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

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Summary: Two synthetic methods for the preparation of tri- or tetrasubstituted 1,2-azaborolyls (Ab) are described. Both tri- and 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-1,2-azaborolyl, 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.[1] 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.[2] For example, Chirik et al. have demonstrated that in dinitrogen activation the end-on versus side-on N_2 coordination is subtly influenced by the substitution pattern of the Cp ligand in low-valent group IV metallocene chemistry,[3] while the recent work by Hou et al. has established that cationic $[(\eta^5\text{-}C_5Me_4SiMe_3)Sc(CH_2SiMe_3)(THF)]^+$ half-sandwich species exhibit olefin polymerization properties that are distinctly different from those of a comparable $\{[\eta^5\text{-}C_5H_3(SiMe_3)_2]Sc(CH_2SiMe_3)(THF)\}^+$ complex.[4] 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.[5] 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 converts the Cp ring into an Ab ligand. The B−N unit in aminoboranes has substantial double-bond character, as evidenced by the fact that the rotational barriers about the B−N bonds in various aminoborane molecules has been determined by variable-temperature NMR spectroscopy in the range of 10−24 kcal mol^{-1}.[6] Taking the much higher rotational barrier of C═C double bonds (∼63 kcal mol^{-1}) into consideration,[7] one can expect that π electrons are more localized in the B−N π bond than in the C═C double bond, which consequently contributes to an Ab ring with less π-electron delocalization, relative to Cp systems. Therefore, the HOMO in the Ab system has more character of a filled nitrogen atomic orbital, while the LUMO of the Ab system resembles more the empty 2p orbital at boron.[8] In this regard, the Ab ligands distinguish themselves from their Cp analogues with more electron-donating and less electron-accepting characters.

In fact, Ab ligands have been investigated as the potential replacement ligand for Cp group in various metal complexes,[8–10] and it has been observed that Ab ligand is more electron-donating than its Cp rival in metal complexes.[9] 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.[8–10] 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.[11] 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_2Zr^{II}-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[12] to the preparation of trisubstituted Ab ligands **6**−**8**, as illustrated in Scheme 1. Dilithiation of *N*-*tert*-butyl-*N*-

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(1) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley: New York, 2002.
(2) (a) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953. (b) Lin, S.; Waymouth, R. M. *Acc. Chem. Res.* **2002**, *35*, 765.
(3) (a) Chirik, P. J. *Dalton Trans.* **2007**, 16. (b) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2858. (c) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.
(4) (a) Li, X. F.; Baldamus, J.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 962. (b) Luo, Y. L.; Baldamus, J.; Hou, Z. M. *J. Am. Chem. Soc.* **2004**, *126*, 13910.
(5) (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355.
(6) (a) Imbery, D.; Jaeschke, A.; Friebolin, H. *Org. Magn. Reson.* **1970**, *2*, 271. (b) Friebolin, H.; Rensch, R.; Wendel, H. *Org. Magn. Reson.* **1976**, *8*, 287.
(7) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985.
(8) Schmid, G. In *Comprehensive Heterocyclic Chemistry II*; Shinkai, I., Ed.; Elsevier: Oxford, U.K., 1996; Vol. 3, Chapter 3.17.
(9) (a) Liu, S. Y.; Lo, M. M. C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174. (b) Liu, S. Y.; Hills, I. D.; Fu, G. C. *Organometallics* **2002**, *21*, 4323.
(10) (a) Ashe, A. J., III; Fang, X. D. *Org. Lett.* **2000**, *2*, 2089. (b) Ashe, A. J., III; Hong, Y.; Fang, X. D.; Kampf, J. W. *Organometallics* **2002**, *21*, 4578.
(11) Schmid, G.; Zaika, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 602.
(12) Schulze, J.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 54.

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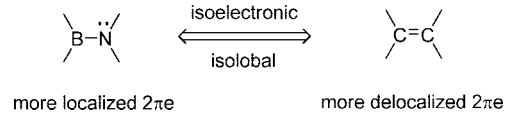
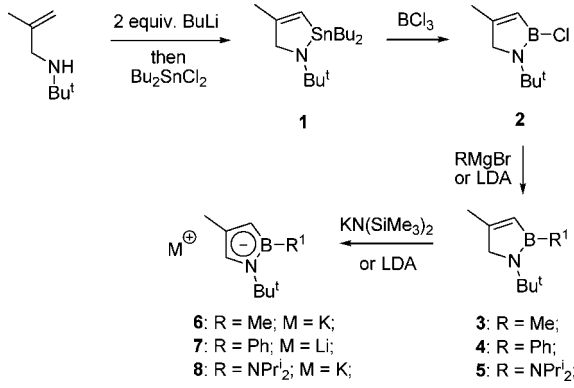
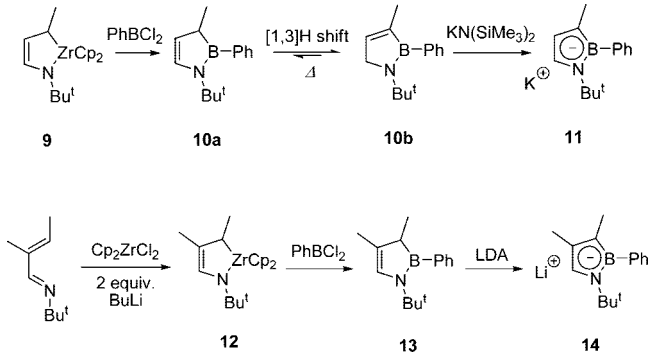


Figure 1. Comparison of B−N and C═C bonds.

Scheme 1. Synthesis via Dilithiation



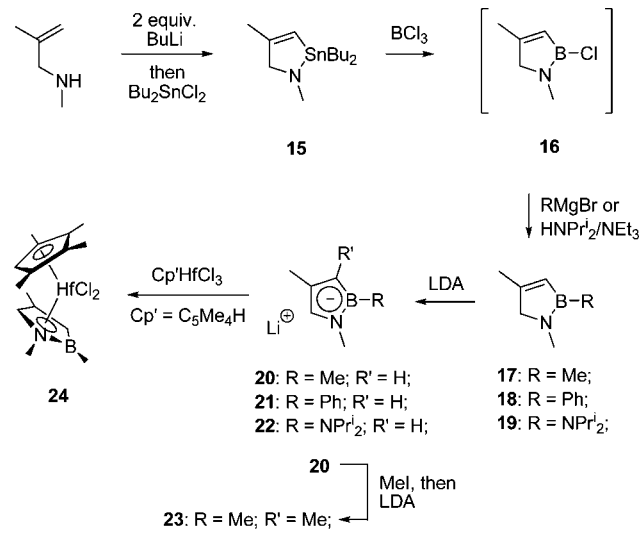
Scheme 2. Synthesis via Cp_2Zr^{II} Cyclization



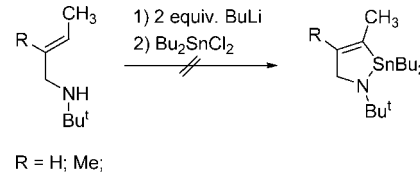
methallylamine[13] with 2 equiv of BuLi followed by addition of Bu_2SnCl_2 affords the corresponding stannacycle **1** in 68% yield. The reaction of **1** with BCl_3 in CH_2Cl_2 gives the B/Sn transmetalated product **2** in 73% yield, which serves as a general precursor for various trisubstituted Ab rings **3**−**5**. Deprotonation of compounds **3**−**5** with $KN(SiMe_3)_2$ 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).[14] 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 α,β-unsaturated imine molecules,[15] generally produced the conjugate acids **10** and **13** in good yields, as shown in Scheme 2. Complex **9** transmetalates with $PhBCl_2$ 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.

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.



(1)

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-1,2-azaborolyl (**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_2SnCl_2. After BCl_3 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 ^1H, ^{13}C, and ^{11}B NMR chemical shift values for lithium tri- and tetramethylated Ab ligands **20** and **23** (Figure 2). The ^{11}B NMR chemical shift values of **20** and **23** are almost identical (**20**, δ 26.8; **23**, δ 26.7), which indicates that there is significant π donation of negative charge to boron in both cases.[9] In ^{13}C NMR spectra, the signals (**20**, δ 86.7; **23**, δ 96.5) for the intra-ring C groups which are α to boron are shifted much more upfield, relative to those of other intra-ring carbons (δ 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

(13) Denmark, S. E.; Amburgey, J. *J. Am. Chem. Soc.* **1993**, *115*, 10386.
(14) (a) Jacobson, M.; Keresztes, I.; Williard, P. G. *J. Am. Chem. Soc.* **2005**, *127*, 4965. (b) Burns, S. A.; Corriu, R. J. P.; Huynh, V.; Moreau, J. J. E. *J. Organomet. Chem.* **1987**, *333*, 281.
(15) Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1743.

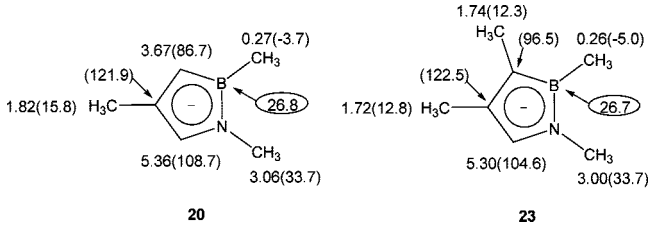


Figure 2. Comparison of ^{1}H, ^{13}C (in parentheses), and ^{11}B NMR (in circles) chemical shift values (in ppm) of lithium salts **20** and **23** in THF-d_8 at 20 °C.

is of great interest, because it provides an attractive approach to convert atmospheric N_2 into more value-added N-containing organic molecules under ambient conditions.[16] In particular, Chirik's hafnocene−N_2 complex based on a tetramethylcyclopentadienyl ligand has been observed to have exclusively side-on coordination with a more elongated N−N bond, which can promote the direct coupling with CO_2.[3b] Therefore, our synthetic studies have been extended to prepare the hafnocene congener with Ab ligand. Reaction of $(C_5Me_4H)HfCl_3$[16c] 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 η^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−N_2 systems is of importance, because it promotes side-on coordination of the dinitrogen molecule by providing suitable space close to the metal center.[3] 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 σ bonds, are quite different (150.0(5) and 135.0(5)°) 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

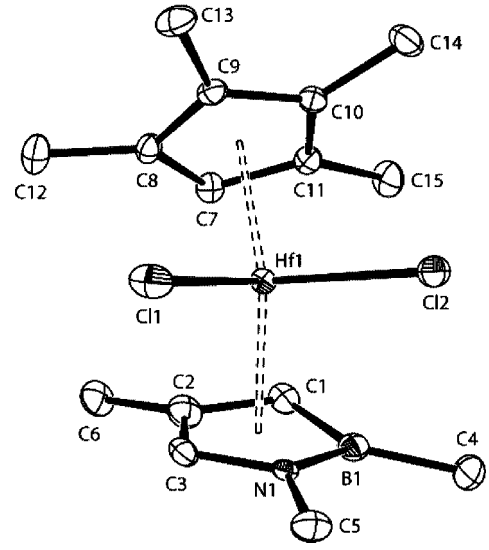


Figure 3. ORTEP view of the hafnium complex **24**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Hf1−C1 = 2.480(2), Hf1−C2 = 2.506(2), Hf1−C3 = 2.464(2), Hf1−B1 = 2.654(3), Hf1−N1 = 2.465(2), Hf1−C7 = 2.445(2), 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); ∠Cl1−Hf1−Cl2 = 93.0(1), ∠C1−B1−C4 = 133.5(2), ∠N1−B1−C1 = 101.8(2), ∠N1−B1−C4 = 124.7(2), ∠B1−N1−C3 = 110.3(2), ∠C3−N1−C5 = 120.9(2), ∠B1−N1−C5 = 127.8(2).

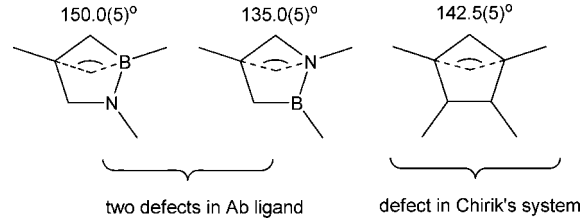


Figure 4. Ab ligand defects in complex **24** as measured by the intersecting angles (in degrees) of two flanking exocyclic σ bonds.

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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(16) (a) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445. (b) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 14051. (c) Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 12690.