Organometallics **1985**, *4*, 1117-1122 1117

Synthesis of Mixed-Metal Clusters by Facile Metal Substitution Reactions

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Received October 11, 1984

The anionic clusters $[Fe_2(CO)_8]^{2-}$, $[Fe_4(CO)_{13}]^{2-}$, $[Ru_4(CO)_{13}]^{2-}$, and $[Fe_3W(CO)_{14}]^{2-}$ react rapidly with 1 equiv of $Co_2(CO)_8$ to produce the metal-substituted clusters $[FeCo(CO)_8]^-$, $[Fe_3Co(CO)_{13}]^-$, $[Ru_3Co(CO)_{13}]^-$, and $[Fe_3Co(CO)_{13}]^-$, respectively. Similarly $[Fe_3(CO)_{11}]^{2-}$ with $[Mn(CO)_5(CH_3CN)]^+$ yields $[Fe_2Mn(CO)_{12}]^-$. Radical spin traps implicate a radical chain reaction with $Co_2(CO)_8$. The crystal structure of one of these products $[N(PPh_3)_2][Fe_3Co(CO)_{13}]$ was determined. The metal framework is pseudotetrahedral. Crystal data for $[PPN][Fe_3Co(CO)_{13}]$: triclinic, space group $P\bar{1}$, $a = 15.255$ (5) Å, $b = 18.750$ (6) Å, $c = 9.266$ (2) Å, $\alpha = 79.20$ (2)°, $\beta = 86.27$ (2)°, $\gamma = 109.48$ (2)°, and $Z = 2$.

Introduction

The synthesis of mixed-metal clusters has been dominated to a large extent by the redox condensation technique.[2] This method involves reaction of a metal carbonylate with a neutral cluster usually resulting in formation of a higher nuclearity species (eq 1).

$$M_n(CO)_x + [M'(CO)_y]^{w-} \rightarrow [M_nM'(CO)_z]^{w-} \quad (1)$$

An alternative approach to mixed-metal clusters is replacement of one metal vertex by an isoelectronic heterometal fragment (eq 2). Although reactions of this type

$$M_n(CO)_x + M'(CO)_y \rightarrow M_{n-1}M'(CO)_z + \text{“}M(CO)\text{”} \quad (2)$$

were observed some time ago,[3] it is not until recently that systematic studies of metal substitution reactions have been undertaken.[4] These reactions have in general required harsh conditions resulting in relatively low product yields and have been limited to capped trimetallic systems. By contrast there are reports of facile substitution reactions at ambient or subambient temperatures involving $Co_2(CO)_8$ and anionic cluster species.[3,5] In this paper we explore the generality of the facile metal substitution reactions and test for the involvement of radical intermediates. Radical intermediates in metal substitution reactions have recently been implicated by means of electrochemical techniques.[6]

Experimental Section

General Methods. All manipulations were performed under an atmosphere of prepurified N_2 using standard Schlenk or high vacuum line techniques.[7] Solids were handled in a Vacuum Atmosphere glovebox under N_2. Solvents were distilled under N_2 from appropriate drying agents: THF, pentane, methylcyclohexane, and diethyl ether from sodium benzophenone, CH_2Cl_2 from P_2O_5, and CH_3CN from CaH_2. Acetone and methanol were deaerated with N_2 prior to use. $Co_2(CO)_8$ (Strem) and $Mn_2(CO)_{10}$ (Strem) were purified by sublimation while [PPN]Cl (Aldrich) [PPN = bis(triphenylphosphine)nitrogen(1+)] and $[PPh_4]Br$ (Aldrich) were used without further purification. The $[PPN]^+$ and $[PPh_4]^+$ salts of $[Fe_4(CO)_{13}]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, and $[Fe_2(CO)_8]^{2-}$ were synthesized by literature procedures.[8-10] Except for $[Fe_2(CO)_8]^{2-}$, the $[PPN]^+$ and $[PPh_4]^+$ salts undergo similar reactions. $[Mn(CO)_5(CH_3CN)][PF_6]$,[11] $[Mn(CO)_3(CH_3CN)_3][PF_6]$,[11] and $[PPN]_2[Fe_3W(CO)_{14}]$[12] were synthesized by literature procedures.

Infrared spectra were obtained on either a Perkin-Elmer 399 or 283 spectrophotometer. Solution cells were 0.1-mm path length, and CaF_2 windows were used. NMR spectra were recorded on a JEOL FX-90 spectrometer (^{13}C, 22.49 MHz) using CD_2Cl_2 (99.5 atom %) which was dried over P_2O_5 and vacuum distilled prior to use.

Reactions of $[Fe_n(CO)_x]^{2-}$ (n = 2, 3, or 4) (x = 8, 11, or 13) with $Co_2(CO)_8$. The following procedure is applicable to all three cluster species but works best for $[Fe_3(CO)_{11}]^{2-}$ or $[Fe_4(CO)_{13}]^{2-}$. An alternative procedure for $[PPh_4]_2[Fe_2(CO)_8]$ is described below. A 200-mg (0.12-mmol) sample of $[PPN]_2[Fe_4(CO)_{13}]$ and 40 mg (0.12 mmol) of $Co_2(CO)_8$ were combined in a reaction vessel. The flask was attached to a high vacuum line, and 10.0 mL of CH_2Cl_2 (freeze–thaw degassed three times) was distilled into the reaction vessel. Reaction proceeded for 10 min at room temperature, the solvent and $Fe(CO)_5$ were vacuum distilled from the reaction, and the quantity of $Fe(CO)_5$ was determined by IR spectroscopy. Diethyl ether (10 mL) was added to the reaction vessel to redissolve the solid and precipitate $[PPN][Co(CO)_4]$, which was collected by filtration and weighed. A spectrum of this solid in a Nujol mull showed only the presence of $[Co(CO)_4]^-$ (ν_{CO} 1890 cm^{-1}) and no other carbonyl-containing species. The cluster was crystallized by layering the filtrate with 25 mL of pentane and allowing slow diffusion. Product was recovered by filtration on a medium porosity frit, washed with two 10-mL aliquots of pentane, and dried in vacuo. The yield of $[PPN][Fe_3Co(CO)_{13}]$ was 80 mg (60%) based on starting $[PPN]_2[Fe_4(CO)_{13}]$. The IR spectrum of this product compares well with a sample of $[Fe_3Co(CO)_{13}]^-$ described in the literature.[13] Anal. Calcd for $Fe_3CoC_{49}H_{30}O_{13}P_2N$: Fe, 14.85; Co, 5.22; N, 1.24. Found: Fe, 13.85; Co, 5.09; N, 1.33. Elemental analysis was not performed on the product from $[PPN]_2[Fe_3(CO)_{11}]$, since its IR spectrum was identical with the spectrum obtained from reaction of $[PPN]_2[Fe_4(CO)_{13}]$ with $Co_2(CO)_8$.

Reaction of $[PPh_4]_2[Fe_2(CO)_8]$ with $Co_2(CO)_8$. A sample of $[Ph_4P]_2[Fe_2(CO)_8]$ (300 mg) was combined with $Co_2(CO)_8$ (100 mg), and methanol (10 mL) was added. The solution slowly turned light brown. (The brown color is caused by formation of $[Fe_3Co(CO)_{13}]^-$.) When no further reaction appeared to occur (15 min), the solution was filtered and the volume of MeOH reduced to ca. 3 mL. A precipitate of a light colored solid formed and was then collected by filtration, washed with cold Et_2O (10 mL, −10 °C), and dried in vacuo. Infrared spectra indicated that the filtrate

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0276-7333/85/2304-1117$01.50/0

contained only $[Fe_3Co(CO)_{13}]^-$ and $[Co(CO)_4]^-$ but no $[FeCo(CO)_8]^-$. Dissolution of the solid in CH_2Cl_2 (3 mL) followed by addition of Et_2O (12 mL) caused precipitation of $[PPh_4][Co(CO)_4]$, which was recovered by filtration. The solvents were removed in vacuo from the filtrate leaving an orange-yellow powder. The powder was redissolved in CH_2Cl_2, and pentane was added slowly to precipitate the product which was recovered by filtration, washed with pentane, and dried in vacuo. The yield of $[Ph_4P][FeCo(CO)_8]$ was 85 mg (42%) based on starting $[Ph_4P]_2[Fe_2(CO)_8]$. The IR spectrum of this product compares very well to ν_{CO} values in the literature.[3] Anal. Calcd for $C_{32}H_{20}FeCoO_8P$: Fe, 8.23; Co, 8.69. Found: Fe, 7.37; Co, 8.76.

Reaction of $K_2Ru_4(CO)_{13}$ with $Co_2(CO)_8$. A 10-mg (0.01-mmol) sample of $K_2Ru_4(CO)_{13}$ and 6 mg (0.02 mmol) of $Co_2(CO)_8$ were combined. THF (5 mL) was added, yielding a red solution. The IR spectrum of the solution showed the presence of a monoanion cluster and $[Co(CO)_4]^-$, ν_{CO} 1890 cm^{-1}. THF was removed in vacuo, and then a 3-mL solution of CH_2Cl_2 containing 25 mg of [PPN]Cl was added to the flask. KCl, $[PPN][Co(CO)_4]$, and excess [PPN]Cl precipitated upon addition of Et_2O, and these solids were removed by filtration. Addition of methylcyclohexane to the CH_2Cl_2/Et_2O solution caused precipitation of a red product which was recovered by filtration. An IR spectrum of the product in THF had ν_{CO} at 2068 (vw), 2020 (vs), 1980 (m, sh), and 1805 (w) cm^{-1}, which compare favorably with those for an authentic sample of $[Ru_3Co(CO)_{13}]^-$ in THF.[13,14]

Reactions of $[Fe_4(CO)_{13}]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ with $[Mn(CO)_5(CH_3CN)][PF_6]$. The syntheses of both clusters were similar and will be described for $[PPh_4]_2[Fe_3(CO)_{11}]$ only. A 150-mg (0.13-mmol) sample of $[PPh_4]_2[Fe_3(CO)_{11}]$ and 50 mg (0.13 mmol) of $[Mn(CO)_5(CH_3CN)][PF_6]$ were combined in an inert atmosphere. CH_2Cl_2 (10.0 mL) (freeze–thaw degassed three times) was introduced. Reaction was allowed to proceed for 1 h at which time the CH_2Cl_2 and $Fe(CO)_5$ were distilled from the flask under vacuum. The quantity of $Fe(CO)_5$ produced was determined by IR spectroscopy. Et_2O (10 mL) was added to the reaction vessel, whereupon the cluster product dissolved and $[PPh_4][PF_6]$ precipitated. The latter salt was recovered by filtration and weighed. The cluster was isolated by layering 25 mL of pentane on the Et_2O and allowing slow diffusion. Crystals were recovered by filtration, washed with pentane, and dried in vacuo, yielding 60 mg of $[PPh_4][Fe_2Mn(CO)_{12}]$ (55%) based on starting $[PPh_4]_2[Fe_3(CO)_{11}]$. The cluster product was recrystallized from a concentrated MeOH solution. The IR spectrum of the product compares well with a sample of $[Fe_2Mn(CO)_{12}]^-$ described in the literature.[18] Anal. Calcd for $Fe_2MnC_{36}H_{20}O_{12}P$: Fe, 13.27; Mn, 6.52; P, 3.68. Found: Fe, 13.91; Mn, 7.35; P. 3.76. No analysis was performed on the product isolated from the $[Fe_4(CO)_{13}]^{2-}$ system since it was thought to be impure. An analogous reaction was performed between $[Mn(CO)_3(CH_3CN)_3]^+$ and $[PPh_4]_2[Fe_3(CO)_{11}]$ in acetone solution. The yield of $[PPh_4][Fe_2Mn(CO)_{12}]$ was 27% based on starting $[PPh_4]_2[Fe_3(CO)_{11}]$.

Single-Crystal X-ray Structure Determination. A crystal of $[(Ph_3P)_2N][Fe_3Co(CO)_{13}]$ was sealed in a capillary and mounted on a Syntex P3 automated diffractometer. Unit-cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data (12 753 points) were collected at room temperature using a variable scan rate, a θ–2θ scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for the combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and the intensities of these standards showed less than 8% variation; therefore corrections for decomposition were not performed. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant data, 2901 reflections were considered observed [$I > 3.0\sigma(I)$]. The heavy-atom positions were determined by direct methods using MULTAN80.[15] Successive least-squares/difference Fourier cycles allowed location of the remainder of the nonhydrogen atoms. Refinement of scale factor, positional, and anisotropic thermal parameters[16] for all non-hydrogen atoms was carried out to convergence. Hydrogen positional parameters were not determined. The final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor, R = 7.6% [$R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$]. Anomalous dispersion corrections were made for Fe and Co. Scattering factors were taken from Cromer and Mann.[17] Unit weights were used throughout.

Table I. Crystal Data for $[PPN][Fe_3Co(CO)_{13}]$

formula	$Fe_3CoP_2NC_{49}H_{30}O_{13}$
mol wt	1129.2
a, Å	15.255 (5)
b, Å	18.750 (6)
c, Å	9.266 (2)
α, deg	79.20 (2)
β, deg	86.27 (2)
γ, deg	109.48 (2)
V, Å^3	2431.0 (12)
$F(000)$	1140
μ(Mo Kα), cm^{-1}	13.39
λ(Mo Kα), Å	0.71069
D_{calcd}, g cm^{-3}	1.542
Z	2
obsd reflctns	2901
R	7.6%
space group	$P\bar{1}$

Table II. Product Yields Based on 1 Equiv of Starting Iron Cluster

reactn	$Fe(CO)_5$	$[Co(CO)_4]^-$	cluster
3	0.61	1.13	0.52[a]
4	0.93	1.07	0.65
7	0.59	0.94[b]	0.55
9	1.18	1.35	0.48

[a] Contaminated with $[Fe_3Co(CO)_{13}]^-$. [b] $[PPh_4][PF_6]$.

Results and Discussion

Metal Substitution. The reaction of $Co_2(CO)_8$ with the iron cluster anions $[Fe_2(CO)_8]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$ is rapid at room temperature in CH_2Cl_2 as evidenced by an immediate color change of the parent iron cluster upon solvent addition. Reaction is complete in less than 1 min. An IR spectrum of the reaction mixture shows the presence of $Fe(CO)_5$ and $[Co(CO)_4]^-$ as well as formation of a monoanionic cluster. $Fe(CO)_5$ and $[Co(CO)_4]^-$ were removed from the mixture by appropriate means, and their quantities were determined by quantitative IR spectroscopy and weight of the recovered solid, respectively. The cluster products were identified as $[FeCo(CO)_8]^{-}$[3] and $[Fe_3Co(CO)_{13}]^{-}$[13] by comparison with literature spectra (eq 3 and 4) and, in the case of $[Fe_3Co(CO)_{13}]^-$, determination of the

$$[PPN]_2[Fe_2(CO)_8] + Co_2(CO)_8 \xrightarrow[25\ °C]{CH_2Cl_2} [PPN][FeCo(CO)_8] + Fe(CO)_5 + [PPN][Co(CO)_4] \quad (3)$$

$$[PPN]_2[Fe_4(CO)_{13}] + Co_2(CO)_8 \xrightarrow[25\ °C]{CH_2Cl_2} [PPN][Fe_3Co(CO)_{13}] + Fe(CO)_5 + [PPN][Co(CO)_4] \quad (4)$$

molecular structure by X-ray methods. In order to write balanced chemical equations an additional mole of CO is required. Presumably, this CO is scavenged from a metal carbonyl species. No CO was evolved in reactions 3 and

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4, and these reactions were not attempted in the presence of added CO.

The quantities of $Fe(CO)_5$ and $[Co(CO)_4]^-$ produced in reactions 3 and 4 are reported in Table II. It can be seen that the amount of $Fe(CO)_5$ produced is slightly less than 1 equiv while for $[Co(CO)_4]^-$ slightly more than 1 equiv is formed (both are based on the amount of starting iron cluster). These values are basically in accord with the necessity for some carbonyl-containing species to donate CO by decomposition. Despite the decomposition, both clusters are formed in greater than 50% yield based on starting iron cluster. This is a significant improvement over the previous preparations of $[Fe_3Co(CO)_3]^-$.

The metal substitution reaction can be extended to second-row clusters. Reaction of $[Ru_4(CO)_{13}]^{2-}$ with $Co_2(CO)_8$ in THF results in a rapid color change from orange to red. Both $[Ru_3Co(CO)_{13}]^-$ and $[Co(CO)_4]^-$ were identified by infrared spectroscopy[13] (eq 5). Owing to the

$$K_2[Ru_4(CO)_{13}] + Co_2(CO)_8 \xrightarrow[25\ ^\circ C]{THF} K[Ru_3Co(CO)_{13}] + K[Co(CO)_4] + Ru_n(CO)_m \quad (5)$$

limited quantities of $[Ru_4(CO)_{13}]^{2-}$ available, no attempt was made to detect $Ru(CO)_5$ or determine the quantity of $[Co(CO)_4]^-$ produced. This reaction is interesting since it is generally believed that bonds between second-row metals are stronger than those between a second- and first-row metal.

Reaction of the preformed mixed-metal cluster dianion $[Fe_3W(CO)_{14}]^{2-}$ with $Co_2(CO)_8$ resulted in the formation of $[Fe_3Co(CO)_{13}]^-$ in low yield. In addition to the cluster product other compounds identified in the reaction mixture were $Fe(CO)_5$, $[Co(CO)_4]^-$, and $W(CO)_6$, but no new cluster species could be identified (eq 6). This result demonstrates that the metal substitution reaction is not necessarily selective toward removal of a single type of metal center.

$$[Fe_3W(CO)_{14}]^{2-} + Co_2(CO)_8 \rightarrow [Fe_3Co(CO)_{13}]^- + [Co(CO)_4]^- + Fe(CO)_5 + W(CO)_6 + \ldots \quad (6)$$

Facile metal substitution is not confined to the action of $Co_2(CO)_8$ on anionic clusters. An analogous substitution process was observed between $[Mn(CO)_5(CH_3CN)]^+$ and $[Fe_3(CO)_{11}]^{2-}$ (eq 7).

$$[PPh_4]_2[Fe_3(CO)_{11}] + [Mn(CO)_5(CH_3CN)][PF_6] \xrightarrow[25\ ^\circ C]{CH_2Cl_2} [PPh_4][Fe_2Mn(CO)_{12}] + Fe(CO)_5 + [PPh_4][PF_6] \quad (7)$$

The product of this reaction $[Fe_2Mn(CO)_{12}]^-$ was identified by comparison of its IR spectrum with an authentic sample prepared by literature methods.[3,18] Because of the limited solubility of the manganese reagent in CH_2Cl_2, this reaction is not as rapid as analgous reactions with $Co_2(CO)_8$. However, in CH_3CN the reaction is essentially complete upon addition of solvent as evidenced by the appearance of the blue color characteristic of $[Fe_2Mn(CO)_{12}]^-$. The yields of $Fe(CO)_5$ and $[PPh_4][PF_6]$ are both approximately 1 equiv based on starting iron cluster (Table II). As with the metal substitution reactions of $Co_2(CO)_8$, additional CO must be provided by some decomposition of one of the reactants. The facility of this reaction is interesting when compared to ligand substitution reactions on the manganese cation.[11,19] Metal substitution is essentially complete upon addition of solvent (CH_3CN). By contrast, simple substitutions of the acetonitrile ligand in $[Mn(CO)_5(CH_3CN)]^+$ by pyridine or phosphines are significantly slower.

Table III. Positional Parameters for $[PPN][Fe_3Co(CO)_{13}]$[a]

atom	*x*	*y*	*z*
Fe1	0.9225 (2)	0.3314 (2)	0.9413 (4)
Fe2	0.9391 (2)	0.2951 (2)	0.6777 (3)
Fe3	0.9556 (2)	0.2020 (2)	0.9184 (3)
Co1	0.8042 (2)	0.2180 (2)	0.8790 (3)
O11	0.9422 (17)	0.4923 (11)	0.8490 (24)
O12	0.1195 (12)	0.3700 (11)	0.9893 (21)
O13	0.8575 (16)	0.3108 (13)	0.2540 (20)
O21	0.8327 (15)	0.3838 (12)	0.5324 (22)
O22	0.0075 (13)	0.2521 (11)	0.4177 (19)
O23	0.1033 (14)	0.4369 (10)	0.6401 (22)
O31	0.1348 (10)	0.2614 (9)	0.7243 (18)
O32	0.0561 (12)	0.1805 (11)	0.1689 (18)
O33	0.9213 (13)	0.0462 (9)	0.8658 (22)
O41	0.7329 (14)	0.3407 (12)	0.8840 (24)
O42	0.8039 (12)	0.1431 (10)	0.6344 (19)
O43	0.8001 (11)	0.1304 (10)	0.1730 (18)
O44	0.6043 (12)	0.1283 (14)	0.9147 (23)
C11	0.9331 (20)	0.4291 (15)	0.8856 (31)
C12	0.0384 (17)	0.3489 (14)	0.9717 (27)
C13	0.8846 (18)	0.3207 (17)	0.1292 (31)
C21	0.8749 (18)	0.3478 (13)	0.5917 (27)
C22	0.9797 (18)	0.2675 (14)	0.5219 (27)
C23	0.0363 (18)	0.3808 (14)	0.6652 (27)
C31	0.0605 (15)	0.2447 (12)	0.7841 (25)
C32	0.0154 (16)	0.1889 (13)	0.0731 (26)
C33	0.9328 (16)	0.1073 (14)	0.8825 (26)
C41	0.7876 (18)	0.3066 (15)	0.8983 (27)
C42	0.8307 (16)	0.1919 (13)	0.7084 (24)
C43	0.8357 (14)	0.1659 (12)	0.0525 (24)
C44	0.6852 (16)	0.1640 (14)	0.9005 (26)

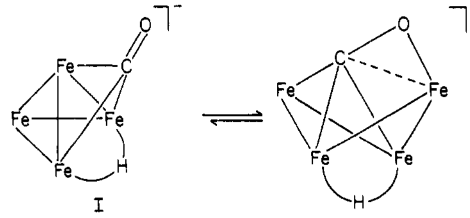
[a] Estimated standard deviations in parentheses.

In acetone solution, $[Mn(CO)_3(CH_3CN)_3]^+$ also reacts with $[Fe_3(CO)_{11}]^{2-}$ to produce the metal substitution product $[Fe_2Mn(CO)_{12}]^-$ (eq 8). This substitution reaction

$$[Fe_3(CO)_{11}]^{2-} + [Mn(CO)_3(CH_3CN)_3]^+ \xrightarrow{acetone} [Fe_2Mn(CO)_{12}]^- + Fe(CO)_5 + \ldots \quad (8)$$

is considerably slower than the analogous reaction with $[Mn(CO)_5(CH_3CN)]^+$ requiring approximately 1 h to react to completion. $Fe(CO)_5$ is again detected as one of the products, but no attempt was made to determine the quantity produced. The yield of $[Fe_2Mn(CO)_{12}]^-$ is low, presumably because of the CO deficiency in the reactants.

Molecular Structure of $[PPN][Fe_3Co(CO)_{13}]$. With our continuing interest in steric and electronic effects in cluster compounds, the molecular structure of $[Fe_3Co(CO)_{13}]^-$ was determined. This molecule is isoelectronic with $[Fe_4(CO)_{13}]^{2-}$ but can also be viewed as replacement of a $[HFe(CO)_4]^+$ vertex with $[Co(CO)_4]^+$ in $[HFe_4(CO)_{13}]^-$. It has recently been demonstrated that $[HFe_4(CO)_{13}]^-$ exists in solution as both a butterfly cluster with a Π-CO and as a protonated tetrahedron (II)[20,21] whereas a butterfly



I

II

$Fe \equiv Fe(CO)_3$

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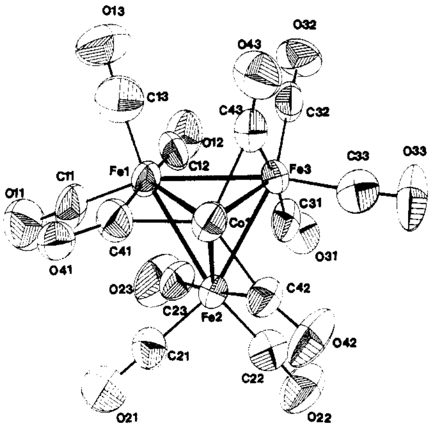

Figure 1. Projection view of $[Fe_3Co(CO)_{13}]^-$ showing thermal ellipsoids at the 50% probability level and the atom numbering scheme. Carbonyl C44–O44, bonded to Co1, has been omitted for clarity.

structure exists in the solid state.[22] Thus it was of interest to investigate the structure of $[Fe_3Co(CO)_{13}]^-$ to determine if the cluster adopted the butterfly geometry with a Π-CO or retained a tetrahedral metal core. The results of the structural determination are shown in Figure 1. Positional parameters for the cluster anion are given in Table III, and derived distances and angles are presented in Table IV. The $[Fe_3Co(CO)_{13}]^-$ cluster is comprised of a tetrahedral metal framework and is isostructural with $[Ru_3Co(CO)_{13}]^-$.[13] Although the positioning of metals differing by one atomic number is often difficult with single-crystal X-ray techniques, in this work the assignment of the Co position appears to be substantiated by the consistency of metal–metal distances and metal–carbon distances and also its position in the analogous $CoRu_3$. The $[Fe_3Co(CO)_{13}]^-$ cluster, like its ruthenium analogue, shows a staggered arrangement of the bridging carbonyls imparting chirality to the cluster. The centrosymmetric space group $P\bar{1}$ requires both enantiomers to be present in the same unit cell. Thus, this represents one of the few examples in which clusters from the first- and second-row transition series are strictly isostructural both with respect to the metal framework and the disposition of the CO ligands on the cluster.

The average Fe–Fe distance is 2.667 (5) Å while the Fe–Co average distance is 2.487 (4) Å. The shorter Fe–Co distances are along edges which are bridged by CO ligands. Other significant bond distances are Co–C44 = 1.74 (2) Å, Co–bridging C = 1.83 (2) Å, Fe–terminal C = 1.76 (3) Å, and Fe–bridging C = 2.02 (2) Å. It is interesting to note that the Fe–Fe bond distances are longer than in other 60-electron iron clusters of like charge such as $[PPN][Fe_4(CO)_{12}(COMe)]$,[23] average Fe–Fe = 2.581 (2) Å, and $[PPN][Fe_4(CO)_{12}(CCH_3)]$,[24] average Fe–Fe = 2.554 (3) Å. However, the average M–M distance in the title structure, 2.577 (6) Å, is similar to the other tetrahedral clusters and is only slightly longer than the average M–M distance of 2.54 Å in $[Fe_4(CO)_{13}]^{2-}$.[25] Thus the average M–M distance of first-row transition-metal clusters with 13 ligands arranged around a tetrahedral metal core appears to fall in the narrow range of 2.54–2.58 Å. These M–M distances can be compared to the more highly strained $[Fe_3Cr(CO)_{14}]^{2-}$ tetrahedral cluster in which the average M–M distance is 2.644 (4) Å.[12]

Table IV. Bond Distances (Å) and Angles (deg) for $[PPN][Fe_3Co(CO)_{13}]$

	Bond Distances		
Co1–Fe1	2.480 (4)	Fe1–Fe2	2.674 (5)
Co1–Fe2	2.512 (4)	Fe1–Fe3	2.682 (5)
Co1–Fe3	2.468 (5)	Fe2–Fe3	2.645 (4)
Co1–C44	1.74 (2)	Fe2–C42	2.04 (2)
Co1–C41	1.80 (3)	Fe2–C21	1.74 (3)
Co1–C42	1.80 (2)	Fe2–C22	1.76 (3)
Co1–C43	1.90 (2)	Fe2–C23	1.76 (2)
Fe1–C41	2.04 (3)	Fe3–C43	1.98 (2)
Fe1–C11	1.76 (3)	Fe3–C31	1.81 (2)
Fe1–C12	1.74 (3)	Fe3–C32	1.77 (2)
Fe1–C13	1.75 (3)	Fe3–C33	1.79 (3)
C11–O11	1.13 (4)	C32–O32	1.13 (3)
C12–O12	1.20 (3)	C33–O33	1.14 (3)
C13–O13	1.16 (3)	C41–O41	1.21 (4)
C21–O21	1.17 (4)	C42–O42	1.22 (3)
C22–O22	1.15 (3)	C43–O43	1.18 (2)
C23–O23	1.17 (3)	C44–O44	1.18 (3)
C31–O31	1.14 (3)		
	Bond Angles		
Co1–C44–O44	179 (3)	Fe2–C22–O22	178 (2)
Co1–C41–O41	143 (2)	Fe2–C23–O23	172 (2)
Co1–C42–O42	144 (2)	Fe3–C43–O43	142 (2)
Co1–C43–O43	139 (2)	Fe3–C31–O31	163 (2)
Fe1–C41–O41	136 (2)	Fe3–C32–O32	178 (2)
Fe1–C11–O11	178 (3)	Fe3–C33–O33	176 (2)
Fe1–C12–O12	172 (2)	Fe1–C41–Co1	80 (1)
Fe1–C13–O13	178 (3)	Fe2–C42–Co1	81 (1)
Fe2–C42–O42	134 (2)	Fe3–C43–Co1	79 (1)
Fe2–C21–O21	179 (2)		

Alternate Reaction Products. Reaction of the triiron cluster $[Fe_3(CO)_{11}]^{2-}$ with $Co_2(CO)_8$ does not result in formation of $[Fe_2Co(CO)_{11}]^-$ but rather a cluster building reaction occurs to form $[Fe_3Co(CO)_{13}]^-$. If this were a straightforward cluster building reaction, it would be described by eq 9. However, eq 9 does not describe the full

$$[Fe_3(CO)_{11}]^{2-} + Co_2(CO)_8 \rightarrow [Fe_3Co(CO)_{13}]^- + [Co(CO)_4]^- + 2CO \quad (9)$$

complexity of this reaction because $Fe(CO)_5$ is formed, and no CO is detected. The quantities of $Fe(CO)_5$ and $[Co(CO)_4]^-$ formed during reaction are included in Table II. It can be seen that both species are produced in excess of 1 equiv based on starting iron cluster. Attempts were made to synthesize $[Fe_2Co(CO)_{11}]^-$ by alternate routes (eq 10 and 11) but were unsuccessful. The only cluster product which

$$Fe_2(CO)_9 + [Co(CO)_4]^- \nrightarrow [Fe_2Co(CO)_{11}]^- \quad (10)$$

$$[Fe_3(CO)_{11}]^{2-} + Co_2(CO)_8 + CO \nrightarrow [Fe_2Co(CO)_{11}]^- \quad (11)$$

could be identified in reaction 10 was $[FeCo(CO)_8]^-$ along with $Fe(CO)_5$ and $[Co(CO)_4]^-$ while only the latter two species were detected in reaction 11. Thus the $[Fe_2Co(CO)_{11}]^-$ cluster does not appear to be stable under the experimental conditions explored thus far. Reasons for this instability are not clear.

An analogous cluster building reaction occurs when the four-iron carbide cluster $[Fe_4(CO)_{12}C]^{2-}$ reacts with $Co_2(CO)_8$ to form $[Fe_4Co(CO)_{15}C]^{2-}$.[26] As in the previous example, $Fe(CO)_5$ is produced, suggesting that a similar pathway is followed in both reactions.

The interaction of $[Mn(CO)_5(CH_3CN)]^+$ with $[Fe_4(CO)_{13}]^{2-}$ proved to be complicated and unpredictable. The

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reaction in CH_2Cl_2 is slower than for $[Fe_3(CO)_{11}]^{2-}$, and no reaction occurs in CH_3CN. In some instances reaction proceeded only to 50% completion when 1 equiv of both reagents was used. In addition, the product obtained from CH_2Cl_2 solution was unpredictable, with $[Fe_2Mn(CO)_{12}]^-$ sometimes identified as the sole product and in other instances a product with CO frequencies at 2000 (vs), 1980 (vs), and 1975 (m, sh) cm^{-1} was observed. Reasons for this irreproducibility are not clear, nor is an explanation available for the apparent instability of the $[Fe_3Mn(CO)_{14}]^-$ cluster. Previous attempts to synthesize this cluster by other methods have also been unsuccessful.[27]

The manganese cation can also participate in cluster building reactions. Reaction of $[Fe_3(CO)_9CCO]^{2-}$ with $[Mn(CO)_5(CH_3CN)]^+$ in CH_2Cl_2 is slow, taking a few hours to react to completion. The product isolated from this reaction is $[Fe_3Mn(CO)_{13}C]^-$ and only a trace amount of $Fe(CO)_5$ is produced.[26]

Reaction Pathway for Metal Substitution. The facility with which the metal substitution reactions of the cluster anions with $Co_2(CO)_8$ suggested that a radical reaction pathway might be involved. Previous kinetic studies on the substitution reactions of $Co_2(CO)_8$ with a variety of ligands have implicated radical intermediates.[28] In addition, EPR spectra of the iron clusters used in this study show the presence of finite concentrations of radical cluster species, which presumably arise from the presence of adventitious O_2 in the solvents.[29] Radical processes have also been invoked in ligand substitution reactions in which catalytic amounts of radical reagents such as sodium benzophenone ketyl are used to initiate reaction.[30] Similarly, electrochemical methods have also been used for ligand substitution[30b,c] and more recently to initiate metal substitution reactions.[6] Finally, radicals derived from homolytic scission of metal–metal bonds in some dimer molecules have been proposed in order to explain metal substitution reactions of the $Co_3(CO)_9CR$ cluster system.[4b,31]

Since the reaction of $[Fe_4(CO)_{13}]^{2-}$ with $Co_2(CO)_8$ appeared to be the most straightforward metal substitution reaction, further investigations were performed on this system. The known radical trap tetramethyl-*p*-benzoquinone (duroquinone) was mixed with both the iron cluster and the $Co_2(CO)_8$, and then CH_2Cl_2 was added. An aliquot of the solution was removed after 2 min, and an infrared spectrum was obtained. Reaction of the iron cluster with $Co_2(CO)_8$ in the presence of duroquinone did proceed to some extent as evidenced by the appearance of both $Fe(CO)_5$ and $[Co(CO)_4]^-$ in the IR spectrum, but an absorption at 1945 cm^{-1} for unreacted $[Fe_4(CO)_{13}]^{2-}$ was still present. No absorptions due to $[Fe_3Co(CO)_{13}]^-$, $Co_2(CO)_8$, or other cobalt carbonyl species were observed. Blank reactions using the reactants individually with duroquinone were run on the same time scale, and no reaction appeared to occur. A considerable amount of insoluble material was formed during the reaction, presumably from decomposition of $Co_2(CO)_8$. These results suggest that the metal substitution reaction is radical in nature, and a significant amount of cobalt radicals are formed during reaction. Iron cluster radicals may also be present.

Radical trapping experiments also were employed for reaction 7. In this instance complete decomposition of both $[Fe_3(CO)_{11}]^{2-}$ and $Co_2(CO)_8$ occurred when the reaction was performed in the presence of duroquinone. Both $Fe(CO)_5$ and $[Co(CO)_4]^-$ are observed as reaction products as well as a considerable amount of insoluble material. Thus formation of the mixed-metal cluster may be radical in nature.

An attempt was made to observe a $^{13}C\{^1H\}$ NMR CIDNP spectrum of reaction 3 but was unsuccessful owing to formation of insoluble [PPN][$Co(CO)_4$] which degraded the quality of the NMR spectra. This experiment did reveal that no significant reaction occurred until the mixture was heated to approximately −40 °C. In order to ascertain whether the radical process was light induced,[32] a reaction was performed at room temperature in the dark on a high vacuum line in an H cell with CH_2Cl_2 as solvent. The IR spectrum of the volatiles showed the presence of $Fe(CO)_5$ in approximately the same quantity (85% of theoretical, see Table II) as when reaction is carried out in the presence of light. Following work-up procedures similar to those described in the Experimental Section, the quantity of $[Co(CO)_4]^-$ recovered was the same as in the presence of light (110% of theoretical) as was the yield of the $[Fe_3Co(CO)_{13}]^-$ cluster (60%).

The facility of the metal substitution reaction with $[Mn(CO)_5(CH_3CN)]^+$ also suggested the possibility of a radical reaction pathway. However, the presence of duroquinone in the reaction mixture had no effect on the reaction. This result does not disprove a radical mechanism.

Since both of the substituted manganese compounds, $[Mn(CO)_5(CH_3CN)]^+$ and $[Mn(CO)_3(CH_3CN)_3]^+$, ultimately yield the same cluster product $[Fe_2Mn(CO)_{12}]^-$, it is possible that both follow similar reaction pathways. The qualitative difference in rates of the two reactions, (7) and (8), are consistent with either an electron-transfer pathway or formation of a Lewis acid–base pair prior to metal substitution. Both pathways would show a decrease in rate as the degree of CO substitution increased. This is caused by an increase in electron density at the metal center which would make reduction of the Mn center more difficult[33] as well as increase its basicity.

The following mechanism (Scheme I) is consistent with our observations for the reaction of anionic iron clusters with $Co_2(CO)_8$. Step 1 involves the one electron reduction of $Co_2(CO)_8$ by the iron cluster anion to form a cobalt carbonyl anion and a $Co(CO)_4$ radical species. There are examples in which the iron cluster anions act as multielectron reducing agents toward other carbonyl containing species.[34,35] Furthermore, the decomposition of a single cluster species can potentially generate a number of cobalt radicals. This might explain the disappearance of all of the $Co_2(CO)_8$ in the presence of the radical trap without the decomposition of all of the iron cluster. Steps 2 through 4 formally correspond to an electron-transfer-catalyzed (ETC) reaction pathway. In step 2 a radical cluster is formed by the addition of $Co(CO)_4\cdot$ to the anion cluster which loses a $Fe(CO)_4$ fragment in step 3 forming the metal-substituted cluster radical. Recent electrochemical studies on capped metal clusters have demon-

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strated that the presence of a heterometal in an analogous nuclearity cluster shifts the reduction potential of the neutral cluster to more negative potentials.[36] This shift in potential appears to apply when either an earlier or later transition metal is placed in one of the cluster vertices. Thus, the cluster radical formed in step 3 $[Fe_{x-1}Co(CO)_y]^{2-}$ should be a good reducing agent making step 4 favorable. In order to explain the influence of duroquinone most of the $Co(CO)_4\cdot$ must be formed in step 1. The $Fe(CO)_5$ may be produced by decomposition of the products of step 1 or 3. Since no $[Fe_3Co(CO)_{13}]^-$ was detected in the product mixture, it is likely that most of the $Fe(CO)_5$ is generated in step 1.

Scheme I

step 1 $[Fe_x(CO)_y)]^{2-} + Co_2(CO)_8 \rightarrow [Fe_x(CO)_y]^{-\cdot} + Co(CO)_4\cdot + [Co(CO)_4]^-$

step 2 $[Fe_x(CO)_y]^{2-} + Co(CO)_4\cdot \rightarrow [Fe_xCo(CO)_{y+4}]^{2-\cdot}$

step 3 $[Fe_xCo(CO)_{y+4}]^{2-\cdot} \rightarrow [Fe_{x-1}Co(CO)_y]^{2-\cdot} + Fe(CO)_4$

step 4 $[Fe_{x-1}Co(CO)_y]^{2-\cdot} + Co_2(CO)_8 \rightarrow [Fe_{x-1}Co(CO)_y]^- + Co(CO)_4\cdot + [Co(CO)_4]^-$

Only a slight modification of the foregoing reaction scheme is necessary to accommodate the formation of cluster building products rather than metal substitution products. Thus the product of step 2 might yield a stable product according to step 5 rather than fragment. For the

step 5 $[Fe_xCo(CO)_{y+4}]^{2-\cdot} + Co_2(CO)_8 \rightarrow [FeCo(CO)_{y+4}]^- + Co(CO)_4\cdot + [Co(CO)_4]^-$

reaction of $[Fe_3(CO)_{11}]^{2-}$ and $Co_2(CO)_8$ to produce a larger cluster, $[Fe_3Co(CO)_{13}]^-$, the significant quantities of $Fe(CO)_5$ produced suggests that some of the product of step 2 does undergo fragmentation (step 3); but the resulting cluster undergoes further decomposition. According to this interpretation metal substitution occurs in reactions 3 and 4 because the cluster building product of step 2 undergoes fragmentation. In the case of reaction 3, a 5-vertex $[Fe_4Co(CO)_n]^{2-\cdot}$ species would result in step 2 and the apparent instability of this species agrees with the observation that iron carbonyl clusters with five vertices are unknown. Similarly, the instability of the presumed intermediate $[Fe_2Co(CO)_{12}]^{2-\cdot}$ agrees with the failure to synthesize $[Fe_2Co(CO)_{11}]^-$.

Conclusion

The metal substitution reactions described in this paper afford useful alternatives to redox condensation reactions for synthesizing anionic mixed-metal cluster compounds. These reactions are generally faster and more selective than related redox condensation reactions making product isolation relatively easy. One of the limiting factors with the metal substitution reactions studied here is the apparent necessity of employing dianionic clusters as starting materials. However, it appears possible that conditions can be found for the use of monoanionic cluster starting materials. Another potential development in this field is the possibility of selectively replacing a specific metal vertex in a preformed mixed-metal cluster.

The chemistry described in this paper indicates that radical processes play a significant role in metal carbonyl cluster chemistry. Furthermore, it is possible that much of the chemistry which has been explored for other cluster compounds may include some radical intermediates. This is consistent with the general notion that cluster compounds have high-lying orbitals which are predominantly metal based and that these clusters can act as "electron reservoirs".[37] This radical chemistry thus parallels the rich redox chemistry of dinuclear metal–metal bonded species.[38]

Acknowledgment. This research was funded by NSF Grant CHE-8204401. C.P.H. was the recipient of an E.I. duPont de Nemours fellowship. We thank Prof. Sheldon Shore for a sample of $[Ru_4(CO)_{13}]^{2-}$.

Registry No. $[PPN][Fe_2(CO)_8]$, 76419-41-5; $[PPN][Fe_3(CO)_{11}]$, 66039-65-4; $[PPN][Fe_4(CO)_{13}]$, 74792-05-5; $Co_2(CO)_8$, 10210-68-1; $[PPN][Fe_3CO(CO)_{13}]$, 72251-85-5; $[PPh_4]_2[Fe_2(CO)_8]$, 95765-14-3; $[PPh_4][FeCo(CO)_8]$, 95765-16-5; $K_2Ru_4(CO)_{13}$, 75215-44-0; $Ru_3Co(CO)_{13}]^-$, 72152-10-4; $[Mn(CO)_5(CH_3CN)][PF_6]$, 37504-44-2; $[PPh_4]_2[Fe_3(CO)_{11}]$, 95765-17-6; $[PPh_4][Fe_2Mn(CO)_{12}]$, 95765-18-7; $[Mn(CO)_3(CH_3CN)_3]^+$, 55029-83-9; $[Fe_3W(CO)_{14}]^{2-}$, 90838-94-1; $[Fe_3Co(CO)_{13}]^+$, 72251-84-4; Co, 7440-48-4; Fe, 7439-89-6; Ru, 7440-18-8; Mn, 7439-96-5; $[Fe_4(CO)_{13}]^{2-}$, 25767-85-5.

Supplementary Material Available: Complete listings of bond angles and distances, positional parameters, anisotropic thermal parameters, and observed and calculated structure factors (70 pages). Ordering information is given on any current masthead.

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