

# Lewis Acid Catalyzed Synthesis of Poly(pyrazolyl)borate Ligands

# Changle Chen and Richard F. Jordan\*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois, 60637

Received June 16, 2010

Summary: Lewis acids catalyze the reaction of Li[MeBH<sub>3</sub>] and Na[BH<sub>4</sub>] with pyrazoles to yield poly(pyrazolyl)borates under mild conditions. The reaction of  $Li[MeBH_3]$  with 2 equiv of 3-mesitylpyrazole ( $Hpz^{Ms}$ ) at 23 °C (2 days) affords  $Li-[MeB(3-mesityl-pz)_2H]$  ( $Li[MeBp^{Ms}]$ ) and Li[MeB(3-mesityl-pz)(5-mesityl-pz)H] ( $Li[MeBp^{Ms*}]$ ) in 88% yield (3:1 isomer ratio) in the presence of  $MeB(O^{i}Pr)_{2}$  (5 mol % vs  $Hpz^{Ms}$ ) but only 28% yield without this additive. Similar enhancements in the yield of  $Li[MeBp^{R}]$  products are observed in the reaction of  $Li[MeBH_{3}]$  with 3-<sup>t</sup>Bu-pyrazole, 3,5-Me<sub>2</sub>-pyrazole (Hpz<sup>\*</sup>), and 3,5-<sup>t</sup>Bu<sub>2</sub>-pyrazole. The reaction of Li[MeBH<sub>3</sub>] with 3 equiv of Hpz<sup>Ms</sup> (THF, 60 °C, 2 days) in the presence of 3 mol %  $MeB(O^{i}Pr)_{2}$  affords  $Li[MeB(3-Ms-pz)_{3}]$  (75%), but only  $Li[MeBp^{Ms}]$  and  $Li[MeBp^{Ms^{*}}]$  without this additive. Similar results were observed for the reaction of Li[MeBH<sub>3</sub>] with 3-CF<sub>3</sub>-pyrazole. The reaction of  $Na[BH_4]$  and 3 equiv of  $Hpz^*$  (THF, 60 °C, 4 h) yields  $Na[B(3,5-Me_2-pz)_2H_2]$  in 93% yield in the presence of  $BF_3 \cdot Et_2O(5 \text{ mol } \% \text{ vs } Hpz^*)$  but only 5% without this additive. Coordination of the pyrazole to the Lewis acid is expected to decrease the  $pK_a$  of the pyrazole and increase the rate of B-H bond protonolysis.

### Introduction

Poly(pyrazolyl)borate ligands have found wide application in coordination chemistry.<sup>1</sup> The most general route to these ligands, developed by Trofimenko, is the hydrogen elimination reaction of pyrazoles (Hpz<sup>x</sup>) with  $BH_4^-$  (eq 1).<sup>2</sup> This reaction can be controlled to yield mono-, bis-, tris-, and tetrakis(pyrazolyl)borates.

$$BH_4^{-} + nHpz^x \rightarrow H_{4-n}B(pz^x)_n^{-} + nH_2$$
  
$$n = 1 - 4$$
(1)

For the synthesis of bis-, tris-, and tetrakis(pyrazolyl)borates, the Trofimenko synthesis often requires an excess of the pyrazole as well as elevated temperatures that necessitate the use of high boiling solvents. In some cases, the isolation of the product is difficult due to the need to remove the excess pyrazole and solvent. Furthermore, the high reaction temperatures preclude the use of thermally sensitive Scheme 1<sup>*a*</sup>



2

pyrazole derivatives.<sup>3</sup> Here we report that Lewis acids catalyze the reaction in eq 1, which enables poly(pyrazolyl)borates to be prepared under mild conditions.

# **Results and Discussion**

MeB(O<sup>i</sup>Pr)<sub>2</sub>-Catalyzed Synthesis of Methyl-bis(pyrazolyl)borates. In the course of studying group 4 metal poly-(pyrazolyl)borate chemistry, we prepared the methylbis(pyrazolyl)borate salts Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>]  $([MeBp^{Ms}]^- = MeB(3-mesityl-pz)_2H^-, [MeBp^{Ms^*}]^- = MeB^-$ (3-mesityl-pz)(5-mesityl-pz)H<sup>-</sup>) by the reaction of Li[MeBH<sub>3</sub>] with 2 equiv of 3-mesitylpyrazole (Hpz<sup>Ms</sup>), as shown in Scheme 1.<sup>4</sup> Surprisingly, we observed that the yield of Li- $[MeBp^{Ms}]$  and Li $[MeBp^{Ms*}]$  varied significantly between experiments. Careful studies showed that the variation in yield was due to the presence or absence of MeB(O<sup>1</sup>Pr)<sub>2</sub>, a contaminant from the synthesis of Li[MeBH<sub>3</sub>] (Scheme 1). NMR monitoring experiments showed that the reaction of Li[MeBH<sub>3</sub>] with Hpz<sup>Ms</sup> to generate a 2:1 mixture of Li[MeB- $(3-Ms-pz)H_2$  and Li[MeB(5-Ms-pz)H\_2] (Ms = mesityl) is complete within 4 h at 23 °C in THF. The subsequent reaction of these species with the second equivalent of Hpz<sup>Ms</sup> to generate a 2.3:1 mixture of Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>] at 23 °C is accelerated by the presence of MeB(O<sup>i</sup>Pr)<sub>2</sub>.<sup>5</sup> For example, addition of 5 mol % (vs Hpz<sup>Ms</sup>) of MeB(O<sup>i</sup>Pr)<sub>2</sub> increases the rate of this step by a factor of ca. 5.<sup>6</sup> The reaction of Li[MeBH<sub>3</sub>] with 2 equiv of Hpz<sup>Ms</sup> on a gram scale

<sup>\*</sup>To whom correspondence should be addressed. E-mail: rfjordan@uchicago.edu.

<sup>(1) (</sup>a) Trofimenko, S. *Polyhedron* **2004**, *23*, 197. (b) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (c) Pettinari, C. *Scorpionates II: Chelating Borate Ligands*; Imperial College Press: London, 2008.

 <sup>(2) (</sup>a) Trofimenko, Š. J. Am. Chem. Soc. 1967, 89, 6288. (b) Trofimenko,
 S. Inorg. Chem. 1970, 11, 2493. (c) Trofimenko, S.; Calabrese, J. C.;
 Thompson, J. S. Inorg. Chem. 1987, 26, 1507.

<sup>(3) (</sup>a) Janiak, C.; Esser, L. Z. *Naturforsch.*, *B* **1993**, *48*, 394. (b) Janiak, C.; Scharmann, T. G.; Guenther, W.; Girgsdies, F.; Hemling, H.; Hinrichs, W.; Lentz, D. *Chem.–Eur. J.* **1995**, *9*, 637.

<sup>(4) (</sup>a) Chen, C.; Lee, H.; Jordan, R. F. *Organometallics* **2010**, ASAP (DOI: 10.1021/om1004034). (b) The formation and interconversion of isomers in Scheme 1 is due to 1,2-borotropic shifts, which are common in these systems, as discussed in ref 1.

<sup>(5)</sup> The isomer ratio varies with temperature but is not influenced by the presence of  $MeB(O^{i}Pr)_{2}$  or other Lewis acids.

Table 1. Influence of MeB(O<sup>i</sup>Pr)<sub>2</sub> (5 mol %, vs pyrazole) on the Generation of Li[MeBp<sup>x</sup>] by the Reaction of Li[MeBH<sub>3</sub>] with 2 equiv of 3-R-pyrazole or 3,5-R<sub>2</sub>-pyrazole at 23 °C in THF (2 days)<sup>*a*</sup>

· · /				
pyrazole	conversion to Li[MeBp <sup>x</sup> ] in the presence of 5 mol % MeB(O <sup>i</sup> Pr) <sub>2</sub> (%)	conversion to Li[MeBp <sup>x</sup> ] in the absence of MeB(O <sup>i</sup> Pr) <sub>2</sub> (%)		
Hpz <sup>Ms</sup> Hpz <sup>tBu</sup>	88 95	28 50		
Hpz* Hpz <sup>tBu2</sup>	$\frac{80}{82^b}$	$     16     20^{b} $		

<sup>*a*</sup> [pyrazole]<sub>initial</sub> = 0.51 M. <sup>*b*</sup> Reaction performed at 60 °C.

Table 2. Influence of MeB(O<sup>i</sup>Pr)<sub>2</sub> (3 mol % vs pyrazole) on the Generation of Li[MeTp<sup>x</sup>] by the Reaction of Li[MeBH<sub>3</sub>] and 3 equiv of 3-R-pyrazole at 60 °C in THF (2 days)<sup>a</sup>

3-R-pyrazole	conversion to Li[MeTp <sup>x</sup> ] in the presence of 3 mol % MeB(O <sup>i</sup> Pr) <sub>2</sub> (%)	$\begin{array}{c} \text{conversion to } \text{Li}[\text{MeTp}^x] \\ \text{in the absence of} \\ \text{MeB}(\text{O}^i\text{Pr})_2(\%) \end{array}$
Hpz <sup>Ms</sup>	75	$0^b$
Hpz <sup>CF3</sup>	67	$0^c$

<sup>*a*</sup> [pyrazole]<sub>initial</sub> = 0.76 M. <sup>*b*</sup> The product is predominantly Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>]. <sup>*c*</sup> The product is predominantly Li[MeBp<sup>CF3</sup>] and Li[MeBp<sup>CF3\*</sup>] ([MeBp<sup>CF3\*</sup>]<sup>-</sup> = MeB(3-CF<sub>3</sub>-pz)<sub>2</sub>H<sup>-</sup>, [MeBp<sup>CF3\*</sup>]<sup>-</sup> = MeB(3-CF<sub>3</sub>-pz)(5-CF<sub>3</sub>-pz)H<sup>-</sup>).

in THF at 23 °C for 3 days with 3 mol % of  $MeB(O^{i}Pr)_{2}$  followed by reaction with TlOAc affords  $Tl[MeBp^{Ms}]$  in 76% isolated yield. For comparison, we synthesized  $Tl[MeBp^{Ms}]$  in 73% yield by the same reaction at 60 °C (3 days) in the absence of a Lewis acid.<sup>4a</sup>

The catalytic effect of MeB(O<sup>1</sup>Pr)<sub>2</sub> on the reaction of Li[MeBH<sub>3</sub>] with pyrazoles (2 equiv) to generate Li[MeBp<sup>x</sup>] compounds is general (Table 1). For the reaction of Li-[MeBH<sub>3</sub>] with 2 equiv of the 3-subsituted pyrazoles Hpz<sup>Ms</sup> and 3-<sup>t</sup>Bu-pyrazole (Hpz<sup>tBu</sup>), the conversion to Li[MeBp<sup>x</sup>] is increased by 2–3 times in the presence of 5 mol % MeB-(O<sup>1</sup>Pr)<sub>2</sub>. For the 3,5-disubstituted pyrazoles 3,5-Me<sub>2</sub>-pyrazole (Hpz<sup>\*</sup>) and 3,5-<sup>t</sup>Bu<sub>2</sub>-pyrazole (Hpz<sup>tBu2</sup>), the conversion to Li[MeBp<sup>x</sup>] is increased by 4–5 times by 5 mol % MeB-(O<sup>1</sup>Pr)<sub>2</sub>.

MeB(O<sup>i</sup>Pr)<sub>2</sub>-Catalyzed Synthesis of Methyl-tris(pyrazolyl)borates. MeB(O<sup>i</sup>Pr)<sub>2</sub> also catalyzes the formation of methyltris(pyrazolyl)borates (MeTp<sup>x</sup>) (eq 2, Table 2). The reaction of Li[MeBH<sub>3</sub>] with 3 equiv of Hpz<sup>Ms</sup> or 3-CF<sub>3</sub>-pyrazole (Hpz<sup>CF3</sup>) in THF at 60 °C for 2 days in the presence of MeB(O<sup>i</sup>Pr)<sub>2</sub> (3 mol % vs pyrazole) affords the corresponding Li[MeTp<sup>x</sup>] products with good conversion. In contrast, in the absence of MeB(O<sup>i</sup>Pr)<sub>2</sub>, only Li[MeBp<sup>x</sup>] products are formed under these conditions. The reaction of Li[MeBH<sub>3</sub>] with 3 equiv of Hpz<sup>Ms</sup> on a gram scale in THF at 60 °C for 3 days with 3 mol % of MeB(O<sup>i</sup>Pr)<sub>2</sub> followed by reaction with TlOAc affords Tl[MeTp<sup>Ms</sup>] in 89% isolated yield. For comparison, Dias synthesized Tl[MeTp<sup>Ms</sup>] in 75% yield by refluxing a mesitylene solution (bp = 165 °C) of Li[MeBH<sub>3</sub>]

 Table 3. Influence of Lewis Acids (5 mol % vs Hpz\*) on the
 Generation of Na[Bp\*] by the Reaction of Na[BH<sub>4</sub>] and 3 equiv of

 Hpz\* (eq 3) at 60 °C in THF (4 h)<sup>a</sup>

Lewis acid	conversion to Na[Bp*] (%)
none	5
ZnCl <sub>2</sub>	5
MgCl <sub>2</sub>	5
$MeB(O^{i}Pr)_{2}$	19
$Cu(CF_3SO_3)_2$	52
$B(C_6F_5)_3$	55
$BF_3 \cdot Et_2O$	$93^{b}$

<sup>*a*</sup>[Hpz\*]<sub>initial</sub> = 0.51 M. <sup>*b*</sup> 5% of Na[Tp\*] is also formed.

and 3 equiv of Hpz<sup>Ms</sup> for 2 days.<sup>7</sup>

$$Li[MeBH_3] + 3Hpz^x \rightarrow Li[MeTp^x] + 3H_2 \qquad (2)$$

Lewis Acid Catalyzed Formation of  $Na[Bp^*]$  ([Bp^\*]<sup>-</sup> =  $H_2B(3,5-dimethylpyrazolyl)_2^{-})$ . The reaction of Na[BH<sub>4</sub>] with Hpz\* (3,5-Me<sub>2</sub>-pyrazole) at 60 °C in THF to generate Na[Bp\*] was used as a test reaction to explore the effectiveness of other Lewis acids as catalysts for the formation of bis(pyrazolyl)borates (eq 3). As summarized in Table 3, a variety of Lewis acids catalyze this reaction. BF<sub>3</sub> is the most effective catalyst among those tested and improves the yield of Na[Bp\*] from 5% (uncatalyzed) to 93%. No Na[Tp\*]  $([Tp^*]^- = HB(3,5-dimethylpyrazolyl)_3^-)$  or other byproducts were observed in these reactions except for the case of  $BF_3 \cdot Et_2O$ , in which case a small amount (5%) of Na[Tp\*] is formed. ZnCl<sub>2</sub> and MgCl<sub>2</sub> are ineffective as catalysts under these conditions, probably due to their insolubility in the reaction medium. For comparison, K[Bp\*] was previously prepared by refluxing a mixture of K[BH<sub>4</sub>] with Hpz\* (3 equiv) in dimethylacetamide (bp 165 °C).<sup>2</sup>

 $Na[BH_4] + 2 \xrightarrow{N-N} H \xrightarrow{H, \bigcirc N-N} H^{+}_{H, \bigcirc N-N} \oplus H^{+}_{H, \bigcirc N-N} \oplus H^{+}_{H, \bigcirc N-N} \oplus H^{+}_{H, \bigcirc N-N}$ (3)

Lewis Acid Catalyzed Formation of Li[MeTp<sup>Ms</sup>] ([Me- $Tp^{Ms}]^{-} = MeB(3-mesitylpyrazolyl)_{3}^{-})$ . The reaction of Li-[MeBH<sub>3</sub>] with 3 equiv of Hpz<sup>Ms</sup> at 60 °C in THF to generate Li[MeTp<sup>Ms</sup>] was used as a test reaction to explore the effectiveness of other Lewis acids in catalyzing the formation of tris(pyrazolyl)borates (Scheme 1). In the absence of Lewis acid, no Li[MeTp<sup>Ms</sup>] is formed under these conditions; after 3 days only Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>] (3:1 mixture, 100%)<sup>5</sup> along with 1 equiv of unreacted Hpz<sup>Ms</sup> were observed. In contrast, in the presence of MeB(O<sup>i</sup>Pr)<sub>2</sub> (3 mol % vs Hpz<sup>Ms</sup>), Li[MeTp<sup>Ms</sup>] is formed in 93% yield after 3 days. The use of stronger boron Lewis acids results in lower yields of Li[MeTp<sup>Ms</sup>]. The reaction with 3 mol % of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> for 3 days generates a mixture of Li[MeTp<sup>Ms</sup>] (35%) and Li-[MeBp<sup>Ms</sup>]/Li[MeBp<sup>Ms\*</sup>] (57%, 3:1 ratio). The <sup>1</sup>H NMR spectrum of the reaction mixture showed that unreacted Hpz<sup>Ms</sup> was present. The <sup>19</sup>F NMR spectrum contained resonances for two new two  $-C_6F_5$  species, but only trace resonance for free  $B(C_6F_5)_3$ . No further reaction was observed at longer times, presumably because the  $B(C_6F_5)_3$  is either sequestered by coordination by the products or consumed by some other side reaction. The reaction with 3 mol % of BF<sub>3</sub>·Et<sub>2</sub>O generates a 30% yield of Li[MeBp<sup>Ms</sup>]/Li[MeBp<sup>Ms\*</sup>]

<sup>(6)</sup> The kinetics of the MeB(O<sup>i</sup>Pr)<sub>2</sub>-catalyzed and uncatalyzed reaction of Li[MeB(3-Ms-pz)H<sub>2</sub>]/Li[MeB(5-Ms-pz)H<sub>2</sub>] with Hpz<sup>Ms</sup> were compared assuming that Li[MeB(3-Ms-pz)H<sub>2</sub>] and Li[MeB(5-Ms-pz)H<sub>2</sub>] react at the same rate. (The 2:1 ratio of these species remained approximately constant during the reaction.) The rate law under this assumption is Rate =  $k[\text{HPz}^{Ms}]{[Li[MeB(3-Ms-pz)H_2]]} + [Li[MeB(5-Ms-pz)H_2]]$ . The estimated second-order rate constants are  $k_{\text{catalyzed}} = 1.0 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{\text{uncatalyzed}} = 2.1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 23 °C in THF. See the Supporting Information for details.

<sup>(7)</sup> Dias, H. V. R.; Wang, X. Y. Polyhedron 2004, 23, 2533.

Table 4. Influence of Lewis Acids (3 mol % vs Hpz<sup>Ms</sup>) on the Generation of Li[MeTp<sup>Ms</sup>] by the Reaction of Li[MeBH<sub>3</sub>] with 3 equiv of Hpz<sup>Ms</sup> at 60 °C in THF<sup> $\alpha$ </sup>

Lewis acid	conversion to Li[MeTp <sup>Ms</sup> ] after 3 h (%)	conversion to Li[MeTp <sup>Ms</sup> ] after 3 days (%)
none	$0^b$	$0^c$
MeB(O <sup>i</sup> Pr) <sub>2</sub>	16	93
$B(C_6F_5)_3$	30	35
$BF_3 \cdot Et_2O$	30	30

<sup>*a*</sup> [Hpz<sup>Ms</sup>]<sub>initial</sub> = 0.76 M. <sup>*b*</sup> The product is Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>] (3:1 mixture, 90%) and Li[MeB(3-Ms-pz)H<sub>2</sub>] and Li[MeB(5-Ms-pz)H<sub>2</sub>] (3:1 mixture, 10%). <sup>*c*</sup> The product is Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>] (3:1 mixture, 100%).

(3:1 mixture) after 3 h, but no additional product is formed after longer reaction times. NMR analysis showed that a complex mixture of species is present.<sup>8</sup> Thus the weak Lewis acid  $MeB(O^{i}Pr)_{2}$  is the best catalyst for Scheme 1 among those studied.

**Reaction Mechanism.** These results are consistent with a mechanism involving Lewis acid catalyzed protonolysis of B–H bonds, as shown for the formation of Li[MeBp<sup>Ms</sup>] in eq 4 (LA = Lewis acid). Coordination of the pyrazole to the Lewis acid is expected to decrease the  $pK_a$  of the pyrazole and thus increase the rate of B–H protonolysis.<sup>9</sup> MeB(O<sup>i</sup>Pr)<sub>2</sub> is an effective catalyst because it does not bind strongly to the (pyrazolyl)borate products and does not undergo side reactions, at least for the cases studied here. Coordination of Hpz<sup>x</sup> to MeB(O<sup>i</sup>Pr)<sub>2</sub> was not detected by NMR under the synthetic conditions studied here. However, the coordination of Hpz<sup>\*</sup> to BF<sub>3</sub> to form the known (Hpz\*)BF<sub>3</sub> adduct under the conditions of eq 3 was confirmed by <sup>1</sup>H and <sup>19</sup>F NMR.<sup>10,11</sup>

$$\underset{LA \sim}{\overset{N}{\underset{H}{\bigcirc}}} + MeB(pz^{Ms})H_2^{-} \longrightarrow MeB(pz^{Ms})_2H^{-} + H_2 + LA$$
(4)

#### Conclusion

Lewis acids catalyze the reaction of Li[MeBH<sub>3</sub>] and Na [BH<sub>4</sub>] with pyrazoles to yield poly(pyrazolyl)borates under mild conditions. This approach may be a useful complement to the classic Trofimenko synthesis of poly(pyrazolyl)borates and other scorpionate ligands.<sup>12–14</sup>

#### **Experimental Section**

General Procedures. All manipulations were performed using standard vacuum line, Schlenk, or glovebox techniques under a

(10) Komorowski, L.; Maringgele, W.; Meller, A.; Niedenzu, A.; Serwatowski, J. Inorg. Chem. 1990, 29, 3845. purified N<sub>2</sub> atmosphere. Nitrogen was purified by passage through activated molecular sieves and Q-5 oxygen scavenger. THF was distilled from sodium benzophenone ketyl. Na[BH<sub>4</sub>], Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, BF<sub>3</sub>·Et<sub>2</sub>O, Hpz\* (3,5-Me<sub>2</sub>-pyrazole), and Hpz<sup>CF3</sup> (3-CF<sub>3</sub>-pyrazole) were purchased from Aldrich and used as received. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was obtained from Boulder Scientific and sublimed twice before use. MeB(O<sup>i</sup>Pr)<sub>2</sub>,<sup>15</sup> Li[MeBH<sub>3</sub>],<sup>16</sup> Hpz<sup>Ms</sup> (3-mesitylpyrazole), Hpz<sup>tBu</sup> (3-<sup>tBu</sup>-pyrazole),<sup>17</sup> and Hpz<sup>tBu2</sup> (3,5-<sup>tBu2</sup>-pyrazole)<sup>18</sup> were prepared by literature procedures. NMR spectra were recorded on Bruker DMX-500 or DMX-400 spectrometers in Teflon-valved NMR tubes. <sup>11</sup>H and <sup>13</sup>C chemical shifts are reported versus SiMe<sub>4</sub> and were determined by reference to the solvent peaks. <sup>11</sup>B chemical shifts are reported relative to external BF<sub>3</sub>·Et<sub>2</sub>O. <sup>19</sup>F chemical shifts are reported relative to external CFCl<sub>3</sub>. Coupling constants are reported in hertz.

<sup>1</sup>H NMR Monitoring of Poly(pyrazolyl)borate Synthesis Reactions. The following procedure for monitoring the generation of Li[MeBp<sup>Ms</sup>] and Li[MeBp<sup>Ms\*</sup>] with 5 mol % MeB(O<sup>i</sup>Pr)<sub>2</sub> as catalyst is representative. An NMR tube was charged with Li [MeBH<sub>3</sub>] (5.4 mg, 0.15 mmol), Hpz<sup>Ms</sup> (55.8 mg, 0.30 mmol), and MeB(O<sup>i</sup>Pr)<sub>2</sub> (2.7  $\mu$ L, 0.015 mmol). THF- $d_8$  (0.5 mL) was added by vacuum transfer at -78 °C. The NMR tube was agitated at 23 °C and monitored periodically by <sup>1</sup>H NMR. The B-Me resonances of the starting Li[MeBH<sub>3</sub>] and poly(pyrazolyl)borate products were monitored. For the generation of Na[Bp\*], the 4-pz <sup>1</sup>H NMR resonances were monitored.

NMR and ESI-MS Data for Li[poly(pyrazolyl)borate] Salts (THF-d<sub>8</sub>). Tl[MeTp<sup>Ms</sup>],<sup>7</sup> Tl[MeTp<sup>tBu</sup>],<sup>7</sup> and Li[MeTp<sup>CF3</sup>]<sup>19</sup> have been characterized previously. <sup>1</sup>H and <sup>11</sup>B NMR and ESI-MS data for the Li<sup>+</sup> pyrazolylborate species studied here are listed below. Broad B–H resonances in the region  $\delta 4-6$  are observed for these species and are not listed here. Li[MeB(3-Ms-pz)H<sub>2</sub>]: <sup>1</sup>H NMR:  $\delta$  7.25 (d, J = 2, 1H, pz), 6.75 (s, 2H, Ms), 5.76 (d, J2, 1H, pz), 2.09 (s, 3H, Me), 1.96 (s, 6H, Me), -0.52 (t, J = 8, 3H, BCH<sub>3</sub>). <sup>11</sup>B NMR:  $\delta - 14.4$  (br). Li[MeB(5-Ms-pz)H<sub>2</sub>]:  $\delta 7.43$  (d, J = 2, 1H, pz), 6.82 (s, 2H, Ms), 5.86 (d, J = 2, 1H, pz), 2.25 (s, 3H, Me), 2.04 (s, 6H, Me), -0.05 (t, J = 8, 3H, BCH<sub>3</sub>). <sup>11</sup>B NMR:  $\delta$  -9.1 (br). ESI-MS: Li[MeB(3-Ms-pz)H<sub>2</sub>]<sub>2</sub><sup>-</sup> and Li  $[MeB(5-Ms-pz)H_2]_2^-$  calcd m/z = 433.3, found 433.2. Li  $[MeBp^{Ms}]: \delta 7.58$  (d, J = 2, 2H, pz), 6.79 (s, 4H, Ms), 5.85 (d, J = 2, 2H, pz, 2.22 (s, 6H, Me), 1.98 (s, 12H, Me), 0.46 (d, J = 5, 3H, BCH<sub>3</sub>). <sup>11</sup>B NMR:  $\delta - 5.7$  (br). Li[MeBp<sup>Ms\*</sup>]:  $\delta 7.46$  (d, J = 2, 1H, pz), 7.38 (d, J = 2, 1H, pz), 6.89 (s, 2H, Ms) 6.85 (s, 1H, Ms), 6.83 (s, 1H, Ms), 5.85 (d, J = 2, 1H, pz), 5.83 (d, J = 2, 1H, pz), 2.30 (s, 3H, Me), 2.28 (s, 3H, Me), 2.27 (s, 3H, Me), 2.07 (s, 3H, Me), 1.97 (s, 3H, Me), 1.82 (s, 3H, Me), -0.03 (d, J = 5, 3H, BCH<sub>3</sub>). <sup>11</sup>B NMR:  $\delta$  -2.2 (br). ESI-MS: MeBp<sup>Ms-</sup> and MeBp<sup>Ms+-</sup> calcd m/z = 397.3, found 397.2. Li[MeTp<sup>Ms</sup>]:  $\delta$  7.80 (d, J = 2.1, 3H, pz), 6.76 (s, 6H, Ms), 5.91 (d, J = 2.1, 3H, pz), 2.20 (s, 9H, Me), 1.90 (s, 18H, Me), 1.14 (s, 3H, BCH<sub>3</sub>). <sup>11</sup>B NMR:  $\delta$  0.6 (br). Li[MeB(3-<sup>t</sup>Bu-pz)H<sub>2</sub>]:  $\delta$  7.33 (d, J = 2.0, 1H, pz), 6.00 (d, J = 2.0, 1H, pz), 1.28 (s, 9H, Me), -0.09 (t, J =5.8, 3H, BCH<sub>3</sub>). Li[MeBp<sup>tBu</sup>]:  $\delta$  7.32 (d, J = 2.0, 2H, pz), 5.86 (d, J = 2.0, 2H, pz), 1.27 (s, 18H, Me), 0.27 (d,  $J = 5.0, 3H, BCH_3$ ). <sup>11</sup>B NMR:  $\delta$  = 5.4 (br). Li[MeB(3,5-Me<sub>2</sub>-pz)H<sub>2</sub>]:  $\delta$  5.69 (s, 1H, pz), 2.19 (s, 3H, Me), 2.11 (s, 3H, Me), -0.26 (t, J = 5.8, 3H, BCH<sub>3</sub>). Li[MeBp\*]: & 5.52 (s, 2H, pz), 2.24 (s, 6H, Me), 2.09 (s, 6H, Me), -0.14 (d, J = 5.4, 3H, BCH<sub>3</sub>). Li[MeB(3,5<sup>-t</sup>Bu<sub>2</sub>-pz)

(19) Dias, H. V. R.; Wang, X. Dalton Trans. 2005, 2985.

<sup>(8)</sup> Li[MeBH<sub>3</sub>] reacts with BF<sub>3</sub> rapidly under these conditions to produce a mixture of species.

<sup>(9) (</sup>a) Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2754. (b) Evans, C. A.; Rabenstein, D. L.; Geier, G.; Erni, I. W. J. Am. Chem. Soc. **1977**, 99, 8106. (c) Johnson, C. R.; Shepherd, R. E.; Marr, B.; Donnell, S. O.; Dressick, W. J. Am. Chem. Soc. **1980**, *102*, 6227. (d) Hoq, M. F.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 1851. (e) Evans, E. J. Chem. Educ. **2004**, *81*, 1191.

<sup>(11)</sup> HO<sup>i</sup>Pr has no effect on the formation of bis- and tris(pyrazolyl) borate products in these reactions.

<sup>(12)</sup> Smith, J. M. Comments Inorg. Chem. 2008, 29, 189.

<sup>(13)</sup> Reglinski, J.; Spicer, M. D. Eur. J. Inorg. Chem. 2009, 12, 1553.

 <sup>(14)</sup> Jernigan, F. E.; Sieracki, N. A.; Taylor, M. T.; Jenkins, A. S.;
 Engel, S. E.; Rowe, B. W.; Jové, F. A.; Yap, G. P. A.; Papish, E. T.;
 Ferrence, G. M. *Inorg. Chem.* 2007, *46*, 360.

<sup>(15)</sup> Rheingold, A. L.; White, C. B.; Trofimenko, S. Inorg. Chem. 1993, 32, 3471.

<sup>(16)</sup>  $\text{Li}[\text{MeBH}_3]$  was synthesized by the procedure reported in Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 774, except that the product was further purified by washing with CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum for at least 12 h. The extended vacuum drying ensures the removal of MeB(O<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>.

<sup>(17)</sup> Trofimenko, S. J.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

<sup>(18)</sup> Wang, Z. X.; Qin, H. L. Green Chem. 2004, 2, 90.

H<sub>2</sub>]:  $\delta$  5.80 (s, 1H, pz), 1.49 (s, 9H, Me), 1.29 (s, 9H, Me), 0.01 (t, J = 5.2, 3H, BCH<sub>3</sub>). Li[MeBp<sup>tBu2</sup>]:  $\delta$  5.68 (s, 2H, pz), 1.38 (s, 18H, Me), 1.24 (s, 18H, Me), -0.20 (d, J = 5.5, 3H, BCH<sub>3</sub>). Li [MeBp<sup>CF3</sup>]:  $\delta$  7.67 (br s, 2H, pz), 6.44 (d, J = 2, 2H, pz), 0.14 (d, J = 5, 3H, BCH<sub>3</sub>). Li[MeBp<sup>CF3</sup>]:  $\delta$  7.49 (br s, 1H, pz), 7.42 (br s, 1H, pz), 6.43 (d, J = 2, 1H, pz), 6.34 (d, J = 2, 1H, pz), 0.01 (d, J = 5, 3H, BCH<sub>3</sub>). Li[MeTp<sup>CF3</sup>]:  $\delta$  7.71 (m, 3H, pz), 6.55 (m, 3H, pz), 0.97 (s, 3H, BCH<sub>3</sub>).

**TI[MeBp**<sup>Ms</sup>]. A mixture of Li[MeBH<sub>3</sub>] (0.87 g, 0.024 mol), Hpz<sup>Ms</sup> (9.0 g, 0.048 mol), and MeB(O<sup>i</sup>Pr)<sub>2</sub> (0.25 mL, 0.0014 mol, 3 mol % vs Hpz<sup>Ms</sup>) in THF (50 mL) was stirred at 23 °C for 3 days. The mixture was allowed to cool to 23 °C. Tl(OAc) (6.5 g, 0.024 mmol) was added, and the mixture was stirred for 3 days at 23 °C. The mixture was filtered through Celite, and the colorless filtrate was dried under vacuum to give a white solid. The solid was washed with hexanes (3 × 30 mL) and dried under vacuum to yield a white solid (11.1 g, 76%). This material is spectroscopically identical to and behaves identically in the synthesis of group 4 metal MeBp<sup>Ms</sup> compounds as Tl[MeBp<sup>Ms</sup>] made in the absence of MeB(O<sup>i</sup>Pr)<sub>2</sub>.

**TI[MeTp<sup>Ms</sup>].** A mixture of Li[MeBH<sub>3</sub>] (0.37 g, 0.010 mol), Hpz<sup>Ms</sup> (5.7 g, 0.031 mol), and MeB(O<sup>i</sup>Pr)<sub>2</sub> (0.18 mL, 0.0010 mol, 3 mol % vs Hpz<sup>Ms</sup>) in THF (50 mL) was stirred at 60 °C for 3 days. The mixture was allowed to cool to 23 °C. Tl(OAc) (2.7 g, 0.010 mmol) was added, and the mixture was stirred overnight at 23 °C. The mixture was filtered through Celite, and the colorless filtrate was dried under vacuum to give a white solid. The solid was washed with hexanes (3 × 10 mL) and dried under vacuum to yield a white solid (7.22 g, 89%). This material is spectroscopically identical to Tl[MeTp<sup>Ms</sup>] made in the absence of MeB(O<sup>i</sup>Pr)<sub>2</sub>.

**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.