Articles

Synthesis of $[AsPh_4][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]$ by Oxidative Chloride Substitution of $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$

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The deprotonation of $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$ with *n*-butyllithium yields the dianionic complex $[Li]_2[Fe_3(CO)_9(\mu_3\text{-}HBCO)]$, which has been spectroscopically characterized. In contrast to the facile reprotonation of closely related ferraboranes, protonation of $[Li]_2[Fe_3(CO)_9(\mu_3\text{-}HBCO)]$ leads to decomposition. On the other hand, reaction of this dianionic complex with 2 equiv of $FeCl_3$ gives a good yield of $[Li][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)$. Metathesis with $[AsPh_4][Cl]$ yields $[AsPh_4][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]$, which has been crystallographically characterized (triclinic, $P\bar{1}$, $a = 9.534(3)$ Å, $b = 13.305(4)$ Å, $c = 15.225(4)$ Å, $\alpha = 104.39(2)°$, $\beta = 103.56(2)°$, $\gamma = 99.23(2)°$, $V = 1768.7(8)$ Å^3, $Z = 2$). Comparison with the analogous osmium clusters, as well as isoelectronic organometallic clusters, reveals relationships among their structures, properties, and energetics.

Introduction

The borylidyne cluster $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$ has been characterized and its chemistry explored by the Shore group.[1-4] In the same time period, we reported the spectroscopic characterization of the analogous iron compound with a very different disposition of the three hydrogen atoms on the trimetal–boron framework, i.e., $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$.[5] Lack of a solid-state structure prevented a definitive comparison with the osmium cluster. We have now succeeded in preparing a dianion of this ferraborane which has been converted into a chloro derivative of the monoanion $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$. Besides demonstrating a new method of functionalizing metallaborane clusters, these new data establish the preferences of hydrogen and CO for boron vs transition element sites on a cluster with a M_3B core and permit a comparison with the isoelectronic organometallic clusters.

Experimental Section

General Data. All reactions were carried out under an atmosphere of prepurified dinitrogen using standard Schlenk techniques.[6] THF, diethyl ether, and hexane were dried and degassed by distillation from sodium benzophenone ketyl. $FeCl_3$, $Fe_2(CO)_9$, $AsPh_4Cl$, *n*-BuLi (1.6 M solution in hexanes), and $BH_3\cdot SMe_2$ (10.0 M), obtained from Aldrich, and (PPN)Cl (bis(triphenylphosphine)nitrogen(1+) chloride, obtained from Johnson Matthey, were used without further purification. IR spectra were recorded on a Nicolet Model 205 spectrometer. ^1H and ^{11}B NMR spectra were obtained using GN-300 and NT-300 spectrometers, respectively. The ^1H NMR spectra were referenced to the solvent peak, and $[N(CH_3)_4][B_3H_8]$ (δ −29.7) was used as an external reference for the ^{11}B spectra.

Preparation of $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$ (I). $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$ was prepared as described previously.[7] The dianion is formed by the slow addition of a stoichiometric amount *n*-BuLi at low temperature. Excess *n*-BuLi or rapid addition results in the decomposition of the ferraborane into uncharacterized products. Thus, to a cold (−78 °C) solution of $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$ (0.020 g, 0.044 mmol) in THF was added *n*-BuLi dropwise over a period of several hours. The dark-brown solution was stirred vigorously, and the progress of the reaction was monitored by IR spectroscopy. The monoanion $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ is produced after the addition of 1 equiv of *n*-BuLi. Addition of further base causes the solution to turn deep red-brown and produces bands in the IR spectrum at 2006 w, 1935 s, 1893 m cm^{-1}, which are attributed to the dianion. The yield of the dianion based on ^{11}B NMR integration is 50%. A THF solution of the dianion can be stored for several days at −40 °C under N_2 and can be used *in situ* for further experiments. Metathesis with (PPN)Cl and $AsPh_4Cl$ and recrystallization from THF/hexanes at −40 °C produce a conveniently handled red-brown powder, but no single crystals suitable for a structure determination were obtained. NMR: ^{11}B (THF, 20 °C) δ 29, J_{BH}

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Table 1. Structure Determination Survey for $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)][AsPh_4]$

	Crystal Data
empirical formula	$C_{34}H_{21}AsBClFe_3O_{10}$
color; habit	dark-red block
crystal size	0.24 × 0.24 × 0.54 mm^3
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimens	a = 9.534(3) Å b = 13.305(4) Å c = 15.225(4) Å α = 104.39(2)° β = 103.56(2)° γ = 99.23(2)°
V	1768.7(8) Å^3
Z	2
fw	878.2
density (calcd)	1.649 g/cm^3
abs coeff	22.73 cm^{-1}
F(000)	876
	Data Collection
diffractometer used	Siemens P4
radiation	Mo Kα (λ = 0.710 73 Å)
temp	233 K
monochromator	highly oriented graphite crystal
2θ range	4.0–50.0°
scan type	Wyckoff
scan speed	variable; 6.00–20.00°/min in ω
scan range (ω)	1.00°
bkgd measmt	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
std reflns	3 measd every 197 reflns
index ranges	$-12 \le h \le 12$ $-17 \le k \le 16$, $0 \le l \le 19$
no. of reflns collected	8441
no. of independent reflns	8134 (R_{int} = 2.1%)
no. of obsd reflns	4541 ($F > 4.0\sigma(F)$)
abs cor	semiempirical
min/max transm	0.7171/0.8661
	Solution and Refinement
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	N/A
extinction cor	N/A
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
no. of params refined	467
final R indices (obsd data)	R = 5.13%, R_w = 5.22%
R indices (all data)	R = 10.76%, R_w = 6.55%
goodness-of-fit	1.01
largest and mean Δ/σ	6.627, 0.014
data-to-param ratio	9.7:1
largest diff peak	0.69 e Å^{-3}
largest diff hole	−0.52 e Å^{-3}

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$)

	x	y	z	U(eq)[a]
As	800(1)	8962(1)	3073(1)	31(1)
Fe(1)	−4903(1)	6753(1)	−1577(1)	37(1)
Fe(2)	−3728(1)	6062(1)	−2872(1)	36(1)
Fe(3)	−2320(1)	6313(1)	−1137(1)	35(1)
Cl	−5600(2)	3948(1)	−2303(1)	52(1)
O(1)	−7906(7)	6638(5)	−2676(5)	83(3)
O(2)	−6011(6)	5636(4)	−361(4)	71(3)
O(3)	−4001(7)	8892(4)	−209(4)	92(3)
O(4)	−3991(7)	8310(4)	−2544(4)	73(3)
O(5)	−1325(7)	7148(5)	−3446(5)	92(3)
O(6)	−2855(5)	4035(4)	−3356(3)	55(2)
O(7)	−6337(7)	5439(5)	−4512(4)	95(3)
O(8)	−839(6)	8443(4)	−1065(4)	86(3)
O(9)	191(6)	5341(5)	−1321(4)	85(3)
O(10)	−1881(6)	6823(4)	903(3)	69(2)
C(1)	−6731(9)	6691(5)	−2242(5)	51(3)
C(2)	−5532(8)	6046(5)	−845(5)	46(3)
C(3)	−4330(9)	8062(6)	−725(5)	57(3)
C(4)	−4125(8)	7469(5)	−2413(4)	47(3)
C(5)	−2267(9)	6747(6)	−3216(5)	55(3)
C(6)	−3214(7)	4828(5)	−3150(4)	45(3)
C(7)	−5306(9)	5697(6)	−3874(5)	56(3)
C(8)	−1444(8)	7601(6)	−1109(5)	57(3)
C(9)	−787(8)	5726(6)	−1247(5)	51(3)
C(10)	−2067(8)	6606(5)	108(5)	47(3)
C(11)	−304(7)	6881(5)	3213(5)	48(3)
C(12)	−490(9)	6150(6)	3713(6)	59(4)
C(13)	180(10)	6436(7)	4665(7)	73(4)
C(14)	1016(9)	7438(6)	5146(6)	63(4)
C(15)	1230(7)	8177(5)	4667(5)	45(3)
C(16)	564(6)	7899(5)	3712(4)	35(2)
C(17)	1786(9)	10945(6)	4541(5)	68(4)
C(18)	2813(12)	11828(7)	5175(7)	94(5)
C(19)	4223(13)	11983(7)	5191(7)	86(5)
C(20)	4681(10)	11252(10)	4575(7)	98(5)
C(21)	3676(8)	10328(6)	3923(6)	61(3)
C(22)	2218(7)	10201(5)	3932(4)	38(2)
C(23)	1625(8)	9113(5)	1418(5)	49(3)
C(24)	2123(8)	8758(6)	642(5)	55(3)
C(25)	2511(8)	7791(6)	461(5)	52(3)
C(26)	2404(9)	7167(6)	1048(6)	62(4)
C(27)	1913(8)	7506(5)	1828(5)	50(3)
C(28)	1508(6)	8465(5)	2004(4)	34(2)
C(29)	−1031(8)	10300(5)	2454(5)	58(3)
C(30)	−2358(10)	10577(6)	2173(6)	68(4)
C(31)	−3663(10)	9961(7)	2150(6)	72(4)
C(32)	−3650(8)	9048(7)	2374(6)	75(4)
C(33)	−2336(8)	8742(6)	2664(6)	59(3)
C(34)	−1038(6)	9376(4)	2698(4)	34(2)
B	−4424(7)	5292(5)	−1977(5)	31(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

≈ 40 Hz; ^{1}H (CD_3CN, 20 °C) δ −12.1, br, Fe–H–B. IR (THF, cm^{-1}) 2006 w, 1935 s, 1893 m.

Protonation of I. Attempted reprotonation of the dianion with CF_3COOH, H_3PO_4 (40%), or H_2O under a variety of conditions was unsuccessful. Although reaction occurred in all cases, complete degradation of the cluster ensued. Among the ultimate products observed were $[HFe_3(CO)_{11}]^-$, $Fe_3(CO)_{12}$, and $[HFe_4(CO)_{12}BH]^-$. No evidence for $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$ or $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ was observed by NMR or FAB mass spectrometry.

Preparation of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]^-$ (II). In a typical reaction, a 0.1 M THF solution of $FeCl_3$ was added via cannula to a solution of I in THF (0.203 g, 0.428 mmol) at −30 °C with stirring. After the addition of 2 molar equiv of $FeCl_3$, bands due to the starting material were replaced with bands in the IR spectrum of the product II, and the reaction mixture was allowed to warm to room temperature. The yield of II was ≈80% based on ^{11}B NMR. Metathesis with (PPN)Cl or $AsPh_4Cl$ followed by extraction with Et_2O gave a green-brown solution. Crystallization from Et_2O/hexane at room temperature or below afforded needlelike crystals. MS (FAB, NBA): p$^-$ at m/z 495, isotopic envelope corresponding to Fe_3ClB, loss of 7 CO. NMR: ^{11}B (THF, 20 °C) δ 76.4, J_{BH} = 60 Hz; ^{1}H (acetone-d_6, $AsPh_4$ salt, 20 °C) δ 7.98–7.82, m, Ph; δ −9.53, partially collapsed q, Fe–H–B. IR (THF, cm^{-1}): 2057 w, 2001 s, 1996 s, 1975 m, 1953 w, 1803 w. Anal. Calcd for $C_{24}H_{21}AsBClFe_3O_{10}$: C, 46.50; H, 2.41. Found: C, 46.52; H, 2.40.

Protonation of II. Hexane (10 mL) was added to $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]^-$ (0.086 g, 0.17 mmol). The reaction was stirred vigorously, and aqueous H_3PO_4 (5 mL, 40%) was added. The hexane layer immediately became light pink-brown. Upon shaking, all of the monoanion reacted to give a brown hexane layer. The latter was transferred via cannula to a Schlenk tube and the solvent removed under vacuum to give a brown solid. The neutral product is very unstable at room temperature and decomposes overnight at −40 °C. The yield of the product was 0.050 g (0.102 mmol, 60%). NMR: ^{11}B (hexane, 20 °C) δ 74.5, J_{BH} = 49 Hz; ^{1}H (C_6D_6, 20 °C) δ −12.0, br, Fe–H–B; δ −25.5, s, Fe–H–Fe. IR (hexane, cm^{-1}): 2105 w, 2071 s, 2052 s, 2040 s, 2026 m, 2017 w, 2001 m, 1847 m.

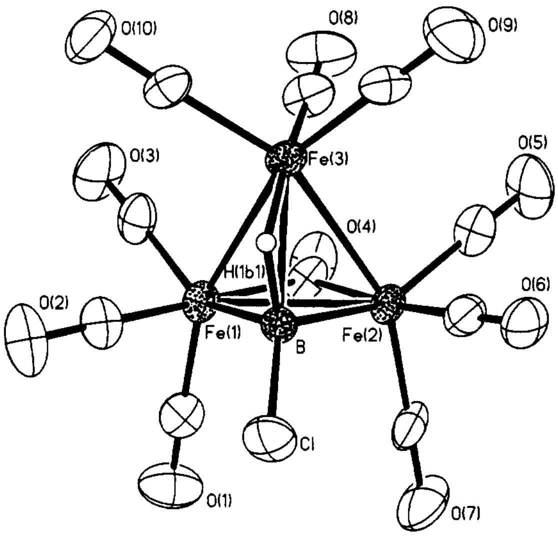

Figure 1. Molecular structure of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]$-$[AsPh_4]$ ((**II**)$[AsPh_4]$). Selected bond distances (Å) and angles (deg): Fe(1)–Fe(2) = 2.540(2), Fe(1)–Fe(3) = 2.596(1), Fe(2)–Fe(3) = 2.577(1), Fe(1)–B = 2.046(7), Fe(2)–B = 2.060(8), Fe(3)–B = 2.137(6), Cl–B = 1.831(6), Fe(1)–B–Cl = 130.4(4), Fe(2)–B–Cl = 127.3(3), Fe(3)–B–Cl = 144.6(4).

Structure of $[AsPh_4][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]$ ($[AsPh_4]$(II)). Slow diffusion of hexane into a diethyl ether solution of $[AsPh_4]$ (**II**) at room temperature led to the formation of dark-red blocklike crystals suitable for an X-ray diffraction study. A summary of the structure determination will be found in Table 1, and Table 2 contains the atomic coordinates. The structure of the anion is shown in Figure 1.

Results

Characterization of I. The spectroscopic data for the dianion are consistent with formulating the compound as $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$ (**I**). That is, the IR data (Figure 2) for $(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$ and $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ show terminal B–H and bridging CO stretching vibrations but there is no evidence for either in **I**. The sequential shift of $\approx$50 cm^{-1} in the mean CO stretching frequencies in forming the mono- and dilitho derivatives suggests the formation of solvated mono- and dianions plus solvated lithium cations.

The ^1H NMR spectrum of the lithium salt of **I** shows a single, broad resonance at δ −12.1 with coupling to ^{11}B (see below), which is only consistent with the presence of a B–H–Fe bridging proton; i.e., B–H terminal protons are observed at much lower fields and Fe–H–Fe protons yield sharp resonances often at considerably higher fields. A correlation of ^{11}B chemical shifts for ferraboranes suggests that $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}BH)]^{2-}$ should have a resonance at $\delta \approx 80$, i.e. a downfield shift of $\approx$30 ppm,[8] whereas deprotonation of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ actually leads to a resonance at δ 29 with $J_{BH} \approx 40$ Hz, i.e. an upfield shift of $\approx$20 ppm and a B–H coupling constant more consistent with a bridging as opposed to a terminal hydrogen atom. The ^{11}B chemical shift of **I** is also consistent with that of the structurally characterized $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$ (δ 19.4)[1–4] if one formulates the dianion as $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$. Further, a good correlation between ^{13}C and ^{11}B NMR shifts exists for closely related compounds.[9–12] The upfield shift of 80 ppm in the ^{13}C resonance associated with the carbyne carbon in going from $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CH)]^-$ (δ 262) to $[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ (δ 182)[13] translates into a 0.33 × 80 = 27 ppm upfield ^{11}B shift on deprotonation of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ if **I** is formulated as $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$. The observed upfield shift is 27 ppm.

These spectroscopic data provide considerable support for the proposed structure of **I** shown in Chart 1.

Reaction of I with $FeCl_3$. In an attempt to couple **I** in the manner of $[Li]_2[Fe_2(CO)_6B_2H_4]$,[14] reaction 1 was

$$2\,[Li]_2[Fe_3(CO)_9(HBCO)] + FeCl_2 \rightarrow \qquad + 2FeCl_3 \rightarrow \qquad (1)$$

carried out. However, although a number of minor products were observed in the ^{11}B and ^1H NMR spectra, the major product formed and subsequently isolated is **II**. Its structure, based on spectroscopic data, and the solid-state structure are shown in Figure 1 and Chart 1. The reaction of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ with $FeCl_3$ does not lead to the formation of **II**. Further, there is no apparent reaction between **I** and $FeCl_2$. The reaction of **I** with $FeCl_3$ alone results in the exclusive formation of **II** in high yield (80%). All of these observations are consistent with describing the reaction as oxidative substitution of chloride. The empirical reactant stoichiometry (Figure 3) suggests that reaction 2 takes place.

$$\underset{\textbf{I}}{[Li]_2[Fe_3(CO)_9(HBCO)]} + 2FeCl_3 \rightarrow$$

$$\underset{\textbf{II}}{[Li][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBCl)]} + 2FeCl_2 + LiCl \qquad (2)$$

Structure of II. The solid-state structure (Figure 1) reveals a ferraborane cluster with a nearly equilateral trimetal base capped asymmetrically by a boron atom with a plane of symmetry containing Cl, B, H, and Fe(3). It verifies the proposed structure of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ and is closely related to that of $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CH)]$.[13] The structural details are consistent with what is known about this well-characterized cluster type.[15] The iron atoms can be viewed as distorted octahedral (Fe(1) and Fe(2) with 4 C, B, and Fe(3) as nearest neighbors and Fe(3) with 3 C, 2 Fe, and H as nearest neighbors), and the boron atom, as distorted tetrahedral (2 Fe, Cl, and H). The CO-bridged Fe–Fe edge distance of the Fe_3B core is slightly shorter than that of the two unbridged Fe–Fe edges.

One point of interest is the structural parameters of the B–H–Fe interaction. We have previously pointed out the substantial range of the bridged B–Fe distance (2.26–1.97 Å) and, hence, the Fe–H–B angle. The value of Fe(3)–B observed here is 2.137(6) Å, compared to 2.046(7) and 2.060-

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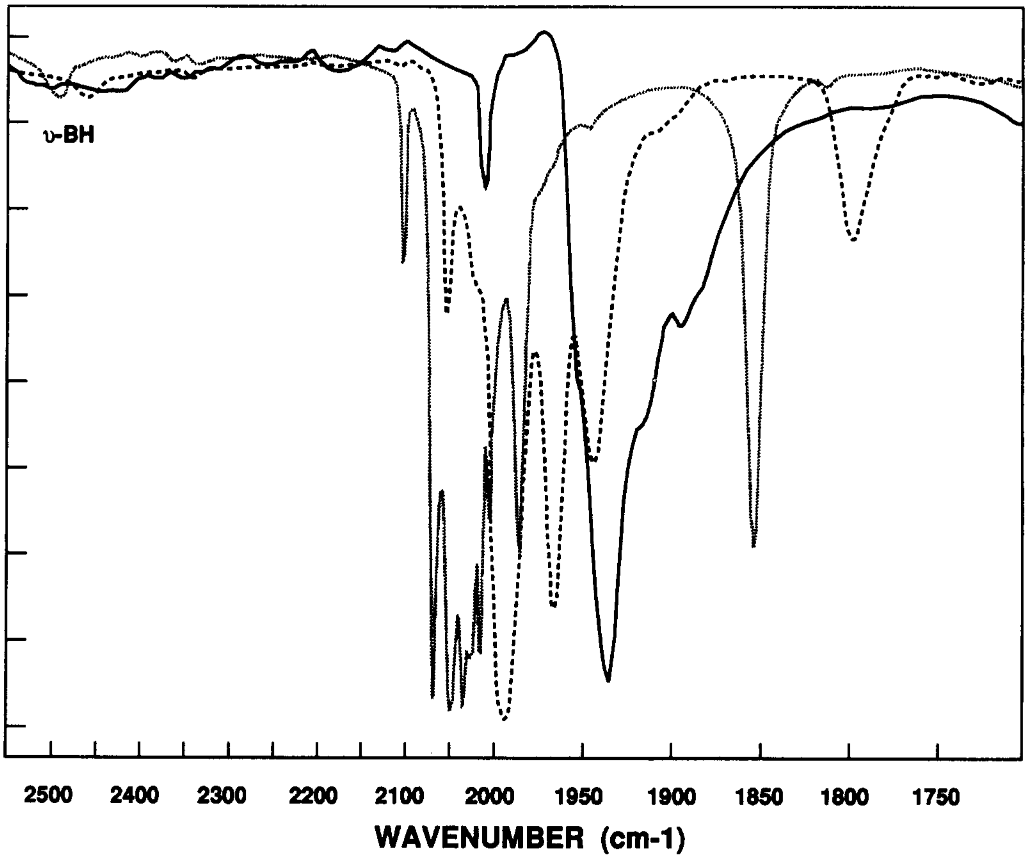
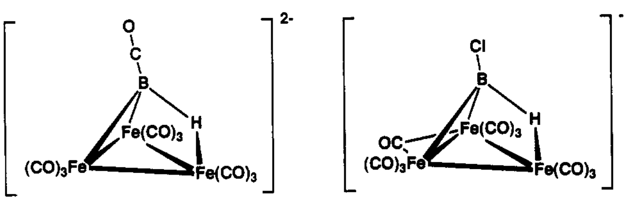


Figure 2. IR spectra in the metal carbonyl region for (μ-H)$Fe_3(CO)_9$(μ-CO)(HBH) (dotted line), $[Fe_3(CO)_9(\mu\text{-CO})(HBH)]^-$ (dashed line), and $[Fe_3(CO)_9(HBCO)]^{2-}$ (solid line).

Chart 1



I II

(8) Å observed for Fe(1)–B and Fe(2)–B, respectively. Consequently, an intermediate three-center interaction similar to that in $HFe_3(CO)_9(\mu_3\text{-}H_3BH)$ exists.[5] A second point of interest is the B–Cl interaction. The B–Cl distance is normal for a single bond (1.831(6) Å vs sum of covalent radii 1.81 Å), but the B–Cl bond vector is bent away from the pseudo-3-fold axis (Fe(3)–B–Cl > Fe(1)–B–Cl ≈ Fe(2)–B–Cl). The latter is presumably caused by the presence of the FeHB bridging hydrogen on the Fe(3)–B edge.

Discussion

Oxidation of $[Fe_3(CO)_9(\mu_3\text{-HBCO})]^{2-}$. Consistent with the work of Grimes and co-workers,[16,17] we have shown that the coordination of $[Fe_2(CO)_6B_2H_4]^{2-}$ to $FeCl_2$ followed by oxidation with $FeCl_3$ leads to a good yield of a coupled cluster product $[Fe_2(CO)_6B_2H_4]_2$.[14] $FeCl_2$ is necessary, as reaction of $[Fe_2(CO)_6B_2H_4]^{2-}$ with $FeCl_3$ alone leads to decomposition. Presumably, two of the dianions coordinate to the Fe(II) center and the entire complex is oxidized. The situation is quite different for **I**. In both the presence and the absence of $FeCl_2$, direct reaction with $FeCl_3$ predominates and leads to the formation of **II** according to reaction 2. As illustrated in Scheme 1, direct oxidation of **I** followed by chloride addition is favored over coordination followed by oxidation. Two-electron oxidation of a cluster dianion is known to provide a route for the introduction of a two-electron donor into a cluster,[18-21] and the reaction of **I** with $FeCl_3$ provides another example in which a functionalized metallaborane is formed.

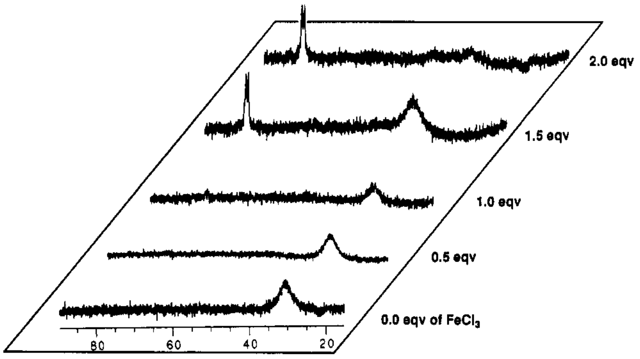


Figure 3. ^{11}B NMR spectra of the reaction of **I** with $FeCl_3$ as a function of the number of equivalents added. Note that the intensities of the spectra are not directly comparable.

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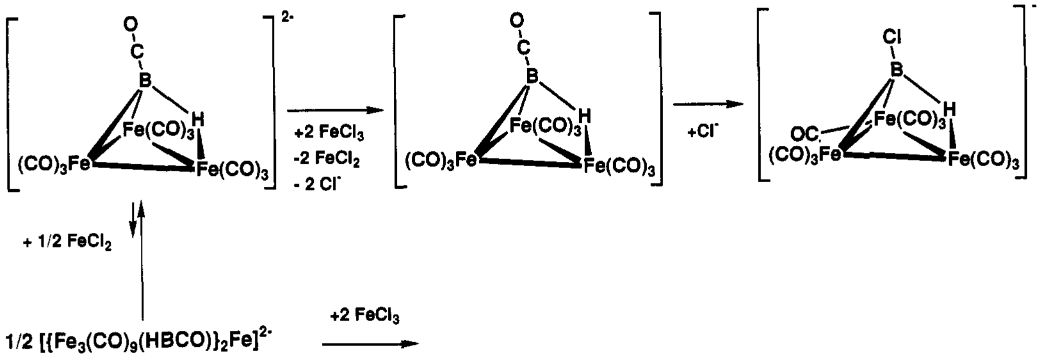
Scheme 1



The different reactivity of $[Fe_2(CO)_6B_2H_4]^{2-}$ and $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$ with respect to $FeCl_3$ is not as surprising when one recalls their differing behaviors with respect to protonation. The former, as well as all other ferraborane anions we have studied (including **II**), is cleanly protonated to give the neutral ferraborane. The latter decomposes on protonation. Insofar as the metal cation resembles a proton, the interaction of **I** with $FeCl_2$ may also be very different from that of $[Fe_2(CO)_6B_2H_4]^{2-}$ with $FeCl_2$. Likewise, the interaction of $FeCl_3$ with **I** and $[Fe_2(CO)_6B_2H_4]^{2-}$ differs in that the former leads to oxidative Cl^- substitution whereas the latter leads to uncharacterized decomposition products.

$(\mu\text{-}H)_2M_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}BH)$ (A) vs $(\mu\text{-}H)_3M_3(CO)_9(\mu_3\text{-}BCO)$ (B). The characterization of **II** establishes the structure of $[Fe_3(CO)_9(\mu_3\text{-}H_3BR)]^-$ (R = H, Cl, CH_3), thereby demonstrating by comparison with $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$ that the site preferences of H and CO in the $H_3M_3(CO)_{10}B$ cluster system depend on the nature of the metal. The characterization of **I**, which is isoelectronic with $[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ and closely related to the ruthenium and osmium analogs,[13,22-26] shows that the number of cluster hydrogens is also an important factor. That is, the protonation of the dianions $[M_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ (M = Fe, Ru, Os) yields either $[M_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CH)]^-$ (=isomer **A**) (i.e., the tenth CO ligand moves from the cluster carbon to the metals) or $[(\mu\text{-}H)M_3(CO)_9(\mu_3\text{-}CCO)]^-$ (=isomer **B**).[13,22-26] The former structure is analogous to that of **II** wherea the latter is analogous to that proposed for **I**. The implications of these observations for the energetics of cluster processes are briefly explored in the following.

The observed isomeric forms for this cluster type as a function of E, M, and the number of protons are listed in Table 3. Structure **B** is favored for Ru and Os independently of the number of protons. Iron is a special element since for **B** it becomes less stable than for **A** as the number of protons increases with both carbon and boron as the capping atom E. We have demonstrated previously[27] that, for constant E, the preference for M–H–M vs E–H–M increases in the order Fe < Ru < Os and that, for constant M, the preference for M–H–M vs E–H–M increases in the order B < C. These preferences constitute one factor involved in the relative stability of structure **A** vs **B**. However, there are two additional factors that must be considered. That is, preferences of E–H vs E–H–M or M–H–M interactions and the greater complexity of the M–CO ligand interaction vs the M–H interaction enter into the problem.

Table 3. Observed Isomeric Forms of Tetrahedral Clusters with Fe_3E and M_3E Cores (M = Ru, Os; E = C, B)

	E = C	E = B
isomer **A**	$[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CH)]^-$	$[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$
	$HFe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CH)$	$(\mu\text{-}H)Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)$
isomer **B**	$[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$	$[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$
	$[M_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$	
	$[(\mu\text{-}H)M_3(CO)_9(\mu_3\text{-}CCO)]^-$	
	$(\mu\text{-}H)_2M_3(CO)_9(\mu_3\text{-}CCO)$	$(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$

As it is with the iron compounds for which both isomer structures **A** and **B** are observed, we compare the isoelectronic clusters (a) $[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ and $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CH)]^-$ and (b) $[Fe_3(CO)_9(\mu_3\text{-}HBCO)]^{2-}$ and $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}HBH)]^-$ by estimating ΔH of the reaction

$$\text{isomer } \mathbf{A} = \text{isomer } \mathbf{B} \tag{3}$$

For case a we have

$$\Delta H = E(\mathrm{FeC(O)Fe}) - E(\mathrm{C{-}CO}) < 0 \tag{4}$$

for the dianion and

$$\Delta H = E(\mathrm{FeC(O)Fe}) + E(\mathrm{C{-}H}) - E(\mathrm{Fe{-}H{-}Fe}) - E(\mathrm{C{-}CO}) > 0 \tag{5}$$

for the monoanion where $E(\ )$ represents an average bond energy for the interaction indicated. We have previously presented an experimental measurement of $[E(\mathrm{FeC(O)Fe}) - E(\mathrm{Fe{-}H{-}Fe})] = -35.0$ kcal/mol, leading to estimates of $E(\mathrm{FeC(O)Fe}) = 48$ and $E(\mathrm{Fe{-}H{-}Fe}) = 83$ kcal/mol.[28] Thus, (4) gives $E(\mathrm{C{-}CO}) \geq 48$ kcal/mol, and (5), $E(\mathrm{C{-}H}) \geq E(\mathrm{C{-}CO}) + 35$ kcal/mol. Taking $E(\mathrm{C{-}H}) = 100$ kcal/mol places limits on the CCO bond energy of $48 \leq E(\mathrm{C{-}CO}) \leq 65$ kcal/mol.

For E = C, the change in isomer stability requires that $E(\mathrm{C{-}H}) - E(\mathrm{C{-}CO}) > E(\mathrm{Fe{-}H{-}Fe}) - E(\mathrm{FeC(O)Fe})$. If $E(\mathrm{C{-}H}) - E(\mathrm{C{-}CO})$ is independent of M, then, for M = Ru and Os, $E(\mathrm{C{-}H}) - E(\mathrm{C{-}CO}) < E(\mathrm{M{-}H{-}M}) - E(\mathrm{MC(O)M})$. In this case, structure **B** is found exclusively. However, published estimates of $E(\mathrm{M{-}H{-}M}) = 98$ (M =

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Ru) and 102 kcal/mol (M = Os)[29] along with M–CO bond strengths[30] suggest that E(M–H–M) – E(MC(O)M) changes little with M. Thus, E(C–H) – E(C–CO) ≈ E(M–H–M) – E(MC(O)M) and average bond energy term values cannot account for the change in isomer stability. On the other hand, E(C–CO) must be ≈65 kcal/mol.

In case b, the analogs of eqs 4 and 5 are

$$\Delta H = E(\mathrm{FeC(O)Fe}) + E(\mathrm{B{-}H}) - E(\mathrm{Fe{-}H{-}B}) - E(\mathrm{B{-}CO}) < 0 \quad (6)$$

for the dianion and

$$\Delta H = E(\mathrm{FeC(O)Fe}) + E(\mathrm{B{-}H}) - E(\mathrm{Fe{-}H{-}Fe}) - E(\mathrm{B{-}CO}) > 0 \quad (7a)$$

or

$$\Delta H = E(\mathrm{FeC(O)Fe}) + E(\mathrm{B{-}H}) - E(\mathrm{Fe{-}H{-}B}) - E(\mathrm{B{-}CO}) > 0 \quad (7b)$$

for the monoanion, where two possibilities exist as the added proton can occupy either an Fe–H–Fe site (eq 7a) or an Fe–H–B site (eq 7b). If (7b) holds, then $\Delta H \approx 0$ and E(FeC(O)Fe) + E(B–H) ≈ E(Fe–H–B) + E(B–CO). If (7a) holds, then E(BH) – E(BCO) > E(Fe–H–Fe) – E(FeC(O)Fe) = 35 kcal/mol. From (6), E(BH) – E(BCO) < E(Fe–H–B) – E(FeC(O)Fe). Taking E(BH) = 90 kcal/mol yields E(Fe–H–B) + E(B–CO) ≈ 138 kcal/mol in the first instance and E(BCO) < 55 kcal/mol in the second. If E(Fe–H–B) ≥ E(Fe–H–Fe), then the two conclusions are the same. As in the case of E = C above, consideration of the osmium system leads to the conclusion that E(BCO) ≈ 55 kcal/mol. Apparently, E(ECO) scales with E(E–H).

For iron, there is a delicate balance between forms **A** and **B**, which is not predicted by summing average bond energies. Although equilibria were not observed in any of these systems, thereby ruling out a more precise definition of the energetics, the different structural forms adopted for these isoelectronic clusters allow limits to be placed on E(E–CO) for E = C and B.

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Supplementary Material Available: A drawing of **II** showing the $[\mathrm{AsPh_4}]^+$ counterion and tables of anisotropic displacement coefficients, additional bond distances and bond angles, and equivalent isotropic displacement parameters of hydrogen atoms for **II** (5 pages). Ordering information is given on any current masthead page.

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