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Synthesis and Reactivity of the Metal-Substituted Borane $(CO)_4CoBH_2·THF$. Preparation of the Ambiphilic Clusters $(CO)_9Co_3C(CH_2)_nOH$ (n = 4, 5)

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The reaction $Co_2(CO)_8 + 2BH_3·THF \rightarrow 2(CO)_4CoBH_2·THF$ (I) + H_2 has been demonstrated to occur cleanly at −15 °C in THF. I has been characterized by low-temperature ^{11}B NMR and infrared spectroscopies as well as classical chemical analysis. The formation of I bears a remarkable similarity to that of $(CO)_4CoSiR_3$. Displacement of the bound THF of I occurs with Lewis bases, and the Lewis acidity of I relative to that of $BH_3·THF$ for SMe_2 has been estimated. Displacement of $[Co(CO)_4]^-$ from I occurs easily; e.g., reaction with PhMgBr yields $PhBH_2$. I readily accepts hydride from $[HFe_2(CO)_8]^-$, losing $[Co(CO)_4]^-$ but reduces the CO ligands of hydride-free metal carbonylate anions. I is a very active reducing agent and above 10 °C cleaves THF and condenses with hydrocarbyl and metal fragments to yield a mixture of clusters including an unusual tailed cluster $(CO)_9Co_3C(CH_2)_nOH$ (n = 4,5) (II). A deuterium labeling experiment showed that four of the n carbons in the hydrocarbyl chain of II arise from THF. The results of an X-ray diffraction study suggest association of II in the solid state. [Crystals of II (the ratio of II with $n = 5/n = 4$ is 4) form in the space group $R\bar{3}$ with unit cell parameters a = 34.409 (15) Å, b = 34.398 (21) Å, c = 8.575 (5) Å; $\alpha = \beta = 90°$, $\gamma = 120°$, V = 8789.8 Å^3, and Z = 18. Solution was by direct methods, and all atoms were refined to $R_1 = 0.077$ and $R_2 = 0.096$ for 1443 independent reflections ($F_o > 3\sigma(F_o)$). Because of the disorder caused by the cocrystallization of species with different chain lengths, the last two atoms at the OH end of the chain could not be fully defined.] Association of II in solution is shown by a ^1H NMR study, thereby demonstrating that II behaves as an ambiphilic cluster.

Introduction

The importance of substituted monoboranes, BH_xR_{3-x}, as synthetic reagents is well documented.[1] The use of organic substituents and a variety of Lewis bases to tailor the reactivity of $BH_xR_{3-x}·L$, L = base, to a particular reaction is also well-known. The interaction of $BH_3·L$ and B_2H_6 with a number of transition-metal and organometallic systems has been studied, and the complex M–B interactions in clusters are known to drastically change the reactivity of the B–H bond.[2-10] However, there has been no report of a mononuclear transition-metal-substituted monoboron hydride, e.g. L_xMBH_2. Hence, the nature of the B–H bond in a monoborane as perturbed by the presence of a direct, single, unsupported M–B bond is unknown. On the other hand, the work of Schmid and Nöth[11] constitutes compelling evidence for the formation of the non-hydridic L_xMBX_2 monoboranes (X = halogen, aryl; M = Mn, Fe, Co), containing direct metal–boron bonds.

A second objective in exploring the preparation and properties of an example of an L_xMBH_2 compound was to gain access to a potential building block for the rational construction of metallaborane cluster systems.[12-14] As demonstrated by Vahrenkamp,[15] species such as L_xMEH_y (E = a main-group atom) are suitable for the designed synthesis of di- and trimetal metallaboranes.

In the following, we describe the preparation and characterization of $(CO)_4CoBH_2·THF$ (I), which is a compound of the type desired. We also describe some aspects of the reactivity of this very labile metal-substituted monoboron hydride, including its condensation into an example of a tailed cluster, i.e., $Co_3(CO)_9C(CH_2)_nOH$, (n = 4, 5) (II). The latter compound permits us to demonstrate that with appropriate functionalization a metal cluster behaves as an ambiphilic species in the solid state as well as in solution.

Results

The reaction of $Co_2(CO)_8$ with $BH_3·THF$ at 25 °C in THF results in the vigorous evolution of gas (H_2 and CO) and the formation of a deep red-brown solution that eventually solidifies. The initial solution contains a variety of products containing reduced carbon and fragments of solvent (see below) while the solid results from the polymerization of the THF. Similar products are produced when hexane is used as a solvent except that longer reaction times are required and the polymerization is inhibited. In order to obtain greater understanding of the origin of these materials, the reaction has been examined at lower temperatures.

Low-Temperature Reaction—^{11}B NMR. The reaction of $BH_3·THF$ with $Co_2(CO)_8$ is very slow below −40 °C because of the decreased solubility of $Co_2(CO)_8$; however, at −25 °C the reaction can be conveniently observed in homogeneous solution. The results of a ^{11}B NMR study of a typical reaction are shown in Figure 1. Under these conditions, $BH_3·THF$ is smoothly lost and a single boron-containing product exhibiting a broad triplet at δ 7.9 ($J_{BH} \approx 110$ Hz) is observed. On the basis of the net integrated ^{11}B signal and with the assumption of equal sensitivities, the yield of the species giving rise to the signal at δ 7.9, I, is ≈80%. The single boron-containing product observed is stable at −20 °C for at least 24 h. As shown in Figure 1, warming the dark red solution results in the loss of the triplet at δ 7.9 and, eventually, the formation of a singlet at $\delta \approx 19$. The latter is consistent with the formation of a species containing two or three B–O bonds,[16] and we often see such a signals in systems where CO reduction is known to take place. The lifetime of I is enhanced by carrying out the reaction in hexane–THF, but eventually the same type

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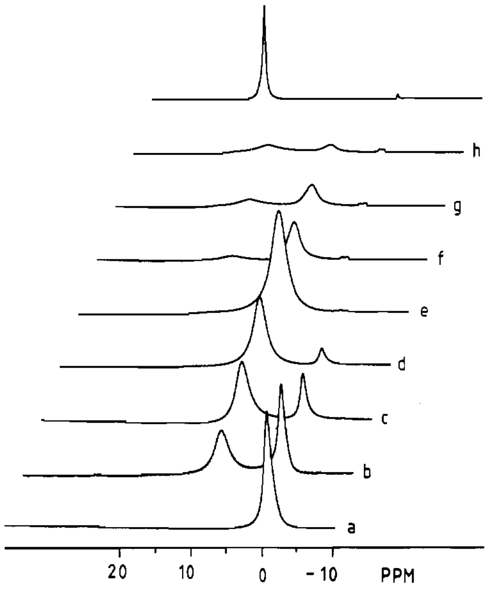

Figure 1. $^{11}B\{^1H\}$ NMR spectra of the reaction of 0.101 g (0.295 mmol) of $Co_2(CO)_8$ with 0.6 mL of 1 M $BH_3·THF$ in 1.2 mL of THF: (a) −40 °C at $t = 0$; (b) −25 °C at $t = {}^1/_2$ h; (c) −25 °C at $t = 1{}^1/_2$ h; (d) −25 °C at $t = 2{}^1/_2$ h; (e) −25 °C at $t = 4$ h; (f) warming to room temperature; (g) warming to room temperature; (h) room temperature; (i) excess MeOH added. The signals at δ −1 and 7.9 correspond to $BH_3·THF$ and I, respectively.

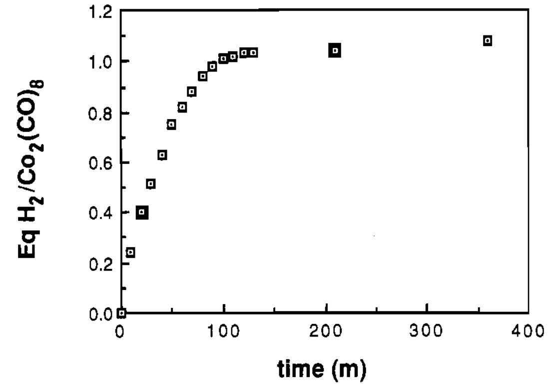

Figure 2. Gas evolution from the reaction $Co_2(CO)_8 + 2BH_3·THF$ (3.2 mmol of $Co_2(CO)_8$) in THF at −15 °C. Analysis of the gas periodically gave a composition 2 ± 1% CO in H_2. The rate of gas evolution is exponential with a half-life of 20 min.

of final product distribution is obtained.

Reaction Stoichiometry. The stoichiometry of the reaction resulting in the production of I was defined in several experiments. First, gases are evolved at low temperature on the addition of $BH_3·THF$ to $Co_2(CO)_8$. The volume of gas produced as a function of time at −15 °C is shown in Figure 2, demonstrating the formation of 1.05 mol of gas per mole of $Co_2(CO)_8$ and a reaction half-life of ≈20 m at this temperature. Gas chromatographic analysis yielded a gas composition of 98% H_2 and 2% CO. Hence 1.0 ± 0.1 mol of H_2 is produced per mole of I formed.

Second, the characteristic absorption band of I at 512 nm was used to define the stoichiometry with respect to $BH_3·THF$ and $Co_2(CO)_8$. This reaction was carried out in 1:1 THF–hexane, so that the measurements could be carried out at 22 °C before significant decomposition of I occurred. The $BH_3·THF$:$Co_2(CO)_8$ ratios used ranged from 0.5 to 2.5, and the spectra were measured as a function of reaction time. The spectra at one of these times are shown in Figure 3. The maximum yield of I was observed for $BH_3·THF$: $Co_2(CO)_8$ = 2.0. The average stoichiometric factor for all times was 2.0 ± 0.3.

Third, the reaction was followed by IR spectroscopy by monitoring the consumption of $Co_2(CO)_8$ using the 1840-cm^{-1} band. This band disappears smoothly with time and requires a total of 2 equiv of $BH_3·THF$ to "titrate" it to zero intensity.

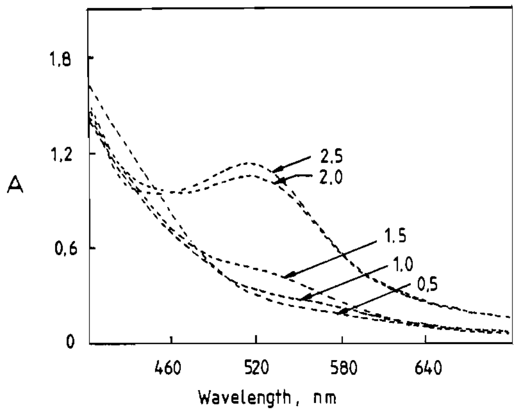

Figure 3. Visible spectra from the reaction $Co_2(CO)_8 + nBH_3·THF$ (0.036 M $Co_2(CO)_8$ in hexane) in hexane/THF = 10.7. The numbers indicate the value of n for each spectrum. For this set of spectra the reaction time was 8.5 h.

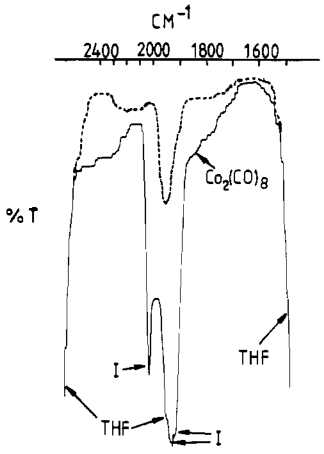

Figure 4. IR spectrum (solid line) of the product of the reaction $Co_2(CO)_8 + 2BH_3·THF$ (1.0 mmol of $Co_2(CO)_8$ in 20 mL of THF at −20 °C after 2 h taken in a single-beam mode at −28 °C. The dashed spectrum is that of pure THF under the same cell conditions.

Finally, an NMR experiment was used to support the spectrophotometric results. The reaction of 3 equiv $BH_3·THF$ and $Co_2(CO)_8$ at −15 °C was followed by ^{11}B NMR. On the basis of the fraction of borane lost, the $BH_3·THF$:$Co_2(CO)_8$ ratio for the reaction producing I is = 1.7. That is, if equal NMR sensitivities for $BH_3·THF$ and I are assumed, the moles of boron appearing in I is 1.7 times the moles of $Co_2(CO)_8$ used. This corresponds to a yield of ≈85% if I contains a B:Co ratio of 1. The combined results establish that the reaction producing I is given in eq 1 where the coefficient of I in the balanced equation is deduced below.

$$2BH_3·THF + Co_2(CO)_8 \rightarrow 2I + H_2 \qquad (1)$$

Characterization of I. It was not possible to isolate I in a pure state. Hence, characterization was by spectroscopic and chemical means at reduced temperatures. The ^{11}B NMR spectrum described above shows that I contains a single type of boron atom. The chemical shift is consistent with either tri- or tetracoordinate boron[17] while the broad triplet observed is consistent with a BH_2 group. The value of J_{BH} is similar to that observed for the B–H terminal bonds in borane–base adducts. The ^{11}B chemical shift and coupling constant observed for I is also in the range of that for $[BH_2·L_2]^+$ cations.[18] However, other evidence (see below) allows us to rule out $[BH_2·THF_2][Co(CO)_4]$ as the formulation of I. A spectrum of I (prepared with $BH_3·THF$) in THF-d_8 (THF/THF-d_8) showed a broad quartet at δ 1.8 with J_{BH} = 100

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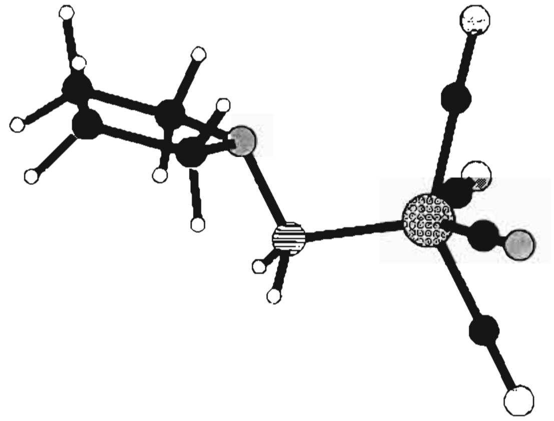

Figure 5. Proposed structure for $(CO)_4CoBH_2 \cdot THF$ (I).

Hz and with the approximate relative intensity expected (Figure 8a). In addition, the number of hydridic hydrogens per boron was determined by the methanolysis of I. Although the methanolysis produces mainly H_2, a significant amount of CO is also evident in the gas chromatographic analysis. After the contribution from CO was subtracted, the results of three experiments (five determinations) yielded an average of 1.54 mol of H_2 produced per mole of $BH_3 \cdot THF$ reacted with $Co_2(CO)_8$. However, the CO produced varied from 0.5 to 0.7 mol per mole of I and increased with increasing reaction time after H_2 evolution had ceased, suggesting that a significant fraction of I decomposed during reaction with MeOH. Hence, 1.5 is the minimum number of BH hydrogens in I.

The absorption in the visible region at 512 nm (Figure 3) demonstrates the presence of a transition metal in I. A single-beam infrared spectrum of I at −28 °C in the CO stretching region is shown in Figure 4. Absorptions at 2040 (s), 1935 (vs) and 1920 (sh) cm^{-1} attributed to I were observed by flowing the low-temperature product mixture from reaction 1 into a temperature-controlled cell. The weak band at 1840 cm^{-1} is due to residual $Co_2(CO)_8$, and warming of the sample yielded a complex spectrum containing $Co_4(CO)_{12}$ and $[Co(CO)_4]^-$ among other unknown products. Clearly I contains carbonyls bound to a metal atom, and the spectrum is very similar to that observed for $HCo(CO)_4$.[19] The energy of the infrared bands suggest that I is a neutral compound, and a $Co(CO)_4$ fragment with C_{4v} symmetry is implied by the number and type of bands observed. The spectrum is definitely not that of $[Co(CO)_4]^-$, thereby ruling out $[BH_2 \cdot 2THF][Co(CO)_4]$ as the formulation of I.

Compound I is soluble in THF, C_6H_6, $C_6H_5CH_3$, 1:1 THF–CH_2Cl_2, and 1:1 and 1:14 THF–hexane. The solubility data also rule out the formulation of I as the salt $[BH_2 \cdot 2THF][Co(CO)_4]$. Hence, we conclude that the monomeric formulation of compound I is $(CO)_4CoBH_2$, i.e., a metal-substituted borane, and the proposed structure of I is shown in Figure 5.

Lewis Base Coordination. If compound I is monomeric, coordination to a Lewis base is probably necessary. Figure 6 summarizes the results of two ^{11}B NMR experiments that reveal a requirement for THF in the formation of I. The reaction of $Co_2(CO)_8$ with $BH_3 \cdot SMe_2$ in CH_2Cl_2 shows the formation of a small amount of a BH_3 adduct of $Co_2(CO)_8$ (δ −49, t, J = 104 Hz), presumably corresponding to BH_3 bound through an oxygen atom of a carbonyl ligand, but no evidence of the ^{11}B signal of I. (A very weak signal at δ −10 is attributed to $(CO)_4CoBH_2 \cdot SMe_2$.) On the other hand, the reaction of $Co_2(CO)_8$ with $BH_3 \cdot SMe_2$ in 1:1 CH_2Cl_2–THF shows a modest yield of I and no evidence of the adduct at δ −49. The reaction of B_2H_6 with $Co_2(CO)_8$ in hexane (not shown) proceeds with the formation of the adduct at δ −49 and other undetermined products, but no evidence for the formation of I is observed. Finally, the reaction of B_2H_6 with $Co_2(CO)_8$ in 14:1 hexane–THF shows the formation of the adduct at δ −49 followed by the formation of I. In the last reaction, the ^{11}B NMR shows that both B_2H_6 and $BH_3 \cdot THF$ are initially present, and thus, the adduct at δ −49 may be a "dead-end" intermediate not leading directly to I. The evidence suggests I should be formulated as monomeric $(CO)_4CoBH_2 \cdot THF$.

Table I. ^{11}B Chemical Shifts (δ) and Coupling Constants (Hz) for $BH_3 \cdot L$ and $(CO)_4CoBH_2 \cdot L$

	shift (coupling const)	
L	$BH_3 \cdot L$	$(CO)_4CoBH_2 \cdot L$
THF	−1 (103)	7.9 (105)
Et_3N	−14 (83)	3.6 (65)
Me_2S	−20 (104)	−10 (130)
bipyridine	−12.8	−2.2

To further establish the presence of the coordinating solvent in I, the displacement of THF from I by other Lewis bases was attempted. At low temperatures, addition of nitrogen bases resulted in the loss of all or part of the signal at δ 7.9 and, as exemplified by the reaction of I with NEt_3, the formation of a triplet in another part of the spectrum. As may be seen in Figure 7, addition of NEt_3 to I results in the rapid loss of the signal at δ 7.9 followed by the appearance of a new broad signal at δ 3.6 that sharpens on ^1H decoupling. Some $BH_3 \cdot NEt_3$ is also formed as evidenced by the upfield quartet. This reaction was also followed by ^1H NMR spectroscopy, and the results are summarized in Figure 8 for two separate reactions. In the first reaction, 2 equiv of $BH_3 \cdot THF$ were used in reaction 1 with THF-d_8 as solvent. At low temperature, before the addition of the amine, the THF signals have shoulders on the downfield side at about 20% of the intensity of the main signal. As the ratio of THF-d_8 to THF is ≈5 and as on a chemical time scale bound and free THF most certainly will be fully scrambled, we attribute these shoulders to THF bound to $(CO)_4CoBH_2$. When 2 equiv of NEt_3 are added, the shoulders disappear and a quartet and triplet characteristic of bound NEt_3 appears and is assigned to $(CO)_4CoBH_2 \cdot NEt_3$ (δ 2.94, q, J = 7.2 Hz; δ 1.19 t, J = 7.2 Hz). In addition, the quartet assigned to the BH protons of I disappears and is replaced with another quartet at higher field (δ 1.6, J_{BH} ≈ 65 Hz). In the second experiment, carried out with 1 equiv of excess $BH_3 \cdot THF$, addition of 3 equiv of NEt_3 at low temperature gave signals shortly after mixing due to free NEt_3, $BH_3 \cdot NEt_3$, and $(CO)_4CoBH_2 \cdot NEt_3$. The last signal is downfield from that of $BH_3 \cdot NEt_3$ as expected from the ^{11}B NMR. At longer times, the signal due to NEt_3 decreased and that due to $(CO)_4CoBH_2 \cdot NEt_3$ increased. This confirms the assignment. Finally, on the basis of integration of the proton signals from the Et groups and the THF, the net yield of $(CO)_4CoBH_2 \cdot NEt_3$ under stoichiometric conditions is calculated to be 99%.

The fact that displacement of THF takes place, forming $(CO)_4CoBH_2 \cdot NEt_3$, also rules against the formulation of I as $[BH_2(THF)_2][Co(CO)_4]$. It has been stated[20,21] that NEt_3 is sterically too large to permit formation of $[BH_2(NEt_3)_2]^+$. As seen in Table I, which contains the ^{11}B chemical shifts of I coordinated to a variety of bases, the difference in chemical shifts between $(CO)_4CoBH_2 \cdot L$ and $BH_3 \cdot L$ is ≈10 ppm with the shift for metal derivative at lower field as expected. These observations are consistent with the formulation of the red $(CO)_4CoBH_2$ product as a base adduct of a metal-substituted borane. Not all Lewis bases displace THF from I. For example, $AsPh_3$ shows no reactivity at −15 °C and only in neat SMe_2 is some $(CO)_4CoBH_2 \cdot SMe_2$ observed (see below).

Reactivity of I

Reaction with Lewis Bases. The simple displacement reaction of THF from I by NEt_3 was presented above; however, more complex reactivity is observed when excess base is used. In fact, with excess L substantial $BH_3 \cdot L$ was observed. Thus, a reaction path consuming more than 1 equiv of the base must exist. The

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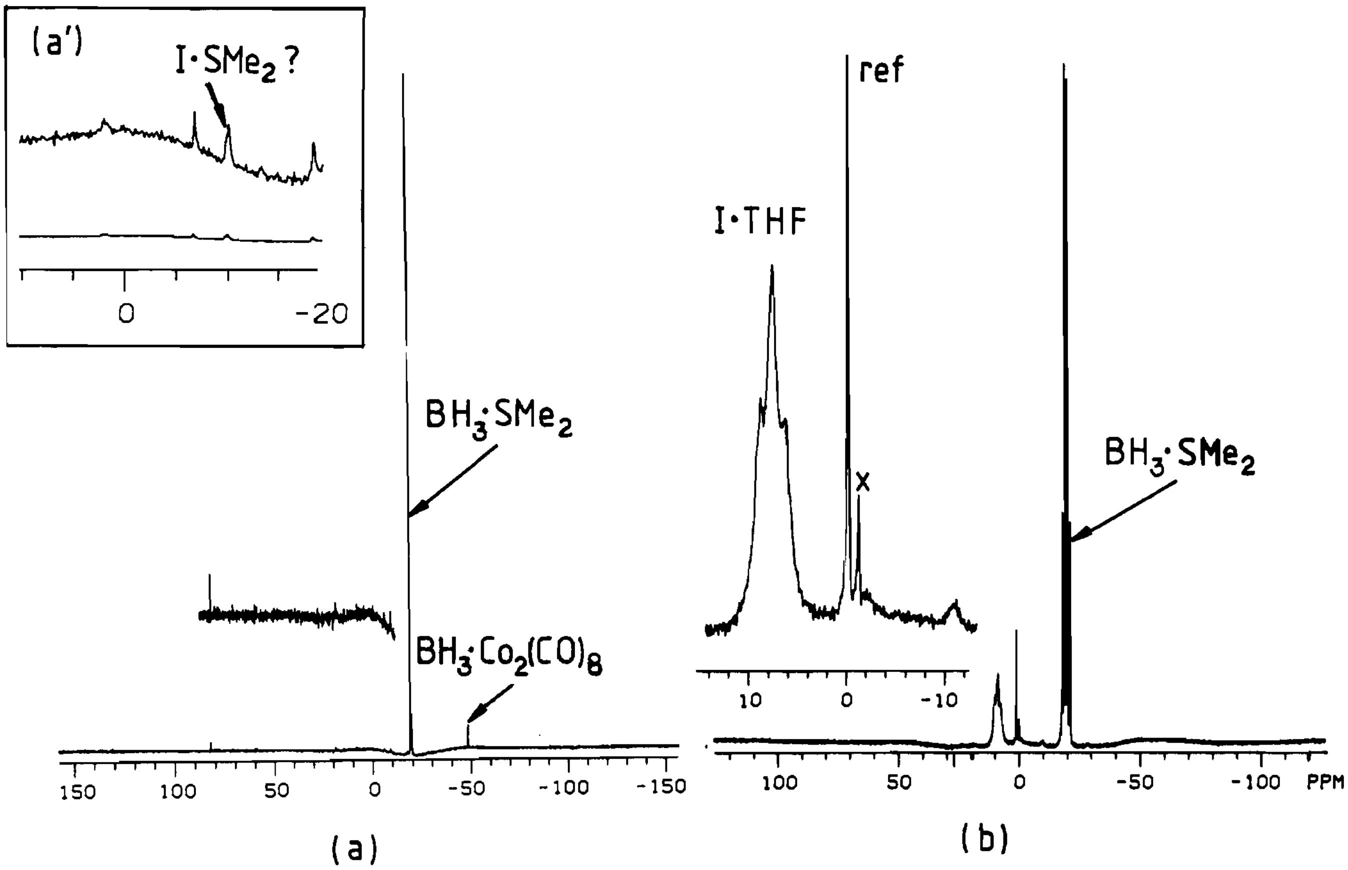

Figure 6. (a) $^{11}B\{^1H\}$ NMR spectrum of the reaction $Co_2(CO)_8 + BH_3\cdot SMe_2$ in CH_2Cl_2 at 22 °C at $t = 30$ min. (b) ^{11}B NMR spectrum of the reaction $Co_2(CO)_8 + 2BH_3\cdot THF$ in $CH_2Cl_2{:}THF = 1$ at 22 °C at $t = 30$ min. The external reference is $BF_3\cdot Et_2O$ and the signal marked X is due to the reference sample.

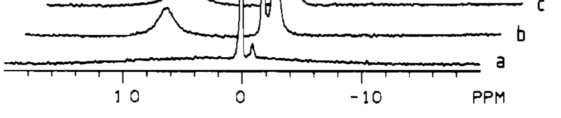

Figure 7. ^{11}B NMR spectra ($\{^1H\}$ except where indicated) of the reaction of I with NEt_3 (I synthesized from 0.08 mmol of $Co_2(CO)_8$ and 0.12 mmol of $BH_3\cdot THF$ in 0.37 mL of THF): (a) external $BF_3\cdot Et_2O$, × = impurity in external reference; (b) $Co_2(CO)_8 + BH_3\cdot THF$ at $t = {}^1/_2$ h at −20 °C; (c) same mixture as in part b at $t = 2.5$ h; (d) mixture from part c 0.125 mL of Et_3N added at $t = 3^1/_4$ h with the spectrum recorded 6 min after addition; (e) same mixture as in part d after 15 min, ^1H coupled; (f) same mixture as in part e 30 min after addition of amine; (g) mixture as in part b at 22 °C for 24 min.

reaction with SMe_2 constitutes the best example of this behavior. Adding 1 or 2 equiv of SMe_2 to a solution of I in THF resulted in no reaction at −20 °C. However, removing the THF at low temperature followed by dissolving I in SMe_2 resulted in reaction at −20 °C. The ^{11}B spectrum showed a signal for $BH_3\cdot SMe_2$, a signal at δ −9 (t, $J_{BH} = 130$ Hz) attributed to $(CO)_4CoBH_2\cdot SMe_2$, and a signal due to $(CO)_4CoBH_2\cdot THF$, plus signals due to unknown products at δ 18.9 (s) and δ 26.4 (d, $J = 148$ Hz) in relative abundances 1:1:3:2:3. On warming, signals for $BH_3\cdot SMe_2$, $(CO)_4CoBH_2\cdot SMe_2$, and the species at δ 26.4 initially increase at the expense of that for $(CO)_4CoBH_2\cdot THF$. Although displacement of THF from I appears to take place, reaction with a second equivalent of SMe_2 must be competitive under the reaction conditions. We suggest that a disproportionation reaction similar to reaction 2 may be taking place. The doublet observed

$$2(CO)_4CoBH_2\cdot THF + 2L \rightarrow [(CO)_4CoBH\cdot 2L_2]^+ + [(CO)_4CoBH_3]^- + THF$$

$$[(CO)_4CoBH_3]^- + L/THF \rightarrow [Co(CO)_4]^- + BH_3\cdot L/THF \qquad (2)$$

at δ 26.4 would then be assigned to $[(CO)_4CoBH\cdot 2L]^+$, and the overall reaction would be analogous to unsymmetrical cleavage of boranes by Lewis bases.[22] Consistent with this interpretation, $[Co(CO)_4]^-$ is a major ultimate product of the reaction of I with Lewis bases. The signal at δ 18.9, which is the only major signal observed after warming the solution to room temperature or after keeping the solution at −20 °C for 7 days, is assigned to a final degradation product containing boron that is always observed in these reactions (see Figure 1). Apparently, when THF is replaced with SMe_2, the reactivity of $(CO)_4CoBH_2$ with respect to CO reduction is further enhanced.

Reaction with Metal Carbonyls. Reaction of I with $[HFe(CO)_4]^-$ gave $BH_3\cdot THF$ as an initial product. $[HFe_3(CO)_{11}]^-$ and $[Co(CO)_4]^-$ were the major metal-containing products. As displacement of $[Co(CO)_4]^-$ by hydride on boron is probably taking place, it seems unlikely that the compound reported as $Na[Co(BH_3)(CO)_4]$ contains a Co–B bond.[23] The reaction of $[HFe_2(CO)_8]^-$ with I also gave $BH_3\cdot THF$ as an initial product and $[HFe_3(CO)_{11}]^-$ and $[Co(CO)_4]^-$ (≈45%) plus $[FeCo_3(CO)_{12}]^-$ as metal-containing products. In the latter case, evidence of CO reduction chemistry was also observed, e.g., formation of $H_3Fe_3(CO)_9CR$.[24]

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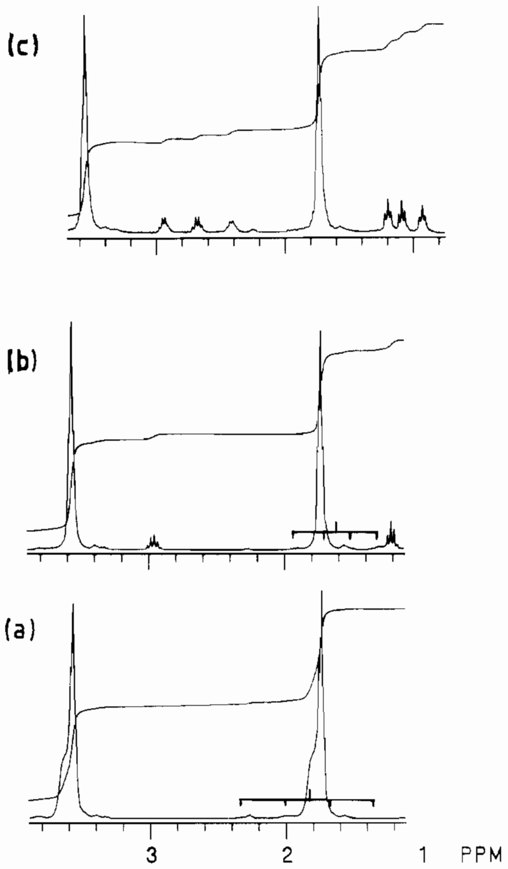

Figure 8. ^{1}H NMR spectra of the reaction of I with NEt$_3$. For spectra a and b, I was prepared with a 1:2 mol ratio of Co$_2$(CO)$_8$ to BH$_3$·THF while for (c) this ratio was 1:3. Both reactions were carried out in THF-d_8 at −20 °C for 4 h followed by the addition of 1 mol of NEt$_3$ for each mole more of BH$_3$·THF. Part a shows the spectrum of I at −35 °C, and the shoulders on the downfield side of the main resonances are attributed to the bound THF in I. The quartet due to the BH protons is indicated. Part b shows the spectrum of the same solution in part a after the addition of 1 equiv of NEt$_3$. Part c shows the spectrum of a similar reaction using a BH$_3$·THF:Co$_2$(CO)$_8$ ratio of 3 rather than 2 shortly after the addition of 1 equiv of NEt$_3$ per equivalent of BH$_3$·THF. The new signals (compared to part b) are due to BH$_3$·NEt$_3$ and NEt$_3$.

The reaction of I with [Fe(CO)$_4$]$^{2-}$ was studied in some detail as simple displacement of [Co(CO)$_4$]$^-$ would lead to [(CO)$_4$FeBH$_2$]$^-$ which we have proposed as an intermediate in the formation of ferraboranes in related systems.[10] Reaction of [Fe(CO)$_4$]$^{2-}$ with I at −15 °C was demonstrated by loss of solid [Fe(CO)$_4$]$^{2-}$ and the formation of 1 mol of [Co(CO)$_4$]$^-$ per mole of I. Evidence for the formation of the desired product was sought by adding BH$_3$·THF as an agent for trapping the [(CO)$_4$FeBH$_2$]$^-$ anion to form [(CO)$_4$FeB$_2$H$_5$]$^-$, a known compound.[25] ^{11}B and ^{1}H NMR studies of the final products showed the formation of [(CO)$_4$FeB$_2$H$_5$]$^-$; however, yields were only ≈40% and [BH$_4$]$^-$ was also a product. A variable-temperature ^{11}B NMR study of the reaction as a function of time with an external reference of known concentration showed the total loss of the signal due to I upon the addition of [Fe(CO)$_4$]$^{2-}$ but no other boron signal of equivalent intensity was generated. On the addition of the second equivalent of BH$_3$·THF, the slow formation of [(CO)$_4$FeB$_2$H$_5$]$^-$ and [BH$_4$]$^-$ at the expense of BH$_3$·THF was observed. Clearly I reacts with [Fe(CO)$_4$]$^{2-}$ by a process other than displacement. The most likely reaction is with the carbonyls of [Fe(CO)$_4$]$^{2-}$ yielding reduced carbon and BO polymers. This process must consume about 2 mol of I per mole of [Fe(CO)$_4$]$^{2-}$, and the remaining [Fe(CO)$_4$]$^{2-}$ then reacts with the added borane to yield [(CO)$_4$FeB$_2$H$_5$]$^-$ by the known route. This suggests that I contains a more highly reducing B–H bond than BH$_3$·THF.

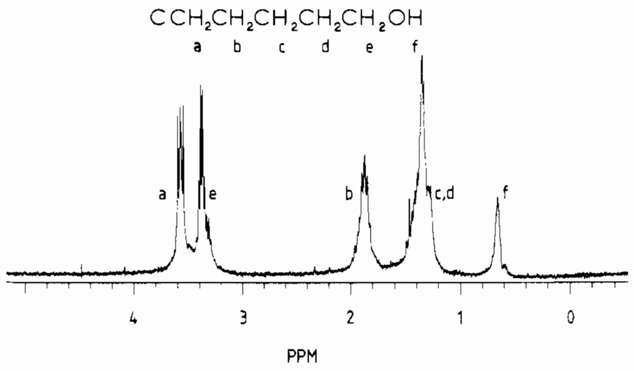

Figure 9. 300-MHz ^{1}H NMR spectrum of Co$_3$(CO)$_9$C(CH$_2$)$_n$OH (n = 4, 5) (II) in C$_6$D$_6$ at 25 °C. When line narrowed, resonance f is a triplet. There is about 20% of Co$_3$(CO)$_9$C(CH$_2$)$_4$OH in this sample.

Reaction of I with [CpFe(CO)$_2$]$^-$ yielded [Co(CO)$_4$]$^-$ (≈100%) and [CpFe(CO)$_2$]$_2$ as the major products. The fate of the boron is unknown.

Other Reactions. In order to test I as a cluster-building precursor, reactions with Fe$_2$(CO)$_9$, Co$_2$(CO)$_8$, and (CpNiCo)$_2$ were explored. In all cases the only products identified were those of the thermal decomposition reaction of I (see below). Displacement of THF with NEt$_3$ before addition of the metal reagents or removal of the THF solvent at low temperature followed by replacement with toluene changed the reaction process but yielded no cluster products containing a boron atom. In some cases, previously known compounds were observed in low yield, e.g., Co$_3$(CO)$_{10}$BH$_2$·NEt$_3$.[26] In the case of Fe$_2$(CO)$_9$ reaction in THF as solvent resulted in polymerization of the THF while reaction in toluene gave the same products observed for the thermal decomposition reaction of I. C$_3$H$_5$Co(CO)$_3$, another known metal fragment source, fails to react at −15 °C with I.

As [Co(CO)$_4$]$^-$ readily forms from I in the presence of bases and as this anion is considered to be a pseudohalogen,[27] we investigated I as an in situ source of [BH$_2$]$^+$. Reaction with PhMgBr yielded PhBH$_2$, which was identified as the NEt$_3$ adduct or the known disproportionation product BPh$_3$. [Co(CO)$_4$]$^-$ was a coproduct as expected. The apparent yield of PhBH$_2$ is ≈75%; however, solvent attack and/or CO reduction is still competitive. Thus, the product mixture was still too complex to justify use of I as a source of [BH$_2$]$^+$. Although I is isoelectronic with [Cp(CO)$_2$FeCH$_2$·SMe$_2$]$^+$, which is a proven methylene-transfer reagent,[28] it appears much less useful in a synthetic sense.

Compound I failed to react with 2-butene or 2,3-dimethyl-2-butene at −15 °C. In the latter case, the yield of H$_2$ on methanolysis is the same before and after addition of the olefin.

Thermal Reactivity. As already commented upon, the thermal decomposition (heating a solution of I to 25 °C) of I results in a complex mixture of products, only three of which have been characterized. Two major products are known compounds (Co$_4$(CO)$_{12}$ and [Co(CO)$_4$]$^-$). Another significant product is Co$_3$(CO)$_9$C(CH$_2$)$_n$OH (n = 4, 5) (II), whose characterization will be described later. The other products have not been fully characterized, but it is clear that they are cobalt carbonyl clusters containing a variety of reduced carbon fragments and/or THF cleavage products. We were unable to separate and characterize these clusters because of very similar physical properties. The reduction of metal-bound carbonyls by boranes is well-known,[29] and evidence of this type of reactivity for I is reported below. In addition to the metal-containing products, a complex mixture of organic products was produced.

Co$_3$(CO)$_9$C(CH$_2$)$_n$OH was characterized by mass spectrometry and infrared and ^{1}H NMR spectroscopy. As II is a derivative

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Table II. Bond Distances (Å) and Angles (deg) for $Co_3(CO)_9C(CH_2)_nOH$ (n = 4, 5)

	Distances		
Co(1)–Co(2)	2.457 (3)	Co(1)–Co(3)	2.462 (3)
Co(1)–C(11)	1.84 (2)	Co(1)–C(12)	1.77 (2)
Co(1)–C(13)	1.79 (2)	Co(1)–C(1)	1.93 (2)
Co(2)–Co(3)	2.475 (4)	Co(2)–C(21)	1.84 (2)
Co(2)–C(22)	1.82 (2)	Co(2)–C(23)	1.79 (2)
Co(2)–C(1)	1.89 (2)	Co(3)–C(31)	1.88 (2)
Co(3)–C(32)	1.78 (2)	Co(3)–C(33)	1.80 (2)
Co(3)–C(1)	1.86 (2)	O(11)–C(11)	1.12 (2)
O(12)–C(12)	1.13 (2)	O(13)–C(13)	1.15 (2)
O(21)–C(21)	1.12 (2)	O(22)–C(22)	1.12 (2)
O(23)–C(23)	1.15 (2)	O(31)–C(31)	1.07 (2)
O(32)–C(32)	1.11 (2)	O(33)–C(33)	1.11 (2)
C(1)–C(2)	1.49 (3)	C(2)–C(3)	1.55 (3)
C(3)–C(4)	1.59 (4)	C(4)–C(5)	1.68 (4)
C(5)–C(6)	1.73 (9)		
	Angles		
Co(2)–Co(1)–Co(3)	60.44 (10)	Co(2)–Co(1)–C(11)	101.8 (5)
Co(2)–Co(1)–C(12)	151.8 (6)	Co(2)–Co(1)–C(13)	96.9 (7)
Co(2)–Co(1)–C(1)	49.3 (7)	Co(3)–Co(1)–C(11)	100.7 (5)
Co(3)–Co(1)–C(12)	97.9 (6)	Co(3)–Co(1)–C(13)	148.8 (7)
Co(3)–Co(1)–C(1)	48.3 (6)	C(11)–Co(1)–C(12)	99.9 (8)
C(11)–Co(1)–C(13)	105.2 (8)	C(11)–Co(1)–C(1)	143.3 (8)
C(12)–Co(1)–C(13)	94.6 (9)	C(12)–Co(1)–C(1)	103.2 (9)
C(13)–Co(1)–C(1)	101.0 (9)	Co(1)–Co(2)–Co(3)	59.88 (9)
Co(1)–Co(2)–C(21)	95.7 (5)	Co(1)–Co(2)–C(22)	99.5 (6)
Co(1)–Co(2)–C(23)	154.5 (6)	Co(1)–Co(2)–C(1)	50.7 (5)
Co(3)–Co(2)–C(21)	101.7 (6)	Co(3)–Co(2)–C(22)	149.0 (6)
Co(3)–Co(2)–C(23)	97.1 (6)	Co(3)–Co(2)–C(1)	48.2 (6)
C(21)–Co(2)–C(22)	103.4 (8)	C(21)–Co(2)–C(23)	100.0 (9)
C(21)–Co(2)–C(1)	141.4 (7)	C(22)–Co(2)–C(23)	96.3 (9)
C(22)–Co(2)–C(1)	101.1 (8)	C(23)–Co(2)–C(1)	106.5 (8)
Co(1)–Co(3)–Co(2)	59.68 (9)	Co(1)–Co(3)–C(31)	97.2 (5)
Co(1)–Co(3)–C(32)	98.7 (6)	Co(1)–Co(3)–C(33)	152.1 (6)
Co(1)–Co(3)–C(1)	50.8 (6)	Co(2)–Co(3)–C(31)	100.3 (6)
Co(2)–Co(3)–C(32)	149.8 (6)	Co(2)–Co(3)–C(33)	97.3 (6)
Co(2)–Co(3)–C(1)	49.2 (7)	C(31)–Co(3)–C(32)	103.4 (8)
C(31)–Co(3)–C(33)	102.8 (9)	C(31)–Co(3)–C(1)	142.3 (9)
C(32)–Co(3)–C(33)	95.4 (8)	C(32)–Co(3)–C(1)	101.2 (10)
C(33)–Co(3)–C(1)	102.8 (8)	Co(1)–C(11)–O(11)	174.9 (16)
Co(1)–C(12)–O(12)	175.0 (18)	Co(1)–C(13)–O(13)	173.4 (21)
Co(2)–C(21)–O(21)	177.4 (16)	Co(2)–C(22)–O(22)	178.2 (17)
Co(2)–C(23)–O(23)	179.2 (20)	Co(3)–C(31)–O(31)	177.7 (16)
Co(3)–C(32)–O(32)	179.0 (17)	Co(3)–C(33)–O(33)	177.8 (20)
Co(1)–C(1)–Co(2)	80.0 (8)	Co(1)–C(1)–Co(3)	80.9 (7)
Co(1)–C(1)–C(2)	126.7 (15)	Co(2)–C(1)–Co(3)	82.6 (9)
Co(2)–C(1)–C(2)	134.0 (13)	Co(3)–C(1)–C(2)	132.8 (16)
C(1)–C(2)–C(3)	113.3 (18)	C(2)–C(3)–C(4)	110.3 (24)
C(3)–C(4)–C(5)	106.9 (26)	C(4)–C(5)–C(6)	107.3 (47)

of a thoroughly studied cluster,[30] only the nature of the alcoholic chain is relevant here. The ^{1}H NMR spectrum is shown in Figure 9 where the assignments indicated were confirmed by integration and by selective ^{1}H–^{1}H decoupling, i.e., a is coupled to b, b and e are coupled to c and d, and e is coupled to f. The chemical shifts of resonances a and e are consistent with a CH_2 group attached to an alkylidyne carbon and OH oxygen respectively. The NMR spectra indicate that the ratio of II (n = 4) to II (n = 5) is $\approx$4 for a sample of the crystalline material in general as well as for the specific crystal used for the X-ray structure determination. As discussed further below, the chemical shifts of the resonances due to protons e and f depend significantly on concentration. The spectroscopic information leaves no doubt that the capping μ_3-C atom of I has a linear hydrocarbon fragment terminating in an OH group. II with n = 4 has been reported previously as the product of the reaction of $MeSiCl_3$ and $[Co(CO)_4]^-$ in THF; however, characterization was by IR and mass spectrometry only.[31]

The molecular structure of II is shown in Figure 10 and consists of three cobalt atoms in a nearly equilateral triangular arrangement, each with three terminal carbonyl groups. In addition there is a triply bridging carbon atom that is one terminus of a six-atom chain that extends in a fairly straightforward manner away from the rest of the molecule. Table II contains pertinent bond distances and angles, and these parameters are consistent with those derived from earlier structural studies of the $(CO)_9Co_3(\mu_3\text{-CR})$ cluster.[32] Because molecules differing in chain length by one carbon cocrystallized, the hydroxyl end of the hydrocarbon chain of II could not be resolved in the crystallographic analysis (see Experimental Section). However, the final structure is sufficiently complete to establish the fact that there is nothing out of the ordinary with the cluster framework.

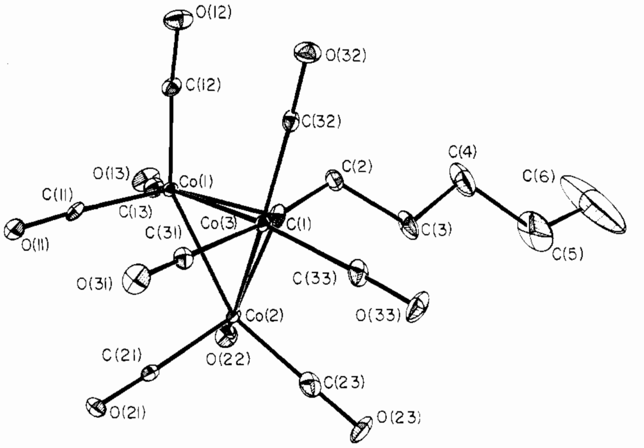

Figure 10. ORTEP drawing of the structure of II. The atoms are represented as 50% thermal elipsoids. Only six atoms are shown in the chain because of the disorder problem (see text).

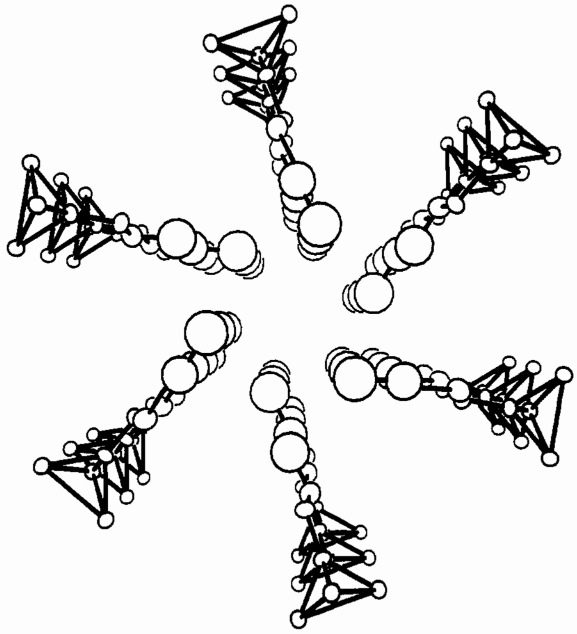

Figure 11. Representation of a hexagonal column of molecules of II showing the packing of the chains in the crystal lattice from the room-temperature determination. The CO ligands of the Co atoms are not shown for clarity.

Despite the disorder problem, the disposition of the individual molecules in the solid is clear. The packing diagram (Figure 11) shows infinite, hexagonal columns of molecules with the OH termini of the alkyl chains lying in the center of each column and the $Co_3(CO)_9$ fragments on the outside. Naturally, the question arises as why the packing for II is so different than that of the same cluster with a CH_3 substituent replacing the long chain. An obvious suggestion is that the packing in the solid state is driven by association of the OH groups plus association of metal cluster units. On the other hand, as only small energies determine

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(32) See, for example: Leung, P.; Coppens, P.; McMullan, R. K.; Koetzle, T. F. *Acta. Crystallogr.* **1981**, *B37*, 1347.

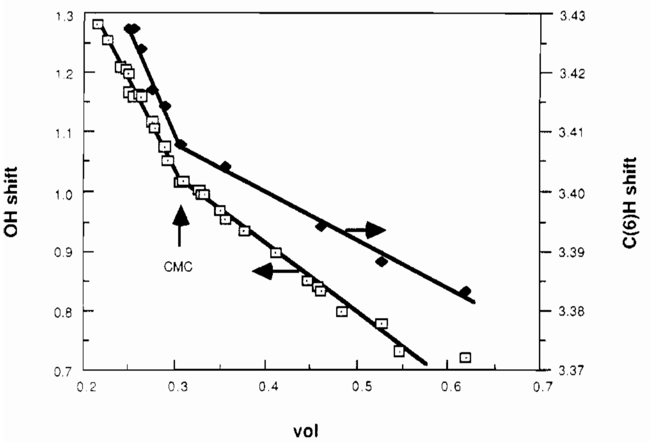

Figure 12. Plot of ^1H NMR shift at 28 °C vs the total volume of C_6D_6 (mL) added to a 0.578 mmol sample of II. The data plotted for the OH proton are combined data obtained from 300- and 100-MHz instruments in separate experiments while those for the C(6) protons are from the 300-MHz instrument alone. The critical micelle concentration is 0.18 M.

packing, the observed solid-state structure does not prove that bipolar interactions between molecules are the determining factor. Hence, we sought evidence for molecular association in solution.

It is well-known that surfactants form micelles in nonpolar solvents.[33] These aggregates, often referred to as reversed micelles, contain the hydrophilic groups in their interior. If the evidence for association from the solid state carries over into solution, II might be expected to form reversed micelles with the metal carbonyl cluster moiety in the outer layer in contact with the solvent. As noted above, several of the ^1H resonances in the NMR of II shift significantly with concentration. Hence, we chose the NMR method to seek evidence for association in solution.[33] The results of a ^1H NMR study are plotted in Figure 12 as chemical shift vs volume of solvent added to a fixed weight of II. The two curves shown are for the OH and adjacent methylene protons. The clear break occurring at the same value of $V = 1/M$ in each curve is evidence for the formation of micelles in solution. The critical micelle concentration (solid arrow in Figure 12, CMC = 0.18 M), the calculated number of molecules of II in each micelle (4) and the calculated monomer–micelle equilibrium constant of (10^4) are all reasonable for a bipolar species in an apolar solvent. For example, the same quantities measured for butylammonium propionate in benzene[33] are 0.05 M, 4, and 10^4. Although the nature of the aggregates in solution depend on the validity of the model used to interpret the NMR observations, the qualitative conclusion that association takes place in solution is clear. Hence, the observations in the solid state involve more than simple crystal packing forces and reflect the nature of the intermolecular interactions of an ambiphilic transition-metal cluster.

Discussion

$(CO)_4CoBH_2$·THF. The reaction in which I is formed is analogous to reaction 3, which is well-known.[34] One suggested mechanism for (3) involves the formation of $R_3SiCo(CO)_4$ and

$$2HSiR_3 + Co_2(CO)_8 \rightarrow 2R_3SiCo(CO)_4 + H_2 \qquad (3)$$

$HCo(CO)_4$ in an initial step followed by the disproportionation of $HCo(CO)_4$ to H_2 and $Co_2(CO)_8$.[35] A similar mechanism is possible for reaction 1. As the $Co(CO)_4$ fragment can be viewed as a pseudohalogen, the proposed first step, reaction 4, is analogous

$$Co_2(CO)_8 + BH_3\cdot THF \rightarrow (CO)_4CoBH_2\cdot THF + HCo(CO)_4 \qquad (4)$$

to the halogenation of borane. In contrast to $RCo(CO)_4$ (R = alkyl), $R_3SiCo(CO)_4$ is quite stable. The fact that I has proved exceedingly prone to cleavage perhaps should have been expected as a Co–B bond may well be weaker than a Co–C bond. However, it is dangerous to use evidence from reactivity as a measure of bond strength.

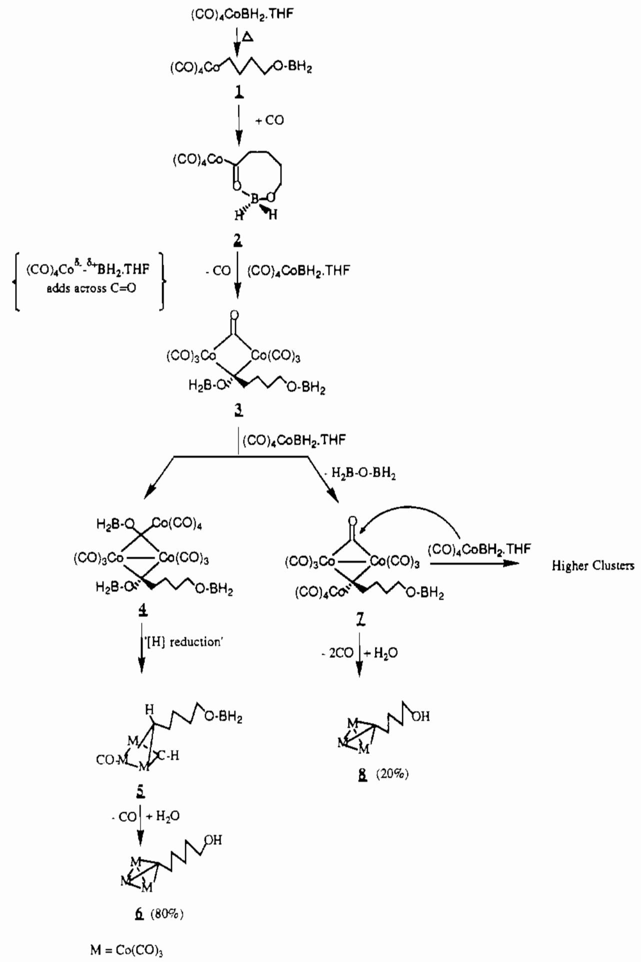

Figure 13. Proposed mechanism for the reaction of I with THF leading to the formation of II.

Reaction 3 plays a key role in the cleavage and derivatization of THF via the agency of silanes.[36] The cleavage of THF by I may proceed in an analogous fashion to that of the silylcobalt compound, i.e., by formation of $BH_2O(CH_2)_4Co(CO)_4$. As demonstrated previously for the silylcobalt system, CO insertion in the Co–C bond followed by reduction to CH_2 serves to explain the longer chains observed. Indeed a reasonable mechanism for the formation of II may be proposed on the basis of these and other known precedents (Figure 13).

As with the silicon system, opening of THF by I and CO insertion into the Co–Carbon bond of the alkyl substituent is facilitated by the anchimeric effect[37,38] of boron coordinating intramolecularly to the oxygen end of the carbonyl to form an eight-membered-ring intermediate (**2**).[31] This coordination also activates the carbonyl toward reduction by addition of I across a C=O bond as shown in **3** (see Figure 13). For example, carbonyl insertion into metal–carbon bonds (the so called migratory insertion reaction) has been shown to be greatly enhanced by coordination of a Lewis acid to the oxygen end of the CO molecule.[39,40] The boron atom in **2** can be viewed as serving a similar

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Table III. Selected Mulliken Populations from the Fenske–Hall Calculation on $RBH_2\cdot THF$

R	q(H)	q(B)	q(O)	$q(O)_{\text{bound-free}}$
H	−0.104	−0.153	−0.018	0.373
$(CO)_4Co$	−0.113	−0.247	−0.008	0.383
CH_3	−0.144	0.048	−0.050	0.343
CH_3S	−0.147	0.045	−0.049	0.342
Cl	−0.155	0.120	−0.060	0.331
CH_3O	−0.188	0.320	−0.075	0.316

function. Note that insertion of a second CO in this fashion after the first has been reduced would call for a nine-membered-ring analogue of **2**. This is unlikely to occur because of the unfavorable transannular steric effects that are known to accompany formation of rings of this size. A third mole of I can add to **3** either at a bridging CO (route a) or at the bridging carbene carbon (route b). In a route a the two carbon atoms in the bridging carbonyl and carbene of **3** end up being incorporated at the metal end of the hydrocarbon chain in the cluster product **6**. Route b involves addition at the carbene carbon to give structure **7**, which rearranges to the final product **8**, yielding a hydrocarbon chain one carbon atom shorter than that of product **6**. Route b is apparently less favorable. As performance of the reaction under 1 atm of CO had no effect on the ratio of chain lenngths observed for II, this branching reaction is included to account for the apparently constant ratio of the two different chain lengths.

It appears that once three cobalt atoms are held in close proximity, e.g., structure **4**, cluster formation occurs, resulting in a trinuclear cluster with no bridging CO groups. Hydrolysis of the terminal $-BH_2$ group takes place on silica gel during chromatography to yield a product mixture of **6** (80%) and **8** (20%). In terms of this mechanism, the relative percentages measure the relative reactivities of the bridging carbonyl and carbene carbon atoms in **3** toward addition of I. Terminal carbonyls are not as reactive toward addition of I, and thus, these products are stable under the reaction conditions. To account for the uncharacterized higher nuclearity products, we suggest further attack of I on the bridging CO of intermediate **3**.

Although the mechanism is speculative, the type of reactivity exhibited by I is not unexpected for a borane. For example, (arylthio)- and (alkylthio)boranes are effective ether cleavage reagents and borane itself will eventually cleave ethers.[41] $PhSBH_2$ reacts with THF to yield $PhS(CH_2)_4OH$ in excellent yields in reasonable reaction times. Thus, like PhS substitution, replacing H on BH_3 with a $Co(CO)_4$ substituent enhances the cleavage of THF. In contrast to PhS, the $Co(CO)_4$ substituent also provides a subsequent reaction path leading to II as well as other products.

The ability of I to coordinate Lewis bases is expected to be different from that of BH_3 itself. To obtain a qualitative measure of the difference, the distribution of BH_3 between THF and SMe_2 was compared to that of $(CO)_4CoBH_2$ between THF and SMe_2 by using ^{11}B NMR intensities to obtain the equilibrium ratios for reaction 5. For R = H, the equilibrium lies to the right whereas

$$SMe_2 + RBH_2\cdot THF \rightarrow RBH_2\cdot SMe_2 + THF \qquad (5)$$

for R = $Co(CO)_4$ it lies to the left. The difference in equilibrium ratios corresponds to ≈5 kcal/mol in free energy. The metal substituted-borane, $(CO)_4CoBH_2$, has less affinity for SMe_2 than BH_3 relative to THF. Apparently $(CO)_4CoBH_2$ is a somewhat harder acid than BH_3 just as BMe_3 is. The larger J_{BH} in $(CO)_4CoBH_2\cdot SMe_2$ vs I is consistent with a larger s character in the BH bond, which in turn is evidence of a weaker interaction with base. The fact that we observed no displacement of THF with 1 equiv of SMe_2, PPh_3, or $AsPPh_3$ is also consistent with this interpretation, although in the last two cases there may be a steric effect operative as well.

In order to further explore the electronic interactions in I, Fenske–Hall calculations were carried out on I and various substituted boranes, $RBH_2\cdot THF$. Mulliken populations pertinent to the discussion are gathered in Table III. One notes that the negative charge on the B–H hydrogen in I is larger than that on $BH_3\cdot THF$ just as that for $MeSBH_2\cdot THF$ is. This correlates with the greater facility of I and $PhSBH_2\cdot THF$ to cleave THF relative to $BH_3\cdot THF$. On the other hand, the negative charge on the boron atom of I is larger than that of $BH_3\cdot THF$ while the negative charge on the oxygen atom of the bound THF molecule is smaller for $(CO)_4CoBH_2$ than for $BH_3\cdot THF$. As the calculated oxygen population for free THF is −0.391, the latter observation suggests that I does have a greater affinity for THF than does BH_3 in spite of the fact that the metal makes the boron considerably more negatively charged. The complexity of donor–acceptor interactions is well-known, and the so-called spillover effect suggests that the ability of substituents at the acceptor site to accept electron density is an important factor governing net acidity.[42] Hence, the ability of a metal carbonyl fragment to accommodate negative charge appears to enhance the ability of $(CO)_4CoBH_2$ to coordinate a Lewis base despite the apparently higher charge density at boron.

$(CO)_9Co_3C(CH_2)_nOH$ (n = 4, 5). The spontaneous formation of organized assemblies has an important role in a number of chemical systems of contemporary interest. For example, so-called ambiphilic moieties with polar and nonpolar regions exhibit spontaneous phase separation into micelles, vesicles, microemulsions, and other organized assemblies.[43] The formation of liquid crystals and related materials (molecular "metals") also involves organization induced by specific structural properties of molecules.[44] Likewise, the whole area of electrically conductive low-dimensional solids depends on regular, interacting chemical assemblies, e.g. the stacking relationships in phthalocyanines.[45] There is no reason why metal clusters should be excluded from such behavior, and indeed, some efforts to promote the association of metal clusters in solution have already been described in the literature.[46] Tanaka et al. have tried to manipulate the redox behavior of iron–sulfur and iron–molybdenum–sulfur clusters by inducing them into aqueous micellar solutions.[47] To facilitate incorporation of the clusters into micelles, clusters having RS^- ligands with R = $C_6H_5C_8H_{17}$ were synthesized. Marchon et al. have explored the liquid crystal behavior of copper (II) n-alkanoates.[48] These compounds have binuclear cores surrounded by four alkyl chains pointing away from the Cu–Cu axis. Above 380 K, the dodecanoate forms a hexagonal columnar lattice, each column of which is made up of stacked binuclear units. We have now provided evidence that by synthetically modifying metal clusters in an understandable fashion, spontaneous assembly in the solid state and in solution can be promoted. This provides a means of generating clusters of clusters as well as other types of organization that may be of value in promoting certain types of reactivity.

Experimental Section

All reactions and manipulations were carried out with standard Schlenk-ware under a dry nitrogen atmosphere.[49] Solvents were dried (THF over KOH pellets, hexanes over molecular sieves), degassed and

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distilled before use. Methanol was degassed before use. $Co_2(CO)_8$ (Alfa) was dissolved in chilled hexanes (−5 °C) and filtered through either a medium frit or degassed Celite over a coarse frit. The orange filtrate gives large orange platelets after overnight storage in the freezer. The dry crystals can be stored in the freezer for long periods under nitrogen. 2,2′-Bipyridyl (Aldrich) and $AsPh_3$ (Aldrich) were dried on a vacuum line. BH_3·THF (1 M, Aldrich), Collman's reagent (Alfa or Aldrich) and 2,3-dimethyl-2-butene (Aldrich) were used as received. Allylcobalt carbonyl,[50] $[HFe_2(CO)_8][M]$,[51] and $K[FeCp(CO)_2]$[52] were prepared by published procedures. Silica gel (Kieselgel 60 PF_{254}, EM Science) made into a water slurry was used to prepare the 2 mm thick–20 cm diameter disks on glass for centrifugal preparative TLC. The disks were baked before use. Solvents for this purpose were nitrogen-degassed over a frit.

IR spectra were recorded in a CaF_2 cell on either a Perkin-Elmer 1420 or 727B spectrophotometer and calibrated by using the polystyrene band at 1601 cm^{-1}. UV–visible spectra were obtained on a Varian DMS-100 spectrometer. ^{11}B NMR spectra were obtained on a Nicolet NT 300 instrument while ^1H spectra were obtained on Magnachem A 200 and GN 300 spectrometers. ^{11}B shifts are reported with respect to $BF_3 \cdot OEt_2$ (δ 0) and ^1H with respect to TMS (δ 0). The mass spectral data were recorded on either a Finnigan MAT 8450 or a AEI MS-902 high-resolution mass spectrometer. A Carle Model 311 gas chromatograph with molecular sieves and Porapak columns in series and argon carrier gas was used to identify CO and H_2 and to determine their ratio.

Synthesis of I. To a flask containing a magnetic stirring bar and 1.04 mmol of $Co_2(CO)_8$ dissolved in 10 mL of THF and cooled to −18 °C, was added 2.08 mmol of BH_3·THF with a syringe. The reaction mixture was stirred at −18 °C for 5–6 h after which time the spectra reported above were obtained. The evolution of gas, identified mainly as H_2, was measured with standard volumetric techniques. The reaction mixture could be stored at −20 °C for at least 24 h with no decomposition. NMR were obtained without allowing the solution to warm up. To obtain the IR spectrum the reaction solution at −20 °C was flowed under nitrogen pressure via cannula into a variable-temperature IR cell. The spectroscopic properties of I are given in the results section.

Alcoholysis of I. In a typical experiment, 2.5 mL (0.52 mmol) of I in THF cooled to −78 °C was injected into an excess of MeOH and stirred vigorously. Volumetric measurement of the evolved gas was carried out along with GC analysis. Five runs gave an average of 1.54 mol of H_2 per mole of I. To obtain information on the products, the reaction of I with catechol was carried out. Volatiles were removed from a THF solution of I (2 mmol) by pumping at low temperature. Fresh THF was added, and a solution of 0.22 g (2 mmol) of catechol in THF was syringed in. There was an immediate gas evolution, and the ^{11}B spectrum showed signals at δ 22.7 (br s) and 16.7 (br s) accounting for ≈50% of the initial boron in the system. Removal of the volatile material followed by extraction with hexane and subsequent sublimation allowed the isolation of a white solid identified as $C_6H_4O_2BOH$ (NMR: ^{11}B δ 22.7 (br s); ^1H (C_6D_6) δ 7.54 (s), 6.86 (m), 6.69 (m), 4.27 (s), 3.34 (s). IR (C_6H_6, cm^{-1}): 3560 (br), 2970 (m), 2940 (sh), 1610 (m), 1510 (s), 1470 (s), 1420 (s), 1360 (m), 1320 (m), 1270 (s), 1250 (s), 1200 (br), 1150 (m), 1090 (m). MS: P = 136, 1 B, $^{12}C_6{}^1H_5{}^{11}B^{16}O_3$, 136.033 obsd, 136.03317 calcd) and a purple solid identified as $Co_4(CO)_{12}$ by IR spectroscopy.

Stoichiometry by UV–Visible Spectrometry. As shown in Figure 3, I exhibits an absorption band at 512 nm while $Co_2(CO)_8$ has a maximum at 350 nm with a shoulder at 420 nm. The former increases and the latter two decrease on the addition of BH_3·THF, using BH_3:$Co_2(CO)_8$ ratios of 0.5, 1.0, 1.5, 2.0, and 2.5 carried out in THF–hexane. To a solution 0.036 M in $Co_2(CO)_8$ in hexane was added an appropriate volume of BH_3·THF. The THF to hexane ratio was 1:10.7 and held constant by appropriate dilution of 1 M BH_3·THF. The absorbance was monitored at five times over a period of 8 h. Samples of either 0.1 or 0.05 mL were withdrawn, diluted volumetrically with hexane, and run within 5 min on the spectrophotometer at room temperature. Under these conditions, the IR spectrum shows some $Co_4(CO)_{12}$ and signals attributable to I (see Figure 4). The ^{11}B NMR spectrum under similar conditions shows I and $BH_3 \cdot Co_2(CO)_8$ (δ −49, q, J_{BH} = 105 Hz).

Base Displacement of THF from I. (a) Et_3N. To a solution of 1.29 mmol of I in 10 mL of THF at −20 °C was added 0.18 mL of Et_3N via a syringe. The reaction was monitored by ^{11}B NMR at low temperature. In a variation of this experiment, I was prepared in THF-d_8 as above. Addition of Et_3N was monitored by ^1H NMR at low temperature. Warming to room temperature and extracting with hexane yielded small amounts of $Co_3(CO)_{10}BH_2 \cdot NEt_3$ as identified by its ^{11}B and IR spectrum.

(b) Me_2S. No reaction was observed at −20 °C. Hence, after removal of THF at low temperature, the residue was dissolved in neat Me_2S and the reaction was observed with variable-temperature ^{11}B NMR spectroscopy. The NMR observations will be found in the Results section above.

(c) Other Bases. The reaction with other bases were examined in similar manner. Reaction with PPh_3 and $AsPh_3$ at −20 °C did not take place; however, on warming a complex reaction occurred. The chemical shifts for the base adducts are given in Table I.

Reaction of I with $[Fe(CO)_4]^{2-}$. In a typical reaction, 1.5 mmol of Collman's reagent, $[Fe(CO)_4]Na_2$, was weighed into a Schlenk tube and cooled to −78 °C and a cold solution of I (1.5 mmol) in THF was added to it via a cannula. The reaction mixture was stirred at −20 °C for 4–5 h. Then 1.5 mmol of BH_3·THF was added, and the reaction mixture was stirred at −20 °C for 4–5 h and then warmed to room temperature. Metathesis with (PPN)Cl produced an Et_2O-soluble part containing major ^{11}B signals at δ 32 (s), 18 (s), −10 (br), −15 (t), and −44 (q). The species corresponding to the first two resonances could be washed out with hexanes and are attributed to B–O-containing compounds resulting from the reduction of CO. The signal at δ −15 is due to $[B_2H_5Fe(CO)_5]^-$ while that at −10 is unknown.[25] The precipitate after the Et_2O extraction was identified as $[Co(CO)_4]^-$ by IR analysis and contained nearly 100% of the Co used in the reaction. Examination of the same reaction with ^{11}B NMR with an external ^{11}B reference for integration at low temperature revealed the rapid loss of I and the production of a large singlet at 17 attributed to B–O species. It is only after the addition of BH_3·THF that the other signals gradually grow in. As $[B_2H_5Fe(CO)_5]^-$ is produced by the reaction of BH_3·THF with $[Fe(CO)_4]^{2-}$ with the production of $[BH_4]^-$ clearly I is entirely consumed before the addition of the borane. The reaction of I with $[Fe_2(CO)_8]^{2-}$ was carried out in similar fashion with similar results; i.e., CO reduction appears to be the primary reaction route.

Reaction with $[HFe_2(CO)_8]^-$. A cold solution of 0.77 mmol of PPN-$[HFe_2(CO)_8]$ in THF was added to a −20 °C THF solution of I (0.77 mmol), and the reaction mixture was stirred at −10 °C overnight and then at room temperature for 24 h. The loss of PPN$[HFe_2(CO)_8]$ was monitored by IR. THF was removed, Et_2O added, and $[Co(CO)_4]^-$ precipitated. The PPN$[Co(CO)_4]$ isolated was 45% of the cobalt used by weight. The ^{11}B spectrum showed evidence for CO reduction (δ 19 (s)) but was otherwise uninteresting. IR spectroscopy of the Et_2O solution showed the presence of $[FeCo_3(CO)_{12}]^-$ and $[HFe_3(CO)_{11}]^-$, and the former was confirmed by FAB mass spectrometry. Repeating the reaction with the sodium salt yielded evidence for $Fe(CO)_5$, $Fe_3(CO)_{12}$, and $Co_4(CO)_{12}$ by IR and $H_3Fe_3(CO)_9CR$ by mass spectrometry. The latter compound is a product of the reaction of iron carbonyls in the presence of hydride and boranes.[28]

Reaction with $K[FeCp(CO)_2]$. A Schlenk tube containing 0.24 g (1.1 mmol) of $[FeCp(CO)_2]^-$ was cooled to −78 °C. To this was added a cold solution of I (1.1 mmol) in THF via a cannula and stirred at −20 °C. The reaction was complete in ca. 5 min as shown by the disappearance of the characteristic bands of $[FeCp(CO)_2]^-$ in the IR spectrum of the reaction solution; however, stirring was continued for 1 h. The ^{11}B NMR of a toluene extract showed evidence of CO reduction (singlets at δ 30 and 18) but no evidence for other metallaboranes. The toluene-insoluble part contained all (90 ± 10%) the cobalt used in the reaction as $K[Co(CO)_4]$. Addition of BH_3·THF to the reaction mixture gave basically the same results; however, in this case, IR and ^1H NMR showed the presence of $[FeCp(CO)_2]_2$ and some $FeCp(CO)_2Co(CO)_4$.

Reaction with PhMgBr. Volatiles were removed from a THF solution of I (2 mmol) at −20 °C. Fresh THF was added (10 mL), and 2 mmol of PhMgBr was syringed into the reaction flask. The reaction mixture was stirred at −20 °C for 5 h and at room temperature for 2 h. Then 2 mmol of Et_3N was syringed into the flask and the reaction mixture stirred overnight at room temperature. The ^{11}B NMR of the Et_2O-soluble portion of the products integrated with respect to a calibrated external standard showed signals at δ 60 (br s, ≈10% B), 45 (br s, ≈10% B), −7 (t, J_{BH} = 95 Hz, ≈2% B), and δ −14 (q, J_{BH} = 92 Hz, 45% B). The last signal is due to $BH_3 \cdot NEt_3$ while the triplet at δ −7 is due to $PhBH_2 \cdot NEt_3$, which is a known compound.[53,54] As $PhBH_2$ is known to disproportionate to Ph_3B and B_2H_6,[55] the broad singlet at δ 60 is assigned to the former[56] while the B_2H_6 appears as the amine adduct. Separation by distillation or column chromatography was unsuccessful; however, the white sublimate from a reaction with no added amine exhibited the same ^{11}B signals at δ 60 and 45, and the ^1H NMR showed Ph resonances as

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well as other complex signals in the δ 1–4 region. Hence, Ph_3B is formed, and the signal at δ 45 is assigned to Ph_2BR, where R is probably alkyl or alkoxy. On the basis of the ^{11}B spectra, the overall yield of $PhBH_2$ before disproportionation and reaction is $\approx$75%. The solid left after Et_2O extraction was metathesized with (PPN)Cl by using THF as a solvent. The THF solution contained no boron, and IR spectroscopy showed the presence of $[Co(CO)_4]^-$ together with another unidentified anionic metal carbonyl. Thus, the reaction of I with PhMgBr appears to produce $PhBH_2$ and $[Co(CO)_4]^-$, but reduction of CO or cleavage of THF still appears to be competitive.

Synthesis of II. First, 2 g (5.8 mmol) of $Co_2(CO)_8$ was dissolved in 20 mL of prechilled THF. In a second Schlenk tube, 12 mL (11.6 mmol) of $BH_3{\cdot}THF$ was syringed into 20 mL of THF chilled to ca. –5 °C. Then the $BH_3{\cdot}THF$ solution was siphoned into the reaction flask over a period of 5 min while being vigorously stirred. The color changed to deep red as a gas was evolved. After mixing, the solution was stirred for 0.5 h at this temperature and then for a further 2.5 h (total 3 h) at room temperature. The color changed to red-brown, and a black precipitate fell out. Reaction progress can be monitored by infrared spectroscopy (the characteristic peak for bridging carbonyls of the starting material at 1840 cm^{-1} recedes into the base line). Stirring was stopped to allow solids to settle.

The supernatant was filtered through 15-cm degassed silica gel in a 2.3-cm-wide column and the filtrate concentrated for centrifugal chromatography (2-mm plate) under nitrogen. Elution with hexanes washed off two red bands, which were discarded. Elution with an increasing methylene chloride gradient elutes a brown-red band, which was crystallized from toluene to give long red needles of product $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_nOH)$ (n = 4, 5) with $[n = 5]/[n = 4] = 4$ (yield $\approx$ 30%). MS, (EI with either regular or DCI probe): 528 amu (weak). Isobutane DCI gave a substantial M + 1 peak at m/e 529. Two carbonyls are very labile, judging from the relatively high intensity of the peak at m/e 472 (–2 CO), successive loss of CO to m/e 276 (–9 CO); $^{12}C_{13}{}^{1}H_{11}{}^{16}O_8{}^{59}Co_3{}^+$, measd 471.824, calcd 471.8449. ^1H NMR (C_6D_6, 300 MHz): δ 3.48 (t, 2 H, CH_2 5), 1.78 (m, 2 H, CH_2 4), 1.26 (m, 4 H, CH_2 3 and 2), 3.28 (q, 2 H, CH_2 1), 0.46 (t, 1 H, OH) ppm; assignment based on homonuclear decoupling. Partially overlapping signals (ca. 10% of the intensity) of the one carbon atom shorter chain $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_4OH)$ are clearly evident. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 200.5 (9 CO), 62.37, 59.27, 37.08, 32.68, 26.22 (5 CH_2) ppm. IR (toluene): 3575 (vw, OH), 2090 (w), 2040 (vs), 2022 (s), 2002 (vw) cm^{-1}.

X-ray Structure of II. Two structure determinations were carried out. The first at 298 K yielded the basic structure, but several atoms of the hydrocarbyl chain could not be refined. The second at 118 K gave a more satisfactory solution, but disorder at the OH end of the chain prevented a complete solution. The second determination is reported here. A deep brown crystal of hexagonal cross section of the compound $Co_3(CO)_9C_6H_{11}O$ having approximate dimensions 0.45 × 0.25 × 0.20 mm was mounted on a glass fiber and was chilled under the cold stream of nitrogen in the diffractometer. The crystal mounting was random in orientation. Preliminary examination was carried out with Mo Kα radiation (λ = 0.71073 Å) on a κ geometry automated Enraf-Nonius CAD4 diffractometer equipped with a graphite-crystal incident-beam monochromator. Indexing the 15 automatically centered reflections resulted in a triclinic cell. DeLauney reduction of this triclinic cell indicated a primitive rhombohedral cell. Data collection and structure solution were carried out in an equivalent triply primitive hexagonal cell. A set of higher angle data (2θ) were obtained by using the initial orientation matrix. Final cell constants and an orientation matrix for data collection were calculated by the least-squares refinement of 25 reflections ($22° < 2\theta < 29°$) measured by the computer-controlled diagonal slit method of centering. Final cell parameters were a = 34.409 (15) Å, b = 34.398 (21) Å, c = 8.575 (5) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, and V = 8789.8 Å^3. For Z = 18 and a formula weight of 528.05, the calculated density is 1.796 g/cm^3. The data were collected at 118 K by using the $\theta/2\theta$ scan technique with a variable scan rate between 4.0 and 56.8° in 2θ (excluding $-h + k + l \neq 3n$). The scan range was determined as a function of θ. The scan width was calculated as ω scan width = 0.8 × 0.350 (tan θ)°. Moving-crystal–moving-counter background counts were made by scanning an additional 25% above and below this range; thus, the ratio of peak counting time to background counting time was 2:1.

Inspection of the data showed no absence due to glide planes. Like that for the room-temperature structure of this compound, the space group assigned was $R\bar{3}$. A total of 5144 reflections ($+h,+k,\pm l$) were measured of which 2621 were space group allowed ($-h + k + l = 3n$, $k > h$). The number of unique observed reflections ($F_o > 3\sigma(F_o)$) was 1443. As a check on the crystal stability, four representative reflections were measured every 60 min of X-ray exposure. As the intensity of these standards remained constant within experimental error, no decay correction was applied. Orientation of three reflections were monitored every 250 reflections, and a new orientation matrix was calculated by centering the 25 reflections if the angular variation was >0.10°.

Data reduction was carried out by the appropriate program of the SDP software.[57] Lorentz and polarization corrections were applied to the data. The linear absorption coefficent is 2.563 mm^{-1} for Mo Kα radiation. Empirical absorption correction was applied to the data by using nine ψ scan curves with $\chi > 83°$. The average correction factor = 0.988. Intensities of equivalent reflections were averaged. The agreement factor for the averaging of 2616 space group allowed data was 1.6% based on I.

The structure was solved by direct methods (MULTAN 78[58]) in space group $R\bar{3}$. A total of 22 non-hydrogen atoms were located from the MULTAN solution. The heavy-atom positions agreed with the Patterson solution. The rest of the atoms of the aliphatic chain were located from a subsequent difference Fourier map.

Several problems were encountered during refinement of the structure. From the NMR and other spectroscopic data as well as chemical reactions of the compound it is known that a seventh atom (oxygen as hydroxyl) exists at the end of the aliphatic chain. However, all attempts to find any atom beyond the sixth atom from difference Fourier peaks and refine any of them as C or O was unsuccessful. The highest peaks from the difference Fourier (0.33 e/Å^3) were included as O and resulted in incredible temperature factors.

Two different disorder models were tested. The temperature factors of the C atoms of the chain increase progressively, and there is a big change in the temperature factor from C(5) to C(6). Assuming appreciable disorder starts from the C(6), refinement of partially occupied C(6′) and an atom bound to it as partially occupied O was not successful, from the crystallographic point of view, as the atoms were not well behaved. Two peaks bonded to C(6) were included as partially occupied O's, but as in all the previous cases, the atoms resulted in extremely big temperature factors.

Attempts to find any reasonable position from the difference Fourier contour map of the region containing C(6) proved to be of no help. Also, several calculated positions (assuming ideal geometry) were included and had to be rejected on the basis of their behavior toward least-squares refinement.

Therefore, the only reasonable model that could be refined has a six-carbon aliphatic chain bonded to all the Co atoms through C(1). However, due to the disorder problem, the distances between C(4)–C(5) and C(5)–C(6) are long compared to a normal C–C single-bond distance. Even though the position of the atoms as located from the difference Fourier are approximately 1.55 Å apart, after refinement they converged to their current positions.

No hydrogen atoms were included in the refinement of the molecule. Full-matrix least-squares refinement was carried out on the non-hydrogen atoms to convergence. All the atoms were refined anisotropically. Atomic form factors used were taken from Cromer and Mann.[59] Anomalous dispersion effects were included in F_c for Co. The values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[60] The final refinement included 244 variables. The converged model had unweighted (R_1) and weighted (R_2) agreement factors of 0.077 and 0.096, respectively, where $R_1 = \sum I|F_o| - |F_c|/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2}$. The highest peak in the final difference Fourier had a height of 0.33 e/Å^3. All calculations were performed on a VAX 11/730 computer. The experimental conditions are summarized in Table IV, and selected bond distances and angles are given in Table II.

Reaction of $Co_2(CO)_8$ with $BH_3{\cdot}THF$ in THF-d_8. Incorporation of Deuterium into the Hydrocarbon Tail of II. First, 2.67 g (7.8 mmol) of $Co_2(CO)_8$ was dissolved in 10 mL of chilled (–10 °C) THF-d_8. In a second Schlenk tube, 11 mL of 1 M $BH_3{\cdot}THF$ was added to 20 mL of THF-d_8 and cooled to –10 °C before being slowly siphoned into the reaction flask. Reaction and workup were exactly as in the preceding experiment. MS (EI) shows deuterium incorporation, 536 amu = M$^+$, immediate loss of 2 CO to 480 anu, then successive loss to CO-free ions from 480 amu. Also present was the nondeuterated $(CO)_9(Co_3(\mu_3\text{-}C\text{-}(CH_2)_5OH)$ (528 amu) with signals ca. half the intensity of the D-incorporated molecule. This was to be expected because the 11 mL of $BH_3{\cdot}THF$ used was deuterium-free, so only partial enrichment was possible. NMR data for $(CO)_9Co_3(\mu_3\text{-}CCD_2(CD_2)_4OH)$ are as follows. ^1H (C_6D_6 200 MHz): δ 3.48 (t, 2 H, CH_2 a), 1.78 (m, 1.2 H, CH_2 b), 1.26 (m, 2.5 H, CH_2 c and d), 3.28 (q, 0.8 H, CH_2 e), 0.46 (t, 1 H, OH) ppm. The noninteger integral values unequivocally locate the positions of deuterium incorporation in the hydrocarbon tail. ^2H (toluene, C_6D_6

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Table IV. Summary of Crystal Data and Intensity Collection Parameters for $Co_3(CO)_9C(CH_2)_nOH$ ($n = 4, 5$)

formula	$Co_3O_{10}C_{15}H_{11}$
fw	528.05
cryst dimens, mm	0.45 × 0.25 × 0.20
space group	$R\bar{3}$
temp, K	118
a, Å	34.409 (15)
b, Å	34.398 (21)
c, Å	8.575 (2)
$\alpha = \beta$, deg	90.0
γ, deg	120.0
V, Å^3	8789.8
Z	18
d_{calc}, g/cm^3 (298 K)	1.796
radiation	graphite-monochromated Mo Kα (0.71073 Å)
scan technique	θ–2θ
max 2θ, deg	56.8
criterion for observn	$F_o > 3\sigma(F_o)$
no. of data measd	5144
no. of unique obsd data	1443
bkgd	profile anal.
merging R value (I), %	1.6%
final no. of variables	244
μ(Mo Kα), mm^{-1}	2.563
R_1	0.077
R_2	0.096
goodness of fit	2.69

reference at 7.15 ppm, 75.4 MHz): δ 3.21 (s, 2 D), 1.76 (s, 2 D), 1.24 (s, 4 D) ppm.

Reaction of II with $(CH_3)_3SiCl$. To 0.15 g (0.28 mmol) of $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_5OH)$ in 10 mL of toluene (−78 °C) were added 2 equiv (0.57 mmol, 0.1 mL) of $(CH_3)_3SiCl$ and excess Et_3N and allowed to warm to room temperature while being stirred. No color change was observed, but a white powder could be seen toward the top of the Schlenk tube. Since the OH signal is very weak in the IR region, this reaction could not be satisfactorily followed by IR spectroscopy; therefore, 4 h reaction time was allowed in order to be certain. The product mixture was stripped of solvent under vacuum, and the solid residual was extracted with 1.5 mL of benzene-d_6. Filtration through a medium frit left behind a white residual, which was discarded. The red filtrate was analyzed by NMR. The OH signal of II at 0.46 ppm is totally absent, implying a practically quantitative conversion of II to $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_nOSi(CH_3)_3)$. MS (EI): observed 600 amu = M$^+$, $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_5OSi(CH_3)_3)$ (80%), and 586 amu = M$^+$, $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_4OSi(CH_3)_3$ (20%). ^{1}H NMR (C_6D_6, 300 MHz): δ 3.49 (m, 4 H), 1.85 (m, 2 H), 1.48–1.39 (m, 4 H), 0.11 (s, 9 H) ppm. A smaller signal at 0.09 ppm (ca. 20%) is due to the product coming from the shorter chain $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_4OH)$: $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 200.53 ppm (9 CO) and δ 62.15, 59.37, 37.08, 32.72, and 26.31 ppm account for all the proton-containing backbone carbons of the hydrocarbon chain. The resonance with highest intensity (−0.46 ppm) belongs to the $-Si(Me)_3$ group. IR spectrum (toluene) was identical with that of II except for the absence of the OH stretching vibration.

Concentration Dependence of ^{1}H NMR Shifts. A freshly sublimed sample of II was placed in an NMR tube and weighed by difference. The sample was dissolved in C_6D_6 and the tube reweighed. After the ^{1}H NMR spectrum (28 °C) was recorded, additional C_6D_6 was added and the weight recorded. Weights were measured after each spectrum to check for solvent loss by evaporation. Volume of solvent present was obtained from the weights by using the density of benzene.

Table V. Fractional Coordinates

atom	x	y	z
Co(1)	0.24527 (8)	0.05181 (7)	0.16350 (23)
Co(2)	0.26910 (8)	0.09820 (8)	0.40033 (24)
Co(3)	0.26058 (9)	0.02237 (8)	0.40311 (24)
O(11)	0.3319 (5)	0.0883 (5)	−0.0031 (15)
O(12)	0.1899 (6)	−0.0343 (5)	0.0138 (18)
O(13)	0.1977 (6)	0.0921 (5)	0.0083 (16)
O(21)	0.3634 (4)	0.1544 (4)	0.3007 (15)
O(22)	0.2293 (5)	0.1548 (5)	0.3352 (16)
O(23)	0.2772 (6)	0.1127 (5)	0.7399 (15)
O(31)	0.3528 (5)	0.0438 (5)	0.3274 (17)
O(32)	0.2083 (6)	−0.0724 (5)	0.3323 (17)
O(33)	0.2592 (6)	0.0125 (5)	0.7406 (15)
C(11)	0.2988 (6)	0.0725 (6)	0.0597 (18)
C(12)	0.2124 (7)	−0.0001 (6)	0.0660 (20)
C(13)	0.2183 (7)	0.0789 (8)	0.0710 (24)
C(21)	0.3281 (7)	0.1331 (6)	0.3418 (19)
C(22)	0.2452 (6)	0.1338 (7)	0.3602 (22)
C(23)	0.2743 (8)	0.1073 (6)	0.6070 (27)
C(31)	0.3193 (7)	0.0366 (6)	0.3527 (20)
C(32)	0.2282 (7)	−0.0360 (6)	0.3607 (19)
C(33)	0.2589 (7)	0.0155 (7)	0.6119 (22)
C(1)	0.2187 (7)	0.0406 (7)	0.3688 (21)
C(2)	0.1701 (7)	0.0198 (7)	0.4058 (23)
C(3)	0.1608 (9)	0.0246 (8)	0.580 (3)
C(4)	0.1085 (10)	−0.0009 (10)	0.612 (4)
C(5)	0.1016 (12)	0.0099 (16)	0.798 (5)
C(6)	0.0449 (27)	−0.0106 (19)	0.826 (13)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

Fenske–Hall Calculations. The Fenske–Hall method is a proven, nonparametrized MO method that is often chosen to characterize the electronic structure of complex systems presently beyond the limits of more exact methods.[61] A minimal basis set was employed in these calculations. Clementi's free-atom double-ζ Hartree–Fock–Slater type orbitals[62] were used for the second-row elements. The STO functions each atoms were of single-ζ form, except for the valence p orbitals and the valence d orbitals on the transition metals; all of which were of double-ζ form. The hydrogen 1s exponent was set at 1.16. The exponents for the transition-metal valence s and p orbitals were set at 2.0. These functions are less diffuse than atomic results but are found to describe bonding in organometallic complexes more accurately.[63]

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Supplementary Material Available: Tables containing positional parameters, refined anisotropic temperature factors, least-squares planes, and a summary of the crystal data and collection parameters (4 pages); a table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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