes to form indan **5** and MeOH as an unobserved byproduct. As reported elsewhere, diborane **1** is unstable in the presence of substoichiometric amounts of MeOH, forming borinic ester **7** and borane **8**;[14] essentially identical chemistry is observed in the case of CumOMe (Scheme 3).

While this instability could explain the low conversions observed in isobutene polymerizations, it should be borne in mind that the polymerization experiments were conducted well below the temperature at which this process is rapid (and at lower concentrations of both initiator and diborane **1**). On the other hand, it is very likely that, after addition of one or several isobutene units to ion-pair **3c**, the resulting ion-pairs are much less stable toward a similar degradation reaction, even at low temperature, and borinic ester **7** and/or borane **8** are insufficiently Lewis acidic to reinitiate polymerization of isobutene.

Different chemistry was observed in the case of diborole **2** and CumOMe. The expected ion-pair **3d** is formed, as verified by comparison to stable ion-pair **4d** (*vide supra*); however, this species is present only in small amounts (Figure 3a). The major species present are diborole **2** along with a compound **9**, assigned as the *exo*-MeOH adduct of diborane **2** (Scheme 3). This is based on the 12-line ^{19}F NMR spectrum in solution at low temperature (see Figure 3a and Table 1) similar to that observed for the characterized mono-THF adduct,[14] as well as a doublet at δ 3.65 (J_{HH} = 3.9 Hz) in the ^{1}H NMR spectrum corresponding to 3H and a doublet of quartets at δ 6.53 (dq, J_{HF} = 18.7 Hz, J_{HH} = 3.9 Hz) integrating to 1H (Figure 3b). Also, significant quantities of indan **5** are present at low temperature in addition to higher oligomers of α-methylstyrene (α-Me-Sty). In particular, the presence of eight methyl signals at high field, along with four AB spin systems, indicates the formation of an indan bearing an additional cumyl group resulting from trimerization of α-Me-Sty and subsequent cyclization.

On warming above −60 °C, both ion-pair **3d** and MeOH adduct **9** decompose (at different temperature) to form indan **5** (from decomposition of **3d** or acid-catalyzed dimerization of α-Me-Sty) and the novel borinic ester **10**, which forms from both compounds **3d** and **9**; this ester results from proton-mediated B−C cleavage of one of the borole rings in **2**.

Borinic ester **10** has been independently prepared from diborole **2** and stoichiometric amounts of MeOH and has been fully characterized.[14b,15] A characteristic feature of compound **10** is that 19 of the 20 F nuclei are chemical shift inequivalent at room temperature [Figure 3a and Table 1 (the signal at δ −133 is due to two F nuclei which are probably accidentally equivalent)]. This is because in the solid state[15] and in solution a strong, dative interaction between the BOMe group and the adjacent borole moiety exists; when coupled with hindered rotation of the biphenyl moiety and/or slow inversion at O, this molecule is asymmetric.

We believe that MeOH adduct **9** forms via coordination of CumOMe to the *exo*-side of diborole **2**, which is sufficiently Lewis acidic to form an unstable ion-pair; the ion-pair eliminates α-Me-Sty to form adduct **9** (Scheme 3). α-Me-Sty is in turn trapped by the cumyl cation (or in general protons) to form indan **5** or higher oligomers of this type. The borinic ester **10** could form either directly from MeOH adduct **9** or indirectly from ion-pair **3d**, and in the latter case by protonation of the counteranion by cumyl cation to form an (unobserved) *endo*-MeOH adduct. It is evident from the VT NMR spectra depicted in Figure 3b that the latter process is faster than the former since *exo*-MeOH adduct **9** persists in solution at temperatures as high as −20 °C, while ion-pair **3d** is largely consumed at this temperature. In view of this additional complexity, and the fact that very little ion-pair **3d** was produced at low temperature, the use of diborole **2** as an initiator with CumOMe in isobutene polymerization was not even studied, especially in view of the low conversions already obtained with diborane **1** (Table 4).

Reactions with Cumyl Azide (CumN$_3$). The reactions of diborane **1** and diborole **2** with CumN$_3$ proved to be quite interesting. As shown in Figure 4a reaction of diborane **1** with CumN$_3$ at −80 °C leads to a more complicated ^{1}H NMR spectrum but a simple five-line pattern in the corresponding ^{19}F NMR spectrum. Ion-pair **3e**, featuring the μ-N$_3$ anion, is definitely present (0.61 equiv), as verified by comparison to its stable analogue **4e**, but in addition to indan **5** (0.19 equiv) another product **11a** (0.20 equiv) is present with signals at δ 10.64 (br t, 1H) 7.6 (m, 3H), 7.2 (m, 2H), 2.85 (s, 3H), and 2.60 (s, 3H). This material corresponds to the iminium salt of *N*-phenylacetone imine, as revealed by generation of an analogous salt from an authentic sample of this imine and Brookhart's acid[16] (see Supporting Information).

Iminium salt **11a** is formed by protonation of this imine by, for example, ion-pair **3e**, where the imine is formed by competing Schmidt rearrangement of CumN$_3$, a process that is known to be catalyzed by Lewis acids, including organoboranes.[17] We thus suspect that the low yields of polymer formed using this initiator result from competitive ionization (which is

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(14) (a) Lewis, S. P.; Henderson, L. D.; Chander, B. D.; Parvez, M.; Piers, W. E.; Collins, S. *J. Am. Chem. Soc.* **2005**, *127*, 46−47. (b) Henderson, L. D. Ph.D. Thesis, The University of Calgary, 2005.

(15) Sciarone, T.; Henderson, L. D.; Lewis, S. P.; Collins, S.; Piers, W. E. Manuscript in preparation.

(16) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

(17) Desai, P.; Schildknegt, K.; Agrios, K. A.; Mossman, C.; Milligan, G. L.; Aube, J. *J. Am. Chem. Soc.* **2000**, *122*, 7226−7232, and references therein.

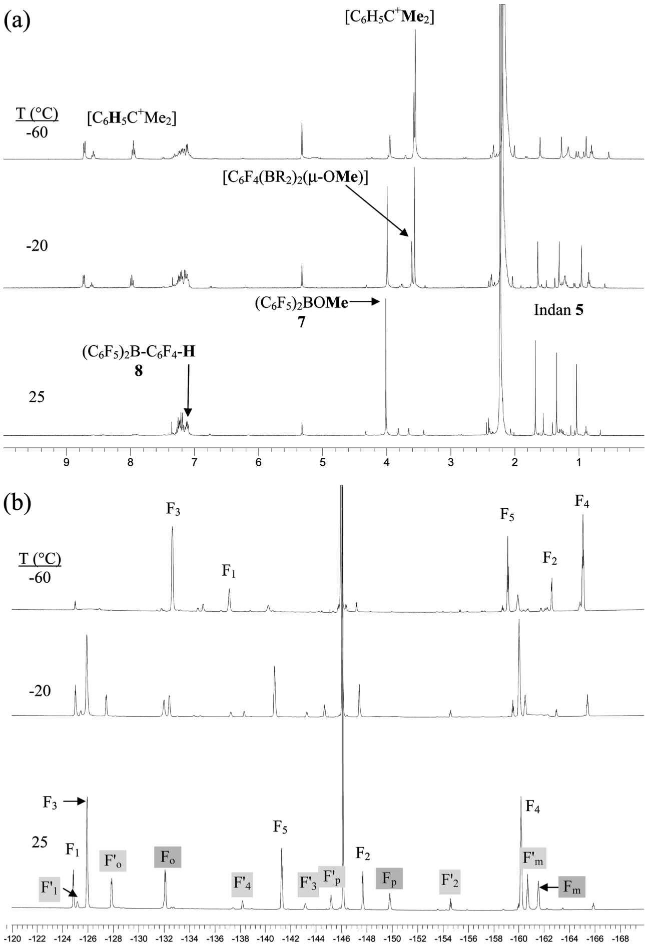

Figure 3. (a) Variable-temperature ^{1}H NMR spectra of ion-pair **3c** formed from diborane **1** and CumOMe in CD_2Cl_2. Signals due to the cumyl cation of ion-pair **3c** are labeled in the top spectrum. The signal due to the μ-OMe group of the anion is nearly coincident with the $-CMe_2$ moiety of the cation at low temperature but is resolved at higher temperature (see middle spectrum). The Me group of borinic ester **7** and the *o*-H of borane **8** are labeled in the bottom spectrum. (b) Variable-temperature ^{19}F NMR spectra of ion-pair **3c** formed from diborane **1** and CumOMe in CD_2Cl_2. Signals due to ion-pair **3c** are labeled in the top spectrum (see Table 1 for labeling scheme), while those due to diborane **1** are labeled analogously. Signals due to borinic ester **7** [$(C_6F_5)_2BOMe$] and borane **8** [$(C_6F_5)_2B$-(o-H)C_6F_4] are labeled in light gray (see Table 1 for labeling scheme) and dark gray (see Table 1 for labeling scheme), respectively, in the bottom spectrum. TFX = tetrafluoro-*p*-xylene added as an internal standard.

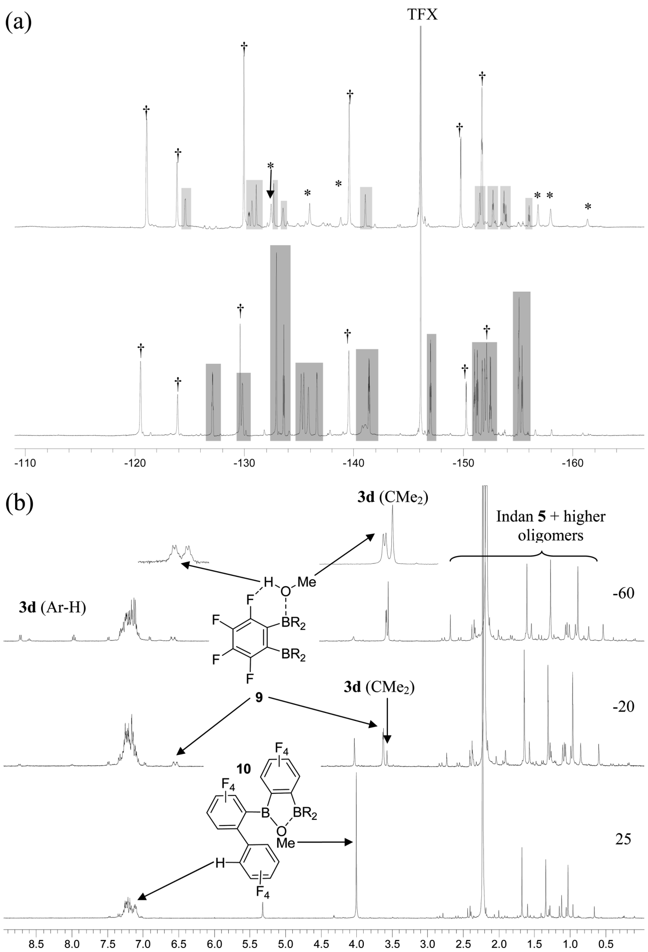

Figure 4. (a) ^{19}F NMR spectra of a mixture of diborole **2** and CumOMe in CD_2Cl_2. Signals due to ion-pair **3d** are indicated with asterisks (top spectrum, −60 °C), while those due to diborole **2** are indicated with daggers (for chemical shifts and assignments see Table 1). Signals due to MeOH adduct **9** are shaded in light gray (see Table 1 for chemical shifts and tentative assignments), while those due to borinic ester **10** formed at higher temperature (bottom spectrum, 25 °C) are shaded in dark gray (see Table 1 for chemical shifts and couplings). (b) Variable-temperature ^{1}H NMR spectra of a mixture of diborole **2** and CumOMe in CD_2Cl_2. Signals due to MeOH adduct **9** are indicated in the inset spectra, and those due to borinic ester **10** are indicated in the bottom spectrum.

stoichiometric in diborane and favored in a polar solvent) versus rearrangement (which is *catalytic* in diborane and less affected by solvent polarity). It is clear any of this unhindered imine generated *in situ* would terminate both initiating and propagating ion-pairs at rapid rates.^{5}

Also, the iminium salt **11a** that is formed represents a source of common ions; as we have recently shown, even in polar media with stable carbocations partnered with WCA, excess common ions *significantly* suppress the rate at which these ion-pairs undergo electrophilic addition reactions.^{18} Therefore, in hydrocarbon (or even polar) media, the presence of variable quantities of common ion will have a negative effect on the rate of polymerization.

On warming a mixture of ion-pair **3e** and iminium salt **11a** above −60 °C, indan **5** formed, but surprisingly additional iminium salt **11a** also was generated. This result implies that ionization of $CumN_3$ by diborane **1** *must be reversible* such that any $CumN_3$ generated undergoes competing, though irreversible rearrangement to imine. This is the first clear indication of reversible ionization with these diboranes and is probably due to the linear and more exposed nature of the azide ion in these compounds (*vide supra*).

Hydrazoic acid is expected to be produced during decomposition of ion-pair **3e** by analogy with the reactions of diborane **1** with CumCl; in this case, it is evident from Figure 4 that the indanyl cation **6**, partnered with the μ-N_3 anion, and benzene are also produced at elevated temperature and that this ion-pair is stable at RT. The ultimate products resulting from this reaction are a mixture of indan **5** (0.22 equiv), iminium salt **11a** (0.43 equiv), and ion pair **6** (0.35 equiv).

Similar chemistry was also observed in the case of $CumN_3$ and diborole **2**, although rearrangement to form iminium salt **11b** was much more prominent compared to ionization to form ion-pair **3f**. The less hindered nature of this diborole will facilitate binding of $CumN_3$ to the *exo*-side, and the resulting

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(18) Chai, J.; Lewis, S. P.; Kennedy, J. P.; Collins, S. *Macromolecules*, published online Sep 20, 2007 http://dx.doi.org/10.1021/ma0711137.

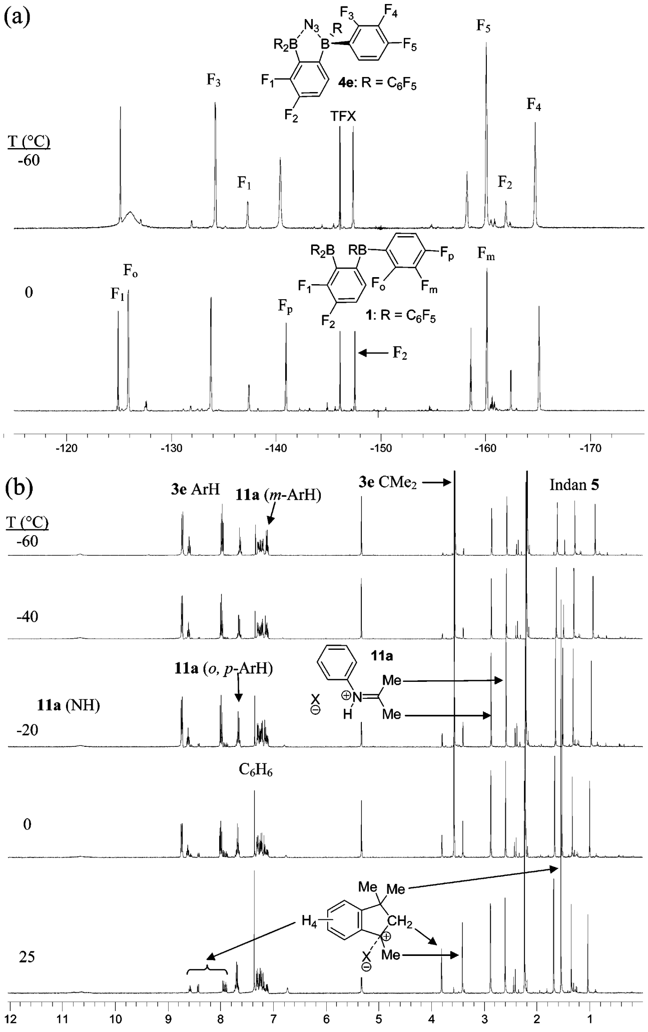


Figure 5. (a) Variable-temperature ^{19}F NMR spectra of a mixture of diborane **1** and $CumN_3$ in CD_2Cl_2. Signals due to ion-pair **3e**, iminium salt **11a**, and indanyl ion-pair **6** (which are coincident; see Table 1 for shifts and assignments) are labeled in the top spectrum, while those due to diborane **1** are indicated with asterisks in the bottom spectrum. (b) Variable-temperature ^{1}H NMR spectra of a mixture of diborane **1** and $CumN_3$ in CD_2Cl_2. Signals due to ion-pair **3e**, iminium salt **11a**, and indanyl ion-pair **6** are labeled in the top, middle, and bottom spectra, respectively.

adduct could be more prone to rearrangement than ionization. In contrast, unhindered donors such as CH_3CN bind to the interior of diborane **1**, and this could facilitate direct ionization in the case of $CumN_3$. Also, ionization could be favored by coordination of diborane to the *terminal* N of $CumN_3$, whereas rearrangement is facilitated by coordination to the *internal* N, a process that would be favored for a less-hindered Lewis acid.

On warming above −60 °C, more indan **5** and iminium salt **11b** were produced, but in addition degradation of diborole **2** was observed. In particular, a compound with a 16-line ^{19}F NMR spectrum is formed at the expense of diborole **2** on warming to room temperature. An identical species was formed by treating a mixture of diborole **2** with HN_3 (generated *in situ* from $[^nBu_4N][N_3]$ and CF_3SO_3H in CD_2Cl_2) but was accompanied by extensive degradation. Evidently, this species forms from the reaction of HN_3 (liberated when forming indan **5**) and diborole **2**. Unfortunately, none of the routes investigated provided material that could be readily purified, so the identity of this degradation product is unknown. [It is interesting to note that attempts to generate this degradation product by protonation of the μ-N_3 salt derived from diborole **2** and $[^nBu_4N][N_3]$ were unsuccessful. This salt is *inert* toward anhydrous HCl in CD_2Cl_2 solution, while use of CF_3SO_3H resulted in degradation but not to the same product.]

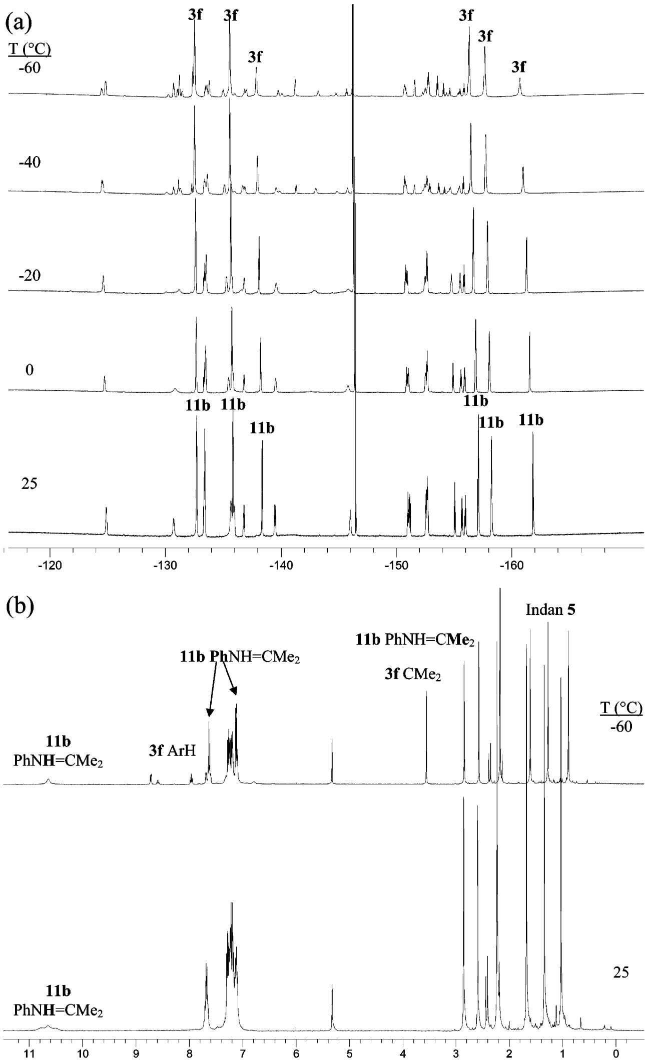


Figure 6. (a) Variable-temperature ^{19}F NMR spectra of a mixture of diborole **2** and $CumN_3$ in CD_2Cl_2. Signals due to ion-pair **3f** and iminium salt **11b** (which are coincident; see Table 1 for assignments) are labeled in the top and bottom spectra, while the remaining signals in the latter spectrum are due to the degradation product. (b) Variable-temperature ^{1}H NMR spectra of a mixture of diborole **2** and $CumN_3$ in CD_2Cl_2. Signals due to ion-pair **3f** and iminium salt **11b** are labeled in the top spectrum.

The above studies are instructive with respect to how chelating diboranes react with cumyl initiators differing in the nature of the ionizable group as well as the substituents on boron. In essence, diborane **1** reacts to give the highest proportion of chelated ion-pair **3**, an effect that is largely independent of anion, despite the higher kinetic and thermodynamic Lewis acidity of diborole **2**.[11] Evidently, initial coordination and ionization is highly sensitive to steric effects in these diboranes, and the cleanliness, or even the course of this reaction, is largely dependent on this issue.

The higher Lewis acidity of diborole **2**, combined with the tendency of donors to coordinate to the *exo*-side of this compound, generally manifests itself in terms of ionization to form unobserved (and unchelated) ion-pairs, which rapidly degrade even at low temperature. Conversely, the chelated ion-pairs that do form from **2** (generally in smaller quantities) appear to be more stable toward degradation than those formed from **1**. In general, for sterically hindered CumX initiators, there is no advantage to the use of diborole **2** and distinct disadvantages considering the regioselectivity of initial initiator binding and ionization.

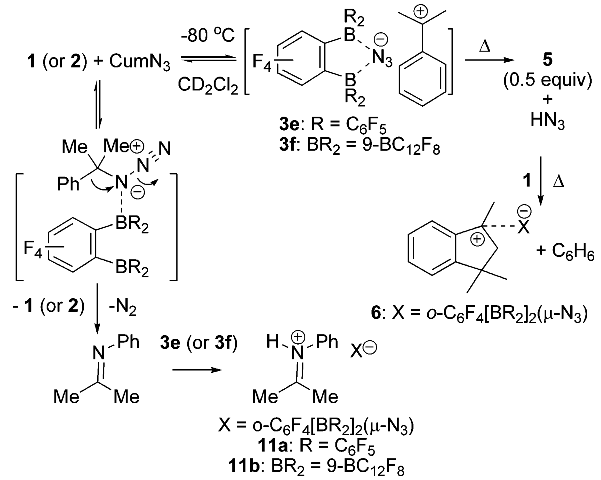
Reactions of CumCl, CumOMe, and CumN$_3$ with 2,4,4-Trimethylpentene (TMP) in the Presence of Diborane 1 and DtBMP. As a model for the polymerization experiments summarized earlier, we decided to investigate the products formed during oligomerization of TMP under conditions that mirrored our experiments. 2,4,4-Trimethyl-1-pentene is known to be an accurate model for reactions occurring in isobutene polymerization,[19] but the nature of the end groups is more readily identified due to facile chain transfer reactions that limit the degree of polymerization.[19,20]

The oligomerization of TMP (28 equiv) in the presence of diborane **1** proceeds rapidly in CH_2Cl_2 or hydrocarbon solution at low temperature to give a complex mixture of oligomeric materials. GC-MS analysis of the crude product mixture indicates formation of TMP-derived dimers (all five isomers[19]) and much smaller amounts of higher oligomers. These higher oligomers (trimers with $m/z = 336$ can be detected by GC-MS) are much less volatile than the dimer, and thus their relative amounts are not accurately represented by GC analysis. The ^{1}H NMR spectrum of the nonvolatile material, which corresponds to ca. 50 wt % of the TMP added, shows multiple, broad, and overlapping olefinic resonances largely consistent with *internal* unsaturation with $X_n \approx 4.7$ for oligomerizations conducted at −78 °C. Complex mixtures of this type are not uncommon when using very strong Lewis acids and uncontrolled protic initiation, although we do note that the degree of polymerization of the involatile material is quite high in comparison to conventional Lewis acids.[19,20]

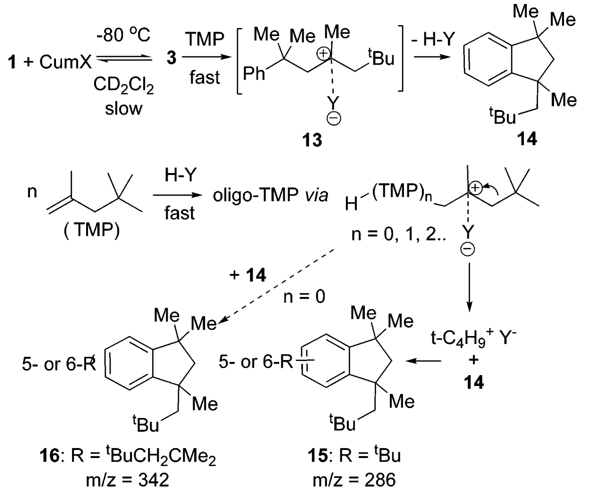
When CumCl, CumN$_3$, or CumOMe was used as initiator under similar conditions (i.e., 1.0 equiv with respect to diborane **1**), in the presence of the hindered pyridine DtBMP (0.24 equiv), TMP oligomers were also formed and the dimer represents the major volatile component in all cases. In general these product mixtures were extremely complex (see Supporting Information for representative GC-MS). Unlike the polymerization experiments involving isobutene and these initiators, conversion of TMP was quite high (>65% based on the amount of nonvolatile material recovered) given the low ratio of monomer to initiator in these experiments.

^{19}F NMR spectra of the crude mixtures prior to chromatography were consistent with the presence of chelated counteranions corresponding to **3a** (X = Cl), **3c** (X = OMe), and **3e** (X = N$_3$) being present (see Supporting Information). However, it was unclear what the countercations were (presumably stable oxonium acids [(MeOH)$_n$H][**1**(μ-X)];[14] these reactions were all quenched with excess MeOH). In the case of CumCl there was also evidence of anion degradation, since borinic ester **7** and the MeOH adduct of borane **8** were detected following a MeOH quench.

Scheme 4



Scheme 5



After separation of diborane **1** and its degradation products by filtration through basic alumina, FT-IR spectroscopy of the crude mixture formed from CumN$_3$ failed to reveal the presence of azide end groups. Substances bearing a cumyl group, which were readily detected by TLC due to their quenching of fluorescence under UV light, were partially separated from the higher oligomers formed by preparative TLC and were identified by a combination of ^{1}H NMR spectroscopy and GC-MS.

As expected, indan **14**[19f] is formed in variable amounts from all three initiators and results from addition of cumyl cation to TMP followed by cyclization (Scheme 5). In addition, we were able to partially purify ring-alkylated indans **15** and **16**, whose identity was confirmed by GC-MS and ^{1}H NMR spectroscopy. These compounds form via electrophilic aromatic substitution on indan **14** by either the 2,4,4-trimethylpentyl or the *tert*-butyl cation. The latter cation can be formed by β-cleavage of the former.[3] [It is likely that this process, which results in concomitant isobutene formation, is responsible for the higher degree of oligomerization of TMP through copolymerization with isobutene.] While only two isomers of *tert*-butylated indan **15** were detected, at least four isomers of indan **16** with m/z values corresponding to 342 were present in some of these mixtures. The two major isomers present had a simple AMX

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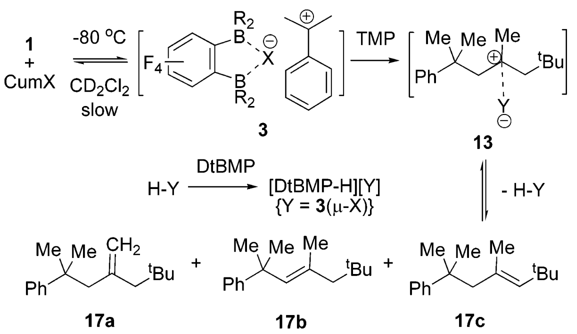
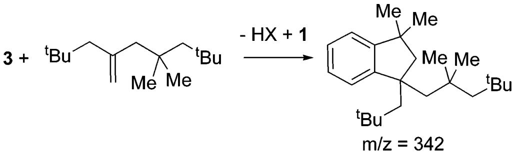
(19) (a) Buchmann, W.; Desmazieres, B.; Morizur, J.-P.; Nguyen, H. A.; Cheradame, H. *Macromolecules* **2000**, *33*, 660−677. (b) Buchmann, W.; Desmazieres, B.; Morizur, J.-P.; Nguyen, H. A.; Cheradame, H. *Macromolecules* **1998**, *31*, 220−228. (c) Coca, S.; Faust, R. *Macromolecules* **1997**, *30*, 649−651. (d) Schuetz, H.; Radeglia, R.; Heublein, G. *Acta Polym.* **1985**, *36*, 415−17. (e) Hasegawa, H.; Higashimura, T. *J. Appl. Polym. Sci.* **1982**, *27*, 171−81. (f) Nguyen A. H.; Kennedy, J. P. *Polym. Bull.* **1981**, *6*, 55−60.

(20) (a) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 427−35. (b) Ivan, B.; Kennedy, J. P *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 89−104. (c) Cheradame, H.; Habimana, J.; Rousset, E.; Chen, F. J. *Macromolecules* **1994**, *27*, 631. (d) Rajabalitabar, B.; Nguyen, H. A.; Cheradame, H.; Chen, F. J. *Eur. Polym. J.* **1995**, *31*, 73. (e) Rajabalitabar, B.; Nguyen, H. A.; Cheradame, H.; Chen, F. J. *Eur. Polym. J.* **1995**, *31*, 297. (f) Rajabalitabar, B.; Nguyen, H. A.; Cheradame, H. *Makromol. Chem. Phys.* **1995**, *196*, 3597. (g) Rajabalitabar, B.; Nguyen, H. A.; Cheradame, H. *Macromolecules* **1996**, *29*, 514.

Scheme 6



spin system for the aromatic protons (i.e., dd, $J = 8$, 2 Hz, 1H, br d $J = 2$ Hz, 1H; d, $J = 8$ Hz, 1H), consistent with the structure invoked for indan **16**; the other two isomers detected by GC-MS could result from addition of cumyl cation to the *exo* (or possibly rearranged) dimer of TMP (both of these compounds were among the major oligomers present[19]), followed by cyclization (eq 2).



(2)

Other than these discrete compounds, it would appear that the balance of the oligo-TMP present (the major nonvolatile component) lacks cumyl end groups and thus is formed via chain transfer. The relative amounts of the various products (i.e., **14**−**16** vs oligo-TMP) were sensitive to the nature of CumX, with CumCl giving the lowest amounts of the indanyl compounds relative to TMP oligomers, and CumOMe the most. Evidently, cumylation of TMP involving ion-pair **3** is occurring, but this process is less efficient compared to chain transfer following, for example, cyclization.

In an attempt to hinder chain transfer, the reaction of $CumN_3$ and TMP in the presence of diborane **1** was also examined at increased levels of DtBMP (1.0 equiv). The net result of this approach was a drastic decrease in total conversion of TMP (ca. 6−7%) with a change in product distribution. Here the major products formed are a mixture of three alkenes, **17a**−**c**, arising from cumylation of TMP followed by elimination (Scheme 6) and indan **5** (arising from analogous trapping of α-Me-Sty by the cumyl cation).

It is surprising to find *internal* alkenes being formed in the presence of DtBMP, which is usually highly selective for *exo*-olefin formation. Although the *exo*-olefin **17a** was the major isomer formed, it is likely that the μ-N_3 counteranion in ion-pair **13** is sufficiently basic to *reversibly* produce the various products (Scheme 6), and it is the resulting adduct of hydrazoic acid and diborane **1** that then reacts irreversibly with DtBMP. [We cannot exclude the participation of adventitious water in this deprotonation process followed by irreversible proton transfer to DtBMP.]

Taken together, these experiments are consistent with (inefficient) cationogenic initiation coupled with effective chain transfer. We suspect the inefficiency of cationogenic initiation is related to relatively slow ionization (due to steric hindrance in these diboranes) coupled with the very high intrinsic reactivity of the ion-pairs formed *in situ*.

Reversible *termination* to form telechelic materials [i.e., $Cum-(CH_2CMe_2)_n-CH_2CMe_2-X$] has been documented for classical (and sterically unhindered) Lewis acids and these types of initiators.[19,20] However, the use of cumyl ethers as initiators in living isobutene polymerization does not result in formation of polymers with OR end groups (only 3° Cl are detected).[21] In these cases either the initiator or the end OR groups are converted by excess Lewis acid into the corresponding chlorides, a reaction that is not possible in the case of diborane **1**. It is also a little surprising that analogous rearrangements of $CumN_3$ or related initiators were not seen in earlier work involving classical Lewis acids and isobutene oligomerization;[20c−f] perhaps this competing process accounts for the observation that, with some Lewis acids, cumylation was efficient, but end-capping by azide ion was not.

Finally, our results to date indicate a strong propensity for these ion-pairs to undergo extensive chain transfer reactions in isobutene polymerization or TMP oligomerization. In the absence of DtBMP, it is clear from model studies involving ion-pairs **3** that this transfer process involves these sterically hindered, though weakly coordinating anions, acting as *bases* toward the propagating chain end, rather than *nucleophiles* as required for a controlled cationic polymerization.

Conclusions

Although diborane **1** and diborole **2** are highly Lewis acidic and irreversibly ionize cumyl-based initiators in polar media, this reaction (both its rate and outcome) is highly dependent on the initial binding of CumX to these hindered diboranes. In general, diborane **1** is much more chemoselective in its reactions with CumX initiators for ion-pair formation and so is better suited to isobutene polymerization employing these compounds. Unfortunately, the chelating anions that form are sterically hindered, the resulting ion-pairs are contact ion-pairs in apolar media, and thus polymerizations involving isobutene appear dominated by counteranion-mediated chain transfer (or even termination) reactions in a manner that appears strongly correlated with the *basicity* of the bridging anion.

Controlled living polymerization of isobutene requires rapid and reversible ionization of the 3° alkyl halide (or pseudohalide) end group, coupled with efficient sequestration of acidic protons by DtBMP or related additives.[12] With $CumN_3$ reversible ionization is observed, but competing Schmidt rearrangement leads to initiator (and probably chain-end) decomposition. Therefore, future work will focus on the use of related initiators that cannot undergo Lewis acid-mediated rearrangement.[19] Also, indirect evidence suggests that even strong Brønsted acids formed during chain transfer can effectively reinitiate chain growth in concert with these diboranes, even in the presence of hindered bases such DtBMP. This result is quite unexpected on the basis of work with classical Lewis acids and will be the subject of future study.[10]

Experimental Section

Unless otherwise noted, all reagents were obtained from commercial sources and purified as required. All synthetic procedures were carried out in glassware previously passivated with dichlorodimethylsilane and were conducted under N_2 using Schlenk techniques or in an Innovative Technology glovebox. Hexanes, diethyl ether, and toluene were purified by distillation from potassium and benzophenone under N_2 and stored over activated 4 Å molecular sieves. Dichloromethane was distilled from P_2O_5 and stored over activated 4 Å molecular sieves. TMP was distilled and

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[21] Mishra, M. K.; Kennedy, J. P. *J. Macromol. Sci., Chem.* **1987**, *A24*, 933−48.

stored over activated 4 Å molecular sieves. DtBMP was sublimed prior to use. Diboranes **1**[6] and **21**[11] were synthesized using modified versions of the original literature methods. Cumyl chloride was prepared by bubbling HCl through predried α-methylstyrene and distilled, degassed, and stored at −28 °C. Cumyl azide was prepared using an existing literature method,[20c] while CumOMe was prepared from cumyl alcohol and MeI as described below. We find the Williamson ether synthesis[22] to be more reliable for the synthesis of CumOMe compared to the more commonly employed acid-catalyzed reactions. In particular, the product is uncontaminated with MeOH, CumOH, or other protic materials, which serve as co-initiators of isobutene polymerization using diborane **1**. *N*-Phenyl-2-iminopropane was prepared according to a literature method.[23] $[(Et_2O)_2H][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ was prepared as described in the literature[16] and stored at −30 °C in the glovebox freezer prior to use.

Routine $^1H/^{19}F$ NMR spectra were obtained on either Varian Mercury or Gemini 300 MHz instruments. All ^1H NMR spectra were referenced with respect to residual deuterated solvent. ^{19}F NMR spectra were referenced with respect to tetrafluoro-*p*-xylene (TFX: −146.21 CD_2Cl_2). Variable-temperature $^1H/^{19}F$ NMR spectra were recorded on a Varian Inova 400 MHz instrument, the thermocouple of which had been calibrated to within 5% of the actual temperature using a methanol standard. The solvent used for variable-temperature studies (CD_2Cl_2) was dried by vacuum transfer from P_2O_5 and stored over activated 4 Å molecular sieves prior to use.

GC analyses were performed using a Hewlett-Packard 5890 instrument equipped with a flame ionization detector and a 30 m × 0.25 mm HP-5 capillary column. A split injection (100:1 split ratio) was performed with the injector at 275 °C and the detector at 300 °C using the following temperature program: 50 °C (5 min) to 250 °C (15 min) at 4 °C/min. Data were recorded using a HP 3395 Series II digital integrator; representative GC traces are included as Supporting Information. GC-MS analyses were performed using a Varian Series 3300 GC-ion-trap MS equipped with a 30 m VXMS-5 column and an identical temperature program using a 10:1 split ratio. A solvent delay of 6 min was employed prior to data collection, and the entire mass range of 0−650 amu was scanned; representative GC-MS data are also included as Supporting Information.

Preparative and analytical TLC was performed using Merck silica gel 60 aluminum-backed plates, eluting with hexane. In the case of preparative TLC no more than 20 mg of crude material was separated on one entire plate.

Polyisobutene samples were analyzed by GPC at 35 °C, eluting with THF at 1.0 mL/min using a Waters chromatograph equipped with a set of linear Ultrastyragel columns, a Waters model 410 refractive index detector (DRI), a Viscotek model 110R differential viscometer (DV), and a Wyatt Technology 18-angle DAWN EOS multiangle light-scattering (MALLS) detector. Data were analyzed with Viscotek's TriSEC (random-coil approximation using data from the DRI, DV, and 90° MALLS detectors) and also Wyatt Technology's ASTRA software using a literature value for dn/dc supplied by Wyatt Technology. Although column calibration using polystyrene standards was not employed, the values of the MW averages of some narrow MWD polyisobutene standards (supplied by American Polymer Standards Inc.) were checked against values provided by this company and were found to be accurate to within ±10% for materials in excess of 10 kg/mol MW. The operator who performed these analyses was initially unaware that some of the samples analyzed were standards.

Preparation of Cumyl Methyl Ether. A solution of 5.0 g (36.7 mmol) of cumyl alcohol in 20 mL of dry THF was added to a suspension of 2.0 g of KH (50.0 mmol) in 150 mL of THF at −78 °C with stirring. The solution was warmed to RT and then refluxed until evolution of H_2 ceased. To the suspension of KH and alkoxide was added 10 mL (excess) of dry MeI at −78 °C. The mixture was allowed to warm to RT, then heated to reflux and refluxed overnight. The suspension was cooled to RT and the THF partially removed at 20 mmHg using a rotary evaporator. The suspension was diluted with hexane and then filtered to remove salts, washing with hexane. The hexane was evaporated at 20 mmHg using a rotary evaporator. The crude product (>80% yield) was purified by high-vacuum (10^{-3} mmHg) Kugelrohr distillation from powdered CaH_2.

Preparation of $[Ph_3C][1,2\text{-}C_6F_4(9\text{-}BC_{12}F_8)_2\text{-}\mu\text{-}Cl]$ (4b). $1,2\text{-}C_6F_4(BC_{12}F_8)_2$ (200 mg, 0.26 mmol) and Ph_3CCl (73 mg, 0.26 mmol) were stirred in CH_2Cl_2 (1 mL) for 18 h. An orange precipitate was formed upon addition of hexanes (10 mL). The supernatant was decanted, and the precipitate was washed with hexanes (20 mL) and dried *in vacuo* to afford the product as an orange powder. Yield: 204 mg (75%). ^1H NMR (300 MHz, CD_2Cl_2, RT): δ 8.25 (t, ^3J = 7.5 Hz, 3H, *p*-C_6H_5), 7.86 (t, ^3J = 8.0 Hz, 6H, *m*-C_6H_5), 7.63 (d, ^3J = 8.3 Hz, 6H, *o*-C_6H_5). ^{19}F NMR (282 MHz, CD_2Cl_2, RT): δ −131.9 (4F, $C_{12}F_8$), −136.0 (4F, $C_{12}F_8$), −137.0 (2F, C_6F_4), −156.5 (4F, $C_{12}F_8$), −157.7 (4F, $C_{12}F_8$), −161.3 (2F, C_6F_4). ^{11}B NMR (128 MHz, CD_2Cl_2, RT): δ 9.9. Anal. Calcd for $C_{49}H_{15}B_2ClF_{20}$ (1040.70): C 56.55, H 1.45. Found: C 56.78, H 1.49.

Preparation of $[Ph_3C][1,2\text{-}C_6F_4(9\text{-}BC_{12}F_8)_2\text{-}\mu\text{-}OMe]$ (4d). $1,2\text{-}C_6F_4(BC_{12}F_8)_2$ (0.030 g, 0.039 mmol) and Ph_3COMe (0.011 g, 0.039 mmol) were weighed into a flask, and CH_2Cl_2 (2 mL) was added. The reaction was stirred for 1 h, and the volatiles were removed *in vacuo*. The resulting product was pure by NMR spectroscopy. The product was crystallized from CH_2Cl_2 layered with hexanes. Yield: 35 mg (85%). ^1H NMR (300 MHz, CD_2Cl_2, RT): δ 8.26 (t, ^3J = 7.5 Hz, 3H, *p*-C_6H_5), 7.87 (t, ^3J = 7.5 Hz, 6H, *m*-C_6H_5), 7.66 (d, ^3J = 7.7 Hz, 6H, *o*-C_6H_5) 2.76 (s, 3H, O*Me*). ^{19}F NMR (282 MHz, CD_2Cl_2, RT): δ −131.9 (s, br, 4F, $C_{12}F_8$), −136.5 (s, br, 4F, $C_{12}F_8$), −139.5 (AA′BB′ spin system, 2F, C_6F_4), −157.8 (d of t, *J* = 18.1, 9.1 Hz, 4F, $C_{12}F_8$), −158.5 (m, 4F, $C_{12}F_8$), −162.5 (AA′BB′ spin system, 2F, C_6F_4). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, RT): δ 7.6 (br s). Anal. Calcd for $C_{50}H_{18}B_2F_{20}O$ (1036.28): C 57.95, H 1.75. Found: C 57.74, H 2.15.

Preparation of $[Ph_3C][1,2\text{-}C_6F_4(B(C_6F_5)_2)_2\text{-}\mu\text{-}N_3]$ (4e). Into a flask containing triphenylmethylazide[24] (0.14 g, 0.48 mmol) and $C_6F_4\{B(C_6F_5)_2\}_2$ (0.40 g, 0.48 mmol) was condensed CH_2Cl_2 (25 mL). The solids rapidly dissolved upon warming to give a yellow-orange solution, which was stirred for 1 h at ambient temperature. The solvent was removed *in vacuo* to afford the crude product as a glass on the walls of the vessel. This was triturated with hexanes (30 mL) for an extended period, affording an orange solid after filtration and drying under reduced pressure. Sonication of the product/hexanes mixture was often employed to aid in the isolation of the product in powder form. Yield: 0.49 g (91%). ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ 8.27 (t, ^3J = 8 Hz, 3H, *p*-C_6H_5), 7.88 (m, 6H, *m*-C_6H_5), 7.66 (d, ^3J = 8 Hz, 6H, *o*-C_6H_5). ^{19}F NMR (282 MHz, CD_2Cl_2, 300 K): δ −133.9 (m, 8F, *o*-C_6F_5), −137.8 (m, 2F, C_6F_4), −159.1 (t, 4F, *p*-C_6F_5), −162.8 (d, 2F, C_6F_4), −165.5 (m, 8F, *m*-C_6F_5). ^{11}B NMR (64 MHz, CD_2Cl_2, 300 K): δ 0.5 (s). Anal. Calcd for $C_{49}H_{15}B_2F_{24}N_3$: C 52.4, H 1.4, N 3.7. Found: C 52.6, H 1.4, N, 3.6.

Preparation of $[Ph_3C][1,2\text{-}C_6F_4(9\text{-}BC_{12}F_8)_2\text{-}\mu\text{-}N_3]$ (4f). $1,2\text{-}C_6F_4(BC_{12}F_8)_2$ (0.030 g, 0.039 mmol) and Ph_3CN_3 (0.011 g, 0.039 mmol) were weighed into a vial, and CH_2Cl_2 (10 mL) was added. The reaction was swirled until all solids were dissolved. Hexanes (10 mL) was layered on top of the reaction mixture, and the vial was capped and placed in the freezer (−40 °C). After 2 days large

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[22] For a recent paper describing the use of a similar procedure to the synthesis of hindered cumyl ethers see: Casarini, D.; Coluccini, C.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **2006**, *71*, 4490−4496.

[23] Kyba, E. P. *Org. Prep. Procedures* **1970**, *2*, 149−156.

[24] Saunders, W. H., Jr.; Ware, J. C. *J. Am. Chem. Soc.* **1958**, *80*, 3328−3332.

orange crystals had formed in the solution. The solution was decanted and the crystals were dried *in vacuo*. Yield: 0.030 g (73%). ^{1}H NMR (300 MHz, CD_2Cl_2, RT): 8.26 (t, J = 7.5 Hz, 3H, p-C_6H_5), 7.87 (t, J = 7.5 Hz, 6H, m-C_6H_5), 7.66 (d, J = 7.7 Hz, 6H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, RT): δ 209.4 (CPh$_3$), 142.2 (C_{Ph}), 141.2 (C_{Ph}), 138.5 (C_{Ph}), 129.2 (C_{Ph}). Signals for the C−F nuclei were not located. ^{19}F NMR (282 MHz, CD_2Cl_2, RT): δ −132.2 (s, br, 4F), −135.9 (s, br, 4F), −138.4 (AA′BB′ spin system, 2F), −157.0 (d of t, 4F, J = 18.1, 9.1 Hz), −157.9 (m, 4F), −161.6 (AA′BB′ spin system, 2F). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, RT): δ 3.5 (br, s). A satisfactory analysis was not obtained.

Preparation of 1,2-$C_6F_4(B(OMe)C_{12}HF_8)(BC_{12}F_8)$ (10). Diborole **2** (250 mg, 0.33 mmol) was dissolved in toluene (5 mL). Dry methanol (13 μL, 0.33 mmol) was injected via syringe. The solution was stirred for 18 h at room temperature, during which the bright yellow color of the starting material disappeared. Toluene was removed under reduced pressure. Any residual toluene was removed by the addition of hexanes and pumping off all volatile materials. The product was obtained as a white powder, pure by NMR spectroscopy. Yield: 185 mg (71%). Recrystallization from toluene (0.5 mL) affords crystalline material (63 mg, 24%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 6.52 (m, 1H, $C_6F_4HC_6F_4B$), 3.04 (s, 3H, B-OMe). (CD_2Cl_2, 298 K): δ 7.11 (m, 1H, Ar^F-H), 4.00 (s, 3H, B-OMe). ^{19}F NMR (282 MHz, C_6D_6, 298 K): δ −127.3 (1F, C_6F_4), −130.4 (1F, $C_6F_4HC_6F_4B$), −131.4 (2F, $BC_{12}F_8$), −133.1 (1F, C_6F_4), −135.7 (2F, $C_6F_4HC_6F_4B$ + $BC_{12}F_8$), −136.0 (1F, $C_6F_4HC_6F_4B$), −136.1 (1F, $BC_{12}F_8$), −138.8 (1F, C_6F_4), −142.2 (br, 1F, $C_6F_4HC_6F_4B$), −145.8 (1F, $C_6F_4HC_6F_4B$), −149.5 (1F, $C_6F_4HC_6F_4B$), −149.8 (1F, $BC_{12}F_8$), −150.3 (1F, $BC_{12}F_8$), −150.8 (1F, $C_6F_4HC_6F_4B$), −151.6 (1F, $C_6F_4HC_6F_4B$), −153.8 (1F, $BC_{12}F_8$), −154.1 (1F, C_6F_4), −154.5 (1F, $BC_{12}F_8$); (CD_2Cl_2, 298 K): δ −127.4 (1F), −130.1 (1F), −133.2 (2F), −133.9 (1F), −135.5 (1F), −135.7 (1F), 136.1 (1F), −136.9 (1F), −141.3 (br, 1F), −141.6 (1F), −147.2 (1F), −151.2 (1F), −151.5 (1F), −151.9 (1F), −152.2 (1F), −152.7 (1F), −155.3 (2F), −155.6 (1F). ^{11}B NMR (128 MHz, C_6D_6, RT): 47.3 (br s, B-borole), 12.3 (br, s, B-OMe). Anal. Calcd for $C_{31}H_4B_2F_{20}O$ (793.96): C 46.90, H 0.51. Found: C 46.72, H 0.67.

General Polymerization Procedure. Nitrogen gas was purified by passing it first through a column packed with a 50:50 v/v mixture of activated 3 Å molecular sieves and BASF R3-11 catalyst followed by a second column packed with alternating layers of activated 3 Å molecular sieves and Sicapent. Isobutylene was purified by passing it through a column packed with a mixture composed of 50:50 v/v activated 3 Å molecular sieves and BASF R3-11 catalyst. The prepurified monomer was next condensed into a graduated collection vessel held at −78 °C under a blanket of nitrogen. The collected monomer was then degassed via three sequential freeze−pump−thaw cycles prior to use. A representative procedure for polymerization is given below with initiation using diborane **1** and CumCl.

A 250 mL round-bottom 24/40 single-neck flask was charged with 11.6 g (17.5 mL) of hexanes, 0.82 g (1 mL) of trioctylaluminum, and a magnetic stir bar inside a glovebox. This was then fitted with a 24/40 vacuum adapter equipped with a Teflon vacuum stopcock and the apparatus connected to a vacuum line. The mixture of solvent and drying agent was degassed using three freeze−pump−thaw cycles and then charged with 5.5 mL monomer via vacuum transfer.

This solution was then stirred at −78 °C for 30 min before vacuum transferring both monomer and solvent to a second, two-neck round-bottom flask attached to the vacuum line through another 24/40 vacuum adapter and equipped with a septum inlet. The contents of this flask were then warmed to −78 °C and stirred for 15 min under N_2 prior to injection of the following solutions listed in order of addition: (1) 1 mL of DtBMP stock solution (0.5 M in hexane); (2) 0.766 mL of a stock solution of diborane **1** (0.065 M in toluene); (3) 0.172 mL of a CumCl stock solution (0.029 M in hexane). Polymerization was allowed to proceed for 1 h at −78 °C under N_2 before quenching with 1 mL of methanol. All volatiles were removed and solids were washed with methanol prior to being taken up in hexanes. The resultant polymer solution was filtered, stripped of solvent, and dried in a vacuum oven at 30 in Hg at 90 °C for 24 h to yield a clear solid or oil.

Reaction of *N*-Phenylacetone Imine with $[(Et_2O)_2H][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$. To a solution of N-phenylacetone imine (2.7 mg, 0.02 mmol) in CD_2Cl_2 (0.5 mL) was added 16.6 mg of oxonium acid at 25 °C. ^{1}H and ^{19}F NMR spectra were recorded, and the former spectrum, overlaid with that due to a mixture of **11a** and **5**, formed from diborane **1** and $CumN_3$ is depicted in the Supporting Information. Aside from the resonances due to diethyl ether and those of the counteranion, the remaining Me and Ar−H resonances overlapped perfectly with those due to **11a**.

General Procedure for Reactions of 1 or 2 with Cum-X in CD_2Cl_2. To a screw-top, septum-sealed, 5 mm NMR tube were added the desired amount of diborane **1** or **2** and TFX in CD_2Cl_2 at room temperature in a glovebox. The spectrum of the resulting solution was then recorded to verify the concentration of diborane with respect to TFX standard. The sample was ejected and cooled in an acetone/dry ice bath under N_2. Cum-X in CD_2Cl_2 was injected slowly via syringe and the tube mixed with a vortex mixer. The tube was immersed into a precooled (−80 °C) probe, and ^{1}H and 19 F spectra were recorded at this temperature. The probe was warmed in 20 °C increments, during which both ^{1}H and ^{19}F NMR spectra were collected to monitor formation and subsequent decomposition of the resulting ion-pairs.

Reaction of Diborane 1 with TMP. A flask was charged with diborane (0.10 g, 0.12 mmol) in 3 mL of CH_2Cl_2 in a glovebox. The flask was taken out of the glovebox and cooled to −78 °C, and TMP (0.375 g, 3.35 mmol) was added slowly. The mixture was stirred at −78 °C for 2 h and quenched with 1 mL of MeOH. The resulting solution was filtered through a short Al_2O_3 column, washing with benzene. The product mixture was analyzed by GC-MS (see Supporting Information). The solution was then concentrated to dryness *in vacuo* to provide a colorless oil. Yield: 0.198 g, 53%. This material was nonvolatile, though contaminated with small quantities of dimer. A representative ^{1}H NMR spectrum is depicted in the Supporting Information indicating $X_n \approx 4.5$.

General Procedure of Reaction of 1, TMP, and Cum-X in the Presence of a Small Amount of DtBMP. To a flask were added diborane (0.100 g, 0.12 mmol), DtBMP (6 mg, 0.029 mmol), CH_2Cl_2 (3 mL), and TMP (0.375 g, 3.35 mmol) in a glovebox in the sequence stated. The flask was taken out of the glovebox and cooled to −78 °C, and Cum-X (1 mL, 0.12 M stock solution in CH_2Cl_2, 0.12 mmol) was added slowly. The mixture was stirred at −78 °C for 2 h and quenched with 1 mL of MeOH. The crude mixtures were worked up as described above and analyzed by GC and/or GC-MS. Then the reaction mixture was concentrated to dryness *in vacuo* and the residue extracted with hexane (3 × 10 mL). The hexane extracts were concentrated to dryness, and a colorless oil was obtained, which was partially separated by preparative TLC eluting with hexane.

Reaction of 1, TMP, and $CumN_3$. Crude yield: 0.265 g, 71%. Preparative TLC afforded two fractions, which appeared as dark bands under UV light. Fraction 1: $R_f \approx 0.90$, two major isomers of **16** contaminated with TMP oligomers. Fraction 2: $R_f, \approx 0.82$; 1,3,3-trimethyl-1-neopentylindan (**14**), contaminated with TMP oligomers and trace amounts of **15**. For GC-MS data of the mixture and these compounds, see the Supporting Information.

Reaction of 1, TMP, and CumOMe. Crude yield: 0.251 g, 67%. Preparative TLC afforded two fractions, which appeared as dark bands under UV light. Fraction 1: $R_f \approx 0.90$, four isomers of **16** contaminated with TMP oligomers. Fraction 2: $R_f \approx 0.82$, mainly isomers of **15** (three compounds by GC-MS) contaminated with TMP oligomers, and trace amounts of **14**. For GC-MS data of the mixture and these compounds, see the Supporting Information.

Reaction of 1, TMP, and CumCl. Crude yield: 0.346 g, 88%. This mixture was not separated by preparative TLC, but GC-MS reveals the presence of compounds **14**−**16** with a product distribution resembling that formed from CumOMe.

Reaction of 1, TMP, and CumN$_3$ in the Presence of Equimolar DtBMP. To a flask was added diborane (0.1 g, 0.12 mmol), DtBMP (25 mg, 0.12 mmol), CH_2Cl_2 (3 mL), and TMP (0.375 g, 3.35 mmol) in a glovebox in the stated sequence. The flask was taken out of the glovebox and cooled to −78 °C, and CumN$_3$ (1 mL, 0.12 M stock solution in CH_2Cl_2, 0.12 mmol) was added slowly. The mixture was stirred at −78 °C for 2 h and quenched with 1 mL of MeOH. Workup as described above provided a colorless oil. Yield: 0.025 g, which consisted of a ca. 4.6:1 molar ratio of **17**:**5** by ^{1}H NMR spectroscopy The mixture was separated by preparative TLC eluting with hexane. Fraction 1: $R_f \approx 0.90$, mixture of **17a**−**c**. Fraction 2: $R_f \approx 0.75$, 1,3,3-trimethyl-1-phenylindan (**5**).

High-field ^{1}H NMR spectra, including 2D COSY and NOESY spectra, gHSQC, and HMBC ^{13}C−^{1}H spectra of compounds **17a**−**c** are included as Supporting Information. High-resolution mass spectrum calcd for $C_{17}H_{26}$ 230.2035, found (EI, 70 eV) 230.2029.

X-ray Crystallography. Data were collected at 160 K on a Bruker SMART 1K CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections for **4f**, for which the crystal was a thin plate, were made on the basis of repeated and symmetry-equivalent reflections; no correction was applied for the approximately equidimensional block crystal of **4e**. The structures were solved by direct methods and refined on all unique F^2 values, with constrained riding H atoms. Each structure contains one CH_2Cl_2 molecule in the asymmetric unit. In **4f** this is ordered, but in **4e** it is extensively disordered; a reasonable approximation was achieved with a model having three components, two of which share C and one Cl atom.

Acknowledgment. The authors thank the American Chemical Society, Petroleum Research Fund, the University of Akron, and the Natural Sciences and Engineering Research Council of Canada for financial support of this work, and the Engineering and Physical Sciences Research Council (UK) for funding of crystallographic equipment. The authors also thank Prof. Mark Soucek of the Department of Polymer Engineering at the University of Akron for access to a GC-MS instrument and Mr. Jon Page of the Institute for Polymer Science at the University of Akron for GPC analyses of polyisobutene samples.

Supporting Information Available: ^{1}H NMR spectra of iminium salt **11a**. ^{19}F NMR spectra of reaction mixtures resulting from oligomerization of TMP using diborane **1** and CumCl, CumN$_3$, and CumOMe. GC-MS analyses of these product mixtures along with selected mass spectra of individual components. ^{1}H NMR spectra of partially purified indans **14**−**16**. 2D COSY, NOESY ^{1}H−^{1}H, and gHSQC, HMBC ^{1}H−^{13}C NMR spectra of alkenes **17a**−**c**. Crystallographic information files for **4e** and **4f**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700672Q