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PHOTOASSISTED SYNTHESIS OF MIXED-METAL CLUSTERS: [PPN][$CoOs_3(CO)_{13}$], $H_2RuOs_3(CO)_{13}$, and $H_2FeOs_3(CO)_{13}$

ERIC W. BURKHARDT and GREGORY L. GEOFFROY *

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

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Summary

The utility of photochemical methods for the directed synthesis of mixed-metal clusters has been explored. The 366 nm photolysis of a solution containing [PPN][$Co(CO)_4$] (PPN = $(Ph_3P)_2N^+$) and $Os_3(CO)_{12}$ gives the new cluster [PPN][$CoOs_3(CO)_{13}$] in 33% yield. Irradiation of a mixture of $Fe(CO)_5$ and $H_2Os_3(CO)_{10}$ yields $H_2FeOs_3(CO)_{13}$ in 95% yield, and photolysis of $Ru_3(CO)_{12}$ in the presence of $H_2Os_3(CO)_{10}$ gives the new cluster $H_2RuOs_3(CO)_{13}$. Details of these syntheses, their probable mechanisms, and the characterization of the new compounds are discussed.

The condensation of a carbonylmetallate with a closed metal carbonyl trimer has been demonstrated to be a valuable method for the preparation of mixed-metal clusters [1—4]. The nucleophile $[Co(CO)_4]^-$ has been found to work particularly well in these syntheses. For example, near-quantitative yields of [PPN][$CoRu_3(CO)_{13}$] (PPN = $(Ph_3P)_2N^+$) are obtained from the reaction of [PPN][$Co(CO)_4$] with $Ru_3(CO)_{12}$ (eq. 1) [2].

$$[PPN][Co(CO)_4] + Ru_3(CO)_{12} \rightarrow [PPN][CoRu_3(CO)_{13}] \qquad (1)$$

However, reactions of this type do not always yield the desired product, and in particular, reactions employing $Os_3(CO)_{12}$ generally give little or none of the expected tetranuclear cluster, e.g. (eq. 2—3) [1,2,5].

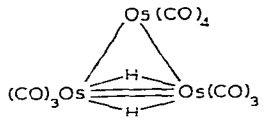
$$[Fe(CO)_4]^{2-} + Os_3(CO)_{12} \xrightarrow{\Delta} \xrightarrow{H^+} \underset{(9\%)}{H_2FeOs_3(CO)_{13}} \qquad (2)$$

$$[Co(CO)_4]^- + Os_3(CO)_{12} \xrightarrow{\Delta} \text{N.R.} \qquad (3)$$

Suspecting that the lack of success with $Os_3(CO)_{12}$ may be due to the relative strength of the Os—CO bonds [1,2,6,7], thus retarding their dissociation, and knowing that photoexcitation generally leads to CO loss from metal carbonyls [8], we decided to try to photoassist reactions of this type. This has been successful in one case and herein we report the preparation of $[CoOs_3(CO)_{13}]^-$ in good yield via photolysis of the reaction mixture shown in eq. 3.

Stone and coworkers have elegantly shown that coordinatively unsaturated metal complexes can add to the formal Os=Os double bond of $H_2Os_3(CO)_{10}$ to give mixed-metal clusters in high yield, e.g., eq. 4 and 5 [9].

$$\underset{(I)}{H_2Os_3(CO)_{10}} + Pt(C_2H_4)(PPh_3)_2 \rightarrow H_2Os_3Pt(CO)_{10}(PPh_3)_2 \qquad (4)$$



(I)

$$H_2Os_3(CO)_{10} + Rh(C_2H_4)_2(acac) \rightarrow H_2Os_3Rh(CO)_{10}(acac) \qquad (5)$$

After failing to obtain a high yield of $H_2FeOs_3(CO)_{13}$ via the reaction shown in eq. 2, we attempted to prepare this cluster via an adaption of Stone's method using photogenerated electrophiles (i.e., "$Fe(CO)_4$"). Indeed, photolysis of a mixture of $Fe(CO)_5$ and $H_2Os_3(CO)_{10}$ gives the desired $H_2FeOs_3(CO)_{13}$ cluster in excellent yield. The analogous new cluster $H_2RuOs_3(CO)_{13}$ results from photolysis of a mixture of $Ru_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$. Details of these and other photochemical studies are reported herein.

Results

1. *Preparation of [PPN][CoOs₃(CO)₁₃].* Repeated attempts to prepare the cluster anion $[CoOs_3(CO)_{13}]^-$ via the thermal reaction between $[Co(CO)_4]^-$ and $Os_3(CO)_{12}$ proved unsuccessful despite considerable effort in varying the reaction conditions [2]. A low yield of the unstable protonated derivative $HCoOs_3(CO)_{13}$ was obtained in an experiment in which $K[Co(CO)_4]$ was allowed to react with the trimer mixture Os_3-, $RuOs_2$-, Ru_2Os- and $Ru_3(CO)_{12}$ followed by acidification [2]. We have now found that the desired $[CoOs_3(CO)_{13}]^-$ anion can be obtained in 33% recrystallized yield as its PPN^+ salt by irradiating a solution of $[PPN][Co(CO)_4]$ and $Os_3(CO)_{12}$ with 366 nm light (eq. 6).

$$[PPN][Co(CO)_4] + Os_3(CO)_{12} \underset{25^\circ C,\ 48\ h}{\xrightarrow[\text{THF}]{h\nu(366\ nm)}} \underset{(33\%)}{[PPN][CoOs_3(CO)_{13}]} \qquad (6)$$

The formation of $[CoOs_3(CO)_{13}]^-$ is evident after 2 h photolysis and the yield slowly increases with increased photolysis time. Even after 48 h when the reaction was stopped, a significant quantity of unreacted $Os_3(CO)_{12}$ remained. In contrast, there was no evidence of reaction when the reagents were refluxed in THF solution for 48 h. $[PPN][CoOs_3(CO)_{13}]$ was characterized by chemical analysis and by its IR spectrum, Table 1, which is similar to that of the analogous $[PPN][CoRu_3(CO)_{13}]$ [2]. The compound is air stable in the solid state

TABLE 1

INFRARED SPECTRAL DATA

Cluster	Solvent	ν(CO) (terminal, cm^{-1})	ν(CO) (bridging, cm^{-1})
$H_2FeOs_3(CO)_{13}$	hexane	2114vw, 2087s, 2073s, 2041vs, 2034m, 2027m, 2017m, 1994w	1875w, 1846m
$H_2RuOs_3(CO)_{13}$	hexane	2110vw, 2082vs, 2067vs, 2057vs, 2029m, 2025m, 2019s, 2008w	1869w(br)
$H_2Ru_4(CO)_{13}$	hexane	2112vw, 2079vs, 2068vs, 2056vs, 2036m, 2024vs, 2008w	1880w(br)
[PPN][$CoOs_3(CO)_{13}$]	THF	2072m, 2017vs, 2007(sh) 1966mw, 1945mw	1825w, 1804m
[PPN][$CoRu_3(CO)_{13}$]	THF	2067w, 2017vs, 1993m, 1974mw	1828w, 1803m

and in solution for moderate periods of time (1—2 d).

2. *Preparation of $H_2FeOs_3(CO)_{13}$.* This cluster has previously been prepared in yields of 9 and 7% by the reactions shown in eqs. 2 and 7 [1,10].

$$H_2Os(CO)_4 + Fe_2(CO)_9 \xrightarrow{\Delta} H_2FeOs_3(CO)_{13} \qquad [10] \qquad (7)$$

We have found that $H_2FeOs_3(CO)_{13}$ can be conveniently synthesized in >90% isolated yield by irradiating a solution of $H_2Os_3(CO)_{10}$ and $Fe(CO)_5$ with 366 nm light, eq. 8. $H_2FeOs_3(CO)_{13}$ was identified by comparison of its IR

$$Fe(CO)_5 + H_2Os_3(CO)_{10} \xrightarrow[\substack{\text{hexane} \\ 25^\circ\text{C, 2 h}}]{h\nu\ (366\ \text{nm})} H_2FeOs_3(CO)_{13} \qquad (8)$$

spectrum to that reported [1,10]. The only other product detected in the reaction was $Fe_3(CO)_{12}$ in low yield.

3. *Preparation of $H_2RuOs_3(CO)_{13}$.* This previously unknown cluster was prepared in 23% isolated yield by irradiating a solution of $Ru_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$ with 366 nm light (eq. 9). The reaction was continued until the IR spec-

$$Ru_3(CO)_{12} + H_2Os_3(CO)_{10} \xrightarrow[\substack{\text{hexane} \\ 25^\circ\text{C, 70 h}}]{h\nu(366\ \text{nm})} H_2RuOs_3(CO)_{13} \qquad (9)$$

trum indicated little unreacted $H_2Os_3(CO)_{10}$ remained. Chromatography of the reaction mixture yielded two other fractions which were identified as $H_2Ru_4(CO)_{13}$ [11] and $H_4Os_4(CO)_{13}$ [12] by their IR data. The new cluster $H_2RuOs_3(CO)_{13}$ was characterized by its IR spectrum, Table 1 and Fig. 1, and by its mass spectrum and its elemental analysis. It appears to be indefinitely air-stable in both the solid state and in solution.

4. *Photolysis of $[V(CO)_6]^-$ and $M_3(CO)_{12}$ (M = Fe, Os) solutions.* In attempts to prepare VFe_3 and VOs_3 cluster anions, equimolar solutions of Na[$V(CO)_6$] and $Fe_3(CO)_{12}$ or $Os_3(CO)_{12}$ were irradiated with 366 nm and metathesized with [PPN]Cl. However, the only crystalline products obtained were [PPN][$HFe_3(CO)_{11}$] and [PPN][$HOs_3(CO)_{11}$], identified by their reported IR

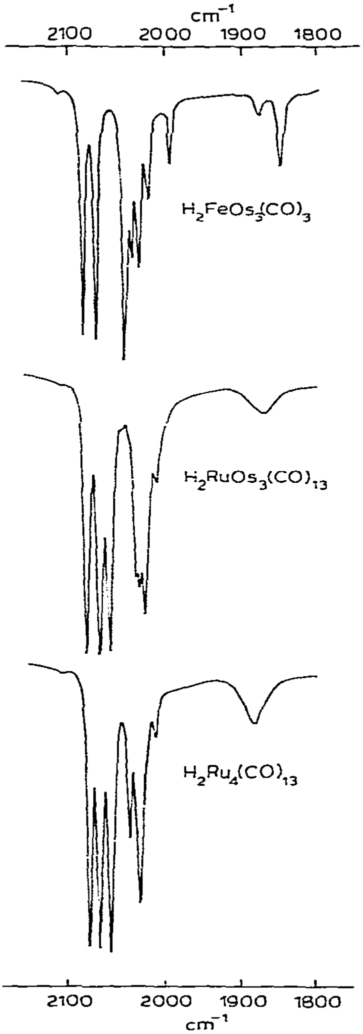


Fig. 1. Infrared spectra of (a) $H_2FeOs_3(CO)_{13}$, (b) $H_2RuOs_3(CO)_{13}$, and (c) $H_2Ru_4(CO)_{13}$ in hexane solution.

data [13,14]. Apparently $[V(CO)_6]^-$ is a sufficiently strong reducing agent to reduce both of these trimers to their respective anions, although the proton source is presently unknown. In this regard it has been recently reported that reduction or photolysis of $Fe_3(CO)_{12}$ in THF solution leads to the formation of $[HFe_3(CO)_{11}]^-$ and the hydride was assumed to derive by abstraction from THF [15].

5. Photolysis of $V(\eta^5\text{-}C_5H_5)(CO)_4/H_2Os_3(CO)_{10}$ *and* $V(\eta^5\text{-}C_5H_5)(CO)_4/Os_3(CO)_{12}$ *solutions.* In an attempt to synthesize VOs_3 clusters, equimolar hexane solutions of $V(\eta^5\text{-}C_5H_5)(CO)_4/H_2Os_3(CO)_{10}$ and $V(\eta^5\text{-}C_5H_5)(CO)_4/Os_3(CO)_{12}$ were irradiated with 366 nm light under a continuous N_2 purge. In each case the IR spectra of the irradiated solutions showed a continual decrease in the bands due to $V(\eta^5\text{-}C_5H_5)(CO)_4$ but the only vanadium-containing product isolated was the $V_2(\eta^5\text{-}C_5H_5)_2(CO)_5$ dimer. This dimer is known to result from photolysis of $V(\eta^5\text{-}C_5H_5)(CO)_4$ [16].

6. Photolysis of $M(CO)_6$ (M = Cr, Mo, W)/$H_2Os_3(CO)_{10}$ solutions. Hexane solutions of $M(CO)_6$ (M = Cr, Mo, W) were irradiated in the presence of $H_2Os_3(CO)_{10}$ in attempts to prepare the corresponding MOs_3 clusters. These, however, were not obtained and only slow decomposition of $M(CO)_6$ resulted. $H_2Os_3(CO)_{10}$ was recovered unchanged.

Discussion

As demonstrated herein by the preparation of $H_2RuOs_3(CO)_{13}$ and $H_2FeOs_3(CO)_{13}$, photolysis of metal carbonyl complexes in the presence of $H_2Os_3(CO)_{10}$ is a viable method for the synthesis of mixed-metal clusters. However, it is not without its limitations, as evidenced by the unsuccessful synthetic attempts described above. Insight into whether or not a particular combination of reactants will give the desired product could perhaps be gained by consideration of the reaction mechanism. Even though $H_2Os_3(CO)_{10}$ absorbs a portion of the incident 366 nm irradiation (ϵ_{366} 1698 M^{-1} cm^{-1}), independent studies have shown that $H_2Os_3(CO)_{10}$ is not very photoactive although it does slowly yield $H_2Os_4(CO)_{13}$ upon prolonged photolysis [17]. On the other hand both $Fe(CO)_5$ and $Ru_3(CO)_{12}$ are highly photosensitive. Photolysis of $Fe(CO)_5$ is known to yield $Fe(CO)_4$ as a primary photoproduct [8], and $Ru_3(CO)_{12}$ has been shown to fragment upon photolysis in the presence of CO to yield $Ru(CO)_5$ [18]. The mechanism of this latter reaction is presently unknown although $Ru(CO)_4$ monomers may initially be formed. Following Stone and coworkers' [9] elegant demonstration of the thermal addition of nucleophilic metal complexes to $H_2Os_3(CO)_{10}$, the clusters $H_2FeOs_3(CO)_{13}$ and $H_2RuOs_3(CO)_{13}$ presumably arise via the initial addition of $Fe(CO)_4$ and $Ru(CO)_4$ to the Os=Os double bond of $H_2Os_3(CO)_{10}$. Further CO loss, either thermally or photochemically induced, must then occur to close the clusters to the final products.

Why then did the reactions which employed $V(\eta^5\text{-}C_5H_5)(CO)_4$ and $M(CO)_6$ (M = Cr, Mo, W) not proceed to give the desired MOs_3 cluster even though each of these metal carbonyls is known to undergo CO loss upon photolysis? We can only surmise that the photogenerated intermediates are not sufficiently nucleophilic to attack $H_2Os_3(CO)_{10}$ or that such addition is retarded by the increased size of the particular intermediate relative to $Fe(CO)_4$ and the small nucleophiles studied by Stone and coworkers [9].

The synthesis of $[CoOs_3(CO)_{13}]^-$ described herein also demonstrates that the carbonylmetalate addition to a metal carbonyl trimer can be photoassisted. The role of light in this reaction is presumably to activate $Os_3(CO)_{12}$ to attack by the carbonylmetalate. The electronic absorption spectrum of $[Co(CO)_4]^-$ is transparent in the region of irradiation (366 nm). Likewise, IR spectra of solutions containing $Os_3(CO)_{12}$ and $[Co(CO)_4]^-$ show only bands attributable to these two species and thus the concentration of any intermediate formed by thermal addition of $[Co(CO)_4]^-$ to $Os_3(CO)_{12}$ is far too low to absorb a sufficient fraction of the incident irradiation. Thus the only viable candidate for photoactivation is $Os_3(CO)_{12}$.

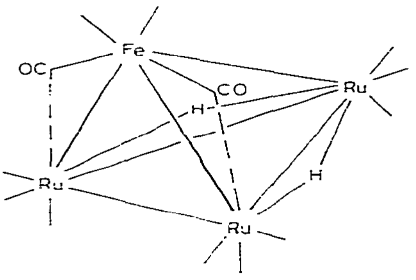
$Os_3(CO)_{12}$ is known to lose CO upon photolysis in preference to cleavage of the Os—Os bonds [19]. In contrast to $Ru_3(CO)_{12}$ [18], photolysis of $Os_3(CO)_{12}$ for 2 h under 6 atm of CO gives no net reaction whereas photolysis of $Os_3(CO)_{12}$ in the presence of PPh_3 rapidly yields the $Os_3(CO)_{12-x}(PPh_3)_x$ (x = 1—3) substitution products [19]. We also find that photosubstitution dominates as irradiation of $Os_3(CO)_{12}$ in CH_3CN solution yields a mixture of the known $Os_3(CO)_{11}(CH_3CN)$ and $Os_3(CO)_{10}(CH_3CN)_2$ clusters [20] and not monomeric products. Thus the photoassisted synthesis of $[CoOs_3(CO)_{13}]^-$ presumably proceeds via photoinduced CO loss from $Os_3(CO)_{12}$ to produce "$Os_3(CO)_{11}$" which is more susceptible to addition of $[Co(CO)_4]^-$ (eq. 10), than is $Os_3(CO)_{12}$.

$$Os_3(CO)_{12} \xrightarrow{h\nu} CO + \text{"}Os_3(CO)_{11}\text{"} \xrightarrow{[Co(CO)_4]^-} [CoOs_3(CO)_{13}]^- + 2\,CO \qquad (10)$$

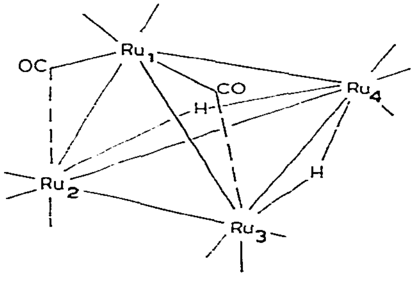
Whether or not this observation has any relevance to the mechanism of the thermal reactions between carbonylmetalates and closed metal carbonyl trimers which give good yields of tetranuclear clusters is not clear [1,2].

Characterization of $H_2RuOs_3(CO)_{13}$ and $[CoOs_3(CO)_{13}]^-$

1. $H_2RuOs_3(CO)_{13}$. The mass spectrum of $H_2RuOs_3(CO)_{13}$ shows a parent ion at *m/e* 1038 with the correct isotopic distribution along with fragment ions corresponding to successive loss of all 13 carbonyls. The infrared spectrum of $H_2RuOs_3(CO)_{13}$ is shown in Fig. 1 and the data summarized in Table 1. Significantly, the IR spectrum of $H_2RuOs_3(CO)_{12}$ is not similar to the IR spectra of the isoelectronic clusters $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, $H_2FeRuOs_2(CO)_{13}$, and $H_2FeOs_3(CO)_{13}$ [1] but instead more closely resembles that of $H_2Ru_4(CO)_{13}$ (Fig. 1). It should be noted that $H_2FeRu_3(CO)_{13}$ (II) [21], and $H_2Ru_4(CO)_{13}$ (III) [22], have similar structures but yet their spectra differ significantly in the bridging CO region. $H_2FeRu_3(CO)_{13}$ shows the two band pattern expected for these structures which arises from symmetric and antisymmetric motions of the two bridging carbonyls. However, only a single broad band is observed in the bridging carbonyl region for $H_2Ru_4(CO)_{13}$ and $H_2RuOs_3(CO)_{13}$. We conclude that the structure of $H_2RuOs_3(CO)_{13}$ is similar to that of $H_2Ru_4(CO)_{13}$ as indicated in IV. Alternative structures with the bridging CO's attached to Os do not appear as likely.



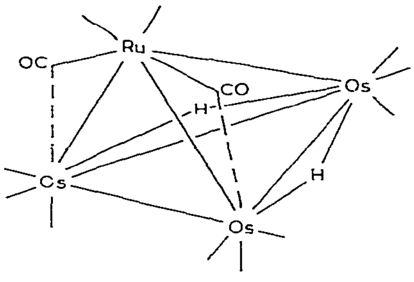
(II)



(III)

The ¹H NMR spectrum of $H_2RuOs_3(CO)_{13}$ shows a broad singlet at δ −20.7 ppm (6.7 Hz half-width) attributable to the two equivalent hydrides in IV. The position of this resonance is consistent with the hydride assigned to a position bridging Os—Os bonds [23]. In the series of compounds $H_2FeRu_3(CO)_{13}$,

$H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$, the chemical shift ordering $\delta(\underset{\mathrm{H}}{\mathrm{Ru{-}Ru}}) > \delta(\underset{\mathrm{H}}{\mathrm{Ru{-}Os}}) > \delta(\underset{\mathrm{H}}{\mathrm{Os{-}Os}})$ was clearly evident with the most upfield



(IV)

resonance at —19.82 ppm assigned to the hydride bridging the Os—Os bond in the C_1 isomer of $H_2FeRuOs_2(CO)_{13}$ [23b].

Why do $H_2Ru_4(CO)_{13}$ and $H_2RuOs_3(CO)_{13}$ show only the single broad band in the bridging CO region instead of the expected two band pattern? Other molecules show an effect similar to this with the most notable example being $Fe_3(CO)_{12}$ for which the IR spectrum in non-polar solvents does not agree with either the crystallographically established C_{2v} structure or with the D_{3h} structure of $Ru_3(CO)_{12}$ [24,25]. Cotton has suggested that this effect arises because the molecule is easily deformable with a range of structures present in solution,

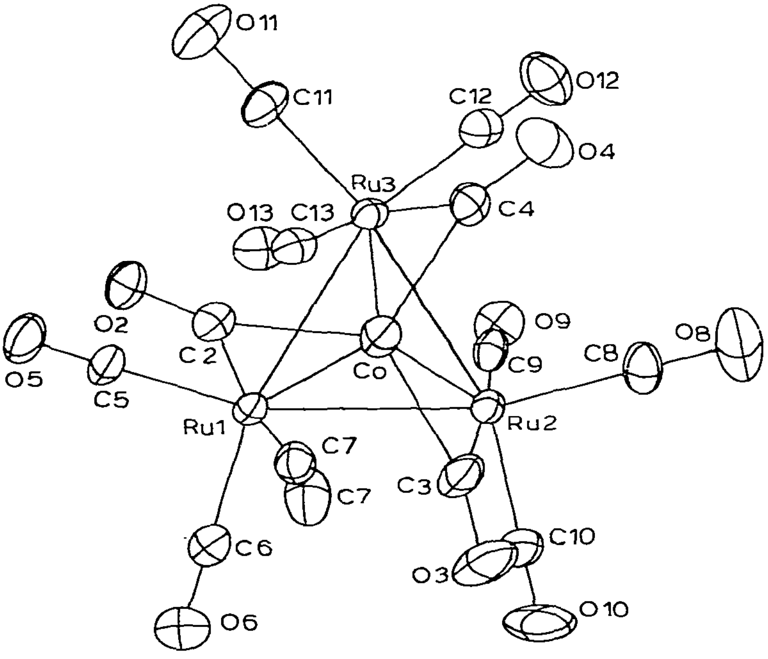


Fig. 2. Structure of the anion $[CoRu_3(CO)_{13}]^-$ [2]. A terminal CO (C(1)—O(1)) attached to Co has been omitted for clarity.

thus, in effect, "washing-out" the limiting C_{2v} spectrum [26,27]. Molecules of this type have been termed "fictile" [28]. Perhaps both $H_2Ru_4(CO)_{13}$ and $H_2RuOs_3(CO)_{13}$ belong to this class of compounds, at least with respect to the bridging and terminal carbonyls attached to the unique Ru atom (Ru(1) in III). Support for this hypothesis comes from a ^{13}C NMR study of $H_2Ru_4(CO)_{13}$. In the ^{13}C NMR spectrum of this complex separate resonances for the bridging and terminal carbonyls attached to Ru1 (cf. III) were not resolvable and, instead, an average signal was observed at temperatures as low as —72° C [29]. This contrasts sharply with $H_2FeRu_3(CO)_{13}$ in which separate resonances for the bridging and terminal carbonyls attached to Fe are clearly observable at —65° C [23]. Resolution of this question will have to await the results of variable-temperature ^{13}C and ^1H NMR studies of $H_2RuOs_3(CO)_{13}$ which are currently underway.

2. *[PPN][CoOs$_3$(CO)$_{13}$].* The band pattern in the infrared spectrum of $[PPN][CoOs_3(CO)_{13}]$ is similar to that of $[PPN][CoRu_3(CO)_{13}]$ [2], although some minor frequently shifts are evident. The structure of $[CoOs_3(CO)_{13}]^-$ is thus presumed to be analogous to that established for $[CoRu_3(CO)_{13}]^-$ [2] as indicated in Fig. 2.

Experimental

General. $Fe(CO)_5$, $Fe_3(CO)_{12}$, $M(CO)_6$ (M = Cr, Mo, W), $V(\eta^5\text{-}C_5H_5)(CO)_4$, $Na[V(CO)_6] \cdot 2\ C_5H_{12}O_2$, hereafter abbreviated $Na[V(CO)_6]$, and [PPN]Cl were obtained from Alfa-Ventron Corp. and were used without further purification. $[PPN][Co(CO)_4]$ [30], $Ru_3(CO)_{12}$ [31], $Os_3(CO)_{12}$ [32], and $H_2Os_3(CO)_{10}$ [33] were prepared by published procedures. All solvents were dried and degassed prior to use. A Blak-Ray B-100A UV lamp (Ultra-Violet Products, San Gabriel, CA) with a 366 nm filter was used as the irradiation source. Infrared spectra were recorded on a Perkin—Elmer model 580 IR spectrophotometer and are accurate to within ±2 cm^{-1}. Chromatographic separations were conducted on SiO_2 using the previously described chromatography apparatus [1]. Electron impact mass spectra were obtained using an AEI-MS9 spectrometer, and ^1H NMR spectra were measured on a Bruker WH-200 spectrometer. Elemental analyses were obtained by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y.

Preparation of H$_2$FeOs$_3$(CO)$_{13}$. A 100 ml hexane solution of $H_2Os_3(CO)_{10}$ (77.2 mg, 0.090 mmol) and $Fe(CO)_5$ (100 μl, ~0.743 mmol) was irradiated with 366 nm light for 2 h under a slow N_2 purge. After 15 min the presence of $H_2FeOs_3(CO)_{13}$ was detected by IR spectroscopy and an orange film of $H_2FeOs_3(CO)_{13}$ began to deposit on the walls of the flask as the reaction proceeded. Evaporation of solvent and unreacted $Fe(CO)_5$ gave an orange residue which was chromatographed on SiO_2. Green $Fe_3(CO)_{12}$ and purple $H_2Os_3(CO)_{10}$ were first eluted in that order using hexane as the eluting solvent. The third band containing orange $H_2FeOs_3(CO)_{13}$ was eluted with a 9/1 hexane/benzene solvent mixture and evaporation of solvent gave an orange microcrystalline product (85.4 mg, 0.0866 mmol, 95% yield).

Preparation of H$_2$RuOs$_3$(CO)$_{13}$. An 80 ml hexane solution of $H_2Os_3(CO)_{10}$ (33.2 mg; 0.039 mmol) and $Ru_3(CO)_{12}$ (24.8 mg; 0.039 mmol) was irradiated with 366 nm for 70 h under a slow N_2 purge. The IR spectrum indicated that the reaction had slowed considerably by this time, and the orange solution was reduced in volume to about 30 ml. Chromatography on SiO_2 with hexane as the eluting solvent gave 4 fractions in the following order: a yellow-brown inseparable mixture of $Ru_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$; red-orange $H_2Ru_4(CO)_{13}$ (4.6 mg; 20% yield based on $Ru_3(CO)_{12}$); orange $H_2RuOs_3(CO)_{13}$ (19.1 mg; 0.018 mmol, 23% yield based on $H_2Os_3(CO)_{10}$); yellow $H_4Os_4(CO)_{12}$. Anal. Found: C, 15.04; H, 0.15. $H_2RuOs_3(CO)_{13}$ calcd.: C, 15.04; H, 0.19%.

Preparation of [PPN][$CoOs_3(CO)_{13}$]. A 150 ml THF solution of $Os_3(CO)_{12}$ (102.6 mg, 0.113 mmol) and [PPN][$Co(CO)_4$] (82.1 mg; 0.114 mmol) was irradiated with 366 nm light for 48 h under a slow N_2 purge during which time the solution changed color from yellow to orange. The THF was removed under vacuum, and the resultant orange residue was dissolved in 50 ml Et_2O. The solution volume was reduced to 20 ml and slow diffusion of petroleum ether (b.p. 40—60°C) into the Et_2O solution in a double tube recrystallizer gave red crystals of [PPN][$CoOs_3(CO)_{13}$] (55.9 mg, 0.036 mmol, 33% yield). Anal. Found: C, 38.22; H, 2.06. [PPN][$CoOs_3(CO)_{13}$] calcd.: C, 38.41; H, 1.96%.

Acknowledgments

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