

$R_2NB_2H_5$.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 isoelectronic 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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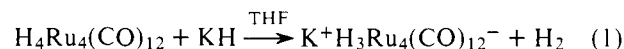
The New Cluster Dianion $\text{H}_2\text{Ru}_4(\text{CO})_{12}^{2-}$. Simple, High-Yield, Stepwise Deprotonation of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$

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

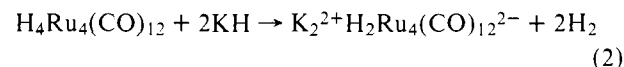
We report here the first stepwise, systematic deprotonation of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in a procedure which is probably generally applicable to a variety of polynuclear metal carbonyl hydride systems. Koepke, Johnson, Knox, and Kaesz reported⁴ removal

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:



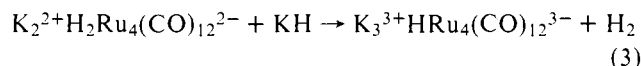
The slightly soluble yellow $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ is gradually consumed by stirring with a stoichiometric amount of KH in THF at ambient temperature for 12 h, or 0.5 h at 50–60 °C. An opaque dark red solution of highly soluble $\text{KH}_3\text{Ru}_4(\text{CO})_{12}$ (**1**) is formed.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



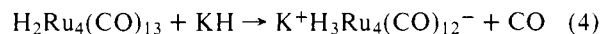
Quantitative evolution of H_2 is observed, with <2% CO impurity. Pure THF solutions of $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ are orange; removal of solvent in vacuo yields $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ (**2a**) as a yellow powder. Metathesis reactions of **2a** with 2 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 apparent 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

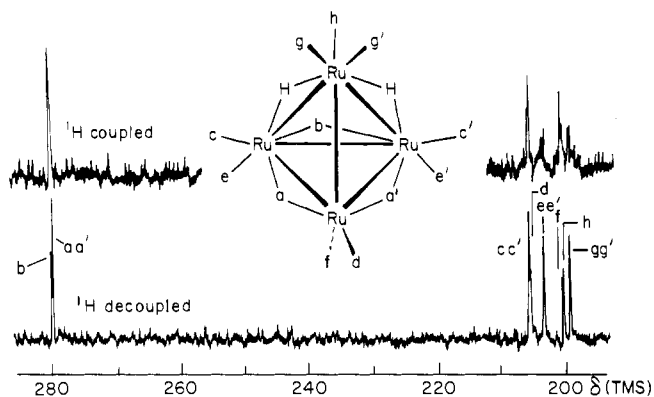


Figure 1. Fourier-transform (22.6 MHz) ^{13}C NMR spectra of $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ in THF-d_8 , -80°C .

A single temperature-invariant peak at τ 29.26 is observed for **2a** in THF-d_8 in the ^1H NMR spectrum. Its ^{13}C NMR (22.6 MHz) spectrum provides evidence for a carbonyl bridged system in a structure of apparent C_s symmetry at the slow exchange limit (Figure 1). At -80°C , eight resonances of 1:2:2:1:2:1:1:2 intensity are observed in the $^{13}\text{C}\{^1\text{H}\}$ spectrum at δ 281.1, 280.9, 205.3, 205.1, 203.3, 200.3, 200.0, and 199.0, respectively. The resonances at δ 281.1 and 280.9 are by far the lowest field carbonyl resonances yet observed for a ruthenium species and are clearly assignable to bridging carbonyls (aa', b). Of the upfield resonances, only those at δ 205.1 and 200.3 remain relatively unaffected by proton coupling. These are assigned to carbonyls d and f, respectively, since they are farthest removed from the two edge-bridging hydrogens. Carbonyls ee' and gg' are expected to couple most strongly to the trans hydrogens and are thus assigned to the resonances at δ 203.3 ($J = 10.3$ Hz) and 199.0 ($J = 5.9$ Hz), respectively.

Variable-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure 2) of **2a** facilitated the shift assignments. At -50°C , the four lowest field resonances have noticeably broadened and attenuated with respect to the four highest field resonances. At -30°C , the high-field peaks have also begun to broaden, while the low-field peaks have collapsed into the baseline. At 60°C , one resonance is observed at the weighted average of the low-temperature shifts.

We account for the spectra in Figure 2 in the following way. Commencing at about -50°C , a selective, cyclic exchange occurs around the Ru_3 basal plane involving only the bridging carbonyls (aa', b) and basal equatorial carbonyls (cc', d).⁹ Such exchange would occur through an unbridged intermediate which is forced to re-form carbonyl bridges about the same cluster face owing to occupation of two of the remaining three tetrahedral edges by bridging hydrogens. Complete exchange averaging occurs at higher temperatures and no unique mechanism is extractable from the data. It is entirely possible that a combination of exchange mechanisms is operative above 0°C . Intranuclear CO and H exchange or intranuclear H exchange coupled with localized axial-equatorial carbonyl exchange about each ruthenium vertex are reasonable routes to the averaging of ligand environments.

Variable-temperature ^{13}C NMR spectra of **1** (not described in detail here) are consistent with the interpretation⁴ of Koepke, Johnson, Knox, and Kaesz of the variable-temperature ^1H NMR spectra of $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$. The presence of two isomers is indicated below -80°C (one of C_{3v} symmetry and the other of C_2 or C_{2v} symmetry) which rapidly interconvert at room temperature. The ^{13}C NMR spectra give no evidence for bridging carbonyls at any of the temperatures observed (-127 to $+27^\circ\text{C}$). Four ^{13}C resonances are observed for **1** at -90°C (δ 201.4, 199.3, 196.5, 193.3). At $+27^\circ\text{C}$, only one sharp peak is seen at δ 198.2. The exchange mechanism is

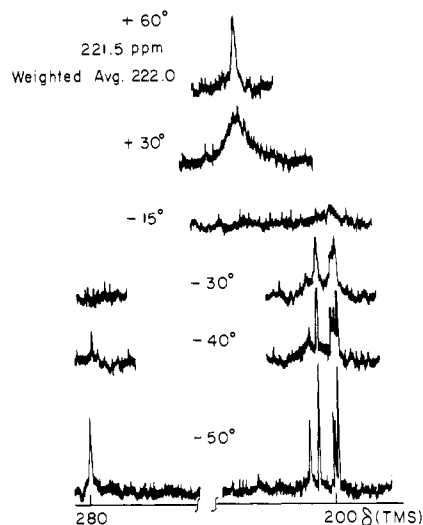


Figure 2. Variable-temperature ^{13}C NMR spectra of $\text{K}_2\text{H}_2\text{Ru}_4(\text{CO})_{12}$ in THF-d_8 .

presumed to occur through intramolecular hydrogen exchange coupled with localized axial-equatorial carbonyl exchange about each ruthenium vertex.

We plan to test the general applicability of this method for selectively generating in high yield cluster anions from their conjugate cluster acids.

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Matrix Infrared Spectrum of the O_2Br Radical. Bonding in the O_2X Species

Sir:

Recently, a number of fluorine- and chlorine-atom matrix reactions with nonmetal oxides have been investigated in this laboratory.¹⁻⁵ During the course of several of these studies, the previously identified dioxygenyl radicals, O_2F^{6-8} and O_2Cl ,⁹ had been observed as secondary reaction products. We have recently extended these investigations to include the corresponding matrix reactions of atomic bromine. However, at the time of this writing, the analogous O_2Br radical had not yet been identified. Consequently, in an attempt to prepare and