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Isobutene Polymerization Using Chelating Diboranes: Polymerization in Aqueous Suspension and Hydrocarbon Solution

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The use of the chelating diboranes o-$C_6F_4[B(C_6F_5)_2]_2$ (**1**) and o-$C_6F_4(9\text{-}BC_{12}F_8)_2$ (**2**: $9\text{-}BC_{12}F_8$ = 1,2,3,4,5,6,7,8-octafluoro-9-borafluorene) for the polymerization of isobutene (IB) in aqueous suspension or in hydrocarbon solution was studied. Polymerizations in aqueous suspension provided polymer of moderate MW and at variable conversion and were dependent on temperature, mode of diborane addition, the presence of surfactant, and the acidity of and nature of the anion present in the aqueous phase. The *T* dependence of MW over the *T* range −80 to −20 °C was studied in aqueous suspension, and higher MW polymer was formed at lower *T*. The hydrolysis and methanolysis of diboranes **1** and **2** was studied by NMR spectroscopy. Reactions of diborane **1** with excess MeOH or water afford solutions containing oxonium acids $[o\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-}OR)][(ROH)_nH]$ (**7**: R = H, $n > 2$; **3**: R = Me, $n = 3$). When diborane **1** is present in excess over water or MeOH, degradation of the diborane is observed. In this case the products are $o\text{-}C_6F_4\{B(C_6F_5)_2\}H$ (**5**) and $(C_6F_5)_2BOH$ **7** or $(C_6F_5)_2BOMe$ **4**, respectively. In the case of diborole **2**, $o\text{-}C_6F_4(9\text{-}BC_{12}F_8)B(2\text{-}C_{12}F_8\text{-}2''\text{-}H)(\mu\text{-}OH)\cdot 7H_2O$ (**17**) and $o\text{-}C_6F_4(9\text{-}BC_{12}F_8)B(2\text{-}C_{12}F_8\text{-}2''\text{-}H)(\mu\text{-}OMe)$ (**11**) were isolated from reactions of **2** with water and MeOH, respectively, and were characterized by X-ray crystallography. None of these degradation products effect IB polymerization in aqueous suspension. As a model for initiation of polymerization, the reaction of diborole **2** with 1,1-diphenylethylene (DPE) was studied. Addition of MeOH at low *T* results in efficient formation of the ion-pair $[Ph_2CMe][o\text{-}C_6F_4(9\text{-}BC_{12}F_8)_2(\mu\text{-}OMe)]$ via protonation of DPE. Polymerizations in hydrocarbon media were exothermic and rapid and gave quantitative yields of polymer even at very low concentrations of diborane **1**. The *T* dependence of MW was studied in hydrocarbon solution and showed non-Arrhenius behavior. This was explained by competitive chain transfer to monomer at elevated *T* and chain transfer to molecular water at lower *T*.

Introduction

Protic or electrophilic initiators that give rise to weakly coordinating anions (WCA),[1] partnered with propagating carbocations in isobutene polymerization,[2] are a topic of significant interest in the context of butyl rubber manufacturing 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**[6] (Chart 1), in combination with cumyl chloride (CumCl), was

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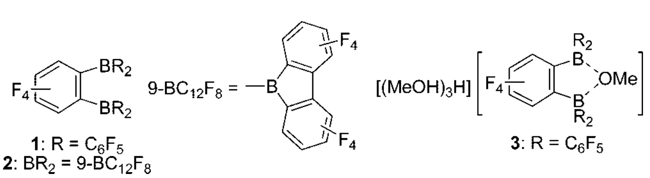
Chart 1



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

effective for isobutene polymerization in the presence of the sterically hindered pyridine 2,6-di-*tert*-butyl-4-methylpyridine (DtBMP).[7] More recently, we have studied the polymerization and allied chemistry of diborane **1** and diborole **2**[8] in combination with cumyl ether and cumyl azide initiators,[9] as well as the roles of DtBMP in polymerizations initiated by diborane **1** and CumCl.[10]

A picture that emerges from these studies is that although these diboranes are effective for ionization of cumyl halide and related initiators, giving rise to weakly coordinating, chelated anions partnered with the cumyl cation,[11] isobutene polymerizations in hydrocarbon media using these initiators and the diboranes are complicated by facile chain transfer. Also, DtBMP is not an entirely innocent additive in polymerizations featuring weakly coordinating anions. The highly Brønsted acidic chain ends are susceptible to termination in the presence of sufficiently high concentrations of this hindered pyridine. (The study of chain transfer processes under these conditions is complicated by the presence of *excess* DtBMP. We have recently discovered a Lewis acidic additive that is an effective scavenger of water in hydrocarbon media, compared to diborane **1**. Future work will focus on the study of chain transfer featuring controlled initiation under these conditions.)

Another picture that emerges from these studies is that both of these diboranes are rather resistant to hydrolysis and the hydrolysis products are not strong Brønsted acids (*vide infra*). Thus, unlike conventional Lewis acids, these polymerizations readily proceed in the presence of variable quantities of dissolved water (*vide infra*), and an excess of DtBMP over Lewis acid (and water) is required to efficiently sequester the Brønsted acid formed from these diboranes and water.

In 2005 we reported that the use of diborane **1** in aqueous isobutene suspension afforded moderate conversions to polymer of moderate MW.[12] Although styrene and related monomers had been earlier polymerized in aqueous suspension[13] and most recently in a controlled fashion using either $BF_3 \cdot OEt_2$[14] or $B(C_6F_5)_3$,[15] this was the first report of significant polymer formation from isobutene in the presence of a large excess of water.

At the time, our understanding of this novel process was largely incomplete: the nature of the initiator was not known nor was it obvious that diborane **1** versus a degradation product was involved in initiation. The only mechanistic information we had was that the novel, stable oxonium acid **3** formed from diborane **1** and excess MeOH (Chart 1)[12] was ineffective as an initiator, as were compounds of comparable Brønsted acidity to **3** (e.g., $[(Et_2O)_2H][B(C_6F_5)_4]$[16]) or Lewis acidity to diborane **1** [$B(C_6F_5)_3$ or 9,10-bis(perfluorophenyl)-9,10-dibora-perfluoroanthracene[17]].

In this paper we report more detailed polymerization studies in both aqueous suspension and hydrocarbon solution using both diborane **1**[18] and diborole **2** that shed considerable insight into the nature of the processes limiting both MW and conversion under these conditions. We also studied and report in detail the reactions of these two compounds with water and MeOH, including the characterization of the degradation products formed and their efficacy as initiators of polymerization. We have also studied the reaction of diborole **2** with 1,1-diphenylethylene (DPE) in the presence of MeOH as a model for protic initiation involving these compounds.

Results and Discussion

Polymerization of Isobutene in Aqueous Suspension. Polymerization of isobutene in aqueous suspension was studied in three aqueous media featuring strong electrolytes, aqueous LiCl (mp −65 °C),[19] 38 wt % sulfuric acid, and 48 wt % fluoroboric acid. The latter two media were initially selected on the basis of low freezing point (ca. −70 and −90 °C, respectively) and commercial availability. In all cases, there was no noticeable reaction between isobutene and any of these media, prior to the introduction of diborane or diborole. Polymerizations were quenched by the addition of an excess of 2-propanol at low *T*; the use of a hydrocarbon-soluble base such as NEt_3 in lieu of 2-propanol did not affect the outcome of these experiments.

It should be noted that these suspensions are unstabilized, and so rapid, mechanical stirring (>500 rpm) was employed to

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Table 1. Isobutene Polymerization in Aqueous LiCl Suspension[a]

entry	initiator (mM)[b]	surfactant[c]	M_w (kg mol^{-1})	PDI	yield (%)
1	**1** (0.322)		22.8	2.30	44
2	**1** (0.322)		29.4	2.38	39
3	**1** (0.322)	DTMB	61.0	2.74	5
4	**1** (0.322)	DTMB	47.4	2.68	4
5	**1** (0.322)	SDS	31.8	2.37	32
6	**1** (0.322)	SDS	34.9	2.47	30
7	**2** (0.627)		91.9	2.27	40
8	**2** (0.627)	SDS	39.5	1.74	25
9	**2** (0.627)	SDS	75.4	2.47	26

[a] The diborane initiator dissolved in 1 mL in toluene was added rapidly to a stirred (500 rpm) mixture of 18.0 mL of isobutene and 18.0 mL of aqueous LiCl [LiCl (23 wt %) NaCl (1.2 wt %) H_2O (75.8 wt %)] at −60 °C unless otherwise noted. [b] The concentration of diborane used is reported with respect to the total volume of the organic phase. [c] Where used, 0.100 g of dodecyltrimethylammonium bromide (DTMB) or sodium dodecylsulfate (SDS) was added to the aqueous phase.

Table 2. Isobutene Polymerization in Aqueous Sulfuric Acid Suspension[a]

entry	initiator	surfactant[b]	M_w (kg mol^{-1})	PDI	yield (%)
1	**1**		28.3	2.05	29
2	**1**		25.3	2.21	27
3	**1**[c]		22.0	3.86	46
4	**1**[c]		27.6	3.38	30
5	**1**[d]		17.4	2.63	24
6	**2**[d]		18.7	3.11	26
7	**1**	SDS	33.8	2.24	17
8	**1**	SDS	37.2	2.69	18
9	**1**	DTMB	83.4	3.16	2
10	**1**	DTMB	69.8	2.86	3
11	**1**	DTMOTf	41.3	2.32	18
12	**1**	DTMOTf	35.8	2.82	14

[a] The diborane initiator dissolved in 1.0 mL of toluene was added rapidly to a stirred (500 rpm) mixture of 18.0 mL of isobutene and 18.0 mL of aqueous H_2SO_4 [H_2SO_4 = 38 wt %] at −60 °C unless otherwise noted. The final concentration of diborane was 0.625 mM. [b] Where used, 0.100 g of DTMB, SDS, or dodecyltrimethylammonium triflate (DTMOTf) was added to the aqueous phase. [c] A stock solution of diborane or diborole in toluene (1.0 mL) was added over 5 min to a suspension of 15.0 mL of isobutene and 15.0 mL of 5.0 M aqueous $LiHSO_4$ at −45 °C. [d] A stock solution of diborane or diborole in toluene (1.0 mL) was added over 10 min to a suspension of 15.0 mL of isobutene and 15.0 mL of 5.0 M aqueous $LiHSO_4$ at −45 °C.

Table 3. Isobutene Polymerization in Aqueous Fluoroboric Acid Suspension[a]

entry	initiator (mM)	surfactant[b]	T (°C)	M_w (kg mol^{-1})	PDI	yield (%)
1	**1** (0.322)		−80	41.4	2.37	58
2	**1** (0.322)		−80	37.2	2.43	54
3	**2** (0.625)		−80	49.4	2.15	58
4	**2** (0.625)		−80	42.4	2.22	64
5	**1** (0.625)[c]		−80	29.3	2.05	61
6	**2** (0.625)[c]		−80	39.5	2.04	29
7	**1** (0.322)	SDS	−80	27.2	2.08	47
8	**1** (0.322)	SDS	−80	36.2	2.34	42
9	**1** (0.322)	$DTMBF_4$	−80	33.4	2.22	47
10	**1** (0.322)	$DTMBF_4$	−80	31.8	2.13	52
11	**1** (0.625)[d]		−80	41.0	1.73	85
12	**1** (0.625)[d]		−80	41.3	1.82	80
13	**1** (0.625)[d]		−73	31.7	2.06	87
14	**1** (0.625)[d]		−73	32.1	2.10	92
15	**1** (0.625)[d]		−60	31.0	2.28	95
16	**1** (0.625)[d]		−60	38.1	2.37	78
17	**1** (0.625)[d]		−40	13.0	2.36	76
18	**1** (0.625)[d]		−22	4.60	2.28	30
19	**1** (0.625)[d]		−22	6.10	2.17	19

[a] The diborane initiator dissolved in 1.0 mL of toluene was added rapidly to a stirred (500 rpm) mixture of 18.0 mL of isobutene and 18.0 mL of aqueous HBF_4 [HBF_4 = 7.0 M] at −80 °C unless otherwise noted. [b] Where used, 0.100 g of SDS or dodecyltrimethylammonium tetrafluoroborate ($DTMBF_4$), was added to the aqueous phase. [c] A stock solution of diborane or diborole in toluene (1.0 mL) was added over 10 min to a suspension of 15.0 mL of isobutene and 15.0 mL of aqueous HBF_4 [d] A stock solution of diborane in toluene (1.0 mL) was added over 1.0 min to a suspension of 10.0 mL of isobutene, 5.0 mL of hexane, and 15.0 mL of aqueous HBF_4.

create a dispersion. On addition of a toluene stock solution of diborane or diborole, an exothermic reaction was noted, depending on the rate of addition, this being particularly pronounced in the case of diborane, while these mixtures took on a milky appearance as reaction progressed. On the other hand, phase separation was observed to occur when stirring was stopped, at least in those suspensions featuring monomer diluted with hexane.

The results of these experiments are summarized in Tables 1−3. Table 1 summarizes the results obtained in aqueous LiCl suspension at −60 °C. Table 2 summarizes the results obtained in 38 wt % sulfuric acid at the same *T* along with a few experiments in aqueous $LiHSO_4$ at somewhat higher *T*, while Table 3 reports results obtained in aqueous fluoroboric acid at −80 °C. These *T* were dictated by the freezing points of the aqueous phase and increased viscosity of the aqueous medium as one approaches the freezing point; in essence, effective dispersal of the monomer was possible only at the *T* indicated.

Polymer yields are higher in aqueous fluoroboric acid, while those in sulfuric acid are lower compared with aqueous LiCl. The first effect is likely related to the significantly lower *T* employed, as experiments in aqueous HBF_4 indicated significant decreases in both MW and conversion at higher *T* (*vide infra*). We speculate that as the *T* is increased, the solubility of water in the organic phase increases to the point where formation of higher order, less acidic, oxonium acids (analogous to **3**) interferes with either initiation or propagation within the droplet.

The lower yields encountered in aqueous sulfuric acid versus aqueous LiCl at the same *T* may be related to the acidity of the aqueous phase. That the acidic nature of these aqueous phases is deleterious is revealed by the experiments with aqueous $LiHSO_4$, where even at higher *T* (−45 °C), conversions are higher while MW is at least comparable to experiments in aqueous H_2SO_4 conducted at lower *T* (Table 2, entries 3/4 vs 1/2). Since the ionic strength of these media are comparable (both are about 5 M in HSO_4), these differences are due to the higher acidity of the latter medium.

Unfortunately, there are no commonly available fluoroborate salts whose aqueous solutions possess low melting temperatures comparable to that of fluoroboric acid. On the other hand, particularly using diborane **1**, conversions of monomer can approach 100% in that medium at low *T* if diluted with hexane (*vide infra*).

As far as polymer MW is concerned, no clear pattern emerges from these data other than that of temperature. Thus, at −80 °C, $\bar{M}_w$ varies between 30 and 40 kg mol^{-1} in aqueous HBF_4, while at −60 °C, $\bar{M}_w$ varies between 20 and 30 kg mol^{-1} in aqueous LiCl or H_2SO_4. Surprisingly, in aqueous $LiHSO_4$ at −45 °C, $\bar{M}_w$ varied between 17 and 28 kg mol^{-1} and was found to be sensitive to the rate of addition of initiator (entries 3−5, Table 2).

Also, rather contradictory results were obtained using diborane **1** versus diborole **2** in the different media. In aqueous LiCl, 3−4 times higher MW polymer was formed at similar levels of conversion using the diborole (Table 1, entry 7 vs 1 and 2). This feature was not observed in aqueous HBF_4 (Table 3, entries 1/2 vs 3/4), although conversion and MW appeared sensitive to the rate of initiator addition (entry 5 vs 6). Almost identical outcomes were observed in aqueous $LiHSO_4$ at −45 °C with either initiator (entry 5 vs 6, Table 2) using a controlled addition rate.

As can be seen from the results in Tables 1−3, the MWD are broad with PDI between 2 and 3, as would be expected for a polymerization process dominated by chain transfer. In the cases reported in Tables 1−3, the polymer featured a unimodal MWD with a low MW tail. The skew or asymmetry of the MWD was sensitive to whether the suspension was quenched at, for example, low T versus warming to room temperature prior to quenching. The latter conditions led to increased formation of low MW oligomers and as a result were generally avoided.

During this work, it became apparent that the rate of addition of initiator to these suspensions was a very significant variable influencing the results. The diborole is bright yellow in solution; formation of donor adducts[8] and/or hydrolysis (*vide infra*) leads to formation of colorless products. When this compound is added rapidly to these suspensions, the yellow color of the diborole persists for some time after the addition is complete, while at sufficiently slow addition rates (5−10 min, depending on T, amount of initiator and medium used), the suspensions remain colorless. Under the former conditions, polymer yields and MW are generally significantly higher than under the latter conditions.

For example, in aqueous HBF_4 suspension with 10.0 mL of monomer diluted by 5.0 mL of hexane, addition of 0.25 mL of 0.01 M diborole within 5 s resulted in the formation of poly(isobutene) (PIB) with $\bar{M}_w = 62.5$ kg mol^{-1} at 36% conversion, while addition of 1.0 mL of 0.01 M diborole over a 5 min period afforded PIB with $\bar{M}_w = 27.7$ kg mol^{-1} at 27% conversion.

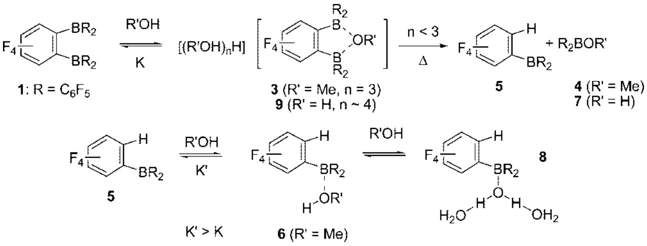
This behavior was also evident using the diborane initiator. Rapid addition of this compound to monomer is highly exothermic and can result in reflux of the monomer. One would normally expect a negative impact on both conversion and MW. However, in those experiments where a slower, controlled addition of this compound was conducted, lower MW polymer was formed at similar conversion (e.g., Table 3, entries 1 and 2 vs 5). If this compound was added sufficiently slowly, only trace amounts of PIB were formed.[18]

Finally, the use of ionic surfactants to stabilize these suspensions was studied. Although the high ionic strength of these aqueous phases mitigates against formation of micelles, it was anticipated that the particle size of the droplets would be more uniform under these conditions, possibly allowing for a more controlled initiation.

In all cases, the use of a surfactant led to a decrease in conversion, and this effect was particularly pronounced in the case of dodecyltrimethylammounium bromide (DTMB) in aqueous LiCl or H_2SO_4 (Table 1, entries 3 and 4 or Table 2, entries 9 and 10). In contrast, when using dodecyltrimethylammounium triflate (DTMOTf) in aqueous H_2SO_4 or dodecyltrimethylammounium tetrafluoroborate ($DTMBF_4$) in aqueous HBF_4, comparable results were obtained to those observed using sodium dodecylsulfate (SDS) in either medium (Table 2, entries 11/12 vs 7/8 and Table 3, entries 9/10 vs 7/8). In either case, one suffers about a 10% drop in conversion under otherwise similar conditions.

The use of SDS or $DTMBF_4$ surfactant led to a statistically insignificant change in $\bar{M}_w$ in aqueous HBF_4 (i.e., 39.3 ± 3.0 vs 32.2 ± 3.8 kg mol^{-1}), while surprisingly a significant increase in $\bar{M}_w$ was observed in aqueous H_2SO_4 using either SDS or DTMOTf (25.8 ± 2.8 vs 37.0 ± 3.2 kg mol^{-1}) and to a lesser extent in aqueous LiCl using SDS (26.1 ± 4.7 vs 33.4 ± 2.2 kg mol^{-1}).

Scheme 1



Part of this is almost certainly related to the lower conversions encountered: experiments using DTMB that featured dramatically lower conversions also provided the highest MW polymer (Table 1, entries 3 and 4 and Table 2, entries 9 and 10).

It is now reasonably well understood that anions tend to preferentially aggregate at the interface in dispersed media of this sort, where they can disrupt local water structure at the interface.[20] Ordering of water structure near an interface results in a local decrease in density, thus facilitating diffusion through the interface. In particular, the Hofmeister series can be used to predict the efficacy of anions for this process, and in the present case, diffusion of water through the interface is expected to increase in the order BF_4[20c] ≪ $ROSO_3$ ∼ HSO_4[20c] ∼ CF_3SO_3 < Br ≪ Cl.

One possible interpretation of the results obtained to date is that lower conversions encountered in stabilized suspension are a reflection of increased diffusion of water into the droplet during chain growth at constant T.

Since $\bar{M}_w$ does not show a consistent trend, it is less clear whether a similar explanation applies. In particular, since all of the experiments using a surfactant featured an uncontrolled addition rate, and this is known to be an important variable influencing polymer MW, it could be that variations in addition, etc., account for any difference in the results observed. We do note that the poor reproducibility in $\bar{M}_w$ between the two experiments conducted with the diborole in the presence of SDS (Table 1, entries 8 and 9) is likely a reflection of this.

Finally, the T dependence of MW and conversion was studied in the case of isobutene polymerization in aqueous HBF_4 suspension. In these experiments, the isobutene was diluted with hexane ([IB] = 8.36 M) since this results in better T control and higher conversion in suspension, as well as in solution polymerizations (*vide infra*). Over the T range −80 to −40 °C, conversions varied between 75% and 95% with no discernible trend, but they do decrease to 20−30% at −22 °C (see Table 3, entries 11−19). Evidently, at sufficiently low T, the MW of the polymer formed is largely independent of T (entries 11−16) but decreases rapidly above −60 °C. We will defer discussion of these results until those obtained in the virtual absence of water are presented (*vide infra*).

Hydrolysis and Alcoholysis of Diborane 1. As mentioned in the Introduction, the reaction of diborane **1** with MeOH has been previously studied, and in the presence of excess MeOH, the novel and stable oxonium acid **3** is formed (Scheme 1).[12] In that study various amounts of MeOH were added to diborane **1**, initially at low T, with the outcome of this reaction being highly solvent and T dependent for amounts of MeOH ≤ 1.0 equiv (Table 4, entries 1−7).

In polar media such as CD_2Cl_2, oxonium acid **3**is present at low T, while in toluene-d_8 at low T, or on warming a CD_2Cl_2

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(20) (a) Pegramnt, L. M.; Record, M. T., Jr. *J. Phys. Chem. B* **2007**, *111*, 5411–5417. (b) Wick, C. D.; Dang, L. X. *J. Phys. Chem. B* **2005**, *109*, 15574–15579. (c) Taylor, R. P.; Kuntz, I. D., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 7963–65.

Table 4. Product Distribution from the Reaction of Diborane 1 with MeOH

entry	MeOH (equiv)	T (K)	solvent	1	3	4	5	6
1	0.5	298	toluene-d_8	50	0	25	25	0
2	0.5	193	CD_2Cl_2	88	12	0	0	0
3	0.5	298	CD_2Cl_2	50	0	25	25	0
4	1.0	213	toluene-d_8	30	17	26	26	0
5	1.0	298	toluene-d_8	0	0	50	50	0
6	1.0	213	CD_2Cl_2	31	39	15	15	0
7	1.0	298	CD_2Cl_2	0	0	50	50	0
8	2.0	298	toluene-d_8	0	0	50	0	50
9	3.0	298	toluene-d_8	0	33	33	0	33
10	4.0	298	CD_2Cl_2	0	100	0	0	0

solution above −60 °C, any oxonium acid present decomposes to form $(C_6F_5)_2BOMe$ **4**[12,21] and $(o\text{-}C_6F_4H)B(C_6F_5)_2$ **5**. The identity of these compounds was verified by independent synthesis (see Supporting Information), while the ^1H, ^{19}F, and ^{11}B chemical shifts and assignments for all of these compounds are reported in Table 5.

Evidently, compounds **4** and **5** arise from chemoselective cleavage of the *o*-phenylene B−C bonds of diborane **1** (Scheme 1). We strongly suspect that this cleavage results from reversible protonation of the anion in **3**, either at O to form an unobserved μ-MeOH adduct or possibly in an irreversible and direct manner involving *ipso* electrophilic aromatic substitution at one of the B−C bonds. In particular, the acidity of the oxonium acid **3** will be sensitive to the number of MeOH molecules that solvate the proton,[22] and a minimum of three are needed to stabilize this compound at room temperature. Presumably, the higher stability of **3** in polar media at low T reflects its ionic constitution, such that protonation to form the neutral degradation products is less facile.

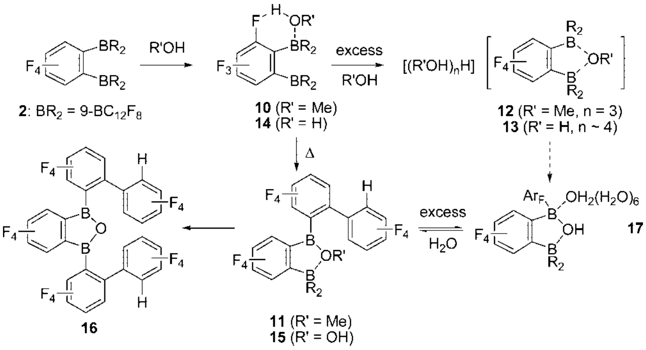
Borane **5** is sufficiently Lewis acidic (and less sterically hindered) that it competes effectively with diborane **1** for MeOH, forming monoadduct **6**. Thus, when ≥1.0 equiv of MeOH is present, a quasi-equilibrium is established between **1**, **3**, **4**, and **6** at low T in toluene-d_8, with ion-pair **3** favored in CD_2Cl_2 at low T (Table 4, entry 4 vs 6). At sufficiently high T, all of diborane **1** is converted into **4** and **5** (or **6**) depending on the amount of MeOH initially present.

If excess MeOH is present (i.e., ≥ 4 equiv) ion-pair **3** is the exclusive product formed at low T and is stable in solution at room temperature. Additional MeOH, over and above that needed to form **3**, exchanges with the MeOH molecules that solvate the proton; this exchange process is rapid at all temperatures in CD_2Cl_2.

The formation of ion-pair **3** from **1** and MeOH is reversible in the sense that ion-pair **3** can serve as a source of MeOH in the presence of excess **1**. This was shown by an experiment where **3** was generated from **1** and excess MeOH (8.0 equiv). Addition of 3.0 equiv of diborane **1** to a solution of **3** (1.0 equiv + 4.0 equiv of MeOH) at room temperature led to formation of **4** (and **6**).

Similar chemistry is also observed on addition of various amounts of water to diborane **1** in toluene-d_8 solution at low T (Scheme 1). Predictably, the stoichiometry of these reactions was rather difficult to control, given the low solubility of water in this solvent as well as it is ultimate physical state at low T.

Scheme 2



However, when ca. 1−2 equiv of water was added, the cleavage products **5** and the known borinic acid **7**[23] were formed at the expense of **1**. When larger amounts of water were added, an aquo complex **8** was formed from **5** in much the same manner as observed in the case of MeOH. Compound **8** has been structurally characterized (see Supporting Information) and is analogous in structure to the known compound $(C_6F_5)_3B \cdot (H_2O)_3$.[24] An oxonium acid **9** analogous to **3** was formed in the presence of excess water, but it was exclusively generated only by adding D_2O to solid diborane **1** at room temperature. This compound was characterized spectroscopically but has not been obtained in pure form.

Hydrolysis and Alcoholysis of Diborole 2. Similar chemistry was investigated with diborole **2**; in the case of MeOH, addition of 1 equiv to diborole **2** in either toluene-d_8 or CD_2Cl_2 at low T results in the formation of *exo*-MeOH adduct **10** (Scheme 2). The formation of **10** had been noted earlier in reactions involving ionization of cumyl methyl ether by diborole **2**.[9] In this case, adduct **10** can be generated at −80 °C in sufficient amounts (19%) to allow for its spectroscopic characterization, though its formation was accompanied by some thermal degradation to borinic ester **11** (*vide infra*, ~ 13%). In particular, the *exo* adduct formulation was confirmed by a cross-peak in the two-dimensional $^{19}F-^1H$ correlation spectrum between the methanol proton (dq at δ 6.58) and a ^{19}F resonance at δ −133.5. The same correlation was established by a 1D selective decoupling experiment. Irradiation of this ^{19}F signal reduces the doublet of quartets structure for the methanol proton to a quartet due to H−H coupling only. In toluene-d_8, *exo*-MeOH adduct **10** was also formed, but no ^{19}F coupling to the methanol proton was apparent from the spectra in this more basic solvent.

Coordination of MeOH to the *exo* side is not unexpected for diborole **2**; even unhindered donors such as acetonitrile have a strong preference for *exo* coordination to this compound.[8] In contrast, unhindered donors such as acetonitrile exhibit *endo*-coordination to diborane **1**.

On warming adduct **10**, reaction to form borinic ester **11** is observed; compound **11** was reported earlier,[9] but has now been structurally characterized and the molecular structure appears in Figure 1, while crystallographic and metrical data are reported as Supporting Information. The characteristic structural feature of ester **11** is that the OMe group bridges to both B atoms in

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(21) This compound has been structurally characterized: Donghi, D.; Maggioni, D.; Beringhelli, T.; D'Alfonso, G.; Mercandelli, P.; Sironi, A. *Eur. J. Inorg. Chem.* **2008**, *10*, 1645–1653.

(22) (a) Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 1948–1958. (b) Fărcaşiu, D.; Hâncu, D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2161–2165. (c) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260–1266.

(23) (a) X-ray structure: Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Organometallics* **2003**, *22*, 1588–1590. (b) See also: Metcalfe, R. A.; Kreller, D. I.; Tian, J.; Kim, H.; Taylor, N. J.; Corrigan, J. F.; Collins, S. *Organometallics* **2002**, *21*, 1719–1726. (c) Preparation/characterization: Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1965**, *393*, 3–9.

(24) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Doerrer, L. H.; Cafferkey, S.; Hursthouse, M. B. *Chem. Commun.* **1998**, *22*, 2529–2530.

Table 5. ^{1}H, ^{19}F, and ^{11}B NMR Chemical Shifts and Assignments for Hydrolysis and Methanolysis Products of Diborane 1

compound (solvent)	δ F1	δ F2	δ F3	δ F4	δ $-B(C_6F_5)_2$ (F_o, F_p, F_m)	δ ^{1}H	δ ^{11}B
1 [X = $B(C_6F_5)_2$] (C_6D_6)	−127.6	−141.6			−128.5, −141.6, −161.5		
3 [$(MeOH)_nH$][*o*-$C_6F_4\{B(C_6F_5)_2\}_2(\mu$-OMe)] (*n* = 3, CD_2Cl_2)	−137.4	−163.8			−132.4, −160.2, −166.1	(MeO*H*) 6.19, (-O*Me*) 3.65, (*Me*OH) 3.53	3.8
$(C_6F_5)_2$BOMe **4** (C_6D_6)					−132.7, −148.8, −160.9	(-O*Me*) 3.24	40.3
5 [X = H] (C_6D_6)	−137.7	−141.0	−153.6	−125.4	−129.0, −143.7, −160.0	(aryl-*H*) 6.66	40.3
6 [X = H] (C_6D_6)	−139.5	−155.2	−156.9	−133.6	−133.8, −153.9, −161.9	(aryl-*H*) 6.49, (MeO*H*) 4.70, (*Me*OH) 2.25	4.6
1 (CD_2Cl_2) −62 °C	−125.1	−147.2			−125.9, −140.3, −159.9		
5 (d_8-toluene) −60 °C	−137.7	−139.7	−154.0	−125.4	−128.4, −141.4 −159.1	(aryl-*H*) 6.66	
$(C_6F_5)_2$BOH **7** (d_8-toluene)					−132.8, −147.8, −160.9	(-O*H*) 6.32	42.2
8 [X = H] (d_8-toluene) −60 °C	−139.0	−154.3	−156.2	−133.4	−134.0, −152.7, −161.2	(aryl-*H*) 6.52, (-O*H*) 6.28, (H_2O) 4.52	
[$(H_2O)_nH$][*o*-$C_6F_4\{B(C_6F_5)_2\}_2(\mu$-OH)] (**9**, *n* ∼ 4, CD_2Cl_2)	−138.9	−163.4			−135.0, −160.3, −166.4		−0.4

the solid state and in solution. However, the bridging is asymmetrical as one would expect with bond lengths of O(1)−B(2) = 1.397(3) Å and O(1)−B(1) = 1.640(3) Å, respectively differing by about 17% with the former being typical of a B−O single bond involving trigonal boron. The five-membered, chelate ring is essentially planar with the sum of the dihedral angles ∠B(1)−C(2)−C(7)−B(2) = −5.4(2)° + ∠C(2)−C(7)−B(2)-O(1) = 2.7(2)° + ∠C(7)−B(2)−O(1)-B(1) = 1.0(2)° + ∠B(2)−O(1)−B(1)−C(2) = −3.7(2)° + ∠C(7)−C(2)−B(1)−O(1) = 5.4(2)° = 0.0(2)°. Both B(2) and O(1) have sp^2 hybridization with the sum of the bond angles about each atom being 359.9(2)° and 360.0(2)°, respectively. Though B(1) is approximately tetrahedral, there is significant angle strain in both the borole, as well as five-membered chelate, rings as is evident from C(8)−B(1)−C(19) and C(2)−B(1)−O(1) angles of 99.5(2)° and 96.8(2)°, respectively. Surprisingly, this chelate structure is preserved in the presence of strong monodentate donors such as pyridine, which coordinate to B(2) rather than the more Lewis acidic borole moiety.[25]

An oxonium acid **12**, analogous to **3**, is formed from diborole **2** if at least four equivalents of MeOH are initially present. As suggested in Scheme 2, formation of **12** may involve adduct **10** as an intermediate, where the latter is sufficiently acidic to protonate free MeOH. The monodentate anion that would result could rearrange to the chelated form, provided excess MeOH is present to stabilize the oxonium acid formed.

In the case of hydrolysis, the chemistry is similar. Controlled addition of stoichiometric water at low *T* leads initially to *exo* adduct **14** which degrades in a similar manner at higher *T* to form borinic acid **15**. On prolonged standing at room temperature in toluene-d_8 solution, this compound degrades to the symmetrical anhydride **16** through cleavage of the remaining borole ring; compound **16** has been structurally characterized as its mono-THF adduct (see Supporting Information). In the presence of excess water, oxonium acid **13** is produced and is stable in solution at room temperature. However, when water was removed rapidly *in vacuo* from these solutions, anhydride **16** was isolated (as a bis hydrate). Slow evaporation of water resulted in the crystallization of borinic acid **15**, isolated as heptahydrate **17**.

Compound **17** has been characterized by X-ray crystallography, and its molecular structure is depicted in Figure 2. It has the same basic chelate structure as observed for **11**, though a water molecule is coordinated to B(2), rendering it tetrahedral. In addition, six additional water molecules are present in the lattice (not shown) involved in a network of hydrogen bonds to each other, O(2), O(1), and several F atoms. Since both B atoms are tetrahedral, the bonds to O(1) are significantly longer at O(1)−B(2) and O(1)−B(1) = 1.520(3) and 1.540(3) Å. In fact both B−O bonds are equivalent in length to that of the dative interaction of O(2)−B(2) at 1.527(3) Å. The five-membered, chelate ring is planar, with the sum of the dihedral angles about all five atoms being −0.1(2)°, while O(1) is approximately sp^2 hybridized at least on comparing the B−O−B angle in this structure [116.7(2)°] to that of ester **11** [113.5(2)°]. (The H atom bonded to O(1) was not located and constrained to a calculated position.)

Since oxonium acid **13** is formed and is stable in the presence of excess H_2O, the eventual isolation of **16**·$(H_2O)_2$ or **17** implies that as water is removed through evaporation, the formation of adduct **14** from **13** must be reversible or that cleavage of **13** to form **15** occurs directly as the degree of solvation of the proton in the oxonium acid is diminished.

Relation of Hydrolysis Chemistry to Isobutene Polymerization. Given the complexity of these reactions as well as the nature of the products formed, it is quite conceivable that any of the Lewis or Brønsted acidic byproduct resulting from hydrolysis of diborane **1** or diborole **2** could be involved in initiation of polymerization in aqueous suspension (or hydrocarbon solution, *vide infra*).

While not all of the stable byproducts described previously have been individually tested, several control experiments suggest that they are probably not involved. As already mentioned, stable oxonium acid **3** does not initiate polymerization of isobutene in aqueous suspension, nor does a mixture of this compound, borane **5**, and borinic ester **4** when previously generated by addition of 2−3 equiv of MeOH to diborane **1**. Also, the combination of borinic acid **7** and excess $B(C_6F_5)_3$ is also ineffective for polymerization in aqueous suspension, while the latter compound is also inactive by itself. Finally, though the presence of excess water no doubt moderates the Brønsted acidity of chelated borinic acid **17**, this compound was also ineffective as an initiator of isobutene polymerization in aqueous suspension.

A related question is to what extent do these decomposition reactions intrude during polymerization in aqueous suspension or hydrocarbon solution. This is rather difficult to answer using isobutene itself, but we did investigate the reaction of 1,1-diphenylethylene (DPE) with MeOH in the presence of diborole **2** as a model for protic initiation.[4f,26]

In fact, using conventionally dried CD_2Cl_2, there was sufficient moisture present that DPE (20 μmol) was converted to a 1:1 mixture of DPE (67% conversion) and indan **18**[27] in the

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[25] Sciarone, T. J. J. Parvez, M., unpublished structural results.

[26] (a) Sauvet, G.; Vairon, J. P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1975**, *52*, 173–87. (b) Ioone, T. W.; Lee-Ruff, E.; Khazanie, P. G.; Hopkinson, A. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, *6*, 607–609. (c) Olah, G. A.; Halpern, Y. *J. Org. Chem.* **1971**, *36*, 2354–2356.

[27] Bergmann, E.; Weiss, H. *Just. Lieb. Ann. Chem.* **1930**, *480*, 49–59.

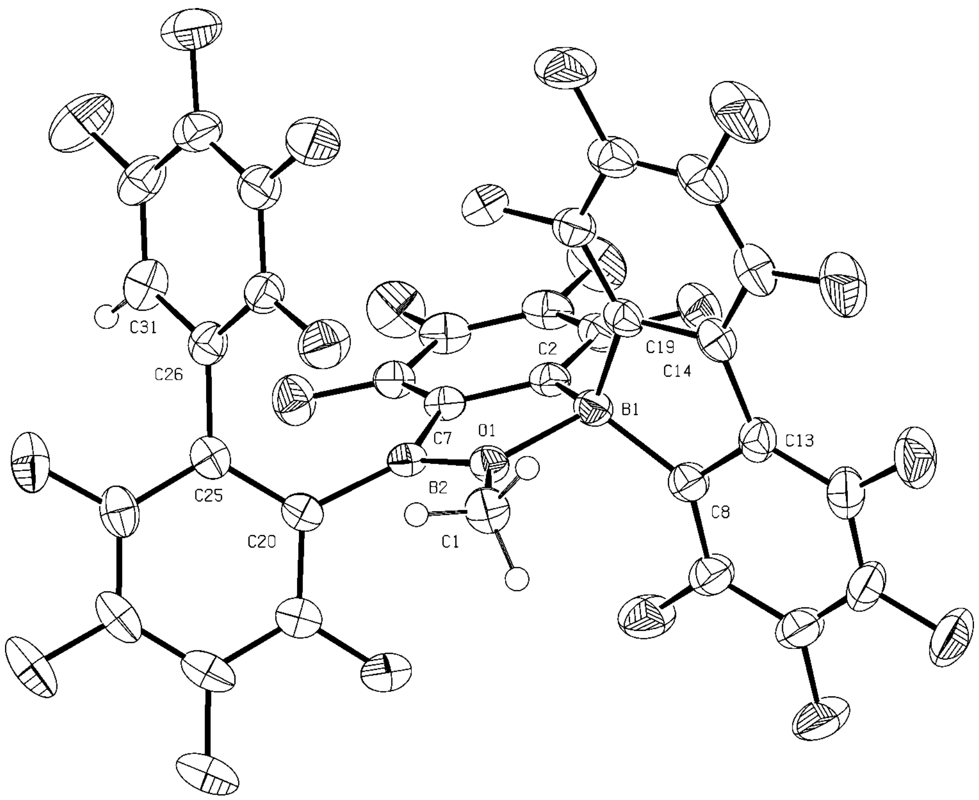
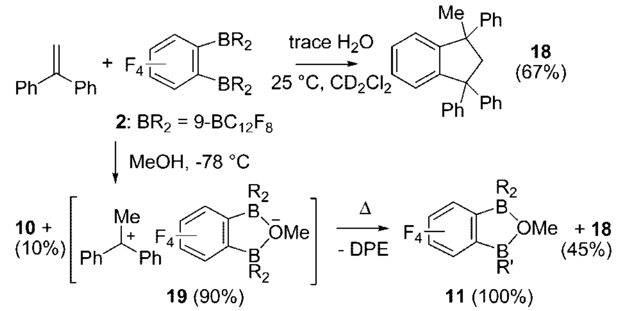


Figure 1. Molecular structure of borinic ester **11** with 50% thermal ellipsoids depicted.

Scheme 3

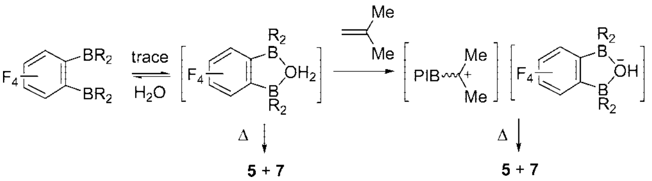


presence of 1 equiv of diborole **2** at room temperature (Scheme 3). Conversion of DPE to **18** may be minimized to ca. 20−30% at room temperature by using CD_2Cl_2 that has been more thoroughly dried and DPE that has been freshly distilled from CaH_2.

Subsequent addition of MeOH (~1.0 equiv with respect to diborole **2**) at −80 °C to this solution led to complete conversion of the remaining DPE to stable ion-pair **19**[28] (ca. 90% conversion of diborole **2**) as well as *exo*-MeOH adduct **10** (ca. 10%). As the temperature was increased, first *exo* adduct **10** (at ca. −40 °C) and then ion-pair **19** (above −20 °C) degraded to form ester **11** and in the latter case indan **18**.

Thus, at low *T* in polar media, protic initiation is reasonably efficient in the case of this model reaction. In particular, competing dimerization of DPE to form the $MeCPh_2CH_2CPh_2$ cation, which is seen in analogous reactions involving CF_3SO_3H or $TiCl_4$,[26a] was not observed. Although DPE is much more basic than isobutene, we are confident that protic initiation in aqueous suspension involves analogous chemistry with diborole **2** or diborane **1** and dissolved water.

This raises the interesting question as to what species is responsible for protonation of isobutene versus degradation via B−C bond cleavage. In our view, monodentate aquo complexes formed from either diborole or certainly diborane are insufficiently acidic for this purpose. For example, $B(C_6F_5)_3$ and compound **5** are both kinetically stronger Lewis acids than diborane **1**, yet neither is effective for protic initiation in aqueous suspension (or hydrocarbon solution). Instead, we believe a μ-aquo complex that is transiently formed from water and diborane **1** is sufficiently acidic to irreversibly protonate isobutene (eq 1). In the absence of a suitable base, degradation to form borane **5** and borinic acid **7** intervenes.



That this structural motif is possible is revealed by the molecular structure for compound **20**, crystals of which were isolated from an attempt to crystallize oxonium acid **12**, evidently from wet MeOH (Figure 3). Compound **20** is a monoaquo adduct of borinic ester **11**, which features the μ-OH_2 interaction invoked above; this compound has defied rational attempts to synthesize it and has only been structurally characterized.

The dative coordination of water to the two B atoms is almost symmetrical with rather long B1−O1 and B2−O1 distances of 1.541(5) and 1.568(5) Å, respectively. Both B atoms are tetrahedral in this structure so that the B1−O2 distance for the MeO moiety is now elongated to 1.523(5) Å compared to that seen in the parent borinic ester **11**. Strain is present within the chelate and borole rings as evident from the B2−O1−B1,

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(28) (a) Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 932–4. (b) Farnum, D. G. *J. Am. Chem. Soc.* **1964**, *86*, 934–5.

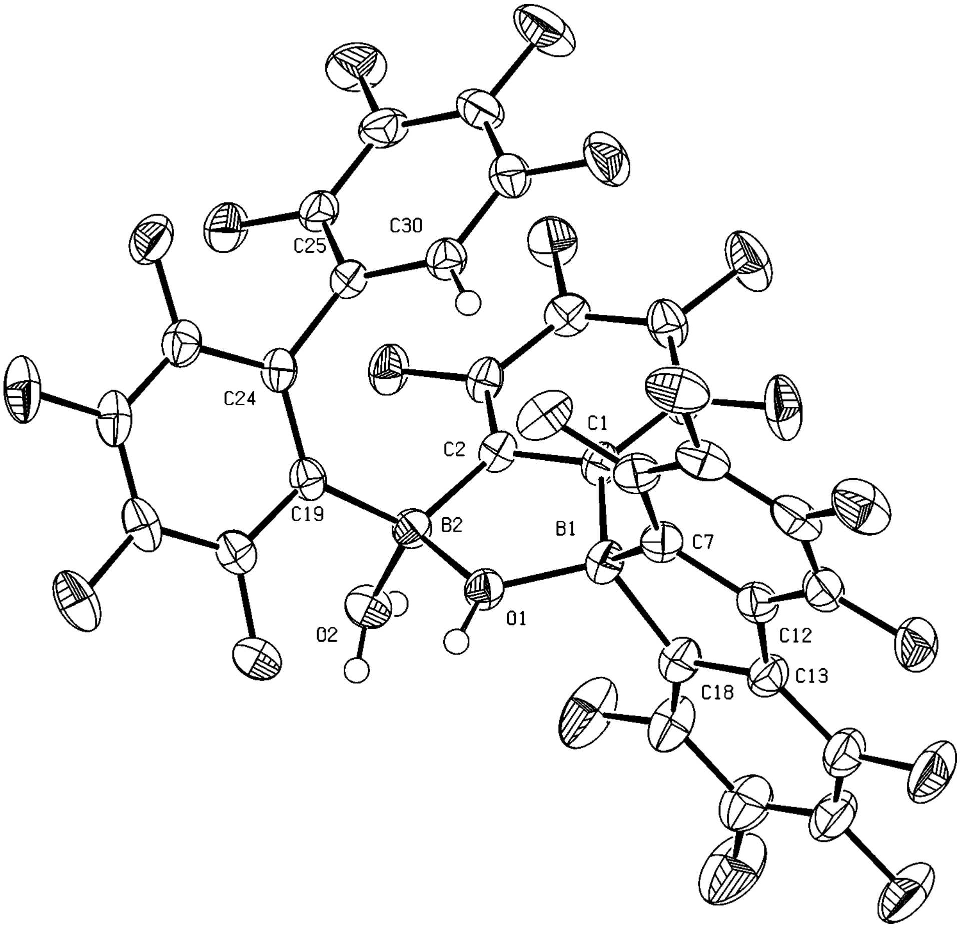

Figure 2. Molecular structure of borinic acid **17** with 50% thermal ellipsoids depicted. Six additional water molecules present in the unit cell are not depicted.

O1−B1−C2, C7−B2−O1, and C20−B2−C31 angles of 116.2(3)°, 98.2(3)°, 97.1(3)°, and 98.5(3)°, respectively. The five-membered chelate ring is puckered, with the sum of the dihedral angles involving B1, O1, B2, C7, and C2 = −5.0(5)°; in essence O1 lies outside the plane defined by the other four atoms by 0.278(2) Å, with the mean deviation from this plane being 0.029(4) Å for B1, B2, C2, and C7.

Polymerization of Isobutene in Hydrocarbon Solution. The aqueous suspension process can be viewed as a series of bulk or solution polymerizations carried out in a dispersed medium, featuring better *T* control and potentially higher conversions due to lower process viscosity. It was therefore of interest to compare our results to polymerizations carried out in solution in the virtual absence of H_2O.

Polymerizations of isobutene undiluted or in hexane solution were conducted on a vacuum line, where both monomer and solvent had been stirred with and then vacuum transferred from tri-*n*-octylaluminum. The total impurity content under these conditions is $<2.5 \times 10^{-5}$ M, as measured by titration using a stock solution of benzophenone ketyl.[18] More recent work has shown that solutions of monomer in CH_2Cl_2 purified in this same manner have residual H_2O contents $\leq 7 \times 10^{-6}$ M, as verified by titration with a solution of $[Ph_3C][B(C_6F_5)_4]$, which serves as a *selective* indicator for H_2O.[29] Undoubtedly, the residual H_2O content in hydrocarbon media is lower than this.

In these polymerizations, toluene solutions of diborane or diborole were added by syringe; these polymerizations were characterized by rapid increases in viscosity, and in the case of neat monomer, it was impossible to avoid "solidification" of the swollen mass. Quantitative conversions of monomer were obtained in hydrocarbon solution except where very low levels of initiator (2 μM) were used. The results obtained are summarized in Table 6.

Essentially, polymerization ceases below ca. 2 μM of compound **1** (entry 7). This is probably an indication that background H_2O levels are between 2 and 20 μM under these conditions. On the other hand, with [**1**] = 2.0 mM, stopping experiments revealed that *at least* 15 mM DtBMP was needed to prevent protic initiation under these conditions (see Experimental Section). Since DtBMP does not react directly with dissolved water, it is clear that the Brønsted acid formed from water and diborane **1** must be *kinetically* competent to protonate isobutene (2.76 M) even when [DtBMP] = 2.0 mM! We are unaware of any precedent for this behavior using classical Lewis acids: we suspect it arises due to the hindered nature of the (strong) Brønsted acid formed in this case.

The first seven entries of Table 6 demonstrate the use of progressively lower amounts of diborane initiator. Entries 3−7 were conducted at the same time using the same stock solution. It can be seen that MW increases significantly as the amount of diborane added is reduced. We suspect this feature arises from better *T* control on dilution of this compound. Entries 8−11 demonstrate that much lower MW polymer is formed in undiluted monomer, a feature that we attribute, in part, to poor *T* and mass transfer control. The conversions in entries 10 and

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(29) Slomkowski, S.; Penczek, S. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1718–1722, and references therein.

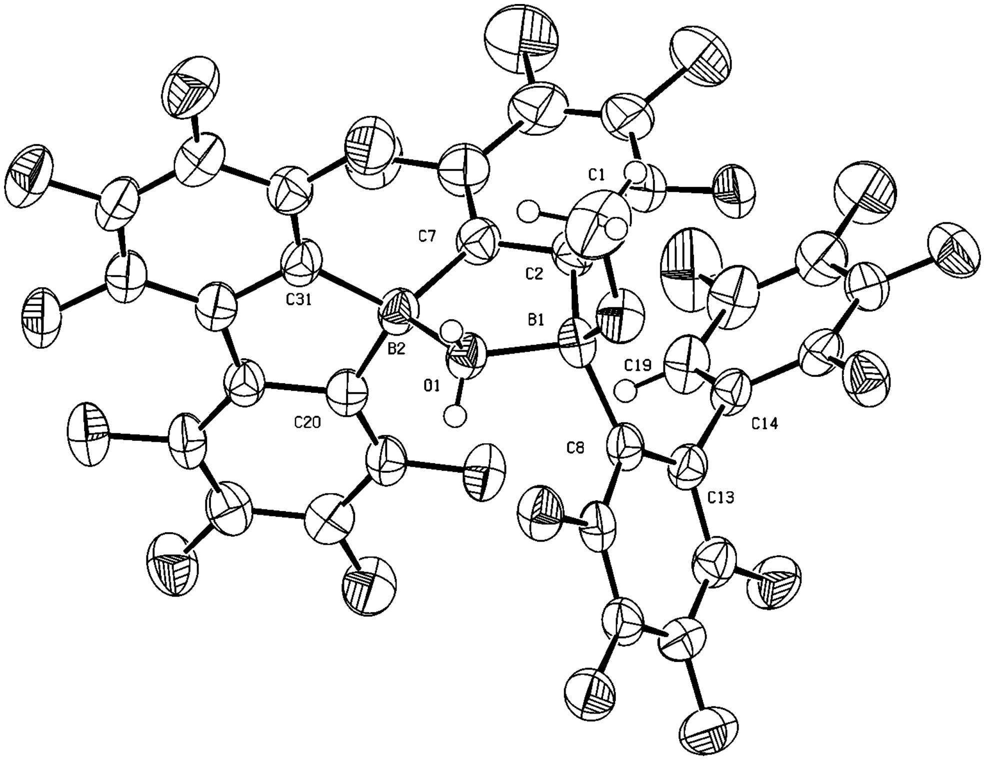

Figure 3. Molecular structure of compound **20** with 50% thermal ellipsoids depicted. Disordered MeOH and CH_2Cl_2 molecules present in the unit cell are not depicted.

11 are not quantitative, suggesting moisture levels may well have been higher in these two experiments.

The final two entries in this table reveal that significantly lower MW polymer is produced using the diborole initiator (compare entries 19/20 vs 3/4). In addition, the MWD of the derived polymers were considerably narrower than those formed using the diborane. Since polymerizations conducted using this initiator were significantly less exothermic than those using the diborane, we have to attribute these differences as being characteristic of this diborole. Similar behavior has also been noted in polymerizations featuring cationogenic initiation.[9]

Note that the behavior of the diborole initiator in hydrocarbon solution is opposite that observed in aqueous suspension; we suggest this is because physical factors (rate of addition, degree of dispersion, nature of the aqueous medium, etc.) limit MW in aqueous suspension rather than, for example, intrinsic factors such as the nature of the counteranion, etc.

The T dependence of MW in hydrocarbon solution was studied over the range −90 to −20 °C. These data appear in Table 6 and are plotted in Figure 4 along with the data obtained in aqueous suspension (Table 3) in the form of Arrhenius plots. Surprisingly, almost identical behavior is seen here as in aqueous suspension!

In hydrocarbon solution, polymer MW is virtually independent of T between −60 and −90 °C, suffering a pronounced decrease at higher T. The limiting slope of this curve at higher T corresponds to an activation energy for MW (ΔE_{MW}) of −5.2 kcal mol^{-1}. This corresponds to a ΔE_{MW} value often attributed to chain transfer to monomer, although it must be admitted that the literature value $\Delta E_{\mathrm{MW}} = -5.9$ kcal mol^{-1} relates to experiments conducted in more polar media.[4i−k]

Although the high MW of the PIB samples formed under anhydrous conditions precluded convenient spectroscopic determination of end-groups, the lower MW materials formed in aqueous suspension could be analyzed by ^{1}H NMR spectroscopy. Although not all samples were analyzed in this fashion, those that were exhibited both *exo*- and *endo*-terminal unsaturation (ca. 60:40 ratio) consistent with chain transfer to monomer. However, these samples were formed at temperatures well below (i.e., −60 to −80 °C) where one would expect this chain transfer process to dominate based on the Arrhenius plots depicted in Figure 4.

The shallow T dependence of MW observed at even lower T has been observed before using conventional Lewis acids in polar media and has been interpreted as arising from a change in MW controlling events.[30] The nature of the process responsible for this "cross-over" behavior is not well understood and has been attributed to, for example, termination to counteranion and polymer precipitation. However, this cannot be the case here; all of these polymerizations are quantitative and characterized by highly efficient chain transfer based on dissolved [H_2O] or even diborane ($I_{\mathrm{eff}} > 1000\%$).

Another explanation, again in polar media ($\epsilon \gg 4$), is that primarily unpaired cations propagate at low T, while ion-pairs dominate the kinetics at higher T so that the T dependence of MW should show a "kink" because of the T dependence of the equilibrium constant governing the concentration of these two species. This theory predicts that polymerizations in apolar media such as hexane ($\epsilon = 2.2$) should not show this phenomenon as the kinetics are dominated by ion-pairs at all accessible temperatures.[31]

Recent work from the group of Bochmann has highlighted the role of dissolved or molecular H_2O in isobutene homo/copolymerizations featuring weakly coordinating (and hydrolytically resistant) counteranions.[4f] Although they did not analyze their MW data in this fashion, a Mayo plot of X_n^{-1} vs [H_2O]/[IB] is linear with a slope corresponding to the transfer (or termination) constant for H_2O, $C_{H_2O} = 126.2$ at −35 °C (see Supporting Information).

In other words, transfer to dissolved H_2O would be 100 times faster than propagation at equivalent concentrations of H_2O and monomer at this T. It should be noted that this result could have

Table 6. Isobutene Polymerization in Hydrocarbon Solution[a]

entry	initiator (mM)	T (°C)	M_w (kg mol^{-1})	PDI	yield (%)
1	**1** (2.0)	−80	340	2.38	100
2	**1** (2.0)	−80	227	3.18	100
3	**1** (0.2)	−80	159	5.68	100
4	**1** (0.2)	−80	170	3.82	100
5	**1** (0.02)	−80	316	1.99	97
6	**1** (0.02)	−80	294	2.03	100
7	**1** (0.002)	−80	518	1.90	3
8	**1** (0.2)[b]	−80	69.0	3.16	100
9	**1** (0.2)[b]	−80	41.3	2.49	100
10	**1** (0.02)[b]	−80	98.6	4.34	31
11	**1** (0.02)[b]	−80	59.4	3.47	39
12	**1** (2.0)	−90	185	2.45	100
13	**1** (2.0)	−90	269	3.24	100
14	**1** (2.0)	−64	194	2.87	100
15	**1** (2.0)	−40	94.8	2.25	100
16	**1** (2.0)	−40	86.4	3.75	100
17	**1** (2.0)	−20	37.0	2.27	100
18	**1** (2.0)	−20	32.3	2.39	100
19	**2** (0.2)	−80	88.6	2.09	100
20	**2** (0.2)	−80	139	2.14	100

[a] The diborane initiator dissolved in 1.0 mL in toluene was added to a magnetically stirred solution of isobutene (2.76 M in hexane) unless otherwise noted. [b] A stock solution of diborane in toluene (1.0 mL) was added to 12.0 mL of isobutene at −80 °C.

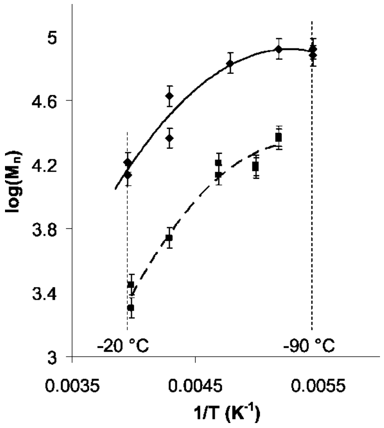

Figure 4. Temperature dependence of MW in hydrocarbon solution (solid curve) and aqueous HBF_4 suspension (dashed curved) initiated by diborane **1**.

been anticipated from the early work of Williams and other workers who studied γ-ray-initiated polymerizations of isobutene;[32] scrupulous purification of monomer and (hydrocarbon) solvent are required where the rate constant for "termination to polar impurities" exceeds that of propagation by a similar magnitude.[5a]

Recent kinetic work has indicated that propagation in isobutene polymerization occurs via ion-pairs with a specific rate constant of ca. 10^8 M^{-1} s^{-1}, which is largely independent of T.[33] With this information, and under the assumption that C_{H2O} is also independent of T (i.e., both processes are characterized by a nonzero activation entropy and a very low activation enthalpy), it is possible to simulate the effect of dissolved [H_2O] on MW as a function of T if this process and chain transfer to monomer are the only ones involved (see Supporting Information).

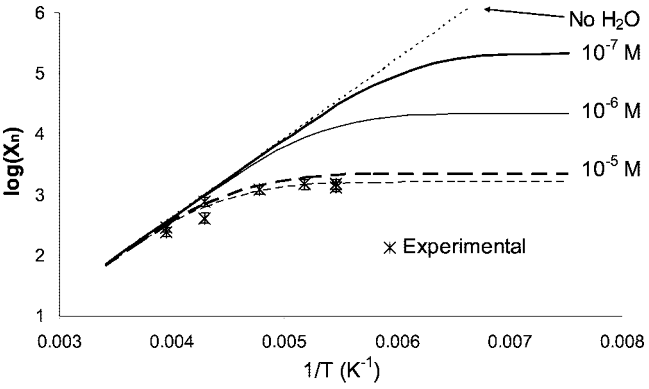

Figure 5. Simulated temperature dependence of MW in hydrocarbon solution initiated by diborane **1** assuming various dissolved [H_2O]. See Supporting Information for assumptions and data.

This analysis is shown in Figure 5, where it is clear that the observed data can be accommodated by a background [H_2O] of about 10^{-5} M. The agreement with the value estimated by titration with benzophenone ketyl is fortuitous since the T dependence of some of these processes is unknown. However, these diboranes do not react as readily with H_2O (in comparison to conventional Lewis acids), so one can envisage that H_2O will act as a potent chain transfer agent.

If so, it is clear that the lower molecular weights seen in aqueous suspension are almost entirely due to the higher levels of dissolved H_2O that are inevitably present. [Some experiments that involved addition of diborole solution (changes from yellow to colorless when "wet") to an aqueous suspension of hexane (5.0 mL) and toluene (10.0 mL) at various rates revealed that the (mutual) rate of diffusion of H_2O into the droplet at −78 °C in fluoroboric acid was $<10^{-4}$ mmol s^{-1}, while background levels of H_2O in the droplet were between 10^{-4} and 10^{-5} M.] Evidently, at least under some conditions at low enough T, there is not enough H_2O present to prematurely terminate chains given the high conversions seen, but many of the other effects can be interpreted in terms of differential lowering of H_2O content as a function of diborane structure (i.e., susceptibility to *degradation* by water) and/or mode and rate of addition.

Conclusions

The work summarized here provides considerable insight into the nature of the initiation, propagation, and chain transfer processes involving aqueous suspension polymerization of isobutene using chelating diboranes **1** and **2**. In addition, experiments in hydrocarbon solution, which serve as a model for the suspension process, highlight the probable role of dissolved water as a potent chain transfer agent in polymerizations involving hydrolytically resistant Lewis acids that give rise to weakly coordinating counteranions. It is evident that chain transfer to water will limit MW in aqueous suspension and to the point where it will prove very challenging to develop an aqueous suspension process for the synthesis of high MW PIB

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or copolymers thereof. In particular, on the basis of the behavior of these diboranes in nearly anhydrous hexane solution, it is clear that the required levels of background moisture in the monomer droplets would have to be in the ppm range.

Experimental Section

Part I. All of the synthetic or NMR scale reactions involving diborane **1** or diborole **2** and various reactants (i.e., MeOH, H_2O, or DPE) were performed at the University of Calgary. Details of these experiments are provided as Part II of the Experimental Section.

All polymerization experiments were conducted at the University of Akron, as were control polymerization experiments involving the hydrolysis products of diborane **1** or diborole **2**. The syntheses of diborane **1** and diborole **2** for use in all polymerization experiments were conducted at the University of Akron according to literature procedures[6c,8] or modifications thereof.[18] Borinic acid **7** was prepared by controlled hydrolysis of $B(C_6F_5)_3$ as described in the literature.[34]

All solvents and reagents were purchased from commercial sources and purified as required. Hexane and toluene used in polymerization experiments were predried by passage through columns of A2 alumina and Q5 deoxo catalyst under N_2[35] or distilled from Na metal and benzophenone under N_2. Dichloromethane was dried and distilled from P_2O_5 under N_2. Further purification of dichloromethane or hexane was achieved by stirring with tri-*n*-octylaluminum under N_2 followed by vacuum transfer just prior to polymerization as explained below. Stock solutions of diborane **1** and diborole **2** were prepared in anhydrous toluene or hexane and stored in an Innovative Technologies glovebox at −30 °C prior to use.

Isobutene was grade 2.0 (99.0%) provided by Praxair and was purified by passage through a column of BASF R3-11 deoxo catalyst and activated molecular sieves 4 Å; initial exposure of the latter to isobutene must be accomplished slowly, and with cooling of the column if needed, to avoid significant exotherm and resulting cracking of isobutene. Isobutene was further purified by vacuum transfer from tri-*n*-octylaluminum just prior to polymerization as explained below.

Routine NMR spectra were recorded on Varian Mercury 300 and Inova 400 MHz instruments. ^1H and ^{19}F NMR spectra are referenced to residual protonated solvent and 2,3,5,6-tetrafluoroxylene (δ −145.7 vs $CFCl_3$), respectively. GPC analyses were performed by a technician affiliated with the Institute of Polymer Science and using a Waters GPC system equipped with a set of five, linear Styragel columns, eluting with THF at 1.002 mL/min at 35 °C. Polymer was detected using a Waters differential refractive index, Viscotek 110 differential viscometer, and Wyatt Technology Dawn EOS, 18-angle light scattering detectors. Data were analyzed using the Astra 4.0 software provided by Wyatt Technology using a dn/dc value for poly(isobutene) of 0.108 mL g^{-1}[36] and assuming 100% mass recovery. This procedure was found to be reliable, and the results were periodically checked through blind analyses of poly(isobutene) standards provided by American Polymer Standards Corp.

Polymerization of Isobutene in Aqueous Suspension. Two different procedures were employed, each involving the addition of a toluene stock solution of diborane **1** and diborole **2** to isobutene monomer, either neat or diluted with hexane:

Procedure A: Uncontrolled Addition of Diborane.[18] A three-neck, 100 mL round-bottom flask, with a central 24/40 and two 14/20 side necks, was charged with 20 mL of LiCl/NaCl/H_2O stock and 0.100 g of surfactant if used. The flask was then fitted with a 14/20 septum, 14/20 gas-inlet adapter, and 24/40 outer/inner air-free adapter with in-line PTFE stopcock, after which it was affixed to a vacuum line. The contents of the flask were then subjected to a single freeze−pump−thaw cycle, and then 18.0 mL of isobutene was vacuum transferred into the flask. The flask was then warmed to −60 °C (through use of a $CHCl_3$/dry ice bath) and sealed under N_2. The flask was then connected to a double manifold and placed back under N_2, after which the 24/40 outer/inner air-free adapter was replaced with a stir bearing/shaft/blade assembly. The flask contents were then stirred under N_2 at −60 °C at about 500 rpm. Next, 1.0 mL of diborane or diborole stock (1.19×10^{-5} mol) was then added rapidly by syringe (**Caution:** can be violently exothermic), after which the reactor contents turned milky white in color. Polymerization was allowed to continue for a full hour before warming the reactor contents to room temperature by diluting the flask with additional water and CH_2Cl_2. During this period very little gas evolution occurred. The organic phase was then extracted with CH_2Cl_2 and dried over $MgSO_4$ before isolating polymer by removal of volatiles under reduced pressure. Yield: 6.10 g (48% conversion).

Procedure B: Controlled Addition of Diborane. A three-neck, 100 mL round-bottom flask, calibrated with a mark corresponding to 10.0 mL and equipped with a central 24/40 and two 14/20 side necks, was fitted with a 14/20 stopper, a 14/20 gas-inlet adapter, and a 24/40 outer/inner air-free adapter with in-line PTFE stopcock, after which it was connected to a vacuum line. Then, 10.0 mL of isobutene was condensed into the flask, and the flask and adapter were removed from the vacuum line. The flask was then connected to a double manifold, after which the 24/40 outer/inner air-free adapter was replaced with a stir bearing/shaft/blade assembly and the remaining 14/20 neck fitted with a septum under a flow of N_2. The flask was then maintained at −78 °C (through use of a acetone/dry ice bath) and kept under slight positive N_2 pressure. The flask contents were then stirred under N_2 at −78 °C at 500 ± 10 rpm, while 5.0 mL of hexane and 15.0 mL of aqueous HBF_4 were added sequentially via syringe. Next, 1.0 mL of diborane or diborole stock (1.19×10^{-5} mol) was then added over periods varying between 30 s and 10 min using a syringe pump at a controlled rate. Polymerization was allowed to continue for a full hour before quenching with 2-propanol and warming the contents to room temperature. The organic phase was diluted with hexane and transferred to a separatory funnel. The aqueous phase was withdrawn, and the organic phase washed with water and then dried over $MgSO_4$. The mixture was filtered, washing with additional hexane before isolating polymer by removal of volatiles *in vacuo* using a rotary evaporator until constant weight was obtained. Samples were transferred to vials and dried overnight in a vacuum oven at 90 °C and 30 in. Hg prior to GPC analysis.

Procedure C: Polymerization of Isobutene in Hexane Solution. A dry 250 mL round-bottom 24/40 single-neck flask was charged with 11.9 g (18 mL) of hexane, 0.82 g (1 mL) of tri-*n*-octylaluminum, and a magnetic stir bar inside a glovebox. This was then sealed with an air-free style adapter equipped with an in-line PTFE vacuum stopcock and the apparatus connected to a vacuum line. The mixture of solvent and drying agent was then degassed by application of three sequential freeze−pump−thaw cycles and subsequently charged with 5.50 mL of isobutene via vacuum transfer. Next, a dry 100 mL, two-neck, round-bottom flask previously silanized with Me_2SiCl_2 and containing a magnetic stir bar and glass stopper was connected to the vacuum line, and the entire assembly was flame-dried under vacuum, refilled with N_2, and then fitted with a septum. The solvent/monomer/drying agent mixture was then stirred at −78 °C for 30 min before vacuum

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Table 7

entry	DtBMP (mM)	M_w (10^3 kg mol^{-1})	PDI	yield (%)
1	20			0
2	20			0
3	15	605	2.3	0.5_0
4	15	753	4.9	0.4_7
5	5	552	3.6	1.4_4
6	5	370	4.2	0.9_8
7	2	287	2.2	6.8_2
8	2	293	2.1	6.0_2
9	2	302	2.5	5.7_6
10		195	3.2	100
11		285	2.4	100

transferring volatile material to the 100 mL flask. The contents of the 100 mL flask were then warmed to −78 °C and stirred for 15 min under a blanket of N_2 prior to injection of 750, 75, or 7.5 μL of a 0.065 M solution of diborane **1** in toluene.

A rapid increase in viscosity occurred immediately upon addition, particularly at higher concentrations of diborane (**Caution:** strongly exothermic), and stirring often ceased entirely while the reaction was allowed to proceed for 1 h at −78 °C under a blanket of nitrogen. The viscous solution was diluted with hexane and washed with a mixture of water and MeOH. The resultant polymer solutions were dried over Na_2SO_4, filtered, and concentrated to dryness *in vacuo*. Polymer samples were dried in a vacuum oven at 30 in. Hg at 90 °C for 24 h prior to analysis.

Stopping Experiments with 2,6-Di-*tert*-butyl-4-methylpyridine (DtBMP). Stopping experiments using DtBMP were conducted in the same fashion as in Procedure C but involved the addition of 1.00, 0.75, 0.50, 0.25, or 0.10 mL of a stock solution of DtBMP (0.5 M in hexane) prior to the addition of diborane **1** (0.065 M in toluene, final concentration = 2.0 mM). Polymerization was allowed to proceed for 1 h at −78 °C before quenching with 1 mL of methanol. All volatiles were removed and the residue washed with methanol prior to being taken up in hexanes. The resultant polymer solutions were filtered, concentrated *in vacuo*, and dried in a vacuum oven at 30 in. Hg at 90 °C for 24 h prior to analysis by GPC. The results are summarized in Table 7.

Impurity Levels in Hydrocarbon Solution. A stock solution of sodium benzophenone ketyl in xylenes/tetraglyme was prepared as follows: A mixture of xylenes (100 mL) and tetraglyme (20 mL) was stirred over molten Na metal under N_2 in a glovebox for several hours. The mixture was cooled, filtered, and stirred over fresh Na metal, and this process was repeated, until the molten Na was shiny and no further decomposition of tetraglyme (which produces a dark brown residue) was noted. Benzophenone was then gradually added to the cooled suspension until the deep blue purple color of the ketyl persisted, and the entire mixture, containing excess Na metal, was stored in a Schlenk storage flask with integral stopcock in a glovebox. Aliquots were removed by syringe and added, outside the glovebox, to an known excess of degassed, standardized aqueous HCl. The excess acid was titrated to a phenolphthalein end-point using a standard aqueous NaOH solution. Stock solutions prepared in this manner maintain their titer for many months provided excess Na is present; a typical concentration is 0.02 M.

A solution of IB and hexane, prepared and purified as described in Procedure C, was warmed to room temperature under N_2 until most of the IB had evaporated. The remaining solution was titrated to a persistent, pale blue end-point using the stock ketyl solution. A typical result was $2.5 \pm 0.3 \times 10^{-5}$ M based on a stoichiometry of 2 mol of ketyl consuming 1 mol of water and the original volume of the hexane/IB solution.

Control Experiments in Aqueous Suspension or Hydrocarbon Solution.

Attempted Polymerization Using Borinic Acid 7 and $B(C_6F_5)_3$. Procedure B was followed using 15.0 mL of undiluted isobutene and 15.0 mL of aqueous HBF_4 at −78 °C. One milliliter of a toluene stock solution containing borinic acid **7** (0.01 M) and $B(C_6F_5)_3$ (0.01 M) was added over 1 min at −78 °C. No exotherm or change in appearance of the mixture was noted. After 1 h the mixture was quenched with 2-propanol and warmed to room temperature; vigorous gas evolution was observed to occur during this process. Extraction of the aqueous phase with hexane did not provide any polymeric material.

Attempted Polymerization Using $B(C_6F_5)_3$. Procedure C was followed using 5.50 mL of isobutene and 18.0 mL of hexane at −78 °C. One milliliter of a toluene stock solution of $B(C_6F_5)_3$ (0.02 M) was added rapidly at −78 °C. No exotherm or change in appearance of the mixture was noted. After 1 h the mixture was quenched with 2-propanol and warmed to room temperature; vigorous gas evolution was observed to occur during this process. Evaporation of the hexane did not provide any polymeric material.

Attempted Polymerization Using Borinic Acid 17. Procedure B was followed using 10.0 mL of isobutene, diluted with 5.0 mL of hexane and 15.0 mL of aqueous HBF_4 at −78 °C. One milliliter of a dichloromethane stock solution containing borinic acid **17** (0.01 M) was added over 1 min at −78 °C. No exotherm or change in appearance of the mixture was noted. After 1 h the mixture was quenched with 2-propanol and warmed to room temperature; vigorous gas evolution was observed to occur during this process. Extraction of the aqueous phase with hexane did not provide any polymeric material.

Attempted Polymerization Using a Mixture Borinic Ester 5 and Borane 4. Procedure C was followed using 5.50 mL of isobutene diluted with 18.0 mL of hexane. A solution of diborane **1** (84 mg) in toluene (10 mL) was treated with ~2.0 equiv of MeOH (1.0 μL) at −78 °C. The solution was warmed to room temperature; a ^{19}F NMR spectrum of this mixture revealed complete conversion of diborane **1** to a mixture of borinic ester **5**, borane **4**, and its MeOH adduct **6**. To the mixture of isobutene and hexane at −78 °C was added 2.0 mL of this solution via syringe so as to give a final concentration of about 2 mM expressed as diborane **1**. No exotherm or change in appearance of the mixture was noted. After 1 h the mixture was quenched with 2-propanol and warmed to room temperature; vigorous gas evolution was observed to occur during this process. Evaporation of the hexane did not provide any polymeric material.

Part II. An Innovative Technologies or Vacuum Atmospheres argon-filled glovebox was used for the storage and manipulation of oxygen- and moisture-sensitive compounds. Thermally unstable compounds were stored in a −35 °C freezer installed on the respective glovebox. All reactions were performed on a double manifold, high-vacuum line using modified Schlenck techniques.[37] Residual oxygen and moisture were removed from Ar by passage through an Oxisorb-W scrubber from Matheson Gas Products. Commonly utilized specialty glassware included a swivel frit assembly, thick-walled (5 mm) Carius tubes, and round-bottom flasks with in-line adaptors all equipped with Teflon stopcocks. All glassware was stored in a 110 °C oven for a minimum of 12 h before immediate transfer into the glovebox antechamber or assembled on the vacuum line and evacuated while hot. Unless otherwise noted, the introduction of solvent in all manipulations was via vacuum transfer with condensation at −78 °C. Liquid nitrogen (−196 °C), dry ice/acetone (−78 °C), dry ice/acetonitrile (−45 °C), and water/ice (0 °C) baths were used for cooling receiving flasks and to maintain low-temperature conditions.

Solvents were purchased from Aldrich or Cambridge Isotopes and dried and deoxygenated before use by the following procedures. Toluene, hexanes, and tetrahydrofuran (THF) solvents were dried and purified using the Grubbs/Dow purification system[35] and stored

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in evacuated 500 mL thick-walled flasks over titanocene[38] (toluene and hexanes) or sodium/benzophenone ketyl (THF). Benzene, d_6-benzene, and d_8-toluene, were dried and stored over sodium/benzophenone ketyl in thick-walled Schlenk tubes under vacuum. Diethyl ether and methylene chloride were predried over $LiAlH_4$ and CaH_2, respectively, and subsequently stored over sodium/benzophenone ketyl and CaH_2, respectively. Methylene chloride-d_2 was predried over 4Å molecular sieves and stored over CaH_2. All of these solvents and reagents were distilled directly into reaction vessels or separate predried Schlenk storage vessels prior to use. Chloroform, chloroform-d, and D_2O were used as received.

Routine NMR spectra were recorded on a Bruker AC-200 MHz, AMX-300 MHz (^{19}F −282.4 MHz), Bruker AC-300 MHz, or Avance DRX-400 [equipped with a gradient $^1H/^{13}C$ probe] spectrometer. All 2D NMR experiments [$^{19}F,^{19}F$-COSY, $^{19}F,^{19}F$-NOESY, $^1H,^{13}C$-HMQC, $^1H,^1H$-NOESY, $^1H,^{19}F$-COSY, or NOESY] were performed using a Bruker Avance AMX-300 MHz or DRX-400 MHz spectrometer. All ^1H NMR spectra were referenced to $SiMe_4$ through the residual ^1H resonance(s) of the solvent: C_6D_6 ($\delta = 7.15$ ppm), d_8-toluene ($\delta = 2.09$, 6.98, 7.02, and 7.09 ppm), d_8-THF ($\delta = 1.73$ and 3.58 ppm), or CD_2Cl_2 ($\delta = 5.32$ ppm). $^{13}C\{^1H\}$ NMR spectra are also referenced relative to $SiMe_4$ through the resonance(s) of the deuterated solvent: C_6D_6 ($\delta = 128.0$ ppm), d_8-toluene ($\delta = 20.4$, 125.2, 128.0, 128.9, and 137.5 ppm), d_8-THF ($\delta = 25.4$ and 67.6 ppm), or CD_2Cl_2 ($\delta = 54.0$ ppm). ^{19}F NMR spectra were referenced externally to C_6F_6: $\delta = -163.0$. Temperature calibration for NMR experiments was achieved by monitoring the ^1H NMR spectrum of pure methanol.[39] For all air- and/or moisture-sensitive compounds and reactions, NMR samples were prepared in the glovebox and the NMR tubes were capped with rubber septa. Unless otherwise stated, all spectroscopic data are reported at room temperature (298 K).

Elemental analyses were performed on a Control Equipment Corporation 440 elemental analyzer by Mrs. Dorothy Fox, Mrs. Roxanna Smith, or Mrs. Olivera Blagojevic at the University of Calgary.

Spectroscopic Studies of the Addition of MeOH to C_6F_4-1,2-$[B(C_6F_5)_2]_2$. In a glovebox, C_6F_4-1,2-$[B(C_6F_5)_2]_2$, **1** (10 mg, 0.012 mmol), was loaded into a 5 mm NMR tube and dissolved in d_8-toluene (0.4 mL) or CD_2Cl_2 (0.4 mL). The sample was capped with a rubber septum, removed from the glovebox, and cooled to −78 °C in a dry ice/acetone bath. Varying equivalents (0.5−10.0 equiv) of dry and degassed methanol (0.72 M in d_8-toluene or CD_2Cl_2) were injected into the NMR tube via gastight syringe at low temperature. The NMR tube was placed in a spectrometer, cooled to −60 °C, and the reaction was monitored up to room temperature. A complete listing of spectral data at various T and stoichiometries is provided as Supporting Information.

(C_6F_4-1,2-$[B(C_6F_5)_2]_2$ + 8.0 MeOH) + 3 C_6F_4-1,2-$[B(C_6F_5)_2]_2$. A solution of **3** was prepared by the addition of MeOH (35 μL, 1.36 mM in d_8-toluene) via gastight syringe to a capped 5 mm NMR tube charged with C_6F_4-1,2-$[B(C_6F_5)_2]_2$, **1** (5 mg, 0.006 mmol), dissolved in d_8-toluene (0.2 mL) at room temperature. To this solution was added an additional 3 equiv of C_6F_4-1,2-$[B(C_6F_5)_2]_2$, **1** (15 mg, 0.018 mmol), dissolved in d_8-toluene (0.3 mL). ^1H NMR (d_8-toluene, 298 K): δ 6.58 (m, 1H, $-C_6F_4H$), 3.65 (s, ~0.3H, μ-O*Me*), 3.37 (br s, 2H, $(C_6F_5)_2BOMe$), 2.55 (br s, 4H, *Me*OH). ^{19}F NMR (d_8-toluene, 298 K): 6% **3**, δ −131.7 (8F, *o*-$B(C_6F_5)_2$), −136.5 (2F, -C_6F_4), −158.4 (4F, *p*-$B(C_6F_5)_2$), −164.2 (2F, $-C_6F_4$), −164.8 (8F, *m*-$B(C_6F_5)_2$); 47% **6**, δ −133.4 (4F, *o*-$B(C_6F_5)_2$(MeOH)), −133.5 (1F,-C_6F_4(MeOH)), −139.6 (1F, $-C_6F_4$(MeOH)), −154.5 (2F, *p*-$B(C_6F_5)_2$(MeOH)), −155.6 (1F, $-C_6F_4$(MeOH)), −156.8 (2F, $-C_6F_4$(MeOH)), −161.9 (4F, *m*-$B(C_6F_5)_2$(MeOH)); 47% **4**, δ −132.3 (4F, *o*-$B(C_6F_5)_2$), 148.5 (2F, *p*-$B(C_6F_5)_2$), 160.6 (4F, *m*-$B(C_6F_5)_2$).

Spectroscopic Studies of the Addition of H_2O to C_6F_4-1,2-$[B(C_6F_5)_2]_2$. In a glovebox solid C_6F_4-1,2-$[B(C_6F_5)_2]_2$, **1** was loaded into a 5 mm NMR tube and dissolved in d_8-toluene (0.4 mL). The sample was capped with a rubber septum, removed from the glovebox and cooled to −78 °C in a dry ice/acetone bath. Varying equivalents of degassed water (0.5 − 8.0 equiv. or a large excess) were injected into the NMR tube via gastight syringe at low temperature. The NMR tube was placed in a spectrometer, cooled to −60 °C and the reaction was monitored up to room temperature. A complete listing of spectral data is provided as Supporting Information.

Spectroscopic Studies of the Addition of MeOH to C_6F_4-1,2-$[B(C_{12}F_8)]_2$. In a glovebox solid C_6F_4-1,2-$[B(C_{12}F_8)]_2$, **2**, was loaded into a 5 mm NMR tube and dissolved in d_8-toluene (0.4 mL). The sample was capped with a rubber septum, removed from the glovebox, and cooled to −78 °C in a dry ice/acetone bath. Varying equivalents of dry and degassed methanol (0.713 M in d_8-toluene) were injected into the NMR tube via gastight syringe at low temperature. The NMR tube was placed in a spectrometer cooled to −60 °C, and the reaction was monitored up to room temperature. A complete listing of spectral data is provided as Supporting Information.

Spectroscopic Studies of the Addition of H_2O to C_6F_4-1,2-$[B(C_{12}F_8)]_2$. In a glovebox solid C_6F_4-1,2-$[B(C_{12}F_8)]_2$, **2**, was loaded into a 5 mm NMR tube and dissolved in d_8-toluene (0.4 mL). The sample was capped with a rubber septum, removed from the glovebox, and cooled to −78 °C in a dry ice/acetone bath. Varying equivalents of water were injected into the NMR tube via gastight syringe at low temperature. The NMR tube was placed in a spectrometer cooled to −60 °C, and the reaction was monitored up to room temperature. A complete listing of spectral data is provided as Supporting Information.

Generation of MeOH Adduct 10. Diborole **2** (15 mg, 20 μmol) was dissolved in CD_2Cl_2 (0.5 mL). The solution was placed in an NMR tube, which was sealed with a rubber septum, and the tube was cooled to −78 °C. A stock solution of MeOH (0.394 M in CD_2Cl_2, 50 μL, 20 μmol) was injected through the septum. The tube was briefly shaken and subsequently introduced in the precooled (−80 °C) NMR probe. Spectra (^1H, ^{19}F) were recorded from −80 to 0 °C with 10 deg intervals

NMR spectroscopic data for **10**: ^1H NMR (300 MHz, CD_2Cl_2, 193 K): δ 6.58 (dq, $J = 19$ Hz, 4.0 Hz, 3.58, 1H, MeO*H*), (d, $J = 3.5$ Hz, 3H, *Me*OH). ^{19}F NMR (282 MHz, CD_2Cl_2, 193 K): δ −124.6 (m, 2F, $BC_{12}F_8$), −130.2 (dd, $J = 24$ Hz, 12 Hz, 1F, C_6F_4), −130.6 (m, 2F, $BC_{12}F_8$), −131.0 (s, br, 2F, $BC_{12}F_8$), −132.6 (s, br, 2F, $BC_{12}F_8$), −133.5 (m, br, 3F, $BC_{12}F_8$+, C_6F_4), −140.8 (m, 2F, $BC_{12}F_8$), −152.4 (t, $J = 20$ Hz, 2F, $BC_{12}F_8$), −153.4 (t, $J = 22$ Hz, 2F, $BC_{12}F_8$), −153.6 (t, $J = 22$ Hz, 1F, C_6F_4), −155.7 (t, $J = 22$ Hz, 1F, C_6F_4). 2D $^1H/^{19}F$ correlation: 6.58, −133.5. Selective decoupling of ^{19}F at δ 133.5 gave δ 6.58 (q, $J = 4.0$ Hz).

^1H NMR (300 MHz, PhMe-d_8, 213 K): δ 4.04 (br s, 1H, MeO*H*), 2.01 (s, 3H, *Me*OH). ^{19}F NMR (282 MHz, PhMe-d_8, 213 K): δ −124.6 (2F, $BC_{12}F_8$), −129.2 (2F, $BC_{12}F_8$), −129.2 (2F, $BC_{12}F_8$), −130.6 (1F, C_6F_4), −130.8 (2F, $BC_{12}F_8$), −132.0 (1F, C_6F_4), −140.1 (2F, $BC_{12}F_8$), −150.2 (2F, $BC_{12}F_8$), −151.7 (2F, $BC_{12}F_8$), −152.2 (1F, C_6F_4), −153.1 (2F, $BC_{12}F_8$), −154.4 (1F, C_6F_4).

X-ray Crystallographic Characterization of Borinic Ester 11.[9] An orange block crystal of dimensions 0.20 × 0.16 × 0.12 mm was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. Details of crystal data and structure refinement are provided as Supporting Information. The data were collected using ω and φ

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scans.[40] The data were corrected for Lorentz and polarization effects and for absorption using a multiscan method.[41] Since the crystal did not show any sign of decay during data collection, a decay correction was deemed unnecessary.

The structure was solved by the direct methods[42] and expanded using Fourier techniques.[43] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97[44] converged with unweighted and weighted agreement factors, $R = 0.0457$ and $wR = 0.1199$ (all data), respectively, and goodness of fit, $S = 1.033$. The weighting scheme was based on counting statistics, and the final difference Fourier map was essentially featureless. Figure 1 was plotted with the aid of PLATON.[45]

X-ray Crystallographic Characterization of Compound 20. A colorless needle of dimensions 0.70 × 0.20 × 0.04 mm was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. Details of crystal data and structure refinement are provided as Supporting Information. The data were collected using ω and φ scans.[40] The data were corrected for Lorentz and polarization effects and for absorption using a multiscan method.[41] Since the crystal did not show any sign of decay during data collection, a decay correction was deemed unnecessary.

The structure was solved by the direct methods[42] and expanded using Fourier techniques.[43] The non-hydrogen atoms were refined anisotropically. The structure contains disordered dichloromethane and methanol molecules of solvation with unequal site occupancy factors of 0.870(5) and 0.716(6), respectively, for the major components. The EADP command was used to refine the U_{ij}'s as constrained parameters of the disordered atoms. The C−O distance was fixed using the command DFIX in the methanol molecule. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97[44] converged with unweighted and weighted agreement factors, $R = 0.0559$ and $wR = 0.1345$ ($I \geq 2\sigma(I)$), respectively, and goodness of fit, $S = 1.057$. The weighting scheme was based on counting statistics, and the final difference Fourier map was essentially featureless. Figure 3 was plotted with the aid of PLATON.[45]

Synthesis of 1,2-C_6F_4(9-$BC_{12}F_8$)(B(H_2O)($C_{12}HF_8$)(μ-OH)·6H_2O (17). Diborole **2** (130 mg, 0.17 mmol) was dissolved in water (2 mL). An aliquot of the solution was dissolved in D_2O for NMR analysis. ^{19}F NMR data for **13** (282 MHz, D_2O, 298 K): δ −134.4 (4F, $BC_{12}F_8$), −136.3 (4F, $BC_{12}F_8$), −139.8 (2F, C_6F_4), −157.4 (4F, $BC_{12}F_8$), −158.2 (4F, $BC_{12}F_8$), −161.4 (2F, C_6F_4). After evaporation of ca. 25% of the water in air, colorless single crystals of compound **17** were deposited. Yield: 69 mg (51%). Anal. Calcd for $C_{30}H_4B_2F_{20}O_2$·6H_2O: C 39.77, H 1.78. Found: C 40.60, H 1.55.

X-ray Crystallographic Characterization of Borinic Acid 17. A colorless prismatic crystal of dimensions 0.20 × 0.18 × 0.12 mm was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. Details of crystal data and structure refinement are provided as Supporting Information. The data were collected using ω and φ scans.[40] The data were corrected for Lorentz and polarization effects and for absorption using a multiscan method.[41]

The structure was solved by the direct methods[42] and expanded using Fourier techniques.[43] The non-hydrogen atoms were refined anisotropically. Of the six molecules of water of hydration, three were disordered over two sites each with site occupancy factors for O6, O7, and O8 of 0.789(3), 0.848(3), and 0.813(3), respectively, while the smaller fractions O6′, O7′, and O8′ had occupancy factors of 0.211(3), 0.152(3), and 0.187(3), respectively. The same U_{ij} values were assigned to the disordered O atoms (using EADP within SHELXL), and H atoms for all water molecules were constrained at geometrically idealized position with O---H distances = 0.82 Å. Other hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97[44] converged with unweighted and weighted agreement factors, $R = 0.0462$ and $wR = 0.1303$ (all data), respectively, and goodness of fit, $S = 1.024$. The weighting scheme was based on counting statistics, and the final difference Fourier map was essentially featureless. Figure 2 was plotted with the aid of PLATON.[45]

Reaction of *2* with Excess Water. Diborole **2** (0.25 g, 0.33 mmol) was dissolved in water (2 mL), and the water was subsequently pumped off. Residual water was removed by redissolution in CH_2Cl_2 and evaporation of the volatiles *in vacuo* to afford an off-white powder. Recrystallization from CH_2Cl_2 gave white crystals (135 mg, 50%). ^{1}H NMR (300 MHz, toluene-d_8, 353 K): δ 6.35 (m, 2H, Ar^F-H), 3.46 (s, br, 4H, H_2O) indicated the presence of a dihydrate of **16**. ^{19}F NMR (282 MHz, toluene-d_8, 353 K): δ −129.3 (2F), −131.3(2F), −137.3(m, 2F), −138.2, −139.4 (2F), −151.0(2F), −152.4(2F), −154.1(2F), −154.3(2F), −155.6. Spectroscopic data for anhydrous **16**: ^{1}H NMR (d_8-toluene, 298 K): δ 6.54 (m, 2H, $C_6F_4\mathit{H}C_6F_4B$). ^{19}F NMR (d_8-toluene, 298 K): δ −122.9 (2F, −$C_6\mathit{F_4}$), −129.2 (2F, $C_6F_4HC_6\mathit{F_4}B$), −137.4 (2F, $C_6F_4HC_6\mathit{F_4}B$), −137.7 (2F, $C_6\mathit{F_4}HC_6F_4B$), −139.4 (2F, $C_6\mathit{F_4}HC_6F_4B$), −141.8 (2F, −$C_6\mathit{F_4}$), −146.8 (2F, $C_6F_4HC_6\mathit{F_4}B$), −151.6 (2F, $C_6\mathit{F_4}HC_6F_4B$),−151.9 (2F, $C_6F_4HC_6\mathit{F_4}B$), −153.6 (2F, $C_6\mathit{F_4}HC_6F_4B$). ^{11}B{^{1}H} NMR (d_8-toluene, 298 K): δ 42.1.

Crystals of a THF adduct of compound **16** were isolated on attempted recrystalization of borinic acid **15** from a mixture of THF and hexane over several days. Crystallographic data for **16**·THF are provided as Supporting Information.

Generation of Ion Pair 19 from 2 and MeOH in the Presence of DPE. Diborole (**2**) (15 mg, 20 μmol) was dissolved in dry CD_2Cl_2 (0.4 mL) and placed in an NMR tube covered with a rubber septum. Dry 1,1-diphenylethene (DPE, freshly distilled from CaH_2) (50 μL, 0.397 M in CD_2Cl_2) was injected through the septum. Upon addition, the solution turned red locally, but after mixing, the solution was yellow again. ^{1}H NMR spectroscopy indicated a 20−30:70−80 mixture of 1,3,3-triphenyl-3-methylindan (**18**) and DPE. The ^{19}F NMR spectrum showed only **2** with <1% degradation. ^{1}H NMR spectroscopic data for indan **18**: ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.33−7.00 (m, 19H, Ph overlap with Ph of $Ph_2C{=}CH_2$), 3.39 (d, J = 14 Hz, 1H), 3.12 (d, J = 14 Hz, 1H), 1.27 (s, 3H, Me), for $Ph_2C{=}CH_2$: δ 7.33−7.00 (10H, Ph, overlap with indan Ph), 5.47 (s, 2H, CH_2).

To generate **19**, the NMR tube described above was immediately cooled to −78 °C and MeOH (50 μL, 0.397 M in CD_2Cl_2) was added. The sample was introduced into a precooled (−80 °C) NMR probe. Spectra (^{1}H and ^{19}F) were recorded at −80, −60, −40, −20, and 0 °C and room temperature.

At −80 °C ion pair [Ph_2CMe][**2**-μ-OMe] (**19**) and methanol adduct **10** were observed in ~90:10 ratio (by ^{1}H NMR integration). NMR spectroscopic data for **19**: ^{1}H NMR (300 MHz, CD_2Cl_2, 213 K): δ 8.31 (t, J = 7.3 Hz, 2H, *p*-H), 7.98 (d, J = 7.5 Hz, 4H, *o*-H), 7.87 (t, J = 7.8 Hz, 4H, *m*-H), 3.67 (s, 3H, Me), 2.68 (s, 3H, μ-OMe). ^{19}F NMR (282 MHz, CD_2Cl_2, 213 K): δ −132.0 (4F,

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$C_{12}F_8$), −136.0 (4F, $C_{12}F_8$), −138.8 (2F, C_6F_4), −156.8 (4F, $C_{12}F_8$), −157.8 (4F, $C_{12}F_8$), −161.3 (2F, C_6F_4). Formation of 1,3,3-triphenyl-3-methylindan (**18**) was confirmed after the experiment by GC-MS ($m/z = 360$). Warming the sample to −40 °C and above resulted in conversion of **19** (and **10**) to **11**, which was the major boron-containing product at the end of the experiment.

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Supporting Information Available: Experimental procedures for the synthesis of borinic ester **4** and borane **5**, NMR spectroscopic data for compounds **6**−**16** formed *in situ* from diboranes **1** or **2** and water or MeOH, Mayo plot of MW^{-1} vs $[H_2O]$:[IB] using data from ref 4f, equation and data used to estimate the *T* dependence of PIB MW at various $[H_2O]$ as depicted in Figure 5, and crystallographic information files for compounds **8**, **11**, **17**, **20**, and **16**·THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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