

tolysis in the presence of methyl radical scavengers such as cyclohexane failed to alter product yields. The variation in reaction times required correlates roughly with the electron affinities of the products,¹¹ which may reflect the electron-transfer aspects of the mechanism. However, we also note that the presence of such electron traps might merely divert another mechanism. Mechanism III has some precedent in the known decomposition of σ -sulfuranes to yield sulfides,⁷ but attempts to produce oxysulfuranes directly have been unsuccessful.¹² Finally, more exotic pathways cannot at this time be completely ruled out.

A complete understanding of the exact mechanism of this new photoreaction must await a quantitative study of the role structure, pK_a , electron affinities, ionization potentials, and excited-state energies play in the excited-state reactivities of the anions involved. Such studies are in progress and will be reported at a later date.

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An Iron-Bridged Diborane(6) Derivative.

Preparation of $K^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$

Sir:

The formation of metal-boron bonds through reaction of transition metal carbonylate ions with BH_3 has been relatively unexamined except for the preparation of species¹ such as $\text{H}_3\text{BRe}(\text{CO})_5^{1-}$, and $\text{H}_3\text{BMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3^{1-}$. Only reactions of monoanions have been reported, and the products were simple BH_3 adducts. A possible exception¹ is $(\text{H}_3\text{B})_2\text{-Re}(\text{CO})_5^{1-}$ which might be $\text{H}_3\text{BHBH}_2\text{Re}(\text{CO})_5^{1-}$.

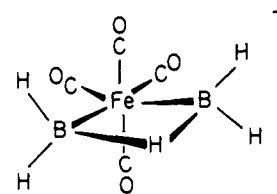
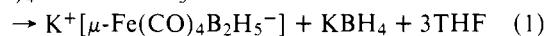
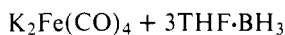


Figure 1. The proposed structure of $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$.

We have examined the reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{THF}\cdot\text{BH}_3$,

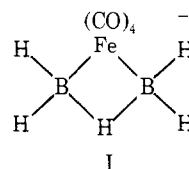


and report the preparation of the $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ ion, the first example of a substituted diborane(6) with a transition metal occupying a bridge site. Working on a 1-mmol scale, $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ was obtained in yields as high as 98% when reactants were employed in $3\text{THF}\cdot\text{BH}_3/\text{K}_2\text{Fe}(\text{CO})_4$ ratio. Unreacted $\text{K}_2\text{Fe}(\text{CO})_4$ and diminished yields of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ were obtained when this ratio was $<3/1$. Solid $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ is dark brown in appearance. It is stable at room temperature for several hours, sealed under vacuum. In THF solution, no decomposition of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ is noted in NMR spectra obtained after several hours at 50°C . Anal. Calcd for $\text{KFe}(\text{CO})_4\text{B}_2\text{H}_5$ (percent by weight): H, 2.16; C, 20.6; B, 9.21; Fe, 23.9. Found: H, 2.07; C, 20.7; B, 8.93; Fe, 23.6.

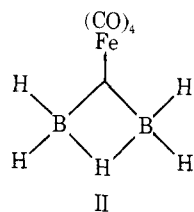
^{11}B and ^1H NMR spectra are consistent with the molecular structure shown in Figure 1. A triplet of doublets is observed upfield of $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ($\delta -15.4$ ppm) in the ^{11}B NMR spectrum. (Note. A negative chemical shift denotes a resonance which occurs at higher field than the reference.)² The triplet arises from coupling of two terminal ^1H atoms with each ^{11}B atom, $J_{\text{BHt}} = 112$ Hz. Each component of this triplet is split into a doublet owing to spin coupling of a single ^1H atom bridging two ^{11}B atoms ($J_{\text{BH}\mu} = 25$ Hz). ^1H decoupling causes collapse of the ^{11}B NMR spectrum to a singlet. This spectrum is independent of temperature in the range studied ($+50$ to -80°C). The ^1H NMR spectrum (^{11}B decoupled) consists of resonances at τ 8.20 and 15.17 ($(\text{CH}_3)_4\text{Si}$, τ 10.00) with relative areas of 4.1/1.0, respectively. These spectra are consistent with those of other bridge substituted diboranes (μ -amino-,³ μ -thio-,⁴ and μ -selenodiboranes⁵).

The infrared spectrum of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ (THF solution) shows a doublet in the BH terminal stretching region at 2450 (w) and 2400 (w) and BH bridge stretches at 1845 (vw) and 1655 (vw). Similar bands are observed in the infrared spectra of $\mu\text{-Se}(\text{CH}_3)\text{B}_2\text{H}_5^{5-}$ and $\mu\text{-NR}_2\text{B}_2\text{H}_5$.^{3a} The CO stretches of $\text{K}^+[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^-$ occur at 2030 (w), 1943 (vs), and 1927 (s). These bands fall in the same region as the CO stretches⁶ of $\text{HFe}(\text{CO})_4^-$, as expected for a single negatively charged species, and are at significantly higher frequencies than the CO stretches of $\text{K}_2\text{Fe}(\text{CO})_4$.⁶

The $\text{Fe}(\text{CO})_4^{2-}$ ion is the conjugate dibase of $\text{H}_2\text{Fe}(\text{CO})_4$. It is a potential four-electron donor in the formation of the $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^{1-}$ ion from $\text{THF}\cdot\text{BH}_3$. One representation of the valence structure of this anion is I in which the iron is



formally d^2sp^3 hybridized and is bonded to the B_2H_5 system through two 2-center Fe-B bonds. This representation is analogous to the commonly held valence description of bonding of nitrogen to the B_2H_5 system in a μ -aminodiborane(6), μ -



$R_2NB_2H_5$.⁷ Another valence structure (II) for $[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]^{1-}$ can also be considered. In this case the iron is formally dsp^3 hybridized and is bonded to the B_2H_5 system through a single 3-center B-Fe-B bond and is the direct iso-electronic analogue of $\eta^2\text{-Fe}(\text{CO})_4\text{C}_2\text{H}_4$.⁸ Such bonding would be expected to be favored when an electrophilic $\text{Fe}(\text{CO})_4$ group is inserted into a boron-boron bond as, for example, in the formation of $\mu\text{-Fe}(\text{CO})_4\text{B}_6\text{H}_{10}$ ⁹ and its derivative¹⁰ $\text{Fe}(\text{CO})_4\text{B}_7\text{H}_{12}^-$. In these cases structural^{10a} and spectroscopic data (infrared¹⁰ and Mössbauer⁹) appear to favor the existence of B-Fe-B 3-center bonding. At this point, we favor II; however, there is insufficient experimental information to distinguish between the two modes of bonding. We plan to examine this point through Mössbauer spectroscopy.

Work on the reactions of the $\text{Fe}(\text{CO})_4^{2-}$ ion is currently being extended to other boron hydrides.

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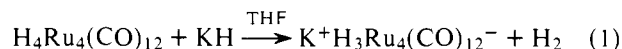
The New Cluster Dianion $\text{H}_2\text{Ru}_4(\text{CO})_{12}^{2-}$. Simple, High-Yield, Stepwise Deprotonation of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$

Sir:

Many methods which produce metal carbonylate cluster species suffer from a lack of specificity, yielding mixtures of products which are separated with difficulty. In general, these nonspecific methods involve reduction of neutral metal carbonyls with basic reactants. Another approach which has received less attention involves deprotonation of a parent hydrido cluster,^{1,2} an approach which has met with considerable success in bridge proton abstraction from boron hydrides and some metalloborane clusters.³

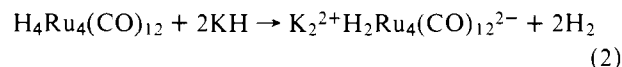
We report here the first stepwise, systematic deprotonation of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in a procedure which is probably generally applicable to a variety of polynuclear metal carbonyl hydride systems. Koepke, Johnson, Knox, and Kaesz reported⁴ removal

of a single proton forming the monoanion $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$ in ethanolic KOH. However, extended reaction times led to cluster degradation.⁴ By using KH as the deprotonating agent, we have observed the evolution of up to 3 equiv of hydrogen. The monoanion is formed in the following stoichiometric reaction:



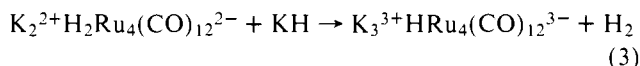
The slightly soluble yellow $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ is gradually consumed by stirring with a stoichiometric amount of KH in THF at ambient temperature for 12 h, or 0.5 h at 50–60 °C. An opaque dark red solution of highly soluble $\text{KH}_3\text{Ru}_4(\text{CO})_{12}$ (**1**) is formed. Hydrogen evolution was quantitative (measured manometrically and identified by mass spectroscopy).

The previously unreported dianion, $\text{H}_2\text{Ru}_4(\text{CO})_{12}^{2-}$, was synthesized by stirring 2 equiv of KH with $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in THF for 0.5 h at 55 °C, and an additional 24 h at ambient temperature:



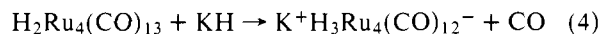
Quantitative evolution of H_2 is observed, with <2% CO impurity. Pure THF solutions of $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ are orange; removal of solvent in vacuo yields $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ (**2a**) as a yellow powder. Metathesis reactions of **2a** with 2 equiv of $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ or $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ give the $[(\text{Ph}_3\text{P})_2\text{N}]_2^{2+}$ or $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2^{2+}$ salts in 80% yield. Analytically pure samples of yellow $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{H}_2\text{Ru}_4(\text{CO})_{12}]$ (**2b**) were obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{EtOH}$. Calcd for $\text{C}_{84}\text{H}_{62}\text{N}_2\text{O}_{12}\text{P}_4\text{Ru}_4$: C, 55.45; H, 3.43; Ru, 22.22. Found:⁵ C, 55.35; H, 3.59; Ru, 21.84. Solutions of $\text{H}_2\text{Ru}_4(\text{CO})_{12}^{2-}$ salts are stable indefinitely under nitrogen at 25 °C, but decompose within 1 h when exposed to air. Conductivity measurements of **2b** in nitromethane ($\Lambda_0 = 167 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) agree well with accepted values⁶ for 2:1 electrolytes.

Preliminary results have shown that a 3rd equiv of H_2 with negligible CO impurity is evolved upon reaction of **2a** with a stoichiometric amount of KH over a period of 3 days at ambient temperature:



Study of this product is continuing but has been hampered because of its low solubility in commonly available solvents.

Interestingly, the reactivity of KH to ruthenium hydrido carbonyl clusters is not limited to proton abstraction. Reaction of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ with KH does not give a direct deprotonation product. Instead, hydride displacement of CO occurs to produce **1**:



In contrast to $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ⁷ and $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$ ⁴ which exhibit only terminal CO infrared absorptions in the range 2100–1900 cm^{-1} , THF solutions of **2a** and **2b** also exhibit low frequency absorptions (1900–1700 cm^{-1}) indicative of bridging carbonyls. Infrared spectra, $\nu(\text{CO})$ (cm^{-1}), in THF: **2a**, 2028 (w), 1998 (s), 1960 (vs), 1911 (m), 1895 (m, sh), 1817 (w), 1770 (w), 1742 (m), 1719 (m); **2b**, 2027 (w), 1985 (s), 1950 (s), 1940 (s), 1899 (m), 1881 (m), 1809 (vw), 1763 (m), 1753 (m, sh). Frequency and intensity differences are probably due to significant ion pairs in the potassium salt.

The significant carbonyl rearrangement to give a bridging system is presumably due to the larger negative charge on the dianion than the precursor species $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$. The rearrangement might represent a mode of averaging charge distribution throughout the cluster framework.⁸