(0.0326 for $F_o^2 > 3\sigma(F_o^2)$) with a goodness of fit of 1.33.

Calculations were done with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference (*International Tables for X-ray Crystallography*; 71, p. 149; Kynoch: Birmingham, 1947; Vol. IV, pp 71, 149): $R = \sum |F_o - |F_c||/\sum F_o$, for only $F_o^2 > 0$, and goodness of fit = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of data and p is the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.014I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. The absorption correction was done by Gaussian integration over an $8 \times 8 \times 8$ grid. Transmission factors varied from 0.431 to 0.732.

Preparation of 5b. A mixture of 5a (200 mg, 0.45 mmol) and AgBF₄ (88 mg, 0.45 mmol) in dichloromethane (25 mL) was allowed to react for 3 h at -20 °C. The resultant solution was filtered and evaporated to give a yellow powder (130 mg, 0.32 mmol, 72%): ¹H NMR (CD₂Cl₂, -10 °C) δ 5.57 (s, 5 H, Cp), 5.54 (s, 5 H, Cp), 2.20 (d, J_{CH} = 10 Hz, 1 H, CH₂), 2.03 (d, J_{CH} = 10 Hz, 1 H, CH₂), 1.99 (s, 3 H, CH₃), 1.51 (d, J_{PH} = 7.2 Hz, 9 H, PMe₃); ³¹P{¹H} NMR (CD₂Cl₂, -10 °C) δ 18.58; ¹⁹F{¹H} NMR (CD₂Cl₂, -10 °C) δ -7.6. Anal. Calcd for C₁₅H₂₄BF₄PSTi: C, 44.81; H, 6.02. Found: C, 44.67; H, 5.84.

Preparation of 5c. A mixture of 5a (200 mg, 0.45 mmol) and AgBPh₄ (200 mg, 0.46 mmol) in dichloromethane (20 mL) was stirred for 3 hours at room temperature. After the solution was filtered to separate the precipitated silver iodide and evaporated to dryness, the yellow residue was dissolved in dichloromethane (15 mL). Pentane (40 mL) was added to make a double-layered solution, which gave a yellow powder on storing at -78 °C. The product (165 mg, 0.26 mmol, 58%) was recovered by tiltration at -78 °C: ¹H NMR (CD₃CN, 0 °C) δ 7.3–6.8 (m, 20 H, Ph), 5.58

(s, 5 H, Cp), 5.56 (s, 5 H, Cp), 2.20 (CH₂), 1.92 (s, 3 H, CH₃), 1.46 (d, J_{PH} = 8 Hz, 9 H, PMe₃); ³¹P{¹H} NMR (CD₃CN, 0 °C) δ 17.23. Anal. Calcd for C₃₉H₄₄BPSTi·CH₂Cl₂: C, 66.78; H, 6.44. Found: C, 66.49; H, 6.36.

Reaction of 5c with CuCl. A mixture of 6c (20 mg, 0.03 mmol) and CuCl (6 mg, 0.06 mmol) in dichloromethane-d_2 was allowed to react at -20 °C. The yellow–red solution obtained after an hour showed a new product (7c) together with CuCl(PMe₃)ₓ in the ¹H NMR spectrum: ¹H NMR (CD₂Cl₂, -20 °C) δ 7.37–7.14 (m, 20 H, Ph), 6.37 (s, 10 H, Cp), 2.26 (s, 3 H, CH₃), 2.10 (s, 2 H, CH₂), 0.92 (d, J_{PH} = 7 Hz, free CuCl(PMe₃)ₓ); ³¹P{¹H} NMR δ -42.87 (br, free CuCl(PMe₃)ₓ, which was characterized by control reactions between CuCl and PMe₃). Addition of excess acetonitrile-d_3 (19 μL) into the above sample broadened the Cp peak and merged the methylene and the methyl peaks into a broad peak in ¹H NMR: ¹H NMR (CD₂Cl₂/CD₃CN, -20 °C) δ 7.34–7.09 (m, 20 H, Ph), 6.28 (br s, 10 H, Cp), 2.19 (br s, CH₂, CH₃), 1.11 (d, J_{CH} = 8 Hz, PMe₃ complex). These peaks broaden reversibly at lower temperatures (-50 °C). In separate experiments an excess of either ethylene or methyl vinyl ether was injected into a solution of 7c at -20 °C. No sign of polymerization was observed upon warming to room temperature. Above room temperature, only decomposition products of 7c were detected.

Supplementary Material Available: Atomic numbering schemes and tables of complete bond distances and angles, final parameters, and anisotropic displacement parameters (9 pages); a table of structure factors (22 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of Reductive Elimination of Hydrocarbons from (μ-H)₃Ru₃(μ₃-CX)(CO)₉ (X = Ph, Et, Cl, CO₂Me, SEt, CHPhCH₂Ph)

Timothy P. Duggan, Matthew J. Golden, and Jerome B. Keister*,[1]

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

The reaction of CO with (μ-H)₃Ru₃(μ₃-CX)(CO)₉ forms the corresponding CH₃X (X = CO₂Me, Ph, Et, CHPhCH₂Ph) and Ru₃(CO)₁₂/Ru(CO)₅; if β-hydrogens are present, alkenes and H₄Ru₄(CO)₁₂ are also products. The rate law (X = Ph, Cl, and Et) is of the following form: rate = $\{k_a k_c P_{CO}/(k_b + k_c P_{CO})\}$[H₃Ru₃(CX)(CO)₉] (X = Ph, k_a = (6.4 ± 0.6) × 10⁻⁶ s⁻¹, k_b/k_c = 0.49 ± 0.14 atm, 100 °C; X = Cl, k_a = (7.5 ± 0.7) × 10⁻⁵ s⁻¹ and k_b/k_c = 3.5 ± 0.9 atm, 100 °C; X = Et, k_a = (7.6 ± 2.5) × 10⁻⁵ s⁻¹, k_b/k_c = 14 ± 7 atm, 125 °C). For X = CO₂Me the rate law is zero order in P_{CO}. Activation parameters for the limiting rate constant k_a were determined (Ph, 35 atm, $\Delta H^\ddagger$ = 131 ± 3 kJ/mol, $\Delta S^\ddagger$ = 6 ± 8 J/(K mol); Cl, 35 atm, $\Delta H^\ddagger$ = 125 ± 9 kJ/mol, $\Delta S^\ddagger$ = 9 ± 25 J/(K mol); Et, 34 atm, $\Delta H^\ddagger$ = 140 ± 19 kJ/mol, $\Delta S^\ddagger$ = 22 ± 49 J/(K mol); CO₂Me, 1 atm, $\Delta H^\ddagger$ = 111.2 ± 1.3 kJ/mol, $\Delta S^\ddagger$ = -0.8 ± 4 J/(K mol)). For X = Ph, Cl, and Et inverse deuterium isotope effects were measured (Ph, 86% d, k_H/k_D = 0.64 ± 0.08, 100 °C, 35 atm; Cl, 85% d, k_H/k_D = 0.56 ± 0.06, 100 °C, 6.8 atm; Et, 80% d, k_H/k_D = 0.46 ± 0.03, 100 °C, 35 atm), but k_H/k_D = 1.01 ± 0.03 (95% d, 70 °C, 1 atm) for X = CO₂Me. The proposed mechanism involves a sequence of C–H reductive eliminations, each of which is preceded by reversible migration of hydrogen from Ru–H–Ru bridging to Ru–H–C bridging. The rate-determining step at high CO pressures is cleavage of the first Ru–H–C bond. For X = CO₂R or SEt anchimeric assistance of the reductive elimination, perhaps through a species containing a (μ₃-H)Ru₂C interaction, is proposed.

Introduction

The reductive elimination of a C–H bond from a transition-metal center is one of the fundamental reactions of organometallic chemistry. This reaction is the final step in many catalytic processes, occurring in both homogeneous and heterogeneous catalytic systems. Numerous studies of the mechanism of this process have been conducted for monometallic complexes.[2–6] A variety of

---

(1) Alfred P. Sloan Fellow, 1987–89.

(2) Halpern, J. *Acc. Chem. Res.* 1982, *15*, 332.

mechanisms have been identified. The most common, especially for Pt, involves a three-center, synchronous elimination.[3,6] Bimolecular[4] and radical[5] processes are also well-documented. Few studies have concerned polymetallic systems, in which both hydride and hydrocarbyl ligands may bridge two or more metal centers. Hydrogenation of $Co_3(CO)_9(\mu_3$-CR), producing alkenes, alkanes, and carbonyl compounds, has been proposed to involve radical intermediates.[7] Radical intermediates have also been proposed for the photoinduced reactions of Co_3-$(CO)_9(\mu_3$-CR) (R = H, Me) with hydrogen to give CH_3R.[8]

In this paper we report a study of the mechanism of reductive elimination of C–H bonds from $(\mu$-H$)_3Ru_3(\mu_3$-CX)(CO)$_9$ (X = Ph, Et, Cl, CO_2Me, SEt, $CHPhCH_2Ph$) under carbon monoxide, yielding ruthenium carbonyls and alkanes or alkenes.[9]

Experimental Section

General Techniques. Infrared spectra were recorded on a Beckman 4250 spectrophotometer. ^{1}H NMR spectra were recorded on Varian EM-390 or JEOL FX-90Q instruments. ^{13}C NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer. Mass spectra were provided by Dr. R. Minard of Penn State University, the Mass Spectrometry Laboratory at Cornell University, or the Instrument Center at the University at Buffalo. Mass spectra recorded at the University at Buffalo were obtained on a VG 70SE instrument; element composition was verified by comparison of experimental spectra with spectra calculated by using the program MSCALC, adapted by J. B. Keister for use on IBM PC computers from MASPAN.[10] Kinetic data were evaluated by using the least-squares program KINPLOT written by Dr. Ronald Ruszczyk, formerly of the University at Buffalo.

Starting Materials. $(\mu$-H$)_3Ru_3(\mu_3$-CX)(CO)$_9$ (X = OCH_3,[11] Cl,[12] CO_2Me,[12] CO_2Et, CO_2CH_2Ph, Ph,[12] p-Tol,[12] and $CHPhCH_2Ph$[13]) were prepared according to previously published methods, except as noted below.

$(\mu$-H$)_3Ru_3(\mu_3$-CX)(CO)$_9$ (X = CO_2Me, CO_2Et, Ph, p-Tol). The syntheses of $(\mu$-H$)_3Ru_3(\mu_3$-CX)(CO)$_9$, X = Ph, Tol, and CO_2Me, were adapted from those described previously,[12] except that $(\mu$-H$)_3Ru_3(\mu_3$-COMe)(CO)$_9$, rather than $(\mu$-H$)_3Ru_3(\mu_3$-CBr)(CO)$_9$, was used as the starting material. This modification has the advantage of convenience and does not significantly affect the yields. The syntheses of $(\mu$-H$)_3Ru_3(\mu_3$-CX)(CO)$_9$, X = CO_2Et or CO_2CH_2Ph, follow the same procedure as that for $(\mu$-H$)_3Ru_3(\mu_3$-CCO$_2$Me)(CO)$_9$ with the use of ethanol or benzyl alcohol to quench the AlCl$_3$ slurry instead of methanol.

$(\mu$-H$)_3Ru_3(\mu_3$-CCO$_2CH_2C_6H_5$)(CO)$_9$: 36% yield; IR (C_6H_{12}) 2114 vw, 2089 s, 2083 m sh, 2038 vs, 2030 m, sh, 1997 w, and 1680 w cm^{-1}; ^{1}H NMR (CDCl$_3$, 22 °C) –18.05 (s, 3 H, MHM), 5.30 (s, 2 H, CO$_2CH_2$Ph), and 7.35 (m, 5 H, C_6H_5) ppm.

$(\mu$-H$)_2Ru_3(\mu_3$-η^2-CHCO$_2CH_2C_6H_5$)(CO)$_9$. This compound was prepared by pyrolysis of $(\mu$-H$)_3Ru_3(\mu_3$-CCO$_2CH_2C_6H_5$)(CO)$_9$ according to the procedure described for the methyl ester;[14] IR (C_6H_{12}) 2105 m, 2078 s, 2054 vs, 2035 s, 2016 m, 2006 s, 1990 m, 1959 vw, 1548 vw, sh, and 1534 w cm^{-1}; ^{1}H NMR (CDCl$_3$, 22 °C) 7.32 (m, 5 H, C_6H_5), 4.90 (s, 2 H, CH_2Ph), 3.99 (s, 1 H, CHCO$_2$Bz), –13.03 (br, 1 H, MHM), and –14.91 (br, 1 H, MHM) ppm.

Preparation of Deuterium-Labeled Clusters. Deuterium-labeled clusters $(\mu$-D$)_3Ru_3(\mu_3$-CPh)(CO)$_9$, $(\mu$-D$)_3Ru_3(\mu_3$-CCl)(CO)$_9$, and $(\mu$-D$)_3Ru_3(\mu_3$-CCO$_2$Me)(CO)$_9$ were prepared from $(\mu$-D)-Ru$_3(\mu$-COMe)(CO)$_{10}$ and $(\mu$-D$)_3Ru_3(\mu_3$-COMe)(CO)$_9$. These starting materials were prepared by appropriate substitution of the deuterated reagents D$_2$O and D$_2$, respectively, in the published procedures.

The percent deuterium enrichments were determined through integration of ^{1}H NMR resonances of the metal hydrides (if visible) with respect to the resonances of the methylidyne substituent or by analysis of the mass spectra using MSCALC.

$(\mu$-D$)_3Ru_3(\mu_3$-CEt)(CO)$_9$. A stirred cyclohexane solution (100 mL) of $(\mu$-D)Ru$_3(\mu$-COCH$_3$)(CO)$_{10}$ (251 mg, 0.4 mmol) is heated at 65 °C as acetylene is bubbled through the solution for 3 h. The solvent is removed by evaporation, and the product residue is then dissolved in decane. The decane solution is placed in a Parr pressure bottle. The Parr bottle was equipped with a gas inlet and pressure regulator to allow for reactions under moderate pressure. The vessel is flushed three times and then is pressurized to 3.8 atm with D$_2$. The bottle is immersed in an oil bath that is then heated at 100 °C for 10 h. The solution is cooled, and the decane is removed by rotory evaporation. The product is purified by TLC on silica, eluting with hexanes, yield 72.2 mg (0.12 mmol), 30%; deuterium enrichment was 80%.

Kinetics of Reductive Elimination of CH_3X from $(\mu$-H$)_3Ru_3(\mu_3$-CX)(CO)$_9$. All reactions were monitored by using IR spectroscopy to follow the decrease in absorbances in the 2150–2000-cm^{-1} region due to the starting material. Three experimental apparatuses were used to allow variation in the CO pressure over the solution. Either pure CO or a mixture of 10% CO in N$_2$, obtained from Linde Corp., were used to adjust the CO partial pressure to the desired value.

High Pressure (3–70 atm). A 300-cm^3 Autoclave Engineers Magnadrive autoclave, equipped with a Love Controls Corp. temperature monitoring and control device, was charged to the desired pressure with CO or CO/N$_2$ mixtures to allow variation of the CO partial pressure from 3.5 to 70 atm. The autoclave was filled with 125 mL of Decalin, was pressurized to the desired pressure, and then was stabilized at the desired temperature (temperature control good to ±1 °C). Once the autoclave had reached the desired temperature, 50 mL of Decalin was withdrawn from the autoclave through the liquid sampling valve. Then a solution of the cluster (typically 0.03–0.05 mmol) in 50 mL of Decalin was introduced from a high-pressure sampling bomb attached to an inlet valve. The solution was approximately 3 × 10^{-3} M in cluster. The autoclave was then flushed thrice with the gas and repressurized to the desired pressure. After the reaction stabilized at the desired temperature, sampling was commenced.

For determination of the dependence of rate upon the partial pressure of CO and of the deuterium kinetic isotope effect, the temperature stability was improved by circulation of fluid from a thermostated bath (100.0 ± 0.2 °C) through the internal cooling coils of the autoclave.

Medium Pressures (1–4 atm). A solution consisting of ca. 0.01–0.02 mmol of the metal cluster in 50 mL of Decalin was placed in a Parr bottle, which was then flushed thrice or more and finally pressurized to 50 psi (35 psig) with either CO or 10% CO in N$_2$, for CO pressures of 3.4 or 0.34 atm, respectively. The Parr bottle apparatus was then immersed completely in a constant-temperature bath (±0.1 °C) filled with oil. To sample the reaction periodically, the Parr bottle was removed from the oil bath and placed in a hood to cool briefly so as to minimize loss of solvent through vaporization. The pressure was then released, and the stopper and gauge were removed. A sample of about 0.5 mL of solution was withdrawn, and the apparatus quickly reassembled, flushed, repressurized, and replaced in the oil bath. Five minutes

(3) (a) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986. (b) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227. (c) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (d) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 6115.

(4) (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376. (c) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33.

(5) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

(6) (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (c) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

(7) Seidler, P. F.; Bryndza, H. E.; Frommer, J. E.; Stuhl, L. S.; Bergman, R. G. *Organometallics* **1983**, *2*, 1701.

(8) Geoffroy, G. L.; Epstein, R. A. *Inorg. Chem.* **1977**, *16*, 2795.

(9) Some of this work has appeared in a preliminary communication: Duggan, T. P.; Barnett, D. J.; Muscatella, M. J.; Keister, J. B. *J. Am. Chem. Soc.* **1986**, *108*, 6076.

(10) (a) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942. (b) Andrews, M. A. Ph.D. Dissertation, University of California, Los Angeles, Los Angeles, CA, 1977.

(11) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* **1983**, *2*, 219.

(12) Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304.

(13) Beanan, L. R.; Keister, J. B. *Organometallics* **1985**, *4*, 1713.

(14) Churchill, M. R.; Janik, T. J.; Duggan, T. P.; Keister, J. B. *Organometallics* **1987**, *6*, 799.

was subtracted from the time of the reaction to correct for the time required for sampling.

Atmospheric Pressure. These experiments were run in foil-wrapped, water-jacketed, glass vessels equipped with two ports for use as gas inlet and outlet, and the third was used for sampling and temperature monitoring; a magnetic stir bar was placed in the reaction vessel. Fluid from a Lauda constant-temperature circulator was passed through the jacket of the vessel to maintain the desired temperature (± 0.2 °C).

Rate constants were determined by computer-calculated least-squares determination of the slope of the plot of ln (absorbance) vs time, using one of the CO stretching frequencies of the reactant cluster. Rate constants were then taken as the average of 2–4 runs, with the error limits taken as the larger of the standard deviation ($n - 1$) of the values or the 95% confidence limits for the least precise run. Activation parameters were determined by computer-calculated least-squares determination of the slope and intercept of the Eyring plot of ln (k/T) vs $1/T$; all runs were used rather than average values at each temperature, and error limits are given as the 95% confidence limits using Student's t values. Values of k_a and k_b/k_c in eq 2 were determined by computer-calculated least-squares determination of the slope and intercept of the plot of $1/k_{obs}$ vs $1/P_{CO}$; all runs were used rather than average values at each pressure, and error limits are given as the 95% confidence limits using Student's t values.

Reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$ with CO. The cluster $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$ (32 mg, 0.043 mmol) was dissolved in ca. 0.5 mL of C_6D_6, and the solution was placed in a 5-mm NMR tube. Dissolved gases were removed by using three freeze–pump–thaw cycles. Then the solution was placed under an atmosphere of CO and the tube was sealed. The reaction was heated in an oil bath at temperatures of 80–110 °C over a period of 7 days. At that time the reaction was shown to be complete by ${}^1H$ NMR spectroscopy.

The ${}^1H$ NMR spectrum of the product mixture contained signals assigned to 2,3-diphenyl-1-propene, cis- and trans-1,2-diphenylpropene, and 1,2-diphenylpropane on the basis of comparison with the spectra of authentic samples of 2,3-diphenyl-1-propene, a mixture of cis- and trans-1,2-diphenylpropene, and 1,2-diphenylpropane. The assignments to cis- vs trans-1,2-diphenylpropene are uncertain. The ${}^1H$ NMR spectrum (C_6D_6, 23 °C) of the product mixture contained the following resonances: 5.47 (d, $J = 1$ Hz, 1 H), 4.98 (dd, $J_1 = 1$ Hz, $J_2 = 1$ Hz, 1 H), and 3.70 (d, $J = 1$ Hz, 2 H) ppm, assigned to 2,3-diphenyl-1-propene, 44%; 2.15 (d, 3 H, J = 1 Hz), 26%, and 2.07 (d, 3 H, J = 1 Hz) ppm, 4%, assigned to trans- and cis-1,2-diphenylpropene, respectively; 1.20 (d, 3 H, $J = 7$ Hz) ppm, assigned to 1,2-diphenylpropane, 27%.

Resonances are also observed at −17.67 s and −17.90 s ppm with relative integrations equal to 9% and 3% of the beginning intensity of the reactant hydride resonance at −17.67 ppm. These are attributed to unreacted starting cluster and $H_4Ru_4(CO)_{12}$, respectively. Most of the $H_4Ru_4(CO)_{12}$ had apparently precipitated out of solution as indicated by the IR spectrum of the insoluble product mixture, which shows primarily $H_4Ru_4(CO)_{12}$ and $Ru_3(CO)_{12}$.

Reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CC}_6H_5)(CO)_9$ with CO. In a 5-mm NMR tube was placed 30 mg (0.046 mmol) of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CC}_6H_5)(CO)_9$ in approximately 0.8 mL of benzene-d_6. To this solution was added approximately 2 μL of cyclohexane as a reference against which resonances due to reactants and products were integrated. After evacuation of other gases through three freeze–pump–thaw cycles, the solution was placed under a CO atmosphere, and the tube was sealed. Initial ${}^1H$ NMR spectra were obtained, and the hydride resonance at −17.44 ppm was integrated with respect to the cyclohexane resonance at 1.50 ppm. The tube was heated to temperatures up to 120 °C over a period of several days, and the reaction monitored periodically by NMR spectroscopy. When the reaction seemed complete, final integrations of the hydride resonance at −17.44 ppm and the methyl protons of the toluene product at 2.22 ppm (91 $\pm$ 5% yield) were obtained. The NMR tube was then opened, and the volatile components were separated by vacuum transfer. Toluene was also confirmed by GC/MS analysis.

Reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ with CO. In a 5-mm NMR tube was placed 32 mg (0.053 mmol) of $(\mu\text{-H})_3Ru_3(\mu_3$-

CEt)(CO)$_9$ in approximately 0.7 mL of benzene-d_6. Then the NMR tube was degassed by three freeze–pump–thaw cycles and was finally filled with a CO atmosphere. The tube was then sealed and was placed in an oil bath at 125–135 °C for 6 days. The ${}^1H$ NMR spectrum was periodically monitored during this period. After 2 days resonances at 1.69 (d, $J = 6$ Hz), 5.0 (m), and 5.8 (m) ppm, attributed to propene (lit. NMR 5.0 (m, 2 H), 5.73 (m, 1 H), 1.72 (d, 3 H, $J = 6.4$ Hz) ppm), were observed, in addition to a hydride resonance at −17.8 ppm, assigned to $H_4Ru_4(CO)_{12}$. However, after 6 days this resonance had disappeared, and only resonances assigned to propane were present (0.84 (t, 6 H), 1.3 (m, 2 H) ppm, $J = 6.2$ Hz) (lit. 0.91, 1.34 ppm, $J = 7.4$ Hz (CCl_4)[15]). No high-field signals were observed.

Crossover Experiment. A solution of $(\mu\text{-D})_3Ru_3(\mu_3\text{-CC}_6H_5)(CO)_9$ (29.7 mg, 86% d in the hydride position by NMR spectroscopy, MSCALC analysis: 4 $\pm$ 6% d_1, 15 $\pm$ 8% d_2, 80 $\pm$ 9% d_3, and 1 $\pm$ 6% d_4) and $(\mu\text{-H})_3Ru_3(\mu_3\text{-CC}_6H_4CH_3)(CO)_9$ (27.5 mg) in 0.7 mL benzene-d_6 was placed in a 5-mm NMR tube. The tube was treated to three freeze–pump–thaw cycles and then was filled to 1 atm with CO. The tube was then sealed and was heated at 100 °C for 4 days. NMR was used to monitor the reaction daily. The tube was opened, and the volatile components were removed by vacuum transfer for GC/MS analysis. The residue was purified by TLC and was found to contain $Ru_3(CO)_{12}$ and a purple solid characterized by IR spectroscopy and mass spectrometry as $Ru_6C(CO)_{14}(C_6D_6)$.[38]

Mass spectrometric analysis of toluene and xylene products gave the following results: toluene (m/e, rel intensity) 92, 74.3; 93, 94.4; 94, 100.0; 95, 63.8; 96, 8.1; 97, 0.6; 98, 0.7; 99, 0.1. MSCALC analysis provided the best fit for 23.8 $\pm$ 0.5% d_0, 28.3 $\pm$ 0.5% d_1, 29.7 $\pm$ 0.5% d_2, and 18.1 $\pm$ 0.5% C_7H_8-d_3. p-xylene 106, 53.9; 107, 25.4; 108, 5.5; 109, 0.4. MSCALC analysis provided the best fit for 69.3 $\pm$ 0.1% d_0, 26.3 $\pm$ 0.1% d_1, 4.4 $\pm$ 0.1% d_2, and 0.01 $\pm$ 0.1% C_8H_{10}-d_3.

In a control experiment $(\mu\text{-D})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ (19.3 mg, 0.030 mmol, deuterium enrichment as above) and $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$ (17.0 mg, 0.28 mmol) were dissolved in benzene-d_6 (0.6 mL) in a tube which was degassed via freeze–pump–thaw cycles and was then sealed. The tube was heated at 100 °C for 44 h. Then the tube was opened, and the solution was evaporated to dryness. TLC separation of the nonvolatile products gave H_4-$Ru_4(CO)_{12}$ (33% d enrichment) and $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ (9 $\pm$ 6% d_0, 34 $\pm$ 8% d_1, 46 $\pm$ 8% d_2, and 11 $\pm$ 6% d_3). No $(\mu$-$H)_3Ru_3(\mu_3\text{-CCl})(CO)_9$ was isolated.

Crossover Experiment: $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Et)(CO)_9/(\mu$-$D)_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ + CO. A solution of 30 mg (0.047 mmol) each of $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCO}_2CH_3)(CO)_9$ (95% deuterium enrichment, as determined by ${}^1H$ NMR spectroscopy) and $(\mu$-$H)_3Ru_3(\mu_3\text{-CCO}_2C_2H_5)(CO)_9$ in 6 mL of benzene-d_6 was placed in a 10-mm NMR tube. Dissolved gases were removed by three freeze–pump–thaw cycles under vacuum, the solution was placed under a carbon monoxide atmosphere, and the tube was sealed. The tube was allowed to stand for 18 days at room temperature, but the H^1 NMR spectrum showed that little reaction had occurred. The tube was then placed in a 40 °C bath and monitored over another 18 days until it was determined that the reaction was complete. The tube was opened, the volatile components were separated and collected by vacuum transfer to a liquid N_2 cooled trap, and the solution was divided into three aliquots placed in ampules and sealed under N_2 atmosphere. One ampule was sent to Cornell Mass Spectrometry Laboratory for GC/MS analysis. Later, a second ampule was sent to the Pennsylvania State University Mass Spectrometry Laboratory to corroborate the first set of results. Results of GC/MS analysis by two independent laboratories showed predominantly unscrambled products of ethyl acetate-d_0 (85% d_0, 15% d_1) and methyl acetate-d_3 (72% d_3, 25% d_2).

Crossover Experiment: $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Bz)(CO)_9/(\mu$-$D)_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ Isomerization. A solution containing 35 mg (0.055 mmol) of $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ (84% D in hydride position) and 35 mg (0.50 mmol) of $(\mu\text{-H})_3Ru_3(\mu_3$-$CCO_2Bz)(CO)_9$ in 50 mL of heptane was placed in a 250-mL, three-necked, round-bottomed flask fitted with an inlet tube for

(15) Brugel, W. *Nuclear Magnetic Resonance Spectra and Chemical Structure*; Academic Press: New York, 1967; Vol. 1.

Table I. Pseudo-First-Order Rate Constants for Reductive Elimination of CH_3Ph from $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ under CO^a

T, °C	P_{CO}, atm	$10^5 k_{obs}$, s^{-1}	T, °C	P_{CO}, atm	$10^5 k_{obs}$, s^{-1}
90^b	35	0.20 ± 0.01	100^d	0.10	0.36 ± 0.01
100^{b,f}	35	0.65 ± 0.03	100^d	0	0.44 ± 0.03
100^b	3.5	0.58 ± 0.02	100^{b,e,f}	35	1.01 ± 0.07^e
100^c	3.4	0.57 ± 0.01	110^b	35	1.98 ± 0.06
100^d	1	0.41 ± 0.03	120^b	35	6.0 ± 0.1
100^c	0.44	0.32 ± 0.01			

^{a} All reactions in Decalin solution. ^{b} Autoclave reaction. ^{c} Parr bottle reaction. ^{d} Kinetic cell reaction. ^{e} Deuterated at the hydride positions. ^{f} Autoclave equipped with cooling coils connected to constant temperature bath.
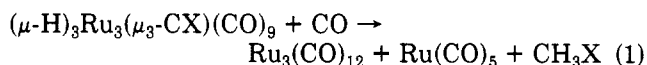
bubbling N_2 through, a reflux condenser topped with a stopcock connected to an oil bubbler, and a magnetic stir bar. With N_2 bubbling through, the solution was heated in an oil bath to 80–90 °C for 3 h, and the reaction monitored by IR spectroscopy. The solvent was removed by rotary evaporator, and the cluster products separated by thin-layer chromatography on silica, eluting with hexanes. The products were extracted with dichloromethane. ^1H NMR spectra were obtained, and the resonances in the hydride region were integrated against the alkyl protons in the respective clusters in order to determine the deuterium content of the products relative to the reactants.

$(\mu\text{-}H)_2Ru(\mu_3\text{-}\eta^2\text{-}CHCO_2Bz)(CO)_9$ (3.99 ppm, 50% H; −13.03 ppm, 47% H; −14.91 ppm, 45% H); $(\mu\text{-}D)_2Ru(\mu_3\text{-}\eta^2\text{-}CDCO_2Me)(CO)_9$ (3.96 ppm, 40% H; −13.04 ppm, 50% H; −14.92 ppm, 46% H).

Results

Reactions involving the reductive elimination of C–H bonds have been investigated for the clusters $(\mu\text{-}H)_3Ru_3$-$(\mu_3\text{-}CX)(CO)_9$ in which X = Ph, CO_2Me, CO_2Et, CO_2Bz, Cl, SEt,[16] Et, $CHPhCH_2Ph$, and Tol.

$(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$. Reaction of this cluster with CO gives toluene and ruthenium carbonyl products (eq 1).

$$(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9 + CO \rightarrow$$
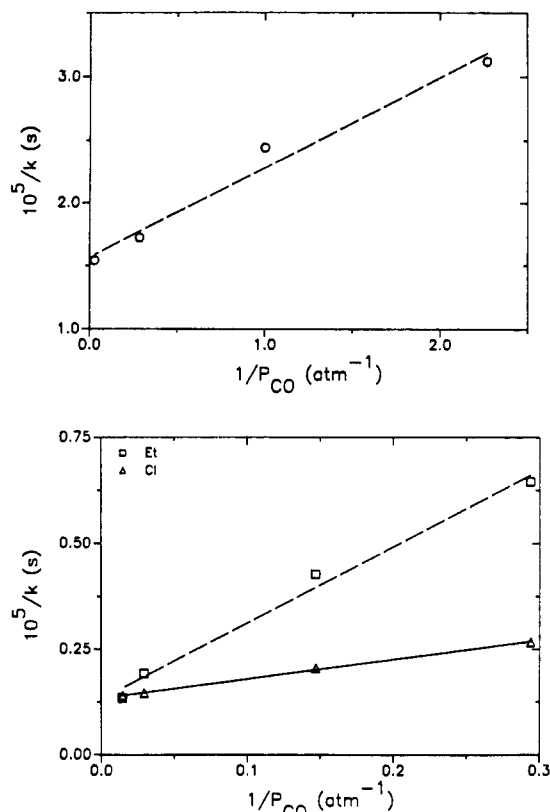$$Ru_3(CO)_{12} + Ru(CO)_5 + CH_3X \quad (1)$$

Since $Ru_3(CO)_{12}$ and $Ru(CO)_5$ are in equilibrium under the reaction conditions, the primary metal-containing product cannot be specified. $Ru_3(CO)_{12}$ is the product isolated at low CO pressures or after releasing the CO pressure and allowing the product solution to stand. The yield of CH_3Ph was determined by ^1H NMR spectroscopy to be 91 ± 5%. In the absence of CO, decomposition is evidenced by the progressive disappearance of absorptions in the carbonyl region of the IR spectrum. The rate of decomposition under nitrogen at 100 °C was found to be approximately the same as that for the reaction of $(\mu$-$H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ with 1 atm of CO (k_{obs} = ca. 4 × 10^{-6} s^{-1}). However, this rate of decomposition is at least an order of magnitude slower than the rate of CO dissociation as determined by substitution experiments with $(\mu$-$H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ and $AsPh_3$.[17] This suggests that at low CO pressures CO dissociation from the cluster provides a decomposition pathway in addition to reductive elimination.

The dependence of the rate of disappearance of $(\mu$-$H)_3Ru_3(\mu_3\text{-}CX)(CO)_9$ upon CO concentration was evaluated. No dependence of the rate upon the CO partial pressure was noted at high P_{CO}, but the rate decreased slightly with decreasing CO pressure at low pressures (Table I). A low-pressure limit was reached at $P_{CO} \simeq 0.1$ atm, where the rate of decomposition apparently exceeds

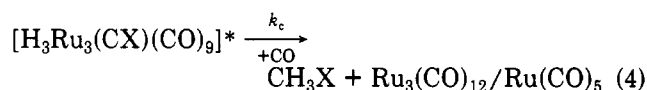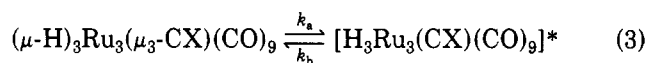(16) Churchill, M. R.; Ziller, J. W.; Dalton, D. M.; Keister, J. B. *Organometallics* **1987**, *6*, 806.

(17) Rahman, Z. A.; Beanan, L. R.; Bavaro, L. M.; Modi, S. P.; Keister, J. B.; Churchill, M. R. *J. Organomet. Chem.* **1984**, *263*, 75.

Figure 1. Plot of $1/k_{obs}$ vs $1/P_{CO}$ (atm^{-1}) for decomposition of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9$, (upper) X = Ph and (lower) X = Cl or Et.

the rate of reductive elimination (i.e., the primary reaction is decomposition in which no ruthenium carbonyl products are observed in the IR spectrum). A plot of the inverse of the observed rate constants at various pressures (Table I) versus the inverse of pressure is shown in Figure 1. Therefore, the rate law is of the form given by eq 2, with k_b/k_c = 0.49 ± 0.14 atm and k_a = (6.4 ± 0.6) × 10^{-6} s^{-1}.

$$\text{rate} = \frac{k_a k_c P_{CO}}{k_b + k_c P_{CO}}[H_3Ru_3(CX)(CO)_9] \quad (2)$$

$$(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [H_3Ru_3(CX)(CO)_9]^* \quad (3)$$

$$[H_3Ru_3(CX)(CO)_9]^* \xrightarrow[+CO]{k_c}$$
$$CH_3X + Ru_3(CO)_{12}/Ru(CO)_5 \quad (4)$$

A mechanism given by eq 3 and 4 accounts for the observed rate behavior. This mechanism involves the reversible formation of an activated intermediate, which reacts with CO in the rate-determining step to reductively eliminate CH_3X. With the steady-state approximation the rate law for this mechanism is given by eq 2.

The deuterium isotope effect was determined by using $D_3Ru_3(CC_6H_5)(CO)_9$ (86% deuterium enrichment). At 100 °C and 35 atm an inverse isotope effect, k_H/k_D = 0.64 ± 0.08 (esd), was determined.

From the temperature dependence of k_{obs} at 35 atm, the activation parameters are $\Delta H^{\ddagger}$ = 131 ± 3 kJ/mol (31.4 ± 0.7 kcal/mol) and $\Delta S^{\ddagger}$ = 6 ± 8 J/(K mol) (1 ± 2 eu).

$(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$. In the presence of CO, $(\mu$-$H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ decomposes to ruthenium carbonyls and propene and propane. Pseudo-first-order rate constants for disappearance of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ are given in Table II. The rate law is of the form in eq 2, with k_a = (7.6 ± 2.5) × 10^{-5} s^{-1} and k_b/k_c = 14 ± 7 atm at 125 °C. At 100 °C and 35 atm, the kinetic isotope effect,

Table II. Pseudo-First-Order Rate Constants for Reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ with CO^a

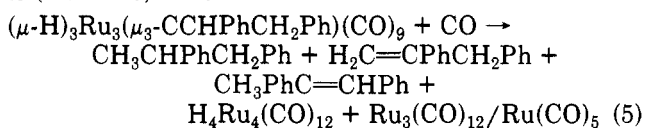| T, °C	P_{CO}, atm	$10^5 k_{obs}$, s^{-1}	T, °C	P_{CO}, atm	$10^5 k_{obs}$, s^{-1}
115	34	1.71 ± 0.31	125	34^b	11.2 ± 2.0
125	3.4	1.55 ± 0.15	125	68	7.4 ± 0.7
125	6.8	2.34 ± 0.33	137	34	19 ± 3
125	34	5.2 ± 0.9			

^{a} All reactions done in Decalin solution. ^{b} Deuterium labeled.

Table III. Pseudo-First-Order Rate Constants for Reductive Elimination of CH_3Cl from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$ under CO^a

T, °C	P_{CO}, atm	$10^5 k_{obs}$, s^{-1}	T, °C	P_{CO}, atm	$10^5 k_{obs}$, s^{-1}
90	35	2.1 ± 0.1	100	34	6.9 ± 0.7
100	3.4	3.76 ± 0.17	100	68	7.2 ± 0.8
100	6.8	4.89 ± 0.26	110	35	19 ± 1
100	6.8	8.3 ± 0.5^b			

^{a} All reactions done in 300-cm^3 autoclave in Decalin. ^{b} Deuterium labeled.

k_H/k_D, is 0.46 ± 0.03, determined by using 80% enriched $(\mu\text{-D})_3Ru_3(\mu_3\text{-CEt})(CO)_9$. From the temperature dependence of k_{obs} at 34 atm, the activation parameters are $\Delta H^{\ddagger}$ = 140 ± 19 kJ/mol (33 ± 5 kcal/mol) and $\Delta S^{\ddagger}$ = 22 ± 49 J/(K mol) (5 ± 11 eu).

$(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$. The reaction of this cluster with CO (1 atm) proceeds according to eq 5. At 100 °C and 35 atm, the pseudo-first-order rate constant for disappearance of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$ is $(6.6 ± 1.3) \times 10^{-5}$ s^{-1}.

$$(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9 + CO \rightarrow$$
$$CH_3CHPhCH_2Ph + H_2C{=}CPhCH_2Ph +$$
$$CH_3PhC{=}CHPh +$$
$$H_4Ru_4(CO)_{12} + Ru_3(CO)_{12}/Ru(CO)_5 \quad (5)$$

$(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$. In the presence of CO, $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$ decomposes to ruthenium carbonyls; no attempt was made to detect the organic product, presumably chloromethane. Pseudo-first-order rate constants are given in Table III. The rate law is of the form in eq 2, with k_a = $(7.5 ± 0.7) \times 10^{-5}$ s^{-1} and k_b/k_c = 3.5 ± 0.9 atm at 100 °C. At 100 °C and 6.8 atm, the kinetic isotope effect, k_H/k_D, is 0.56 ± 0.06, determined by using 85% enriched $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCl})(CO)_9$. From the temperature dependence of k_{obs} at 35 atm, the activation parameters are $\Delta H^{\ddagger}$ = 125 ± 9 kJ/mol (30 ± 2 kcal/mol) and $\Delta S^{\ddagger}$ = 9 ± 25 J/(K mol) (2 ± 6 eu).

In the absence of CO decomposition of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$ occurs, with complete disappearance of carbonyl absorptions from the IR spectrum. The rate constant for decomposition of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$ under N_2 at 100 °C was $(4.36 ± 0.38) \times 10^{-5}$ s^{-1}.

$(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2R)(CO)_9$, R = Me, Et, CH_2Ph. Reaction with CO forms the acetate ester and ruthenium carbonyl products. Triruthenium dodecacarbonyl is the primary carbonyl product, especially at lower pressures of CO. However, at higher pressures of CO, fragmentation occurs, forming $Ru(CO)_5$.

Unlike kinetics for $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$, X = Ph, Cl, and Et, the rate law for the reaction is first order in cluster concentration and zero order in P_{CO} at all pressures examined. First-order rate constants are given in Table IV. Also unlike other clusters, no detectable deuterium kinetic isotope effect was found, k_H/k_D = 1.01 ± 0.03 with 95% enriched $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ at 70 °C and 1 atm. From the temperature dependence of k_{obs} at 1 atm, the activation parameters are $\Delta H^{\ddagger}$ = 111.2 ± 1.3 kJ/mol (22.6 ± 0.3 kcal/mol) and $\Delta S^{\ddagger}$ = -0.8 ± 4 J/(K mol) (-0.2 ± 0.9 eu).

Table IV. Pseudo-First-Order Rate Constants for Reductive Elimination of Methyl Acetate from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ under CO (1 atm)^a

T, °C	$10^5 k_{obs}$, s^{-1}	T, °C	$10^5 k_{obs}$, s^{-1}
40.9	0.182 ± 0.004	70.8	8.66 ± 0.36
50.2	0.655 ± 0.010	70.9^b	8.56 ± 0.27^b
60.2	2.32 ± 0.09	79.9	22.6 ± 0.09
70.2	7.9 ± 0.5		

^{a} All reactions in Decalin solution under 1 atm of CO. ^{b} Deuterated at the hydride positions.
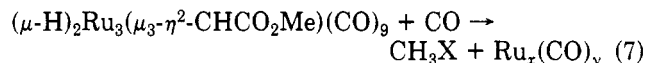
Table V. Rate Constants for Isomerization of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ to $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9{}^a$

T, °C	$10^5 k_{obs}$, s^{-1}	T, °C	$10^5 k_{obs}$, s^{-1}
50.2	0.66 ± 0.03	70.6	10.4 ± 0.5
60.6	2.21 ± 0.16	80.0	32 ± 2

^{a} All reactions in Decalin solution under N_2 atmosphere.
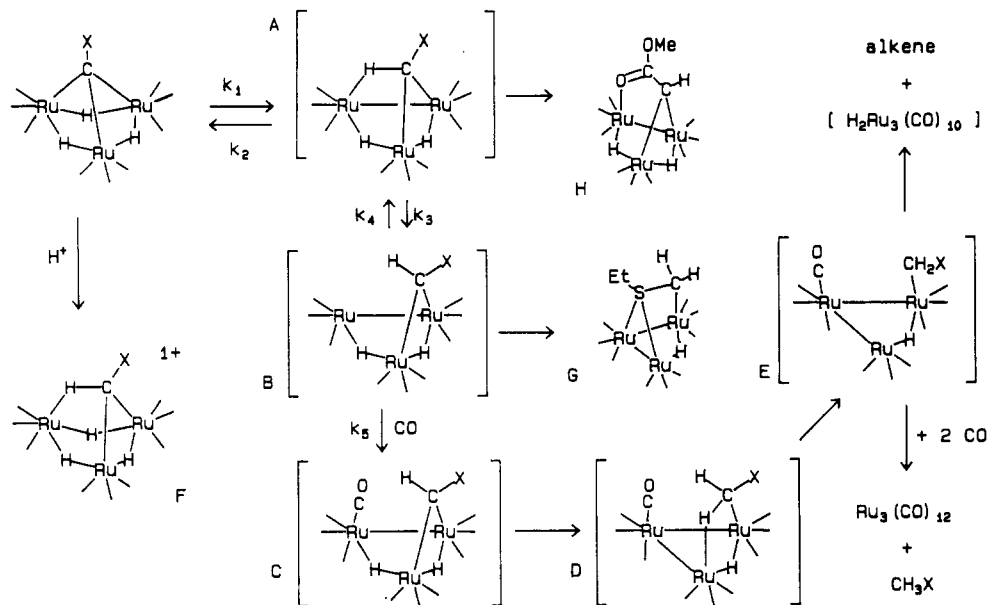
Crossover experiments were performed to determine the molecularity of C–H bond reductive elimination. Equimolar amounts of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Et)(CO)_9$ and $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCO}_2Me)$ were reacted together with CO. Results of GC/MS analysis by two independent laboratories showed predominantly unscrambled products of ethyl acetate-d_0 (85% d_0, 15% d_1) and methyl acetate-d_3 (72% d_3, 25% d_2). After correction for 95% enrichment of the deuterated cluster, the results are consistent with a mechanism involving no less than two intramolecular C–H bond eliminations and no more than one intermolecular C–H bond elimination.

Pyrolysis of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2R)(CO)_9$, R = Me, Et, or Bz, under a nitrogen atmosphere leads to cluster rearrangement involving the migration of one hydride to the methylidyne carbon (eq 6). The rate constant at 50 °C

$$(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2R)(CO)_9 \rightarrow$$
$$(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2R)(CO)_9 \quad (6)$$

$$(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9 + CO \rightarrow$$
$$CH_3X + Ru_x(CO)_y \quad (7)$$

for rearrangement of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ to $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9$ is the same as that for the reductive elimination of methyl acetate in the presence of CO, indicating a common rate-determining step. At higher temperatures the rate constant for disappearance of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ is larger than that found for the reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ with CO, probably due to an increasing contribution from CO dissociation and decomposition. From the temperature dependence of k_{obs} (Table V), the activation parameters are $\Delta H^{\ddagger}$ = 125 ± 9 kJ/mol (30 ± 2 kcal/mol) and $\Delta S^{\ddagger}$ = 40 ± 25 J/(K mol) (9 ± 6 eu). Continued heating of $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9$ in the absence of CO leads to decomposition to methyl acetate (34% by ^{1}H NMR spectroscopy) and $Ru_3(CO)_{12}$. No evidence of formation of the isomer $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9$ is found when the reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ is conducted under an atmosphere of CO. In the presence of CO, $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9$ decomposes to methyl acetate and ruthenium carbonyls; at 70.5 °C and P_{CO} = 1 atm, k_{obsd} = $(1.0 ± 0.2) \times 10^{-4}$ s^{-1} for this reaction (eq 7), as compared with k_{obsd} = $(8.7 ± 0.4) \times 10^{-5}$ s^{-1} at 70.8 °C for the reaction of CO with $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ to produce methyl acetate.

A crossover experiment on the rearrangement of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2R)(CO)_9$ under nitrogen was attempted. Equimolar amounts of $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ (84% deuterium enriched) and $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Bz)(CO)_9$ were
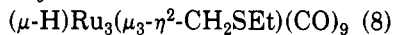
Figure 2. Proposed mechanism for elimination of alkenes and alkane from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$. Structures in brackets are proposed intermediates; other structures have been characterized by spectroscopic or crystallographic methods.

reacted together under a nitrogen atmosphere. The products showed almost complete scrambling: (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Bz)(CO)$_9$ (3.99 ppm, 50% H; −13.03 ppm, 47% H; −14.91 ppm, 45% H); (μ-D)$_2$Ru$_3$(μ_3-η^2-CDCO$_2$Me)(CO)$_9$ (3.96 ppm, 40% H; −13.04 ppm, 50% H; −14.92 ppm, 46% H). If both reactions, rearrangement and reaction with CO, occur by a common first step, then the crossover results are inconsistent with those of the elimination under CO and suggest that there may exist a pathway for intermolecular exchange of protons between the pyrolysis products (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$R)(CO)$_9$; under this circumstance, less scrambling will occur when the concentrations of these products remain low, i.e., when the products react with CO.

Since isomerization of (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$Me)(CO)$_9$ to (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Me)(CO)$_9$ may be viewed as being a proton migration, we considered the possibility that the reaction might be base catalyzed. However, the addition of 5 equiv of NEt$_3$ was found to have no effect on the rate of the isomerization.

(μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$. Our group has previously reported that pyrolysis of (μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$ causes migration of two hydrides to the methylidyne carbon, according to eq 8.[16] The same product is observed even

$$(\mu\text{-H})_3Ru_3(\mu_3\text{-CSEt})(CO)_9 \rightarrow$$
$$(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^2\text{-CH}_2SEt)(CO)_9 \quad (8)$$

under a CO atmosphere. The yield under a nitrogen atmosphere is 46%. At 70.6 °C the first-order rate constant for the rearrangement is 2.2 × 10^{-4} s^{-1} in Decalin.

Discussion

The structure[18] of the clusters (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$ consists of a triangular metal framework capped on one face by the methylidyne carbon, which is symmetrically bonded to all three metal nuclei. Each edge of the metal framework is also bridged by one hydride such that the octahedral coordination sphere on each metal atom consists of facially oriented two hydrides and the methylidyne carbon and three facially oriented and terminally bound

carbonyls which complete the coordination sphere at each metal center. Since there are cis relationships between the two hydrides bound to each metal, as well as between the hydrides and the Ru–CX bond, reductive elimination of either molecular hydrogen or of C–H bonds is geometrically feasible.

When the methylidyne substituent X is a good π donor (X = OMe or NMe$_2$), reactions with CO proceed by reductive elimination of molecular hydrogen, forming (μ-H)Ru$_3$(μ-CX)(CO)$_{10}$.[19] However, for all other substituents examined (X = CO$_2$R, SEt, Ph, Cl, Et, or CHPhCH$_2$Ph) the preferred reaction is the reductive elimination of C–H bonds.

Reactions of (μ-H)$_3$Ru$_3$(μ_3-CR)(CO)$_9$ with CO generally produce alkanes, CH$_3$R, or alkanes and alkenes if hydrogens are present on the β carbon. The metal-containing products are Ru$_3$(CO)$_{12}$/Ru(CO)$_5$ mixtures or H$_4$Ru$_4$(CO)$_{12}$ if alkenes are formed. For example, (μ-H)$_3$Ru$_3$(μ_3-CPh)(CO)$_9$ and CO form toluene (>90%) and Ru$_3$(CO)$_{12}$. (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$Me)(CO)$_9$ and CO gives methyl acetate (>80%). On the other hand, (μ-H)$_3$Ru$_3$(μ_3-CCHPhCH$_2$Ph)(CO)$_9$ reacts with CO (1 atm) to give 2,3-diphenyl-1-propene, cis- and trans-1,2-diphenyl-1-propene, and 1,2-diphenylpropane; H$_4$Ru$_4$(CO)$_{12}$ and Ru$_3$(CO)$_{12}$ were metal products. (μ-H)$_3$Ru$_3$(μ_3-CEt)(CO)$_9$ reacts with CO at low pressures to form propene and propane.

In earlier work we have shown that pyrolysis of (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$R)(CO)$_9$ or (μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$ in the absence of CO yields the isomerized products in which one ((μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Me)(CO)$_9$) or two ((μ-H)Ru$_3$(μ_3-η^2-CH$_2$SEt)(CO)$_9$) C–H eliminations have occurred. (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Me)(CO)$_9$ reacts with CO to give methyl acetate and Ru$_3$(CO)$_{12}$.

Mechanism for Reductive Elimination of CH$_3$X from (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$ under CO. The proposed mechanism for CO-induced reductive elimination of alkane or alkene from (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$ is shown in Figure 2. We have assumed that the sequence of events is the same for all derivatives X, except for the nature of intermediate A, for which a different structure is proposed

(18) Churchill, M. R.; Duggan, T. P.; Keister, J. B.; Ziller, J. W. *Acta Crystallogr.* **1987**, *C43*, 203, and references therein.

(19) (a) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977. (b) Bavaro, L. M.; Keister, J. B. *J. Organomet. Chem.* **1985**, *287*, 357.

in the case of X = CO_2R or SEt. In the following discussion evidence will be presented to support this proposal.

The first step in the reductive elimination involves the reversible formation of an intermediate, [$(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-HCX})(CO)_9$], containing an agostic[20] hydrogen bridging Ru and C. Since it involves no change in the electron count for the cluster, this migration is expected to have a low activation energy. The next step, which is rate-determining at high CO pressure, is the cleavage of the agostic hydrogen–metal bond; this completes the first hydrogen migration to the methylidyne carbon and creates an unsaturated metal center. Addition of CO to this unsaturated metal atom forms a saturated alkylidene cluster, (μ-H)$_2$Ru$_3$(μ-CHX)(CO)$_{10}$. This alkylidene can isomerize by another hydride migration from a metal–metal to a metal–carbon bridging position to a tautomer (μ-H)Ru$_3$(μ-HCHR)(CO)$_{10}$, having one bridging hydride and an alkyl group bridging through carbon and an agostic hydrogen. As in the first step, this isomerization does not change the electron count for the cluster, which thus remains saturated. Cleavage of the agostic hydrogen bond generates a terminal alkyl group and an unsaturated metal center, which rapidly adds CO to form (μ-H)Ru$_3$(CH$_2$X)(CO)$_{11}$. Reductive elimination of the third hydride and the alkyl then generates an unsaturated cluster Ru$_3$(CO)$_{11}$, which with subsequent addition of the third CO ligand gives Ru$_3$(CO)$_{12}$. Alternatively, β-hydrogen elimination from HRu$_3$(CH$_2$X)(CO)$_{10}$ would produce H$_2$Ru$_3$(CO)$_{10}$ and alkene.

Sequential Reductive Elimination of C–H Bonds.
Evidence supporting the sequential reductive elimination of C–H bonds in the elimination of CH$_3$X is provided by the isolation of stabilized alkyidene and alkyl intermediates. Pyrolysis of (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$R)(CO)$_9$ (R = Me, Et, or Bz) in the absence of CO produces the alkylidene (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$R)(CO)$_9$, stabilized by coordination of the acyl moiety.[14] Pyrolysis of (μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$, even under a CO atmosphere, generates (μ-H)Ru$_3$(μ_3-η^2-CH$_2$SEt)(CO)$_9$ by migration of two hydrides to the alkylidyne carbon; again, the alkyl is stabilized by coordination of the donor substituent.[16]

Pyrolysis of the osmium analogues has been reported by Strickland and Shapley. The reaction of ester- and amide-functionalized alkylidyne triosmium clusters leads to isomerization to acyl-coordinated alkylidenes.[21] No elimination of CH$_3$X from the triosmium clusters is observed in the presence of CO, nor is CO inhibition of conversion seen, indicating that no unsaturated intermediates are formed.

Precedence for sequential hydride transfers is also found in the tautomeric interconversion of osmium cluster-bound methyl and methylene ligands and the subsequent formation of a methylidyne species upon loss of CO.[22] Intermediates C and D in Figure 2 are modeled upon this system.

Increasing Rates for Successive C–H Eliminations.
Several pieces of evidence suggest that in general the rate constants for successive C–H eliminations increase.

First, the rate-determining step in the reductive elimination of methyl acetate from (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$Me)(CO)$_9$

involves the formation of the first C–H bond. Subsequent steps, including the reaction of the saturated product (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Me)(CO)$_9$ with CO, are faster.

Second, (μ-H)$_2$Ru$_3$(μ_3-η^2-CHSEt)(CO)$_9$, which would be structurally analogous to (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Me)(CO)$_9$, is not observed as an intermediate in the rearrangement of (μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$ to (μ-H)Ru$_3$(μ_3-η^2-CH$_2$SEt)-(CO)$_9$, suggesting that the second hydride migration occurs faster than the first hydride migration.

A third indication of the increasing ease of successive reductive eliminations is the qualitative order of increasing ease of decomposition of an analogous Os cluster series under CO: (μ-H)$_3$Os$_3$(μ_3-CH)(CO)$_9$ < (μ-H)$_2$Os$_3$(μ-CH$_2$)-(CO)$_{10}$ < (μ-H)Os$_3$(μ-η^2-CH$_3$)(CO)$_{10}$.[22]

Finally, structural evidence suggests a decreasing Ru–CH$_n$X bond strength as n increases. Structural investigations of clusters (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$ show that the length of the Ru–CX bond increases in the order X = Cl < Me < p-tolyl;[18] this trend is the same as the order of decreasing bond strength for H–CH$_2$X, suggesting a parallel between Ru–CX and H–CH$_2$X bond strengths. Similarly, a comparison of (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$ (X = Cl, Me, or p-tolyl) with (μ-H)$_2$Ru$_3$(μ_3-η^2-CHCO$_2$Me)(CO)$_9$ and (μ-H)Ru$_3$(μ_3-η^2-CH$_2$SEt)(CO)$_9$ shows increasing Ru–C bond length with successive C–H eliminations. This suggests decreasing Ru–C bond strengths in the order Ru–μ_3-CX > Ru–μ-CHX > Ru–CH$_2$X.[16]

Thus, the rate-determining step in the reductive elimination of CH$_3$X from H$_3$Ru$_3$(CX)(CO)$_9$ under CO is assumed to involve the transfer of the first hydride to the methylidyne carbon, thereby creating an unsaturated intermediate. This intermediate then adds CO and goes on to rapidly and sequentially eliminate CH$_3$X. For X = CO$_2$Me or SEt, the Lewis base site on the methylidyne substituent coordinates instead of CO.

Molecularity of Reductive Elimination of CH$_3$X.
The double-labeling crossover experiment has been used to probe the molecularity of elimination reactions. Unfortunately, studies with cluster hydrides can be complicated (1) by exchange of label between starting materials by processes unrelated to the elimination and (2) because synthesis of deuterium-labeled materials is hampered by the exchange of some cluster hydrides with silica.[23] Both problems have arisen during this work.

Evidence supporting intramolecular C–H bond formation was obtained from the predominant retention of label in the reaction of a mixture of H$_3$Ru$_3$(CCO$_2$Et)(CO)$_9$ and D$_3$Ru$_3$(CCO$_2$Me)(CO)$_9$ with CO (ethyl acetate (85% d_0, 15% d_1) and methyl acetate (72% d_3, 25% d_2)). After correction for 95% enrichment of deuterated cluster, these results are consistent with at least two intramolecular, and no more than one intermolecular, C–H reductive eliminations.

A crossover experiment on the isomerization reaction was attempted in order to focus upon the first hydride migration. Equimolar amounts of D$_3$Ru$_3$(CCO$_2$Me)(CO)$_9$ (84% deuterium enriched) and H$_3$Ru$_3$(CCO$_2$Bz)(CO)$_9$ were allowed to react together under a nitrogen atmosphere. Results showed complete scrambling of hydrogen and deuterium in the products. These results suggest that scrambling may be occurring between products of the initial hydride migration or between starting materials when substantial quantities of the clusters are present.

Evidence for an additional pathway for scrambling of label was obtained with (μ-H)$_3$Ru$_3$(μ_3-C(aryl))(CO)$_9$. The toluene and xylene products from the reaction of (μ-

(20) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(21) (a) Strickland, D. S., Ph.D. Thesis, University of Illinois, 1983. (b) Strickland, D. S.; Shapley, J. R. *J. Organomet. Chem.*, submitted for publication.

(22) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225; **1978**, *100*, 6544; **1978**, *100*, 7726. (b) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.

(23) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Adv. Chem. Ser.* **1978**, *167*, 215.

D)$_3$Ru$_3$(μ_3-CC$_6$H$_5$)(CO)$_9$ with (μ-H)$_3$Ru$_3$(μ_3-CC$_6$H$_4$Me)(CO)$_9$ displayed extensive scrambling of label. Since (μ-D)$_3$Ru$_3$(μ_3-CC$_6$H$_5$)(CO)$_9$ and (μ-H)$_3$Ru$_3$(μ_3-CC$_6$H$_4$Me)(CO)$_9$ cannot be separated by chromatography, we were unable to determine whether exchange between starting materials could occur under reaction conditions. However, a control experiment using (μ-D)$_3$Ru$_3$(μ_3-CPh)(CO)$_9$ and (μ-H)$_3$Ru$_3$(μ_3-CCl)(CO)$_9$ showed loss of label from the former, indicating that exchange between the cluster starting materials was possible.

Because of the predominant retention of label in the reductive elimination of acetate esters, we favor an intramolecular mechanism. The low values for $\Delta S^\ddagger$ for (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$, X = Ph, Cl, and Et at high pressure and X = CO$_2$Me at 1 atm are consistent with an intramolecular rate-determining step.

Rate Law for Reductive Elimination. The rate laws found for elimination of alkane or alkene from (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$, X = Ph, Cl, and Et, show a slight CO pressure dependence according to eq 2. For these clusters at high CO pressure and for (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$Me)(CO)$_9$ at all pressues the rate law is zero order in P_{CO}. The low activation energy for C–H bond formation from (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$Me)(CO)$_9$ and (μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$ and the anomalous kinetic isotope effect for (μ-H)$_3$Ru$_3$(μ_3-CCO$_2$Me)(CO)$_9$ indicate that the mechanism differs in some important respect for these clusters which have Lewis base sites within the molecule. We will return to this point later.

The rate law for the detailed mechanism of Figure 2 is given by eq 9. At high CO pressures the rate-determining

$$\text{rate} = [k_1k_3k_5[\text{CO}]/(k_2k_4 + (k_2 + k_3)k_5[\text{CO}])] \times [\text{H}_3\text{Ru}_3(\text{CX})(\text{CO})_9] \quad (9)$$

step is the formation of the unsaturated alkylidene cluster by cleavage of the agostic Ru–H–C bond. Then the observed rate constant at high CO pressure becomes k_1k_3/k_2 if $k_2 \gg k_3$.

The Agostic Hydrogen. The step of most interest in the proposed mechanism is the reversible formation of the agostic Ru–H–C bond prior to the rate-determining step. The rate law established for reductive elimination from (μ-H)$_3$Ru$_3$(μ_3-CX)(CO)$_9$, X = Ph, Cl, and Et, indicates a preequilibrium prior to addition of the first CO ligand, and the small dependence of the rate upon CO is inconsistent with a CO–associative rate-determining step at low P_{CO}. The rate-determining step at high P_{CO} is therefore proposed to be an intramolecular rearrangement, either reductive elimination to form a C–H bond or cleavage of the Ru–H–C bond, to generate a vacant coordination site. However, irreversible reductive elimination of a hydride and a Ru–C bond cannot account for an inverse kinetic isotope effect at high P_{CO}, since reductive eliminations of this kind typically show normal kinetic isotope effects in the range 1.3–3.5.[2] Therefore a second preequilibrium step is proposed, an intramolecular rearrangement that does not create an unsaturated metal center. The inverse kinetic isotope effect at high P_{CO} implies that the vibrational modes associated with hydrogen in the transition state are of higher frequencies than those in the ground state. Inverse kinetic isotope effects have been determined recently for reductive elimination from monometallic complexes; these unusual values have been explained as due to reversible formation of an agostic bond.[6] While other intramolecular rearrangements of the cluster might account for the inverse kinetic isotope effect found here, we propose reversible migration of a hydrogen from a position bridging two Ru atoms in the ground state to a position bridging a Ru atom and the alkylidyne carbon atom; this proposal

is based primarily upon the existence of stable analogues of the proposed intermediate and upon the magnitudes of the inverse kinetic isotope effects.

The hydrocarbyl cluster Fe$_3$(CO)$_9$CH$_4$ has been shown to exist in solution as a mixture of tautomers, (μ-H)$_3$Fe$_3$-(CO)$_9$(μ_3-CH) (isomer A), (μ-H)$_2$Fe$_3$(CO)$_9$(μ_3-HCH) (isomer B), and (μ-H)Fe$_3$(CO)$_9$(μ_3-H$_2$CH) (isomer C).[24] The relative amounts of the isomers are [A] > [B] > [C], with low-energy barriers between Fe–H–Fe and Fe–H–C interactions. Finally, in the presence of excess phosphine, methane is eliminated. The reaction is similar to that of the ferraborane system [(μ-H)Fe$_3$(BH$_2$R)(CO)$_9$]$^-$, in which BH$_3$L is one of the elimination products, and may suggest that displacement of main-group fragments is enhanced by the presence of MHX interactions.[25] A theoretical analysis has recently been made of the interconversion of endo-hydrogen interactions, Fe–H–Fe and Fe–H–E, and deprotonation of the clusters Fe$_3$(CO)$_9$EH$_x$ (E = B, x = 5; E = C, x = 4).[26]

Because of the greater differences between the energies of M–H–M and M–H–C bonds for M = Ru, the concentration of intermediate A in Figure 2 would be expected to be too low to allow characterization by NMR spectroscopy. However, an analogue to our proposed intermediate, [(μ-H)$_3$Ru$_3$(μ_3-η^2-HCEt)(CO)$_9$]$^+$ (Figure 2, structure F), can be obtained by protonation of (μ-H)$_3$Ru$_3$-(μ_3-CEt)(CO)$_9$.[27]

There is also evidence that such a hydride migration from Ru–H–Ru bridging to Ru–H–C bridging can be rapid. Proton site exchange between CH and Ru–H–Ru positions, proposed to occur through Ru–H–C bridging, occurs with free energies of activation of <90 kJ/mol.[28,29]

The preequilibrium migration of hydrogen between metal–metal and metal–carbon edges nicely accounts for the inverse kinetic isotope effect observed for reductive elimination from (μ-H)$_3$Ru$_3$(μ_3-CPh)(CO)$_9$. The inverse isotope effect is due to the higher force constant for hydrogen in the transition state than in the Ru–H–Ru bridge of the ground state. Three preequilibria could account for a high force constant for the hydrogen: (1) formation of a terminal hydride prior to the rate-determining C–H elimination, (2) formation of a normal C–H bond prior to the rate-determining step (which must not involve CO addition), and (3) formation of the agostic Ru–H–C bond.

Equation 10 can be used to calculate equilibrium isotope effects in the formation of possible intermediates.[30] Here,

$$\log (k_H/k_D) = (0.0810/T)(\nu_{GS} - \nu_I) \quad (10)$$

ν_{GS} and ν_I are the vibrational frequencies (cm^{-1}) of the hydrogen atom in the ground state and in the intermediate, respectively. The formula assumes that the experimental average ratio ν_H/ν_D is 1.35, rather than $2^{1/2}$. We will assume that only the stretching frequency of the hydrogen being transferred need be considered. The calculated isotope effects for the formation of the possible intermediates from a metal–metal bridging hydride, Ru–H–Ru (ν_{GS} = 1350 cm^{-1}),[31] are 0.72 for a terminal Ru–H (ν_I = 2000

(24) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842.

(25) Housecroft, C. E.; Fehlner, T. P. *J. Am. Chem. Soc.* **1986**, *108*, 4867.

(26) Lynam, M. M.; Chipman, D. M.; Barreto, R. D.; Fehlner, T. P. *Organometallics* **1987**, *6*, 2405.

(27) Bower, D. K.; Keister, J. B. *J. Organomet. Chem.* **1986**, *312*, C33.

(28) VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077.

(29) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1984**, *3*, 1322.

(30) Thornton, E. K.; Thornton, E. R. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; ACS Monograph Series No. 167; Van Nostrand Reinhold Co.: New York, 1970; Chapter 4, p 216.

(31) Oxton, I. A. *Spectrochim. Acta* **1982**, *38A*, 181.

**Table VI. Limiting Rate Constants for Reactions of
$(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$, X = CO$_2$Me, Ph, CHPhCH$_2$Ph, Cl,
and Et, with CO at 100 °C**

X	$10^5 k_{obs}$, s^{-1}	X	$10^5 k_{obs}$, s^{-1}
CO$_2$Me	190^a	Ph	6.5
Cl	6.8	Et	0.3^a
CHPhCH$_2$Ph	6.6 ± 1.3		

^{a} Extrapolated by using activation parameters.

cm^{-1}), 0.54 for an agostic Ru–H–C (ν_I = 2600 cm^{-1}), and 0.44 for a fully formed C–H (ν_I = 3000 cm^{-1}). The intermediate containing the terminal Ru–H is least likely since the observed isotope effect for reductive elimination of CH$_3$Ph is smaller than calculated value. Of the two remaining intermediates, the agostic case is favored because of the precedents for such an intermediate and because formation of a terminal C–H would generate an unsaturated metal center which should react rapidly with CO.

Since the isotope effect on the rate constant for reductive elimination (eq 9, $k_{obs} \sim k_1 k_3/k_2$ at high P_{CO}) is the product of the deuterium equilibrium isotope effect on k_1/k_2 and the deuterium kinetic isotope effect on k_3, it is not possible to fully interpret the values for the isotope effects measured for different complexes. The deuterium kinetic isotope effect on k_3 cannot be estimated and might be either greater or less than 1.
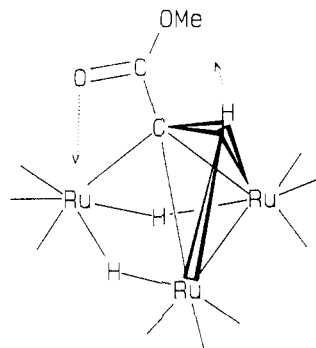
An inverse isotope effect has been reported for deprotonation of and subsequent H$_2$ elimination from $(\mu\text{-H})_3Fe_3(\mu_3\text{-CCH}_3)(CO)_9$, leading to the anionic species $[(\mu\text{-H})Fe_3(\mu_3\text{-}\eta^2\text{-CCH}_2)(CO)_9]^-$.[32]

Effect of the Methylidyne Substituent upon the Rate of Reductive Elimination. The methylidyne substituent clearly exerts a great influence upon the rate of reductive elimination. Rate constants for $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$, X = CO$_2$Me, Ph, Cl, Et, and CHPhCH$_2$Ph, at 100 °C are given in Table VI. The rate constant for isomerization of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CSEt})(CO)_9$ to $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^2\text{-CH}_2SEt)(CO)_9$ (2.2 × 10^{-4} s^{-1}, 70.6 °C) is twice as large as the rate constant for isomerization of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2Me)(CO)_9$ to $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2Me)(CO)_9$ (1.0 × 10^{-4} s^{-1}). Thus, the trend in relative rates for C–H elimination is

X = SEt > CO$_2$Me $\gg$ Cl $\sim$ CHPhCH$_2$Ph $\sim$ Ph > Et

The rates for elimination when X = Ph, Cl, Et, and CHPhCH$_2$Ph are all rather similar; only for the SEt and CO$_2$Me derivatives are the rates unusually rapid. It appears that the presence of a Lewis base site on the methylidyne substituent facilitates hydride migration. Indeed, the isomerization reactions of the osmium clusters $(\mu\text{-H})_3Os_3(\mu_3\text{-CC(O)R})(CO)_9$, forming $(\mu\text{-H})_2Os_3(\mu_3\text{-}\eta^2\text{-CC-(O)R})(CO)_9$, where the relative rates are R = OEt < NEt$_2$, demonstrate the large effect that the donor character of the substituent has on the rate of reductive elimination of C–H bonds.[21] Within the subset of the clusters having Lewis base substituents, the rate for isomerization appears to increase with the nucleophilicity of the Lewis base site.

Acceleration of the rate for reductive elimination by an internal Lewis base site cannot be due simply to trapping of the unsaturated intermediate by the internal Lewis base rather than by CO, since the rate enhancement is large even relative to the rate at the high-pressure limit, where CO attack is not rate limiting. The effect must be due to assistance by the internal Lewis base in the migration step itself. Furthermore, this must also account for the kinetic isotope effect being closer to 1. Thus, a different transition

Figure 3. Intermediate proposed in the isomerization of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCO}_2R)(CO)_9$ to $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2R)(CO)_9$, containing a Ru$_2$C face-bridging agostic hydrogen.

state is required. From the intermediate A in Figure 2, it would seem that the X substituent is oriented anti to the developing unsaturated metal center; it is difficult to see how internal attack by the Lewis base site could assist in C–H elimination in this case.

An alternative intermediate in Figure 3 could explain the lower activation barrier for elimination and also the higher kinetic isotope effect. This intermediate contains a face-bridging agostic hydrogen. Although there is as yet no direct evidence for such a bonding mode, Fehlner has recently proposed the existence of such a bond as one of two possibilities in the structure of FeCo$_2$(HCPh)(CO)$_9$.[33] In such an intermediate the methylidyne substituent is oriented over a metal atom rather than over a M$_2$C face. Simultaneous M–H–C bond cleavage and bond formation between the Lewis base center and a second metal atom can therefore account for the low activation energy. Since the force constants for μ_3-hydrogens are lower than μ-hydrogens, the kinetic isotope effect will be higher (closer to 1) in the transition state following this intermediate.

β-Hydrogen Elimination. If the alkylidyne substituent possesses hydrogen atoms on the β-carbon, then the preferred pathway from the agostic alkyl $(\mu\text{-H})Ru_3(\mu\text{-HCHX})(CO)_{10}$ appears, at least at low pressures, to be β-hydrogen elimination, forming alkene and presumably H$_2$Ru$_3$(CO)$_{10}$, rather than coordination of CO and reductive elimination of alkane to form Ru$_3$(CO)$_{11}$. It is established that the products from the reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$ with CO are alkenes (2,3-diphenylpropene, cis- and trans-1,2-diphenylpropane) and alkane (1,2-diphenylpropane). The Ru-containing products, H$_4$Ru$_4$(CO)$_{12}$ and Ru$_3$(CO)$_{12}$, are both products of decomposition of H$_2$Ru$_3$(CO)$_{11}$ in the absence of CO,[34] suggesting that H$_2$Ru$_3$(CO)$_{10}$ (as yet, this compound is unknown) may be a product of β-hydrogen elimination. The internal alkene products may be formed prior to alkene dissociation or may be formed by Ru-catalyzed isomerization of the terminal alkene; H$_4$Ru$_4$(CO)$_{12}$ is a known alkene isomerization catalyst,[35] and other products of the reaction may also be catalysts for isomerization. Previous studies of related triosmium systems also support the favorability of β-hydrogen elimination relative to reductive elimination.[36,37]

(32) Dutta, T. K.; Meng, X.; Vites, J. C.; Fehlner, T. P. *Organometallics* **1987**, *6*, 2191.

(33) Barreto, R. D.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 4471.
(34) Nevinger, L. R.; Keister, J. B.; Maher, J. *Organometallics*, in press.
(35) (a) Frediani, P.; Bianchi, M.; Piacenti, F. *Chim. Ind. (Milan)* **1971**, *53*, 80. (b) Valle, M.; Osella, D.; Vaglio, G. A. *Inorg. Chim. Acta* **1976**, *20*, 213.
(36) Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316.
(37) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056.
(38) Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *Chem. Commun.* **1967**, 1057.

Intermolecular Tautomerization of Metallacyclic Imines to Enamines Formed from Tantalum Alkyne Complexes and Nitriles

Jamie R. Strickler and David E. Wigley*

*Carl S. Marvel Laboratories of Chemistry, Department of Chemistry,
University of Arizona, Tucson, Arizona 85721*

Received December 13, 1989

The electrophilic metal center in $(DIPP)_3Ta(PhC≡CPh)$ (1; DIPP = 2,6-diisopropylphenoxide) coordinates a variety of nitriles to afford the $η^1$-nitrile adducts $(DIPP)_3(RC≡N)Ta(PhC≡CPh)$ (2, R = CH_3; 3, R = CH_2CH_3; 4, R = CMe_3; 5, R = Ph). Those complexes of nitriles containing α-hydrogens (2 and 3) react further to form the metallacyclic enamine complexes $(DIPP)_3Ta(CPh=CPhC(=CHR)NH)$ (6, R = H; 7, R = CH_3). Deuterium labeling and crossover experiments support these products as having arisen through an *inter*molecular metallacyclic imine to enamine tautomerization.

Introduction

The metal-promoted coupling of unsaturated organic substrates constitutes a powerful strategy for carbon–carbon bond formations in organic synthesis.[1] Among the reductants employed for such reactions are the middle-to low-valent early transition metals.[2–9] Of particular recent interest are the coupling reactions involving at least one nitrile, which have provided convenient routes to vicinal diamines,[10] polyfunctionalized aromatic compounds,[11] and

Scheme I

Ta = (DIPP)₃Ta

related products derived from metallacyclic intermediates.[12] These reactions often proceed by the initial formation of a metallacyclic imine, which may subsequently rearrange[13] or dimerize.[14] Herein, we investigate the metallacyclization reactions of d² alkyne complexes of tantalum[15–18] with nitriles and present evidence for an *inter*molecular tautomerization of tantalacyclic imines to enamines.

Results

The $η^1$-nitrile adducts 2–5 can be isolated from the reaction of the alkyne complex $(DIPP)_3Ta(PhC≡CPh)$ (1;

(1) For overviews, see: (a) Seebach, D.; Weidmann, B.; Widler, L. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Otto Salle Verlag: Frankfurt am Main, FRG, 1983; Vol. 3, pp 217–353. (b) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. (c) Ho, T.-L. *Synthesis* **1979**, 1. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(2) (a) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788 and references therein. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *Ibid.* **1985**, *107*, 2568. (c) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917.

(3) (a) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *Ibid.* **1978**, *100*, 2716. (c) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *Ibid.* **1982**, *104*, 4712. (d) Straus, D. A.; Grubbs, R. H. *Ibid.* **1982**, *104*, 5499.

(4) (a) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. (b) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29.

(5) Mattia, J.; Sikora, D. J.; Macomber, D. W.; Rausch, M. D.; Hickey, J. P.; Friesen, G. D.; Todd, L. J. *J. Organomet. Chem.* **1981**, *213*, 441 and references therein.

(6) (a) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (b) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Ibid.* **1987**, *109*, 6068. (c) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203.
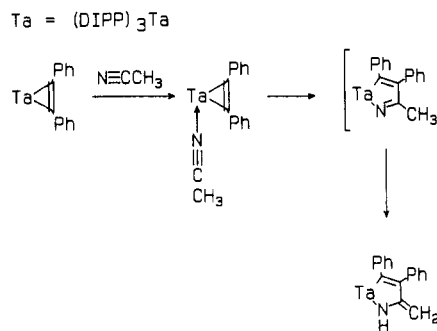
(7) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349.

(8) (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987**, *109*, 2544. (c) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1986**, *108*, 7411. (d) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *Ibid.* **1986**, *108*, 7441.

(9) (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551. (b) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *Ibid.* **1989**, *111*, 8014.

(10) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152.

(11) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137.

(12) (a) Doxsee, K. M.; Farahi, J. B. *J. Am. Chem. Soc.* **1988**, *110*, 7239. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *Ibid.* **1989**, *111*, 4486.

(13) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

(14) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. *Tetrahedron Lett.* **1987**, 3245.

(15) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

(16) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.

(17) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266.

(18) Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860.