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The First General Method for the Synthesis of Transition-Metal π Complexes of an Electronically Diverse Family of 1,2-Azaborolyls

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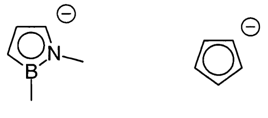
*Summary: A general method for the synthesis of new families of transition-metal-free 1,2-azaborolides (**3**) has been developed, based on a readily available precursor (**1**). These azaborolides react with a variety of transition-metal electrophiles to produce an unprecedented array of η^5-azaborolyl adducts (**4**) (substituents bound to boron: nitrogen, oxygen, hydrogen, carbon, and phosphorus).*

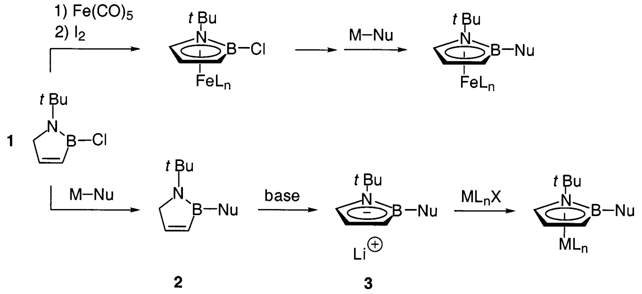
We have initiated a program focused on developing the chemistry of η^5-1,2-azaborolyls,[2−4] ligands that are of particular interest due to their isoelectronic relationship with the ubiquitous cyclopentadienyl group.[5] Thus, ready access to an electronically diverse set of azaborolyl complexes may enhance our fundamental understanding of metal-based reactivity as well as provide more active and/or selective catalysts.



During the 1980s, Schmid pioneered the development of 1,2-azaborolyl/transition-metal chemistry, focusing exclusively on adducts in which the boron substituent is carbon-based (i.e., methyl or phenyl).[3] Recently, we described the first azaborolyl complexes in which the group on boron is hydrogen, nitrogen, oxygen, fluorine, phosphorus, or sulfur.[2] Furthermore, we established that the electronic character of the boron-bound substituent is transmitted to the metal.

Unfortunately, the route that we employed to produce 1,2-azaborolyl adducts of iron is not readily generalizable to the synthesis of complexes with other transition metals (Scheme 1, top). In analogy with cyclopentadienyl (as well as Schmid's azaborolyl) chemistry, an approach that exploits the reaction of an azaborolide with a transition-metal electrophile should provide a more versatile pathway (Scheme 1, bottom).

Scheme 1. Approaches to the Synthesis of Transition-Metal Complexes of η^5-1,2-Azaborolyls



In this communication, we describe the synthesis of a wide range of B-heteroatom-substituted 1,2-azaborolides **3** (Scheme 1; e.g., Nu = NR$_2$, OR, H, PR$_2$), the first examples of transition-metal-free azaborolides which bear substituents that are not carbon-based. In addition, we demonstrate that these isolable reagents react with a spectrum of transition-metal (zirconium, chromium, and rhodium) electrophiles to generate (η^5-azaborolyl)metal complexes, which we have investigated crystallographically and spectroscopically.

The chloride of heterocycle **1**[6] can be displaced by any of an array of nucleophiles, thereby producing B-substituted derivatives **2** in generally excellent yield (Table 1, step A). Deprotonation of **2** with sterically demanding lithium 2,2,6,6-tetramethylpiperidide (LiTMP) furnishes the desired lithium 1,2-azaborolide (step B), wherein the boron bears a nitrogen, oxygen, hydrogen, carbon, or phosphorus substituent.

With these new families of 1,2-azaborolides in hand, it was incumbent upon us to demonstrate that they are indeed suitable, versatile precursors to azaborolylmetal complexes. We therefore reacted them with a range of transition-metal electrophiles.

With respect to early-transition-metal chemistry, we decided to focus our attention on the synthesis of zirconocene derivatives, since *B*-methyl and *B*-phenyl 1,2-azaborolylzirconium complexes serve as active catalysts for Ziegler−Natta polymerizations.[7,8] Furthermore, electronic tuning of the zirconium adducts of another

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[1] To whom correspondence concerning X-ray crystallography should be directed.

[2] Liu, S.-Y.; Lo, M. M.-C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174−176.

[3] For overviews of 1,2-azaborolyl chemistry, see: (a) Schmid, G. In *Comprehensive Heterocyclic Chemistry II*; Shinkai, I., Ed.; Elsevier: Oxford, U.K., 1996; Vol. 3, Chapter 3.17. (b) Schmid, G. *Comments Inorg. Chem*. **1985**, *4*, 17−32.

[4] For two recent contributions to 1,2-azaborolyl chemistry, see: (a) Ashe, A. J., III; Fang, X. *Org. Lett.* **2000**, *2*, 2089−2091. (b) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **2001**, *20*, 5413−5418.

[5] (a) *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley: New York, 1998, Vols. 1−2. (b) *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: New York, 1995.

[6] Heterocycle **1** is available on a multigram scale in three steps from commercially available compounds.[2]

[7] For an example of the application of 1,2-azaborolyl complexes to olefin polymerization, see: Nagy, S.; Krishnamurti, R.; Etherton, B. P. U.S. Patent 5 902 866, May 11, 1999.

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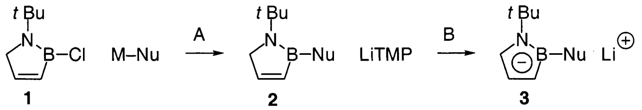
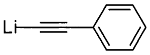
Table 1. Synthesis of a Diverse Array of Lithium 1,2-Azaborolides via Nucleophilic Substitution Followed by Deprotonation

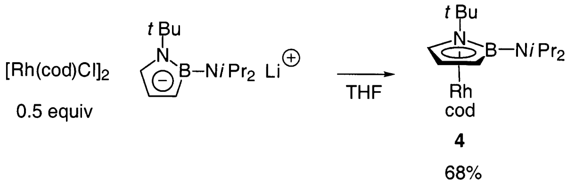


Entry	M–Nu	Yield of Step A (%)[a]	Yield of Step B (%)[a]
1	Li–N*i*Pr$_2$	91	66
2	K-O-*t*Bu	89	54
3	LiEt$_3$BH	58[b]	59
4		88	69
5	K–PPh$_2$	95	69

[a] Average of two runs; ~95% purity by NMR. [b] ~90% purity by NMR.

class of boron-based Cp analogues, boratabenzenes, has been shown to provide excellent control of polymerization/oligomerization activity.[9–11] Thus, the capacity to generate an electronically diverse set of azaborolyl complexes should open the door to new avenues of investigation in metallocene-catalyzed processes. We were pleased to determine that $ZrCpCl_3$ reacts with the entire spectrum of lithium 1,2-azaborolides (**3**) to produce the desired zirconocene derivatives in good yields (Table 2).

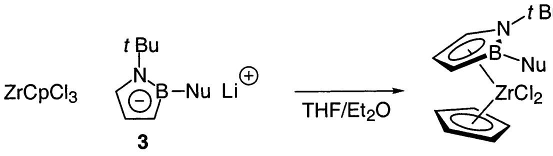
We have established that halide complexes of late transition metals also undergo substitution by 1,2-azaborolides to provide η^5-azaborolyl complexes. For example, the reaction of $[Rh(cod)Cl]_2$ with the N*i*Pr$_2$-substituted heterocycle proceeds smoothly to furnish the desired rhodium adduct in 68% yield (eq 1).[12] The

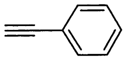


(1)

crystal structure of this complex (Figure 1) is consistent with donation by the nitrogen "lone pair" to the heteroaromatic ring. Thus, the nitrogen is sp^2 hybridized (sum of bond angles 360.0°), the N*i*Pr$_2$ group adopts a conformation that permits a π interaction between nitrogen and boron ($\angle$N1–B1–N2–C10 = 9.8(4)°), and the B–N bond distance is short (1.427(2) Å; sum of covalent radii 1.51 Å).

Table 2. Synthesis of 1,2-Azaborolylzirconium Complexes with a Range of Boron Substituents



Entry	Nu	Yield (%)[a]
1	N*i*Pr$_2$	65
2	O*t*Bu	59
3	H	75
4		72
5	PPh$_2$	66

[a] Isolated yield; average of two runs.

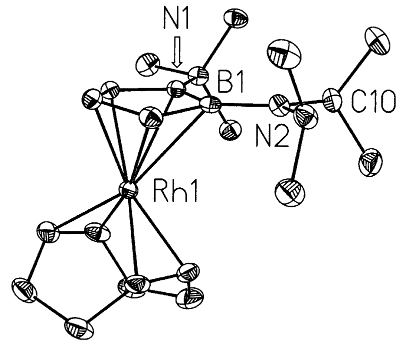
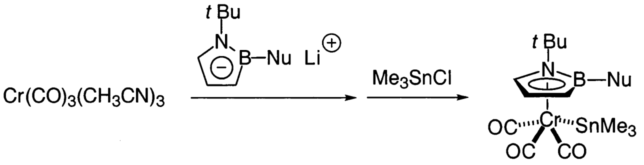
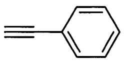


Figure 1. ORTEP illustration, with thermal ellipsoids drawn at the 35% probability level, of the 1,2-azaborolyl-rhodium complex **4**.

Table 3. Synthesis and CO Stretching Frequencies of 1,2-Azaborolylchromium Complexes with a Range of Boron Substituents



Entry	Nu	Yield (%)[a]	ν(CO) (cm^{-1})
1	N*i*Pr$_2$	47	1819, 1894, 1958
2	O*t*Bu	51	1830, 1900, 1965
3	H	92	1868, 1899, 1968
4		85	1871, 1894, 1965
5	PPh$_2$	63[b]	1865, 1905, 1966

[a] Isolated yield; average of two runs. [b] Product slowly decomposes in solution; ~95% purity by NMR.

We were also interested in demonstrating that 1,2-azaborolides can react with non-halide-based transition-metal electrophiles to generate η^5-azaborolyl complexes. We chose to investigate reactions with $Cr(CO)_3(CH_3$-

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(8) For recent reviews of Ziegler–Natta polymerization, see: (a) *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: New York, 2000. (b) Kaminsky, W.; Arndt, M. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Hermann, W. A., Eds.; VCH: New York, 1996. (c) *Ziegler Catalysis*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, 1995. (d) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170.

(9) (a) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291–2292. (b) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305–9306. (c) Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 6037–6046. (d) Rogers, J. S.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 1288–1298. (e) Bazan, G. C.; Cotter, W. D.; Komon, Z. J. A.; Lee, R. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1371–1380.

(10) For reviews on boratabenzene chemistry, see: (a) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199–236. (b) Fu, G. C. *Adv. Organomet. Chem.* **2001**, *47*, 101–119.

(11) For a review of the influence of cyclopentadienyl-ring substituents on Ziegler–Natta catalysts based on group 4 metallocenes, see: Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1–29.

(12) In preliminary studies, other azaborolides (**3**) have reacted analogously.

CN)$_3$, since, if the complexations were successful, the CO stretching frequencies of the products would furnish additional insight into how the substituent on boron impacts the electronic nature of the metal.[13] We were pleased to determine that this approach to η^5-azaborolyl adducts is also effective. Thus, treatment of Cr(CO)$_3$(CH$_3$CN)$_3$ with an azaborolide, followed by stannylation of the resulting anion with Me$_3$SnCl, provides the desired complexes (Table 3). The CO stretching frequencies of the azaborolylchromium adducts are consistent with effective transmission of electronic effects from the boron-bound N*i*Pr$_2$ and O*t*Bu substituents to chromium.

In summary, we have developed a general method for the synthesis of new families of transition-metal-free 1,2-azaborolides (**3**) from a readily available precursor (**1**), and we have demonstrated that these azaborolides react with a variety of transition-metal electrophiles to produce η^5-azaborolyl adducts with an unprecedented diversity of substituents on boron (nitrogen, oxygen, hydrogen, carbon, and phosphorus). These advances open the door to a wide range of studies of azaborolyl-metal complexes that, in view of the richness of the chemistry of the isoelectronic cyclopentadienylmetal complexes, will doubtlessly lead to the discovery of interesting new reactivity.

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Supporting Information Available: Text giving experimental details and tables giving crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2001.