Pentamethylcyclopentadienyl−Borollide Complexes of Tantalum: New Group 4 Metallocene Mimics[†]

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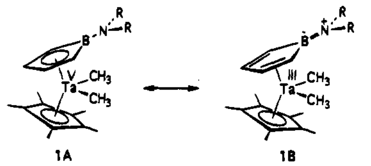
One approach to further the design of a new generation of homogeneous Ziegler−Natta olefin polymerization initiators consists of substituting, within a catalytically active complex, a dianionic 6 π electron donor in place of the monoanionic cyclopentadienyl (Cp) ligand.[1a] Ultimately, this substitution aims at changing the overall molecular charge, or the metal−ligand combination, without perturbing the important structural features that permit polymerization. Reactivity differences of complexes prepared in this way thus provide valuable insight into the influence that charge and metal have on the olefin insertion step.[1]

Borollide ligands are close structural relatives of Cp. The dianionic charge in these molecular fragments can be readily understood in terms of an isoelectronic boron anion for neutral carbon atom substitution in the five-membered aromatic ring. Herberich's reagent, $Li_2[C_4H_4B\text{-}N(CHMe_2)_2]\cdot(THF)$, is conveniently prepared in multigram quantities and provides a suitable starting material for borollide-supported organotransition metal chemistry.[2] It has been used to prepare mononuclear complexes, such as $[\eta^4\text{-}C_4Me_4B\text{-}N(CHMe_2)_2]_2Cr(CO)_2$ or $[\eta^4\text{-}C_4Me_4B\text{-}N(CHMe_2)_2]_2Mn(CO)$, in which the bonding of the borollide ring has been described as akin to that of a diolefin. Consequently, the metal in these complexes is regarded as low valent.[3] Early, or high oxidation state, transition metal complexes are unknown except for those of general composition $Cp^*[\eta^5\text{-}C_4H_4B\text{-}N(CHMe_2)_2]MCl_2Li(OEt_2)_2$ (M = Zr, Hf; Cp* = C_5Me_5) where the borollide ring is *pentahapto* coordinated. These complexes are interesting because of their ability to induce heterolytic bond cleavage.[4] We report herein the synthesis, characterization, and reactivity of $Cp^*[\eta^5\text{-} C_4H_4B\text{-}N(CHMe_2)_2]\text{-}TaMe_2$, a complex that is isoelectronic and isostructural to zirconocene reagents.

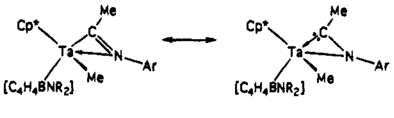
Addition of triflic acid to Cp^*TaMe_3Cl in ether at −30 °C produces CH_4 and $Cp^*TaMe_2Cl(OSO_2CF_3)$ quantitatively. Further reaction of $Cp^*TaMe_2Cl(OSO_2CF_3)$ with $Li_2[C_4H_4B\text{-}N(CHMe_2)_2]\cdot(THF)$ produces dark blue $Cp^*[\eta^5\text{-}C_4H_4B\text{-}N(CHMe_2)_2]TaMe_2$ (**1** in Scheme 1) in 40% isolated yield. Use of $Cp^*TaMe_2Cl(OSO_2CF_3)$ in this step is critical in order to avoid reduction of the metal center. X-ray diffraction analysis of **1**[5] reveals that the overall molecular geometry resembles a bent metallocene with a pentahapto-coordinated borollide ring, a rather weak Ta−B interaction (Table 1), and normal bond distances between Ta and both the Cp* and methyl ligands.[6] The short B−N distance and the sum of the angles about the sp^2-hybridized nitrogen (359(1)°) are in agreement with significant $p^\pi-p^\pi$ bonding between N and B. These observations imply that the metal−ligand bonding description contains contributions from both Ta(V)−(dianionic borollide) (**1A**) and Ta(III)−diolefin (**1B**) resonance structures.[7]

Table 1. Selected Structural Data for **1**−**4**

compd	Ta−B (Å)	B−N (Å)	Cp*−Ta−Bo (deg)
1	2.70(1)	1.44(1)	135.0
2	2.70(2)	1.46(2)	132.7
3	2.67(1)	1.44(2)	136.7
4	2.537(6)	1.567(7)	137.0


1A **1B**

Addition of 2,6-dimethylphenyl isocyanide (ArNC) to **1** results in clean migratory insertion of the isocyanide functionality into the Ta−Me bond to produce yellow $Cp^*[\eta^5\text{-}C_4H_4B\text{-}N(CHMe_2)_2]Ta(\eta^2\text{-}MeCNAr)(Me)$ (**2**). This reactivity is similar to reactions between ArNC and Cp_2ZrMe_2[8] or Cp_2TiMe_2.[9] Solid-state characterization of **2** (Scheme 1 and Table 1) reveals no significant differences in Ta−borollide distances relative to **1**. Note that the η^2-N−C bond distance of 1.34(2) Å in **2**, which is between the ranges observed for single (1.47 Å) and double (1.28 Å) C−N bonds, suggests a contribution from an amido−carbene resonance form.[10]



Hydrogenolysis of the Ta−Me bond in **1** is fast (2−3 atm, C_6D_6) and results in formation of CH_4 and unidentifiable organometallic products. Addition of excess PMe_3 under the same conditions results in quantitative formation of air-stable $Cp^*[\eta^5\text{-}C_4H_4B\text{-}N(CHMe_2)_2]Ta(PMe_3)(H)_2$ (**3**). We have compared the reactivity of **1** and Cp_2ZrMe_2 toward hydrogenolysis and have found that, in equimolar mixtures, all of **1** is converted (7 h, 1 atm of H_2, C_6D_6) into **3**, whereas no obvious consumption of the zirconium compound has occurred.[11] Perhaps the increased electron density on the metal in **1** as evidenced by the Ta(III) resonance contribution permits an oxidative addition reactivity pathway which is absent in Cp_2ZrMe_2. Solid-state metrical parameters of **3** (Scheme 1) show that the phosphorus atom in PMe_3 is essentially contained (4(1)° deviation) in the $Cp^*_{centroid}\text{−}Ta\text{−}C_4B_{centroid}$ plane, and therefore we suspect that the hydrides are located on the two sites adjacent to PMe_3. Additionally, the borollide ring is rotated so that the bulky

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[†] Dedicated to Professor Richard R. Schrock on the occasion of his fiftieth birthday.

[1] Dicarbollide complexes: (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (c) Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098. Trimethylenemethane complexes: Bazan, G. C.; Rodriguez, G.; Cleary, B. P. *J. Am. Chem. Soc.* **1994**, *116*, 2177.

[2] Herberich, G. E.; Hostalek, M.; Laven, R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *23*, 317.

[3] Herberich, G. E.; Hessner, B.; Ohst, H. *J. Organomet. Chem.* **1988**, *348*, 305.

[4] Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Shaeffer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489.

[5] The complete crystallographic details for compounds **1**−**4** have been deposited as supplementary material.

[6] (a) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578. (b) Gibson, V. C.; Kee, T. P.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1990**, 313. (c) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037. (d) Mayer, J. M.; Wolczanski, P. T.; Santarsiero, B. D.; Olson, W. A.; Bercaw, J. E. *Inorg. Chem.* **1983**, *22*, 1149.

[7] This effect is also present in the aminoborollide complexes of Zr and Hf (ref 4) and obeys the series N > O > P other substituents on boron. These p interactions weaken the boron−metal bond and make the ligands similar to dienes. For a detailed discussion, see: Herberich, G. E.; Englert, U.; Hostalek, M.; Laven, R. *Chem. Ber.* **1991**, *124*, 17.

[8] $Cp_2ZrR(\eta^2\text{-acyl})$: Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. $Cp_2ZrR(\eta^2\text{-iminoacyl})$: Bristow, G. S.; Lappert, M. F.; Atwood, J. L.; Hunter, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, K. W., Eds.; Pergamon: Oxford, 1982; Chapter 23, p 600.

[9] Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297.

[10] For a detailed discussion, see: Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Hoffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. For related work, see: Berg, F. J.; Petersen, J. L. *Organometallics* **1993**, *12*, 3890 and references therein.

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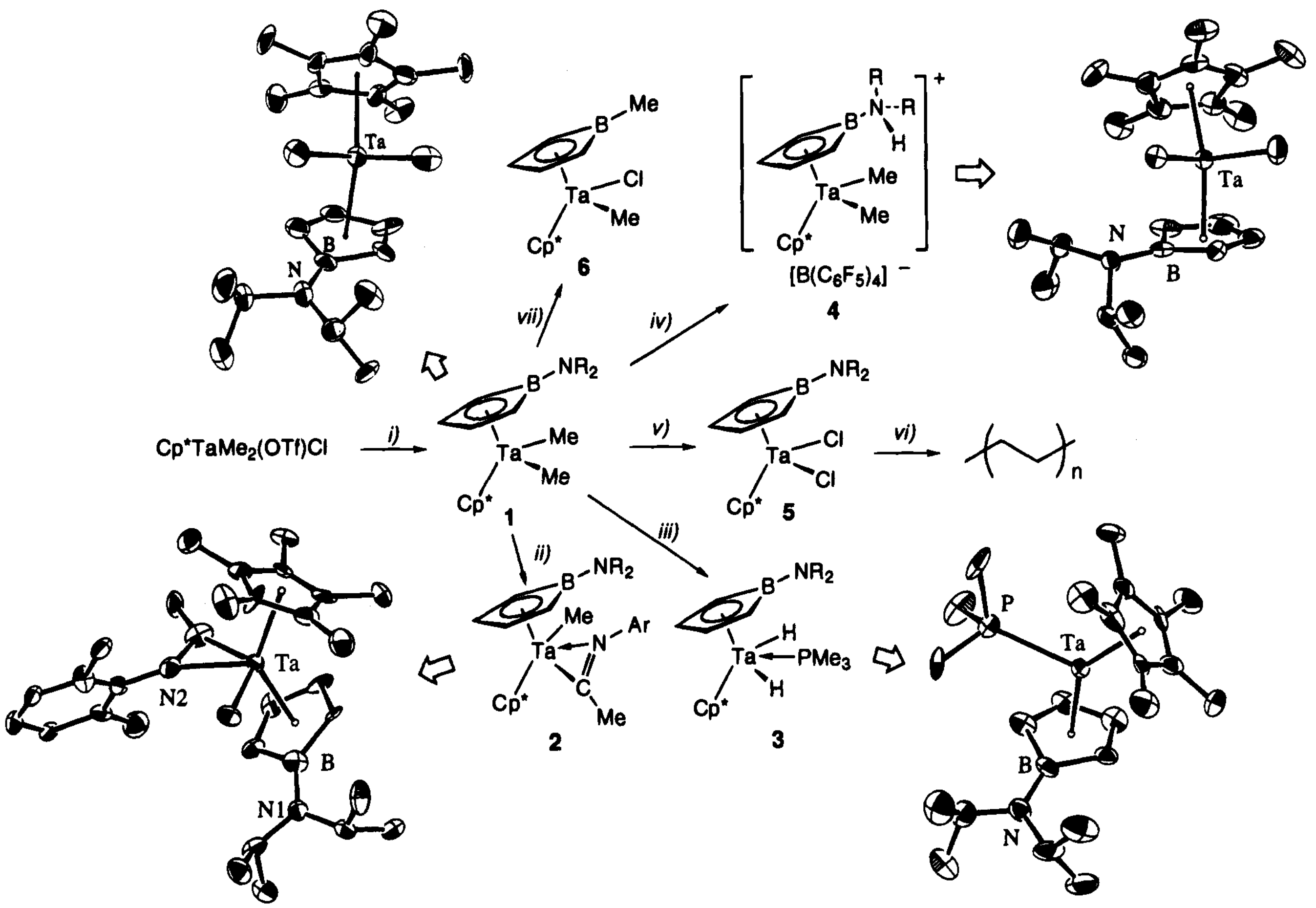
Scheme 1



[a] (i) 1.0 equiv of $Li_2[C_4H_4B\text{-}N(CHMe_2)_2]\cdot(THF)$, diethyl ether (−30 °C); (ii) 1.0 equiv of 2,6-dimethylphenyl isocyanide, diethyl ether or benzene (25 °C); (iii) 2−3 atm of H_2, excess PMe_3, benzene (25 °C); (iv) 1.0 equiv of $[PhNMe_2H][B(C_6F_5)_4]$, CH_2Cl_2; only the tantalum-containing fragment is shown for **4**; (v) *hν*, 48 h, CH_2Cl_2 or $CHCl_3$; (vi) 500 equiv of MAO, 1 atm of ethylene, 6 h, toluene (25 °C); (vii) excess $[HNMe_3]Cl$, 12 h, CH_2Cl_2 (25 °C). ORTEP diagrams are shown at the 50% probability level.

diisopropylamine functionality is directed away from the sterically demanding Cp* and PMe_3 ligands.

Protonolysis of group 4 metallocene alkyls is of practical importance in the formation of α-olefin polymerization catalysts. In the case of **1**, addition of $[PhNMe_2H][B(C_6F_5)_4]$ in CH_2Cl_2 results in quantitative protonation of the exocyclic amine functionality to $[Cp^*(\eta^5\text{-}C_4H_4B\text{-}NH(CHMe_2)_2)TaMe_2]^+[B(C_6F_5)_4]^-$ (**4**). Interatomic distances and angles in **4** are consistent with this formula and are significantly different from those of **1**, **2** or **3** (Table 1). Particularly notable are the stronger Ta−B interaction, the elongated B−N distance, and the tetrahedral disposition of substituents around N. The bond distances and angles of **3** illustrate how protonation at nitrogen effectively interrupts the B−N π interaction and thereby eliminates any contribution from a Ta(III)−diolefin resonance contribution in **3** (*i.e.*, analogous to **1B**).

Photolysis of **1** in CH_2Cl_2 or $CHCl_3$ results in formation of green $Cp^*[\eta^5\text{-}C_4H_4B\text{-}N(CHMe_2)_2]TaCl_2$ (**5**) in 15−30% yield (the reaction proceeds quantitatively by ^1H NMR experiments in CD_2Cl_2, but solubility of the product prevents higher isolated yields) to provide a valuable nonprotic route for methyl substitution. When activated with excess methylaluminoxane, both **1** and **5** polymerize ethylene (at 1 atm and 25 °C) with catalytic activities of 0.6 and 2 (kg PE/h[Ta]mol), respectively. These activities are significantly lower than those obtained using zirconocene-based catalysts but are in the range observed by Nakamura using $Cp^*(\eta^4\text{-}1,3\text{-butadiene})TaR_2$ (R = Me, 1.9 kg PE/h[Ta]mol; Cl, 5.9 kg PE/h[Ta]mol).[12] These data suggest that resonance contribution **1B** may be significant not only to describe structural features but for reactivity as well.

It is not known at the present time whether borollide complexes containing exocyclic substituents that do not participate in π-bonding to boron (*i.e.*, analogous to **4**) would exhibit more electrophilic behavior than compounds such as **1** or **5**. Unfortunately, the preparations of suitable ligands for such complexes are difficult and of low yield, making substitution at boron an attractive alternative. To this end, we have found that reacting **1** with excess $[HNMe_3]Cl$ results in formation of $[H_2N^iPr_2]Cl$ and purple $Cp^*[\eta^5\text{-}C_4H_4BMe]TaMeCl$ (**6**, in Scheme 1), which is isolated in excellent yield (75−85%). How this reaction proceeds is presently unclear. Our current thinking is that protonation occurs at nitrogen (as in **4**), followed by nucleophilic attack of Cl^- on B, and finally, Me for Cl scrambling between Ta and B.[13] These mechanistic questions, as well as reactivity studies of **6** and its derivatives, are the subjects of ongoing investigations.

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Supplementary Material Available: Complete experimental procedures for preparation of compounds in Scheme 1 and X-ray crystallographic determination of **1**−**4** (84 pages); listing of observed and calculated structure factors (scale factor for each set is 10) (96 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[12] Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990.

[13] It appears that this exchange mechanism is facile in these complexes; for example, addition of $Li(N^iPr_2)$ to **6** yields **1** quantitatively: Donnelly, S. J.; Bazan, G. C., unpublished results.