J. Am. Chem. Soc. 1994, 116, 4489–4490 4489

Pentamethylcyclopentadienyl Aminoborollide Derivatives of Zirconium and Hafnium: A New Class of Amphoteric Molecule Having Both Lewis Acidic and Lewis Basic Sites

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Received December 2, 1993

Electron-deficient "bent metallocene" derivatives of early transition, lanthanide, and actinide elements have been shown to promote important transformations such as olefin polymerization and carbon–hydrogen bond activation. Whereas the 14-electron, d^0 derivatives, *e.g.*, Cp^*_2MR ($Cp^* = (\eta^5\text{-}C_5Me_5)$; M = Lu, Y,[2] Sc[3]) and $[Cp'_2MR]^+$, ($Cp' = (\eta^5\text{-}C_5H_5)$,[4] $(\eta^5\text{-}C_5Me_5)$;[5,6] M = Zr, Hf, Th), are particularly reactive, these compounds are voracious Lewis acids that tend to dimerize and tightly bind or react irreversibly with most polar solvents. Moreover, the cationic compounds of the group 4 transition metals require the use of an appropriate, noncoordinating anion such as $[B(C_6F_5)_4]^-$. As pointed out originally by Jordan,[7] replacement of a uninegative, 6 π electron cyclopentadienyl ligand with a dianionic, 6 π electron ligand may be used to make the overall charge on the complex one unit more negative. The new types of bent metallocene-like compounds so obtained may display similar reactivity without some of the attendant difficulties. For example, the dicarbollide ligand $(C_2B_9H_{11})^{2-}$ has been incorporated to generate (a) anionic group 3 complexes such as $Li[Cp^*(C_2B_9H_{11})ScR]$,[8] analogous to neutral Cp^*_2ScR; (b) group 4 neutral complexes such as $Cp^*(C_2B_9H_{11})MCH_3$ (M = Zr, Hf),[7] analogous to cationic $[Cp'_2MCH_3]^+$; and (c) a group 5 complex such as $(\eta^5\text{-}C_5H_4Me)(C_2B_9H_{11})Ta(CH_3)_2$,[9] analogous to the cationic $[Cp'_2Ta(CH_3)_2]^+$.[10] The dicarborollide dianions $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ and $[2\text{-}(SiMe_3)\text{-}3\text{-}(CH_3)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ have also been incorporated to afford anionic group 4 complexes such as $Li(THF)_2\text{–}[(SiMe_3)_2C_2B_4H_4]_2ZrCl(THF)$ and $Li(THF)\text{–}[(SiMe_3)(CH_3)C_2B_4H_4]_2HfCl(THF)$, analogous to group 4 cations $[Cp'_2MR]^+$.[11]

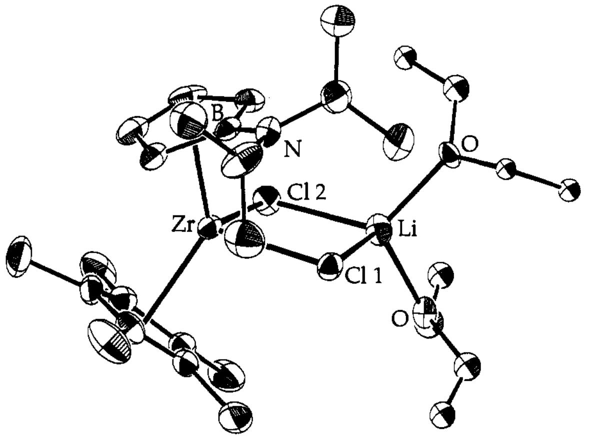
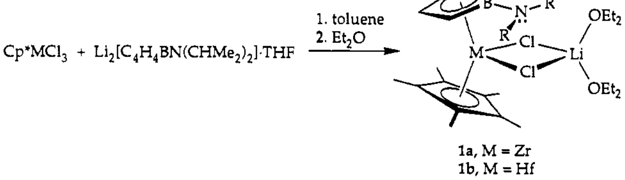


Figure 1. ORTEP diagram of $Cp^*(C_4H_4BN^iPr_2)ZrCl\cdot LiCl(Et_2O)_2$ (**1a**).

Although dicarbollide complexes are similar to their bis(cyclopentadienyl) analogs in reactivity, the increase in overall negative charge generally reduces their electrophilicity. Moreover, crystal structure determinations for several dimeric dicarbollide complexes have revealed bridging interactions involving a B–H bond of the dicarbollide cage with the Lewis acidic metal that further reduce their reactivity.[7,8] We have therefore examined the dianionic aminoborollide ligand, $[C_4H_4BN(CHMe_2)_2]^{2-}$, introduced by Herberich,[12] as a possible replacement for dicarbollide. Since there are no B–H bonds, the problems associated with the formation of unreactive dinuclear complexes characteristic of the dicarbollide ligand are circumvented. Reported herein are the syntheses of $Cp^*[\eta^5\text{-}C_4Me_4BN(CHMe_2)_2]MCl_2\text{-}Li(OEt_2)_2$ (M = Zr (**1a**), Hf(**1b**)) and the structure of the zirconium derivative. An unusual feature of these new compounds is the Lewis basic nitrogen adjacent to the Lewis acidic group 4, d^0 metal centers. It occurred to us that this combination could be used to cooperatively induce the heterolytic cleavage of H–X (X = halide, alkoxide, amide, alkyl, *etc.*) and C–X (X = halide, *etc.*) bonds.[13] The reaction of **1a** or **1b** with HCl illustrates this new type of reactivity, proceeding readily to zwitterionic $Cp^*[\eta^5\text{-}C_4H_4BN^+H(CHMe_2)_2]M^-Cl_2$ (M = Zr (**2a**), Hf (**2b**)). Comparisons of the structure of **2b** to that for **1a** reveal some of the novel features of the bonding between the aminoborollide ligand and an early transition-metal center.

Treatment of Cp^*ZrCl_3 or Cp^*HfCl_3 with $Li_2[C_4H_4BN(CHMe_2)_2]\cdot THF$ in toluene, followed by filtration and precipitation with petroleum ether, yields purple or red solids, which analyze approximately as $Cp^*[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]MCl\cdot LiCl$. These complexes are poorly soluble in aliphatic or aromatic hydrocarbon solvents in the absence of donor bases such as diethyl ether or tetrahydrofuran. X-ray quality crystals of the bis(diethyl etherate) adduct **1a** were obtained by slow recrystallization from ether (eq 1). The molecular structure of **1a** (Figure 1) indicates



(1)

1a, M = Zr
1b, M = Hf
R = $CHMe_2$

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[2] Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

[3] (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 274.

[4] Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

[5] (a) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (b) Turner, H. W. Eur. Pat. Appl. 277 004, 1988. (c) Turner, H. W. Eur. Pat. Appl. 277 003, 1988. (d) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. (e) Xinmin, Y.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (f) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

[6] Lin, Z.; LeMarechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.

[7] Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

[8] Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126.

[9] Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098.

[10] (a) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577. (c) Schrock, R. R., Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[11] (a) Siriwardane, U.; Zhang, H. M.; Hosmane, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9637. (b) Zhang, H.; Jia, L.; Hosmane, N. S. *Acta. Crystallogr.* **1993**, *C49*, 453.

[12] (a) Herberich, G. E.; Boveleth, W.; Hessner, B.; Hostalek, M.; Köffer, D. P. J.; Ohst, H.; Söhnen, D. *Chem. Ber.* **1986**, *119*, 420. (b) Herberich, G. E.; Ohst, H. *Z. Naturforsch.* **1983**, *B38*, 1388. (c) Herberich, G. E.; Negele, M.; Ohst, H. *Chem. Ber.* **1991**, *124*, 25. (d) Herberich, G. E.; Hessner, B.; Ohst, H.; Raap, I. A. *J. Organomet. Chem.* **1988**, *348*, 305.

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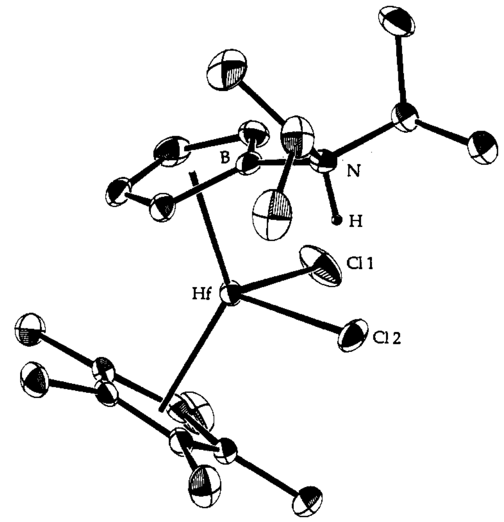
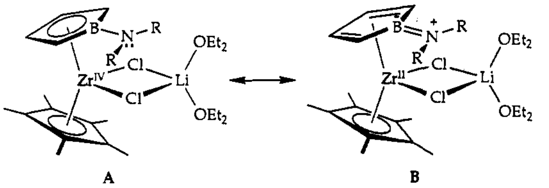
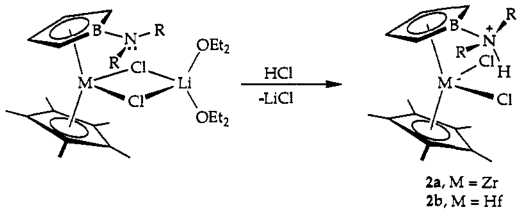


Figure 2. ORTEP diagram of $Cp^*(C_4H_4BN(H)^iPr_2)HfCl_2$ (**2b**).

that the borollide ligand is η5-bound to zirconium (structure **A**), and the bulky $\{N(CHCMe_2)_2\}$ group is rotated to the side of the metallocene wedge so that it points away from both the Cp* ring and one of the coordinated ether molecules. The two methine carbons, the nitrogen atom, and the boron of the borollide are in the same plane (sum of angles about N = 360(1)°), an arrangement that results in a pπ–pπ interaction between the boron and nitrogen atoms (resonance structure **B**).



Protonation of borollide nitrogen of **1a** or **1b** with 1 equiv of HCl affords zwitterionic dichlorides **2a** or **2b** (eq 2).



(2)

An X-ray structure determination for **2b** (Figure 2) reveals that, as for **1a**, the borollide ligand is *pentahapto* coordinated, but the nitrogen is pyramidal (sum of angles about N = 344(1)°). Although the hydrogen atom on the nitrogen was not reliably located, the difference map did show a region of positive density between the nitrogen atom and Cl2. For this reason, the position of the hydrogen shown in the ORTEP drawing was calculated by setting the N–H bond distance at 0.95 Å. The Cl2–Hf–B–N torsion angle of –2.2(4)° is in agreement with this site for the hydrogen (the analogous Cl1–Zr–B–N torsion angle in **1a** is approximately –27°).

Protonation of the nitrogen lone pair effectively eliminates any contribution from resonance structure **B** for the metal–borollide bonding for **2b**. Consistent with this picture is the longer N–B distance for **2b** (1.580(8) vs 1.433(11) Å for **1a**) and its shorter metal–boron distance (2.625(6) vs 2.714(9) Å for **1a**).[14] Indeed **2b**, having the tetrahedral $[NHR_2]^+$ substituent at boron, more closely resembles the 1-methyl- and 1-phenylborollide derivatives reported by Herberich.[12d] Moreover, the much higher reduction potentials for early transition metals result in metal–borollide bonding better described by resonance structure **A**, even for the unprotonated aminoborole derivatives **1**.

These aminoborollide derivatives of zirconium and hafnium represent an unusual class of molecules having both Lewis acidic and Lewis basic sites held in relatively close proximity, yet constrained from interacting directly. Preliminary experiments suggest that heterolysis of bonds other than HCl may also proceed. For example, the carbon–iodine bond of methyl iodide is cleaved smoothly, yielding $Cp^*[\eta^5\text{-}C_4H_4BN^+(CH_3)(CHMe_2)_2]M\text{-}Cl(I)$. The even more Lewis acidic, 14-electron derivatives $Cp^*[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]MR$ (R = H, alkyl, aryl, *etc.*) should prove to be even more reactive, and we are presently exploring synthetic routes to these compounds. We also recognize the similarities of these alkyl derivatives to $[Cp_2ZrR]^+$, the active catalytic species in Ziegler–Natta polymerization.[15]

Acknowledgment. The work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431), by the National Science Foundation (Grant No. CHE-9203076), and by Exxon Chemicals Americas. G.B. acknowledges the financial support of an NSERCC Fellowship.

Supplementary Material Available: Experimental details describing the syntheses of **1a**, **1b**, **2a**, and **2b**; listings of crystal data, data collection, and refinement parameters with tables of final refined parameters, assigned hydrogen atom parameters, complete distances and angles, and intermolecular distances less than 3.5 Å (33 pages); observed and calculated structure factors (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) A similar "bifunctional acid–base system", capable of dissolving ionic compounds (*e.g.*, sodium hydride) in hydrocarbon solution, has recently reported by Floriani and co-workers: Jacoby, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 3595.

(14) The Zr–B distances (2.437–2.521 Å) for the dicarbollide complex $(\eta^5\text{-}C_5Me_5)(C_2B_9H_{11})Zr(CMe{=}CMe_2)$ are somewhat shorter than these distances (ref 7). Where direct comparisons can be made, it appears that metal–boron distances for borollide complexes are consistently longer than metal–boron distances for the corresponding dicarbollide complexes (see ref 11).

(15) Andrew F. Kiely, Roger W. Quan, work in progress.