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A Continuum Resulting from Equilibrium between Two Structural Extremes in Tungstenocene and Niobocene Boryl and Hydridoborate Complexes. π-Bonding in a d^2 Boryl System and the First d^0 Boryl Complex

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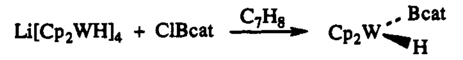
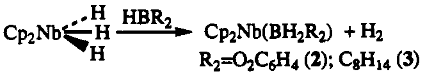
We report the preparation and structures of three early metal complexes containing transition metal-boron bonding interactions, $Cp_2W(H)(BO_2C_6H_4)$ (**1**), $Cp_2Nb[BH_2(O_2C_6H_4)]$ (**2**), and $Cp_2Nb[BH_2(C_8H_{14})]$ (**3**), that demonstrate a continuum between hydridoborate and boryl complexes. Our structural and spectroscopic data indicate that compound **1** contains a boryl ligand, while compound **3** possesses a complexed hydridoborate.[1] Compound **2** lies on the continuum between these two structural extremes. ^1H and ^2H NMR data of partially deuterated **2** reveal large perturbations upon isotopic substitution,[2-4] and careful analysis of this effect demonstrated that the continuum results from a rapid *equilibrium* between two discrete species, a conventional hydridoborate and a novel d^0 boryl.



$$\mathrm{Li[Cp_2WH]_4 + ClBcat \xrightarrow{C_7H_8} Cp_2W(Bcat)(H)} \quad (1)$$

The tungstenocene complex $Cp_2W(H)(Bcat)$ (**1**) was prepared by reaction of $[LiCp_2W(H)]_4$[5] with chlorocatecholborane in toluene solvent (eq 1). Complexes **2** and **3** were prepared by addition of catecholborane (55 °C, 2 h) or 9-borabicyclononane (9-BBN) (20 °C, 2 h) to a toluene/pentane slurry of Cp_2NbH_3. Disubstituted hydridoborate complexes are rare, and $[H_2Bcat]^-$ is not stable. A dialkyl-substituted system of uranium has been prepared from Na[H-BBN],[6] but no previous catecholate-substituted systems are known.



$$\mathrm{Cp_2NbH_3 \xrightarrow{HBR_2} Cp_2Nb(BH_2R_2) + H_2} \quad (2)$$
$$\mathrm{R_2{=}O_2C_6H_4\ (\mathbf{2});\ C_8H_{14}\ (\mathbf{3})}$$

X-ray structural studies were conducted on all three compounds. Figure 1A shows ORTEP drawings with metric parameters (Å) concerning bonding of the boron-containing ligands. The W–B distance of 2.190(7) Å is significantly shorter than that predicted by differences in covalent radii of boron and carbon[7] and by a 2.31-Å distance in a tungstenocene alkyl hydride[8] or distances of 2.19–2.22 Å for $Cp_2W–C(sp^2)$ bonds.[9-11] Consistent with this relationship, the catecholate substituent on boron is oriented to enable the directed HOMO of the metallocene fragment[12] to overlap with the boron p-orbital, providing a W–B π-bond, similar to the Ta–C or Hf–N π-bond in the isoelectronic $Cp_2Ta(H)$(alkylidene)[13] and $Cp^*{}_2Hf(H)(NHMe)$.[14] Geometries dictated by π-interactions[15] and short M–B distances may not be related directly, but the two observations appear general. Our previously reported $CpFe(CO)_2Bcat$ showed both features, and the several structurally characterized Ir(III) catecholboryl compounds[16-18] display Ir–B distances that are equal to or *shorter* than those in the corresponding Ir(III)–aryl compounds.

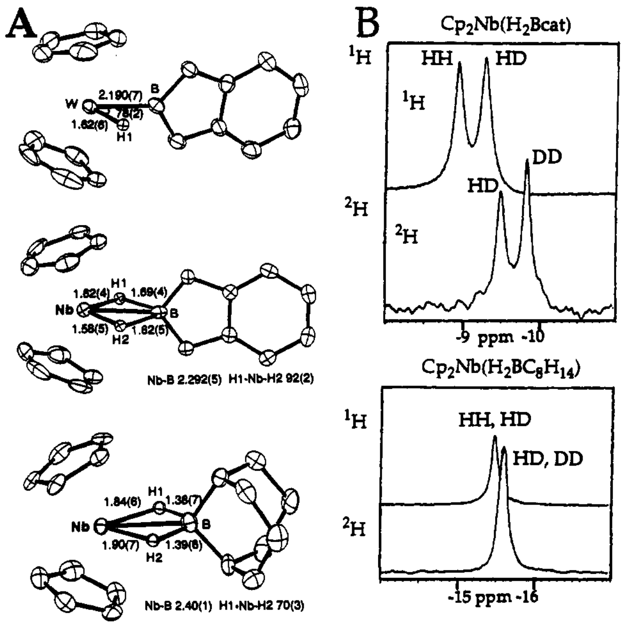


Figure 1. (A) ORTEP drawings of **1** (top), **2** (middle), and **3** (bottom). (B) ^1H and ^2H NMR spectra (–70 °C) of a sample of **2** (top) and a sample of **3** (bottom) containing no deuterium, a single deuterium, and two deuterium atoms in the hydride positions. ^1H NMR spectra were referenced to protiated toluene and ^2H NMR spectra to toluene-d_1 to minimize intrinsic isotope effects.

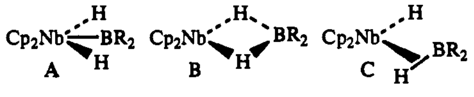


Figure 2. Extremes in the continuum for bonding in **2** and **3**.

Figure 2 shows three potential structural extremes in the bonding of hydridoborate ligands. Our structural and spectroscopic data indicates that complex **2** possesses a significant contribution from structure **A**, while complex **3** results from predominantly structure **B**. The Nb–B bond length in **2** is 2.292(5) (Å), significantly shorter than typical metallocene hydridoborate M–B distances, such as the d^1 $Cp_2Ti(BH_4)$ (2.36 Å),[19] or a series of d^0 metallocene hydridoborates (>2.5 Å).[20,21] Rather the Nb–B bond length corresponds more closely to the distance for a niobocene boryl complex as determined by covalent radii.[7] When formulated as a d^0 species possessing two terminal hydrides and a boryl ligand, no π-interaction could exist in **2**. The dialkyl-substituted complex **3** displays a W–B distance that is an additional 0.1 Å longer than that in **2**. Although steric factors may help to lengthen the Nb–B distance in **3**,[22] it is likely that the lack of

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π-donating substituents in **3** makes the boron center more electrophilic, the B–H interaction stronger, and the complex more similar to the structural extrene B in Figure 2.

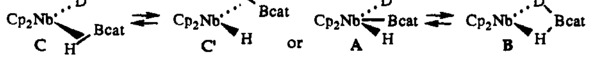
The hydrides in **1**–**3** were located and refined. Although approximate as determined by X-ray diffraction, the B–H distances in **2** are 0.4–0.5 Å longer than those in d^0 metallocene hydridoborates and are similar to the W–H distance in **1** and the Nb–H distances in Cp_2NbH_3 (1.65(6)).[23] The H–M–H angle in **2** is intermediate between the 50–60° angles in d^0 hydridoborates[1] and the 126° angle for the two outside hydrogens in group V metallocene trihydrides.[23] These data corroborate a dominant contribution from A in the structure of **2**. The Nb–H bond lengths in **3** are longer, the B–H distances are shorter, and the H–Nb–H angle is smaller than that in **2**, indicating a larger contribution from B.

We propose that ^{11}B NMR spectroscopy is a simple and conclusive test for determining the position on the continuum between A and B. Comparison of the ^{11}B NMR chemical shift to known boryl ligands containing identical substituents will indicate the degree of interaction with the hydrogens to create a four-coordinate borate rather than three-coordinate boryl complex. Four-coordinate borates resonate far upfield of the corresponding three-coordinate and neutral species. The differences in chemical shifts for alkoxy-substituted boranes are not as large as they are for alkylboranes, and other examples of $[H_2Bcat]^-$ complexes are not known. Nevertheless, the four-coordinate pyridine complex of catecholborane resonantes 20 ppm upfield of free catecholborane, confirming that a substantial upfield shift would be expected for form B of complex **2**.

The ^{11}B resonance for catecholate-substituted niobium compound **2** is essentially identical (δ 59) to that of the *bona fide* catecholboryl complex **1** (δ 57) and is similar to or downfield of those for iridium, rhodium, and iron.[2,15,17] In contrast, the alkyl-substituted system **3** shows a chemical shift of δ 57 that reflects a large upfield shift relative to known dialkylboryl or diaryl compounds of iridium, rhodium,[24] and iron,[15] all of which resonate at greater than δ 100 ppm.[25] The chemical shift of **3** therefore reflects a large contribution of hydridoborate structure B.

Isotopic perturbation of equilibrium[2–4] has been used to probe hydrogen complexes and agostic interactions.[26–28] Perturbations in the chemical shifts are observed for partially deuterated compounds in these experiments because of a difference in chemical shift between two rapidly exchanging positions on the same molecule and a preference by the deuterium for one of the two chemically inequivalent locations. ^1H, ^2H, and ^{11}B data for **2** revealed large perturbations upon isotopic substitution and demonstrate a rapid *equilibrium* between structures A and B of the niobocene complex **2**. Thus, the continuum suggested by NMR spectroscopy of unlabeled material is attributed to two species in rapid equilibrium, rather than a single species that exists as a resonance hybrid of two structures.

The exchange between unsymmetric compounds C and C′ in eq 3 is degenerate in the absence of isotopic perturbation and will provide different results from the exchange between the two different complexes A and B that are symmetric in the absence of isotopic substitution. Figure 1B shows ^1H and ^2H NMR spectra (−70 °C to reduce quadrupolar broadening) for a sample of **2** and **3** containing all three possible isotopic combinations at the hydride position. The portion of compound **2** that contains a single deuterium in the hydride position displayed ^1H and ^2H NMR chemical shifts that were similar, while the fully deuterated material displayed a perturbation that was larger than that for singly deuterated material. This behavior is inconsistent with the topology of degenerate exchange within an unsymmetric structure such as C. Such an exchange would give ^1H and ^2H NMR resonances for monodeuterated material that are perturbed in opposite directions and a ^2H NMR resonance for fully deuterated material that is similar in chemical shift to the ^1H NMR resonance of the protiated material. Instead, a rapid equilibrium between the two structures A and B, each residing at its own minimum in the potential energy surface with hydrides in chemically equivalent positions, is consistent with the ^1H and ^2H NMR spectroscopic results in Figure 1B.[29] These isotopic perturbation results demonstrate the importance of obtaining both ^1H and ^2H NMR spectra when concluding that a *degenerate* equilibrium exists.



(3)

The rapid time scale and solid phase of X-ray diffraction is likely to reveal only a single form of the two species in the rapid equilibrium detected by the slower, solution-phase NMR spectroscopy.[30] Crystallographic data for **2** provides a structure that does not display disorder or large thermal ellipsoids and possesses the dominant characteristics of a Nb(V) boryl complex. It is likely, therefore, that this structure corresponds to the component in the equilibrium that most resembles the structural extreme A. Although the H–Nb–H angle cannot be clearly defined by X-ray diffraction, the value of 92°, along with the orientation of the boryl substituents, allows for a weak B–H interaction to remain in the species best described as a d^0 niobium(V) boryl.

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Note Added in Proof: Niobocene and Tantalocene fragments bonded to catechol-substituted boron centers were discussed recently after review of this manuscript. Data for these compounds support metal–boron bond lengths and ^{11}B NMR chemical shifts predicted in this paper for d^0 boryl systems. Smith, M. R.; Lantero, D. R.; Motry, D. H. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA, 1994; American Chemical Society: Washington, DC, 1994; INOR 38.

Supplementary Material Available: Spectroscopic and analytical data for **1**–**3** and full ORTEP drawings, positional parameters, anisotropic thermal parameters, intramolecular distances and angles, torsion or conformation angles, tables of least squares planes, and experimental details for X-ray structural studies of **1**–**3** (47 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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(22) Oxidative addition of 9-BBN to square planar Ir(I) gives a boryl compound with a distance that is 0.5–0.7 Å longer than those in similar, but not directly analogous, octahedral catecholboryl compounds. References 16–18.

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(25) Although not stable enough to isolate in pure form, the diphenylboryl analog of **1** $Cp_2W(H)(PBh_2)$ has been identified spectroscopically and displays a ^{11}B NMR resonance at δ 114, indicating that dialkyl and diaryl d^2 boryl complexes display shifts that are similar to those of analogous d^6 boryl systems.[15]

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(29) A reviewer has noted that this equilibrium draws analogy to the general trend that addition of alkylboranes to Rh(I) hydrides provides hydridoborate complexes, while addition to Ir(I) gives Ir(III) boryl compounds. Unfortunately, there are not currently published examples of the same ligand sphere and borane substitution for the two metals that would allow for direct comparison.[17,24] Baker, R. T.; Ovenall, D. W.; Harlow, R. L.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *Organometallics* **1990**, *9*, 3028.

(30) Infrared spectroscopy provides a potential method to observe both forms of compound **2**. We have investigated the IR spectra of **2** and **3** in hydrocarbon solvents, Nujol, and KBr. Compound **3** clearly shows only a single band involving the hydrides (comparison with **3**-d_2) at 1605 cm^{-1} in pentane. In contrast, two bands were observed for compound **2** (1622, 1725 in pentane; 1675, 1742 in KBr). Yet, these bands are broad; and we are reluctant to assign these to the two forms of **2**, since it is difficult to distinguish one of them from a band due to Cp_2NbH_3 (1720 cm^{-1} in pentane, 1710 in KBr) that may result from hydrolysis.