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Synthesis of *endo*-Cp2TaH2(BO2C6H4) and *exo*-Cp2TaH2(BO2C6H4): Regioisomers of the First Tantalum Boryl Complexes[†]

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Recent interest in the chemistry of complexes containing simple metal—boron linkages[1,2] has been fueled by successful metal-mediated functionalization of organic molecules by boron reagents.[3-6] Whereas most efforts have been directed toward late transition metal and lanthanide systems, our interests have been centered on the chemistry of the early transition metal compounds bearing olefin and hydride ligands, where a wealth of mechanistic information suggests the possibility of unique reactivity with respect to hydroboration and the formation of metal—boron bonds. During the course of our work on olefin complexes of groups 4 and 5,[7] we have found that the anionic tantalum complex, {Cp2TaH2Li}$_x$,[8] reacts cleanly with halo-borane reagents to form the first documented tantalum boryl complexes, whose syntheses and structures are the subject of this communication.

Addition of toluene solutions of chlorocatecholborane to {Cp2TaH2Li}$_x$ (1), suspended in toluene at −78 °C, gives a precipitate (LiCl) and a pale tan toluene solution which, upon filtration and evaporation of solvent, affords good yields of an off-white microcrystalline solid (57% yield as an isomeric mixture). ^{1}H and ^{11}B NMR spectra (C6D6) of the reaction mixture indicate formation of two products that can be cleanly separated by fractional crystallization from toluene (eq 1).[9]
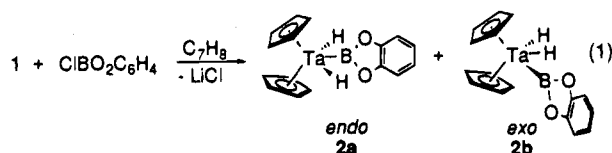
The two products are readily identified by their characteristic ^{1}H NMR spectra as *endo*-Cp2TaH2(BO2C6H4) (**2a**) and *exo*-

† A portion of this work was presented at the 207th National Meeting of the American Chemical Society in San Diego CA (Abstract: INOR 038).

(1) For reviews on metal—boron chemistry,[1a,b] see: (a) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, A., Eds.; Pergamon: Oxford, 1982; Vol. 6, Vol. 6, Chapter 41.1, pp 879. (b) Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 819. (c) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908. (d) Nguyen, P.; Blom. H. P., Westcott, S. A.; Taylor, H. J.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 9329.

(2) This description of "simple" bonds between metals and boron excludes the vast metallocarborane literature. For reviews, see: (a) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, A., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.5. (b) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53.

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(9) Isolated yields of **2a** and **2b** after separation by fractional crystal-lization were 19% and 23%, respectively. ^{11}B NMR (96.234 MHz, C6D6): **2a**, δ 70.0, Δν$_{1/2}$ = 250 Hz; **2b**, δ 64.7, Δν$_{1/2}$ = 190 Hz. See supplementary material for complete spectral data.
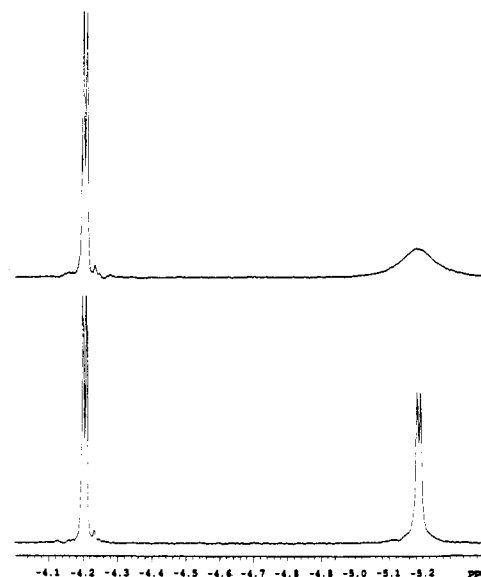

Figure 1. ^{1}H (top) and ^{1}H{^{11}B} (bottom) NMR spectra showing the hydride region for **2b** (500 MHz, C6D6).
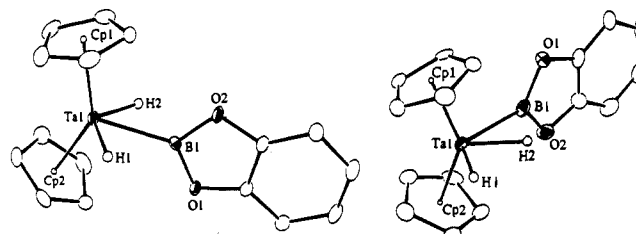

Figure 2. ORTEP drawings of **2a** (left) and **2b** (right), showing 25% probability thermal ellipsoids. Selected bond distances (Å) and angles (°). **2a**: Ta1−B1 2.263(6), Ta1−H1 1.64(6), Ta1−H2 1.54(5), B1−H1 2.11(6), B2−H2 1.75(5); B1−Ta1−H1 63 (2), B1−Ta1−H2 51-(2), H1−Ta1−H2 113(3). **2b**: Ta1−B1 2.295(11), Ta1−H1 1.76(12), Ta1−H2 1.78(10), B1−H2 1.45(10), H1−H2 2.31(20); B1−Ta1−H1 120(4), B1−Ta1−H2 39(3), H1−Ta1−H2 81(6).

Cp2TaH2(BO2C6H4) (**2b**).[10] For the less soluble product (**2a**), the chemically equivalent hydride ligands appear as a single resonance that integrates as two protons versus the cyclopen-tadienyl and catecholate resonances. For **2b**, the high-field region exhibits two resonances (Figure 1): a doublet at δ-4.20 ($|J_{HH}|$ = 5.6 Hz) and a broad resonance at δ −5.15. Since this feature likely resulted from hydride coupling to quadrupolar B or Ta nuclei, we recorded the ^{1}H{^{11}B} NMR spectrum to distinguish between these two possibilities. The well-resolved doublet observed at δ −5.15 clearly shows that boron nuclei are responsible for the observed broadening (Figure 1).[11]

The readily separable isomers **2a** and **2b** were crystallo-graphically characterized, and the resulting molecular structures with relevant metrical parameters are shown in Figure 2.[12] Despite their proximity to heavy tantalum nuclei, hydride positions could be located in difference Fourier maps and refined isotropically for both compounds. In each isomer, the boryl

(10) The *exo* and *endo* terminology is analogous to that used for defining regiochemistry for Cp*2Nb(H)(η^2-CH2=CH2) and related compounds: Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

(11) (a) The magnitude of the coupling in **2b** is temperature independent and similar to that observed in Cp2TaH3 ($|J_{HH}|$ = 9.5 Hz).[11b] Attempts to observe chemical exchange of the hydride positions using spin saturation transfer techniques were inconclusive. (b) Heinekey, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 6074.

(12) **2a**·(C7H8)$_{1/2}$: a = 10.594(6) Å, b = 10.902(8) Å, c = 14.545(8), β = 92.07(5)°, *P*2$_1$/*n* (No. 14-nonstandard setting), *Z* = 4, 2686 unique data ($F_o \geq 2\sigma(F_o)$), R1(*w*/R2) = 2.11(5.03). **2b**: a = 15.859(4) Å, b = 18.131(5) Å, c = 10.025(3), *Pbca* (No. 61), *Z* = 8, 3325 unique data ($F_o \geq 2\sigma(F_o)$), R1(*w*/R2) = 4.52(9.62).

fragment adopts a geometry where the catecholate oxygens and cyclopentadienyl ligands are effectively eclipsed when viewed down the Ta—B vector. Similarities are also observed in the Ta—B distances in **2a** (2.263(6) Å) and **2b** (2.296(11) Å), which compare favorably to the Nb—B distance in $Cp_2Nb(H_2BO_2C_6H_4)$ (**3**). Significantly, the Ta—B distances are shorter than the Nb—B distance (2.411(5) Å) in $Cp_2Nb(H_2BC_8H_{14})$ (**4**), which is almost certainly a true borohydride complex.[13]

Two structural features support the description of *endo* isomer **2a** as an authentic d^0 boryl complex. First, B⋯H contacts to the hydride ligands (1.75(5) and 2.11(6) Å) are longer than those found in archetypal borohydride complexes (B—H = 1.10–1.20 Å)[14,15] and the related niobium complexes **3** (1.69 and 1.62 Å) and **4** (1.38 and 1.39 Å). Second, $\angle H(1)-Ta-H(2)$ (113(3)°) in **2a** is closer to $\angle H_{exo}-Ta-H'_{exo}$ in Cp_2TaH_3 (126°)[16] than the corresponding N—Nb—H angles in **3** (92(2)°) and **4** (70(3)°).

For the *exo* isomer, difference maps revealed two peaks near the expected positions for the *exo* (H(1)), *endo* (H(2)), and hydride ligands. While the position of H(1) is chemically reasonable, as $\angle H(1)-Ta-B$ in **2b** (120(4)°) compares favorably to $\angle H_{exo}-Ta-H'_{exo}$ in Cp_2TaH_3 (126°), the position of H(2) is unusual when both the disparity between $\angle H(1)-Ta-H(2)$ (81(6)°) and $\angle H(2)-Ta-B$ (39(3)°) and the short B⋯H(2) distance (1.45(10)Å) are considered. Unfortunately, the relatively large uncertainties in the hydride positions and the usual caveats concerning hydride positions in heavy atoms structures prevent a quantitative analysis in this case. Thus, we cannot absolutely rule out the possibility that the hydride positions, particularly H(2), are crystallographic artifacts;[17] however, $^{11}B-$ ^1H coupling for this resonance (^1H NMR) lends support to a B⋯H(2) interaction.[18,19] Lastly, the sum of the angles about boron, defined by the tantalum center and catecholate oxygens (360.0(22)°), is consistent with sp^2 hybridization at boron and suggests that the limiting structure that better represents **2b** is a boryl hydride (Ta^V), rather than an agostic borane (Ta^{III}), formulation.[20]

Electronic bases favoring locked geometries in the formally d^0 tantalum complexes **2a** and **2b** are not immediately obvious;[21] however, in both cases filled metal—hydride bonding orbitals of proper symmetry for π-back-bonding to the empty boron p orbital exist and could account for the observed solid-state structures.[22] To probe the solution geometries, we synthesized

analogous complexes (**5a** and **5b**) using B-chloro-5-methyl-catecholborane where the C_{2v} symmetry of the boryl fragment is broken. While the cyclopentadienyl resonances for **5b** broaden dramatically upon cooling, suggesting the onset of decoalescence, we have not reached the low-temperature limit for this fluxional process (-80 °C). Considering the parallels to metal—amide chemistry, low barriers to rotation are not surprising since the static structure corresponding to that adopted by $(\eta^5-C_5Me_5)_2Hf(H)(NHMe)$ in the solid state is not observed in solution.[23]

Formation of regioisomeric products in group 5 metallocene chemistry is rare, but has precedence in addition of silanes to Cp_2TaH_3 where mixtures of *endo* and *exo* isomers are observed.[24] Fine balances in regioselectivity have also been observed in the reactivity of carbon monoxide with zirconium metallocene complexes. CO adds preferentially to the central lobe of the $1a_1$ LUMO[25] of $(\eta^5-C_5Me_5)_2ZrH_2$ to form a product where the hydride ligands are chemically equivalent,[26] while formation of an *exo* acyl isomer as the kinetic product in the carbonylation of $Cp_2Zr(CH_3)_2$ argues strongly for initial "side-on" approach of CO ligand to the $1a_1$ orbital.[27] We view the reaction in eq 1 as proceeding by initial attack of the *filled* $1a_1$ orbital of the tantalum anion on the empty p orbital of the borane. On purely electronic grounds we might expect the *exo* isomer to be the favored one, while steric arguments suggest favored attack at the central site.

To our knowledge, this is the first case where group 5 regioisomers have been cleanly separated and structurally characterized. Furthermore, **2a** and **2b** represent the first unambiguous examples of group 5 boryl complexes. Significantly, **2b** (the major product of eq 1) appears to be the kinetic isomer and is gradually converted to **2a** on heating, which explains our difficulties in preparing **2b** via thermal or photochemical reactions of Cp_2TaH_3 and catecholborane. We are currently investigating the details of the isomerization of **2b** to **2a**, as well as the reactivity of these species, and are pursuing synthesis of other early transition metal boryl complexes.

Supplementary Material Available: Experimental details for the synthesis of **2a** and **2b**, including ^1H and ^{11}B NMR and IR data, and atomic coordinates, thermal parameters, and bond distances and angles for **2a** and **2b** (15 pages); observed and calculated structure factors (38 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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(17) (a) One reviewer suggested using the "low-angle-data" technique of Ibers and La Placa[17b] to improve the position of H(2) in **2b**. The position of the peaks in difference maps at varying resolution in $\lambda^{-1}\sin\theta$ were identical, within experimental error, to the refined positions of H(1) and H(2). A *weak* H(2)⋯B interaction could cause this distortion and account for the spectroscopic observations.[18] (b) La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

(18) We assign the broad resonance at δ -5.18 (300 MHz) in the ^1H NMR spectrum of **2b** to H(2) since this is the only resonance in either isomer that is significantly perturbed on deuterium substitution (^2H NMR: δ -5.49, 46.044 MHz). Perturbation of the other ^1H and ^2H hydride resonances was minimal (comparable to those in $Cp_2TaH_nD_{2-n}$).

(19) For **2b**, two infrared absorptions are observed at 1771 and 1703 cm^{-1}. These appear to be hydride stretches; however, definitive assignment is prevented as one of the corresponding deuteride stretches is partially obscured by catecholate and cyclopentadienyl absorptions.

(20) (a) On the basis of borohydride structures[11] and related "agostic" alkyl structures,[20b] significant lengthening of the Ta—B distance and/or distortion of the boryl geometry might be expected for a structure with substantial "agostic borane" character. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references within.

(21) If all electronic contributions are ignored, preliminary calculations of the energy profile for rotation about the Ta—B bond in **2b** support the notion that the "eclipsed" conformation, observed in the solid-state structure, is disfavored on steric grounds. However, steric barriers for rotation about this bond appear to be small.

(22) Similar π-back-bonding of CO to filled metal—hydride orbitals was suggested to rationalize the magnitude of the C—H coupling observed for the adduct $Cp^*_2ZrH_2(CO)$ ($|J_{CH}| = 23$ Hz): Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244 and references within.

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