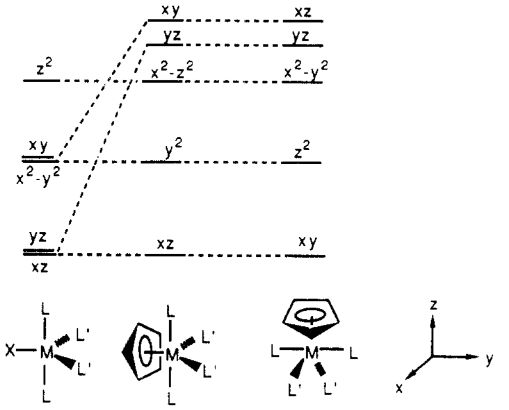

Figure 4. Qualitative relationship between the metal d orbitals in a tbp coordination compound and in pseudo tbp structure where one of the equatorial ligands is a six-electron-donor aromatic ring (the diagram is identical for ring = arene, Cp (shown), or cyclobutadiene).

a tbp complex is drastically changed when a six-electron donor such as Cp or an arene occupies one equatorial position. Looking at these two limiting geometries as tbp and sp is geometrically reasonable but electronically unacceptable. One of the two orbitals that is responsible for making the equatorial positions in the tbp structure better for π acceptors (xy) is sequestered by the π interaction with the organic ring and so is another orbital (yz) (see Figure 4, left and middle diagrams). Upon proper reorientation of the axes, the right-hand diagram is obtained, which presents the same relative ordering of the ideal four-legged piano stool, as expected.

Figure 4 allows one to rationalize (on the basis of the better π-donation properties of the z^2 orbital) why, in a 18-electron structure with two trans π donors and two trans π acceptors, the π donors will prefer the positions with the smaller θ (pseudoaxial position in the tbp description) and the π acceptors will prefer the positions with the larger θ, whereas the reverse is true for 17-electron and low-spin 16-electron complexes, but it failes to explain why a π acid will have a larger θ value when trans to another π acid with respect to when it is trans to another non-π-acidic ligand *within the same structure*, as for instance in MoCp(C_3F_7)$(CO)_3$. A more in-depth analysis of the electronic structure seems to be necessary to explain this effect.

Acknowledgment. I thank the Camille and Henry Dreyfus Foundation (New Faculty Award), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the General Research Board of the University of Maryland for support of this work and Professors B. W. Eichhorn, R. Hoffmann, and J. A. Tossell for helpful comments.

O-Protonation of the $(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_{10}$ Anion. Rearrangement of $(\mu\text{-H})Ru_3(\mu\text{-COH})(CO)_{10}$ to $H(\mu\text{-H})Ru_3(CO)_{11}$. Kinetics of Reductive Elimination of Hydrogen from $H(\mu\text{-H})Ru_3(CO)_{11}$

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The kinetic product from protonation of $[(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_{10}]^-$ with CF_3SO_3H is $(\mu\text{-H})Ru_3(\mu\text{-COH})(CO)_{10}$. This product rearranges to $H(\mu\text{-H})Ru_3(CO)_{11}$ within 20 s at 25 °C. Alternatively, $H(\mu\text{-H})Ru_3(CO)_{11}$ is the only product formed by protonation with CF_3CO_2H. Products were characterized by ^1H NMR spectroscopy at low temperatures and by FT-IR spectroscopy at ambient temperature. $H(\mu\text{-H})Ru_3(CO)_{11}$ is isostructural with the Os analogue, having one bridging and one terminal hydride ligand; these hydrides undergo exchange on the NMR time scale ($\Delta G^{\ddagger}$ = 51.9 kJ/mol at 236 K). $H(\mu\text{-H})Ru_3(CO)_{11}$ decomposes rapidly (k(298 K) = $(1.27 \pm 0.19) \times 10^{-2}\ s^{-1}$) to $Ru_3(CO)_{12}$ and hydrogen. Activation parameters ($\Delta H^{\ddagger}$ = 124 (6) kJ/mol, $\Delta S^{\ddagger}$ = 136 (20) J/(K mol)) and the deuterium kinetic isotope effect (k_H/k_D = 1.12 (0.09) at 298 K) were determined by using stopped-flow FT-IR spectroscopy.

Introduction

Transition-metal complexes of the hydroxycarbyne ligand (COH), although generally unstable with respect to the tautomeric hydrido carbonyl complexes, are possible intermediates in carbon monoxide reduction.[1] Complexes of doubly bridging,[2] triply bridging,[3] and quadruply bridging[4] COH ligands are known, in all cases formed by O-protonation of metal carbonyl anions.

O-Protonation of a carbonyl ligand was first reported in 1978, when $(\mu\text{-H})Fe_3(\mu\text{-COH})(CO)_{10}$ was identified by NMR spectroscopy as the product from anhydrous protonation of $[(\mu\text{-H})Fe_3(\mu\text{-CO})(CO)_{10}]^-$ at low temperatures.[5] Protonation of the analogous osmium anion at room temperature forms the unusual cluster $H(\mu\text{-H})Os_3(CO)_{11}$,

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containing both bridging and terminal hydrides, but low-temperature protonation with DSO_3F gives $(\mu\text{-}H)Os_3(\mu\text{-}COD)(CO)_{10}$.[6] Protonations of $[(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]^-$ at room temperature give $Ru_3(CO)_{12}$[7] or $[HRu_6(CO)_{18}]^-$.[8]

In 1980 one of us reported in a preliminary communication that the kinetic product of protonation of $[(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]^-$ is $(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$ but that this cluster rearranges rapidly to $H(\mu\text{-}H)Ru_3(CO)_{11}$, characterizations of both products relying on ^1H NMR spectroscopy at low temperature; the latter product decomposes at room temperature, forming hydrogen and $Ru_3(CO)_{12}$.[9] Recently, a study of the deuterium kinetic isotope effect for the rearrangement of $(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$ to $H(\mu\text{-}H)Ru_3(CO)_{11}$, followed by NMR spectroscopy at low temperature, has been reported.[6] Since $H(\mu\text{-}H)Ru_3(CO)_{11}$ is one of the few examples of clusters containing terminal hydride ligands and since it has been suggested as a possible intermediate in water-gas shift catalysis,[7] we were interested in its reactivity for reductive elimination of hydrogen. In this paper we report the full details of the protonation reaction, including characterization of the unstable products for the first time by FT-IR spectroscopy and measurements of the kinetics for the conversion of $H(\mu\text{-}H)Ru_3(CO)_{11}$ to $Ru_3(CO)_{12}$.

Experimental Section

Chemicals. $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ was prepared by a published method;[10a] $[NEt_3D][(\mu\text{-}D)Ru_3(\mu\text{-}CO)(CO)_{10}]$ was prepared by the same method by using D_2O (Aldrich, 99.8 atom % D). Trifluoroacetic acid (the deuterium content for the acid used in the determination of the kinetic isotope effect was 99 atom % D) and trifluoromethanesulfonic acid were obtained from Aldrich and were used as received. Unless otherwise specified, all solvents were used as received.

Infrared Spectrum of $H(\mu\text{-}H)Ru_3(CO)_{11}$. Low-temperature infrared spectra were recorded by using a Beckman 4250 spectrophotometer equipped with a Beckman RIIC Model VLT-2 variable-temperature accessory. A solution of $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (19 mg, 0.026 mmol) in dichloromethane (1 mL) was cooled with a dry ice–acetone bath under a nitrogen atmosphere. Then trifluoromethanesulfonic acid (5 mL) was added, and the solution was stirred. The solvent was removed by vacuum transfer, with the temperature still maintained at −77 °C. Then pentane (3 mL) was added under a nitrogen atmosphere. The resulting red-orange solution was sampled by using a syringe and then quickly transferring the sample to the infrared cell, which had previously been cooled to −40 °C. Spectra were recorded, and the the cell was slowly warmed to 25 °C, with periodic recording of spectral changes. IR (pentane, −40 °C): 2089 w, 2079 m ($Ru_3(CO)_{12}$), 2064 vs ($H(\mu\text{-}H)Ru_3(CO)_{11}$ + $Ru_3(CO)_{12}$), 2054 s, 2027 s ($H(\mu\text{-}H)Ru_3(CO)_{11}$ + $Ru_3(CO)_{12}$), 2013 w br ($Ru_3(CO)_{12}$), 2000 w br, 1973 w, 1966 w cm^{-1}. The IR spectrum of the solution at 25 °C was mainly that of $Ru_3(CO)_{12}$. IR (pentane, 25 °C): 2077 m, 2061 vs, 2030 s, 2013 m cm^{-1}.

The spectrum was also obtained at room temperature by using stopped-flow FT-IR spectroscopy. When dichloromethane solutions of $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (2 mM) and CF_3CO_2H (26 mM) were mixed, the spectrum of $H(\mu\text{-}H)Ru_3(CO)_{11}$ was obtained (Figure 3i): 2127 (vw), 2087 (m), 2065 (vs), 2051 (s), 2028 (m), 2020 (m), 1994 (m) cm^{-1}.

NMR Spectra of $H(\mu\text{-}H)Ru_3(CO)_{11}$. ^1H spectra were recorded on a JEOL FX-90 instrument. In each case the NMR tube was prepared by loading $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (ca. 40 mg) into the tube in a drybox and capping the tube with a rubber septum. Solvent was added via syringe. Then a spectrum was recorded at a probe temperature of ca. −65 °C. The tube was removed, the acid was added via a microliter syringe, and the tube was immediately replaced in the probe. ^1H NMR (CF_3SO_3H, MeOH-d_4, 223 K): −11.93 (br, 1 H), −18.74 (br, 1 H) ppm. ^1H NMR (CD_2Cl_2, CF_3CO_2H, 216 K): −11.79 (d, 1 H), −18.55 (d, 1 H) ppm; J = 1.7 Hz.

Determination of the Yield of $Ru_3(CO)_{12}$ from the Decomposition of $H(\mu\text{-}H)Ru_3(CO)_{11}$ under CO. To a sample of $[NEt_4][(\mu\text{-}H)Ru_3(CO)_{11}]$ (93.2 mg, 0.146 mmol) under a CO atmosphere in a Schlenk flask was added methanol (freshly distilled, 10 mL). This solution was cooled with use of a dry ice–acetone bath, and then 12 mL of a 1.4×10^{-2} M solution of trifluoromethanesulfonic acid in methanol was added via an addition funnel. The solution was stirred for a few minutes and was then warmed to room temperature. As the solution warmed over a ca. 10-min period, the color of the solution changed from deep red to brown-yellow and a yellow precipitate formed. The final solution was yellow. The solvent was reduced in volume by vacuum transfer. The solid residue was collected on a tared frit and washed with methanol. The solid was identified by its IR spectrum as $Ru_3(CO)_{12}$ (73.2 mg, 87.8%). The filtrate was evaporated to dryness. The residue was purified by using thin-layer chromatography on silica with hexane as eluent; extraction of the single yellow band yielded 6.6 mg (7.9%) of $Ru_3(CO)_{12}$ (total recovery 95.7%).

Determination of the Gas Composition from the Decomposition of $H(\mu\text{-}H)Ru_3(CO)_{11}$. Solid $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (recrystallized from methanol; 311.1 mg, 0.4189 mmol) was placed in a reaction tube equipped with a Teflon vacuum stopcock and stirbar. A solution of trifluoroacetic acid (39 μL, 0.51 mmol) in methanol (10 mL, freshly distilled) was degassed on the vacuum line by using three freeze–pump–thaw cycles and was then vacuum-transferred into the reaction vessel. After it was thawed, the solution changed from purple-red to red-brown and gas was evolved. The noncondensible gas was collected by Toepler pump in a section of the vacuum line of known volume (64 mmHg, 303 K, 0.0899 L; gas yield 0.304 mmol). A sample of the gas was isolated and submitted for mass spectrometric analysis to the Mass Spectrometry Laboratory at Pennsylvania State University; the gas composition was determined to be 88% hydrogen and 12% carbon monoxide (yield of hydrogen 64%).

The solution remaining after decomposition was filtered under an inert atmosphere. The orange solid that was collected was washed with methanol and dichloromethane and was identified as $Ru_3(CO)_{12}$ (195.7 mg). The brown filtrate was evaporated to dryness, and the residue was dissolved in dichloromethane and was purified by thin-layer chromatography on silica with dichloromethane–hexane mixtures as eluents. Fractions were identified by IR spectroscopy: band 1, 4.1 mg, $Ru_3(CO)_{12}$ + $H_4Ru_4(CO)_{12}$; band 2, 9.9 mg, $Ru_3(CO)_{12}$ + $H_2Ru_4(CO)_{13}$. Additional $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ (12.4 mg) were recovered from the portion of the residue that remained after extraction with dichloromethane.

Variable-Temperature ^1H NMR Spectra. A sample was prepared by using $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (31 mg, 0.042 mmol) in dry dichloromethane-d_2 and then adding trifluoroacetic acid (3.4 mL, 0.051 mmol). The tube was immediately placed into the cold probe. Spectra were recorded at 216, 226.4, 231.0, 236.0, and 254.9 K, all temperatures being measured by the method of van Geet.[11] At higher temperatures the resonances were too broad to be observed. Rate constants at each temperature were determined by comparison of the experimental spectra with spectra calculated by using the program DNMR3.[12] Free energies of activation were calculated at each temperature (226.4 K, k =

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Table I. First-Order Rate Constants for Hydrogen Elimination from $H(\mu\text{-}H)Ru_3(CO)_{11}$

T, K	$10^2 \times [CF_3CO_2H]$, M	10^2k, s^{-1}	T, K	$10^2 \times [CF_3CO_2H]$, M	10^2k, s^{-1}
303.2	1.83	3.1 (0.5)[a]	298.0	5.2	1.24 (0.04)[a]
300.2	2.6	1.71 (0.03)[a]	298.0	1.3	1.37 (0.05)[a,c]
298.0	1.3	1.20 (0.09)[a]	298.0	1.3	1.22 (0.05)[a,c,d]
298.0	2.6	1.13 (0.10)[a]	291.5	1.83	0.50 (0.07)[a]
298.0	2.6	0.90 (0.14)[b]	273.2	0	0.011 (0.002)[b,e]

[a] Solutions were saturated with carbon monoxide. [b] Solutions were saturated with nitrogen. [c] These values were obtained from experiments on the same day with use of identically prepared solutions. [d] Deuterium labeled. [e] Determined by using ^1H NMR spectroscopy for detection.

5 s^{-1}, $\Delta G^\ddagger = 51.9$ kJ/mol; 231.0 K, $k = 8$ s^{-1}, $\Delta G^\ddagger = 52.1$ kJ/mol; 236.0 K, $k = 16$ s^{-1}, $\Delta G^\ddagger = 51.9$ kK/mol; 254.9 K, $k = 103$ s^{-1}, $\Delta G^\ddagger = 52.3$ kJ/mol. Least-squares determination of the slope and intercept of the Eyring plot for these data gave $\Delta H^\ddagger = 49$ (±6) kJ/mol (11.8 (±1.5) kcal/mol) and $\Delta S^\ddagger = -12$ (±26) J/(K mol) (−3 (±6) eu) at the 95% confidence limit and with use of Student's *t* values.

Kinetics of Hydrogen Elimination by ^1H NMR Spectroscopy. To a solution of $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (33 mg, 0.044 mmol) and an internal standard (either $(\mu\text{-}H)Ru_3(\mu\text{-}COMe)(CO)_{10}$ or $(\mu\text{-}H)Os_3(\mu\text{-}CNMeCH_2Ph)(CO)_{10}$ (ca. 30 mg)) in dichloromethane-d_2 was added trifluoroacetic acid (3.5 mL, 0.045 mmol). The tube was immediately placed in the NMR probe at −80 °C, and the spectrum was recorded. Then the tube was removed and was placed in an ice bath. At 20–30-min intervals over a 4-h period the tube was removed and the spectrum recorded at −80 °C. The total time for the reaction in the ice bath was 220 min. A plot of ln (integral of $H(\mu\text{-}H)Ru_3(CO)_{11}$ vs standard) vs time yielded the rate constant of $(1.11 \pm 0.17) \times 10^{-4}$ s^{-1}.

FT-IR Spectroscopy. The rate measurements and associated IR spectra were carried out with use of a prototype FT-IR stopped-flow cell developed by J.M., in collaboration with Hi-Tech Scientific Ltd. (Brunel Road, Salisbury, Wiltshire, England SP2 2PU) and Specac Analytical Accessories Ltd. (Unit 3, Lagoon Road, St. Mary Cray, Orpington, Kent, England BR5 3QX). The design is based upon that of the Hi-Tech SFA-11 rapid kinetics accessory, with the place of the UV–visible spectrometer mixing cell being taken by an IR mixing cell. The dead time for the mixer, with normal hand-push, is estimated as 20–30 ms. The cell windows are made of ZnSe, and in these experiments the path length of 1 mm was set by PTFE gaskets.[24] A more complete description of the cell and its operation is in preparation.

FT-IR measurements were conducted on a Nicolet 7199 spectrometer, at a resolution of 4 cm^{-1}. A series of macros, written with use of the Nicolet FT-IR control instructions, were used to collect data a various frequencies and to process and plot the spectra. All spectra were collected at the rate of 0.42 s per spectrum; the slower reactions allowed CAT operation, with 10 scans per reading.

The temperature of the Nicolet FT-IR machine's cell compartment was found to be between 27 and 30 °C. The temperature of the IR cell itself was thermostated at temperatures between 18 and 30 °C to within ±0.3 °C.

Kinetics of Hydrogen Elimination from $H(\mu\text{-}H)Ru_3(CO)_{11}$ by FT-IR Spectroscopy. Solutions of $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ (2×10^{-3} M) and of trifluoroacetic acid (2.56×10^{-2}–1.05×10^{-1} M) in dichloromethane (distilled from calcium hydride under nitrogen and saturated with carbon monoxide) were prepared. Kinetics were determined by using stopped-flow methods, with detection by FT-IR spectroscopy, described above, and monitoring the decrease of the absorption at 2087 cm^{-1} due to $H(\mu\text{-}H)Ru_3(CO)_{11}$. Rate constants were determined by computer-calculated (program KINPLOT, written by Dr. R. Rusczcyk, formerly of the University at Buffalo) least-squares determination of the slope of the plot of ln (absorbance) vs time. Three or four determinations were made for each set of conditions. The rate constants (Table I) are reported as the mean for each set with error limits as the larger of the standard deviation ($n - 1$) or the 95% confidence limit for the least precise measurement of the set.

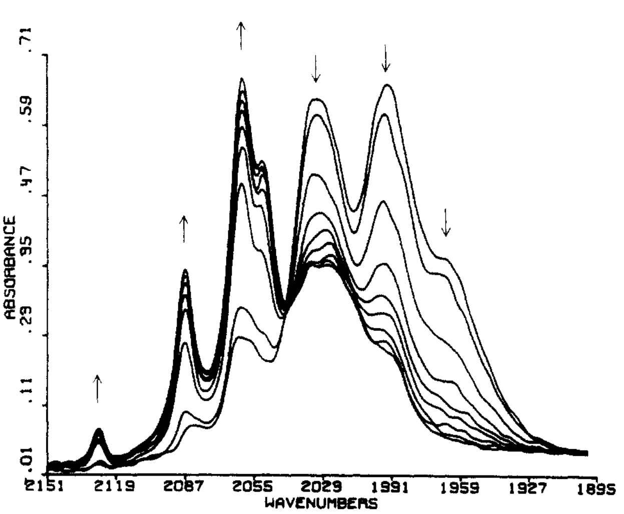

Figure 1. IR spectra during the protonation of $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ with CF_3CO_2H.

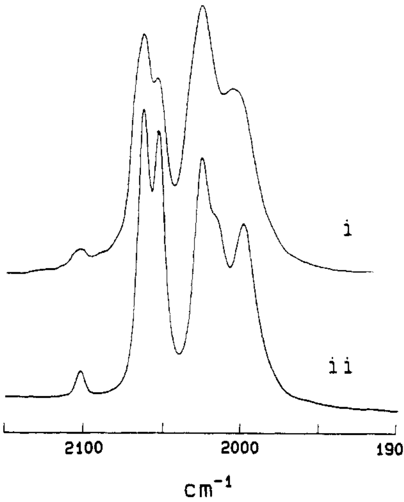

Figure 2. IR spectra of (i) $(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$ and (ii) $(\mu\text{-}H)Ru_3(\mu\text{-}COMe)(CO)_{10}$.

Under continuous-flow conditions it was possible to observe reactions in the cell within 20–30 ms of initiation of the reaction; thus, in Figure 2i, the spectrum shows $(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$, formed from $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ and CF_3SO_3H in dichloromethane within this time scale. CF_3SO_3H was the only acid we tried that provided complete conversion to $(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$. Unfortunately, this acid is not soluble in dichloromethane, thus precluding quantitative measurements. However, protonation of $[NEt_4][(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]$ with CF_3CO_2H occurred within 1 s of mixing, cleanly forming $H(\mu\text{-}H)Ru_3(CO)_{11}$. Figure 1 shows the buildup of $H(\mu\text{-}H)Ru_3(CO)_{11}$ from such a mixture. In the presence of CO the spectrum cleanly decays into that for $Ru_3(CO)_{12}$; in the absence of CO, peaks attributed to $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ are also noted, but the rate constant is the same within experimental error (Table I). No effect of acid concentration was noted on the hydrogen elimination reaction. The rate law for the reaction was found to be first-order for greater than 3 half-lives.

Results and Discussion

$(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$. Protonation of $[(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}]^-$ (0.001 M) in dichloromethane solution with trifluoromethanesulfonic acid (0.01 M) gives as the kinetic product $(\mu\text{-}H)Ru_3(\mu\text{-}COH)(CO)_{10}$ within the 20–30 ms of mixing in the stopped-flow apparatus. This product was previously characterized by its ^1H NMR spectrum[6,9] at 208 K, which consists of singlets at −14.60 and +16.11 ppm (cf. $(\mu\text{-}H)Fe_3(\mu\text{-}COH)(CO)_{10}$,[5] −18.4 and +15.0 ppm, and $(\mu\text{-}H)Ru_3(\mu\text{-}COMe)(CO)_{10}$,[10a] hydride resonance −14.85 ppm).

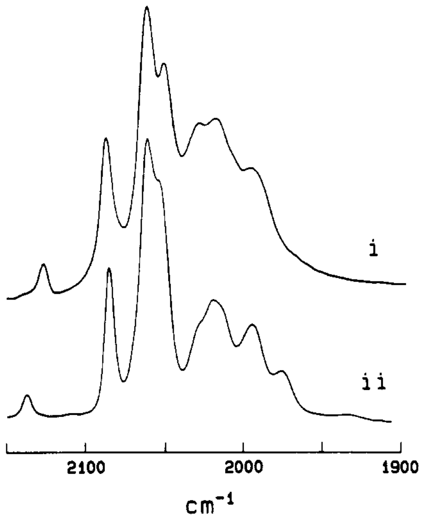

Figure 3. IR spectra of (i) H(μ-H)Ru$_3$(CO)$_{11}$ and (ii) H(μ-H)Os$_3$(CO)$_{11}$.

Its IR spectrum, obtained by stopped-flow FT-IR spectroscopy (Figure 2i: 2100 (w), 2058 (vs), 2050 (s), 2021 (vs), and 2000 (s, br) cm^{-1}), is very similar to that of (μ-H)Ru$_3$(μ-COMe)(CO)$_{10}$ (Figure 2ii), suggesting that these are isostructural (Figure 5i). Attempts to obtain the ^{13}C NMR spectrum of (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$ were unsuccessful, due to the difficulty in obtaining a pure sample.

H(μ-H)Ru$_3$(CO)$_{11}$. At 298 K (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$ rapidly rearranges to H(μ-H)Ru$_3$(CO)$_{11}$ ($t_{1/2}$ ca. 5 s). Alternatively, protonation of [(μ-H)Ru$_3$(μ-CO)(CO)$_{10}$]$^-$ with CF$_3$CO$_2$H cleanly forms H(μ-H)Ru$_3$(CO)$_{11}$, without the formation of observable quantities of (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$ (Figure 1). The IR spectrum of this unstable product (Figure 3i) was obtained under stopped-flow conditions in dichloromethane; the spectrum is very similar to that of H(μ-H)Os$_3$(CO)$_{11}$ (Figure 3ii), suggesting structural analogy (Figure 5ii). This product is characterized by its ^{1}H NMR spectrum at 216 K, which consists of doublets at −11.98 and −18.74 ppm, assigned to terminal and bridging hydrides, respectively, with an interhydride coupling constant of 1.7 Hz; at higher temperatures the hydride resonances are broadened, and above 250 K the compound decomposes by loss of hydrogen, yielding largely Ru$_3$(CO)$_{12}$. The ^{1}H NMR spectrum is quite similar to that of the Os analogue (−10.25 and −19.96 ppm, J = 3.8 Hz).[13] Several attempts to record the ^{13}C NMR spectrum were unsuccessful, due to the difficulty in obtaining a pure sample by protonation of the anion in the NMR tube at low temperature.

Rate constants for exchange of the two hydride ligands of H(μ-H)Ru$_3$(CO)$_{11}$ were determined from line broadening near the slow-exchange limit. From the limited data available (four points), an Eyring plot provides values of $\Delta H^\ddagger = 49\ (\pm 6)$ kJ/mol and $\Delta S^\ddagger = -12\ (\pm 27)$ J/(K mol). The value of $\Delta G^\ddagger$ at 236 K, 51.9 kJ/mol (estimated error limits ±0.2 kJ/mol), is quite close to the value of $\Delta G^\ddagger$(240 K) = 54.0 kJ/mol for hydride fluxionality in H(μ-H)Os$_3$(CO)$_{11}$.

Mechanism for Isomerization of (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$ to H(μ-H)Ru$_3$(CO)$_{11}$. Pribich and Rosenberg[6] have studied the kinetics of rearrangement of (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$, formed by protonation with HSO$_3$F in CD$_2$Cl$_2$, to H(μ-H)Ru$_3$(CO)$_{11}$, using NMR spectroscopy.

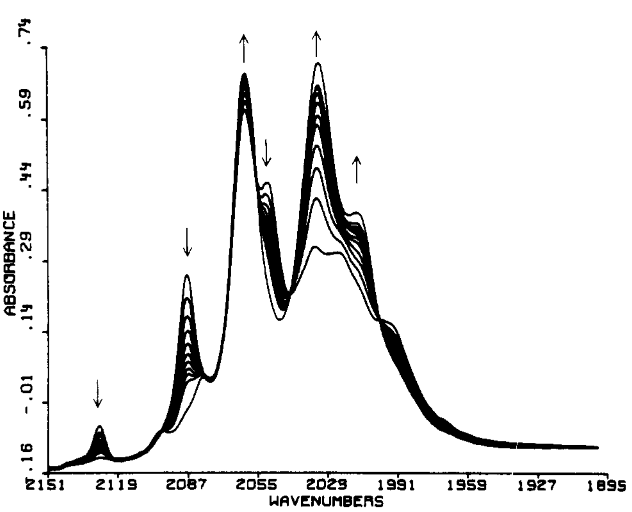

Figure 4. IR spectra during the conversion of H(μ-H)Ru$_3$(CO)$_{11}$ to Ru$_3$(CO)$_{12}$.

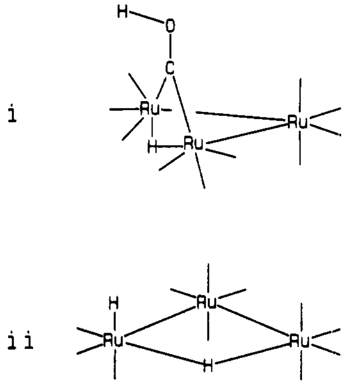

Figure 5. Proposed structures for (i) (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$ and (ii) H(μ-H)Ru$_3$(CO)$_{11}$.

They report a very large kinetic isotope effect of 47 at −40 °C, with a rate constant of ca. 3 × 10^{-4} s^{-1}. These authors described the rearrangement as an intramolecular proton transfer from the carbonyl oxygen atom to the metal core.

A large isotope effect has also been measured for the reverse process, proton migration from a metal core to a coordinated ligand.[23] Isomerization of H(μ-H)Os$_3$(CO)$_{10}$(CNMe) (isoelectronic and isostructural with H(μ-H)Ru$_3$(CO)$_{11}$) to (μ-H)Os$_3$(μ-CNHMe)(CO)$_{10}$ (isoelectronic and isostructural with (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$) displays a deuterium kinetic isotope effect of 27 at 30 °C. The reaction is favored by coordinating solvents and is base-catalyzed. The fact that the isotope effect was reduced to a value close to 1 by the addition of a base catalyst was taken to indicate that separate intra- and intermolecular proton transfer mechanisms were operative in the uncatalyzed and base-catalyzed isomerizations, respectively.

These isomerizations appear to be closely related to the much slower tautomerization of Ru$_3$(μ_3-NOH)(CO)$_9$ to (μ-H)Ru$_3$(μ-NO)(CO)$_{10}$, reported by Gladfelter and coworkers.[14] Protonation of Ru$_3$(NO)(CO)$_{10}^-$ with CF$_3$SO$_3$H gives Ru$_3$(μ_3-NOH)(CO)$_{10}$, but weaker acids, such as CF$_3$CO$_2$H, yield (μ-H)Ru$_3$(NO)(CO)$_{10}$. This study found anion-assisted isomerization, such that addition of PPN[CF$_3$CO$_2$] caused immediate isomerization of Ru$_3$(μ_3-NOH)(CO)$_{10}$ to (μ-H)Ru$_3$(NO)(CO)$_{10}$.

The mechanism for rearrangement of (μ-H)Ru$_3$(μ-COH)(CO)$_{10}$ to H(μ-H)Ru$_3$(CO)$_{11}$ is therefore presumed

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to be an intramolecular proton transfer from oxygen to the metal core when HSO_3CF_3 is used in the protonation but may involve base-catalyzed proton transfer when CF_3CO_2H is used. Unfortunately, crossover experiments using isotope labeling are not feasible in this system.

Kinetics for Reductive Elimination of Hydrogen. Near ambient temperature and in the presence of carbon monoxide, $H(\mu\text{-}H)Ru_3(CO)_{11}$ decomposes cleanly to $Ru_3(CO)_{12}$ (97% isolated yield). Figure 4 shows the changes in the 2150–1900-cm^{-1} region of the IR spectrum during this reaction. Under a nitrogen atmosphere $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ are formed in addition to $Ru_3(CO)_{12}$, and the gaseous products are hydrogen (64% yield) and CO. The kinetics of conversion of $H(\mu\text{-}H)Ru_3(CO)_{11}$ to $Ru_3(CO)_{12}$ in dichloromethane solution were found to be first order in $H(\mu\text{-}H)Ru_3(CO)_{11}$, and the rate constant is independent of either CO concentration or the concentration of trifluoroacetic acid (Table I). The value of the first-order rate constant at 298 K was $(1.27 \pm 0.19) \times 10^{-2}$ s^{-1} (from all measurements at 298 K). Measurements of rate constants for $D(\mu\text{-}D)Ru_3(CO)_{11}$ found $k_H/k_D = 1.12$ ($\pm$0.09). The activation parameters, derived from all data, are $\Delta H^\ddagger = 124$ (6) kJ/mol (29.7 (1.4) kcal/mol) and $\Delta S^\ddagger = 136$ (20) J/(K mol) (33 (5) eu).

These results should be compared with the kinetics of hydrogen elimination from $H(\mu\text{-}H)Os_3(CO)_{11}$.[15] The rate law is identical with that found here for the Ru analogue, but the activation parameters ($\Delta H^\ddagger = 93$ kJ/mol; $\Delta S^\ddagger = -35$ J/(K mol)) and kinetic isotope effect ($k_H/k_D = 1.8$ (2)) are quite different. The mechanism proposed for the Os cluster involves rate-determining reductive elimination through a three-center transition state.

The large positive $\Delta S^\ddagger$ value for hydrogen elimination from $H(\mu\text{-}H)Ru_3(CO)_{11}$ and the negative value reported for $H(\mu\text{-}H)Os_3(CO)_{11}$ might be taken to indicate different mechanisms for the two. However, mechanistic distinctions based upon comparisons of activation entropies are complicated by the larger error limits associated with the measurements, compared with the errors associated with the determinations of rate constants. This is of some concern for the data from $H(\mu\text{-}H)Ru_3(CO)_{11}$ since the values obtained for the activation parameters are strongly influenced by the measurement at 273 K, which is determined under different concentrations and by a method of monitoring different from those used for the higher temperature data. Since compensating errors are introduced in the values for $\Delta H^\ddagger$, it is not unreasonable to put more trust in comparisons of $\Delta G^\ddagger$ values at the same temperature, if the extrapolations from the temperatures of experimental determinations are not too large.

Three mechanisms for hydrogen elimination should be considered: (1) rate-determining intramolecular reductive elimination of hydrogen,[16] (2) rate-determining CO dissociation, followed by bimolecular reductive elimination (such as that found for the reaction of $H_2Os(CO)_4$, yielding $H_2Os_2(CO)_8$),[17] and (3) a rate-determining intramolecular rearrangement, such as hydride migration or Ru–Ru bond cleavage. The large positive entropy of activation, suggestive of a dissociative mechanism, would seem inconsistent with mechanism 3 but perhaps most consistent with (2) (cf. $\Delta S^\ddagger = 85$ J/(K mol) for CO dissociation from $Ru_3(CO)_{12}$[18]). The low value for k_H/k_D is more consistent with mechanism 2 than with (1) but is not definitive. We see no evidence for inhibition of the elimination by CO, but this cannot be taken to rule out (2). Crossover experiments are not feasible in this system. However, since no higher cluster products such as $[HRu_6(CO)_{18}]^-$ (which is formed upon protonation with sulfuric acid at room temperature[8]) are formed, it seems unlikely that a bimolecular mechanism involving elimination of hydrides of different molecules is occurring.

Table II. Comparison of Activation Parameters for Hydrogen Replacement by CO in Cluster Systems

compd	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/(K mol)	$\Delta G^\ddagger$(298 K), kJ/mol
$H(\mu\text{-}H)Ru_3(CO)_{11}$[a]	124	136	84
$H(\mu\text{-}H)Os_3(CO)_{11}$[b]	93	−35	104
$(\mu\text{-}H)_3Ru_3(\mu_3\text{-}COMe)(CO)_9$[c]	130	33	120
$(\mu\text{-}H)_3Os_3(\mu_3\text{-}COMe)(CO)_9$[d]	159	67	139

[a] This work. [b] Reference 15. [c] Reference 19. [d] Reference 20.

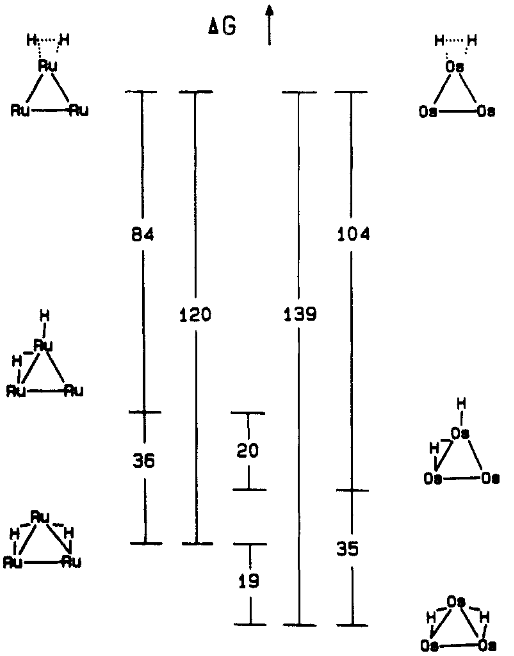

Figure 6. Free energy diagram relating $(\mu\text{-}H)_3M_3(\mu_3\text{-}COMe)(CO)_9$ (lowest pair of structures), $H(\mu\text{-}H)M_3(CO)_{11}$ (middle structures), and the proposed transition state (highest free energy structures) for reductive elimination of hydrogen (M = Ru, Os).

On the other hand, the differences between the *free energies* of activation for the analogous pairs $H(\mu\text{-}H)M_3(CO)_{11}$ and $(\mu\text{-}H)_3M_3(\mu_3\text{-}COMe)(CO)_9$ (Table II) suggest that there is a common mechanism for Ru and Os cluster pairs. Reductive elimination from $(\mu\text{-}H)_3M_3(\mu_3\text{-}COMe)(CO)_9$ (M = Ru,[19] Os[20]) is proposed to occur through a three-center transition state involving a single metal center;[21] this same mechanism has been proposed for $H(\mu\text{-}H)Os_3(CO)_{11}$.[15] Comparison of the pairs $H(\mu\text{-}H)M_3(CO)_{11}$ and $(\mu\text{-}H)_3M_3(\mu_3\text{-}COMe)(CO)_9$ (M = Ru, Os) shows that in each case the free energy of activation for hydrogen elimination from a Ru cluster is 19–20 kJ/mol lower than for its Os analogue. These values are entirely as expected from the thermodynamic considerations. We have de-

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termined that the Os-H-Os bond energy is 17 kJ/mol greater than the Ru-H-Ru bond energy[22] in the pair $(\mu\text{-H})_3M_3(\mu_3\text{-COMe})(CO)_9$. Furthermore, the free energy of activation for hydrogen elimination from $H(\mu\text{-H})M_3(CO)_{11}$ is 36 kJ/mol lower than the value for the corresponding $(\mu\text{-H})_3M_3(\mu_3\text{-COMe})(CO)_9$ for both Ru and Os pairs. Since the M-H-M bond has been estimated to be ca. 45 kJ/mol more stable than the combination of M-H and M-M bonds,[22] the lower free energies of activation for reductive elimination from $H(\mu\text{-H})M_3(CO)_{11}$, compared with the corresponding values for $(\mu\text{-H})_3M_3(\mu_3\text{-COMe})(CO)_9$, may be largely attributed to the relative ground-state energies (Figure 6). Terminal hydride ligands are kinetically and thermodynamically more reactive than are bridging hydrides.

There still is no detailed understanding of the kinetics and thermodynamics of hydride reactivity in cluster systems. Clearly, bridging hydrides are not always energetically more favorable than terminal hydrides, otherwise $H_2Ru_3(CO)_{11}$ should have a different structure than it does. The accumulation of additional quantitative data on hydride reactivity in clusters having a variety of hydride coordination modes is necessary to determine the relationships between structure and reactivity.

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Tetrafluoroethyl Complexes Derived from Insertion of the Tetrafluoroethylene Ligand into an Iridium–Hydride Bond

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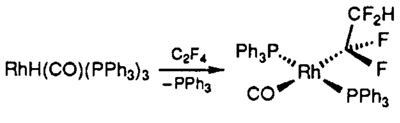
The reaction of $IrH(CO)(PPh_3)_3$ with tetrafluoroethylene gives the hydride olefin complex $IrH(C_2F_4)(CO)(PPh_3)_2$. Further reactions of $IrH(C_2F_4)(CO)(PPh_3)_2$ with a coordinating ligand L (L = C_2F_4, CO, C_2H_4) result in the insertion of the coordinated olefin into the iridium–hydrogen bond and formation of tetrafluoroethyl complexes, $Ir(CF_2CF_2H)(L)(CO)(PPh_3)_2$. Thermal displacement of the ethylene ligand in $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ gives the four-coordinate complex $Ir(CF_2CF_2H)(CO)(PPh_3)_2$. The X-ray crystal structure of the dicarbonyl complex $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ is described. $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.868$ (5) Å, $b = 11.5727$ (5) Å, $c = 17.083$ (9) Å, $\alpha = 103.9$ (4)°, $\beta = 94.14$ (4)°, $\gamma = 113.09$ (3)°, and $Z = 2$ with $d(\text{calcd}) = 1.699$ g cm^{-3} for a molecular weight of 873.83. The structure was refined to give $R = 0.0400$ and $R_w = 0.0407$, and in contrast to the geometry displayed in solution, which has trans triphenylphosphines, has a cis arrangement of triphenylphosphine ligands. The $Ir-CF_2CF_2H$ bond distance is 2.145 (8) Å.

Introduction

The tetrafluoroethylene ligand has proved to be an excellent precursor for σ-bonded transition-metal fluorocarbon complexes.[1] One possibility is the insertion of tetrafluoroethylene into a metal–ligand bond. This reaction has been demonstrated for several different types of ligands but is observed most frequently for the hydride ligand.[2] Metal hydrides react with a large number of olefins and acetylenes, giving products that are a result of formal insertion of the olefin or acetylene into the metal–hydride bond.[3]

The reaction of hydride–carbonyl complexes with alkenes has relevance to the intermediate species in transition-metal-catalyzed hydroformylation,[2c,d] and the insertion of olefins into transition-metal–hydrogen bonds is an important step in a number of other catalytic processes, such as hydrogenation, oligomerization, and polymerization. The reaction of tetrafluoroethylene with rhodium hydrides has been shown to give σ-bonded fluorocarbon complexes in a number of cases (eq 1).[2c,d] Rh-



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