## Anionic Multisubstituted 1,2-Azaborolyl Ligands: Syntheses, Characterization, and Coordination Chemistry

Xiangdong Fang\* and Jalil Assoud<sup>†</sup>

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Summary: Two synthetic methods for the preparation of tri- or tetrasubstituted 1,2-azaborolyls (Ab) are described. Both triand tetrasubstituted Ab rings can be conveniently attained via either dilithiation-directed or  $Cp_2Zr^{II}$ -mediated cyclization followed by transmetalation in good yields. In particular, anionic 1,2,4-trimethyl-1,2-azaborolyl and 1,2,3,4-tetramethyl-1,2azaborolyl, readily prepared through our methods, have been demonstrated as good supporting ancillary ligands in group IV metal complexes.

Cyclopentadienyl (Cp) and its derivatives constitute one of the most important groups of ancillary ligands utilized in transition-metal complexes, as demonstrated in olefin polymerization and selective organic synthesis.<sup>1</sup> It has been noted that in many Cp-based half-sandwich and metallocene complexes, simple modification of Cp-ring substituents may induce significant changes in reactivity and selectivity of the metal center.<sup>2</sup> For example, Chirik et al. have demonstrated that in dinitrogen activation the end-on versus side-on N2 coordination is subtly influenced by the substitution pattern of the Cp ligand in lowvalent group IV metallocene chemistry,<sup>3</sup> while the recent work by Hou et al. has established that cationic  $[(\eta^5-C_5Me_4-$ SiMe<sub>3</sub>)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)]<sup>+</sup> half-sandwich species exhibit olefin polymerization properties that are distinctly different from those of a comparable  $\{ [\eta^5 - C_5 H_3 (SiMe_3)_2] Sc(CH_2 SiMe_3) - Sc(CH_2$ (THF)}<sup>+</sup> complex.<sup>4</sup> On the other hand, the desire to modulate and control the reactivity and selectivity of the metal catalysts has stimulated the design and syntheses of numerous Cp analogues.<sup>5</sup> In this respect, we have initiated a program directed toward the development of multisubstituted monoanionic 1,2-azaborolyl (Ab) ligands that closely relate to the omnipresent Cp counterparts. The application of these Ab ligands in metal complexes may ultimately offer new directions in designing new metal catalysts with novel synthetic properties.

In principle, the formal replacement of a C=C bond unit in a Cp ligand with an isoelectronic and isolobal B-N unit

\* To whom correspondence should be addressed. E-mail: xdfang@ uwaterloo.ca. Tel: 01-519-888-4567, ext. 36229. Fax: 01-519-746-0435. <sup>†</sup> To whom correspondence concerning X-ray crystallographic data should

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In fact, Ab ligands have been investigated as the potential replacement ligand for Cp group in various metal complexes,<sup>8-10</sup> and it has been observed that Ab ligand is more electrondonating than its Cp rival in metal complexes.<sup>9</sup> However, those previous studies were rather synthetically limited. For instance, the scope with respect to the ring substituents afforded by current synthetic methods is almost entirely restricted to B- and N-substituted Ab ligands.<sup>8-10</sup> To the best of our knowledge, the report for C-substituted Ab ligand was extremely sporadic, as only one such compound has been isolated and characterized to date.<sup>11</sup> To address this synthetic challenge, we have established that both unprecedented tri- and tetrasubstituted Ab rings can be conveniently obtained through either dilithiation-directed or Cp<sub>2</sub>Zr<sup>II</sup>-mediated ring cyclization followed by B/Sn or B/Zr transmetalation, respectively.

A simple and effective preparatory method, which provides multisubstituted Ab ligands on a large synthetic scale, would greatly facilitate the exploration of the coordination chemistry of these ligands. We have now extended Schmid's dilithiation method<sup>12</sup> to the preparation of trisubstituted Ab ligands **6**–**8**, as illustrated in Scheme 1. Dilithiation of *N-tert*-butyl-*N*-

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more localized 2πe

Figure 1. Comparison of B-N and C=C bonds.



Scheme 2. Synthesis via Cp<sub>2</sub>Zr<sup>II</sup> Cyclization



methallylamine<sup>13</sup> with 2 equiv of BuLi followed by addition of Bu<sub>2</sub>SnCl<sub>2</sub> affords the corresponding stannacycle **1** in 68% yield. The reaction of **1** with BCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> gives the B/Sn transmetalated product **2** in 73% yield, which serves as a general precursor for various trisubstituted Ab rings **3–5**. Deprotonation of compounds **3–5** with KN(SiMe<sub>3</sub>)<sub>2</sub> or LDA furnishes the desired trisubstituted Ab ligands **6–8**.

Unfortunately, attempts to apply the above dilithiation protocol in terminally methylated allylamine systems proved to be unsuccessful (eq 1).<sup>14</sup> This prompted us to further explore other synthetic routes for tri- and tetrasubstituted Ab systems such as 11 and 14. Gratifyingly, we found that B/Zr transmetalation of the 1,2-azazircona-4-cyclopentenes 9 and 12, readily available from  $Cp_2Zr^{II}$ -mediated cyclization of  $\alpha$ , $\beta$ -unsaturated imine molecules,<sup>15</sup> generally produced the conjugate acids 10 and 13 in good yields, as shown in Scheme 2. Complex 9 transmetalates with PhBCl<sub>2</sub> to yield a mixture of 10a and 10b (10a:10b = 1:3) after vacuum distillation at 70 °C. The isomerization between 10a and 10b is likely to be the result of a [1,3]H shift, because the controlled NMR experiment indicates that the direct B/Zr transmetalation unambiguously gives 10a as the sole product. Thus, the formation of 10b must occur during the step of vacuum distillation at elevated temperature.

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Scheme 3





Interestingly, in the sterically more hindered system 12, the analogous [1,3]H shift was not observed and only directly transmetalated product 13 was isolated in 70% yield. Subsequent deprotonation with  $KN(SiMe_3)_2$  or LDA gives the expected ligands 11 and 14, respectively.



The versatility of the synthetic methods established above has been tested in the syntheses of the unprecedented anions 1,2,4-trimethyl-1,2-azaborolyl (20) and 1,2,3,4-tetramethyl-1,2azaborolyl (23) (Scheme 3), which are both isoelectronic and isostructural with 1,2,4-trimethylcyclopentadienyl and tetramethylcyclopentadienyl ligands, respectively. In this respect, compound 15 is obtained in 60% yield by the sequential reaction of N-methyl-N-methallylamine with 2 equiv of BuLi and Bu<sub>2</sub>SnCl<sub>2</sub>. After BCl<sub>3</sub> transmetalation with 15, 16 can be isolated by careful vacuum distillation, which quickly crystallizes at -78 °C. However, the characterization of 16 proves to be extremely difficult, due to its fast decomposition at room temperature. Thus, colorless crystalline 16 is dissolved in ether at -78 °C and subsequently treated with various nucleophiles to afford 17-19, which can be deprotonated by LDA to give trisubstituted Ab ligands 20–22. In particular, 20 can be further methylated and deprotonated to form the tetramethylated Ab ligand 23 in 50% yield.

It is of interest to compare the <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR chemical shift values for lithium tri- and tetramethylated Ab ligands **20** and **23** (Figure 2). The <sup>11</sup>B NMR chemical shift values of **20** and **23** are almost identical (**20**,  $\delta$  26.8; **23**,  $\delta$  26.7), which indicates that there is significant  $\pi$  donation of negative charge to boron in both cases.<sup>9</sup> In <sup>13</sup>C NMR spectra, the signals (**20**,  $\delta$  86.7; **23**,  $\delta$  96.5) for the intra-ring C groups which are  $\alpha$  to boron are shifted much more upfield, relative to those of other intra-ring carbons ( $\delta$  104.6–122.5), suggesting a major negative charge resting at the ring C(3). Interestingly, the introduction of a methyl group at C(3) in **23** seems to further delocalize the negative charge between C(3) and C(5).

The functionalization of activated group IV transition-metal dinitrogen complexes with nonpolar reagents such as dihydrogen

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**Figure 2.** Comparison of <sup>1</sup>H, <sup>13</sup>C (in parentheses), and <sup>11</sup>B NMR (in circles) chemical shift values (in ppm) of lithium salts **20** and **23** in THF- $d_8$  at 20 °C.

is of great interest, because it provides an attractive approach to convert atmospheric N<sub>2</sub> into more value-added N-containing organic molecules under ambient conditions.<sup>16</sup> In particular, Chirik's hafnocene—N<sub>2</sub> complex based on a tetramethylcyclopentadienyl ligand has been observed to have exclusively sideon coordination with a more elongated N—N bond, which can promote the direct coupling with CO<sub>2</sub>.<sup>3b</sup> Therefore, our synthetic studies have been extended to prepare the hafnocene congener with Ab ligand. Reaction of (C<sub>5</sub>Me<sub>4</sub>H)HfCl<sub>3</sub><sup>16c</sup> with 1 equiv of the lithium salt **20** in refluxing toluene for 4 days and subsequent recrystallization in hexane furnished the desired Ab complex **24** as colorless block crystals in 65% yield (Scheme 3).

The molecular structure of 24 is illustrated along with selected bond lengths and bond angles in Figure 3. The Hf center in complex 24 adopts a pseudotetrahedral coordination geometry, in which the Hf atom becomes more tightly bound to N and C atoms (2.46–2.51 Å) but is loosely coordinated to B (2.65 Å) in the Ab ligand. Thus, the Ab coordination is more shifted toward  $\eta^4$ . Perhaps the most striking structural feature of 24 is that the trimethyl Ab ligand possesses two possible different cavities for the wedge of hafnocene complex 24, as demonstrated in Figure 4. This type of ligand defect in Chirik's bis(tetramethylcyclopentadienyl) metallocene-N2 systems is of importance, because it promotes side-on coordination of the dinitrogen molecule by providing suitable space close to the metal center.<sup>3</sup> Interestingly, the defects involving the B and N atoms in the Ab ligand 20, as measured by the intersecting angles (in degrees) of two flanking exocyclic  $\sigma$  bonds, are quite different  $(150.0(5) \text{ and } 135.0(5)^\circ)$  from that observed in the tetramethylcyclopentadienyl system (142.5(5)°). Thus, it is tempting to expect that cavity-size tuning may be feasible in the dinitrogen functionalization with the Ab metallocene analogues.

In summary, we have developed two synthetic methods for the preparation of tri- and tetrasubstituted Ab rings, which provide, for the first time, easy access to a wide array of B-, N-, and C-substituted Ab ligands. Ligand **20** readily converts into its hafnium metallocene complex **24**. Our study supplies new strategies for tuning the reactivity and selectivity of metal catalysts by implementing both electronic and steric controls in Ab systems. In this regard, we have synthesized a variety of half-sandwich metal alkyl complexes based on our ligand



**Figure 3.** ORTEP view of the hafnium complex **24.** Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Hf1-C1 = 2.480(2), Hf1-C2 = 2.506(2), Hf1-C3 = 2.464(2), Hf1-B1 = 2.654(3), Hf1-N1 = 2.465(2), Hf1-C7 = 2.445(2), Hf1-C8 = 2.501(2), Hf1-C9 = 2.545(2), B1-N1 = 1.473(3), C1-C2 = 1.443(3), C2-C3 = 1.380(3), B1-C1 = 1.503(3), N1-C3 = 1.402(3), B1-C4 = 1.574(4), C7-C8 = 1.417(3), C8-C9 = 1.424(3), C9-C10 = 1.419(3);  $\angle$ Cl1-Hf1-Cl2 = 93.0(1),  $\angle$ C1-B1-C4 = 133.5(2),  $\angle$ N1-B1-C1 = 101.8(2),  $\angle$ N1-B1-C4 = 124.7(2),  $\angle$ B1-N1-C3 = 110.3(2),  $\angle$ C3-N1-C5 = 120.9(2),  $\angle$ B1-N1-C5 = 127.8(2).



Figure 4. Ab ligand defects in complex 24 as measured by the intersecting angles (in degrees) of two flanking exocyclic  $\sigma$  bonds.

systems. Further studies on the polymerization and copolymerization properties of this new family of metal catalysts are in progress.

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**Supporting Information Available:** Text giving experimental details and characterization data for all compounds and a CIF file giving X-ray crystallographic data for complex **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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