Facile Reduction of an Unsaturated Chromaborane

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*Summary: The reduction of $Cp*_2Cr_2B_4H_8$ (**1**) by Na/Hg to yield $[Na][Cp*_2Cr_2B_4H_8]$ (**2**) and its oxidation back to **1** is described. Although **2** has not been crystallographically characterized, changes in the paramagnetic ^{11}B NMR spectra of mixtures of **1** and **2** as a function of composition show that both species have closely related structures. The facile reduction and the lack of cluster structure change support the characterization of **1** as an electronically unsaturated metallaborane cluster.*

Introduction

We have described the chromaborane $Cp*_2Cr_2B_4H_8$ (**1**) as an electronically unsaturated cluster in the sense that it lacks one cluster bonding pair of the six formally required to support its observed cluster geometry.[1,2] Compensation for the missing pair by further condensation of the cluster fragments via additional capping is not possible, and Cr−Cr multiple bonding is apparently not an option either. Ready addition of Lewis bases to form Cr_2B_4 clusters with saturated cluster bonding provides empirical support for the electronic unsaturation of **1**.[3] More recently, we have described $Cp*_2Mo_2Cl_2B_3H_7$ as unsaturated in the same sense.[4] In both the Cr and Mo compounds a molecular orbital (MO), that is principally MM bonding and MB antibonding and is filled in metallaboranes containing later transition metals, lies at high energy and is unoccupied.[4,5] The characteristics of this MO correlate nicely with small changes in cluster core geometry on going from unsaturated to saturated derivatives (shorter MM distance, longer MB distances).

The addition reactions of **1** with electron donors is a better proof of unsaturation than formal rules or MO calculations, but the addition of even a relatively simple ligand such as CO constitutes a large perturbation.[2,3,6] Thus, we sought additional empirical evidence supporting the description of **1** electronically as unsaturated. We have now investigated the ease of electron addition to **1** to form the radical anion and its oxidation back to the original molecule. As the desired information is the extent of structural change on reduction, chemical reducing agents were chosen rather than electrochemical studies in order to enhance the possibilities of full

characterization as well as to facilitate an investigation of the reactivity of the radical anion.

Experimental Section

General Procedures. All reactions were carried out under an argon or nitrogen atmosphere using Schlenk or drybox techniques.[7] Glassware was flame-dried, and solvents were purified by distillation under a nitrogen atmosphere before use: ether, hexane, toluene, and THF were distilled from sodium/benzophenone. **1** was prepared as reported elsewhere.[2] ^1H and ^{11}B NMR spectra were measured on a Varian 300 FT-NMR spectrometer (^{11}B NMR; 96.2 MHz). ^1H and ^{11}B NMR were referenced to residual solvent protons and external $[NMe_4][B_3H_8]$ (−29.7 ppm), respectively. IR spectra were recorded on a Nicolet 205 FT-IR spectrometer. Mass spectra were obtained on a Finnigan MAT Model 8400 mass spectrometer.

Reaction of $Cp*_2Cr_2B_4H_8$ with Na/Hg. A solution of **1** (40 mg, 0.094 mmol) in THF (5 mL) was treated with Na/Hg (Na, 7 mg, 0.30 mmol; Hg, ∼2 g) at room temperature. The brown solution changed slowly to dark brown. After it was stirred for 1 h, the THF solution was transferred to another Schlenk flask by cannula. The solvent was removed under reduced pressure. The resulting solid was washed with hexane (5 mL × 3), and dried in vacuo to yield a highly air-sensitive pale brown powder of $[Na][(Cp*Cr)_2B_4H_8]$ (**2**; 24 mg, 0.053 mmol, 57%). IR (KBr, cm^{-1}): ν(BH) 2430 w, br; 2376 w, br. Because no chromocene-free product could be obtained (see below) chemical analysis was not attempted.

The ^{11}B NMR spectrum of **2** in THF is temperature-dependent. A single broad singlet was observed for **2** with a chemical shift that varied approximately linearly from 57 ppm (fwhm = 1280 Hz) at −80 °C to 13 ppm (fwhm = 730 Hz) at 22 °C. The ^1H NMR spectrum in THF-d_8 consistently exhibits two broad signals that are temperature dependent. A singlet at δ −6.5 (fwhm = 60 Hz) is assigned to an impurity of $Cp*_2$-Cr commonly observed on the decomposition of **1**. This signal remains unaffected during the oxidation of **2** (see below). A singlet at δ 3.3, (fwhm = 35 Hz) at −60 °C varies nearly linearly to δ 2.7, (fwhm = 20 Hz) at 22 °C. Another unidentified impurity was observed at δ −9.1 on one occasion.

The chemical shifts of the signals assigned to **2** varied significantly depending on sample history, i.e., the number of manipulations and age. The purest sample of **2** had δ 13 in the ^{11}B spectrum and δ 3.6 in the ^1H spectrum at 22 °C. For this reason, the time dependence of the ^1H and ^{11}B NMR spectra of **2** were examined in THF-d_8. A solution of $(Cp*Cr)_2B_4H_8$, (**1**; 20 mg, 0.047 mmol) in THF-d_8 (2.5 mL) was treated with Na/Hg (Na: 5 mg, 0.217 mmol) at room temperature. The reaction mixture was stirred for 15 min, and the THF solution was transferred by cannula to an NMR tube capped with a septum. The ^1H NMR and ^{11}B NMR spectra were then monitored over a period of 118 h. Some $Cp*_2Cr$ was

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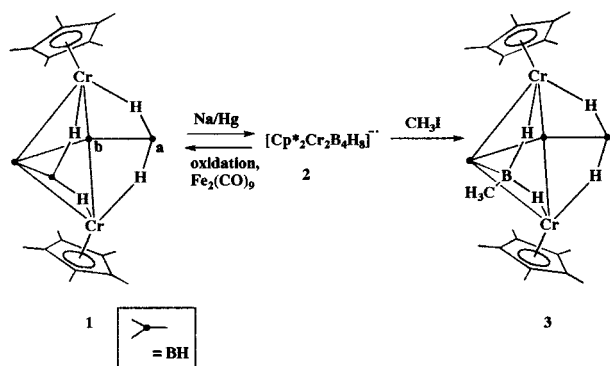(3) Hashimoto, H.; Shang, M.; Fehlner, T. P. *Organometallics* **1996**, *15*, 1963.

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Scheme 1

Table 1. ^{11}B NMR Data of Mixtures of 1 and 2

$f_p{}^a$	δ(B(a)), ppm	fwhm,^{b} Hz	δ(B(b)), ppm	fwhm,^{b} Hz
0	34.6	263	126.4	102
0.015	34.3	263	109	537
0.17	31.2	289	c	c
0.36	27.4	662	c	c
0.47	25.2	772	c	c
0.54	23.8	823	c	c
0.63	22.1	776	c	c
0.69	21.0	779	c	c
0.75	19.7	791	c	c
0.98	15.2	727	c	c
1.0	14.8	707	c	c

^{a} Mole fraction of paramagnetic **2**. ^{b} Coupled. ^{c} Not observed.

present at the beginning, and its signal intensity remained constant over the course of the experiment. The broad signal due to **2** shifted as air slowly diffused through the septum until, ultimately, the two normal signals of diamagnetic **1** were observed.

Reaction of Cp*$_2$Cr$_2$B$_4$H$_8$ with Li Metal and with K Metal. A solution of **1** (40 mg, 0.094 mmol) in THF (5 mL) was treated with Li metal (3 mg, 0.43 mmol) at room temperature. After the mixture was stirred for 1 day, the supernatant was transferred into an NMR tube and the ^{11}B NMR spectrum was measured. As was the case with Na/Hg, **2** was observed; however, the reaction was not satisfactory, as clean reduction depends on the state of the surface of the Li metal. A similar attempt with K metal apparently resulted in complete decomposition, as no signal was observed in the ^{11}B NMR spectrum.

Reaction of [Na][(Cp*Cr)$_2$B$_4$H$_8$] with PPN$^+$Cl$^-$. To a suspension of PPN$^+$Cl$^-$ was added the solution of **2** in THF at room temperature. The reaction mixture was stirred for 1 day. There was no color change observed. After filtration to remove a white precipitate, a ^{11}B NMR spectrum showed the presence of **2**. However, the observed chemical shift, δ 29.7, suggests substantial oxidation had taken place even though the change in cation may also contribute to the downfield shift. Slow evaporation under an argon flow gave dark brown crystals; however, no crystal suitable for X-ray analysis was found.

Reaction of [Na][(Cp*Cr)$_2$B$_4$H$_8$] with MeI. To a solution of **2** (32 mg, 0.075 mmol) in THF (5 mL) was added MeI (5 μL, 0.080 mmol) by microsyringe at room temperature. After removal of solvent, the resulting residue was extracted with hexane. After filtration, the hexane extract gave a mixture of **1** (~80%) and Cp*$_2$Cr$_2$B$_4$H$_7$CH$_3$ **3** (~20%). Similar solubilities of **1** and **3** in hexane prevented separation by fractional crystallization; however, spectroscopic measurements on the mixture were sufficient to identify **3**. MS (EI): spectrum of **1** + p$^+$ m/z 440, isotopic distribution corresponding to 4 B, 2 Cr, exact mass m/z 440.2312 (obsd), 440.2333 (calcd) for C$_{21}$H$_{40}$B$_4$Cr$_2$ (weighted average of Cr isotopes). ^{11}B NMR (THF, 22 °C, δ): spectrum of **1** + 128.4, d, J = 130 Hz, {^{1}H} s, 1B; ≈ 125, sh, position obscured by **1**; 46.8, br s, fwhm = 160 Hz, {^{1}H} s, fwhm = 107 Hz, 1B; 35.7, br s, fwhm = 260 Hz, {^{1}H} s, fwhm = 100 Hz, 1B. These data are consistent with methyl substitution at a boron atom lying on the open face of **1**, i.e., B(a) (Scheme 1).

Reaction of [Na][(Cp*Cr)$_2$B$_4$H$_8$] with Fe$_2$(CO)$_9$ and Co$_2$(CO)$_8$. To a solution of **2** which had been obtained from the reaction of **1** (30 mg, 0.070 mmol) with Na/Hg (Na, 10 mg, 0.435 mmol; Hg, ca. 2 g) in THF (5 mL) was added the solution of Fe$_2$(CO)$_9$ (25 mg, 0.068 mmol) or Co$_2$(CO)$_8$ (25 mg, 0.073 mmol) in THF (3 mL) at room temperature. Each reaction mixture was stirred for 3 h, after which time the ^{11}B NMR spectrum showed only the signals due to **1**.

Results and Discussion

The spectroscopic and chemical evidence shows that the principal product of the reaction of **1** with Na/Hg is the one-electron-reduced compound [Na][Cp*$_2$Cr$_2$B$_4$H$_8$] (**2**). As summarized in Scheme 1, reaction of **1** with 1 equiv of Na/Hg (or Li) results in the formation of a single boron-containing species which is soluble in THF but insoluble in hexane and toluene. The temperature-dependent, broad singlet observed in the ^{11}B NMR as well as the temperature-dependent broadened singlet in the ^{1}H NMR confirms that the product is paramagnetic. The ^{1}H resonance is assigned to the Cp* methyl groups and is found at a low chemical shift relative to normal Cp* ligands. The fact that NMR spectra are observed implies rapid electron relaxation. The BH stretching modes in the IR fall at somewhat lower frequencies than those of the neutral precursor, consistent with an anionic species and require that the amount of **1** present be less than ~15%. Oxidation of the product by traces of air or chemical means leads to the re-formation of **1**. On the other hand, reaction of **1** with CH$_3$I leads to the formation of Cp*$_2$Cr$_2$B$_4$H$_7$CH$_3$ (**3**).

As all attempts to obtain a solid-state structure of **2** failed, it may seem that the question addressed by the experiment is unanswerable. However, to answer it we only need qualitative information on the structural effects of the addition of an electron to **1**. Is there a large change in cluster structure or not? As it turns out, the NMR properties of a solution of **2**, as it is oxidized back to **1**, provide the answer to this question. The usefulness of paramagnetic NMR spectra of mixtures of redox pairs has been described previously.[8-11]

The ^{11}B NMR data for the slow oxidation of **2** to **1** are given in Table 1. The observation of only one signal for the B(a) boron atoms rather than superimposed signals for two species throughout the composition range indicates a rapid symmetrical electron transfer between **2** and **1**. Thus, the observed chemical shift for B(a) is the mean of the chemical shifts for **1** and **2** weighted for the mole fractions of each; i.e., it will depend linearly

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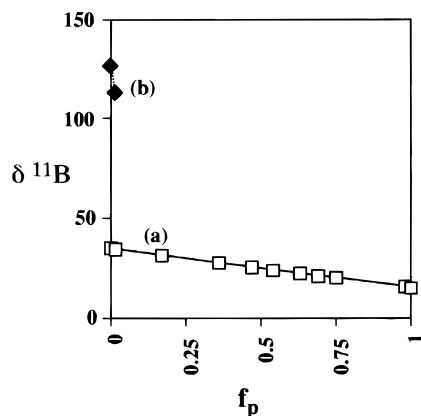
Figure 1. Plot of the chemical shift of the two boron signals observed in mixtures of $Cp^*_2Cr_2B_4H_8$ (**1**) and $[Na][Cp^*_2Cr_2B_4H_8]$ (**2**) in THF as a function of the mole fraction of **2** (f_p). The solid diamonds are the chemical shifts of B(b) and the open squares those of B(a), as designated in Scheme 1 and Chart 1.
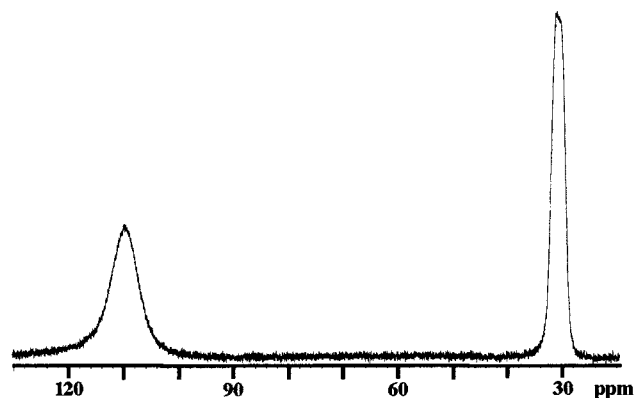

Figure 2. ^{11}B NMR spectrum of a mixture of $Cp^*_2Cr_2B_4H_8$ (**1**) with approximately 2% $[Na][Cp^*_2Cr_2B_4H_8]$ (**2**) in THF showing the much larger effect of the paramagnetic center on the lower field signal of the boron atoms directly bonded to the chromium atoms, B(b), than on the higher field signal of the boron atoms bonded through bridging hydrogens to the chromium atoms, B(a). Atom designations are given in Scheme 1 and Chart 1.

on the mole fraction of **2**. This is demonstrated in Figure 1. The calculated paramagnetic shift is −19.8 ppm, and the paramagnetic line width is 444 Hz. Because of its width the signal for the B(b) borons is only observed for a solution with a tiny amount of **2** (Figure 2). However, the limited data indicate a large negative paramagnetic shift (estimated to be −700) with a correspondingly large paramagnetic line width. Al-

Chart 1
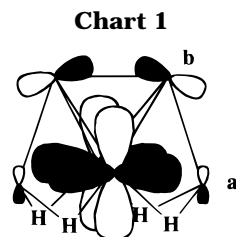
though not quantitative, the observations are sufficient to show that the B(b) borons are more strongly affected by the paramagnetic center than are the B(a) borons. It is also clear that electron exchange between **1** and **2** is rapid, which requires both species to have closely related structures. Apparently, the addition of an electron to **1** does not appreciably affect the cluster structure. The ^1H NMR data for the Cp* protons are in qualitative agreement.

The paramagnetic shifts are related to the actual spin density on the resonating nuclei; i.e., they reflect the properties of the HOMO of **2**, which is the LUMO of **1** if structural differences are small.[12,13] The LUMO of **1** produced by a Fenske−Hall MO calculation is shown in Chart 1 (view down the Cr−Cr axis).[5] It is principally MM δ bonding and MB antibonding and has 69% Cr character and 25% B character with 80% of the latter on B(b). Consistent with these calculated properties, the measured paramagnetic effects are much larger for B(b) than for B(a).

Conclusion

The formation and partial characterization of the radical anion of **1** provides corroboration of our description of chromaborane **1** as an electronically unsaturated cluster. The existence of rapid electron transfer between the two species implies little structural consequence to the addition of an electron to **1**, as expected for an unsaturated species. Further, the properties of the LUMO of **1** agree with the differing magnitudes of the paramagnetic effects on the two types of boron atoms, thereby supporting the MO description of the origin of the electronic unsaturation.

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