Substitution on Metallaboranes at Boron. Syntheses of *closo*-1-X-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H$], X = Cl and OH, and *closo*-1,5-Cl_2-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2$] from *closo*-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H_2$][†]

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The reaction of *closo*-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H_2$], **1**, with metal chlorides results in the formation of either *closo*-1-Cl-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H$], **2**, or *closo*-1,5-Cl_2-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2$], **3**, depending on chlorination reagent. Hydrolysis of **1**, yields *closo*-1-OH-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H$], **4**. Isolated yields of **2** and **4** are modest to good, and all compounds have been characterized spectroscopically as simple substitution derivatives of **1**. The substituent effects have been probed by ^{11}B NMR measurements and compared with those for other substituted borane and metallaborane clusters. The observation of an enhanced antipodal effect shows that **1** possesses a characteristic property of a five-atom closo cage suggesting delocalized cluster bonding that includes both the boron and metal centers.

Introduction

Some of the earliest information on the reactivity of the polyhedral boranes originated in studies of the electrophilic substitution of cage B−H terminal bonds.[1] Correlations with calculated parameters associated with electronic structure, e.g., charge distribution, gave fundamental insights into the nature of these new compounds.[2] Such studies, including those aimed toward peralkylation or halogenation,[3] continue to be of significant interest as they permit the suitable modification of physical properties to solve, for example, problems associated with practical applications of complex cage assemblies.[4] Further, derivative chemistry has been shown to be crucial in some instances, e.g., modification of the reactivity of carborane fragments such that multiple stacking reactions are possible.[5,6]

Very little similar information is known for metallaboranes although the metallacarboranes, already mentioned, constitute one exception[7,8] and there are other notable cases.[9−11] The properties of metallaboranes are considerably different from those of pure boranes, and it is not at all clear yet what factors will dominate the substitution chemistry. The absence of any systematic derivative chemistry has also inhibited the further development of these compounds. That is, the functionalization of a cage permits a greatly expanded reactivity; e.g., cluster carboxylates can be used as ligands to form large cluster assemblies.[12,13] Of course, derivative chemistry requires useful synthetic routes to the parent compounds, and the absence of simple, high yield routes to most metallaboranes lies behind the lack of a developed derivative chemistry.

Recently we reported a new synthetic approach to a number of metallaboranes containing the Cp*Co fragment, Cp* = η^5-C_5Me_5.[14−16] These compounds can be easily made in 0.1 g quantities from $[Cp^*CoCl]_2$ and commercially available monoboranes, and their availability presents an opportunity for the systematic study of their chemistry. Here we report the results of an investigation of the reactivity of *closo*-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H_2$], **1**, with a focus on substitution at the cluster B−H terminal bonds by the electronegative Cl and OH groups.[14,16]

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk line techniques.[17] Solvents were predried over 4-Å molecular sieves (tetrahydrofuran, CH_2Cl_2) or KOH (hexanes, toluene) and purged with N_2 prior to distillation. Diethyl ether, tetrahydrofuran (THF), hexanes, toluene, and pentane were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from CaH_2. The starting material *closo*-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2Co_3B_2H_2$], **1**, was prepared according to published procedures.[16] The metal halides $FeCl_2$ and $CoCl_2$ were dried by heating them under vacuum.

NMR spectra were measured at 300 MHz, and solvent was used as reference for ^1H and ^{13}C NMR spectra whereas a sealed tube containing $[(NMe_4)(B_3H_8)]$ (δ −29.7 ppm) was used as an external reference for ^{11}B NMR spectra. Infrared spectra were measured on a Nicolet 205 FT-IR spectrometer. Mass spectra were measured on a Finnigan MAT Model 8400 or JEOL JMS-AX505HA mass spectrometer.

[†] Dedicated to Prof. Dr. Walter Siebert on the occasion of his 60th birthday.

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***closo*-1-Cl-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], 2.** A toluene solution (4 mL) of **1** (≈85 mg, 0.14 mmol) was combined with a toluene solution (4 mL) of $[Cp^*CoCl]_2$ (180 mg, 0.39 mmol), and the mixture was heated to reflux (110−115 °C). The reaction mixture was checked periodically by ^{11}B NMR spectroscopy to monitor conversion of **1** to products. After all the **1** was exhausted (24 days) the solvent and volatiles were removed by pumping. Addition of hexane to the residue did not dissolve boron-containing products appreciably; therefore, a toluene extraction was carried out, to yield 41 mg of crude product (≈45%). The major species in the mixture was *closo*-1-Cl-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], **2**, which was purified by column chromatography on silica gel at −19 °C. It elutes in hexane with ca. 1% toluene.

Spectroscopic and analytical data for **2** follow. MS (EI): $P^+ = 642$, 2 boron atoms, 1 Cl atom. NMR: ^{11}B, hexanes, 18 °C, δ 61.41 (br, fwhm = 400−470 Hz, {^1H}, s, fwhm = 200−300 Hz), 121.03 (s, fwhm = 50 Hz, {^1H}, fwhm = 50 Hz); ^1H, C_6D_6, 18 °C, δ 1.694 (s, ≤ 3 Cp*), −20.9 (s, fwhm = 54 Hz, 2 BHCo), $^{13}C\{^1H\}$, C_6D_6, 18 °C, δ 11.36 (C*C*H$_3$), 92.92 (*C*CH$_3$). IR (CH_2Cl_2, NaCl, cm^{-1}): 2452 w, 2443 sh, BH; 1707, 1660, 1605.

***closo*-1,5-Cl_2-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2$], 3.** A THF solution (5 mL) of **1** (18 mg, 0.030 mmol) was chilled to −30 °C. To it was added a THF solution of $FeCl_3$ (0.07 M, 0.42 mL, 0.03 mmol). The solution was stirred at −20 °C for a few minutes before allowing it to warm to ambient temperature. After ≈2 h the ^{11}B NMR spectrum revealed weak product signals, and another portion of $FeCl_3$ was then added (0.42 mL of 0.07 M solution, 0.03 mmol). The reaction mixture was stirred overnight. The ^{11}B NMR spectrum after a total of 15 h revealed complete consumption of **1**, and the solvent was removed in vacuum. The product is insoluble in hexanes, toluene, and diethyl ether but dissolves in THF and CH_2Cl_2. Significant impurity signals in the ^{11}B NMR were observed in the crude product. Multiple washing of a single sample with hexanes reduced intensities of these species relative to that of **3** by an order of magnitude but did not completely remove them. A filtered solution was layered with hexane, and after a week at room temperature block-like, air-stable crystals of *closo*-1,5-Cl_2-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2$], **3**, formed but were found to be twinned.

Spectroscopic and analytical data for **3** follow. MS (EI): $P^+ = 676$, 2 B atoms, 2 Cl atoms. NMR: ^{11}B, THF, 22 °C, δ 123.9 (fwhm = 60−70 Hz, {^1H}, fwhm = 60−70 Hz, 1 B); ^1H, $(CD_3)_2CO$, 22 °C, δ 1.76 (s, fwhm = 5 Hz, 3 Cp*), −20.39 (s, fwhm = 140 Hz, 2 BHCo); $^{13}C\{^1H\}$, $(CD_3)_2CO$, 20 °C, δ 11.08 (C*C*H$_3$), 99.14 (*C*CH$_3$). IR (THF, KBr, cm^{-1}): no bands observed in range 2700−1700 cm^{-1}.

The reaction of **1** with $CoCl_2$ provides an alternate route to **3** albeit in a more complex mixture. In a small round-bottom flask **1** (16 mg, 0.026 mmol) was combined with $CoCl_2$ (13 mg, 0.10 mmol). THF was added (3 mL), and the solution was stirred overnight. After 12 h the yellowish-brown reaction mixture was filtered to remove a dark gray residue, and the ^{11}B NMR spectrum of the THF filtrate showed the presence of **3** as well as a number of other boron-containing compounds.

***closo*-1-OH-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], 4.** Solid **1** (184 mg, 0.303 mmol) was dissolved in THF (9 mL). At room temperature, N_2-purged H_2O (0.08 mL, 4 mmol) was added. The solution was then heated to reflux (ca. 70 °C). The ^{11}B NMR spectrum was checked after 3, 6, and 14 days and indicated that reaction was taking place slowly. An excess of N_2-purged H_2O (0.32 mL, 18 mmol) was then added. After an additional 6 days of heating of the solution, all of **1** had been consumed, and the major product was *closo*-1-OH-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], **4**. The yield of filtered, crude product was 0.095 g (50%). Column chromatography was performed with hexane/20% toluene (silica gel, 5 cm h × 3.5 cm d, −18.7 °C). The toluene solution containing **4** was applied to the column and eluted with hexane/20% toluene. It moved part of the way down the column. Elution with toluene gave a light brown fraction that did not contain **4**. Elution with ether gave a yellow fraction with no ^{11}B NMR signal, followed by a brown fraction that contained **4**. In an alternative approach, it was found that **1** converts to **4** in roughly 50% NMR yield within 18 h by bubbling air into a THF solution for ∼30 s, and then leaving it open to the atmosphere.

Spectroscopic and analytical data for **4** follow. HRMS (FAB): $P^+ = 624$, 2 boron atoms, calculated for $^{12}C_{30}{}^1H_{49}{}^{11}B_2{}^{59}Co_3O$, *m/e* 624.1965, observed, *m/e* 624.1953. NMR: ^{11}B, diethyl ether, 18 °C, δ −3.06 (d, J_{BH} = 120 Hz, fwhm = 300 Hz, {^1H}, s, fwhm = 140 Hz), 48.28 (s, fwhm = 250 Hz, {^1H}, s, fwhm = 250 Hz); ^1H, C_6D_6, 18 °C, 7.0 (br, OH), 2−3 (br, BH_t), 1.79 (s, fwhm = 2−4 Hz, ≤ 3 Cp*), −20.3 (br d, fwhm = 140 Hz, 2 BHCo); $^{13}C\{^1H\}$, C_6D_6, 19 °C, δ 11.30 (C*C*H$_3$), 93.61 (*C*CH$_3$). IR (KBr pellet, cm^{-1}): 2472 w (BH), 2985−2967 w, 2901 m, 2867−2848 w.

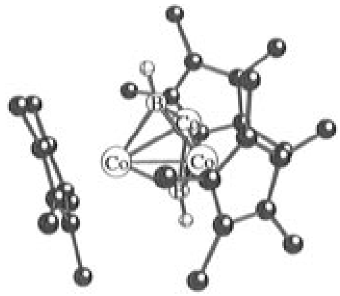

Figure 1. Ball and stick representation of the X-ray solid state structure of closo-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H_2$], **1**. The methyl and the framework hydrogen atoms were not located in the structure determination and are not shown.

Attempted Deprotonation of 1. To a stirred hexanes solution containing **1** (21 mg, 0.034 mmol) was added NEt_3 (0.2 mL, ∼40-fold excess). Observation by ^{11}B NMR spectroscopy indicated that no reaction had occurred after >15 h at ambient temperatures. The **1** recovered from the NEt_3 experiment was redissolved in hexanes and chilled to −20 °C. Then *n*-BuLi (∼0.017 mmol) was added as a dilute hexane solution. The ^{11}B NMR spectra measured after 1 h, 3 h, and overnight indicated no reaction had occurred. After more than a 10-fold excess of *n*-BuLi (0.16 mmol more) was added and the mixture was stirred 3 h and then overnight, there was still no reaction.

Thermolysis of 1. A sample of **1** (15 mg, 0.024 mmol) was dissolved in THF, transferred to a Schlenk tube equipped with reflux condenser, and refluxed at 72−77 °C. After a total of 10 days of heating the ^{11}B NMR spectrum revealed a majority of unreacted **1** but also minor amounts of **4**, $[(Cp^*Co)_3B_3H_5]$,[16] and $[(Cp^*Co)_3B_4H_4]$.[18,19]

T_1 Measurements. The spin-lattice relaxation times (T_1, s) for the ^{11}B resonances of **1** and **3** at 300 MHz were determined by a standard inversion recovery technique.[20] BH_3·THF was used for calibration of pulse widths. The T_1 values were obtained from plots of the equation $\ln(A_\infty - A) = \ln 2(A_\infty) - \tau/T_1$, where A_∞ is the limiting value of A at large τ and A is the amplitude following the 90° pulse at time τ. The ^{11}B T_1 value of **1** is 1.4 ms in toluene-d_8 and that of **3** is 10.7 ms in acetone-d_6 at 22 °C.

Results and Discussion

Reactivity of *closo*-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H_2$], 1. Like many *closo*-boranes, **1**, shown in Figure 1, is relatively unreactive. It is thermally stable in that the majority of **1** survives heating in toluene at 110 °C for 3 days, or in dry THF at 77 °C for 10 days. However, there is evidence of slow cluster degradation and the formation of larger clusters which is behavior typical of metal clusters in general.[21] In contrast to ferraboranes containing M−H−B bridging hydrogens, which can be deprotonated to yield mono- and dianions,[22] **1** does not undergo bridge deprotonation. Even *n*-BuLi at room temperature fails to remove the proton. This is consistent with the

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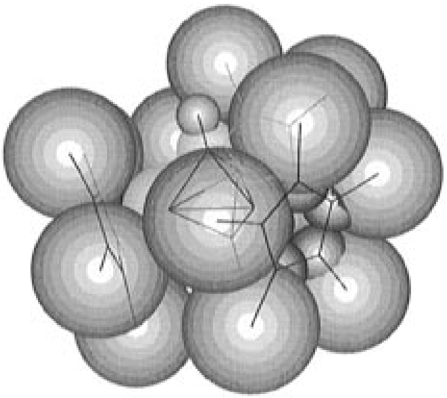

Figure 2. Space-filling representation of the structure of **1** on the same scale as Figure 1.

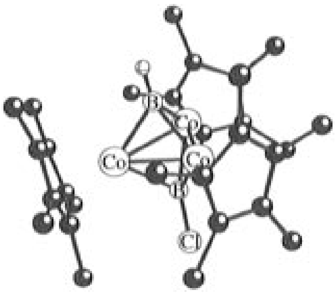

Figure 3. Ball and stick representation of the proposed structure of *closo*-1-X-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], X = Cl, **2**.

view that the Cp* ligand is a better donor than, for example, a set of CO ligands resulting in a lower acidity of the bridging hydrogens.[23] However, the Co−Co edges and Co_3B faces are well shielded by the three Cp* ligands (Figure 2), and kinetics may well play a role here as it does in other cluster systems.[24,25] Under forcing conditions, the terminal hydrogen atom on the capping boron atom may be formally replaced by either hydroxide or chloride. Hence, substitutions at boron in this metallaborane were examined more thoroughly.

Substitution of H on 1 by Cl. In testing for further reactivity of **1** with [Cp*CoCl]$_2$, slow substitution of a terminal H by Cl was observed. Other M−Cl species carry out similar chemistry (see below); however, this was the only reagent found to cleanly yield the monochloro derivative, *closo*-1-Cl-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], **2**. The composition of the product was determined by mass spectrometry. The complex isotopic parent ion distribution envelope fits the expected pattern for a compound with two boron atoms and one chlorine atom. In the ^{11}B NMR spectrum two signals are observed, a narrow one at lower field than **1** with no BH coupling and a broad one at higher field with $BH_{terminal}$ coupling, as expected for a monosubstituted product. The ^{1}H NMR signature is very similar to that of **1** with a metal-based proton signal at high field and a single Cp* resonance (confirmed by the ^{13}C NMR spectrum). The IR spectrum shows the presence of a $BH_{terminal}$ hydrogen. The structure of **2** is clearly that of **1** with one terminal B−H replaced by Cl (Figure 3).

In an attempt to simplify the synthesis of **2** other sources of Cl were investigated. The substitution reaction of **1** with either $FeCl_3$ or $CoCl_2$ is much more facile but gives a dichloro derivative instead of the monochloro derivative observed with [Cp*CoCl]$_2$ as the Cl source. Even reactions with less than a stoichiometric amount of $FeCl_3$ yielded the disubstituted product. The spectroscopic data are consistent with assigning the product as the dichloro derivative, *closo*-1,5-Cl_2-[2,3,4-(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2$], **3**. The mass spectrum exhibits a distribution of parent ion intensities consistent with the presence of two boron and two chloride atoms in the product. A single resonance is observed in the ^{11}B NMR of **3** with no measurable coupling to hydrogen. Its chemical shift and width are similar to the low field resonance found for **2**. As with **1** and **2**, the three Cp* ligands give rise to only one signal in the ^{1}H NMR (confirmed by the ^{13}C NMR); however, it does broaden significantly at low temperature, suggesting a somewhat higher barrier for the fluxional process involving the bridging hydrogens. On the other hand, the broad signal at δ −20.4 ppm, due to the two framework hydrogen atoms, narrows at lower temperatures as does that of **1**. There is a substantial, reversible solvent shift in going between dichloromethane-d_2 and acetone-d_6. No evidence for a $BH_{terminal}$ hydrogen is found in the IR spectrum. The structure of **3** is that of **1** with both $BH_{terminal}$ hydrogens replaced with Cl atoms.

Substitution of H on 1 by OH. The hydroxide derivative is slowly formed by the reaction of **1** with excess H_2O and more rapidly with moist air. The B−$H_{terminal}$ bond is more reactive with respect to hydrolysis than that of a typical ferraborane. On the other hand, there is no evidence of cage cleavage which reflects the robust nature of this metallaborane cluster. The spectroscopic data are consistent with the product being the mono-hydroxo derivative, *closo*-1-OH-[(η^5-C_5Me_5)$_3$(μ-H)$_2$$Co_3B_2H$], **4**. In this case the composition is established by a high-resolution FAB mass spectrum of the parent ion. The ^{11}B NMR spectrum exhibits two types of boron resonances, one with coupling to a terminal hydrogen at higher field and the other with no terminal hydrogen coupling at a lower field. The ^{1}H NMR spectrum shows a hydride resonance at high field and two additional broad resonances. The signal at δ 2−3 ppm, though distorted by overlapping signals, shows coupling characteristic of terminal hydrogen on boron. The other, at 7.0 ppm, is tentatively assigned to the OH proton. The 7 ppm upfield shift of the $BH_{terminal}$ proton resonance on going from **1** to **4** is expected as the associated boron resonance shifts 107 ppm to higher field. There is a single Cp* resonance at 1.78 ppm and a single Cp* resonance in the ^{13}C NMR. The solid state IR spectrum confirms the presence of a $BH_{terminal}$ fragment. The structure of **4** is that of **1** with one $BH_{terminal}$ hydrogen replaced with an OH group.

Placement of the Bridging Hydrogens in 1. The new results on these derivatives of **1** demands a reevaluation of the placement of the bridging hydrogens in **1** itself.[16] These hydrogens were not located in the X-ray structure and are fluxional down to −90 °C in the ^{1}H NMR. The small decrease in the width of the framework hydrogen ^{1}H resonance with decreasing temperature was interpreted as due to weak B−H_{bridge} coupling between the hydrogens and the capping boron atoms. Selective ^{1}B{^{1}H} experiments were ambiguous concerning the framework hydrogen coupling due to the large intrinsic width (200 Hz) of the ^{11}B resonance but placed an upper limit of 20 Hz on the coupling constant. However, as we noted[14] the chemical shift is at rather high field compared to $Cp_4Co_4B_2H_4$ with Co_3 face-bridging hydrogens (δ = −15.6)[26] and $Cp_2Co_2B_4H_6$ with CoCoB face-bridging hydrogens (δ = −12.6).[27] It is more in line with that of $Cp_2Co_2(PPh_2)B_2H_5$ with a Co−B edge-

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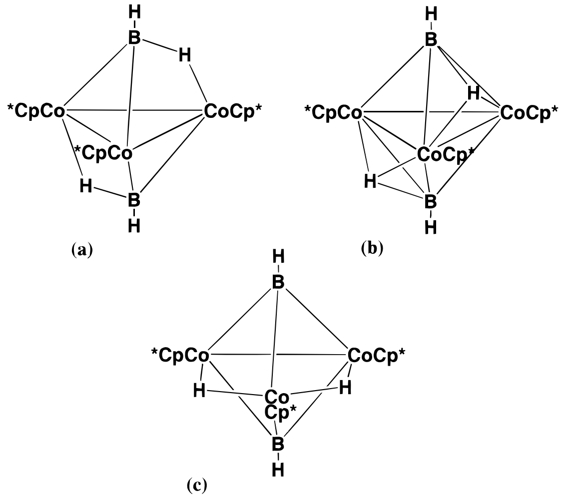
Chart 1



bridging hydrogen ($\delta = -21.5$).[28] In all these cases the positions of the bridging hydrogens were established by the X-ray structure studies. Thus, we suggested edge-bridging positions in the communication (Chart 1a). Subsequently, the $B-H_{bridge}$ coupling was judged too small for this hydrogen to be Co-B edge-bridging in that $[Fe_3(CO)_{10}(HBCl)]^-$ exhibits $J_{FeHB} = 60$ Hz.[29] Thus, we settled on face-bridging positions in the full publication of the synthetic work (Chart 1b). The smaller intrinsic peak width of the ^{11}B NMR signal corresponding to the resonance of the substituted boron atom in **2** relative to **1** (50 vs 200 Hz) reduces the upper limit on the coupling constant to $\approx$5 Hz. In addition, the very small change in the ^1H chemical shift of the framework hydrogens on substitution (-20.8, -20.9, -20.4, -20.3 ppm for **1**−**4**, respectively) strongly suggests that these bridging hydrogens are effectively associated with the Co atoms only. That is, the substituent strongly affects the chemical shift of the substituted boron atom but not the framework hydrogens. We have previously observed for $[Fe_3(CO)_{10}(HBX)]^-$ that $\delta_{Fe-H-B} = -11.1$ and -9.3 for X = H, Cl, respectively, thereby showing that a true bridging hydrogen is measurably affected by Cl substitution in a geminal position.[29,30] Thus, these new observations on derivatives of **1** point toward a fluxional edge-bridged structure (Chart 1c) as a better representation of the actual situation. Whether these framework hydrogens lie in or out of the Co_3 plane is a moot point.

Nature of the Chloride-Substitution Reactions. Main group and transition metal halides have been used extensively to catalyze the halogenation and alkylation of borane and carborane cages.[1,31,32] A systematic study of the nature of metal halide catalyzed alkylations of pentaborane(9) details the factors important in one class of these reactions.[33] Recently, we have uncovered two instances of the conversion of $B-H_{terminal}$ bonds to B−Cl bonds in metallaboranes using a transition metal chloride as a stoichiometric source of the Cl atoms. Except for the use of mercury halides in the halogenation of nonaborane anions,[34] we are unaware of other reports of the use of metal halides as direct halogenation reagents for boranes in general or metallaboranes in particular.

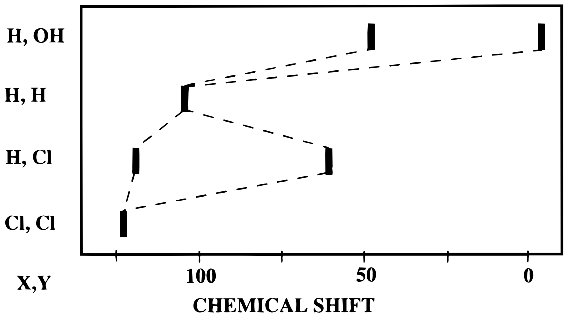


Figure 4. Comparison of the ^{11}B NMR chemical shifts for *closo*-1,5-XY-[2,3,4-(η^5-$C_5Me_5)_3(\mu$-$H)_2Co_3B_2$], **1**−**4**.

The first example of chlorination of a metallaborane by a metal chloride from our laboratory arose from an investigation of the oxidative coupling of $[Fe_3(CO)_9BCO]^{2-}$ using $FeCl_2$/$FeCl_3$ as the coupling agents. In the course of this work we found that the dianion reacts cleanly with $FeCl_3$ alone in a 1:2 mole ratio to yield $[Fe_3(CO)_{10}(HBCl)]^-$.[29] Later, in the synthesis of cobaltaboranes from $[Cp^*CoCl]_2$ and BH_3·THF, we found that 2 mol of the latter reagent is converted to BH_2Cl as the byproduct of the synthesis of the cobaltaborane clusters. Both cases represent formal substitution of a hydrogen atom at a $B-H_{terminal}$ bond by Cl, although the work suggests that the actual reaction is much more involved than direct substitution. The present study constitutes a third example in which a compound containing a M−Cl moiety serves as a chlorination reagent. $[Cp^*CoCl]_2$ acts as a mild chlorinating agent in converting **1** to **2** whereas $FeCl_3$ and $CoCl_2$ react much more vigorously and yield the dichloro product **3**. In the case of the mildly active chlorination reagent $[Cp^*CoCl]_2$ there was no degradation of the cluster or other side reactions. However, with the more active agents $FeCl_3$ and $CoCl_2$, significant degradation took place. In spite of this, the results suggest metal chlorides as reasonable chlorination reagents for metallaboranes.

Effects of Substituents on ^{11}B NMR Parameters. The effect of halogen substituents on the ^{11}B chemical shifts of carborane cages, for example, have been empirically correlated and provide information of structural value.[32,35,36] We and others have drawn connections between substituent shifts and the cage electronic structure.[3,37,38] Thus, chemical shift data for **1**−**4** provide a good relative measure of the perturbation of the metallaborane cage by the OH and Cl substituents.

The ^{11}B chemical shifts for **1**−**4** are compared in Figure 4. The low field chemical shift of the boron atom of the parent compound is consistent with its highly metallic environment.[39] Upon substitution by Cl there is a shift of +17 ppm which compares well with the shift of +19 ppm in going from $[Fe_3(CO)_{10}(HBH)]^-$ to $[Fe_3(CO)_{10}(HBCl)]^-$.[29,30] The other boron atom of **2** experiences a large shift of −43 ppm, which may be attributed to an antipodal effect.[40,41] The existence of an antipodal effect for Cl in this closed metallaborane cage, despite no direct bonding between the boron atoms, shows that

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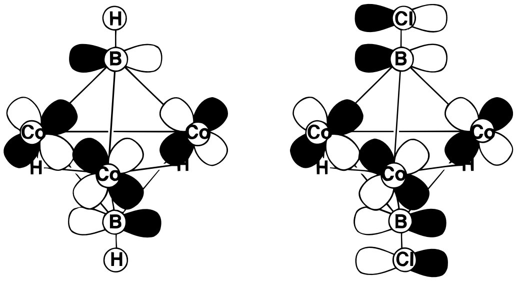
the B_2Co_3 core possesses an essential property of a B_n cage. Curiously, the antipodal upfield shift in **2** is considerably larger than the −9.3 ppm shift observed for the main group cage 2-Cl-1,6-$C_2B_4H_5$.[37,42] As expected, the chemical shift observed for **3** is very similar to that observed for the substituted boron of **2**.

For **4** there is a large upfield shift (56 ppm) on the replacement of H by OH. There is an enormous antipodal shift of 107 ppm if one uses the parent compound as reference. However, note that the differences in chemical shift between the two resonances of **2** and **4** are very similar (61 vs 51 ppm), and it is quite likely that there are two effects operative here, i.e., a perturbation of the entire cage as well as the specific, cross-cage perturbation. The former is small in 2-Cl-1,6-$C_2B_4H_5$ (Cl substitution results in a +9.9 shift in B(2), +2.3 in B(3,5), and −9.3 ppm in B(4)), and apparently the three metal atoms in the trigonal plane connecting the two capping boron atoms amplify both of these effects.

To obtain additional information on the perturbation of the boron atoms by Cl substitution, the T_1 relaxation times were measured for **1** and **3**.[43] As already mentioned above the intrinsic line width of the ^{11}B resonance of the chlorine substituted boron atom is substantially smaller than that of **1** (50 vs 200 Hz). Consistent with the reduced line width, the ^{11}B T_1 value of **3** is an order of magnitude larger than that of **1** (10.7 vs 1.4 ms); i.e., replacing H with a quadrupolar Cl atom decreases rather than increases the relaxation rate. Typical ^{11}B T_1 values range from 130 ms for 1,6-$[Fe_4Rh_2(CO)_{16}B]^-$ to 24 ms for B_2H_6 to 13 ms for $B(OMe)_3$ to 2 ms for $[(Me_2N)_2B]_2$ illustrating the connection between the asymmetry in the electronic environment around boron and the efficiency of quadrupolar relaxation.[35,44] Clearly the boron atom in **1** is in a very asymmetrical electronic environment relative to a normal borane cage and the replacement of H by Cl reduces this asymmetry. A simple model that accounts for the observations is shown in Chart 2. The overall interaction between a capping BCO fragment and a trimetal fragment has been studied previously and was shown to involve a B 2pπ interaction with the M_3 metal triangle. The bonding situation for the boron atom in **1** must be closely related.[45] In **1** the boron atom interacts in σ and π fashions with the trimetal fragment relative to the C_3 axis; however, the interaction with the H ligand can be σ only. On the other hand, in **3**, the lone pairs on the Cl substituents do permit π interactions. In **3** the boron atom is now surrounded by a near tetrahedral arrangement of four atoms with both σ and π capabilities thereby yielding a more balanced electronic environment and a reduced rate of relaxation.

Chart 2



(1) **(3)**

Summary

Exo-cluster substitution at B−H in metallaboranes can be carried out cleanly provided the appropriate reagent is used. Chlorination by metal chlorides and direct hydrolysis produce derivatives that should be useful in preparing functionalized clusters for assembly into larger arrays. The substituted compounds exhibit properties associated with the isolobal borane cluster and show that both metal and boron atoms participate intimately in the cluster bonding network.

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