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Kinetics and Mechanism of Oxidative Addition and Reductive Elimination of Hydrogen on Triruthenium Clusters

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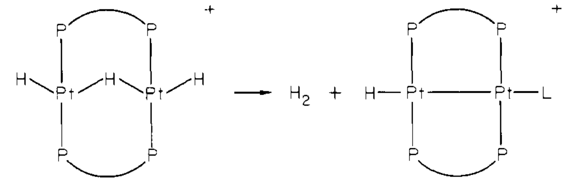
Abstract: The kinetics of the reversible reaction $HRu_3(\mu\text{-COMe})(CO)_{10} + H_2 \rightleftarrows H_3Ru_3(\mu_3\text{-COMe})(CO)_9 + CO$ has been studied. The reaction of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ with carbon monoxide has a rate law which is first order in metal cluster and zero order in carbon monoxide pressure; on the basis of the rate law, activation parameters, and deuterium kinetic isotope effect, the rate-determining step is proposed to be reductive elimination of molecular hydrogen through a three-center transition state. The reaction of $HRu_3(\mu_3\text{-COMe})(CO)_{10}$ with hydrogen involves dissociation of a carbonyl ligand prior to the rate-determining step, which is proposed to be the oxidative addition of molecular hydrogen. The relative rates for reactions of the unsaturated intermediate $HRu_3(COMe)(CO)_9$ with hydrogen and with carbon monoxide were determined. Comparisons between these results and studies of metal surfaces and of mononuclear metal complexes are discussed.

Tremendous progress has been made over the last decade in the syntheses and characterizations of metal carbonyl clusters and products from their reactions with hydrogen, olefins, acetylenes, and other small molecules.[1] Interest in these reactions has been sparked by the hope that clusters might possess unique catalytic activity and by the proposal[2] that clusters might be used as soluble models for metal surfaces. However, in spite of advances in cluster synthesis, very few mechanistic studies of cluster reactions, necessary for a basic understanding of cluster chemistry and for modeling of metal surface reactions, have been reported. Studies of ligand substitutions,[3] cluster fragmentations,[4] and cluster-catalyzed olefin hydrogenation and isomerization[5] have been reported. No studies have heretofore focused upon the elementary steps of fundamental importance to catalysis—oxidative addition, insertion, reductive elimination—that have been extensively investigated for mononuclear metal complexes.

One of the most important reactions in catalysis, either homogeneous or heterogeneous, is the activation of molecular hydrogen. This process has been thoroughly investigated for mononuclear complexes[6] and for metal surfaces.[7] The most widely accepted mechanism for oxidative addition of hydrogen at a single metal center involves a three-center transition state with concerted bond making and bond breaking, resulting in a cis metal dihydride product. Reductive elimination of hydrogen can proceed either through the microscopic reverse process[8-10] or through a bimolecular path.[11]

A number of examples of addition of hydrogen to metal clusters have been reported.[12] Suggested mechanisms for this process have included (a) a three-center transition state at a single metal site,[13] (b) addition across a multiple metal–metal bond,[14] and (c) homolytic cleavage of a metal–metal single bond, followed by binuclear addition of hydrogen.[15] Only one kinetic study of reductive elimination of hydrogen from a dinuclear metal complex has been reported (eq 1); the rate of the reaction was found to be first order in incoming ligand, but the mechanism remains unknown.[16]



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We recently reported[17] that the clusters $HM_3(\mu\text{-COMe})(CO)_{10}$ (M = Fe, Ru, Os) undergo reversible addition of hydrogen according to eq 2. To define the mechanism of this process we have

$$HM_3(\mu\text{-COMe})(CO)_{10} + H_2 \rightleftarrows H_3M_3(\mu_3\text{-COMe})(CO)_9 + CO \quad (2)$$

carried out and report here the first study of the kinetics and mechanism of oxidative addition and reductive elimination of hydrogen at a metal cluster for the above system where M = Ru.

Experimental Section

Chemicals. The clusters $HRu_3(\mu\text{-COMe})(CO)_{10}$ and $H_3Ru(\mu_3\text{-COMe})(CO)_9$ were prepared by published procedures.[17] The deuterium-labeled analogue $D_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (isotopic purity >90% by ^1H NMR) was prepared in the same way with deuterium gas (Matheson, 99.5% isotopic purity) and $DRu_3(\mu\text{-COMe})(CO)_{10}$, which was prepared with D_2O in place of H_2O in the literature procedure.[17] Hydrogen (Linde) and carbon monoxide (Matheson) were CP grade and were used as received. Decane was used as received from Aldrich.

Kinetics. The hydrogenation and carbonylation reactions were monitored by infrared spectroscopy on a Perkin-Elmer 467 instrument. For the hydrogenation the band for $HRu_3(\mu\text{-COMe})(CO)_{10}$ at 2054 cm^{-1} was used, while for carbonylation the 2078 cm^{-1} absorption of $H_3Ru_3(\mu_3\text{-}$

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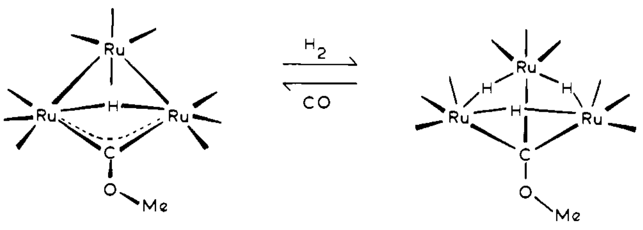

Figure 1. Equilibrium between $(\mu\text{-H})Ru_3(\mu\text{-COMe})(CO)_{10}$ and $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_9$.

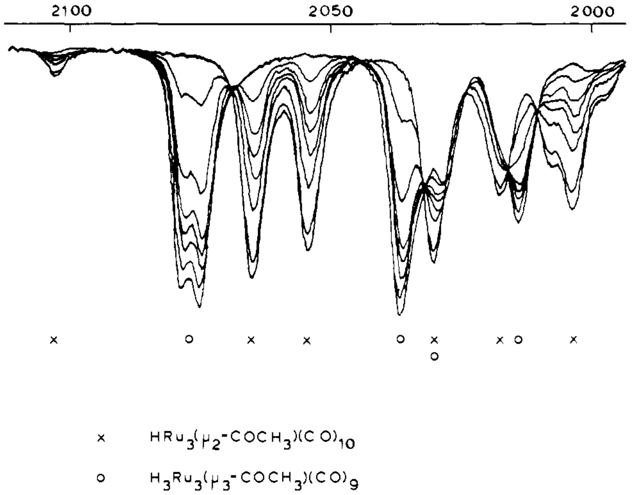

Figure 2. Changes in the infrared spectrum between 2150 and 2000 cm^{-1} during the hydrogenation of $(\mu\text{-H})Ru_3(\mu\text{-COMe})(CO)_{10}$ (denoted by ×) to $(\mu\text{-H})_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (denoted by O) in decane.

COMe)(CO)$_9$ was followed. Solutions generally were prepared with a cluster concentration of 1.6×10^{-3} M in decane and were sampled in 0.5-mm KBr solution cells.

Reactions of 1 atm pressure were conducted in a Schlenk flask equipped with a gas inlet tube, which was inserted into the solution as close to the bottom of the vessel as was feasible, and a reflux condenser topped with a gas outlet to an oil bubbler. The flask was immersed in a Lauda constant temperature bath (±0.1 °C). Gas was bubbled through the solution and samples were withdrawn via syringe through the side arm of the flask.

Reactions at 1–4 atm pressure were conducted in a Parr pressure bottle[18] which was immersed in the constant temperature bath. Sampling necessarily required opening the bottle; after each sampling, the bottle was flushed 3 times and then filled to the desired pressure.

Reactions at up to 70 atm were conducted in an Autoclave Engineers 300 cm^3 Magnadrive unit, equipped with a Love Controls Corp. Model 165-766-713 temperature controller (±1 °C) and with a liquid sampling system through which 1-mL samples were withdrawn periodically for analysis.

Rate constants were determined by a computer-calculated least-squares procedure and error limits were taken as the standard deviations from the least-squares fit.

Equilibrium constants were determined by allowing a solution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ of known concentration to reach equilibrium under a mixture of carbon monoxide and hydrogen of known composition (Matheson mixtures, preanalyzed) in the Parr bottle. The absorbances of the 2054- and 2074-cm^{-1} peaks were used to calculate the relative amounts of $HRu_3(\mu\text{-COMe})(CO)_{10}$ and $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$.

Results

In decane solution $HRu_3(\mu\text{-COMe})(CO)_{10}$ reacted quantitatively with hydrogen at 1 atm and 40–70 °C to give $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (Figure 1).[17] This reaction could be quantitatively reversed with carbon monoxide at 3 atm and 60–80 °C. Isobestic points (Figure 2) were noted in the terminal carbonyl region of the infrared spectrum during both reactions, implying that no measurable quantity of an intermediate is formed during the forward or reverse reactions. Under mixtures of hydrogen and carbon monoxide the system proceeded to equilibrium; over the range 60–80 °C the equilibrium constant, invariant within experimental error, was found to be 1.1 ± 0.1 for eq 3.

$$HRu_3(\mu\text{-COMe})(CO)_{10}\ (\text{solution}) + H_2\ (g) \rightleftarrows H_3Ru_3(\mu_3\text{-COMe})(CO)_9\ (\text{solution}) + CO\ (g)$$

$$K_{eq} = 1.1 \qquad (3)$$

Table I. Rate Constants for Carbonylation of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$[a]

temp, °C	P_{CO}, atm	k_{obsd},[d] s^{-1}
59.4	3.7[b]	$1.40 \pm 0.07 \times 10^{-6}$
59	62[c]	$1.50 \pm 0.02 \times 10^{-6}$
68.6	3.7[b]	$4.8 \pm 0.2 \times 10^{-6}$
70	68[c]	$6.2 \pm 0.2 \times 10^{-6}$
76.5	3.7[b]	$1.27 \pm 0.03 \times 10^{-5}$
80.2	3.7[b]	$2.50 \pm 0.10 \times 10^{-5}$

[a] Initial concentration of cluster was 1.6×10^{-3} M in decane. [b] Pressure bottle. [c] Autoclave. [d] Error limits are given as 1 standard deviation.

To convert the equilibrium constant for eq 3 from the gaseous standard states for carbon monoxide and hydrogen to the equilibrium constant for these molecules when dissolved in solution the ratio of the Henry's law constants for carbon monoxide (K_{CO}) and for hydrogen (K_{H_2}) in decane at the desired temperature must be known. A formula, due to Gjaldbaek,[19] allows the calculation of the solubilities of these gases in a number of nonpolar solvents, including heptane but not decane; however, the ratio of the solubilities of these gases is almost constant in these hydrocarbon solvents. When the ratio of K_{CO}/K_{H_2} in heptane at 60 °C, calculated from Gjaldbaek's formula as 2.4, is used, the equilibrium constant K'_{eq} for all species in solution is then given by eq 4 and has a value of 2.4

$$K'_{eq} = \frac{[H_3Ru_3(\mu_3\text{-COMe})(CO)_9][CO]}{[HRu_3(\mu\text{-COMe})(CO)_{10}][H_2]} = K_{eq}\frac{K_{CO}}{K_{H_2}} = 2.6 \qquad (4)$$

The rate of carbonylation of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ at 3.8–70 atm of carbon monoxide was determined by monitoring the 2078 cm^{-1} absorption in the infrared spectrum. Plots of ln(abs) vs. time were linear for greater than 3 half-lives at temperatures between 60 and 80 °C, signifying a rate law is first order in cluster. Above 80 °C some decomposition was noted. The first-order rate constants k_4 (Table I) were independent of carbon monoxide pressure between 3.8 and 70 atm. From an Eyring plot of ln (k_4/T) vs. $1/T$ the activation parameters for the carbonylation were determined to be $\Delta H_4^{\ddagger} = 31.0 \pm 0.8$ kcal/mol (130 kJ/mol) and $\Delta S_4^{\ddagger} = +8 \pm 2$ eu (33 J/(K mol)). The deuterium kinetic isotope effect was measured at 75.0 °C from the rates of carbonylation of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ and of $D_3Ru_3(\mu_3\text{-COMe})(CO)_9$ (>90% isotope purity by ^{1}H NMR) under 3.7 atm of carbon monoxide, and the value of k_4^H/k_4^D was determined to be 1.40 ± 0.10.

Unlike the carbonylation of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$, for hydrogenation of $HRu_3(\mu\text{-COMe})(CO)_{10}$ linear plots of ln(abs) vs. time were not obtained. The rate behavior observed depended upon the experimental design in a way that can be fully explained by inhibition of the reaction by the carbon monoxide produced. For those runs in which hydrogen was bubbled through the solution, the plot showed an increasing rate with increasing conversion; furthermore, the slope of the plot was found to increase with increasing flow rate of hydrogen. On the other hand, in the autoclave under 70 atm of hydrogen, the rate of the reaction decreased with increasing conversion; however, if the atmosphere was vented during the run and the autoclave was repressurized, the rate increased to a value higher than the rate found at 0% conversion. In the autoclave, the buildup of carbon monoxide with increasing conversion resulted in a decreasing rate; in the open system, because carbon monoxide was not instantaneously swept out, the instantaneous concentration of carbon monoxide was proportional to the amount of unreacted $HRu_3(\mu\text{-COMe})(CO)_{10}$,

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Table II. Rate Constants[a] for Hydrogenation of $HRu_3(\mu\text{-COMe})(CO)_{10}$ to Equilibrium under Carbon Monoxide-Hydrogen Mixtures

temp, °C	P_{H_2}/P_{CO}	k_{obsd},[d] s^{-1}	$k_{obsd\text{-}calcd}$, s^{-1} [b]
58.6	3.18	$8.2 \pm 0.4 \times 10^{-6}$	5.9×10^{-6}
80.2	0.926	$6.79 \pm 0.15 \times 10^{-5}$	5.0×10^{-5}
80.2	3.00	$1.35 \pm 0.02 \times 10^{-4}$	1.1×10^{-4}
80.2	8.52	$2.21 \pm 0.20 \times 10^{-4}$	2.3×10^{-4}
73.8	0.926	$2.32 \pm 0.04 \times 10^{-5}$	2.5×10^{-5}
73.8	0.926	$2.46 \pm 0.07 \times 10^{-5}$ [c]	2.5×10^{-5}

[a] Determined from plots of ln $(A_t - A_{eq})$ vs. time. [b] Calculated from eq 9. [c] Rate constant for carbonylation of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ to equilibrium. [d] Determined using a least-squares fit. Error limits are given as 1 standard deviation.

and the rate correspondingly increased with increasing conversion. The fastest rates of hydrogenation were obtained from the open system near the end of the reaction; from the slope of the ln(abs) plot at >75% conversion, the rate constant was estimated to be $2.7 \pm 1.4 \times 10^{-4}$ s^{-1} at 40.5 °C. In the autoclave at 40 °C and 70 atm of hydrogen, the slope of the ln(abs) plot was 5.6×10^{-5} s^{-1} at <10% conversion, and replacement of the atmosphere at 44% conversion gave a new initial slope of 1.0×10^{-4} s^{-1}.

When mixtures of hydrogen and carbon monoxide (to maintain a constant P_{CO}) were used at 1 atm with the gas bubbled through the solution, the hydrogenation of $HRu_3(\mu\text{-COMe})(CO)_{10}$ proceeded to equilibrium. Plots of ln $(A_t - A_{eq})$[20] vs. time were linear for 3 half-lives or more. The rate constants k_{obsd} (Table II) decreased with a decreasing hydrogen to carbon monoxide ratio.

Discussion

The results obtained are consistent with the following mechanism:

$$HRu_3(\mu\text{-COMe})(CO)_{10} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HRu_3(COMe)(CO)_9 + CO \quad (5)$$

$$H_2 + HRu_3(COMe)(CO)_9 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H_3Ru_3(\mu_3\text{-COMe})(CO)_9 \quad (6)$$

Both oxidative addition and reductive elimination of hydrogen are proposed to proceed through a three-center transition state at a single metal site. The evidence in support of these proposals is as follows.

The reductive elimination of hydrogen from $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ is a well-behaved first-order reaction involving rate-limiting loss of hydrogen. Rate-limiting loss of carbon monoxide, followed by bimolecular reductive elimination,[11] can be discounted because the rate constant for substitution by $AsPh_3$, which proceeds by a CO-dissociative mechanism, is ca. 400 times faster at *25 °C* than the rate of hydrogen elimination at *60 °C*.[21] The activation parameters for loss of hydrogen are not significantly different from those reported for unimolecular reductive elimination from mononuclear metal species. For example, reported values for reductive elimination from $H_2Fe(CO)_4$ are $\Delta E_a = 26 \pm 2$ kcal/mol and $\Delta S^* = +19$ eu,[10] while for $[H_2Ir(CO)_2(PMePh_2)_2][BPh_4]$ the activation parameters are $\Delta H^* = 20.3 \pm 0.6$ kcal/mol and $\Delta S^* = -5 \pm 2$ eu.[8] The kinetic isotope effect of $k_4{}^H/k_4{}^D = 1.4$ is also consistent with the proposed transition state; values for unimolecular reductive elimination from $[H_2Ir(CO)_2(PMePh_2)_2]^+$ and $H_2Co[P(OMe)_3]_4{}^+$ are 2.1 ± 0.6[8] and 1.51[9], respectively. While the activation parameters reported for reductive eliminations of hydrogen from single metal centers vary over a wide range, the activation parameters and kinetic isotope effect for reductive elimination from $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ are consistent with a similar three-center transition state involving simultaneous bond making and bond breaking. Thus, there is no evidence from our data that reductive elimination of hydrogen from a cluster is different in kind than from a mononuclear dihydride, even though in the ground state the cluster has bridging rather than terminal hydride ligands. However, the mechanism may involve prior conversion to an isomer having terminal hydrides; numerous studies of hydride mobility on clusters have found generally low activation energies for interconversion of terminal and μ_2- and μ_3-bridging hydride ligands.[22] Although we cannot discount the possibility that a mechanism involving more than one metal might have kinetic parameters very similar to those found for mononuclear processes, there is no reason to suppose that this is the case.

Because of the sensitivity of the rates of hydrogenation to the experimental procedure, the rate of reaction of $HRu_3(\mu\text{-COMe})(CO)_{10}$ with hydrogen could not be determined directly. Assuming the above mechanism, the rate law for hydrogenation should be given by eq 7. Under our experimental conditions, even

$$\text{rate} = \left[\frac{k_1}{\dfrac{k_2 P_{CO}}{k_3 P_{H_2}} + 1} \right] [HRu_3(\mu\text{-COMe})(CO)_{10}] \quad (7)$$

when no carbon monoxide was added, the term $k_2P_{CO}/k_3P_{H_2}$ was not negligible. In a closed system, as in the autoclave, the partial pressure of carbon monoxide is lowest at $t = 0$ and increases with increasing conversion, thus decreasing the rate. When hydrogen gas is bubbled through the solution, the amount of carbon monoxide present at any instant is proportional to the amount of unreacted $HRu_3(\mu\text{-COMe})(CO)_{10}$; thus, the rate increases with increasing conversion and higher flow rates, which remove carbon monoxide more rapidly, producing higher rates of reaction. At a high enough flow rate in the open system or at a high enough hydrogen pressure, the slope of the first-order plot should approach k_1, the rate constant for dissociation of carbon monoxide from $HRu_3(\mu\text{-COMe})(CO)_{10}$. The highest value of the slopes of these plots that we obtained at 40 °C was $2.7 \pm 1.4 \times 10^{-4}$ s^{-1}. An attempt to measure the rate of ^{13}CO incorporation was thwarted by the complexity of the infrared spectrum of the ^{13}C-enriched product. However, this can be compared with the first-order rate constant of 1.4×10^{-4} s^{-1} for substitution of one carbonyl ligand on $HRu_3(\mu\text{-COMe})(CO)_{10}$ by $AsPh_3$, a process involving CO dissociation in the rate-determining step.[23] At this time the most that can be inferred from these data is that the limiting rate of hydrogenation of $HRu_3(\mu\text{-COMe})(CO)_{10}$ is about the same, within experimental error, as the rate of substitution by $AsPh_3$ and that both may proceed through the same initial step—CO dissociation. This same mechanism of CO dissociation followed by oxidative addition of hydrogen has been suggested to be important in ethylene hydrogenation catalyzed by $H_4Ru_4(CO)_{12}$.[5a]

From the proposed mechanism the integrated rate law for conversion of $HRu_3(\mu\text{-COMe})(CO)_{10}$ to an equilibrium mixture with $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ under carbon monoxide and hydrogen is given by eq 8, where A_t, A_{eq}, and A_0 are the concentrations of $HRu_3(\mu\text{-COMe})(CO)_{10}$ at times t, ∞, and 0, respectively.

$$\ln \frac{A_t - A_{eq}}{A_0 - A_{eq}} = \left[\frac{k_1 k_3 P_{H_2} + k_2 k_4 P_{CO}}{k_3 P_{H_2} + k_2 P_{CO}} \right] t \quad (8)$$

If the value of k_1 at 40 °C is taken as the rate constant for substitution of $HRu_3(\mu\text{-COMe})(CO)_{10}$ by $AsPh_3$ (1.4×10^{-4} s^{-1}), then using the extrapolated value for k_4 at 40 °C of 7.7×10^{-8} s^{-1} and $K_{eq} = k_1k_3/k_2k_4 = 1.1$, the ratio k_3/k_2 is calculated to be 6.0×10^{-4}. If the ratio of the Henry's law constants of carbon monoxide to hydrogen (K_{CO}/K_{H_2}) is taken as 2.4,[19] the competition ratio k_3'/k_2', where $k_3' = k_3K_{H_2}{}^{-1}$ and $k_2' = k_2K_{CO}{}^{-1}$, of 1.4×10^{-3} represents the competition of hydrogen and carbon monoxide in solution for the unsaturated intermediate $HRu_3(COMe)(CO)_9$. This should be contrasted with the competition ratio of hydrogen to trimethyl phosphite of 1.7 obtained for the mononuclear Co-

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(20) A_t is the absorbance of the 2054-cm^{-1} peak at time t while A_{eq} is the absorbance at equilibrium.

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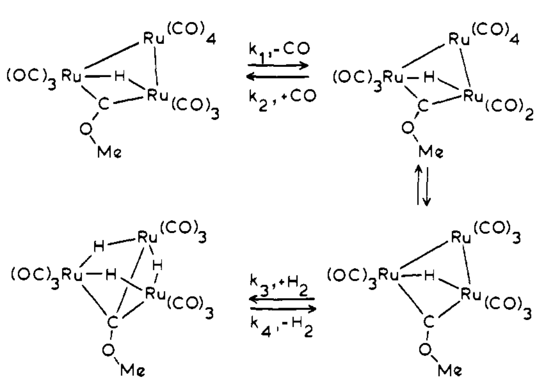

Figure 3. Proposed reaction sequence interconverting (μ-H)Ru_3(μ-COMe)$(CO)_{10}$ and (μ-H)$_3Ru_3$(μ_3-COMe)$(CO)_9$. The two intermediates $HRu_3(COMe)(CO)_9$ are interconverted via intramolecular ligand migrations.

$[P(OMe)_3]_4{}^+$.[9] While trimethyl phosphite is somewhat larger than carbon monoxide and might be expected to compete less effectively, this difference seems much too great to be explained as being due to steric effects.

A possible explanation for the very poor competition between hydrogen and carbon monoxide for the unsaturated $HRu_3(COMe)(CO)_9$ is that the two reactions may proceed through transition states differing significantly in structure. One intriguing possibility is that carbon monoxide dissociation and association might occur at a different metal center than oxidative addition and reductive elimination of hydrogen. For example, CO dissociation from one of the Ru atoms bridged by the hydride ligand would give an intermediate with unequal numbers of carbonyl ligands on each metal (two, three, and four) and a carbonyl migration from the nonbridged Ru atom would be required before addition of hydrogen would give the product (Figure 3).[24] If there were a significant difference in energy between the two isomers of $HRu_3(COMe)(CO)_9$, then carbon monoxide could react much faster than hydrogen because of the population differences between the two intermediates. A second possibility is that the bridging mode of the COMe ligand is different in the two transition states.[26]

From the small value of k_3/k_2, the rate constant k_{obsd} in eq 8 for conversion to the equlibrium mixture reduces to eq 9:

$$k_{obsd} = \left[k_4\left(\frac{k_1 k_3 P_{H_2}}{k_2 k_4 P_{CO}} + 1 \right) \right] \Bigg/ \left[\frac{k_3 P_{H_2}}{k_2 P_{CO}} + 1 \right] \approx k_4\left(K_{eq} \frac{P_{H_2}}{P_{CO}} + 1 \right) \quad (9)$$

As can be seen in Table II, there is good agreement between k_{obsd} at a given temperature and $k_{obsd-calcd}$ calculated from k_4, K_{eq}, P_{H_2}/P_{CO}, and eq 9.

In summary, the data obtained in our study are consistent with the mechanism proposed in eq 5 and 6. These data specifically exclude mechanisms for carbonylation of $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ involving rate-determining CO dissociation and bimolecular reductive elimination of hydrogen or rate-determining attack by CO on the cluster since either of these would give rise to a rate law with CO dependence in the numerator. By microsopic reversibility and the observation of CO inhibition of hydrogenation, rate-determining Ru–Ru bond cleavage prior to CO dissociation can be excluded as a possibility for this cluster hydrogenation. However, it is impossible to infer anything about the structure of the intermediate $HRu_3(COMe)(CO)_9$, in particular whether the COMe ligand is μ_2- or μ_3-bridging, whether any structural change other than loss of CO or H_2 are involved in its formation (e.g., reversible Ru–Ru bond cleavage, followed by rate-determining CO or H_2 dissociation), or what the coordination number is at each metal site. There is no direct kinetic evidence, other than the extremely poor ability of hydrogen to compete for the unsaturated intermediate, which would suggest that oxidative addition or reductive elimination of hydrogen are in anyway different for a cluster than for a mononuclear metal center.

Although oxidative addition and reductive elimination of molecular hydrogen seem mechanistically similar for these metal clusters and for mononuclear complexes, the question remains as to just how similar these processes are to adsorption and desorption of hydrogen on metal surfaces. Adsorption and desorption of hydrogen and of carbon monoxide on Ru metal dispersed on supports, on Ru metal foils, and on Ru single crystals have been investigated. While it is difficult to make comparisons between studies of molecular metal complexes in solution and studies of metal surfaces under high vacuum, there is clearly a need to relate such studies if the metal cluster–metal surface analogy is to be useful.

On Ru metal surfaces hydrogen dissociatively chemisorbs to a stoichiometry of 1 H atom:1 Ru surface atom.[27] Thermal desorption experiments indicate two states for adsorbed hydrogen atoms on the Ru (001) surface; the β_2 state at low coverages and the β_1 state at higher coverages may represent different sites.[28] On the Fe (110) surface,[29] and most likely on Ru, the surface-bound hydrogen atoms occupy bridging positions. Adsorption of hydrogen on a clean Ru surface takes place with no measurable activation energy. Theoretical treatments of dissociative chemisorption of hydrogen suggest that the axis of the hydrogen molecule is parallel to the surface in the transition state.[30] The rate law for desorption of hydrogen from the Ru (001) surface is second order in adsorbed hydrogen atoms, and the activation energy for desorption increases from a value of 11 kcal/mol at high coverage to 26 kcal/mol at low coverage.[31] The kinetics for hydrogen desorption have been interpreted in terms of surface recombination of mobile hydrogen atoms. No measurable deuterium isotope effect is observed for desorption from Ru (001);[28] however, for other metals, for example, Ni,[32] the heat of adsorption of deuterium gas is as much as 0.6 kcal/mol greater than that for hydrogen gas, implying a substantial kinetic isotope effect (~1.8) for desorption.

Carbon monoxide adsorption and desorption on Ru metal have been extensively investigated. At low temperatures carbon monoxide adsorbs nondissociatively on a clean Ru (001) surface.[28,33] Desorption of carbon monoxide is first order in adsorbed carbon monoxide. Two peaks are observed in the thermal desorption. The β_3 peak (low coverage) has a desorption energy of 28 kcal/mol, and the value for the β_2 peak (higher coverage) is 24 kcal/mol. The existence of two states for adsorbed carbon

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[24] Substitution by triphenylphosphine on $MnRe(CO)_{10}$ to give $(OC)_5MnRe(CO)_4PPh_3$ has been proposed to involve CO dissociation from Mn, CO migration from Re to form a carbonyl-bridged intermediate, and then attack of triphenylphosphine at Re.[25]

[25] Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.

[26] A referee has suggested that the large value for k_1/k_4 of 1800 at 40 °C is also unusual and does not parallel data obtained from metal surface studies. Our proposal accounts for this large ratio since k_1 applies to CO dissociation from a metal atom differing in both its oxidation state and ligand environment from the metal atom on which hydrogen is replaced by CO. The relative metal–carbonyl and metal–hydride bond strengths are very sensitive to such differences. The proper numbers for comparison to CO and hydrogen adsorbed on surfaces would be the rates of CO dissociation and hydrogen elimination from the same metal atom. An estimate of the rate of CO dissociation from the $Ru(CO)_4$ unit may be taken as 3.5×10^{-6} s^{-1} at 40 °C, which is one-third of the rate constant found for $Ru_3(CO)_{12}$.[3i] The ratio of 45 for this number to k_4 is not very different from results of studies of some mononuclear complexes, e.g., $Ir(CO)Cl(PPh_3)_2$[6b] or $[Ir(CO)_2L_2][BPh_4]$.[8] Since there are large differences between the steric and electronic environments of the metal atoms of surfaces and those in clusters, there is no reason to expect that the comparison between rates of surface reactions and of reactions of clusters to be any closer than between rates for metal complexes with significantly different ligands.

[27] Sinfelt, J. H. *J. Catal.* **1973**, *29*, 308.

[28] Peebles, D. E.; Schreifels, J. A.; White, J. M. *Surf. Sci.* **1982**, *116*, 117 and references therein.

[29] Barõ, A. M.; Erley, W. *Surf. Sci.* **1981**, *112*, L759.

[30] (a) Johansson, P. K. *Surf. Sci.* **1981**, *104*, 510. (b) Weinberg, W. H.; Merrill, R. P. *Ibid.* **1972**, *33*, 493.

[31] Schwarz, J. A. *Surf. Sci.* **1979**, *87*, 525 and references therein.

[32] Wedler, G.; Bröcker, F. J.; Fisch, G.; Schroll, G. *Z. Phys. Chem. (Wiesbaden)* **1971**, *76*, 212.

[33] Schwarz, J. A.; Kelemen, S. R. *Surf. Sci.* **1979**, *87*, 510 and references therein.

monoxide has been attributed to CO–CO repulsive interactions at higher coverages.[28] Infrared studies of carbon monoxide adsorbed on the Ru (001) surface indicate a linear CO bonded through carbon.[34]

Coadsorption of hydrogen and carbon monoxide on Ru metal has also been examined.[28] Preadsorbed carbon monoxide blocks hydrogen adsorption on the Ru (001) surface, and preadsorbed hydrogen blocks carbon monoxide adsorption but less strongly. Carbon monoxide does not displace preadsorbed hydrogen, nor does hydrogen displace preadsorbed carbon monoxide. There is evidence for strong CO–H repulsive interactions on the surface, and segregation of CO and H atoms on the surface has been proposed.

Our study of the $HRu_3(\mu\text{-COMe})(CO)_{10}/H_3Ru_3(\mu_3\text{-COMe})(CO)_9$ system is most closely related to the results from coadsorption of carbon monoxide and hydrogen on Ru metal. For both the cluster and the metal surface replacement of carbon monoxide by hydrogen and vice versa involve dissociation of the preadsorbed (coordinated) species as the first step. On both the cluster and the surface hydrogen dissociatively chemisorbs (oxidatively adds) to give bridging hydrogen atoms; the coincidentally identical stoichiometry of 1 H:1 Ru is probably not significant. The activation energies for desorption of carbon monoxide or hydrogen from Ru metal are similar in magnitude to "desorption" from the appropriate Ru cluster.[26] In both systems interactions between the hydrogen atoms and the other adsorbed species (ligands) affect the binding energies. On the Ru (001) surface repulsive interactions between H and CO are suggested; in the cluster series the stability of $H_3Ru_3(\mu_3\text{-CX})(CO)_{9-n}L_n$ with respect to loss of hydrogen decreases in the order $CX = COMe > CNR_2 > CO^-$ and $L = SbPh_3 > CO$.[17]

Significant differences between the cluster system and Ru metal are also noted. Hydrogen atom migration on the Ru metal surface is important in the desorption kinetics,[31] but on the small Ru_3 cluster the hydrogen atoms are already close together so that migration is not required.[35] No measurable deuterium isotope effect for desorption of hydrogen from the Ru (001) surface is observed,[28] whereas $k_H/k_D = 1.4$ for reductive elimination of hydrogen from $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$; however, for other metals differences in the heats of adsorption would suggest k_H/k_D for desorption on the order of 2.[32] Another significant difference is that adsorption of hydrogen on a clean Ru surface proceeds with no measurable activation energy,[28] but there appears to be a substantial barrier for oxidative addition of hydrogen to either an unsaturated mononuclear complex or to an unsaturated cluster. This, however, may be due to the impossibility of studying the molecular metal cluster equivalent of a "clean" metal surface. Not only are there always large numbers of other ligands present on a molecular species, but a metal complex in solution, even an "unsaturated" complex, is always involved in a large number of interactions with solvent molecules.[36] Adsorption of molecules on molecular metal clusters or on mononuclear metal complexes is more likely to be relevant to adsorption on fully covered metal surfaces, analogous to the situation existing for metal catalysts under operating conditions, than to adsorption on clean metal surfaces under high vacuum.

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Registry No. $HRu_3(\mu\text{-COMe})(CO)_{10}$, 71737-42-3; $HRu_3(COMe)(CO)_9$, 85849-96-3; $H_3Ru_3(\mu_3\text{-COMe})(CO)_9$, 71562-47-5; H_2, 1333-74-0; CO, 630-08-0; deuterium, 7782-39-0.

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(34) (a) Pfnür, H.; Hoffman, F. M.; Ortega, A.; Menzel, D.; Bradshaw, A. M. *Surf. Sci.* **1980**, *93*, 431. (b) Weaire, D. *Ibid.* **1981**, *103*, L115.

(35) The hydride ligands for $H_3Ru_3(\mu_3\text{-COMe})(CO)_{9-n}(AsPh_3)_n$ (n = 1, 2) are static on the NMR timescale at room temperature.[17]

(36) It should be noted that oxidative addition of hydrogen by the unsaturated fragment $Fe(CO)_4$ has been observed in a 10% hydrogen in argon matrix at 10 K.[37]

(37) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410.