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Articles

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Acceleration of CO Dissociation by a Heterometallic Center: Substitutional Reactivity of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$

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The substitutional reactivity of the mixed-metal clusters $FeRu_2(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ has been investigated as a comparison to $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$. The reactions are first order in cluster with only a very small dependence on the entering ligand (L = PPh_3 or $P(OMe)_3$), consistent with a dissociative interchange mechanism. The activation parameters and all other data are consistent with CO dissociation as the rate-determining step. $FeRu_2(CO)_{12}$ undergoes substitution to $FeRu_2(CO)_{10}L_2$ (both ligands substituted on ruthenium) with no evidence for a monosubstituted cluster. Substitution on $Fe_2Ru(CO)_{12}$ leads initially to $Fe_2Ru(CO)_{11}L$ (substitution on ruthenium) and subsequently to $Fe_2Ru(CO)_{10}L_2$ (substitution on iron and ruthenium). CO dissociation from $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ occurs more rapidly than from $Fe_3(CO)_{12}$ or from $Ru_3(CO)_{12}$, suggesting a metal center effect on CO dissociation.

Mixed-metal cluster complexes are very well suited to provide information on two important questions about metal cluster reactivity: (1) the effect of one metal center on reactivity at other metal centers and (2) the site of reactivity.[1] Heterobimetallic complexes have been very useful in examining the reactions of bimetallic species.[2-7] The advantages of mixed-metal clusters to determine the site of reactivity have been exploited in the detailed investigations of $H_2FeRu_3(CO)_{13}$.[8,9] Studies on $Ir_4(CO)_{12}$ and substituted derivatives have indicated that ligand substitution is influenced by adjacent metal centers.[10-15]

The clusters of group 8 metals, $M_3(CO)_{12}$, offer one of the few examples of clusters where the substitutional reactivity for each metal (M = Fe, Ru, Os) has been examined.[16-23] The substitution reactions occur by CO dissociation with some component of dissociative interchange.[16,17] The reactivity of these clusters is different from that of the mononuclear carbonyls, $M(CO)_5$.[24] To further examine this cluster effect on reactivity, we have examined the substitution reactions of the mixed-metal clusters $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$.[25] These are ideal because the PPh_3 substitution products $Fe_2Ru(CO)_{11}PPh_3$ and $FeRu_2(CO)_{10}(PPh_3)_2$ have been structurally characterized.[26] Each involves solely substitution on ruthenium atoms in equatorial positions. We have examined the kinetics of the substitution reactions, which indicate CO dissociation at a rate more rapid than from either $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$, an interesting adjacent metal center effect on CO dissociation from clusters.

Table I. Infrared Spectra of $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, and Their Substituted Products

complex	ν_{CO}, cm^{-1}	color
$Fe_2Ru(CO)_{12}$[a]	2055 (s), 2042 (vs), 2000 (m), 1840 (vw)	purple
$Fe_2Ru(CO)_{11}PPh_3$[a]	2085 (m), 2025 (s), 2010 (s), 1990 (sh), 1875, 1810 (w)	blue
$Fe_2Ru(CO)_{11}P(OMe)_3$[b]	2075 (w), 2025 (s), 2010 (vs), 1960 (s), 1810, 1765 (w)	blue
$Fe_2Ru(CO)_{10}(P(OMe)_3)_2$[b]	2065 (w), 2010 (s), 1990 (vs)	purple
$Fe_2Ru(CO)_{10}(PPh_3)_2$[b]	2010 (m), 1995 (vs), 1965 (sh), 1940 (sh), 1775 (w, br)	green
$FeRu_2(CO)_{12}$[a]	2067 (s), 2042 (vs), 2032 (s), 1987 (w)	orange
$FeRu_2(CO)_{11}PPh_3$[26,c]	2095 (m), 2040 (s), 2025 (vs), 1975 (m)	purple
$FeRu_2(CO)_{11}P(OMe)_3$[26,c]	2095 (m), 2045 (s), 2025 (vs), 1995 (s), 1970 (m)	red
$FeRu_2(CO)_{10}(PPh_3)_2$[a]	2050 (w), 2020 (s), 1998 (vs), 1965, 1940 (sh), 1890 (m), 1735 (w)	violet
$FeRu_2(CO)_{10}(P(OMe)_3)_2$[a]	2075 (m), 2020 (s), 1998 (vs), 1962, 1920 (sh)	red

[a] C_6H_{12}. [b] CH_2Cl_2. [c] C_6H_{14}.

Experimental Section

Iron pentacarbonyl (Aldrich Chemical Co.) and triruthenium dodecacarbonyl (Strem Chemical Co.) were used without further purification. Triphenylphosphine was recrystallized from ethanol, trimethyl phosphite

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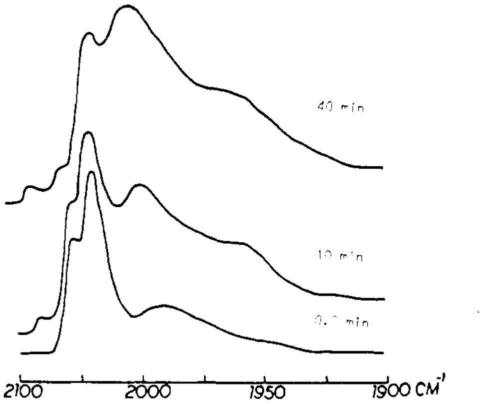

Figure 1. Infrared spectra taken during reaction of $Fe_2Ru(CO)_{12}$ with PPh_3 at 45 °C in 1,2-dichloroethane. The absorption at 2085 cm^{-1}, which grows and then disappears, corresponds to $Fe_2Ru(CO)_{11}PPh_3$ with PPh_3 substituted on Ru. The 40-min spectrum shows the dominance of $Fe_2Ru(CO)_{10}(PPh_3)_2$ (main absorption at 1995 cm^{-1}).

Table II. Rate Constants for Substitution of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$[a]

cluster	L	cluster:L ratio[b]	$10^{-5}k$, s^{-1}	temp, °C
$Fe_2Ru(CO)_{12}$	PPh_3	1:30	16.6 ± 1.6	35
			35.0 ± 2.3	40
			68.0 ± 6.8	45
		1:80	73.3 ± 5.0	45
	$P(OMe)_3$	1:50	68.3 ± 7.1	45
		1:100	69.7 ± 2.8	45
$FeRu_2(CO)_{12}$	PPh_3	1:6	13.2 ± 1.2	35
			27.5 ± 1.5	40
		1:50	16.4 ± 1.1	35
			33.0 ± 2.8	40
			64.4 ± 6.0	45
	$P(OMe)_3$	1:30	35.8 ± 2.4	40
		1:90	43.4 ± 3.4	40

[a] In 1,2-dichloroethane. Error limits represent 95% confidence limits. [b] The cluster concentration is 5 × 10^{-4} M.

was purified by vacuum distillation, and 1,2-dichloroethane was stirred over NaOH and distilled from P_2O_5. Hexane, cyclohexane, and methylene chloride were stirred over H_2SO_4, washed with $NaHCO_3$ solution, stirred over $CaCl_2$, and distilled from CaH_2. All preparative-scale thin-layer chromatography was accomplished by using 1.0 mm thick silica gel plates.

$Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ were prepared as previously described.[25] $Ru_3(CO)_{12}$ (0.50 g) and $Fe(CO)_5$ (10 mL) were heated in a nitrogen-purged pressure bottle at 110 °C for 24 h. After the vessel had cooled to room temperature, the volatile components were removed under vacuum. The solution was filtered in the drybox, and excess $Fe(CO)_5$ was removed under vacuum. The residue was dissolved in CH_2Cl_2 and chromatographed with cyclohexane as eluant. The mixture afforded $Ru_3(CO)_{12}$ (yellow), $FeRu_2(CO)_{12}$ (orange, 30–40 mg), $Fe_2Ru(CO)_{12}$ (purple, 10–20 mg), and a trace of $H_2FeRu_3(CO)_{13}$. Infrared spectra are reported in Table I.

$Fe_2Ru(CO)_{11}PPh_3$ was prepared by a method developed by Bruce and co-workers.[27] $Fe_2Ru(CO)_{12}$ (30 mg, 5.46 × 10^{-2} mmol) and PPh_3 (14.3 mg, 5.46 × 10^{-2} mmol) were dissolved in 30 mL of THF and stirred under nitrogen. A catalytic amount of Na/Ph_2CO (0.02 M in THF) was added dropwise. Formation of $Fe_2Ru(CO)_{11}PPh_3$ was monitored by appearance of the absorbance at 2085 cm^{-1}. The solvent was removed under vacuum, and the product was purified by TLC using a 4:1 cyclohexane/CH_2Cl_2 solution (yield 90%).

The kinetic reactions were accomplished under a nitrogen atmosphere in foil-wrapped vessels in darkened hoods and followed by infrared spectroscopy with a Beckman 4240 spectrophotometer and matched 1.0-mm NaCl cells. All kinetic reactions were performed under pseudo-first-order conditions. Typically 5 mL of a (2–6) × 10^{-4} M solution (hexane or 1,2-dichloroethane as solvent) of the mixed-metal cluster was stirred under N_2 at the desired temperature. The ligand, PPh_3 or $P(OMe)_3$, was added directly to this solution. A Haake FS constant-temperature circulator was used to maintain the reaction at the desired temperature to within ±0.1 °C.

Table III. Activation Parameters for Substitution on $M_3(CO)_{12}$ and $M_2M'(CO)_{12}$ with PPh_3

cluster	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Fe_3(CO)_{12}$[a]	29.5 ± 0.8	18.8 ± 2.8
$Fe_2Ru(CO)_{12}$[b]	26.8 ± 0.4	6.7 ± 0.4
$FeRu_2(CO)_{12}$[b]	26.0 ± 1.1	8.6 ± 3.7
$Ru_3(CO)_{12}$[c]	32.2 ± 1.7	22.7 ± 3.7

[a] Reference 16. [b] This work. [c] Reference 17.

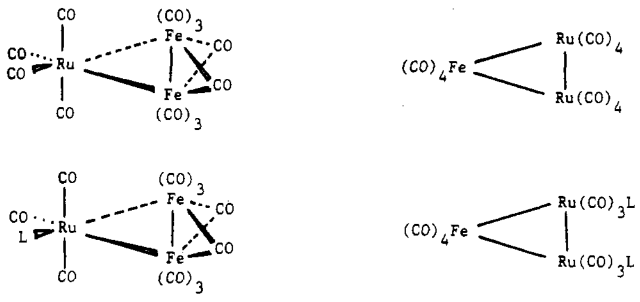

Figure 2. Structures of the unsubstituted mixed-metal clusters $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ (top) and the substituted clusters $Fe_2Ru(CO)_{11}PPh_3$ and $FeRu_2(CO)_{10}(PPh_3)_2$ (bottom).

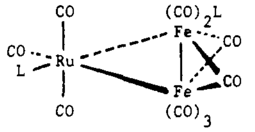

Figure 3. Suggested structure of $Fe_2Ru(CO)_{10}(PPh_3)_2$.

The reactions of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ with PPh_3 and $P(OMe)_3$ were studied between 35 and 45 °C. In these reactions the kinetic data were obtained by monitoring the decrease in absorbance at 2055 and 2067 cm^{-1} due to $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$, respectively, for at least 3 half-lives.

Plots of ln A_t vs. time yielded pseudo-first-order rate constants (Table II). Eyring plots provided the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table III).

Results and Discussion

The synthesis of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ by reaction between $Fe(CO)_5$ and $Ru_3(CO)_{12}$ and separation by thin-layer chromatography provides small quantities of both. As previously discussed the infrared spectra indicate that the structures of these complexes are different with $Fe_2Ru(CO)_{12}$ adopting the $Fe_3(CO)_{12}$ structure and $FeRu_2(CO)_{12}$ adopting the $Ru_3(CO)_{12}$ structure.[26] Both are shown in the top half of Figure 2. The products, $Fe_2Ru(CO)_{11}PPh_3$ and $FeRu_2(CO)_{10}(PPh_3)_2$, have been previously prepared and x-ray crystal structures reported.[26] The structures of these substituted complexes are shown in the bottom half of Figure 2. In these reactions the PPh_3 has substituted the ruthenium atoms, but not the iron. Under the conditions of the kinetic reactions, $FeRu_2(CO)_{12}$ reacts with PPh_3 or $P(OMe)_3$ to give the disubstituted complex with a phosphorus donor on each ruthenium in equatorial positions. No evidence of a monosubstituted intermediate is observed. Reaction of PPh_3 with $Fe_2Ru(CO)_{12}$ gives initially the monosubstituted cluster $Fe_2Ru(CO)_{11}PPh_3$ with the PPh_3 on the ruthenium (blue, 2085 cm^{-1}). A subsequent reaction leads to a new product, $Fe_2Ru(CO)_{10}(PPh_3)_2$ (green, 1995 cm^{-1}):

$$Fe_2Ru(CO)_{12} \xrightarrow[-CO]{+PPh_3} Fe_2Ru(CO)_{11}PPh_3 \xrightarrow[-CO]{+PPh_3} Fe_2Ru(CO)_{10}(PPh_3)_2 \quad (1)$$

Infrared spectra taken during the course of reaction 1 are shown in Figure 1 for reaction in 1,2-dichloroethane. The reaction is somewhat more rapid in hexane and leads to precipitation of $Fe_2Ru(CO)_{10}(PPh_3)_2$. Purification can be effected by TLC (4:1, C_6H_{12}:CH_2Cl_2). This product was also prepared by reaction of independently prepared $Fe_2Ru(CO)_{11}PPh_3$ with PPh_3. Crystals

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Table IV. Comparison of Rate Constants for Reactions of $M_3(CO)_{12}$ and $M_2M'(CO)_{12}$ with PPh_3 at 30 °C

cluster	$10^{-5}k$, s^{-1}	solvent
$Fe_3(CO)_{12}$	4.0	hexane
$Fe_2Ru(CO)_{12}$	17.8	hexane
$Ru_3(CO)_{12}$	0.86[a]	methylcyclohexane
$FeRu_2(CO)_{12}$	10.4	hexane

[a] Reference 17.

of sufficient size for X-ray diffraction have not yet been prepared, but by analogy with the osmium analogue we believe that $Fe_2Ru(CO)_{10}(PPh_3)_2$ has one PPh_3 substituted on Ru and one on an Fe.[28] The suggested structure is shown in Figure 3. The reaction of $Fe_2Ru(CO)_{12}$ with $P(OMe)_3$ proceeds similarly to the reaction with PPh_3 with formation of $Fe_2Ru(CO)_{11}P(OMe)_3$ and $Fe_2Ru(CO)_{10}(P(OMe)_3)_2$. The infrared spectra are shown in Table I.

Kinetic studies show that the reactions are first order in metal cluster and essentially independent of the nature or concentration of the entering ligand. The results are shown in Table II. The very small dependence on the entering ligand is best accommodated by some component of dissociative interchange in a dissociative process as is observed for the $M_3(CO)_{12}$ complexes.[30] The activation parameters (shown in Table III) are also consistent with a dissociative process. While we have not made a full investigation of the solvent effect, the more rapid reaction in hexane in comparison to 1,2-dichloroethane is consistent with previous studies of CO dissociation.[30] Rate-determining dissociation of a CO or a metal–metal bond would be possible in these clusters. A mechanism of metal–metal bond breaking (either homolytic or heterolytic) would have to be irreversible—not a rapid preequilibrium—to fit the observed rate law. A rapid preequilibrium of metal–metal bond cleavage must show a dependence on the concentration of the entering ligand (essentially a competition exists between metal–metal bond formation and ligand substitution).[30] After ligand substitution the metal–metal bond would have to rapidly re-form to give the observed products with no cluster degradation. We thus disfavor a rate-determining cleavage of a metal–metal bond. Thus, as for substitution of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$,[16,17] dissociation of CO apparently leads to substitution on $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$.

The substitution of each of the clusters, $Fe_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, and $Ru_3(CO)_{12}$, occurs by a CO dissociative process with virtually identical rate laws. The reactivity of these four clusters is compared in Table IV. The mixed cluster systems undergo substitution more readily than either of the homotrimeric species. *Thus CO dissociation is facilitated by the presence of a heterometallic center in these trinuclear clusters.* There is no readily discernible effect of the changing geometries on the reactivity, but we note that these clusters are fluxional on the time scale of the substitution. Dissociation of CO from either Fe or Ru is possible in the mixed cluster systems. The initial products involve substitution on Ru, but our previous work has shown that the site of substitution of a metal–metal-bonded complex need not represent the site of ligand dissociation.[6,11,12] The more rapid substitution of $Fe_3(CO)_{12}$ in comparison to $Ru_3(CO)_{12}$ could be used as evidence of CO dissociation from the Fe center. However, the difference is small and CO dissociation from mononuclear complexes occurs much more readily for ruthenium than for iron.[24] No evidence from the data thus far can be used to differentiate between iron centers activating ruthenium centers toward CO dissociation or ruthenium centers activating iron centers toward CO dissociation. Iron activation of CO dissociation from ruthenium would follow smoothly the increasing rate as the iron content in the cluster increases:

$$Ru_3(CO)_{12} < FeRu_2(CO)_{12} < Fe_2Ru(CO)_{12}$$

The rates of second substitution provide conflicting evidence about the site of substitution. For $FeRu_2(CO)_{12}$ no monosubstituted product is observed. This is similar to observations on the effect of ligand substitution on a metal center that is undergoing CO dissociation with an enhanced second substitution.[11] Thus the PPh_3 on Ru enhances further CO dissociation just as for the second substitution on $Ru_3(CO)_{12}$. This is thus more consistent with CO dissociation on ruthenium. However, for $Fe_2Ru(CO)_{12}$ the second substitution occurs at a rate that is comparable to the rate of the first substitution. This is consistent with the site of substitution being different from the site of CO dissociation or being at an iron center in $Fe_2Ru(CO)_{12}$. Perhaps it is most accurate to suggest that dissociation of CO from Fe and Ru centers is not very different and subtle factors may alter the site of CO dissociation. We are continuing with a study of $Fe_2Os(CO)_{12}$ and $FeOs_2(CO)_{12}$ to try to clarify the site of CO dissociation from these group 8 trimetallic clusters.

This study of substitution of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ has shown an acceleration of CO dissociation by a heterometallic center in a trinuclear cluster. Such a kinetic effect could arise from ground-state or transition-state effects. We know of no data currently existing that can be used to differentiate between these two for these cluster complexes.

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Registry No. $FeRu_2(CO)_{12}$, 12388-68-0; $Fe_2Ru(CO)_{12}$, 20468-34-2; CO, 630-08-0; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9.

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(28) The infrared spectrum of $Fe_2Ru(CO)_{10}(PPh_3)_2$ (Table I) is nearly identical with that of the osmium analogue (2065 (w), 2015 (m), 1990 (vs), 1960 (sh), 1935 (sh), 1760 cm^{-1} (w, br)) whose structure has been determined.[29]

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