Acc. Chem. Res. **1980**, *13*, 469–476

Summary

We have evolved a useful and apparently general method of creating a quaternary carbon atom in a six-membered ring, surrounded by functionalized groups. The appearance of such a system in a large and diverse number of natural products or their synthetic precursors, such as steroids, tetracyclic diterpenoids, trichothecanes,[42] compounds related to pentalenolactone,[43] picrotoxin,[44] the erythromycins,[45] spirocycles,[27,28] aspidosperma alkaloids,[46] and many others,[26] makes this a very exciting discovery indeed. We are currently involved in applying our new methodology to the synthesis of a number of these targets.[47]

I am grateful to Professor A. J. Birch for introduction to this interesting area of chemistry and to the Science Research Council and Cancer Research Campaign for financial support.

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Synthesis, Molecular Dynamics, and Reactivity of Mixed-Metal Clusters

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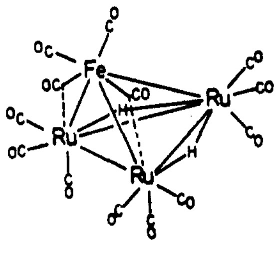
Transition-metal cluster compounds are currently under intense scrutiny, largely due to their numerous potential applications in catalysis. Clusters can function as homogeneous catalysts in which special reactivity features may occur as a result of adjacent metals[1–3] or may serve as "storehouses" for the release of catalytically active fragments. Clusters are also being employed to model substrate bonding and the reactions of substrates on metal surfaces.[4–6] Furthermore, they are useful precursors for the preparation of novel heterogeneous catalysts; they are absorbed onto a catalytic support and then decomposed to yield small metal crystallites.[7,8]

Mixed-metal clusters such as $H_2FeRu_3(CO)_{13}$ (1) and $H_3CoRu_3(CO)_{12}$ (2) are especially interesting in these regards.[9] Mixed-metal clusters have been successfully employed for the preparation of bimetallic heterogeneous catalysts.[7] From a chemical viewpoint, mixed-metal dimers and clusters should show unique reactivity features as a result of combining the different reactivity properties of the constituent metals. For example, dimers and clusters which have early–late transition-metal combinations (e.g., Zr with Rh) are expected to be able to polarize and activate substrates such as CO. From a mechanistic viewpoint, the low symmetry which mixed-metal clusters inherently possess can allow a differentiation of specific sites of reactivity and can provide important insight into mechanistic detail. Mixed-metal clusters are also ideally suited for studies of fluxional processes in which the carbonyls, hydrides, and even the metals themselves undergo rearrangement. In such clusters, the majority of ligands are in chemically nonequivalent positions and are thus distinguishable by NMR spectroscopy.



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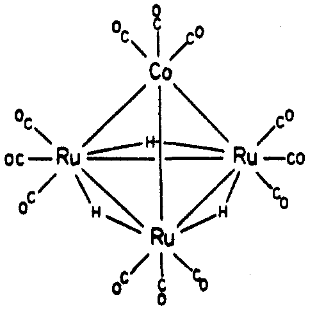

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Mixed-metal carbonyl clusters have been under study in this laboratory from several viewpoints. We have been interested in developing better methods for the synthesis of mixed-metal clusters and have more recently been evaluating features of their reactivity with a variety of substrates. We have chosen to concentrate our reactivity studies on one particular cluster, $H_2FeRu_3(CO)_{13}$ (1) and to examine its reactivity in as much detail as possible. It has been our aim to fully understand the kinds of chemical reactions which this cluster

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Table I
Synthesis of Mixed-Metal Tetranuclear Clusters via the Combination of a Carbonylmetalate with a Closed-Metal Carbonyl Trimer

tetranuclear cluster	carbonylmetalate	trimer	yield, %	ref
$H_2FeRu_3(CO)_{13}$	$[Fe(CO)_4]^{2-}$	$Ru_3(CO)_{12}$	49–55	10
$H_2FeRu_2Os(CO)_{13}$	$[Fe(CO)_4]^{2-}$	$Ru_2Os(CO)_{12}$	36	10
$H_2FeRuOs_2(CO)_{13}$	$[Fe(CO)_4]^{2-}$	$RuOs_2(CO)_{12}$	74	10
$H_2FeOs_3(CO)_{13}$	$[Fe(CO)_4]^{2-}$	$Os_3(CO)_{12}$	9	10
$H_2Fe_2Ru_2(CO)_{13}$	$[Fe(CO)_4]^{2-}$	$Fe_2Ru(CO)_{12}$		10
$[HFeRu_3(CO)_{13}]^-$	$[HFe(CO)_4]^{2-}$	$Ru_3(CO)_{12}$	47	16
$H_2Ru_4(CO)_{13}$	$[Ru(CO)_4]^{2-}$	$Ru_3(CO)_{12}$		*a*
$H_4Ru_xOs_{4-x}(CO)_{12}$	$[Os(CO)_4]^{2-}$	$Ru_3(CO)_{12}$		10
$(x = 1-3)$	$[Ru(CO)_4]^{2-}$	$Os_3(CO)_{12}$		10
$HCoRu_3(CO)_{13}$	$[Co(CO)_4]^-$	$Ru_3(CO)_{12}$	63	11
$HCoRu_2Os(CO)_{13}$	$[Co(CO)_4]^-$	$Ru_2Os(CO)_{12}$	38	11
$HCoRuOs_2(CO)_{13}$	$[Co(CO)_4]^-$	$RuOs_2(CO)_{12}$	25	11
$[CoRu_3(CO)_{13}]^-$	$[Co(CO)_4]^-$	$Ru_3(CO)_{12}$	95	11
$[CoOs_3(CO)_{13}]^-$	$[Co(CO)_4]^-$	$Os_3(CO)_{12}$	33	21
$[CoFeRu_2(CO)_{13}]^-$	$[Co(CO)_4]^-$	$FeRu_2(CO)_{12}$	47	11
$[CoFe_2Ru(CO)_{13}]^-$	$[Co(CO)_4]^-$	$Fe_2Ru(CO)_{12}$	16	11
$[CoFe_3(CO)_{13}]^-$	$[Co(CO)_4]^-$	$Fe_3(CO)_{12}$	18	11

[a] Gladfelter, W. L.; Geoffroy, G. L. Unpublished results.

undergoes as well as their mechanisms, with the expectation that this knowledge will prove applicable to other cluster systems.

Directed Synthesis of Mixed-Metal Clusters

Studies of mixed-metal clusters have been hampered by their relative lack of availability. Most mixed-metal clusters have been prepared by nongeneral methods in which chance has played an important role, and often their yields have been quite low.[9] We initially set out to develop synthetic methods which would allow the directed synthesis of mixed-metal clusters, ideally in high yield.

Our approach has been to use monomeric organometallic complexes as building blocks. Thus a dimer would be formed by the appropriate combination of two monomers, a trimer by the addition of a monomeric complex to a preformed dimer, a tetramer through the addition of a monomer to a preformed trimer, etc. Most of our research to date has focused on the latter step. In particular, we have found that the addition of a carbonylmetalate to a closed metal carbonyl trimer is a valuable synthetic method for certain mixed-metal clusters, as illustrated in eq 1 for the preparation of $H_2FeRu_3(CO)_{13}$.

$$Ru_3(CO)_{12} + [Fe(CO)_4]^{2-} \xrightarrow[\text{THF}\atop 2\text{ h}]{\Delta} \xrightarrow{H^+} \underset{(49\%)}{H_2FeRu_3(CO)_{13}} \tag{1}$$

We realized the possibility of this approach upon considering the outcome of a photochemical experiment in which we were attempting to synthesize $H_2Ru(CO)_4$ via photolysis of $Ru_3(CO)_{12}$ under an H_2 atmosphere. Regardless of how these experiments were conducted, the formation of $H_2Ru_4(CO)_{13}$ was always observed. In attempting to rationalize the formation of this compound, we postulated the combination of "$Ru(CO)_4$" or $H_2Ru(CO)_4$ with $Ru_3(CO)_{12}$. It was a simple extension to substitute a carbonylmetalate as a more powerful nucleophile. The first reaction subsequently examined is that shown in eq 1 which gave a good yield of $H_2FeRu_3(CO)_{13}$.[10]

This reaction was then extended to the preparation of mixed-metal clusters containing three different transition metals via the reactions shown in eq 2 and 3. These gave moderate to good yields of the new

$$Ru_2Os(CO)_{12} + [Fe(CO)_4]^{2-} \xrightarrow{\Delta} \xrightarrow{H^+} \underset{(36\%)}{H_2FeRu_2Os(CO)_{13}} \tag{2}$$

$$RuOs_2(CO)_{12} + [Fe(CO)_4]^{2-} \xrightarrow{\Delta} \xrightarrow{H^+} \underset{(74\%)}{H_2FeRuOs_2(CO)_{13}} \tag{3}$$

clusters $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ which at the time of their preparation were the first examples of clusters with three different metals in their framework. Since then other trimetallic clusters have been prepared[11-14] and, in a truly elegant study, Richter and Vahrenkamp[14] prepared and characterized the first tetrametallic cluster, $MoWFeCo(\eta\text{-}C_5H_5)_2(CO)_7(\mu\text{-}AsMe_2)(\mu\text{-}S)$. After our initial studies we discovered that Knight and Mays[15] had earlier examined similar reactions of the $M_3(CO)_{12}$ (M = Fe, Ru, Os) trimers with $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ and had prepared a series of mixed Mn/Ru, Mn/Os, Re/Ru, and Re/Os clusters.

Table I lists the various tetranuclear clusters that have been prepared in our laboratory via the reaction of a carbonylmetalate with a closed metal carbonyl trimer.[10,11,16] The success of this reaction approach is highly dependent on the particular trimer/carbonylmetalate combination employed. If the carbonylmetalate is too strongly reducing, condensation rather than addition occurs and the desired tetranuclear cluster is not isolated in good yield, if at all. In general, reactions which employed $Fe_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$, and

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Table II
Fragmentation of Mixed-Metal Tetranuclear Clusters with Carbon Monoxide at 1-atm Pressure[22]

initial cluster	fragmentation products	typical conditions
$HCoRu_3(CO)_{13}$	$Ru_3(CO)_{12}$, $Ru(CO)_5$, $Co_2(CO)_8$[a]	25 °C, 1 h, hexane, 100% convn
$H_2Ru_4(CO)_{13}$	$Ru_3(CO)_{12}$, $Ru(CO)_5$, H_2	25 °C, 1 h, hexane, 30% convn
$[CoRu_3(CO)_{13}]^-$	$Ru_3(CO)_{12}$, $[Co(CO)_4]^-$	25 °C, 96 h, CH_2Cl_2, 100% convn
$[HFeRu_3(CO)_{13}]^-$	$[HRu_3(CO)_{11}]^-$, $Fe(CO)_5$	25 °C, 96 h, THF, 90% convn
$H_2FeRu_3(CO)_{12}(PMe_2Ph)$	$FeRu_2(CO)_{11}(PMe_2Ph)$, $Ru(CO)_5$ $Ru_3(CO)_{11}(PMe_2Ph)$ (trace), H_2	25 °C, 185 h, CH_2Cl_2, 40% convn
$H_2FeRu_3(CO)_{13}$	$Ru_3(CO)_{12}$, $Fe(CO)_5$, H_2	50 °C, 42 h, hexane, 10% convn
$H_2FeRu_2Os(CO)_{13}$	$Ru_2Os(CO)_{12}$, $Fe(CO)_5$, H_2	25 °C, 16 days, hexane, 5% convn
$H_2FeRuOs_2(CO)_{13}$	$RuOs_2(CO)_{12}$, $Fe(CO)_5$, H_2	50 °C, 24 days, hexane, 5% convn

[a] Plus other unidentified Co-containing products.

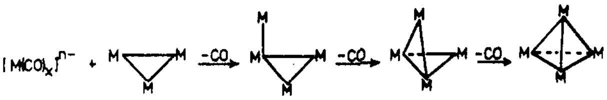
$FeRu_2(CO)_{12}$ gave poor results because of the ease with which these trimers can be reduced and fragmented.[10,11] Likewise, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ and $[V(CO)_6]^-$ have not proven useful in these syntheses since they are strong reducing agents.

Syntheses employing $Ru_3(CO)_{12}$ have worked extremely well. Perhaps the most impressive synthesis of any mixed-metal cluster yet reported comes from the combination of $[Co(CO)_4]^-$ with $Ru_3(CO)_{12}$ to give a nearly quantitative yield of $[CoRu_3(CO)_{13}]^-$ (eq 4).[11]

$$[Co(CO)_4]^- + Ru_3(CO)_{12} \xrightarrow{\Delta} \underset{(>95\%)}{[CoRu_3(CO)_{13}]^-} \quad (4)$$

The success of this reaction is further enhanced by the low reducing power of $[Co(CO)_4]^-$.

Although the exact mechanism of the carbonylmetalate/trimer reaction is unknown, it likely involves initial attack of the nucleophilic carbonylmetalate on either an electropositive carbon of a bound carbon monoxide or directly on one of the trimer metal atoms. In either case, a sequence of reactions such as that shown in eq 5 must occur, and each of these steps involves loss of CO.



(5)

In essence, as the synthesis proceeds, metal–carbonyl bonds in the trimer are replaced by metal–metal bonds. Since Os–CO bonds are considerably stronger than the Ru–CO and Fe–CO bonds in their respective trimers,[17] reactions employing $Os_3(CO)_{12}$ have not worked as well as those with $Ru_3(CO)_{12}$. However, in at least one case we have found that the reaction of a carbonylmetalate with $Os_3(CO)_{12}$ can be photoassisted. Although little or no reaction of $[Co(CO)_4]^-$ occurs with $Os_3(CO)_{12}$ upon heating, irradiation with 366-nm light gives a respectable yield of the desired $[CoOs_3(CO)_{13}]^-$ cluster (eq 6).[18] This reaction apparently proceeds via photoinduced loss of CO from $Os_3(CO)_{12}$, making it more susceptible to $[Co(CO)_4]^-$ attack.

$$[Co(CO)_4]^- + Os_3(CO)_{12} \xrightarrow[366\text{ nm}]{h\nu} \underset{(33\%)}{[CoOs_3(CO)_{13}]^-} \quad (6)$$

A few syntheses directed toward the preparation of pentanuclear clusters via the addition of a carbonylmetalate to a tetranuclear cluster have been attempted. Although the desired objective was not achieved in these studies, several interesting reactions occurred. In an attempt to prepare pentanuclear clusters with an $FeCo_3C$ core, $[Fe(CO)_4]^{2-}$ was added to a series of $RCCo_3(CO)_9$ clusters. These reactions gave, after protonation, the corresponding series of $RCFeCo_2H(CO)_9$ clusters (eq 7).[19] Likewise, addition of carbonylmetalates to a series of preformed mixed-metal tetranuclear clusters gave the metal-exchange reactions illustrated in eq 8–10 rather than the desired M_5 clusters.[20] We suspect that reactions 7–10 proceed through the desired pentanuclear intermediates but that these are not sufficiently stable to allow isolation and that instead degradation to the observed tetranuclear clusters occurs.

$$[Fe(CO)_4]^{2-} + RCCo_3(CO)_9 \xrightarrow{\Delta} \xrightarrow{H^+} RCFeCo_2H(CO)_9 \quad (7)$$

$$H_2FeRu_3(CO)_{13} + [PPN][Co(CO)_4] \rightarrow [PPN][CoFeRu_2(CO)_{13}] \quad (8)$$

$$H_2Ru_4(CO)_{13} + [Co(CO)_4]^- \rightarrow \xrightarrow{H^+} H_3CoRu_3(CO)_{12} \quad (9)$$

$$HCoRu_3(CO)_{13} + [Fe(CO)_4]^{2-} \rightarrow \xrightarrow{H^+} H_2FeRu_3(CO)_{13} \quad (10)$$

Reactivity of $H_2FeRu_3(CO)_{13}$ and Related Mixed-Metal Clusters

With Carbon Monoxide. Since transition-metal cluster compounds are currently being examined as catalysts for a variety of reactions involving carbon monoxide,[21] it is essential that the basic reactivity patterns of clusters with CO be understood. We thus set out to examine the reactions of a series of mixed-metal clusters with CO with the aim of understanding the types of reactions that occur as well as their mechanistic course. It was our finding that most of the clusters studied fragment in the presence of CO, under rather mild conditions (1 atm of CO, 25–50 °C), generally to produce monomeric and trimeric products (Table II and eq 11–13).[22] Despite the fact that nu-

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$$H_2FeRu_3(CO)_{13} + CO \xrightarrow[42\ h,\ 10\%\ conv]{50\ °C} Ru_3(CO)_{12} + Fe(CO)_5 + H_2 \quad (11)$$

$$[HFeRu_3(CO)_{13}]^- + CO \xrightarrow[THF,\ 90\%\ conv]{25\ °C,\ 96\ h} [HRu_3(CO)_{11}]^- + Fe(CO)_5 \quad (12)$$

$$[CoRu_3(CO)_{13}]^- + CO \xrightarrow[CH_2Cl_2,\ 100\%\ conv]{25\ °C,\ 96\ h} Ru_3(CO)_{12} + [Co(CO)_4]^- \quad (13)$$

merous product distributions are possible, especially for the clusters which possess three different metals, fragmentation generally proceeds to give a specific trimer/monomer pair. $H_2FeRu_2Os(CO)_{13}$, for example, reacts to give only $Ru_2Os(CO)_{12}$ and none of the $RuOs_2$, $FeRu_2$, or FeRuOs trimers; furthermore, $Fe(CO)_5$ is the only monomeric product observed from this reaction.

The reactivity of a particular cluster toward CO is greatly dependent on its metal composition (Table II). $HCoRu_3(CO)_{13}$, for example, shows complete fragmentation in <1 h when stirred at 25 °C, whereas only 10% fragmentation is observed for $H_2FeRu_3(CO)_{13}$ when maintained at 50 °C for 42 h, both under 1 atm of CO pressure. The clusters become more resistant to fragmentation with increasing third-row metal content, as illustrated by the data given in Table II for $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$, presumably because of the greater strength of metal–metal bonds which involve third-row metals.[17]

In order to define the mechanistic course of these reactions, a series of kinetic studies on $H_2FeRu_3(CO)_{13}$ and $H_2Ru_4(CO)_{13}$ was undertaken. The rate law obtained for fragmentation of both clusters is given in eq 14.[22] Specific rate constants and activation parameters

$$-d[\text{cluster}]/dt = \{k_1 + k_2[CO]\}[\text{cluster}] \quad (14)$$

are listed in Table III. Under the conditions of our experiments, the first-order term is negligible and the reactions are essentially second order overall.

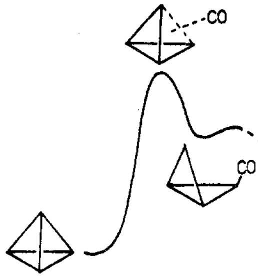
The mechanism which is most consistent with this rate law and with the activation parameters involves association of CO with the intact cluster concerted with cleavage of one of the metal–metal bonds. The latter is necessary since the initial cluster is coordinatively saturated. The activation profile envisaged for this process is shown in Scheme I. A comparison of the activation parameters indicates that the relative degree of CO association and M–M bond cleavage in the transition state varies from $H_2Ru_4(CO)_{13}$ to $H_2FeRu_3(CO)_{13}$. The larger value of $\Delta H^{\ddagger}$ (20.0 kcal/mol) and the less negative values of $\Delta S^{\ddagger}$ (−25.4 cal/(mol K)) imply that in the transition state M–CO bond formation occurs to a lesser extent for $H_2FeRu_3(CO)_{13}$ than for $H_2Ru_4(CO)_{13}$ ($\Delta H^{\ddagger}$ = 12.5 kcal/mol; $\Delta S^{\ddagger}$ = −36.6 cal/(mol K)). This is consistent with the notion that Ru is larger than Fe and there is more room on the surface of intact $H_2Ru_4(CO)_{13}$ to accommodate the incoming CO than in $H_2FeRu_3(CO)_{13}$. The relative degree of CO association with M–M bond cleavage in the transition state will surely vary with the metal composition of the cluster and may account for the greatly different reactivities observed for the compounds listed in Table II.

Table III
Kinetic Parameters for the Reaction of $H_2FeRu_3(CO)_{13}$ and $H_2Ru_4(CO)_{13}$ with CO[a]

cluster	temp, °C	k_1, s^{-1}	k_2, M^{-1} s^{-1}	$\Delta H^{\circ\ddagger}$, kcal/mol	$\Delta S^{\circ\ddagger}$, cal/(mol K)
$H_2FeRu_3(CO)_{13}$	70	6×10^{-7}	3.0×10^{-4}	20.0	−25.4
$H_2Ru_4(CO)_{13}$	30	0	5.7×10^{-3}	12.5	−36.6

[a] [Cluster] = 6×10^{-4} M, *n*-heptane solution; $[CO]_{70\,°C} = 1.42 \times 10^{-2}$ M, $[CO]_{30\,°C} = 1.25 \times 10^{-2}$ M.

Scheme I



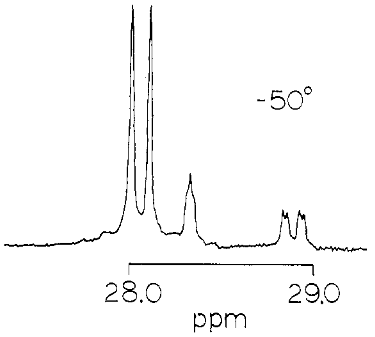


Figure 1. ^{1}H NMR spectrum at −50 °C of $H_2FeRu_3(CO)_{12}(PMe_2Ph)$ in $CDCl_3$ solution.

With Tertiary Phosphines and Phosphites.

$H_2FeRu_3(CO)_{13}$ reacts with a series of tertiary phosphine and phosphite ligands to yield mono- and disubstituted clusters (eq 15).[23] These substitution reactions proceed cleanly and give only trace amounts of side products unless the reactions are carried out under forcing conditions. The ^{1}H and ^{31}P NMR spectra of these derivatives have allowed a determination of specific sites which the PR_3 ligands occupy. Figure 1, for example, shows the −50 °C ^{1}H NMR spectrum of $H_2FeRu_3(CO)_{12}(PMe_2Ph)$ which indicates the presence of two substitutional isomers. The intense doublet at τ 28.07 ppm ($J_{P\text{-}H}$ = 10.3 Hz) is attributed to the two equivalent hydrogens of the C_s isomer shown below while the pseudotriplet at τ 28.35 ppm and the doublet of doublets at τ 28.93 ppm ($J_{P\text{-}H}$ = 9.7 Hz; $J_{H\text{-}H}$ = 2.6 Hz) are assigned to H_A and H_B, respectively, of the C_1 isomer.

$$H_2FeRu_3(CO)_{13} + PR_3 \rightarrow H_2FeRu_3(CO)_{12}(PR_3) + H_2FeRu_3(CO)_{11}(PR_3)_2 \quad (15)$$

$$PR_3 = PMe_3, PMe_2Ph, PMePh_2, PEt_2Ph, PPh_3, P(i\text{-}Pr)_3, P(OMe)_3, P(OEt)_3, P(OEt)_2Ph$$

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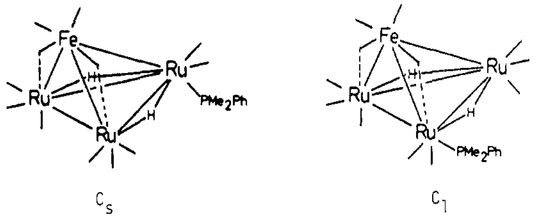
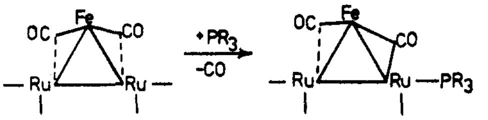
(23) Fox, J. R.; Gladfelter, W. L.; Wood, T. G.; Smegal, J. A.; Foreman, T. K.; Geoffroy, G. L. *J. Am. Chem. Soc.*, submitted for publication.



Similar substitutional isomers result for the other monosubstituted derivatives, but the relative ratios of these two isomers depend on both the ligand's size and its basicity as illustrated by the data given in Table IV.[23,24] With large ligands such as PPh_3 and $P(i\text{-}Pr)_3$, substitution occurs to give only the C_s isomer regardless of the ligand basicity. Presumably there is less steric hindrance in this substitution site. For smaller ligands, basicity becomes the controlling factor and the C_1 isomer becomes more abundant as the basicity of the ligand increases. This effect is best illustrated by comparing the ligands PMe_3 and $P(OMe)_3$ (Table IV). The former is highly basic and it gives a $C_1 \rightleftarrows C_s$ equilibrium constant of 0.4 whereas the smaller but less basic $P(OMe)_3$ gives $K_{C_1 \rightleftarrows C_s} = 10$.

The increased abundance of the C_1 isomer with increased ligand basicity presumably occurs because the semibridging carbonyl attached to the substituted metal can become more full-bridging and remove the excess electron density released by the basic phosphine.



Consistent with this hypothesis is the increased downfield chemical shift of one of the bridging carbonyls in the ^{13}C NMR spectrum of $H_2FeRu_3(CO)_{12}(PMe_2Ph)$ (δ 249) compared to $H_2FeRu_3(CO)_{13}$ (δ 229) and also the shift to lower energy of the bridging carbonyl infrared absorption in the C_1 isomer ($\sim$1806 cm^{-1} vs. $\sim$1850 cm^{-1}).

A kinetic study of the reaction of PPh_3 with $H_2FeRu_3(CO)_{13}$ gave the rate equation shown in eq 16 with

$$-d[H_2FeRu_3(CO)_{13}]/dt = k_1[H_2FeRu_3(CO)_{13}] \quad (16)$$

$\Delta H^{\circ\ddagger} = 25.7$ kcal/mol, $\Delta S^{\circ\ddagger} = 4.8$ cal/(mol K), and $k_1 = 6.96 \times 10^{-4}\ s^{-1}$ at 50 °C.[23] The zero-order dependence on $[PPh_3]$, the positive value of $\Delta S^{\circ\ddagger}$, and the decrease in the reaction rate under a CO atmosphere all imply a dissociative mechanism in which the rate-determining step is loss of CO from $H_2FeRu_3(CO)_{13}$ (eq 17). This

$$H_2FeRu_3(CO)_{13} \underset{k_2}{\overset{k_1\ (\text{slow})}{\rightleftarrows}} H_2FeRu_3(CO)_{12} + CO \quad (17)$$

would generate unsaturated $H_2FeRu_3(CO)_{12}$ that could rapidly add PPh_3 to give the monosubstituted derivative (eq 18).

$$H_2FeRu_3(CO)_{12} + PPh_3 \xrightarrow[\text{fast}]{k_3} H_2FeRu_3(CO)_{12}(PPh_3) \quad (18)$$

With Alkynes. Isomeric products also result from the reaction of $H_2FeRu_3(CO)_{13}$ with internal alkynes (eq 19).[25]

$$H_2FeRu_3(CO)_{13} + RC{\equiv}CR' \rightarrow H_2 + CO + \underset{\text{(isomers)}}{FeRu_3(CO)_{12}(RC{\equiv}CR')} \quad (19)$$

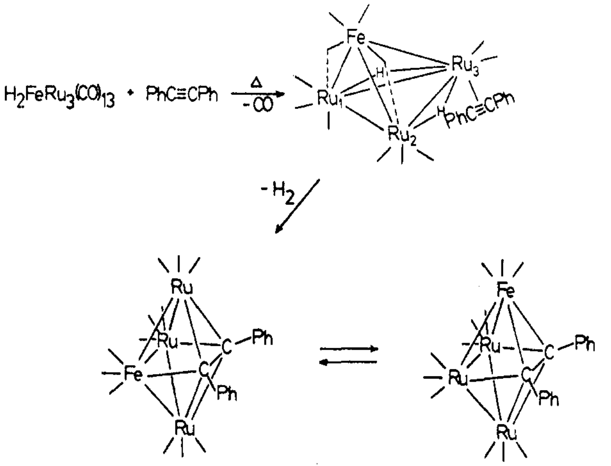
H_2 is evolved during the course of these reactions, and the isomeric $FeRu_3(CO)_{12}(RC{\equiv}CR')$ products are conveniently separated by liquid chromatography on silica gel. Two isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ and $FeRu_3(CO)_{12}(MeC{\equiv}CMe)$ are obtained from the respective reactions with $PhC{\equiv}CPh$ and $MeC{\equiv}CMe$. Reaction with $MeC{\equiv}CPh$ gives three isomers of $FeRu_3(CO)_{12}$ $(MeC{\equiv}CPh)$.

Table IV
Effect of Ligand Size and Basicity on the $C_1 \rightleftarrows C_s$ Equilibrium of $H_2FeRu_3(CO)_{12}L$

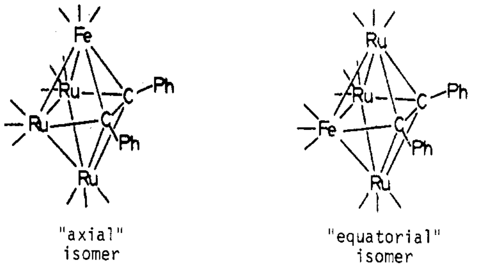
L	cone/ Angle,[a] deg	basicity,[a] cm^{-1}	$K_{C_1 \rightleftarrows C_s}$
$P(i\text{-}Pr)_3$	160	2059.2	>100
PPh_3	145	2068.9	>100
$PMePh_2$	136	2067.0	11
PEt_2Ph	136	2063.7	11
$P(OMe)_3$	107	2079.5	10
$P(OEt)_2Ph$	116	2074.2	5.5
PMe_2Ph	122	2065.3	1.8
PMe_3	118	2064.1	0.4

[a] Reference 24.

Scheme II



The structures of the isomers of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ have been determined by X-ray diffraction.[25] They are isomorphous and differ only in the positioning of the Fe atom. In the "axial" isomer the



Fe is cis to both alkyne carbon atoms whereas in the equatorial isomer Fe is cis to one carbon and trans to the other. Three isomers of $FeRu_3(CO)_{12}(MeC{\equiv}CPh)$ arise because in the equatorial isomer the methyl substituent can occupy a position cis or trans to the Fe atom.

The isomers of these $FeRu_3(CO)_{12}(RC{\equiv}CR')$ clusters

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(24) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(25) Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L.; Day, V. W.; Meguid, S.-A.; Tavanaiepour, I. *J. Am. Chem. Soc.*, submitted for publication.

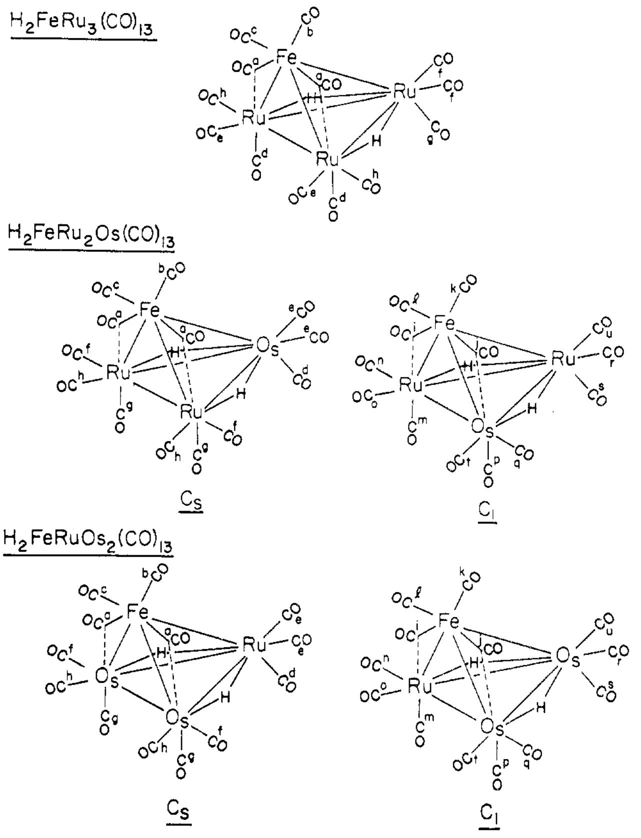


Figure 2. Carbonyl labeling schemes for $H_2FeRu_3(CO)_{13}$ and the C_s and C_1 isomers of $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$.

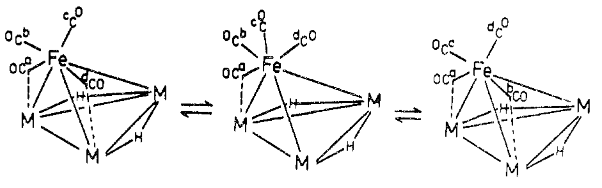
readily interconvert upon heating to yield an equilibrium mixture, e.g., eq 20.[25] For $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ the equilibrium mixture contains about 90% of the axial isomer. It is noteworthy that although the axial isomer of $FeRu_3(CO)_{12}(PhC{\equiv}CPh)$ is the more thermodynamically stable, the equatorial isomer is formed in greater yield in the synthesis of the compound. This suggests that the $FeRu_3(CO)_{12}(RC{\equiv}CR')$ derivatives form via the sequence of reactions outlined in Scheme II. The first step presumably involves dissociation of CO from $H_2FeRu_3(CO)_{13}$ to generate unsaturated $H_2FeRu_3(CO)_{12}$ which rapidly adds the alkyne at the unique Ru atom in the same substitution site to which large phosphorus ligands add. From this site, the alkyne can swing under the cluster and insert into a Ru–Ru bond to give the kinetic equatorial isomer which then subsequently rearranges to the more thermodynamically stable axial isomer. Although rates have not been measured, the reaction of $H_2FeRu_3(CO)_{13}$ with alkynes occurs on the same time scale as the reaction of $H_2FeRu_3(CO)_{13}$ with phosphines, in accord with the postulate that the rate-determining step involves CO dissociation.

$$\underset{\text{equatorial}}{FeRu_3(CO)_{12}(PhC{\equiv}CPh)} \xrightarrow[K_{eq} \simeq 9.0]{70\ ^{\circ}C} \underset{\text{axial}}{FeRu_3(CO)_{12}(PhC{\equiv}CPh)} \quad (20)$$

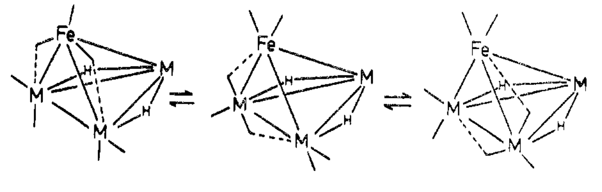
Molecular Dynamics of Mixed-Metal Clusters

The molecular dynamics of the series of clusters $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$, in which Ru is progressively replaced by Os, have been extensively studied in our laboratory. Several distinctly different fluxional processes have been observed.[26] The trimetallic $FeRu_2Os$ and $FeRuOs_2$ clusters exist in the isomeric forms shown in Figure 2 which also gives their corresponding symmetry labels and carbonyl labeling schemes. The low-temperature limiting ^{13}C NMR spectra of these derivatives are shown in Figure 3. The limiting ^{13}C NMR spectrum of $H_2FeRuOs_2(CO)_{13}$ is particularly illustrative. Examination of the structures shown in Figure 2 illustrates that of the 26 carbonyls in the two isomers of $H_2FeRuOs_2(CO)_{13}$, 21 are in distinctly different chemical environments. Each should thus show its own separate, characteristic ^{13}C NMR resonance. Indeed, 19 separate resonances are resolvable in the static ^{13}C NMR spectrum of this derivative (Figure 3), and explicit carbonyl assignments have been derived for each.[26] Similar assignments were made for $H_2FeRu_3(CO)_{13}$ and $H_2FeRu_2Os(CO)_{13}$. Significantly, the terminal carbonyls bound to the different metal atoms in this series group together in characteristic chemical shift regions. The chemical shift decreases relative to Me_4Si upon descending the triad: Fe (204–211 ppm) > Ru (184–180 ppm) > Os (168–177 ppm).

Scheme III



Scheme IV



As the temperature is raised, three distinctly different fluxional processes have been found to occur in each of these clusters.[26] As the temperature is raised from the low-temperature limiting spectrum, the first process to occur is bridge-terminal interchange localized on iron. The mechanism which we have proposed for this exchange is shown in Scheme III and involves opening one of the carbonyl bridges, a subsequent trigonal twist of the resultant $Fe(CO)_3$ unit, and finally re-formation of the CO bridge.

The next exchange process to occur at slightly higher temperatures in each of these clusters involves migration of the carbonyls around the Fe–M–M triangle which possesses the bridging carbonyls. The intermediates in this cyclic movement are presumably the tautomers which have the semibridging carbonyls bound mainly to Ru or Os (Scheme IV).

The third and final process is unique, involving a subtle shift in the metal framework. This process and its implications are best illustrated by consideration of the drawings shown in Scheme V which depict the metal framework of $H_2FeRuOs_2(CO)_{13}$, the two bridging CO's, and the two bridging hydrides. The asymmetry of the cluster is grossly exaggerated for clarity. The process basically involves movement of the Fe atom

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(26) Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.*, **1980**, *19*, 2579.

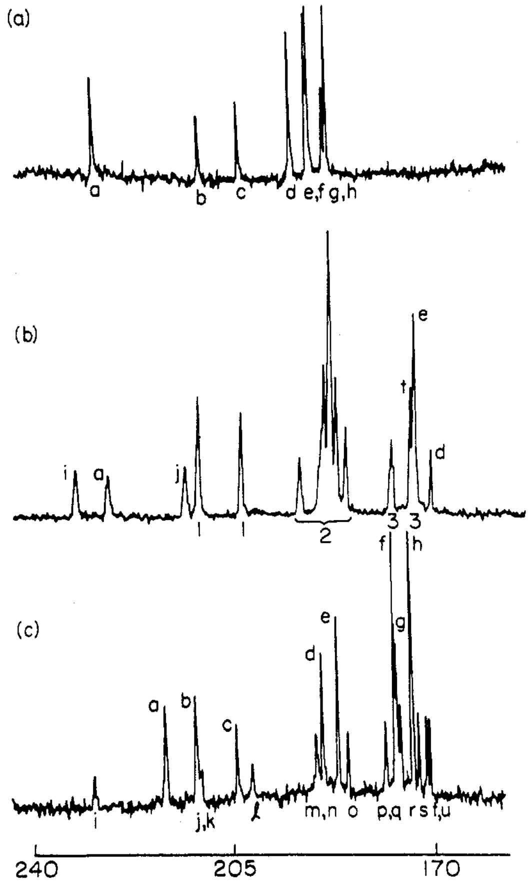
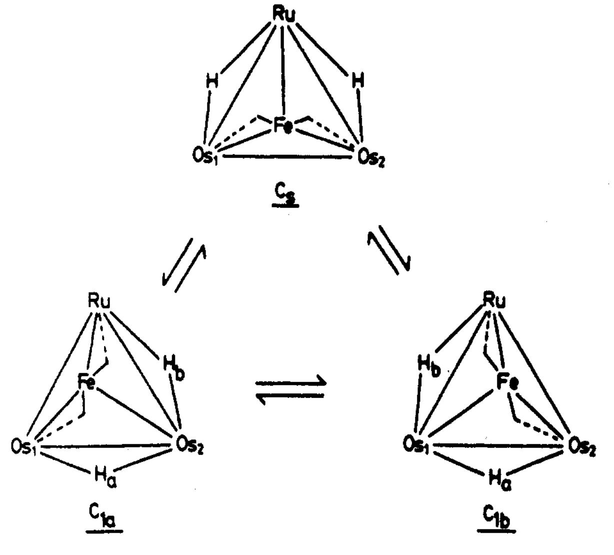
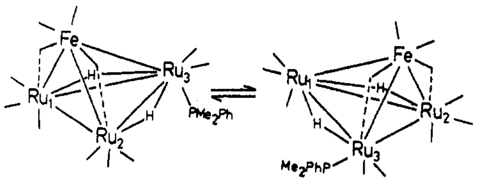


Figure 3. Low-temperature limiting ^{13}C NMR spectra of (a) $H_2FeRu_3(CO)_{13}$ (−95 °C), (b) $H_2FeRu_2Os(CO)_{13}$ (−90 °C), and (c) $H_2FeRuOs_2(CO)_{13}$ (−60 °C).

Scheme V



Scheme VI



away from one metal and closer to another with a concomitant shift of the bridging carbonyls. It must also involve a slight elongation or compression of all the M–M bonds, and it must be accompanied by a shift in position of one of the bridging hydrides.

With reference to Scheme V, starting with the C_{1a} enantiomer, if the Fe moves away from Os-1 toward Os-2, it generates the C_{1b} enantiomer. Movement of Fe away from Ru in either of the C_1 enantiomers and toward both Os atoms gives the C_s isomer. Each time the cluster rearranges, the carbonyls execute the cyclic process about a different Fe–M–M face and hence involve different carbonyl ligands in that process. *The cyclic processes coupled with the framework rearrangement lead to total exchange of all the carbonyl ligands of the cluster.*

The actual magnitude of the shifts within the metal framework must be relatively small. Analysis of the crystal structure published for $H_2FeRu_3(CO)_{13}$[27] shows that the greatest change expected in any one bond length during rearrangement is 0.11 Å. We tend to view the rearrangement process somewhat as a breathing motion of the metal framework, but one which has coupled to it motions of the carbonyls and hydride ligands.

This subtle rearrangement process has profound consequences in regard to the fluxionality of the $H_2FeRu_3(CO)_{12-x}(PR_3)_x$ derivatives discussed above. The effect is most dramatic for $H_2FeRu_3(CO)_{12}(PMe_2Ph)$ which exists in both the C_1 and C_s isomeric forms with $K_{C_1 \rightleftarrows C_s} \sim 1.8$. However, these two isomers rapidly interconvert, as evidenced by the variable-temperature ^1H NMR spectra of this derivative.[28] As the temperature is raised above −50 °C, the resonances shown in Figure 1 broaden, coalesce at ~20 °C, and sharpen to a doublet (J_{P-H} = 9.6 Hz) at 70 °C. The latter implies that at this temperature the $C_1 \rightleftarrows C_s$ isomerization is rapid on the ^1H NMR time scale and that the two hydrogens see an average chemical environment. Computer simulation of the ^1H NMR spectral changes gives a rate constant of $k = 500\ s^{-1}$ at 20 °C for the $C_1 \rightleftarrows C_s$ isomerization. This is an extremely fast rate of isomerization for a process in which two substitutional isomers interconvert, especially since the phosphine ligand is bound to Ru atoms in distinctly different environments in the two isomers.

How does this interconversion occur? The doublet in the high-temperature limiting spectrum implies that the isomerization must occur by a purely intramolecular process and cannot involve dissociation–reassociation of the phosphine. We believe that the isomerization occurs by a rearrangement process analogous to that discussed above for the unsubstituted $H_2FeRu_{3-x}Os_x(CO)_{13}$ clusters, as outlined in Scheme VI. Consider the C_s isomer first, in which the phosphine ligand is attached to the unique Ru atom Ru-3. If the Fe moves away from Ru-1 toward Ru-3 and the hydride and carbonyls shift appropriately, the C_1 isomer is generated. In order to bring the phosphine into the required equatorial position, rotation of the $Ru(CO)_2-(PMe_2Ph)$ unit must accompany the rearrangement. Note, however, that the phosphine has remained attached to the same Ru atom but that this Ru has altered its environment via the rearrangement process. In essence, the phosphine appears to exchange positions, but *the exchange occurs by the phosphine staying attached to*

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(27) Gilmore, C. J.; Woodward, P. *J. Chem. Soc. A*, **1971**, 3453.

(28) Gladfelter, G. L.; Fox, J. R.; Smegal, J. A.; Wood, T. G.; Geoffroy, G. L. *J. Am. Chem. Soc.*, submitted for publication.

Ru-3 with the cluster rearranging around the ligand.

Summary and Outlook

A composite picture of the reactivity of $H_2FeRu_3(CO)_{13}$ can now be assembled with the information now available. By far the most rapid process that this cluster undergoes involves intramolecular exchange of the carbonyl ligands and the hydrides and rearrangement of the metal framework. These fluxional processes occur with rate constants ranging from 10 to 50 s^{-1} at 50 °C. On a far slower time scale, $H_2FeRu_3(CO)_{13}$ undergoes thermal dissociation of CO to yield $H_2FeRu_3(CO)_{12}$. This species can subsequently add phosphines and phosphites to give substituted derivatives, as well as alkynes to first yield substituted clusters followed by rearrangement to give the *closo*-$FeRu_3(CO)_{12}(RC{\equiv}CR')$ products, ^{13}CO to effect $^{13}CO/^{12}CO$ exchange, and H_2 to give $H_4FeRu_3(CO)_{12}$. The first step, dissociation of CO, occurs with a rate constant of 6.96×10^{-4} s^{-1} at 50 °C. Thus, $H_2FeRu_3(CO)_{13}$ undergoes the various fluxional processes 1000–10000 times between each CO dissociative event. Finally, on a much slower time scale, $H_2FeRu_3(CO)_{13}$ undergoes fragmentation with CO to produce $Ru_3(CO)_{12}$, $Fe(CO)_5$, and H_2 by a mechanism which we believe involves association of CO with intact $H_2FeRu_3(CO)_{13}$ concerted with breakage of one of the metal–metal bonds. Recent photochemical experiments indicate that CO dissociation, but not fragmentation, can be photoinduced. This reaction appears to offer potential for the synthesis of unusual substituted derivatives.[29]

Obviously there is still much to be learned concerning the chemistry of $H_2FeRu_3(CO)_{13}$ and related mixed-metal clusters. An important feature for which good information is not at all available concerns the relative strength of the metal–metal bonds in clusters of this type. How does an Fe–Ru bond compare in strength to Fe–Fe and Ru–Ru bonds? This question could presumably be directly addressed by a series of microcalorimetric studies or indirectly by a detailed kinetic examination of the reactions of a series of isostructural mixed-metal clusters with CO. We know nothing concerning the redox properties of these particular clusters, and that should be a subject for further study. Will they retain their integrity on oxidation/reduction or might they open to yield "butterfly" clusters upon two-electron reduction? An interesting question concerns exactly which CO is labilized in the CO dissociation step: i.e., a CO bound to Fe or Ru; axial Ru or equatorial Ru? Even though we know to which site ligands prefer to add to give the substituted products, this implies nothing about the specific CO initially lost. Finally, it must yet be determined if mixed-metal clusters such as these have any useful catalytic properties. That will be one aspect of our future studies.

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(29) Foley, H. C.; Geoffroy, G. L. Unpublished observations.