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Synthesis and Characterization of the Mixed-Metal Alkylidyne Clusters $RCFeCo_2(CO)_9H$ ($R = CH_3, C_2H_5, C_6H_5$)

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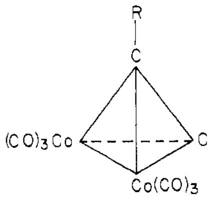
Reaction of $RCCo_3(CO)_9$ ($R = CH_3, C_2H_5, C_6H_5$) with $Na_2[Fe(CO)_4]$ in THF solution leads to the formation of the new mixed-metal alkylidyne clusters $RCFeCo_2(CO)_9H$ ($R = CH_3, C_2H_5, C_6H_5$) in yields of 31–48%. Spectral data suggest that these have structures similar to those of the parent $RCCo_3(CO)_9$ cluster, i.e., an $FeCo_2$ triangle triply bridged by the alkylidyne carbon. The possible location of the hydride ligand is discussed on the basis of electron-count, infrared, and ^1H and ^{13}C NMR spectra. The reaction of $HCCo_3(CO)_9$ with $Na_2[Fe(CO)_4]$, which gave a complex mixture of products, is also discussed.

Introduction

Reaction of closed metal carbonyl trimers with carbonylmetalates has been shown[1-4] to be a useful synthetic route to tetranuclear clusters in which the carbonylmetalate adds to the face of the original trimer. This type of reaction has been particularly useful for the synthesis of mixed-metal clusters. In principle, clusters with more than four framework atoms could be prepared by the addition of carbonylmetalates to the triangular faces of tetranuclear and larger clusters.[5] In order to test this hypothesis we attempted to prepare pentanuclear clusters with an $FeCo_3C$ skeleton by the addition of $[Fe(CO)_4]^{2-}$ to a series of alkylidyne $RCCo_3(CO)_9$ ($R = H, CH_3, C_2H_5, C_6H_5$) clusters of structure **1**.[6-9] However, the pentanuclear $FeCo_3C$ clusters were not isolated from these reactions, but rather the first examples of a new class of mixed-metal alkylidyne clusters, $RCFeCo_2(CO)_9$ ($R = CH_3, C_2H_5, C_6H_5$), were obtained. The synthesis and characterization of these clusters is described herein.



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Experimental Section

The complexes $RCCo_3(CO)_9$ ($R = H$,[10] CH_3,[11] C_2H_5,[12] C_6H_5[11]) were prepared by published procedures. $Na_2[Fe(CO)_4]\cdot 1.5C_4H_8O_2$, hereafter referred to as $Na_2[Fe(CO)_4]$, was obtained from Alfa Ventron Corp. and was used without further purification. Tetrahydrofuran (THF) and hexane were dried and deoxygenated by distillation from CaH_2 under N_2. All other solvents were deoxygenated either by evacuation through a liquid N_2 cooled trap or by purging N_2 through the solvent. Reactant solutions were prepared in an N_2-filled glovebox, and all reactions and manipulations of the compounds were conducted under an N_2 atmosphere.

Chromatography was carried out with the low-pressure chromatography apparatus previously described.[2] The column was thoroughly flushed with deoxygenated hexane prior to chromatography of the reaction mixtures.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer with 0.5-mm path length NaCl solution IR cells. Values reported are ± 1 cm^{-1}. The cells were fitted with serum caps and purged with N_2 in order to record spectra of the air-sensitive compounds. Mass spectra were obtained with an AEI-MS 9 spectrometer with a 70 eV ionization source. Electronic absorption spectra were measured on a Cary 17 spectrophotometer with 1-cm path length quartz cells. A JEOL PS-100-FT Fourier transform NMR spectrometer was used to obtain both ^1H and ^{13}C NMR spectra. $[Cr(acac)_3]$ (10^{-3} M) was added as a shiftless relaxation agent for the ^{13}C NMR measurements.

Preparation of $C_2H_5CFeCo_2(CO)_9H$. A 50-mL THF solution of $C_2H_5CCo_3(CO)_9$ (0.93 g, 2 mmol) was added dropwise over a 15-min period to a refluxing 125-mL THF solution of $Na_2[Fe(CO)_4]$ (1.40 g, 4 mmol). The color of the reactant solution changed from yellow-orange to deep red-brown during the addition, and the solution was refluxed for 1 h after the $C_2H_5CCo_3(CO)_9$ addition was complete. Removal of solvent by evaporation under vacuum gave a dark red-brown solid to which was added 50 mL of deoxygenated hexane. The hexane remained colorless until 50 mL of deoxygenated 40% aqueous H_3PO_4 was added, and then it acquired a red-black color as the residue was dissolved and extracted. After the solution was stirred for 10 min, the hexane was removed under N_2. The extraction was repeated two or three times, and when complete the acid layer was red-pink.

The hexane extract was concentrated under vacuum and chromatographed on silica gel. Elution with deoxygenated hexane gave a red-purple band of $C_2H_5CCo_3(CO)_9$ followed by a green band of $Fe_3(CO)_{12}$. An immobile red fraction remained at the top of the column and was subsequently removed by elution with deoxygenated methanol. Evaporation of the methanol under vacuum followed by acidification and extraction as before gave a maroon solid. Purification by sublimation at 50 °C (10^{-3} mm Hg) gave a 46% yield (0.417 g, 0.91 mmol) of $C_2H_5CFeCo_2(CO)_9H$. Anal. Calcd for $C_2H_5CFeCo_2(CO)_9H$: C, 30.80; H, 1.64; Co, 25.19. Found: C, 31.10; H, 1.28; Co, 24.19.

When the reaction of $C_2H_5CCo_3(CO)_9$ (0.140 g, 0.30 mmol) and $Na_2[Fe(CO)_4]$ (0.180 g, 0.52 mmol) was conducted at room temperature for 1.25 h with the workup described above, a 23% yield (0.031 g, 0.07 mmol) of $C_2H_5CFeCo_2(CO)_9H$ was obtained.

Preparation of $CH_3CFeCo_2(CO)_9H$. Reaction of $CH_3CCo_3(CO)_9$ (0.103 g, 0.23 mmol) and $Na_2[Fe(CO)_4]$ (0.070 g, 0.20 mmol) in refluxing THF for 1.25 h followed by workup in a manner similar to that described above gave a 43% yield (0.045 g, 0.10 mmol) of $CH_3CFeCo_2(CO)_9H$ after sublimation at 50 °C (10^{-3} mm Hg). Reaction at room temperature of $CH_3CCo_3(CO)_9$ (0.462 g, 1.01 mmol) with $Na_2[Fe(CO)_4]$ (0.526 g, 1.52 mmol) gave a 19% yield (0.084 g, 0.19 mmol) of $CH_3CFeCo_2(CO)_9H$.

Preparation of $C_6H_5CFeCo_2(CO)_9H$. Reaction of $C_6H_5CCo_3(CO)_9$ (0.446 g, 0.86 mmol) and $Na_2[Fe(CO)_4]$ (0.650 g, 1.88 mmol) in refluxing THF for 2 h followed by the workup described above gave a 31% yield (0.140 g, 0.27 mmol) of $C_6H_5CFeCo_2(CO)_9H$. The corresponding reaction at room temperature of $C_6H_5CCo_3(CO)_9$ (0.135 g, 0.26 mmol) and $Na_2[Fe(CO)_4]$ (0.100 g, 0.29 mmol) gave a 19% yield (0.025 g, 0.05 mmol) of $C_6H_5CFeCo_2(CO)_9H$.

Reaction of $HCCo_3(CO)_9$ with $Na_2[Fe(CO)_4]$. Reaction of $HCCo_3(CO)_9$ (1.06 g, 2.40 mmol), whose purity was established by infrared and mass spectral analysis, with $Na_2[Fe(CO)_4]$ (1.37 g, 3.96 mmol) in refluxing THF for 1.25 h followed by the workup described above gave trace quantities (<1% by weight) of two fractions which contained $RCFe_2Co(CO)_9H_2$ and $RCFe_3(CO)_9H_3$ clusters and 0.131 g of a mixture of $RCFeCo_2(CO)_9H$ clusters (see Results). Reaction of $HCCo_3(CO)_9$ (0.318 g, 0.72 mmol) and $Na_2[Fe(CO)_4]$ (0.37 g, 1.07 mmol) in THF maintained at 25 °C for 1.5 h gave 0.16 g of the mixture of $RCFeCo_2(CO)_9H$ clusters.

Results

General Synthetic Procedure. The synthesis of each of the $RCFeCo_2(CO)_9H$ alkylidyne clusters was carried out by the

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Table I. Spectroscopic Data

compd	IR,[a] ν(CO), cm^{-1}	UV-vis,[b] λ_{max}, nm (ϵ_{max}, L mol^{-1} cm^{-1})	^1H NMR,[c] δ
$CH_3CFeCo_2(CO)_9H$	2101 m, 2065 m, 2053 s, 2047 s, 2037 s, 2018 m, 2014 m, 1994 w, 1989 m	495 (1370), 375 sh (3190)	H_M: −9.82 CH_3: 2.57 ($J_{CH_3-H_M}$ = 2.5 Hz)
$C_2H_5CFeCo_2(CO)_9H$	2101 m, 2065 m, 2053 s, 2046 s, 2038 s, 2017 m, 2014 m, 1994 w, 1989 m	530 (1390), 390 sh (4270)	H_M: −9.97 CH_3: 0.90 ($J_{CH_3-CH_2}$ = 7.0 Hz) CH_2: 2.75 ($J_{CH_2-CH_3}$ = 7.0 Hz); ($J_{CH_2-H_M}$ = 2.6 Hz)
$C_6H_5CFeCo_2(CO)_9H$	2106 mw, 2101 m, 2067 ms, 2056 s, 2047 s, 2037 s, 2024 m, 2015 w, 1998 mw, 1990 m, 1982 mw	540 sh, 400 sh	H_M: −9.00 C_6H_5: complex multiplet centered at 7.17 ppm[d]

[a] Hexane solution. [b] Isooctane solution. [c] H_M = metal hydride resonance. [d] Multiplet structure is identical with that centered at 6.03 ppm in the spectrum of $C_6H_5CCo_3(CO)_9$.

Table II. Mass Spectral Data

compd	parent ion isotopic distribution, *m/e* (rel intens)	other principal fragments, *m/e*
$CH_3CFeCo_2(CO)_9H$	452 (12), 454 (100), 455 (18), 456 (6)	426, 398, 370, 342, 314, 286, 258, 230, 202
$C_2H_5CFeCo_2(CO)_9H$	466 (11), 468 (100), 469 (17), 470 (5)	440, 412, 384, 356, 328, 300, 272, 244, 216
$C_6H_5CFeCo_2(CO)_9H$	514 (9), 516 (100), 517 (20), 518 (4)	488, 460, 432, 404, 376, 348, 320, 292, 264

dropwise addition of a THF solution of the appropriate $RCCo_3(CO)_9$ cluster to a THF solution of $Na_2[Fe(CO)_4]$ under an N_2 atmosphere. After the specified reaction time (1–2 h), the solvent was removed under vacuum, and the residue was acidified with 40% H_3PO_4 and extracted into hexane. The hexane solution was then chromatographed on silica gel.

These $RCFeCo_2(CO)_9H$ clusters are somewhat acidic and readily deprotonate on basic silica gel during chromatography, remaining at the top of the column as a dark red band. They can be removed from the silica as anions by changing the eluting solvent to methanol after the other components have been eluted with hexane. The nature of the accompanying cation is unknown. Removal of the methanol by evaporation under vacuum followed by protonation and extraction of the residue as before gives the neutral $RCFeCo_2(CO)_9H$ clusters. Mass spectra of the reaction mixtures before chromatography exhibited mass peaks due to the $RCFeCo_2(CO)_9H$ clusters, indicating their presence prior to chromatographic separation. Identical chromatographic behavior was shown by the isolated and purified compounds.

Of the various spectroscopic techniques used to identify the products of the reactions, the most useful were infrared and mass spectroscopy. Previously described compounds were identified mainly by comparison with their reported infrared spectra. The new $RCFeCo_2(CO)_9H$ clusters were primarily characterized by their mass spectra which showed parent ions with the correct *m/e* values and the expected isotopic distribution. In each case, ions corresponding to successive loss of nine carbonyls were observed. $C_2H_5CFeCo_2(CO)_9H$ was further characterized by elemental analysis, but $CH_3CFeCo_2(CO)_9H$ and $C_6H_5CFeCo_2(CO)_9H$ proved too thermally unstable to analyze. Spectroscopic data for the new clusters are set out in Tables I and II.

Preparation of $C_2H_5CFeCo_2(CO)_9H$. Reaction of $C_2H_5CCo_3(CO)_9$ with $[Fe(CO)_4]^{2-}$ proceeded cleanly to give $C_2H_5CFeCo_2(CO)_9H$ as the only detectable product. Unreacted $C_2H_5CCo_3(CO)_9$ and $Fe_3(CO)_{12}$, resulting from protonation of $[Fe(CO)_4]^{2-}$, were also isolated. When the reaction was conducted in refluxing THF, the yield of $C_2H_5CFeCo_2(CO)_9H$, based on the initial quantity of $C_2H_5CCo_3(CO)_9$ employed, was 46%. The yield decreased to 23% with a concomitant increase in the amount of unreacted $C_2H_5CCo_3(CO)_9$ recovered when the reactants were maintained at room temperature (~22–25 °C).

Preparation of $CH_3CFeCo_2(CO)_9H$. $CH_3CFeCo_2(CO)_9H$ was prepared by allowing $CH_3CCo_3(CO)_9$ to react with $[Fe(CO)_4]^{2-}$. Stirring these reactants at room temperature for 1–2 h gave five compounds upon chromatography of the acidified reaction mixture. These were, in order of elution, red-purple $CH_3CCo_3(CO)_9$ (5%), a pink compound, green $Fe_3(CO)_{12}$, blue $Co_4(CO)_{10}(CH_3C{\equiv}CCH_3)$[13-15] (9%), and maroon $CH_3CFeCo_2(CO)_9H$ (19%). The mass spectrum of the pink compound exhibited a parent peak at *m/e* 452. The position of the parent ion and the isotopic distribution correspond to a compound with the molecular formula $CH_3CFe_2Co(CO)_9H_2$, but insufficient material was isolated for complete characterization.

The yield of $CH_3CFeCo_2(CO)_9H$ was increased to 43% by carrying out the reaction in refluxing THF. $CH_3CCo_3(CO)_9$, $Fe_3(CO)_{12}$, the pink compound, and a trace of an unidentified yellow compound were also isolated. No $Co_4(CO)_{10}(CH_3C{\equiv}CCH_3)$ was detected.

Preparation of $C_6H_5CFeCo_2(CO)_9H$. Unreacted $C_6H_5CCo_3(CO)_9$, $Fe_3(CO)_{12}$, and $C_6H_5CFeCo_2(CO)_9H$ in 19% yield were the only compounds isolated from the reaction of $C_6H_5CCo_3(CO)_9$ with $[Fe(CO)_4]^{2-}$ at room temperature. When the reaction was conducted in refluxing THF, the yield of $C_6H_5CFeCo_2(CO)_9H$ increased to 31%, and trace amounts of two unidentified products were isolated in addition to unreacted $C_6H_5CCo_3(CO)_9$ and $Fe_3(CO)_{12}$.

Reaction of $HCCo_3(CO)_9$ with $[Fe(CO)_4]^{2-}$. The reaction of $HCCo_3(CO)_9$ with $[Fe(CO)_4]^{2-}$ gave a complex mixture of products. Prior to chromatography, the product mixture from a reaction maintained at room temperature exhibited a peak at *m/e* 780 in its mass spectrum. Peaks due to the stepwise loss of 11 carbonyls from this species were clearly evident with four additional carbonyl-loss peaks partially obscured by other ions. The mass position, isotopic distribution of the *m/e* 780 ion, and the carbonyl-loss pattern suggest the presence of a species with the formula $H_3Fe_3Co_3(CO)_{15}C$. We were never able to isolate this compound, however, as it presumably decomposed during the chromatographic separation of the product mixture.

Separation of this mixture by silica gel chromatography gave five distinct bands. The first was red-purple and corresponded in color and chromatography characteristics to unreacted $HCCo_3(CO)_9$. However, the infrared and mass spectra of the material isolated from this band revealed it to be a mixture of $RCCo_3(CO)_9$ clusters with R = H, CH_3, C_2H_5, and C_3H_7 with the former two in greater abundance.[16] The mass spectrum of the pink material isolated in trace quantity from the second band also indicated it to be a mixture of compounds. The mass positions and isotope patterns are consistent with the formula $RCFe_2Co(CO)_9H_2$ with R = C_2H_5, C_3H_7, and possibly CH_3.[17] Further characterization was not possible because of the very small amount of material isolated. The third band was green $Fe_3(CO)_{12}$, and the fourth contained a trace quantity of an unidentified pink compound.

The chromatography characteristics and infrared spectrum of the final red band were similar to the other $RCFeCo_2(CO)_9H$ clusters described herein. However, we were unable to obtain a satisfactory mass spectrum for this material. The mass spectrum exhibited a complex series of peaks up to *m/e* 500 with the only identifiable patterns at *m/e* 454 and 440, possibly due to $CH_3CFeCo_2(CO)_9H$ and $HCFeCo_2(CO)_9H$. It may be that one of the compounds initially present in the sample ($HCFeCo_2(CO)_9H$?) pyrolyzes on the mass probe even at the relatively low temperature used (~100 °C). The ^1H NMR spectrum of this fraction exhibited a doublet at 2.57 ppm (J_{M-H} = 2.5 Hz) attributable to $CH_3CFeCo_2(CO)_9H$, Table I, and singlets at 4.03, 2.20, 0.95, and 0.37 ppm which could not be assigned.

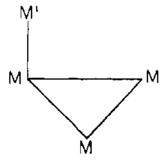
When this reaction was carried out in refluxing THF for 1–2 h, the same five bands resulted upon chromatography of the acidified reaction mixture, in addition to trace amounts of an unidentified yellow fraction between bands one and two and a brown fraction just leading the $Fe_3(CO)_{12}$ band. The mass spectrum of this brown fraction exhibited peaks at *m/e* 452, 466, and 480 consistent with the formulation $RCFe_3(CO)_9H_3$ with R = CH_3, C_2H_5, and C_3H_7, but insufficient material was isolated for further characterization.[18]

Properties. The $RCFeCo_2(CO)_9H$ clusters are dark maroon solids which give orange-red or orange solutions. They are soluble in most organic solvents, although they are somewhat unstable in alcohols and halogenated hydrocarbons. Solid samples and solutions of the clusters can be handled in air for short periods of time; solutions show signs of decomposition within 15–30 min and solids within 30–45 min. The compounds slowly decompose even under an N_2 atmosphere and are best stored under an atmosphere of CO at 0 °C. Under these conditions, $C_2H_5CFeCo_2(CO)_9H$ showed no signs of decomposition after several weeks, but some decomposition of $C_6H_5CFeCo_2(CO)_9H$ was evident after a period of several days. $CH_3CFeCo_2(CO)_9H$ and $C_2H_5CFeCo_2(CO)_9H$ can be purified by sublimation at 50 °C (10^{-3} mmHg), but $C_6H_5CFeCo_2(CO)_9H$ is less stable under the sublimation conditions and is not readily purified. Satisfactory elemental analysis was obtained only for $C_2H_5CFeCo_2(CO)_9H$ and only when a sample was mailed under an atmosphere of CO. The other two compounds apparently decomposed even under these conditions during shipment.

Discussion.

Synthesis. The mixed-metal alkylidyne clusters $RCFeCo_2(CO)_9H$ (R = CH_3, C_2H_5, C_6H_5) described herein resulted from the reaction of $[Fe(CO)_4]^{2-}$ with the appropriate $RCCo_3(CO)_9$ clusters. The spectral data summarized below indicate that the structures of these clusters are similar to those of the parent $RCCo_3(CO)_9$ compounds,[6–9] possessing an $FeCo_2$ triangle bridged by an alkylidyne carbon atom.

The mechanism by which these mixed-metal alkylidyne clusters result from the reaction of $[Fe(CO)_4]^{2-}$ with $RCCo_3(CO)_9$ is not well understood. Similar reactions of $[Fe(CO)_4]^{2-}$ with $Ru_3(CO)_{12}$, $Ru_2Os(CO)_{12}$, and $RuOs_2(CO)_{12}$ followed by protonation gave the tetranuclear clusters $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$.[1,2] It was suggested that the first step in these reactions is nucleophilic attack of the carbonylmetalate at the electropositive carbon of a coordinated carbonyl ligand.[2,3] Elimination of CO would give a species such as **2** which could collapse through **3** to give the tetrahedral cluster **4**.



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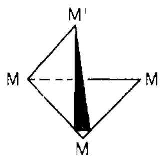

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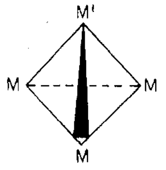

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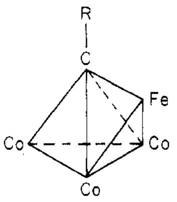
The formation of the mixed-metal alkylidyne clusters reported herein can be rationalized in a similar manner, but with the alkylidyne carbon atom as an additional site of attack. It does not appear that the preferred site of addition is on the Co_3 face, since clusters with an $FeCo_3C$ framework were not isolated, but rather on one of the Co_2C faces to produce an intermediate of possible skeletal structure **5**. Elimination of



5

a cobalt–carbonyl fragment would lead from **5** to the observed $RCFeCo_2(CO)_9H$ clusters, and indeed, evidence for the formation of $HCo(CO)_4$ was obtained in several experiments.[19] It may be that a cluster with structure **5** persists as an anion but that it readily fragments upon protonation.

In the reactions of $[Fe(CO)_4]^{2-}$ with $CH_3CCo_3(CO)_9$ and $HCCo_3(CO)_9$, compounds with an Fe_2CoC skeleton were detected by mass spectroscopy but were formed in insufficient quantities to allow full characterization. These clusters could result by the reaction of $[Fe(CO)_4]^{2-}$ with the initially formed $[RCFeCo_2(CO)_9]^-$ anions in a manner similar to that described above followed by elimination of another cobalt–carbonyl fragment. Further reaction of $[Fe(CO)_4]^{2-}$ with the Fe_2CoC clusters would account for the $RCFe_3(CO)_9H_3$ clusters that were detected, but not conclusively identified, in one of the reactions employing $HCCo_3(CO)_9$.

The $H_3Fe_3Co_3(CO)_{15}C$ carbide cluster which was detected in the mass spectrum of the reaction mixtures resulting from addition of $[Fe(CO)_4]^{2-}$ to $HCCo_3(CO)_9$ is similar to $[Co_6(CO)_{15}C]^{2-}$ which was isolated by Chini and co-workers[20,21] from the reaction of $ClCCo_3(CO)_9$ with $[Co(CO)_4]^-$. The carbide carbon in $[Co_6(CO)_{15}C]^{2-}$ was shown[21] to derive from the alkylidyne carbon atom of $ClCCo_3(CO)_9$. The alkylidyne carbon atom in $C_2H_5CFeCo_2(CO)_9H$ and $C_6H_5CFeCo_2(CO)_9H$ should be less susceptible to attack than in $HCCo_3(CO)_9$ and $CH_3CCo_3(CO)_9$ due to the larger substituents. This may explain why the reactions of the former two clusters with $[Fe(CO)_4]^{2-}$ proceeded to give fewer products than the reactions of the latter two.

We do not at all understand the mechanism by which alkylidyne clusters with R = CH_3, C_2H_5, and C_3H_7 result from the reaction of $[Fe(CO)_4]^{2-}$ with $HCCo_3(CO)_9$, but we are currently examining these reactions for their possible relevance to CO hydrogenation.

Spectroscopic Characterization. The molecular formulas of the mixed-metal alkylidyne clusters were established by their mass spectra and that of $C_2H_5CFeCo_2(CO)_9H$ was established by chemical analysis. The infrared, electronic absorption, and ^1H NMR spectra of these clusters are similar to those of the isoelectronic $RCCo_3(CO)_9$ clusters and suggest that the two

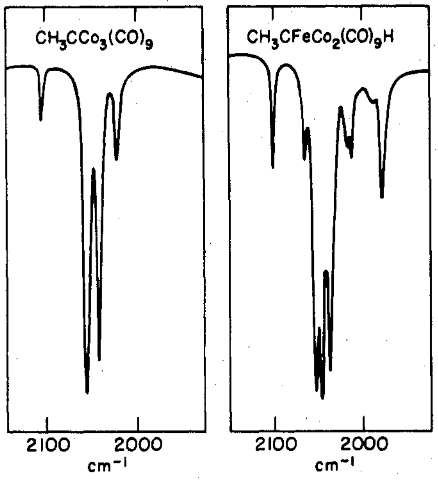


Figure 1. Infrared spectra of $CH_3CCo_3(CO)_9$ and $CH_3CFeCo_2(CO)_9H$ in hexane solution.

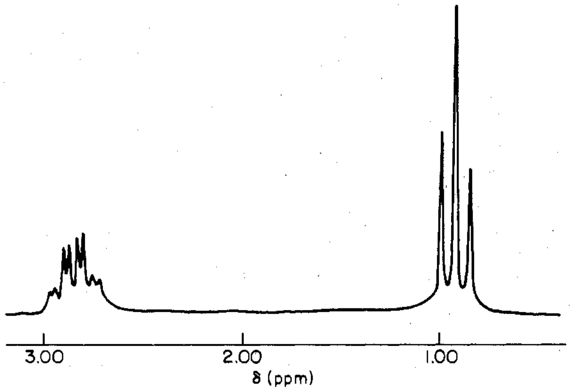


Figure 2. ^1H NMR spectrum of $C_2H_5CFeCo_2(CO)_9H$ in C_6D_6 solution.

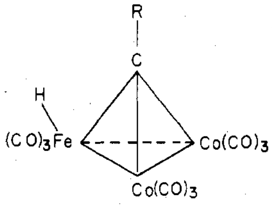
series of compounds have similar structures.

The electronic absorption spectra of the $RCFeCo_2(CO)_9H$ clusters exhibit broad bands in the visible spectral region, Table I, similar to those previously observed[22] in the spectra of the parent $RCCo_3(CO)_9$ clusters. These latter bands were attributed to transitions localized within the triangular Co_3 framework.[22] The presence of a similar spectral feature in the mixed-metal clusters strongly suggests that these also possess a triangular array of metals.

The carbonyl-region infrared spectra of the $RCFeCo_2(CO)_9H$ clusters are also similar to those of the $RCCo_3(CO)_9$ clusters, except that the former exhibit a greater number of bands due to their lower symmetry, Figure 1 and Table I. No bands attributable to bridging carbonyls were observed in any of the spectra.

^1H NMR data for the $RCFeCo_2(CO)_9H$ clusters are summarized in Table I. Each cluster shows the expected resonances for the substituent on the alkylidyne carbon and a broad resonance 9–10 ppm upfield of Me_4Si, indicative of a metal hydride ligand. A coupling of approximately 2.5 Hz was observed between the hydride ligand and the hydrogen atoms on the carbon adjacent to the alkylidyne carbon, as illustrated by the spectrum of $C_2H_5CFeCo_2(CO)_9H$, Figure 2. Similar coupling was observed in the spectrum of $HCOs_3(CO)_9H_3$ (J = 1.1 Hz)[23] but not in the spectrum of $CH_3CRu_3(CO)_9H_3$.[24] The ^{13}C NMR spectrum of $CH_3CFeCo_2(CO)_9H$[25] exhibits a broad singlet at 179.2 ppm (width at half-height = 1.7 ppm) which remains invariant through the temperature range 30 to −50 °C, the lowest temperature investigated. The carbonyl ligands are likely undergoing rapid exchange within this temperature range, as has been previously observed[26] for a number of $RCCo_3(CO)_9$ clusters.

The location of the hydride ligand cannot be deduced from the available spectroscopic data, and the four structures **6**–**9** must be considered. In order for each metal atom in the $RCFeCo_2(CO)_9H$ cluster to possess a filled 18-electron valence shell, the hydride ligand should be terminally bound to iron as in structure **6**. However, the hydride resonances in the ^1H NMR spectra are quite broad with widths at half-height of approximately 0.9 ppm. The broadening is presumably due to coupling with the cobalt nuclei which have a quadrupole moment and a nuclear spin of $^7/_2$. Such coupling would be expected for the static structures **7**–**9** in which the hydride bridges an iron–cobalt or a cobalt–cobalt bond, or the $FeCo_2$ face. Coupling could also result if the hydride ligand were fluxional at room temperature. Recent X-ray[27] and neutron[28] diffraction studies of $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ have established that the hydride ligand bridges the Co_3 face in this compound, and presumably the unsubstituted cluster $HFeCo_3(CO)_{12}$ also possesses a face-bridging hydride. This latter cluster has been shown[22] to be electronically similar to the $RCCo_3(CO)_9$ clusters, and hence a face-bridging position for the hydride in the $RCFeCo_2(CO)_9H$ complexes discussed herein seems likely. Unfortunately, ^1H NMR resonances due to the metal hydride of the parent[29] and substituted[27] $FeCo_3$ clusters have not been observed, and a comparison to the spectra reported herein cannot be made.



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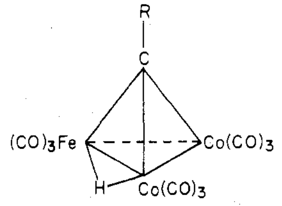

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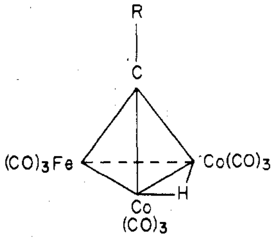

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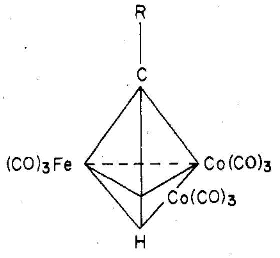

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(17) ν(CO) (hexane): 2101 (m), 2054 (vs), 2047 (vs), 2038 (s), 2017 (m), 1988 (m), 1985 (m) cm^{-1}.

(18) ν(CO) (hexane): 2101 (w), 2053 (vs), 2050 (vs), 2035 (vs), 2025 (s), 1845 (m) cm^{-1}.

(19) In several experiments, the THF solvent was vacuum distilled at 25 °C from the acidified reaction mixture and collected in a 77 K trap. The infrared spectrum of the distillate showed bands at 2073, 2046, 2027, 1866, and 1859 cm^{-1} attributable to $Co_2(CO)_8$ which presumably derived from $HCo(CO)_4$ that was vacuum transferred with the solvent.

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An Example of *Pseudo* Five-Coordination in Copper(II) Complexes

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A series of potential pentadentate *bicyclic* macrocyclic ligands has been prepared by the nucleophilic addition of various dialkoxides to the copper(II) complex of tetrabenzo[*b,f,j,h*][1,5,9,13]tetraazacyclohexadecine (TAAB). The resulting complexes can be classified as pseudo square pyramidal with potential N_4S, N_4N', and N_4O donor sets with S, N′, and O occupying the axial coordination position. The complexes are all monomeric exhibiting characteristic magnetic moments for an $S = {}^1/_2$ system in the solid state. The optical spectra, as well as the X-band ESR spectra of the five donor atom macrocyclic Cu(II) complexes, are essentially identical while Q-band ESR data indicate a very slight variation in symmetry among the series. The spectroscopic differences between $Cu(TAAB)^{2+}$, a nonbridged four-coordinate $Cu(TAAB)(OCH_3)_2$ compound, a bridged four-coordinate $Cu(TAAB)[O(CH_2)_5O]$ compound, and the five-coordinate series $Cu(TAAB)[O(CH_2)_2X(CH_2)_2O]$ (X = S, NCH_3, O) compounds are discussed in terms of both a "cage effect" and the potential effect of the axial donor atom.

Introduction

Our interest in the evolution of small-molecule copper(II) systems capable of duplicating some of the aspects of protein metal chemistry has prompted our investigation of a large number of copper(II) complexes of various stereoelectronic environments.[1] Quite often our motivation has led to some very intriguing coordination chemistry, even though not always lending insight toward the metalloenzyme function. We report one such system here.

For various reasons, we recently considered the possibility of a five-coordinate copper(II) site to explain the redox stability and selective anion binding properties of the metal site in the metalloenzyme galactose oxidase.[1a,b] Copper(II) complexes with pentadentate ligands have been of considerable recent interest.[2–8] The requirements of our model system study included a pentadentate ligand which would clearly *impose* a five-coordinate environment for copper(II). Of the pentadentate ligands reportedly coordinated to copper(II), the only ones which incorporated the salient features desired were the "cagelike" compounds previously prepared by Busch and co-workers.[7,8] The other pentadentate systems coordinated to copper(II) were linear ligands where considerable doubt existed regarding the behavior of coordination of the ligand during the subsequent chemical studies we had planned.[2–6]

The bicyclic, "cagelike", pentadentate ligands of Busch and co-workers[7,8] were prepared by the nucleophilic addition of dialkoxides to $Cu(TAAB)^{2+}$ (Figure 1a), to produce a complex of copper(II) in which the metal atom was in close proximity of either an N_4S or N_4N' donor set (Figure 1b). By modifying this earlier synthetic approach we have been able to extend the series of cagelike complexes to include donor sets of N_4X, where X = S, O, $N(CH_3)$, and the special case where a CH_2 group was X. The more extended series allowed a closer evaluation of the coordination properties of the fifth, central donor atom, an understanding we needed prior to our evaluation of these systems as chemical models for copper(II) in proteins. We report now the synthetic modification we employed and the subsequent characterization of these compounds.

Experimental Section

Materials. $Cu(TAAB)(NO_3)_2$ was prepared by the method of Busch and co-workers.[9] All other chemicals and solvents were commercially obtained, were of reagent grade, and were used without further purification except for the solvents tetrahydrofuran and methylene chloride. Tetrahydrofuran was dried by distillation from Na/K alloy and benzophenone in an argon atmosphere. Methylene chloride was dried by distillation from $CaCl_2$ in an argon atmosphere.

Preparation of Dialkoxide. $HOCH_2CH_2XCH_2CH_2OH$ (X = S, O, $N(CH_3)$, CH_2) was mixed with an excess of metallic sodium in dried tetrahydrofuran under an argon atmosphere. The reaction mixture was stirred for approximately 48 h or until the reaction appeared complete as evidenced by no further H_2 evolution. The excess sodium was removed and the corresponding disodium dialkoxide filtered as a white precipitate and stored under argon.

Preparation of the Bridged Copper Complexes. This procedure represents a substantial modification of that reported by Busch and co-workers.[7,8] The synthesis was similar for all of the bridged