Organometallics 1990, 9, 2368–2374

Syntheses of Dinuclear Carbonylates of the Iron Subgroup: $[M_2(CO)_8]^{2-}$ (M = Ru, Os) and $[FeRu(CO)_8]^{2-}$. Structures of $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$ and $[PPh_4]_2[Fe_2(CO)_8]\cdot 2CH_3CN$

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Received January 4, 1990

The homonuclear dianions $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$ are prepared by a procedure that involves the reductive disproportionation of CO_2 in its reaction with an alkali-metal salt of $[M(CO)_4]^{2-}$ (M = Ru, Os) to form $M(CO)_5$, which then reacts with additional $[M(CO)_4]^{2-}$ in situ to give $[M_2(CO)_8]^{2-}$. The dianion $[FeRu(CO)_8]^{2-}$ is prepared by a procedure with two distinct steps: (1) $[Ru(CO)_4]^{2-}$ reacts with CO_2 in a 1:2 molar ratio to form $Ru(CO)_5$; (2) $[Fe(CO)_4]^{2-}$ is then added to the system, and it reacts with $Ru(CO)_5$ to form $[FeRu(CO)_8]^{2-}$. The dinuclear dianions are isolated as the tetraphenylphosphonium salts. They are air- and moisture-sensitive. From a single-crystal X-ray analysis, the structure of $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$ has been determined. The dianion $[FeRu(CO)_8]^{2-}$ has a structure which closely resembles that of $[Ru_2(CO)_8]^{2-}$; however, there is disorder at the metal atom sites. The structure consists of a trigonal-bipyramidal fragment, $M(CO)_4$ (M = 0.78 Ru, 0.22 Fe), bound at an equatorial site to a four-sided-pyramidal fragment, $M'(CO)_4$ (M′ = 0.78 Fe, 0.22 Ru), bound at a basal site. For the purpose of comparing dianion structures with a common countercation, the structure of $[PPh_4]_2[Fe_2(CO)_8]\cdot 2CH_3CN$ has been determined from a single-crystal X-ray analysis. The structure of $[Fe_2(CO)_8]^{2-}$ is in agreement with that previously obtained by Bau from $[(Ph_3P)_2N]_2[Fe_2(CO)_8]\cdot 2CH_3CN$. It consists of two $Fe(CO)_4$ units, trigonal-bipyramidal fragments joined at apical sites in a staggered configuration. Crystal data for $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$: space group *Cc*, monoclinic, $a = 19.233$ (3) Å, $b = 16.535$ (3) Å, $c = 16.251$ (4) Å, $\beta = 98.81$ (2)°, $V = 5107$ Å^3, mol wt 1100.8, $\rho_{calcd} = 1.416$ g cm^{-3} for $Z = 4$. $\mu = 6.8$ cm^{-1} for Mo Kα. A total of 4646 unique reflections were collected at −50 °C over the range $4 \leq 2\theta \leq 50°$ with 3359 reflections $\geq 2\sigma(I)$ used in the final refinement. $R_F = 0.049$ and $R_{wF} = 0.047$. Crystal data for $[PPh_4][Fe_2(CO)_8]\cdot 2CH_3CN$: space group $P\bar{1}$, triclinic, $a = 9.389$ (3) Å, $b = 12.086$ (6) Å, $c = 12.931$ (11) Å, $\alpha = 71.37$ (4)°, $\beta = 76.75$ (4)°, $\gamma = 69.83°$, $V = 1293.4$ Å^3, mol wt 1096.6, $\rho_{calcd} = 1.351$ g cm^{-3} for $Z = 1$. $\mu = 6.7$ cm^{-1} for Mo Kα. A total of 4534 unique reflections were collected at −50 °C over the range $4 \leq 2\theta \leq 50°$ with 3168 reflections $\geq 3\sigma(I)$ used in the final refinement. $R_F = 0.030$ and $R_{wF} = 0.044$.

Introduction

The dinuclear iron carbonylate $[Fe_2(CO)_8]^{2-}$ has been well characterized.[1-4] It shows a rich and varied chemistry. Many derivatives[1-3,5] have been prepared, some of which have been applied to modeling Fischer–Tropsch catalysis.[5] Preparative reactions for $[Fe_2(CO)_8]^{2-}$ are indicated by reactions 1,[1] 2,[2a,b] and 3.[2c]

$$[Fe(CO)_4]^{2-} + Fe(CO)_5 \rightarrow [Fe_2(CO)_8]^{2-} + CO \quad (1)$$

$$Fe_2(CO)_9 + 4[OH]^- \rightarrow [Fe_2(CO)_8]^{2-} + [CO_3]^{2-} + 2H_2O \quad (2)$$

$$Fe_2(CO)_9 + 3[OH]^- \rightarrow [HFe_2(CO)_8]^- + [CO_3]^{2-} \rightarrow [Fe_2(CO)_8]^{2-} + [HCO_3]^- \quad (3)$$

A common method for obtaining dinuclear carbonylates[6] is the reaction of a basic metal carbonylate with a neutral mononuclear carbonyl complex: eq 1 for example. However, the preparation of $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$ has been more challenging[7] because of the absence, until relatively recently, of a convenient preparative method for the pentacarbonyls $Ru(CO)_5$ and $Os(CO)_5$. Prior to the work of Cooper and co-workers,[8] available methods involved high-temperature and high-pressure[9] or photolytic conditions,[10] which resulted in the low-yield isolation of the neutral metal pentacarbonyls, making their use as starting materials impractical.

In a preliminary communication[11] we reported syntheses and structures of $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$. Our approach to preparing these species is an extension of Cooper and Maher's[8] work, which provides convenient syntheses of $Ru(CO)_5$ and $Os(CO)_5$ from $[M(CO)_4]^{2-}$ (M = Ru, Os) by the reductive disproportionation of CO_2. The structures of the tetraphenylphosphonium salts of $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$ differ significantly in the solid state. While the structure of $[Os_2(CO)_8]^{2-}$ (Figure 1a) is like that observed[4a] for $[Fe_2(CO)_8]^{2-}$, two $Os(CO)_4$ units, trigonal-bipyramidal fragments joined at axial sites in a staggered arrangement (D_{3d} point symmetry), the structure[10] of

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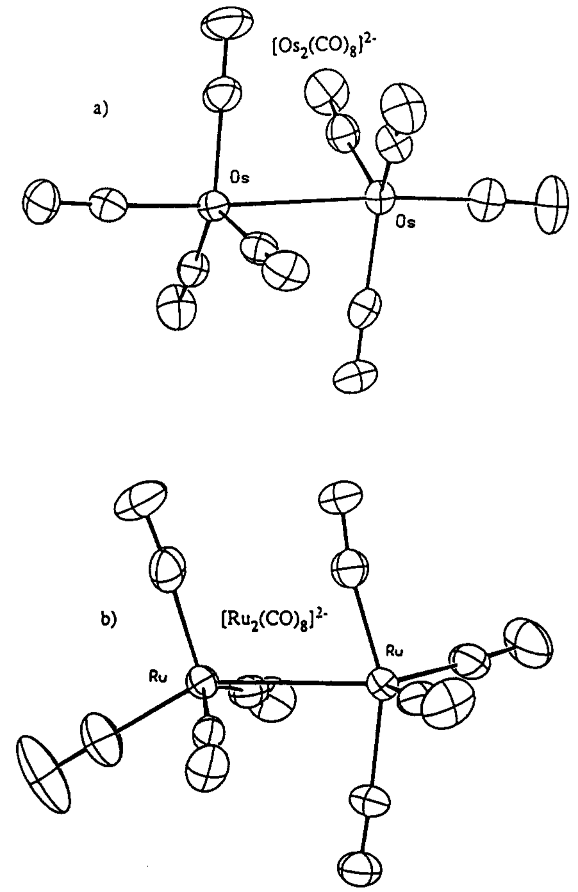

Figure 1. Structures (ORTEP plots, 30% probabilities) of (a) $[Os_2(CO)_8]^{2-}$ and (b) $[Ru_2(CO)_8]^{2-}$.

$[Ru_2(CO)_8]^{2-}$ consists of a trigonal-bipyramidal fragment, $Ru(CO)_4$, bound at an equatorial site to a four-sided-pyramidal fragment, $Ru(CO)_4$, bound at a basal site (C_s point symmetry; Figure 1b). The structure of $[Ru_2(CO)_8]^{2-}$ represents a previously unobserved and apparently unanticipated configuration for homodinuclear carbonylates and carbonyls.

Described here are details of the syntheses and properties of $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$. In view of the different solid-state structure of $[Ru_2(CO)_8]^{2-}$ compared to those of $[Fe_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$, we prepared and obtained the structure of $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$, which is reported here along with its preparation. Additionally, for the purpose of comparing structures of dianions with a common counterion, the structure of $[Fe_2(CO)_8]^{2-}$ as the tetraphenylphosphonium salt was redetermined.

Results and Discussion

I. Syntheses and Properties. A "one-pot" synthetic route for syntheses of $[Ru_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$ has been developed. It is outlined in the sequence of reactions

$$2[\text{alk met}]_2[M(CO)_4] + 2CO_2 \rightarrow [\text{alk met}]_2[M(CO)_4] + M(CO)_5 + [\text{alk met}]_2[CO_3] \tag{4a}$$

$$[\text{alk met}]_2[M(CO)_4] + M(CO)_5 \rightarrow [\text{alk met}]_2[M_2(CO)_8] + CO \tag{4b}$$

alk met = Na, M = Ru; alk met = Na, K, M = Os

The nucleophilicities of the dianions $[M(CO)_4]^{2-}$ are the driving forces for these reactions. In the initial reaction system containing an equimolar mixture of CO_2 and Na^+ or K^+ salt of $[M(CO)_4]^{2-}$ (eq 4a), $^1/_2$ equiv of $[M(CO)_4]^{2-}$ is converted to $M(CO)_5$ at −78 °C. $M(CO)_5$ and the remaining $[M(CO)_4]^{2-}$ subsequently react with each other (eq 4b) when the reaction mixture is warmed to room temperature to form $[M_2(CO)_8]^{2-}$ (M = Ru, Os).

Synthesis of the dianion $[FeRu(CO)_8]^{2-}$ employs a procedure which is based in part upon that outlined above. However, $[Fe(CO)_4]^{2-}$ must be added to the reaction mixture after $Ru(CO)_5$ is generated:

$$[Ru(CO)_4]^{2-} + 2CO_2 \rightarrow Ru(CO)_5 + [CO_3]^{2-} \tag{5a}$$

$$[Fe(CO)_4]^{2-} + Ru(CO)_5 \rightarrow [FeRu(CO)_8]^{2-} + CO \tag{5b}$$

Since $[Fe(CO)_4]^{2-}$ is a stronger nucleophile[12] than $[Ru(CO)_4]^{2-}$, and since $[Ru(CO)_4]^{2-}$ is a stronger reducing agent[12] than $[Fe(CO)_4]^{2-}$, the yield of $[FeRu(CO)_8]^{2-}$ is optimized by combining $Ru(CO)_5$ with $[Fe(CO)_4]^{2-}$. This choice favors nucleophilic displacement of CO from the metal pentacarbonyl over reduction of the pentacarbonyl to the tetracarbonylate dianion. If the reagents are reversed, then reduction of $Fe(CO)_5$ to $[Fe(CO)_4]^{2-}$ occurs as in reaction 6a. In the initial stages of this reaction

$$[Ru(CO)_4]^{2-} + Fe(CO)_5 \rightarrow [Fe(CO)_4]^{2-} + Ru(CO)_5 \tag{6a}$$

$Ru(CO)_5$ can be distilled from the reaction mixture. As $[Fe(CO)_4]^{2-}$ is formed, it can combine with unreacted $Fe(CO)_5$ to form $[Fe_2(CO)_8]^{2-}$ as well as react with $Ru(CO)_5$ to form $[FeRu(CO)_8]^{2-}$, which leads to mixtures of dinuclear species (reactions 6b–d).

$$Fe(CO)_5 + [Fe(CO)_4]^{2-} \rightarrow [Fe_2(CO)_8]^{2-} + CO \tag{6b}$$

$$Ru(CO)_5 + [Ru(CO)_4]^{2-} \rightarrow [Ru_2(CO)_8]^{2-} + CO \tag{6c}$$

$$Ru(CO)_5 + [Fe(CO)_4]^{2-} \rightarrow [FeRu(CO)_8]^{2-} + CO \tag{6d}$$

Tetranuclear side products such as $[Ru_4(CO)_{13}]^{2-}$ and $[FeRu_3(CO)_{13}]^{2-}$ can be minimized but not eliminated from reactions 4 and 5. Yields of the dinuclear dianion salts are dependent upon the alkali-metal counterions employed. Several factors appear to be involved, such as the relative solubilities of the salts and the relative nucleophilicities and reducing abilities of the anions present. Thus, relatively pure $Na_2[Ru_2(CO)_8]$, containing some $Na_2[Ru_4(CO)_{13}]$, was prepared. On the other hand, attempts to prepare $K_2[Ru_2(CO)_8]$ gave almost exclusively $K_2[Ru_4(CO)_{13}]$, which was probably formed from the sequence of reactions

$$[Ru_2(CO)_8]^{2-} + Ru(CO)_5 \rightarrow [Ru_3(CO)_{11}]^{2-} + 2CO \tag{7a}$$

$$[Ru_3(CO)_{11}]^{2-} + Ru(CO)_5 \rightarrow [Ru_4(CO)_{13}]^{2-} + 3CO \tag{7b}$$

Although $K_2[Os_2(CO)_8]$ could be prepared in an impure state, its synthesis required longer reaction times and higher reaction temperatures than $Na_2[Os_2(CO)_8]$ because of the low solubility of $K_2[Os(CO)_4]$ in THF.

Alkali-metal salts of the homodinuclear and heterodinuclear dianions are soluble in CH_3CN. They are also soluble in THF. Sodium and potassium salts have negligible solubility in diethyl ether or hydrocarbons. Rapid decomposition with the evolution of CO occurs in halogenated hydrocarbons.

Tetraphenylphosphonium salts of the dinuclear dianions were obtained through the following metathesis reactions in THF:

$$[\text{alk met}]_2[M_2(CO)_8] + 2[PPh_4]Br \rightarrow [PPh_4]_2[M_2(CO)_8] + 2[\text{alk met}]Br \tag{8}$$

alk met = Na, M = Ru; alk met = Na, K, M = Os

$$Na_2[FeRu(CO)_8] + 2[PPh_4]Br \rightarrow [PPh_4]_2[FeRu(CO)_8] + 2NaBr \tag{9}$$

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Table I. Crystal Data for $[(C_6H_5)_4P]_2[FeRu(CO)_8]\bullet CH_3CN$ and $[(C_6H_5)_4P]_2[Fe_2(CO)_8]\bullet 2CH_3CN$

chem formula	$C_{58}H_{43}FeRuNO_8P_2$	$C_{60}H_{46}Fe_2N_2O_8P_2$
mol wt	1100.8	1096.6
color of cryst	red	red
space group	*Cc*	$P\bar{1}$
molecules/unit cell	4	1
temp, °C	−50	−50
a, Å	19.233 (3)	9.389 (3)
b, Å	16.535 (3)	12.086 (6)
c, Å	16.251 (4)	12.931 (11)
α, deg		71.37 (4)
β, deg	98.81 (2)	76.75 (4)
γ, deg		69.83 (3)
V, Å^3	5107.1	1293.4
cryst dimens, mm	0.35 × 0.20 × 0.30	0.30 × 0.15 × 0.25
ρ_{calcd}, g cm^{-3}	1.416	1.351
radiation	Mo Kα (0.710730 Å)	Mo Kα (0.710730 Å)
abs coeff, cm^{-1}	6.8	6.7
transmission (max, min), %	99.9, 88.1	99.9, 98.5
scan mode	$\omega-2\theta$	$\omega-2\theta$
data collecn limits (2θ), deg	4–50	4–50
no. of unique rflns	4646	4534
no. of rflns used in struct	3359 ($\geq 2\sigma(I)$)	3168 ($\geq 3\sigma(I)$)
no. of variables refined	625	319
$R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.049	0.030
$R_{wF} = (\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2)^{1/2}$	0.047	0.044
$w = [\sigma(\lvert F_o\rvert)^2 + (k\lvert F_o\rvert)^2)]^{-1}$	$k = 0.04$	$k = 0.04$
largest shift/esd, final cycle	0.03	0.01
largest peak, e Å^{-3}	0.83	0.29
GOF	1.59	1.34

Table II. Positional Parameters and Their Estimated Standard Deviations for $[FeRu(CO)_8]^{2-}$ of $[PPh_4]_2[FeRu(CO)_8]\bullet CH_3CN$[a]

atom	*x*	*y*	*z*	*B*, Å^2
M[b]	0.19903 (6)	0.22384 (5)	0.93584 (7)	2.93 (1)
M′[c]	0.32571 (6)	0.15917 (7)	1.02194 (8)	2.85 (2)
C11	0.6823 (5)	0.2433 (5)	0.5419 (6)	3.1 (2)
C12	1.1826 (6)	0.3222 (7)	−0.1143 (6)	4.3 (3)
C13	0.6223 (5)	0.3440 (7)	0.4100 (6)	4.1 (2)
C14	0.7508 (5)	0.3128 (6)	−0.6427 (7)	3.7 (2)
O11	0.1754 (4)	0.2759 (4)	1.1082 (4)	4.5 (2)
O12	0.1671 (5)	0.6197 (5)	0.3470 (5)	7.6 (3)
O13	0.5727 (4)	0.3811 (5)	0.3863 (5)	6.1 (2)
O14	0.7782 (4)	0.3322 (5)	0.3001 (4)	5.6 (2)
C21	0.8784 (6)	0.3607 (7)	0.6203 (8)	4.8 (3)
C22	0.7567 (5)	0.4089 (6)	0.5425 (6)	3.1 (2)
C23	0.8740 (5)	0.3860 (6)	0.4485 (7)	4.2 (3)
C24	1.3412 (5)	0.2669 (6)	0.0284 (7)	3.9 (2)
O21	0.4120 (5)	0.1254 (6)	1.1829 (5)	7.5 (2)
O22	0.7189 (3)	0.4577 (4)	−0.4387 (5)	4.2 (2)
O23	0.9081 (4)	0.4158 (5)	0.4053 (6)	6.6 (2)
O24	0.3560 (4)	0.3340 (4)	0.0362 (5)	4.5 (2)

[a] Positional parameters for $[P(C_6H_5)_4]^+$ and CH_3CN are given in the supplementary material. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Occupancies: 0.78 Ru, 0.22 Fe. [c] Occupancies: 0.78 Fe, 0.22 Ru.

Table III. Positional Parameters and Their Estimated Standard Deviations for $[Fe_2(CO)_8]^{2-}$ of $[PPh_4]_2[Fe_2(CO)_8]\bullet 2CH_3CN$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Fe	0.05173 (4)	−0.02362 (3)	−0.10322 (3)	3.403 (8)
C11	−0.1351 (3)	0.0671 (2)	−0.1340 (2)	4.42 (7)
C12	0.1321 (3)	−0.0490 (2)	−0.2317 (2)	4.75 (7)
C13	0.1872 (3)	0.0484 (2)	−0.1031 (2)	4.03 (6)
C14	0.0771 (3)	−0.1793 (2)	−0.0301 (2)	4.19 (7)
O11	−0.2568 (2)	0.1266 (2)	−0.1564 (2)	6.40 (6)
O12	0.1913 (3)	−0.0662 (2)	−0.3165 (2)	7.89 (8)
O13	0.2797 (2)	0.0939 (2)	−0.1093 (2)	6.11 (5)
O14	0.0989 (3)	−0.2829 (2)	0.0139 (2)	6.48 (7)

[a] See footnote *a* of Table II.

Table IV. Bond Distances (Å) and Their Estimated Standard Deviations for $[FeRu(CO)_8]^{2-}$ and $[Fe_2(CO)_8]^{2-}$

	$[FeRu(CO)_8]^{2-}$		
M–M′[a]	2.827 (1)	C11–O11	1.151 (10)
M–C11	1.881 (9)	C12–O12	1.162 (11)
M–C12	1.826 (10)	C13–O13	1.151 (10)
M–C13	1.849 (11)	C14–O14	1.180 (10)
M–C14	1.838 (10)	C21–O21	1.142 (11)
M′–C21	1.788 (11)	C22–O22	1.157 (10)
M′–C22	1.810 (10)	C23–O23	1.143 (11)
M′–C23	1.784 (12)	C24–O24	1.147 (10)
M′–C24	1.807 (10)		
	$[Fe_2(CO)_8]^{2-}$		
Fe–Fe	2.792 (1)	C1–O1	1.165 (4)
Fe–C1	1.776 (2)	C2–O2	1.158 (4)
Fe–C2	1.736 (3)	C3–O3	1.155 (4)
Fe–C3	1.772 (3)	C4–O4	1.165 (4)
Fe–C4	1.775 (2)		

[a] Occupancies: M, 0.78 Ru, 0.22 Fe; M′, 0.78 Fe, 0.22 Ru.

Table V. Bond Angles (deg) and Their Estimated Standard Deviations for $[FeRu(CO)_8]^{2-}$ and $[Fe_2(CO)_8]^{2-}$

	$[FeRu(CO)_8]^21^-$		
M′–M–C11[a]	84.9 (3)	C11–M–C14	156.7 (4)
M′–M–C12	129.4 (3)	C12–M–C13	111.2 (4)
M′–M–C13	118.7 (3)	C12–M–C1	93.4 (4)
M′–M–C14	72.6 (3)	C13–M–C14	98.1 (4)
M–M′–C21	127.1 (4)	C21–M′–C22	93.0 (4)
M–M′–C22	74.1 (3)	C21–M′–C23	103.8 (5)
M–M′–C23	109.0 (3)	C21–M′–C24	93.7 (4)
M–M′–C24	72.2 (3)	C22–M′–C23	109.5 (4)
C11–M–C12	96.3 (4)	C22–M′–C24	136.2 (4)
C11–M–C13	98.1 (4)	C23–M′–C24	110.8 (4)
	$[Fe_2(CO)_8]^{2-}$		
Fe–Fe–C1	85.0 (1)	C1–Fe–C3	119.6 (1)
Fe–Fe–C2	174.3 (1)	C1–Fe–C4	117.6 (1)
Fe–Fe–C3	81.4 (8)	C2–Fe–C3	93.0 (1)
Fe–Fe–C4	85.4 (9)	C2–Fe–C4	96.5 (1)
C1–Fe–C2	98.9 (1)	C3–Fe–C4	119.5 (1)

[a] Occupancies: M, 0.78 Ru, 0.22 Fe; M′, 0.78 Fe, 0.22 Fe.

These salts are insoluble in THF, while higher nuclearity impurities are soluble, thereby allowing removal of these impurities by extraction or filtration procedures. The tetraphenylphosphonium salts are then extracted from the precipitates with use of CH_3CN as a solvent. NaBr, insoluble in CH_3CN, remains behind. In practice, metathesis reactions were carried out with molar ratios $[PPh_4]Br:[alkmet]_2[M_2(CO)_8] = (1.4–1.7):1$ rather than the stoichiometric ratio of 2:1 in order to minimize the possibility of contaminating the final product with unreacted $[PPh_4]Br$.

The tetraphenylphosphonium salts of the dianions are stable solids at room temperature in the absence of air or water. They decompose slowly in CH_3CN at room temperature. The mixed-metal dianion is less stable in CH_3CN than the homonuclear dianions. Halogenated hydrocarbons cause rapid decomposition with the evolution of CO.

II. Structures. The structures of $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$ and $[PPh_4]_2[Fe_2(CO)_8]\cdot 2CH_3CN$ have been determined from single-crystal X-ray studies. Crystal data and positional parameters are given in Tables I–III. Bond distances and bond angles are given in Tables IV and V.

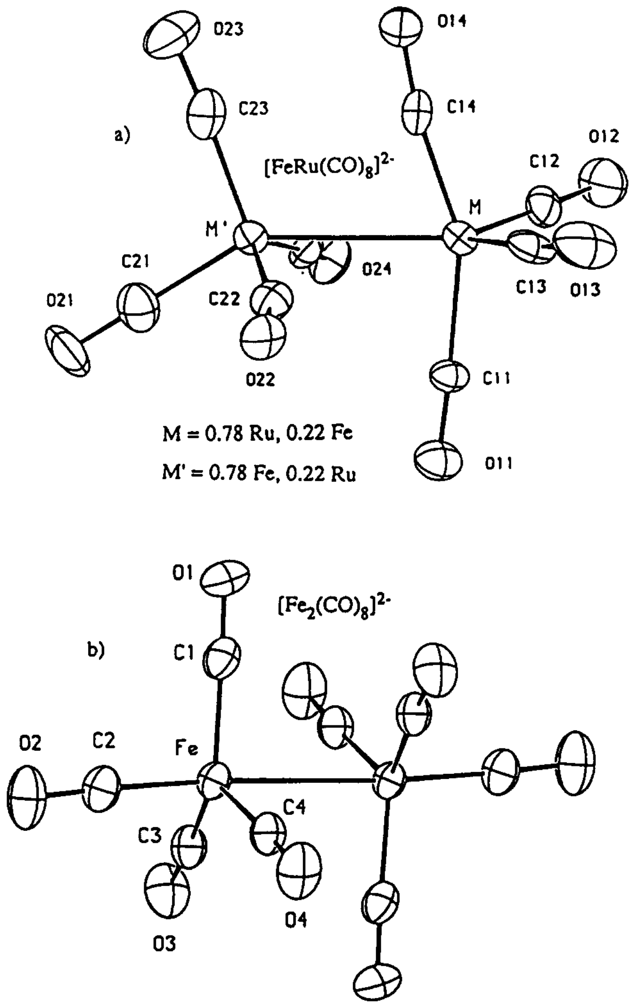


Figure 2. Structures (ORTEP plots, 30% probabilities) of (a) $[FeRu(CO)_8]^{2-}$ and (b) $[Fe_2(CO)_8]^{2-}$.

ORTEP plots of $[FeRu(CO)_8]^{2-}$ and $[Fe_2(CO)_8]^{2-}$ are presented in Figure 2.

In the case of $[FeRu(CO)_8]^{2-}$, there is some disorder of the metal atoms. The atom labeled M (Figure 2a) has 0.78 ruthenium and 0.22 iron occupancies, whereas the atom labeled M′ has the ruthenium and iron occupancies reversed. The structure of this dianion closely resembles[10] that of $[Ru_2(CO)_8]^{2-}$ (Figure 1b) with the important exception that the Fe–Ru distance, 2.827 (1) Å, is 0.109 Å shorter than the Ru–Ru distance, 2.936 (1) Å. It is 0.037 Å longer than the average of the Fe–Fe and Ru–Ru distances, 2.864 Å, in $[Fe_2(CO)_8]^{2-}$ and $[Ru_2(CO)_8]^{2-}$. The M–C distances (1.826 (10)–1.881 (9) Å) are longer than the M–C distances (1.784 (12)–1.810 (10) Å).

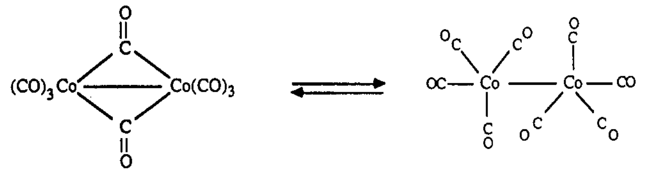
The structure of $[FeRu(CO)_8]^{2-}$ has pseudo-C_s symmetry. It consists of a trigonal-bipyramidal fragment, $M(CO)_4$, bound at an equatorial site to a four-sided-pyramidal fragment, $M'(CO)_4$, bound at a basal site. In the structure of $[Ru_2(CO)_8]^{2-}$ (Figure 1b) the Ru atom adopts both trigonal-bipyramidal and four-sided-pyramidal coordination geometry. It is of interest that the site which is principally the Fe atom in $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$ displays four-sided-pyramidal coordination geometry rather than the trigonal-pyramidal coordination observed for Fe in $[(Ph_3P)_2N][Fe_2(CO)_8]\cdot 2CH_3CN$.[4a]

Because of this difference in structures and the fact that the reported[4a] structure of $[Fe_2(CO)_8]^{2-}$ was determined with a different counterion than the $[PPh_4]^+$ counterion employed with $[FeRu(CO)_8]^{2-}$ and $[Ru_2(CO)_8]^{2-}$, the structure of $[Fe_2(CO)_8]^{2-}$ was redetermined as the $[PPh_4]^+$ salt. Shown in Figure 2b is the structure of $[Fe_2(CO)_8]^{2-}$. Structural parameters of $[Fe_2(CO)_8]^{2-}$ agree well with those previously reported.[4a]

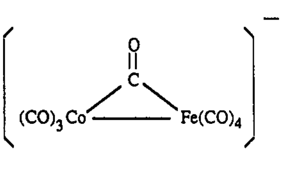
The two least-squares planes associated with the $[FeRu(CO)_8]^{2-}$ structure (Figure 2a) are of interest in that they show the spatial relationship between the $M(CO)_4$ and $M'(CO)_4$ units. The vertical plane is the pseudo mirror plane of the molecule. It passes through atoms C11 and C14 and atom M of the trigonal-bipyramidal fragment. This plane also passes through atoms C21, C23, and M′ of the four-sided-pyramidal fragment. The largest deviation from this vertical plane is by M′, 0.068 Å. The horizontal least-squares plane passes through the atoms C13, C12, M′, and M. The largest deviation from this horizontal plane is by M′, 0.075 Å. The dihedral angle between these planes is 90.7 (7)°.

Bond angles around the apical carbon (C23) of the four-sided-pyramidal fragment are C23–M′–C24 = 110.7 (4)°, C23–M′–C21 = 103.8 (4)°, C23–M′–C22 = 109.5 (5)°, and C23–M′–M = 109.0 (3)°. In the trigonal-bipyramidal fragment, the angle between the equatorial sites on M is C13–Ru–C12 = 111.2 (4)°. Axial carbonyls on M are tipped over the M′–M bond with acute angles of M′–M–C11 = 84.9 (3)° and M′–M–C14 = 72.6 (3)°. Respective M–C–O and M′–C–O angles involving these carbonyls indicate essentially linear arrangements. Two of the carbonyls on M′ are also tipped over the M′–M bond with the angles M–M′–C24 = 77.2 (3)° and M–M′–C22 = 74.1 (3)°. Similar tipping of terminal carbonyls without a significant decrease in the metal–C–O angles has been observed in saturated[4a] and unsaturated dinuclear carbonyls.[13,14] There are no obvious close nonbonded contacts that could account for the difference in geometries of the halves of the dianions. The closest intermolecular distance observed is 3.1 Å between C2 of CH_3CN and O21.

III. Spectra. Although solid-state structures of $[M_2(CO)_8]^{2-}$ (M = Fe, Ru, Os) contain only terminally bound carbonyl groups, the isoelectronic analogues $Co_2(CO)_8$[15] and $[FeCo(CO)_8]^-$[4a] in the solid state have molecular structures (I, II) that contain carbonyl bridges. IR spectra of rhodium[16a] and iridium[16b] carbonyls in argon matrices indicate that $Rh_2(CO)_8$ has the $Co_2(CO)_8$ structure (Ia) and that



Ia Ib



II

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Table VI. Infrared Spectra (cm^{-1}) of Tetraphenylphosphonium Salts of $[M_2(CO)_8]^{2-}$ (M = Os, Ru, Fe) and $[FeRu(CO)_8]^{2-}$ in the CO Stretching Region (in CH_3CN)[a]

$[Os_2(CO)_8]^{2-}$	$[Ru_2(CO)_8]^{2-}$	$[Fe_2(CO)_8]^{2-}$	$[FeRu(CO)_8]^{2-}$
1988 vw	1977 vw	1992 vw	
		1953 w, sh	
1940 m	1930 m	1914 m	1916 m
1866 s, br	1866 s, br	1865 s, br	1862 s, br
			1835 m, sh

[a] Abbreviations: s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder.

$Ir_2(CO)_8$ has only terminally bound carbonyls. In *n*-hexane solution the doubly bridged form (Ia) of $Co_2(CO)_8$ exists in facile equilibrium[15] with an isomer that has been assigned a structure of D_{3d} point symmetry (Ib), like that of $[Fe_2(CO)_8]^{2-}$ and $[Os_2(CO)_8]^{2-}$. This so-called "high-temperature form" of $Co_2(CO)_8$ exists in relatively high concentration at room temperature but diminishes in concentration with decreasing temperature.[15b]

Infrared spectra (Figure 3 and Table VI) of the tetraphenylphosphonium salts of $[Os_2(CO)_8]^{2-}$, $[Ru_2(CO)_8]^{2-}$, $[FeRu(CO)_8]^{2-}$, and $[Fe_2(CO)_8]^{2-}$ in the CO stretching region in CH_3CN each contain two principal bands, a broad, strong band at about 1865 cm^{-1} and a sharp, medium-intensity band that varies from 1940 cm^{-1} for $[Os_2(CO)_8]^{2-}$ to 1914 cm^{-1} for $[Fe_2(CO)_8]^{2-}$. These main features are similar in appearance in all of the spectra. IR spectra in Nujol are also similar in appearance, except that the bands in general are broader and the strong band at about 1865 cm^{-1} is slightly split. We see no distinction between spectra that can be related to the different structural types observed in the solid state. In solution there might be an equilibrium between these different structural types.

Experimental Section

All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of dry, pure N_2. Tetrahydrofuran (THF) and Et_2O were dried by distillation from sodium–benzophenone ketyl into storage bulbs equipped with Teflon Kontes stopcocks and containing sodium–benzophenone ketyl. CH_3CN and CH_2Cl_2 were dried over P_4O_{10} with continuous stirring for 2–3 days followed by distillation into storage bulbs. Hexane was stirred over concentrated H_2SO_4 for 2–3 days followed by extraction with distilled H_2O and then dried with use of the same treatment as that for CH_3CN. NH_3 was dried by stirring it over Na and stored in a Pyrex tube.

Benzophenone (J. T. Baker) and $Ru_3(CO)_{12}$ (Strem Chemicals) were used as received. $Na_2[Ru(CO)_4]$[18a] and $Na_2[Os(CO)_4]$[18b] were prepared by procedures reported in the literature. CO_2 (Liquid Carbonic) was passed sucessively through −78 and −110 °C traps and stored in a −196 °C trap. HCl and HBr (Matheson Gas Products) were passed through a −78 °C trap and stored in a Pyrex tube equipped with a Kontes Teflon stopcock at −78 °C. In a N_2-filled glovebox Na and K were cut, washed with hexane, and stored. $[PPh_4]Br$ (Alfa Inorganics) was heated on a vacuum line to maintain dryness and stored in a drybox.

Infrared spectra were obtained with a Mattson Polaris FTIR spectrometer. Solution spectra were obtained in Perkin-Elmer liquid cells with 0.1- or 0.5-mm Teflon spacers and KBr windows. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, NY, Oneida Research Services, Whitesboro, NY, and Analytische Laboratorien, Elbach, West Germany.

Preparation of $K_2[Os(CO)_4]$. A 356.8-mg (0.39-mmol) quantity of $Os_3(CO)_{12}$ and 92.5 mg (2.37 mmol) of K were weighed in the glovebox and placed in a reaction vessel equipped with a stirbar and a vacuum adapter. Anhydrous NH_3, ca. 25 mL, was condensed into the reaction vessel at −78 °C. The reaction mixture was warmed to −36 °C and stirred until the characteristic blue solution of K–NH_3 changed to a yellow solution containing a white precipitate. This usually required about 1 h of reaction time. The reaction can be carried out at −78 °C as well, but it is 3–4 times slower at that temperature. NH_3 was recovered from the reaction vessel, and the tan-white product was dried in vacuo for approximately 2 h. Unreacted $Os_3(CO)_{12}$ was extracted by washing the product in THF and filtering it on the vacuum line with use of a vacuum-line extractor[22] (yield 80%, based on $Os_3(CO)_{12}$). Anal. Calcd for $C_4K_2O_4Os$: C, 12.63; K, 20.56; Os, 49.99. Found: C, 12.85; K, 18.74; Os, 49.43. IR (ν_{CO}, Nujol): 1720 br cm^{-1}.

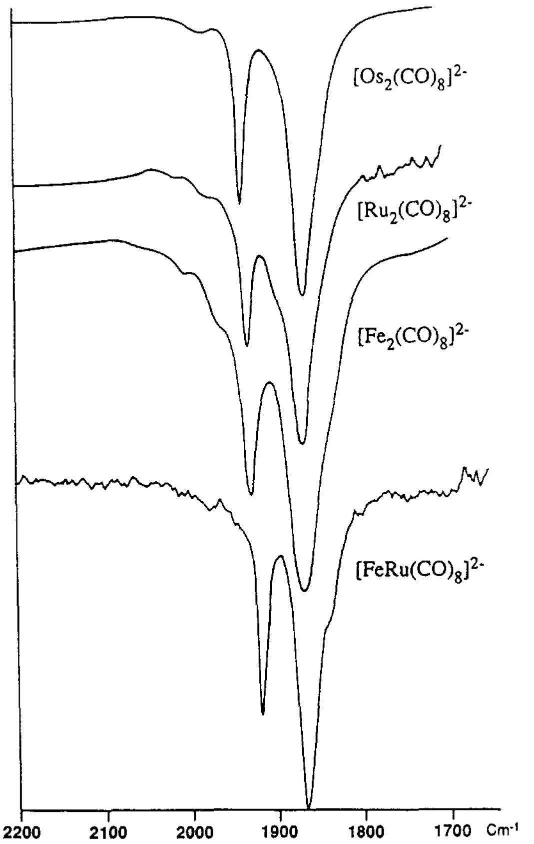

Figure 3. Infrared spectra in CH_3CN.

Preparation of $K_2[Ru(CO)_4]$. The synthesis of $K_2[Ru(CO)_4]$ is similar to that of $K_2[Os(CO)_4]$. In a typical experiment 188.7 mg (0.295 mmol) of $Ru_3(CO)_{12}$ and 70.1 mg (1.79 mmol) of K were used. $K_2[Ru(CO)_4]$ is a cream white solid obtained in 86% yield (221 mg). It is extremely sensitive to air and moisture but can be stored in the drybox for an extended period of time. Anal. Calcd for $C_4K_2O_4Ru$: C, 16.49; K, 26.84; Ru, 34.69. Found: C, 16.68; K, 26.89; Ru, 34.46. IR (ν_{CO}, Nujol): 1720 br cm^{-1}.

Preparation of $[PPh_4]_2[Ru_2(CO)_8]$. In the glovebox, 264.3 mg (1.02 mmol) of freshly prepared $Na_2Ru(CO)_4$ was placed in a reaction vessel along with a Teflon-coated stirbar. The reaction vessel was attached to a vacuum adapter, removed from the glovebox, and evacuated on a vacuum line. THF (15 mL) was condensed into the flask at −78 °C along with 1.02 mmol (1 equiv) of prepurified CO_2 at −196 °C. The reaction vessel was warmed to −78 °C and covered with aluminum foil ($Ru(CO)_5$ is light sensitive), and the mixture was stirred for 12 h. Unreacted CO_2 was pumped away at −78 °C for 1 h in vacuo. After the stopcock was closed, the reaction mixture was warmed to room temperature and stirred for 5 h. The gas evolved during the reaction was collected and analyzed as CO (0.6 mmol, 118% theoretical). The reaction mixture was filtered into a collection bulb through a vacuum extractor to remove Na_2CO_3 formed during the reaction. The bulb was then connected to a fresh extractor (in the drybox), and the THF solution was reduced to ~2 mL. Addition of excess hexane to the solution caused precipitation of a yellow-orange solid. The yellow-orange powder was isolated by filtration followed by washing with several portions of fresh hexane and dried for

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1 h in vacuo. The yield was 230 mg (0.487 mmol, 95.5% of theory) of crude $Na_2[Ru_2(CO)_8]$.[19]

In the glovebox, 99.2 mg (0.21 mmol) of crude $Na_2Ru_2(CO)_8$ and 151 mg (0.36 mmol) of $[PPh_4]Br$ were placed in a reaction flask equipped with a Teflon-coated stirbar. The vessel was then attached to a vacuum extractor and evacuated. Approximately 10 mL of THF was condensed into the flask at −78 °C. The mixture was warmed to room temperature and stirred for 4 h to give a red solution and a red precipitate. Usually a negligible amount of CO was produced during this reaction. The solution was then filtered, and the precipitate was washed several times with fresh THF until the washings were colorless. The vacuum extractor was then placed in the glovebox, and a clean collection bulb was attached to it. After the apparatus was evacuated, CH_3CN was condensed into the flask and the precipitate was washed several times until only a white precipitate of NaBr remained on the frit. The collection bulb was connected to a clean extractor, and the volume of CH_3CN was reduced to 2 mL. Addition of 10 mL of Et_2O induced precipitation of red $[PPh_4]_2[Ru_2(CO)_8]$, which was washed several times with fresh diethyl ether. The compound was dried in vacuo for 1 h. The yield was 149 mg (0.135 mmol), which represents a 75% yield of $[PPh_4]_2[Ru_2(CO)_8]$ based on $[PPh_4]Br$. Anal. Calcd for $C_{56}H_{40}P_2O_8Ru_2$: C, 60.87; H, 3.65; P, 5.61; Ru, 18.29. Found: C, 60.09; H, 4.15; P, 5.84; Ru, 18.71. IR (ν_{CO}, CH_3CN): 1977 vw, 1930 m, 1866 s, br cm^{-1}.

Preparation of $[PPh_4]_2[Os_2(CO)_8]$. This compound was prepared and isolated with use of the same procedure, but under slightly different conditions, as that described for the preparation of $[PPh_4]_2[Ru_2(CO)_8]$. Both $Na_2[Os_2(CO)_8]$ and $K_2[Os_2(CO)_8]$ were employed in the metathesis reactions. A typical preparation of $Na_2[Os_2(CO)_8]$ employed 107 mg (0.307 mmol) of $Na_2Os(CO)_4$ and 0.308 mmol of CO_2. Reaction conditions employed involved stirring the reaction mixture, protected from light, for 12 h at −78 °C. After unreacted CO_2 was pumped away at −78 °C, the mixture was stirred at room temperature for 5 h. During this time 0.15 mmol of CO evolved, representing 98% of the theoretical yield. The bulb was connected to an extractor in the drybox, and the apparatus was evacuated. The THF solution was filtered, and the solvent was removed. The collection flask was connected to a fresh extractor in the drybox. The yellow product was dissolved in a minimum amount of THF. Addition of 10 mL of dry hexane caused crude $Na_2[Os_2(CO)_8]$ to precipitate as a fine yellow powder, which was then collected by filtration and dried on the vacuum line for 1 h; an 85-mg (0.13 mmol, 85% of theory) yield of product was obtained. Crude $K_2[Os_2(CO)_8]$ was obtained from the starting materials $K_2[Os(CO)_4]$ (414.6 mg, 1.09 mmol) and prepurified CO_2 (1.08 mmol). The reaction mixture was stirred in the dark for 15 h at −78 °C. Then the unreacted CO_2 was pumped away at −78 °C for 1 h and the reaction mixture was stirred in an oil bath preheated to 60 °C for 48 h. A 0.055-mmol amount of CO (102% of theory) was produced during this period. Crude $K_2[Os_2(CO)_8]$, in 342-mg (0.501 mmol, 91.9% of theory) yield, was isolated in the same manner as that for $Na_2[Ru_2(CO)_8]$.

The salt $[PPh_4]_2[Os_2(CO)_8]$ was prepared and isolated by following the procedure described above for the isolation of $[PPh_4]_2[Ru_2(CO)_8]$. When the metathesis reaction involving 163 mg (0.250 mmol) of $Na_2[Os_2(CO)_8]$ and 168 mg (0.400 mmol) of $[PPh_4]Br$ was performed in THF at room temperature, a yield of 189 mg (0.149 mmol) was obtained (74% yield based on $[PPh_4]Br$). The metathesis reaction involving 303 mg (0.439 mmol) of $K_2[Os_2(CO)_8]$ and 301 mg (0.718 mmol) of $[PPh_4]Br$ gave a yield of 253 mg (0.197 mmol) of $[PPh_4]_2[Os_2(CO)_8]$ (71% based on $[PPh_4]Br$). Anal. Calcd for $C_{56}H_{40}P_2O_8Os_2$: C, 52.41; H, 3.14; P, 4.83; Os, 29.64. Found: C, 52.2; H, 3.37; P, 4.77; Os, 29.66. IR (ν_{CO}, CH_3CN): 1988 vw, 1940 m, 1866 s, br cm^{-1}.

Preparation of $[PPh_4]_2[FeRu(CO)_8]$. A 206-mg (0.80-mmol) amount of $Na_2[Ru(CO)_4]$ was placed in a 50-mL reaction bulb equipped with a stirbar and a vacuum adapter. The apparatus was evacuated on the vacuum line, and dry THF (10 mL) was distilled into the reaction vessel. A 1.60-mmol quantity of CO_2, measured volumetrically, was condensed into the reaction vessel at −196 °C. The reaction apparatus was covered in foil and the mixture stirred at −78 °C for 12 h. Unreacted CO_2 was pumped away at −78 °C for 1 h. The bulb was connected to one end of a two-necked vacuum-line adapter. The other end was connected to a reaction bulb containing 120 mg (0.56 mmol) of $Na_2[Fe(CO)_4]$. The whole system was wrapped in foil to ensure the absence of light. THF and $Ru(CO)_5$ were condensed into the bulb containing $Na_2[Fe(CO)_4]$ by cooling the bulb to −196 °C while the bulb containing $Ru(CO)_5$ was warmed to room temperature. After the condensation was complete, the reaction mixture was stirred for 24 h in the dark at ambient temperature. During this time 0.98 mmol (123% of theory) of CO was produced. The solvent was removed, and the flask was connected to a vacuum-line extractor in the drybox. After the apparatus was evacuated, the solid was dissolved in a minimum amount of THF and the salt was precipitated by the addition of 10 mL of hexane. This yellow-brown solid was collected by filtration, washed with fresh hexane, and dried in vacuo for 1 h. A 200-mg (0.468-mmol) yield of crude $Na_2[FeRu(CO)_8]$ (84% based on $Na_2(CO)_4$) was obtained.

A metathesis reaction with 150 mg (0.351 mmol) of $Na_2[FeRu(CO)_8]$ and 206 mg (0.492 mmol) of $[PPh_4]Br$ was performed in THF at ambient temperature by employing the same procedure described above for $[PPh_4][Ru_2(CO)_8]$. A 186-mg (0.175-mmol) yield of $[PPh_4]_2[FeRu(CO)_8]$ was obtained (71% based on $[PPh_4]Br$). Anal. Calcd for $C_{56}H_{40}P_2O_8FeRu$: C, 63.47; H, 3.80; P, 5.85; Ru, 9.54; Fe, 5.27. Found: C, 63.80; H, 4.05; P, 5.74; Ru, 9.24; Fe, 5.09. IR (ν_{CO}, CH_3CN): 1916 m, 1865, s, br, 1835 m, sh cm^{-1}.

Preparation of $[PPh_4]_2[Fe_2(CO)_8]$. In the drybox 1.36 g (7.47 mmol) of benzophenone and 0.172 g (7.49 mmol) of sodium were weighed and added to a 100-mL flask that contained a glass-coated magnetic stirbar. The flask was connected to a vacuum-line extractor and removed from the drybox. After evacuation of the apparatus 30 mL of dry THF was condensed into the reaction flask. The mixture was stirred until all of the sodium had dissolved. At this point 0.5 mL (0.728 g, 3.72 mmol) of $Fe(CO)_5$ was condensed into the flask at −78 °C and the mixture was warmed to room temperature and stirred. After 2 h the blue color had dissipated and a white precipitate of $Na_2[Fe(CO)_4]$ was suspended in solution. The reaction solution was cooled to −196 °C, and the evolved carbon monoxide was pumped away. The solution was warmed to −78 °C, and another 0.5 mL of $Fe(CO)_5$ was condensed into the flask. Then the reaction solution was warmed to room temperature and stirred for 4 h. The volume of the THF was reduced to 5 mL, and 25 mL of dry hexane was condensed into the flask at −78 °C to induce precipitation. The solution was filtered, leaving a brown-red solid on the frit. The solid was washed with several portions of fresh hexane to free it of benzophenone and was dried on the vacuum line for 2–3 h. Solid $Na_2[Fe_2(CO)_8]$ is yellow-green when all of the THF is removed. A yield of 1.31 g of $Na_2[Fe_2(CO)_8]$ was obtained.

The salt $[PPh_4]_2[Fe_2(CO)_8]$ was prepared and isolated by following the procedure described above for the isolation of $[PPh_4]_2[Ru_2(CO)_8]$. When the metathesis reaction with 0.506 g (1.33 mmol) of $Na_2[Fe_2(CO)_8]$ and 1.10 g (2.62 mmol) of $[PPh_4]Br$ was performed in THF at room temperature, a yield of 1.08 g (1.06 mmol) of $[PPh_4]_2[Fe_2(CO)_8]$ was obtained (81% based on $[PPh_4]Br$). Anal. Calcd for $C_{56}H_{40}P_2O_8Fe_2$: C, 66.29; H, 3.97; P, 6.11; Fe, 11.01. Found: C, 66.02; H, 4.00; P, 6.00; Fe, 10.75. IR (ν_{CO}, CH_3CN): 1992 vw, 1953 w, sh, 1914 m, 1862 s, br cm^{-1}.

X-ray Crystal Structure Determinations. Single crystals were grown by slow diffusion of Et_2O into saturated CH_3CN solutions of $[PPh_4]_2[RuFe(CO)_8]$ and $[PPh_4]_2[Fe_2(CO)_8]$. Crystals of suitable size were mounted under N_2 in glass capillaries. All crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, obtained at −50 °C, well distributed in reciprocal space and lying in a 2θ range of 24–30°. Crystallographic parameters are given in Table I. The diffraction symmetry (C_{2h}, $2/m$) and the systematic absences (hkl for $h + k = 2n + 1$, $h0l$ for $h, l = 2n + 1$) are consistent with either the centrosymmetric space group $C2/c$ or the noncentrosymmetric space group Cc. Diffraction statistics favor Cc. The structure was solved in this space group. Attempted solution of the structure

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[19] When $K_2[Ru(CO)_4]$ was the starting material, $K_2[Ru_4(CO)_{13}]$ was the principal product.

[20] Bricker, J. C.; Payne, M. W.; Shore, S. G. *Organometallics* **1987**, *6*, 2345.

in $C2/c$ gave a clearly unreasonable result.

All data were corrected for Lorentz and polarization effects, decay (1.1% for $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$, 0.8% for $[PPh_4]_2[Fe_2(CO)_8]\cdot 2CH_3CN$), and absorption (empirically from ψ-scan data). Both structures were solved by employing a combination of MULTAN 11/82 and difference Fourier techniques with analytical scattering factors used throughout the structure refinement and both real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. All the crystallographic computations were carried out on a PDP 11/44 computer using the Structure Determination Package (SDP).[21] After all of the non-hydrogen atoms were located and refined, the hydrogen atoms of the phenyl groups were placed at calculated positions (C–H = 0.95 Å, $B(H) = B(C) + 1$ Å^2). Then with the positional and thermal parameters of all of the hydrogens fixed, the non-hydrogen atoms were refined anisotropically for an additional three cycles. In the solution of the structure of $[PPh_4][FeRu(CO)_8]\cdot CH_3CN$ metal atom sites were initially assigned to Fe or Ru on the basis of peak intensities. After refinement of these atoms and location and refinement of the remaining non-hydrogen atoms, R_F was 0.059 and the equivalent isotropic thermal parameters were $B(Fe) = 1.77$ Å^2 and $B(Ru) = 3.60$ Å^2. When the assignments were reversed, R_F was 0.102 and the thermal parameters were $B(Ru) = 6.08$ Å^2 and $B(F) = 0.141$ Å^2, which indicated that the initial assignments were more reasonable, but with some disorder. A disordered model was developed by employing the program DISORD. In the final structure the occupancies of the two metal sites are 0.78 Ru, 0.22 Fe and 0.78 Fe, 0.22 Ru. Final refinements were carried out by using anisotropic thermal parameters for non-hydrogen atoms.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE88-00515. W.Q. thanks the College of Mathematics and Physical Sciences of The Ohio State University for a postdoctoral fellowship.

Supplementary Material Available: Listings of bond distances and bond angles of $[P(C_6H_5)_4]^+$ and CH_3CN, positional parameters of $[P(C_6H_5)_4]^+$ and CH_3CN, anisotropic thermal parameters, and hydrogen atom positional parameters for $[PPh_4]_2[FeRu(CO)_8]\cdot CH_3CN$ and $[PPh_4]_2[Fe_2(CO)_8]\cdot 2CH_3CN$ (15 pages); listings of structure factor amplitudes (66 pages). Ordering information is given on any current masthead page.

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[21] SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, to apply corrections, and to solve and refine the structures.

[22] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986; pp 190–2.