Synthesis of Tetrahedral Mixed-Metal Clusters of the Iron Triad. Preparation and Characterization of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$

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Abstract: Several new mixed-metal clusters of the Fe–Ru–Os triad have been prepared through the addition of carbonylmetalates to closed metal trimers. Addition of $Na_2[Fe(CO)_4]$ to $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$, followed by acidification, yielded $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$, the first examples of clusters comprised of three different transition metals. $H_2Fe_2Ru_2(CO)_{13}$ was prepared by allowing $Na_2[Fe(CO)_4]$ to react with $Fe_2Ru(CO)_{12}$ or by addition of $[Ru(CO)_4]^{2-}$ to $Fe_3(CO)_{12}$. Addition of $[Ru(CO)_4]^{2-}$ to $Os_3(CO)_{12}$ or $[Os(CO)_4]^{2-}$ to $Ru_3(CO)_{12}$ gave an inseparable mixture of $H_4Ru_4(CO)_{12}$, $H_4Ru_3Os(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, $H_4RuOs_3(CO)_{12}$, and $H_4Os_4(CO)_{12}$. An improved synthesis of $H_2FeRu_3(CO)_{13}$ is reported and an alternative route to $H_2FeOs_3(CO)_{13}$ is described. The new clusters have been characterized by their NMR, infrared, electronic absorption, and mass spectra and the spectral evidence suggests tetrahedral structures similar to the known structures of $H_2FeRu_3(CO)_{13}$ and $H_2Ru_4(CO)_{13}$.

Transition metal cluster complexes have become a very important class of compounds, principally because of their potential in catalysis. Clusters have been shown to behave as catalysts in their own right and they hold considerable promise for serving as models for catalytic surfaces.[1] Clusters comprised of two or more different transition metals in the cluster framework are particularly interesting in this regard because of possible bimetallic effects.[2] Further, mixed-metal clusters have nonequivalent bonding sites. As such they are ideally suited for modeling studies which employ variable temperature NMR to follow the movements of substrates over their surfaces.

One of the problems which has hampered studies of mixed-metal clusters is their relative lack of availability. Only a very few isostructural series have been achieved, and general synthetic methods for mixed-metal clusters are lacking.[3,4] Carbonylmetalates have been widely used as synthetic reagents in cluster chemistry and several of the reported reactions[5-10] appear to be adaptable to design. This is particularly true of the reactions of Knight and Mays[10] who prepared a series of group 7–group 8 tetrameric mixed-metal clusters through the addition of a carbonylmetalate to a closed $M_3(CO)_{12}$ trimer. Specifically, they studied reactions of $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ with the $M_3(CO)_{12}$ (M = Fe, Ru, Os) trimers and prepared, by reactions similar to that shown in eq 1, the tetrahedral clusters $H_3ReOs_3(CO)_{13}$ and $H_3MnOs_3(CO)_{13}$ and the open clusters $H_3MnOs_3(CO)_{16}$, $H_3ReOs_3(CO)_{16}$, $HReOs_3(CO)_{15}$, and $H_2Re_2Ru_2(CO)_{16}$.

$$[Re(CO)_5]^- + Os_3(CO)_{12} \longrightarrow \xrightarrow{H_3PO_4} H_3ReOs_3(CO)_{13} \quad (1)$$

By reactions of this type we have now prepared $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$, the first examples of clusters comprised of three different transition metals,[11] and the new clusters $H_2Fe_2Ru_2(CO)_{13}$, $H_4RuOs_3(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, and $H_4Ru_3Os(CO)_{12}$. We have also synthesized $H_2FeRu_3(CO)_{13}$ in 49% yield, greatly improved over previously published[12,13] pyrolysis procedures. We now report details of the preparation and characterization of these clusters and discuss those factors of primary importance in synthetic reactions of this type.

Results

General Synthetic Procedure. Our approach for the designed synthesis of any specific tetrahedral cluster is to add the appropriate carbonylmetalate to the face of the appropriate metal trimer. To synthesize $H_2FeRu_3(CO)_{13}$, for example, $[Fe(CO)_4]^{2-}$ is added to $Ru_3(CO)_{12}$. The experimental synthesis of each of the particular mixed-metal clusters described below was carried out in essentially the same manner. A THF solution of the trimer was added dropwise to a THF solution of the carbonylmetalate under an N_2 atmosphere. After heating, the solvent was removed by evaporation under vacuum, and the residue acidified with phosphoric acid and extracted into hexane. The hexane solution was then dried over anhydrous $MgSO_4$ and chromatographed on silica gel. Specific details concerning the reaction times, temperatures, and chromatography are given in the Experimental Section. Variation of reaction conditions usually resulted in a significant redistribution of products, as illustrated by the variations discussed below for the synthesis of $H_2FeRu_3(CO)_{13}$ and $H_2FeOs_3(CO)_{13}$. Of the various spectroscopic techniques used to identify the products of the reactions, the most useful were infrared and mass spectroscopy. Chemical ionization (CI) mass spectroscopy served to characterize mixtures of products, whereas electron impact (EI) mass spectroscopy was used to present a detailed spectrum of a single pure product. Previously described clusters were identified mainly by comparison to their reported infrared data. Mass spectral and infrared data for the new clusters prepared in this work are set out in Tables I and II, respectively.

Preparation of $H_2FeRu_3(CO)_{13}$. Reaction of $Ru_3(CO)_{12}$ with $Na_2[Fe(CO)_4]$ leads to formation of the known[12,13] $H_2FeRu_3(CO)_{13}$. The product was identified by its infrared and mass spectrum, and a 49% yield was obtained when the THF solution of $Ru_3(CO)_{12}$ and $Na_2[Fe(CO)_4]$ was refluxed for 75 min. Increasing the reaction time or lowering the reaction temperature decreased the $H_2FeRu_3(CO)_{13}$ yield and increased the amount of $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$, the major by-products. When a tenfold excess of $Na_2[Fe(CO)_4]$ was used instead of a stoichiometric amount, the $H_2FeRu_3(CO)_{13}$ yield decreased significantly (14%). When the order of reagent addition was reversed, the number of by-products increased although $H_2FeRu_3(CO)_{13}$ remained the principal product. Traces of $FeRu_2(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ were isolated in addition to the Ru_4 clusters.

Varying the workup conditions also changed the product distribution. In the initial experiments the THF reaction solution was directly acidified with 85% H_3PO_4, but this procedure often resulted in an increased amount of by-products, especially the tetranuclear Ru_4 clusters. The preferred workup which evolved is to first evaporate the THF under vacuum and

Table I. Mass Spectral Data

Cluster	Parent ion isotopic distribution (rel intensity)	Other principal fragments[a]
$H_2Fe_2Ru_2(CO)_{13}$	687 (7), 686 (31), 685 (23), 684 (69), 683 (58), 682 (98), 681 (100), 680 (82), 679 (78), 678 (58), 677 (35), 676 (36), 675 (19), 674 (18)	658, 630, 602, 574, 546, 518, 490, 462, 434, 404,[b] 376, 348, 320
$H_2FeRu_2Os(CO)_{13}$	824 (18), 823 (12), 822 (29), 821 (18), 820 (47), 819 (59), 818 (76), 817 (82), 816 (94), 815 (100), 814 (88), 813 (94), 812 (65), 811 (47), 810 (41), 809 (35), 808 (24), 807 (18), 806 (18), 805 (12)	790, 762, 734, 705,[c] 677, 649, 621, 593, 565, 537, 508,[c] 408, 452
$H_2FeRuOs_2(CO)_{13}$	911 (13), 910 (28), 909 (20), 908 (65), 907 (53), 906 (93), 905 (98), 904 (100), 903 (88), 902 (93), 901 (58), 900 (55), 899 (38), 898 (25), 897 (20), 896 (13), 895 (8)	880, 852, 824, 796, 768, 740, 712, 684, 654,[b] 626, 598, 570, 542

[a] Mass number is that computed by using 56, 104, and 192 mass units for Fe, Ru, and Os, respectively. [b] Concomitant loss of CO and 2 H. [c] Concomitant loss of CO and 1 H.

Table II. Infrared Spectral Data

Cluster	Color	ν_{CO} (terminal)	ν_{CO} (bridging)
$H_2FeRu_3(CO)_{13}$	Red	2084 s, 2072 s, 2062 w, 2040 vs, 2030 m, 2020 w, 1991 m	1883 w, 1855 m
$H_2FeRu_2Os(CO)_{13}$	Orange-red	2111 vw, 2085 s, 2073 s, 2041 vs, 2026 m, 2016 w, 1991 m	1887 w, 1877 w, 1861 m, 1849 m
$H_2FeRuOs_2(CO)_{13}$	Orange	2121 w, 2086 s, 2073 s, 2041 vs, 2032 m, 2024 m, 2013 w, 1993 m	1882 w, 1870 w, 1855 m, 1842 m
$H_2Fe_2Ru_2(CO)_{13}$	Red	2105 vw, 2084 s, 2072 m, 2066 m, 2057 s, 2041 vs, 2031 m, 2015 s, 2003 w, 1979 m	1888 br, w, 1860 br, w
$H_2FeOs_3(CO)_{13}$	Yellow-orange	2086 s, 2072 s, 2040 vs, 2032 m, 2025 m, 2015 w, 1994 w	1875 w, 1848 m
$H_2Ru_4(CO)_{13}$	Red	2083 s, 2078 s, 2056 s, 2033 m, 2026 s, 2008 w	1880
$H_4Ru_4(CO)_{12}$	Yellow	2081 s, 2067 vs, 2030 m, 2024 s, 2009 w	
$H_4Os_4(CO)_{12}$	Pale yellow	2086 m, 2069 s, 2022 s, 2000 m	
$H_4M_{4-n}M'_n(CO)_{12}$ M = Ru, M′ = Os, $n = 1$–4	Yellow	2081 s, 2063 s, 2022 s, 1994 w	

then add hexane and 20% H_3PO_4 successively. The acid layer is then extracted with hexane until the hexane layer is colorless. Extraction of the reaction residue from syntheses employing $Os_3(CO)_{12}$ was accomplished using benzene owing to the low solubility of the osmium clusters in hexane.

It is interesting to note that only trace amounts of mixed-metal Fe-Ru trimers were formed in any of the reactions regardless of the reaction conditions. In the previously described preparations[12,13] of $H_2FeRu_3(CO)_{13}$, these mixed-metal trimers were the predominant products.

Preparation of $H_2Fe_2Ru_2(CO)_{13}$. Previous attempts[12] using pyrolysis reactions to prepare $H_2Fe_2Ru_2(CO)_{13}$ and $H_2Fe_3Ru(CO)_{13}$, the remaining two members of the homologous series $H_2Fe_nRu_{(4-n)}(CO)_{13}$, have failed. A rational synthesis of $H_2Fe_2Ru_2(CO)_{13}$ should derive from the reaction of $[Fe(CO)_4]^{2-}$ with the known[12,13] mixed-metal trimer $FeRu_2(CO)_{12}$. When these reactants were stirred in THF solution at 25 °C for 3 h and the usual workup procedure was followed, a mixture of $H_2Fe_2Ru_2(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, $H_4Ru_4(CO)_{12}$, $Fe_2Ru(CO)_{12}$, and $Ru_3(CO)_{12}$ resulted. Although $H_2Fe_2Ru_2(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$ could easily be separated from the remainder of the products by chromatography on silica gel, we were not able to separate these two Fe-Ru clusters from each other. $H_2Fe_2Ru_2(CO)_{13}$ does appear to elute slightly faster than $H_2FeRu_3(CO)_{13}$ with hexane as the eluent, and it is likely that the two clusters could be separated by very extensive recycle chromatography. This, however, was not attempted. The new cluster was identified by infrared and mass spectral data. The infrared spectra obtained from successive 100-mL cuts from the eluting $H_2Fe_2Ru_2(CO)_{13}/H_2FeRu_3(CO)_{13}$ fraction clearly show the presence of two clusters and also that bands due to $H_2FeRu_3(CO)_{13}$ increase in relative intensity with the later cuts. The mass spectrum of the solid material obtained after evaporation of the solvent from the recombined cuts showed parent ions at 728 and 682 mass units assignable to $H_2FeRu_3(CO)_{13}$ and $H_2Fe_2Ru_2(CO)_{13}$, respectively, in an intensity ratio of about 4:1.

Attempted Preparation of $H_2Fe_3Ru(CO)_{13}$. Using the reaction approach employed in this study, the unknown cluster $H_2Fe_3Ru(CO)_{13}$ could be prepared either by the reaction of $[Ru(CO)_4]^{2-}$ with $Fe_3(CO)_{12}$ or by reaction of $[Fe(CO)_4]^{2-}$ with $Fe_2Ru(CO)_{12}$. When these two reactions were conducted using precautions to maintain anaerobic conditions, they both produced a product distribution similar to that described in the above synthesis of $H_2Fe_2Ru_2(CO)_{13}$. Although H_2Fe_2-

$Ru_2(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$ were formed in substantial quantities, there was no indication of the presence of the desired $H_2Fe_3Ru(CO)_{13}$. $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $H_2Ru_4(CO)_{13}$, and $H_4Ru_4(CO)_{12}$ were isolated in addition to the Fe-Ru tetramers from the reaction of $[Ru(CO)_4]^{2-}$ with $Fe_3(CO)_{12}$.

Preparation of $H_4RuOs_3(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, and $H_4Ru_3Os(CO)_{12}$. We initially set out to synthesize $H_2RuOs_3(CO)_{13}$ by the reaction of $[Ru(CO)_4]^{2-}$ with $Os_3(CO)_{12}$. This reaction gave a very surprising result. After the reaction mixture was refluxed for 5 h and the usual workup followed, one very broad yellow band was obtained during chromatography on silica gel. Infrared spectra of various cuts taken from this band were virtually identical and all exhibited four relatively broad bands in the terminal CO region, in a pattern similar to the bands of $H_4Ru_4(CO)_{12}$[14] and $H_4Os_4(CO)_{12}$.[14] The EI mass spectrum of the solid material obtained from the chromatography was quite complex, but the mass peak at 1108 confirmed that the highest molecular weight compound was indeed $H_4Os_4(CO)_{12}$. The chemical ionization mass spectrum of the solid, however, gave ions for five compounds at 720, 810, 900, 990, and 1080 mass units in relative ratios of 6:5:3:2:1, respectively. These mass peaks can be assigned to $H_4Ru_4(CO)_{11}$, $H_4Ru_3Os(CO)_{11}$, $H_4Ru_2Os_2(CO)_{11}$, $H_4RuOs_3(CO)_{11}$, and $H_4Os_4(CO)_{11}$. This analysis is consistent with previous studies[15] of metal carbonyls which have shown that CI mass spectrometry in the negative mode gives mass peaks corresponding to the parent ion minus one carbonyl. Thus the entire homologous series $H_4Ru_nOs_{(4-n)}(CO)_{12}$ was formed in this single reaction. These five Ru-Os tetramers appear to have similar solubility and chromatographic properties, and in our hands no evidence of even partial separation has been achieved. It is interesting to note that only the tetrahydrides were produced in this particular reaction. This result is consistent with previous studies[14,16,17] which have shown an increasing preference of Ru and Os to yield the $H_4M_4(CO)_{12}$ structure. When the reaction time in the synthesis was shortened to 60 min, a very small amount of what appeared to be $H_2Os_4(CO)_{13}$[17] and $H_2Ru_4(CO)_{13}$ was isolated in addition to the products described above.

Addition of $[Os(CO)_4]^{2-}$ to $Ru_3(CO)_{12}$ produced somewhat different results. Chromatography of the reaction mixture gave two separate fractions. The first that eluted was yellow and contained $H_4RuOs_3(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, and $H_4Ru_3Os(CO)_{12}$, but the second red fraction yielded a mixture of as yet unidentified compounds. The mass spectrum of this fraction was complex but appeared to show parent ion peaks at approximately 1084, 900, and 855 mass units.

We considered the possibility that the observed distribution of products was formed by successive fragmentation of initially produced clusters into $HM(CO)_4$ or $H_2M_2(CO)_8$ units. These fragments could then recombine in various ways to give complete scrambling of the metals and the product distribution observed. However, when $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$ were refluxed for 1 h in THF, no scrambling occurred and the $H_4M_4(CO)_{12}$ clusters were recovered unchanged, suggesting that this type of reaction is not responsible for the distribution of products.

Preparation of $H_2FeOs_3(CO)_{13}$. This cluster previously had been prepared by Moss and Graham[18] in 7% yield by the reaction of $H_2Os(CO)_4$ with $Fe_2(CO)_9$. We prepared $H_2FeOs_3(CO)_{13}$ from the reaction of $[Fe(CO)_4]^{2-}$ with $Os_3(CO)_{12}$ in a maximum yield of 9% by maintaining the reaction mixture at 46 °C for 3 h. Our decreased yield, relative to the synthesis of $H_2FeRu_3(CO)_{13}$, is accompanied by a much greater variety of products, including $H_2Os_3(CO)_{10}$ and $Fe_2Os(CO)_{12}$ in significant quantities. The product distribution for this reaction is extremely sensitive to reaction conditions. When the temperature was increased to that of refluxing THF, $H_2Os_3(CO)_{10}$ became the principal product with a yield of 28%. When the temperature was lowered to 28 °C and the reaction time reduced to 30 min, only a trace of $H_2Os_3(CO)_{10}$ was formed, and $H_2FeOs_3(CO)_{13}$ and $Fe_2Os(CO)_{12}$ were isolated in yields of 7 and 2%, respectively. Increasing the reaction time in the latter example to 10 h did not significantly alter the product distribution or yields. In all of these reactions, most of the Os is recovered as unreacted $Os_3(CO)_{12}$.

Attempted Preparation of $H_2Fe_3Os(CO)_{13}$. The synthesis of the unknown $H_2Fe_3Os(CO)_{13}$ was attempted by allowing $[Os(CO)_4]^{2-}$ to react with $Fe_3(CO)_{12}$. After refluxing the reaction mixture for 1 h and workup in the usual manner the only products isolated were $Fe_2Os(CO)_{12}$, $H_2Os_4(CO)_{13}$, and $H_4Os_4(CO)_{12}$. No evidence for formation of $H_2Fe_3Os(CO)_{13}$ was obtained.

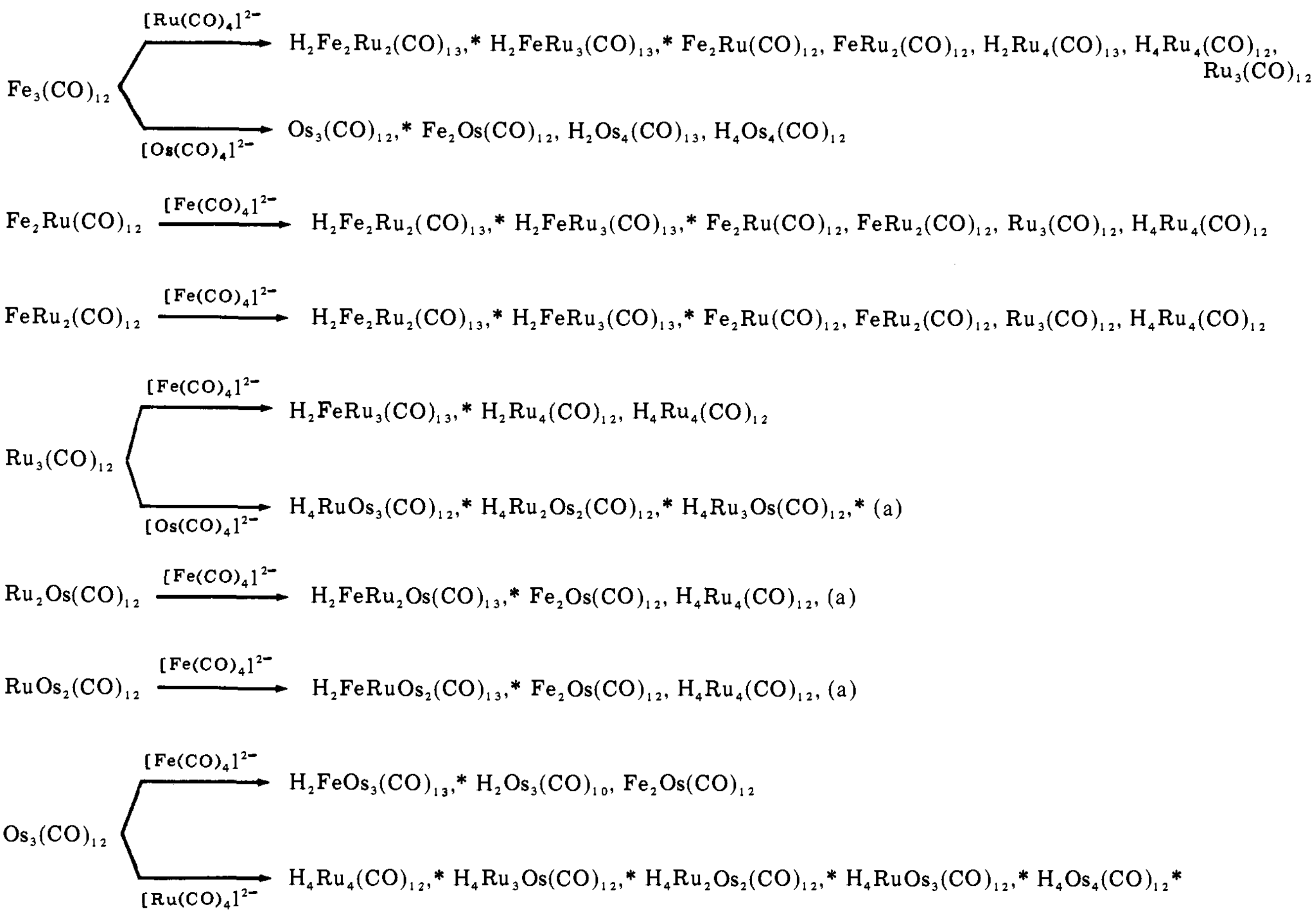
Preparation of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$. As a rigorous test of the adaptability of this synthetic method to designed synthesis, we set out to prepare $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$, the first examples of clusters comprised of three different transition metals. The logical approach was to add $[Fe(CO)_4]^{2-}$ to the mixed-metal trimers $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$. These trimers have been reported[19] to result from the pyrolysis of $Ru_3(CO)_{12}$ with $Os_3(CO)_{12}$. In our hands this pyrolysis gave a 1:2:2:1 mixture of Ru_3-, Ru_2Os-, $RuOs_2$-, and $Os_3(CO)_{12}$, as evidenced by CI mass spectroscopy, which could not be easily separated by liquid chromatography. In a typical cluster synthesis, a dried and deoxygenated THF solution of this trimer mixture was added to a THF solution of $Na_2[Fe(CO)_4]$ and refluxed for 75 min. After the usual workup, chromatography on silica gel afforded two principal fractions. The first consisted of unreacted trimers, a trace of $H_4Ru_4(CO)_{12}$, and $Fe_3(CO)_{12}$ formed from unreacted $[Fe(CO)_4]^{2-}$. The second fraction contained the tetrameric mixed-metal clusters from which orange-red $H_2FeRu_2Os(CO)_{13}$ and orange $H_2FeRuOs_2(CO)_{13}$ were eluted in that order in yields of 36 and 74%, respectively, based on the initial quantity of mixed-metal trimers. Confirmation of our hypothesis that the new clusters were formed by addition of $[Fe(CO)_4]^{2-}$ to $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$, rather than from random scrambling, comes from the observation that treatment of a 1:1 mixture of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with $[Fe(CO)_4]^{2-}$ under similar reaction conditions did not give either of the new species.

Discussion

Synthesis. The basic reaction approach employed in this study for the synthesis of tetrahedral clusters is the controlled addition of a carbonylmetalate to a metal trimer. The reactions examined and their resulting products are summarized in Scheme I. The principal products are indicated with an asterisk and specific yields are given in the Experimental Section. In general, the greatest success in preparing the desired tetrahedral cluster was realized when $[Fe(CO)_4]^{2-}$ was added to $Ru_3(CO)_{12}$, $Ru_2Os(CO)_{12}$, and $RuOs_2(CO)_{12}$. Although these reactions are obviously complex and the mechanism is at best poorly understood, the majority of our observations can be best rationalized by consideration of the following mechanistic path.

The first step in a reaction of this type must involve addition of the carbonylmetalate to a single atom of the metal trimer. Such addition can proceed by attack of the nucleophilic carbonylmetalate at a metal atom of the trimer or by attack at the electropositive carbon of a bound carbon monoxide, much as has been demonstrated for the reaction of nucleophiles such as OH^- and NR_3 with metal carbonyls.[20] Elimination of carbon monoxide would then yield a tetramer with structure **1**. Subsequent attack at the other metal atoms with consequent elimination of carbon monoxide would lead through **2** to a closed tetrahedral cluster **3**. This mechanistic pathway has

Scheme I



$$Fe_3(CO)_{12} \xrightarrow{[Ru(CO)_4]^{2-}} H_2Fe_2Ru_2(CO)_{13},^{*}\ H_2FeRu_3(CO)_{13},^{*}\ Fe_2Ru(CO)_{12},\ FeRu_2(CO)_{12},\ H_2Ru_4(CO)_{13},\ H_4Ru_4(CO)_{12},\ Ru_3(CO)_{12}$$

$$Fe_3(CO)_{12} \xrightarrow{[Os(CO)_4]^{2-}} Os_3(CO)_{12},^{*}\ Fe_2Os(CO)_{12},\ H_2Os_4(CO)_{13},\ H_4Os_4(CO)_{12}$$

$$Fe_2Ru(CO)_{12} \xrightarrow{[Fe(CO)_4]^{2-}} H_2Fe_2Ru_2(CO)_{13},^{*}\ H_2FeRu_3(CO)_{13},^{*}\ Fe_2Ru(CO)_{12},\ FeRu_2(CO)_{12},\ Ru_3(CO)_{12},\ H_4Ru_4(CO)_{12}$$

$$FeRu_2(CO)_{12} \xrightarrow{[Fe(CO)_4]^{2-}} H_2Fe_2Ru_2(CO)_{13},^{*}\ H_2FeRu_3(CO)_{13},^{*}\ Fe_2Ru(CO)_{12},\ FeRu_2(CO)_{12},\ Ru_3(CO)_{12},\ H_4Ru_4(CO)_{12}$$

$$Ru_3(CO)_{12} \xrightarrow{[Fe(CO)_4]^{2-}} H_2FeRu_3(CO)_{13},^{*}\ H_2Ru_4(CO)_{12},\ H_4Ru_4(CO)_{12}$$

$$Ru_3(CO)_{12} \xrightarrow{[Os(CO)_4]^{2-}} H_4RuOs_3(CO)_{12},^{*}\ H_4Ru_2Os_2(CO)_{12},^{*}\ H_4Ru_3Os(CO)_{12},^{*}\ (a)$$

$$Ru_2Os(CO)_{12} \xrightarrow{[Fe(CO)_4]^{2-}} H_2FeRu_2Os(CO)_{13},^{*}\ Fe_2Os(CO)_{12},\ H_4Ru_4(CO)_{12},\ (a)$$

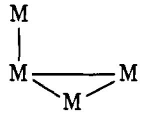
$$RuOs_2(CO)_{12} \xrightarrow{[Fe(CO)_4]^{2-}} H_2FeRuOs_2(CO)_{13},^{*}\ Fe_2Os(CO)_{12},\ H_4Ru_4(CO)_{12},\ (a)$$

$$Os_3(CO)_{12} \xrightarrow{[Fe(CO)_4]^{2-}} H_2FeOs_3(CO)_{13},^{*}\ H_2Os_3(CO)_{10},\ Fe_2Os(CO)_{12}$$

$$Os_3(CO)_{12} \xrightarrow{[Ru(CO)_4]^{2-}} H_4Ru_4(CO)_{12},^{*}\ H_4Ru_3Os(CO)_{12},^{*}\ H_4Ru_2Os_2(CO)_{12},^{*}\ H_4RuOs_3(CO)_{12},^{*}\ H_4Os_4(CO)_{12}{}^{*}$$

* principal product(s)
(a) plus unidentified product(s)

been proposed previously by Knight and Mays[10] to account for their synthesis of tetrahedral clusters from the reaction of $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ with metal trimers. Indeed, they actually isolated the intermediates $[ReOs_3(CO)_{16}]^-$ and $[ReOs_3(CO)_{15}]^-$, having probable structures **1** and **2**, enroute



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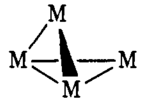

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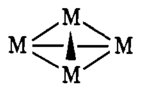
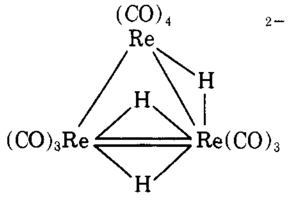


3

to $H_3ReOs_3(CO)_{13}$ of structure **3**. Further support for a mechanism of this type comes from recent studies of Ciani and co-workers[21-23] who prepared $[H_4Re_4(CO)_{15}]^{2-}$ with structure **1** which partially converted to $[H_4Re_4(CO)_{13}]^{2-}$ of structure **3** when heated. A second important product of this particular reaction was $[H_3Re_3(CO)_{10}]^{2-}$, with structure **4**, which resulted from apparent elimination of $[HRe(CO)_5]$.



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In the mechanism outlined above it is apparent that a crucial step involves formation of the first metal-metal bond. The probability of occurrence of this first addition depends on the nucleophilicity of the carbonylmetalate and on the relative strength of the metal-carbonyl bonds in the trimers. Greater nucleophilicity should lead to more rapid reaction with addition competing more effectively with other reaction paths, giving a greater yield of the desired product. The relative nucleophilicity of $[Fe(CO)_4]^{2-}$, $[Ru(CO)_4]^{2-}$, and $[Os(CO)_4]^{2-}$ has unfortunately not been determined. It has been shown, however, that $[CpFe(CO)_2]^-$ is an order of magnitude more nucleophilic than $[CpRu(CO)_2]^-$,[24] and Collman[25] has suggested that $[Fe(CO)_4]^{2-}$ is one of the strongest nucleophiles known, thereby suggesting that the nucleophilicity order is $[Fe(CO)_4]^{2-} > [Ru(CO)_4]^{2-}$. The apparent greater nucleophilicity of $[Fe(CO)_4]^{2-}$ could partially account for the greater success in the reactions which employed this anion.

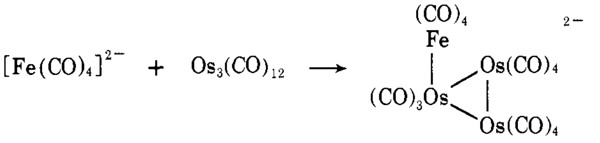
The second important factor which influences addition of the carbonylmetalate is the metal-carbonyl bond strength in the trimer. Obviously the stronger is the M-CO bond, the more difficult it will be to substitute CO by $[M(CO)_4]^{2-}$. A comparison of the reactivity of the $M_3(CO)_{12}$ trimers toward tertiary phosphines has led Chini[26] to suggest that the ordering of the M-CO bond strength is Os-CO > Ru-CO > Fe-CO. The relative strength of the Os-CO bond may account for the low yield of $H_2FeOs_3(CO)_{13}$ when compared to the 49% yield of $H_2FeRu_3(CO)_{13}$. At this point one might conclude that the order of trimer reactivity toward carbonylmetalate addition is $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$. This may indeed be the case, but it also appears to be the relative order of ease of reduction of the trimers, an unwanted reaction which gives rise to other products.

Examination of the reactions shown in Scheme I shows that many of the products arise through reduction of the trimers by the carbonylmetalate, as illustrated by the general reaction shown in eq 2.

$$M_3(CO)_{12} + [M'(CO)_4]^{2-} \rightarrow [M(CO)_4]^{2-} + M'_3(CO)_{12} + M'_nM_{3-n}(CO)_{12} \quad (2)$$

This reduction can produce mixed-metal trimers as well as carbonylmetalate exchange. The latter can then lead to the synthesis of unwanted tetrahedral clusters. For illustration, addition of $[Ru(CO)_4]^{2-}$ to $Fe_3(CO)_{12}$ gave $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $H_2Fe_2Ru_2(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, $H_2Ru_4(CO)_{13}$, and $H_4Ru_4(CO)_{12}$ rather than the desired $H_2Fe_3Ru(CO)_{13}$. The tetrameric ruthenium clusters $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ often appeared as products in the syntheses which employed $Ru_3(CO)_{12}$. This may result by initial reduction of a portion of the $Ru_3(CO)_{12}$, generating $[Ru(CO)_4]^{2-}$ which can then add to $Ru_3(CO)_{12}$ to give the Ru_4 clusters. The relative reducing power of these carbonylmetalates has not been measured nor has the trimer susceptibility toward reduction, and an accurate correlation with reactivity cannot be made. Several workers,[27] however, have shown that third-row $[Re(CO)_5]^-$ is much more reducing than first-row $[Mn(CO)_5]^-$. This is consistent with our experimental evidence which showed reduction products in greater abundance when $[Ru(CO)_4]^{2-}$ or $[Os(CO)_4]^{2-}$ were employed and suggests that these two carbonylmetalates are stronger reducing agents than is $[Fe(CO)_4]^{2-}$, which yielded relatively little reduction.

A notable exception to the latter, however, comes from the reaction of $[Fe(CO)_4]^{2-}$ with $Os_3(CO)_{12}$ which under some conditions gave $H_2Os_3(CO)_{10}$ as the principal product. We believe that formation of $H_2Os_3(CO)_{10}$ arises through initial production of $[FeOs_3(CO)_{15}]^{2-}$, of structure **1**, and this anion subsequently decomposes to yield $Fe(CO)_5$ and $[Os_3(CO)_{10}]^{2-}$, eq 3.



$$\longrightarrow Fe(CO)_5 + [Os_3(CO)_{10}]^{2-} \xrightarrow{H^+} H_2Os_3(CO)_{10} \quad (3)$$

Support for this proposal comes from the report of Ciani and co-workers[23] that when $[H_4Re_4(CO)_{15}]^{2-}$, of structure **1**, was heated it gave $H_3Re_3(CO)_{10}{}^{2-}$, **4**, with a structure analogous to that of $H_2Os_3(CO)_{10}$.

In summary, the success of this particular reaction approach for the designed synthesis of specific mixed-metal clusters depends on three important factors: the nucleophilicity of the carbonylmetalate, the strength of the M–CO bonds in the trimer, and the reducing power of the carbonylmetalate relative to the metal trimer. The reactions which employed $[Fe(CO)_4]^{2-}$ gave greater success, principally because of its apparent greater nucleophilicity and its relatively low reducing power. Likewise the reactions which employed $Os_3(CO)_{12}$ did not proceed to high-yield syntheses presumably because of the resistance of the Os–CO bond to substitution.

Spectroscopic Characterization. The clusters prepared in this study have been characterized principally by their infrared and mass spectra. Mass spectral data for $H_2Fe_2Ru_2(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$ are set out in Table I. The spectrum of each cluster exhibits the parent ion followed by ions corresponding to successive loss of all 13 carbonyls. Ions corresponding to loss of hydrogen in addition to CO were observed at the mass positions indicated in the table, and a fragment consisting of only the tetrametallic framework was prominent in each spectrum. For the purpose of identification, the mass position of the parent ion and a comparison of the observed isotopic distribution to the calculated distribution are of equal importance. Each metal possesses its own characteristic isotopic abundance. Hence the isotopic distribution is a very sensitive probe of the chemical formulation. This is particularly apparent with the Fe–Ru–Os mixed clusters and is illustrated by the distribution of the parent ion of $H_2FeRuOs_2(CO)_{13}$, shown in Figure 1. Chemical ionization mass spectroscopy, because it produces virtually no cluster fragmentation, is especially valuable for elucidation of the components of a mixture of clusters. CI mass spectroscopy, for example, was the only means by which the mixture of $H_4Ru_4(CO)_{12}$, $H_4Ru_3Os(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, $H_4RuOs_3(CO)_{12}$, and $H_4Os_4(CO)_{12}$ could be resolved. The EI mass spectrum showed an almost continuum of mass peaks below the parent ion of $H_4Os_4(CO)_{12}$.

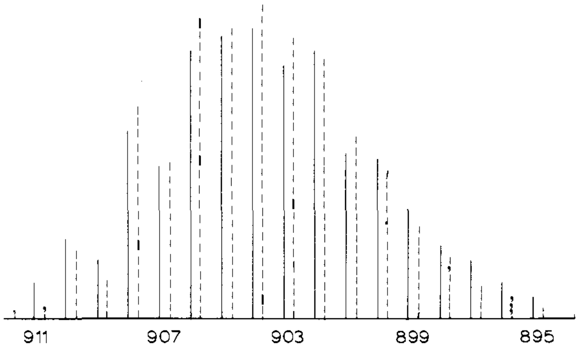
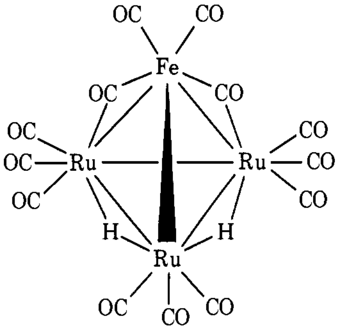


Figure 1. Comparison of observed (—) and calculated (- - -) isotopic distribution of the parent ion for $H_2FeRuOs_2(CO)_{13}$.

Infrared spectroscopy is particularly useful as a structural probe, principally through comparison of measured spectra to the spectra of clusters with known structures. In particular, the infrared spectrum of $H_2FeRu_3(CO)_{13}$ has been most useful for assigning structures to $H_2Fe_2Ru_2(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$. The crystal structure of $H_2FeRu_3(CO)_{13}$, as determined by Woodward and Gilmore,[28] is illustrated in **5** and shows a pseudotetrahedral arrangement of the metal atoms with two asymmetric, or semibridging, carbonyls. The Ru–C/Fe–C bond length ratio for these semibridging carbonyls is 1.29. The hydrides were not located in the structure but their positions was inferred from a comparison of Ru–Ru bond lengths. The infrared spectrum of this cluster is summarized in Table I and is shown in Figure 2a, and it exhibits both bridging and terminal carbonyl bands. The structurally analogous cluster $H_2Ru_4(CO)_{13}$ also possesses semibridging carbonyls with a bond length ratio of 1.22.[29] Although the structures of $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$ have not been determined by x-ray diffraction, available spectroscopic evidence points to a tetrahedral arrangement of the metals with each possessing three terminal carbonyls.[30]



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$H_2Fe_2Ru_2(CO)_{13}$. Mass spectral data for this cluster strongly support the formulation given which is fully consistent with the cluster 60 election rule. Its infrared spectrum is similar to that of $H_2FeRu_3(CO)_{13}$, especially in the bridging carbonyl region where it shows the same two-band pattern, and we propose that it has the structure shown in **6**. Structures in which

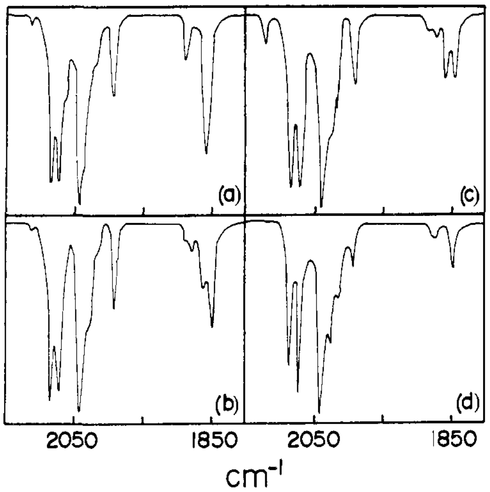
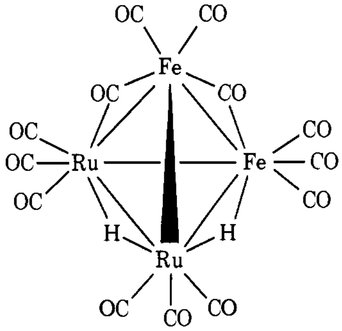


Figure 2. Carbonyl region infrared spectra of (a) $H_2FeRu_3(CO)_{13}$, (b) $H_2FeRu_2Os(CO)_{13}$, (c) $H_2FeRuOs_2(CO)_{13}$, and (d) $H_2FeOs_3(CO)_{13}$ measured in cyclohexane solution.



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two carbonyls bridge the Fe-Fe bond, as is common in many di- and triiron compounds, appear less likely for it is difficult to rationalize an electron precise arrangement of the remaining ligands.

$H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$. These two clusters have been characterized by a variety of spectroscopic means. Their mass spectra clearly indicate the formulation given and their infrared, NMR, and electronic absorption spectra strongly suggest structures similar to that of $H_2FeRu_3(CO)_{13}$. The electronic absorption spectra of the three clusters, Figure 3, are virtually identical, showing only a spectral blue shift as the osmium content increases. This similarity argues for a common pseudotetrahedral metal framework. The spectral shift is consistent with the notion that the bands are due to metal-metal transitions that increase in energy as the strength of the metal-metal bonds increases with incorporation of more third-row character. A similar shift is observed in the spectra of $Fe_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$.[12,26,31]

The carbonyl region infrared spectra of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ are shown in Figure 2 along with the spectra of $H_2FeRu_3(CO)_{13}$ and $H_2FeOs_3(CO)_{13}$ for comparison. All the spectra are virtually identical, especially in the terminal carbonyl region, and differ in the bridging region only by a splitting of the two bands of $H_2FeRu_3(CO)_{13}$ and $H_2FeOs_3(CO)_{13}$ into four bands in the spectra of the trimetallic clusters. The similarity of the infrared spectra strongly suggests a disposition of ligands similar to that of $H_2FeRu_3(CO)_{13}$. The splitting in the bridging carbonyl region is significant, however, and suggests the existence of structural isomers. The two bands in the bridging region in the spectrum of $H_2FeRu_3(CO)_{13}$ arise from symmetric, **7**, and asymmetric, **8**, motions of the bridging carbonyls. The asymmetric stretch

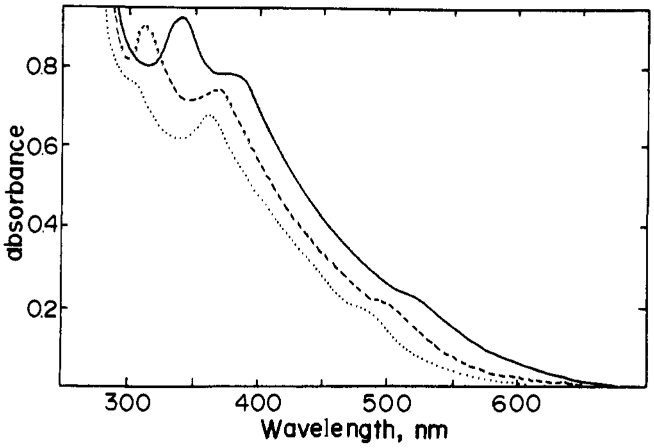
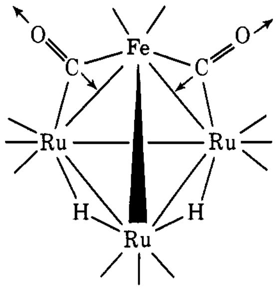


Figure 3. Electronic absorption spectra of $H_2FeRu_3(CO)_{13}$ (—), $H_2FeRu_2Os(CO)_{13}$ (- - -), and $H_2FeRuOs_2(CO)_{13}$ (· · ·) measured in hexane solution.



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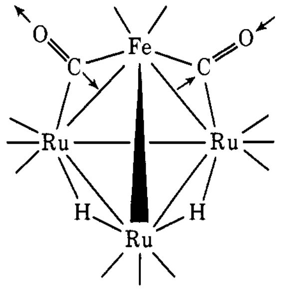

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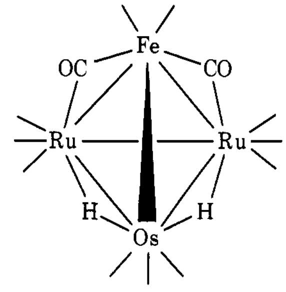
presumably gives rise to the more intense peak at lower energy. Substitution of an osmium for one ruthenium in $H_2FeRu_3(CO)_{13}$ gives $H_2FeRu_2Os(CO)_{13}$, which can exist in the two isomeric forms **9** and **10**. In **9** the two carbonyls both bridge



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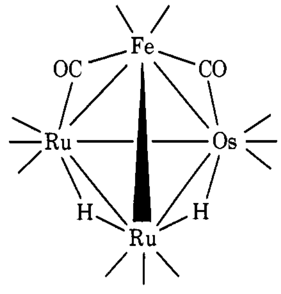

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Fe-Ru bonds but in **10** one carbonyl bridges an Fe-Ru bond and the other bridges an Fe-Os bond. Each isomer **9** and **10** should give rise to a two-band bridging carbonyl infrared pattern similar to that of $H_2FeRu_3(CO)_{13}$.[32] Our observation of four bands for $H_2FeRu_2Os(CO)_{13}$ in this region suggests that the sample is a mixture of isomers **9** and **10** and that the four bands result from combination of the two bands of each isomer.

This conclusion is further supported by the detailed analysis of the spectra shown in Figure 4. The energy separation between the asymmetric and symmetric vibrations is 28 cm^{-1} for $H_2FeRu_3(CO)_{13}$ and 27 cm^{-1} for $H_2FeOs_3(CO)_{13}$ with the vibrations of the latter occurring 7-8 cm^{-1} lower in energy. The four-band patterns observed for $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ can each be separated into two sets of two bands, each with the correct relative intensities for symmetric and asymmetric vibrations and separated by 26-28 cm^{-1}. Furthermore, from this analysis we can propose assignments for the particular isomers. Since the vibrations for $H_2FeO_3(CO)_{13}$ are lower in energy than the corresponding

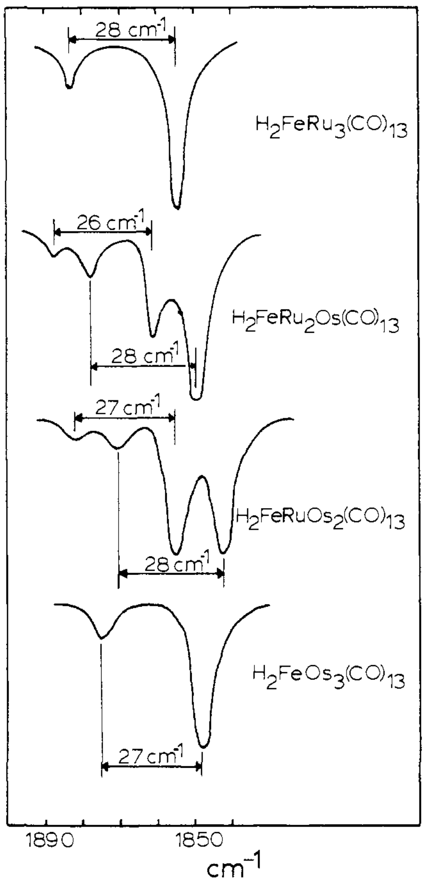

Figure 4. Detailed comparison of the bridging carbonyl infrared spectra of $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, $H_2FeRuOs_2(CO)_{13}$, and $H_2FeOs_3(CO)_{13}$.

vibrations of $H_2FeRu_3(CO)_{13}$, it seems reasonable to assign the lowest energy set of bands in the spectrum of $H_2FeRu_2Os(CO)_{13}$ to isomer **10** which has one CO bridging an Fe–Os bond and the higher energy set of bands to isomer **9** which has no Fe–Os carbonyl bridges. A similar argument can lead to assignment of the analogous isomers of $H_2FeRuOs_2(CO)_{13}$.

The existence of the structural isomers is further supported by ^1H NMR data. At 90 °C, $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ show sharp singlets at 29.0 and 29.7 ppm, respectively. These compare to the singlet of $H_2FeRu_3(CO)_{13}$ at 28.4 ppm and provide additional evidence for the structural similarity. As the temperature is lowered, the singlets in the spectra of the trimetallic clusters broaden, coalesce, and at −50 °C are resolved into the patterns expected for a mixture of two isomers. For example, the −50 °C spectrum of $H_2FeRu_2Os(CO)_{13}$ shows a pair of slightly split doublets at 28.9 ($J_{H-H} \sim 2.0$ Hz) and 29.2 ppm assignable to isomer **10** and a sharp singlet at 29.1 ppm assignable to **9**. The −50 °C spectrum of $H_2FeRuOs_2(CO)_{13}$ shows a similar pattern. The details and complete line-shape analysis of the variable temperature ^1H and ^{13}C NMR spectra of these clusters will be forthcoming in a future publication.

$H_4Ru_3Os(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, and $H_4RuOs_3(CO)_{12}$. Although these clusters could not be separated from each other or from the parent clusters $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$ by chromatography, their presence was clearly confirmed by CI mass spectroscopy which showed ion for each of the three. The infrared spectrum of the product mixture showed no bridging carbonyl vibrations but rather a broad terminal carbonyl pattern similar to that of $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$. It is likely that these three clusters have structures analogous to that proposed[14,30] for $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$. This is further supported by the electronic absorption spectra shown in Figure 5 in which the mixture shows a broad spectrum with a maximum between the maxima of $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$.

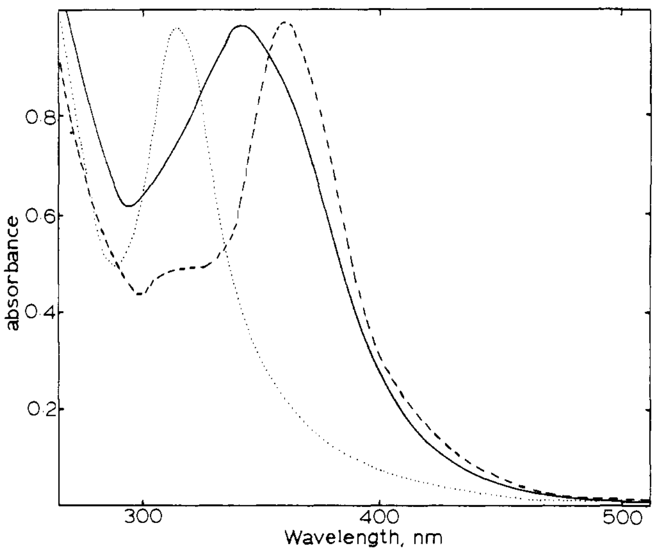

Figure 5. Electronic absorption spectra of $H_4Os_4(CO)_{12}$ (···), $H_4Ru_4(CO)_{12}$ (- - -), and the synthetic mixture of $H_4Ru_{4-n}Os_n(CO)_{12}$ (n = 1–4) (—) measured in hexane solution.

Summary

The syntheses reported herein clearly demonstrate that the synthetic approach of building tetrahedral clusters through the controlled addition of a carbonylmetalate to a closed metal trimer is of considerable importance for designed synthesis. There are limitations to these reactions, however, and the success of a particular synthesis is dependent on the nucleophilicity and the reducing power of the carbonylmetalate, as well as the metal–carbonyl bond strength of the trimer. We are currently evaluating the scope of this reaction approach and have found, for example, that it can be extended into the cobalt subgroup. We have recently prepared the new cluster $HCoRu_3(CO)_{13}$ by a reaction of this type. As will become apparent in future publications, these mixed-metal clusters are ideally suited for variable temperature NMR investigations into cluster dynamics.

Experimental Section

$Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Fe(CO)_5$, and $Na_2[Fe(CO)_4]\cdot 1.5C_4H_8O_2$, hereafter abbreviated $Na_2[Fe(CO)_4]$, were obtained from Alfa-Ventron Corp. and were used without further purification. The following compounds were prepared by published procedures: $Fe_3(CO)_{12}$,[33] $Fe_2Ru(CO)_{12}$,[12] $FeRu_2(CO)_{12}$,[12] $Ru_2Os(CO)_{12}$,[19] $RuOs_2(CO)_{12}$,[19] $H_4Ru_4(CO)_{12}$,[14] $H_2Ru_4(CO)_{13}$,[16] $H_4Os_4(CO)_{12}$,[14] $Na_2[Ru(CO)_4]$,[34] and $Na_2[Os(CO)_4]$.[35] Tetrahydrofuran (THF) was dried by distillation from $LiAlH_4$ under N_2, and unless otherwise stated all other solvents were used as obtained. Solutions of the reactants were prepared in an N_2-filled glove box, and all reactions were carried out under an N_2 atmosphere. Unless otherwise stated, an inert atmosphere was maintained up to the point of the first hexane extraction after acidification of the reaction mixture.

In the preparations described below the conditions given are those for the reaction which gave the highest yield of the desired cluster. The effects of varying the reaction conditions are discussed in the Results section.

Preparation of $H_2FeRu_3(CO)_{13}$. A 60-mL solution of $Ru_3(CO)_{12}$ (100 mg) was added dropwise over a 15-min period to a refluxing and stirred 120-mL THF solution of $Na_2[Fe(CO)_4]$ (70 mg). The color of the solution turned red upon initial addition and reflux was continued for 1 h. The solvent was immediately removed from the deep red solution by evaporation on a vacuum line. Hexane (60 mL), deoxygenated by an N_2 purge, was added to the brown residue and followed by addition of 40 mL of deoxygenated 20% H_3PO_4. The hexane layer remained colorless until addition of acid after which it became deep red-brown. The hexane layer was pipetted into another flask containing anhydrous $MgSO_4$, and the mixture was filtered, concentrated, and chromatographed on silica gel. Using hexane as the eluent three main fractions were obtained. The first was yellow and contained mainly $Ru_3(CO)_{12}$ and a small amount of $H_4Ru_4(CO)_{12}$. The second fraction was green $Fe_3(CO)_{12}$. The third fraction, which eluted very slowly with hexane and was usually stripped from the column with benzene, contained red $H_2FeRu_3(CO)_{13}$ (61 mg, 49% yield). In a few subsequent preparations a very small amount of $H_2Ru_4(CO)_{13}$ was produced and eluted between $Fe_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$.

Preparation of $H_2Fe_2Ru_2(CO)_{13}$. A. A 60-mL THF solution of $FeRu_2(CO)_{12}$ (80 mg) was added dropwise to a stirred 120-mL THF solution of $Na_2[Fe(CO)_4]$ (80 mg). The reaction mixture was stirred for 3 h at room temperature during which time the solution changed from orange to deep red. Workup of the reaction was conducted in a manner exactly analogous to that described in the preparation of $H_2FeRu_3(CO)_{13}$ except that increased precautions for maintaining anaerobic conditions were used. Chromatography of the hexane extract on silica gel using hexane as the eluent yielded four fractions. The first was yellow and contained $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. The green band that followed contained $Fe_3(CO)_{12}$ and $FeRu_2(CO)_{12}$. The third was a small purple band of $Fe_2Ru(CO)_{12}$, and the final fraction was red-brown containing both $H_2FeRu_3(CO)_{13}$ and $H_2Fe_2Ru_2(CO)_{13}$.

B. A 60-mL THF solution of $Fe_3(CO)_{12}$ (105 mg) was added dropwise to a stirred 120-mL THF solution of $Na_2[Ru(CO)_4]$ (100 mg). The mixture was stirred for 5 h at room temperature. After the usual workup, the dark-red hexane solution was chromatographed on silica gel using hexane as the eluent and gave four fractions. The first was yellow $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ (9 mg combined wt). The second was a greenish-brown layer containing $FeRu_2(CO)_{12}$ and $Fe_3(CO)_{12}$ and an unidentified compound (42 mg combined wt). The third fraction contained both purple $Fe_2Ru(CO)_{12}$ and red $H_2Ru_4(CO)_{13}$ (8 mg combined wt). Finally, the fourth fraction contained $H_2FeRu_3(CO)_{13}$, $H_2Fe_2Ru_2(CO)_{13}$, and a small amount of an unidentified product (27 mg combined wt).

C. A 60-mL THF solution of $Fe_2Ru(CO)_{12}$ was dropped slowly into a THF solution of $Na_2[Fe(CO)_4]$ at room temperature. An instantaneous reaction occurred and the solution of $Fe_2Ru(CO)_{12}$ changed to dark red. After addition was complete, no further color change occurred for 1.5 h. After the usual workup, chromatography on silica gel with hexane as the eluent yielded green $Fe_3(CO)_{12}$, purple $Fe_2Ru(CO)_{12}$, and a brown mixture of $H_2Fe_2Ru_2(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$, in that order.

Preparation of $H_4RuOs_3(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, and $H_4Ru_3Os(CO)_{12}$. A. A 60-mL THF solution of $Os_3(CO)_{12}$ was added dropwise to a refluxing and stirred 100-mL THF solution of $Na_2[Ru(CO)_4]$. The reaction mixture was stirred for 5 h at reflux, after which time the solvent was removed and hexane and 20% H_3PO_4 were added in the usual manner. These clusters exhibit low solubility in hexane, and it was necessary to extract most of the acidified material into diethyl ether. Chromatography of the product mixture on silica gel with hexane as the eluent yielded one broad yellow band which was shown by infrared, electronic absorption, and mass spectroscopy to contain $H_4Ru_4(CO)_{12}$, $H_4Ru_3Os(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, $H_4RuOs_3(CO)_{12}$, and $H_4Os_4(CO)_{12}$. In a subsequent reaction, the solution of $[Ru(CO)_4]^{2-}$ and $Os_3(CO)_{12}$ was stirred at room temperature for 1.5 h instead of at reflux. Upon chromatography of the diethyl ether extract of the acidified reaction mixture, a red band eluted after the yellow fraction, and a final small amount of an orange compound was eluted with benzene/hexane. The red band was $H_2Ru_4(CO)_{13}$ and the final band was probably $H_2Os_4(CO)_{13}$.

B. A 60-mL THF solution of $Ru_3(CO)_{12}$ was dropped slowly into a 120-mL THF solution of $Na_2[Os(CO)_4]$. The reaction mixture was refluxed for 1.5 h, after which time the color was deep red. After workup, chromatography on silica gel using hexane as the eluent gave two fractions. The first was yellow and consisted of $H_4Ru_3Os(CO)_{12}$, $H_4Ru_2Os_2(CO)_{12}$, and $H_4RuOs_3(CO)_{12}$. The second fraction was a red mixture of as yet unidentified compounds.

Preparation of $H_2FeOs_3(CO)_{13}$. A 60-mL solution of $Os_3(CO)_{12}$ (105 mg) was added dropwise to a 120-mL THF solution of $Na_2[Fe(CO)_4]$ (60 mg). The reaction mixture was stirred at 46 °C for 3 h after which time the solvent was removed. After the usual workup, chromatography on silica gel with hexane as the eluent yielded purple, green, light purple, and orange fractions corresponding to $H_2Os_3(CO)_{10}$ (18 mg), $Fe_3(CO)_{12}$, $Fe_2Os(CO)_{12}$ (8 mg), and $H_2FeOs_3(CO)_{13}$ (10 mg), respectively. Most of the osmium was recovered as unreacted $Os_3(CO)_{12}$ (65 mg).

Attempted Preparation of $H_2Fe_3Os(CO)_{13}$. A 60-mL THF solution of $Fe_3(CO)_{12}$ was added to a 120-mL THF solution of $Na_2[Os(CO)_4]$. The mixture was stirred at room temperature for 5 h after which time the solution was deep red. After the usual workup, chromatography yielded green, light purple, and yellow fractions corresponding to $Fe_3(CO)_{12}$, $Fe_2Os(CO)_{12}$, and $H_2Os_4(CO)_{13}$.

Preparation of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$. A 60-mL partially dissolved THF solution of $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ (535 mg combined wt, ~180 mg of $Ru_2Os(CO)_{12}$, ~180 mg of $RuOs_2(CO)_{12}$) was added dropwise into a 125-mL THF solution of $Na_2[Fe(CO)_4]$ (350 mg) at reflux. The reaction mixture was refluxed for an additional 2 h. After the usual workup, chromatography on silica gel using hexane as the eluent yielded two principal fractions. The first contained in order of elution a trace of purple $H_2Os_3(CO)_{10}$, a broad yellow band of trimers and $H_4Ru_4(CO)_{12}$, green $Fe_3(CO)_{12}$, and light purple $Fe_2Os(CO)_{12}$. The second fraction was a broad red-orange band containing $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$.

The final band was stripped from the column with benzene. The individual components were separated using the pressurized chromatography column described below. After separation, yields of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ were 64 (36%) and 143 mg (74%), respectively.

Anal. Calcd for $H_2FeRu_2Os(CO)_{13}$: C, 19.19; H, 0.24. Found: C, 19.32; H, 0.25. Calcd for $H_2FeRuOs_2(CO)_{13}$: C, 17.27; H, 0.22. Found: C, 17.28; H, 0.23 (Galbraith Laboratories).

Chromatography. One of the essential features in the preparations described above is chromatographic separation of the reaction mixtures. A typical atmospheric pressure column used to separate 100–200 mg of product was 2 × 50 cm in size and packed with silica gel (Davison chromatographic grade H, 60–200 mesh). The clusters were eluted with hexane or hexane/benzene mixtures and the progress of separation was monitored visually or by infrared spectroscopy of selected fractions.

Chromatography was also conducted using a 1.5 × 125 cm column packed with silica gel (Woelm, 0.032–0.063 mm) and pressurized to 60 psig. A much more efficient and convenient separation was obtained using this apparatus, and, for example, complete visual separation of the trimetal clusters was obtained.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer using 0.5-mm NaCl solution IR cells. Values reported are accurate to ± 2 cm^{-1}. Electron impact mass spectra were obtained using an AEI-MS9 spectrometer with a source voltage maintained at 70 eV. Probe temperatures varied between 100 and 200 °C depending on the cluster examined. Chemical ionization mass spectra were recorded on a Scientific Research Instrument Corp. Biospect mass spectrometer operated in the negative ion mode using methane as the reagent gas at a pressure of 1 Torr. The solids probe used was maintained at 100 °C. NMR spectra were obtained using either a Varian A-60A or a Jeol PS-100-FT Fourier transform spectrometer. Electronic absorption spectra were recorded on a Cary 17 spectrophotometer.

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The Infrared Laser Induced Isomerization of $Fe(CO)_4$. The First Non-Berry Pseudorotation

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Abstract: A combination of matrix isolation and IR laser induced photochemistry has been used to identify the intramolecular ligand exchange process occurring in the highly reactive C_{2v} molecule $Fe(CO)_4$, which has a structure similar to SF_4. UV photolysis of $Fe(CO)_5$, ~40% enriched with $^{13}C^{18}O$, in an Ar matrix at 20 K generated a statistical mixture of the different isomers of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$. These isomers were distinguishable by their different IR absorption bands in the "C–O stretching" region. Irradiation of the matrix with a cw CO IR laser at a frequency corresponding to the absorption of one particular isomer of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$ promoted the selective intramolecular rearrangement of this isomer, generating a nonstatistical distribution of $^{13}C^{18}O$. The permutational process occurring in this rearrangement could be identified directly from the interconversion of the three isomers of $Fe(^{12}C^{16}O)_2(^{13}C^{18}O)_2$. The laser-induced ligand exchange in $Fe(CO)_4$ involves a non-Berry pseudorotation (permutational mode h_3^{ww}), and differs from the thermal rearrangement of SF_4, which involves the more familiar Berry pseudorotation (permutational mode h_4^{ww}). This difference can be rationalized using an angular overlap MO model. The photophysics of the laser rearrangement is briefly discussed. A broad asymmetric red/near-IR absorption, $\bar{\nu}_{max}$ 13 000 cm^{-1}, is reported for $Fe(CO)_4$. Irradiation with light, 13 000–9000 cm^{-1}, is shown to cause nonselective isomerization of $Fe(^{12}C^{16}O)_{4-x}(^{13}C^{18}O)_x$. A possible mechanism is proposed for this near-IR isomerization.

Matrix isolation is a powerful method for studying intramolecular rearrangement processes.[1] The particular advantage of the technique is that molecules are held rigidly,[2] only rearranging when excited by either irradiating[1-3] or heating the matrix. In this paper we show how a combination of matrix isolation and IR laser induced photochemistry can be used to identify the rearrangement mode of the unstable C_{2v} molecule $Fe(CO)_4$.

The majority of selective IR laser induced reactions which have so far been reported occur in the gas phase. They involve individual molecules overcoming a high activation barrier by rapidly absorbing many low-energy photons, usually from a high-intensity (~10^8 W/cm^2) CO_2 laser beam. For example, the dissociation[4] of $^{32}SF_6$ requires absorption of approximately 40 photons[5] at ~948 cm^{-1}. On the other hand, the energy barriers for reactions in low-temperature matrices are often relatively low and can be overcome by individual molecules absorbing only one IR photon. We recently described[6] how a low-power cw CO laser (~1 W/cm^2 at ~1925 cm^{-1}) promoted the reaction between $Fe(CO)_4$ and CH_4 at 20 K.

$$Fe(CO)_4 + CH_4 \xrightarrow{\text{IR laser}} Fe(CO)_4CH_4$$

The reaction was remarkably selective. Using a sample of $Fe(CO)_4$ enriched with ^{13}CO it was possible to react selectively isomers of $Fe(CO)_{4-x}(^{13}CO)_x$ which differed only in the positions of the ^{13}CO groups around the central Fe atom. It was this result which prompted the present study.

$Fe(CO)_4$ can be prepared[7] in an Ar matrix at 20 K by UV photolysis of $Fe(CO)_5$.

$$Fe(CO)_5 \underset{\text{Nernst}}{\overset{\text{UV}}{\rightleftharpoons}} Fe(CO)_4 + CO$$

The $Fe(CO)_5$ is rapidly regenerated when the matrix is exposed to the unfiltered radiation from the Nernst glower of the IR spectrometer.[7] If, however, the $Fe(CO)_4$ is produced by *prolonged* UV photolysis of $Fe(CO)_5$, the reaction is only partially reversed by the Nernst glower.[7] There is substantial IR evidence[1,7] to suggest that this is the result of the photoejected CO molecule diffusing away from the $Fe(CO)_4$ fragment during the prolonged photolysis. The present experiments have been performed using this "irreversible" $Fe(CO)_4$.

The structure of $Fe(CO)_4$ was determined from the IR spectrum of the $^{13}C^{16}O$ enriched compound.[8] It has a C_{2v} structure, similar to SF_4, with bond angles of ~145 and ~120°. These bond angles are close to the angles 135 and 110° predicted by Burdett[9] for the minimum energy configuration of $Fe(CO)_4$ in the *lowest triplet state*. Very recent experiments

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