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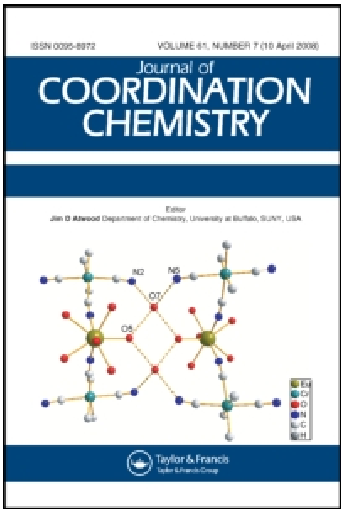

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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KINETICS AND MECHANISM FOR INTRAMOLECULAR ISOMERIZATION OF HRu_3 (μ_3-η^3-EtSCCMeCMe)$(CO)_9$ TO Ru_3(μ-SEt) (μ_3-η^3-CCMeCHMe)$(CO)_9$

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To cite this Article Paw, Witold , Bower, David K. , Bierdeman, David J. , Keister, Jerome B. and Schulman, Edward M.(1996) 'KINETICS AND MECHANISM FOR INTRAMOLECULAR ISOMERIZATION OF HRu_3 (μ_3-η^3-EtSCCMeCMe)$(CO)_9$ TO Ru_3(μ-SEt) (μ_3-η^3-CCMeCHMe)$(CO)_9$', Journal of Coordination Chemistry, 39: 3, 199 — 210
To link to this Article: DOI: 10.1080/00958979608024328
URL: http://dx.doi.org/10.1080/00958979608024328

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J. Coord. Chem., 1996, Vol. 39, pp. 199–210
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KINETICS AND MECHANISM FOR INTRAMOLECULAR ISOMERIZATION OF $HRu_3(\mu_3-\eta^3-EtSCCMeCMe)(CO)_9$ TO $Ru_3(\mu-SEt)(\mu_3-\eta^3-CCMeCHMe)(CO)_9$

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(Received 23 January 1996; Revised 13 March 1996; In final form 29 March 1996)

The kinetics for isomerization of $HRu_3(\mu_3-\eta^3-EtSCCMeCMe)(CO)_9$ to $Ru_3(\mu-SEt)(\mu_3-\eta^3-CCMeCHMe)(CO)_9$ were determined. The overall process involves C—H elimination, C—S and Ru—Ru bond cleavage and $Ru_2(\mu-S)$ bond formation. Activation parameters were determined from the temperature dependence ($\Delta H^\ddagger = 127(3)$ kJ/mol, $\Delta S^\ddagger = 56(11)$ J/mol-K) and from the pressure dependence (0–207 MPa, $\Delta V^\ddagger_0$ +12.7(1.1) cm^3/mol, $\Delta\beta^\ddagger = +0.037(0.012)$ cm^3/(mol–MPa)) of the rate constant. The data are consistent with an intramolecular reaction involving significant metal-metal or carbon-sulfur bond cleavage in the transition state. The activation volume is too large to be accommodated by C—H elimination alone and CO dissociation is not involved.

Keywords: isomerization; kinetics; mechanism; volume of activation; transition metal cluster

INTRODUCTION

Transformations of organic fragments on transition metal clusters frequently give unique products which display structural features unprecedented in the chemistry of monometallic complexes. Some of these structures have been proposed as models for hydrocarbons chemisorbed on metal surfaces.[1] Only infrequently have the mechanisms of these transformations been investigated,

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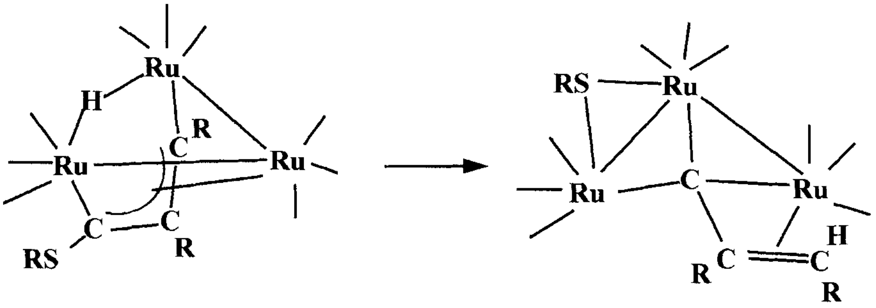

FIGURE 1 Structural changes in the rearrangement of (μ–H) $Ru_3(\mu_3$-η^3-EtSCCMeCMe$(CO)_9$ to $Ru_3(\mu$-SEt$)(\mu_3$-η^3-CCMeCHMe$)(CO)_9$

even for relatively simple processes. Some years ago our group reported an example of hydrocarbon chain growth *via* alkylidyne-alkyne coupling on triruthenium clusters, forming the 1,3-allylidene species $HRu_3(\mu_3$–η^3–XCCRCR$')(CO)_9$.[2] For X = OMe, hydrogenation of the coupled product gives an alkylidyne of longer chain length, $H_3Ru_3(\mu_3$-CCHRCH$_2$R$')(CO)_9$. However, thermally induced isomerization (Figure 1) of $HRu_3(\mu_3$-η^3-EtSCCRCR$')(CO)_9$ forms $Ru_3(\mu$-SEt$)$ $(\mu_3$-η^3-CCRCR$'$H$)(CO)_9$, an apparent intermediate in the hydrogenation process.[3]

In this paper we present a study of the kinetics (including determination of the activation volume) and mechanism of this novel isomerization, which involves C—H elimination, C-SEt and Ru-Ru bond cleavage and μ-Ru$_2$-S bond formation.[4]

EXPERIMENTAL

Materials

$HRu_3(\mu_3$-η^3-EtSCCMe$)(CO)_9$[3] and $H_3Ru_3(\mu_3$-CBr$)(CO)_9$[5] were synthesized according to published procedures. Decane was purchased from Aldrich and used as received.

Kinetics at 1 atm Pressure

The procedure for these measurements was previously reported.[3] Three or four runs were determined at each temperature. The reported rate constants are average values with the error limit as the standard deviation. The enthalpy and entropy of activation were determined from a computer calculated linear least squares fit using the program Psi-Plot. Error limits for the enthalpy and entropy of activation are reported as the 95% confidence limits using 13 different measurements.

Variable Pressure Kinetic Measurements

The apparatus for variable pressure kinetic measurements of very slow reactions was assembled as described in Reference 6b. The components are a hydraulic pressure generator, a 40 cm^3 high pressure reaction vessel, tubing and valves, all supplied by Newport Scientific Inc and a pressure gauge (HEISE). The head of the reaction vessel was customized to have separate inlets for compression and for sampling. The reaction solution was contained in a hypodermic syringe with the barrel and piston adapted to fit the reaction vessel chamber and to minimize dead space (to be occupied by air after assembly). The wide gauge needle connected to this syringe had an opening just below the sampling inlet and was sealed by a compression fitting within the head. A glycerol/water mixture (1:1 v/v) was used for compression. The reaction vessel was thermostatted in a constant temperature bath. Samples were periodically removed by releasing the pressure and inserting a very narrow gauge syringe needle through the wide-bore needle of the syringe containing the reaction solution such that the sampling needle nearly reached the plunger, thus insuring that the solution which was removed had remained at constant temperature and composition in the interior of the reaction vessel. IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer.

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A solution of 10–15 mg of $HRu_3(\mu_3\text{-}\eta^3\text{–EtSCCMeCMe})(CO)_9$ in 8–10 mL of decane was placed in the syringe. After assembly the system was compressed to the desired pressure and thermostatted for *ca.* 2 h at 48.0°C. At 3–12 h intervals, the pressure was released and 0.25 mL of the reaction solution was withdrawn with the use of a gas-tight syringe equipped with a narrow gauge needle. Sampling typically required 10–15 min. Each kinetic run was continued for 2–2.5 half-lives but only points corresponding to one half-life were taken for the plots. Plots of ln(absorbance) *vs* time displayed curvature due to a non-zero final absorbance A_∞; however, the data at later times were unreliable due to cumulative errors introduced in the sampling procedure and to errors in measurement of the absorbance values, thus preventing an accurate experimental determination of A_∞. Fitting of the data over the entire 2–2.5 half-lives to an exponential equation with adjustable A_∞ gave a better fit to the experimental plot of absorbance *vs* time, but more poorly fixed the value of the rate constant (because of the greater weight placed upon less reliable data and compensating A_∞) than did fits using only data over the first half-life. Consequently, rate constants were determined by linear least squares fits of ln(absorbance) *vs.* time using data over the first half-life. The range of pressures was 500 – 30,000 psi (3 – 207 MPa). Polynomial fitting of ln k *vs.* P to Equation (1) was performed using the program Psi-Plot (Poly Software International). Error limits for $\Delta V^\ddagger_0$ and $\Delta\beta^\ddagger$ are 95%

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confidence limits. A similar fit using rate constants determined by fits of the absorbance *vs.* time over 2–2.5 half-lives and with adjustable A_∞ gave essentially the same value of $\Delta V^{\ddagger}_0$ (+13.0(2.3) cm^3/mol) and a similar value of $\Delta\beta^{\ddagger}$ (+0.023(0.012) cm^3/mol-MPa), but with much larger uncertainties.

Synthesis of (μ-H)$_3$Ru$_3$(μ_3-CSBu)(CO)$_9$

This procedure is analogous to that reported for the synthesis of (μ-H)$_3$Ru$_3$(μ_3-CSEt)(CO)$_9$.[3] Butanethiol (110 μL, 1.028 mmol) and triethylamine (86 μL, 0.6168 mmol) were added to a solution of (μ-H)$_3$Ru$_3$(μ_3-CBr)(CO)$_9$ (133.7 mg, 0.2056 mmol) (*ca.* 5:3:1 molar ratio) in 5 mL of dry cyclohexane. The solution was stirred under nitrogen at room temperature for 8 h. Solvent was removed by vacuum. Products were purified by TLC on silica gel, eluting with 5:1 C_6H_{12}/CH_2Cl_2. The primary product, (μ-H)$_3$Ru$_3$(μ_3-CSBu)(CO)$_9$, (75.0 mg, 0.1137 mmol) was obtained in 55% yield. IR (C_6H_{12}): ν(CO) 2107.6 w, 2081.8 *vs*, 2079.2 *vs*, 2037.3 *vs*, 2028.6 m, 2019.2 s, 2005.0 w cm^{-1}.

(μ-H)Ru$_3$(μ_3-η^3-BuSCCEtCEt)(CO)$_9$

(μ-H)$_3$Ru$_3$(μ_3-CSBu)(CO)$_9$ (68.2 mg, 0.103 mmol), cyclohexane (6 mL) and 3-hexyne (115 μL, 1.01 mmol) were added to a 25-mL flask equipped with stir bar and nitrogen gas inlet. The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. Then the solvent was removed by vacuum transfer and the solid residue was purified by TLC on silica gel, eluting with hexanes. The second, yellow band was extracted with dichloromethane. Evaporation yielded yellow-orange (μ-H)Ru$_3$(μ_3-η^3-BuSCCEtCEt)(CO)$_9$ (15.5 mg, 20%). IR (C_6H_{12}): ν(CO) 2094.0 s, 2068.2 *vs*, 2060.9 m, 2045.6 *vs*, 2036.3 m, 2025.0 m 2015.5 m 2008.3 *vs*, 1975 w cm^{-1}. ^{1}H NMR (CDCl$_3$, 25°C): 3.15 (m, 2H$_{a,a'}$), 2.83 (m, 2H$_{b,b'}$), 2.40 (m, 2H$_{c,c'}$), 1.73 (m, 2H$_{d,d'}$), 1.45 (t,3H$_e$), 1.26 (m,2H$_{f,f}$), 1.02 (t,3H$_g$), 1.00 (t, 3H$_h$), –20.50 (s, 1H$_i$) ppm, J_{cg} 7.4 Hz, J_{cf} 7.4 Hz, J_{ab} 7.0 Hz, J_{bf} 7.2 Hz, J_{fi} 7.4 Hz.

Crossover reaction of (μ-H)Ru$_3$(μ_3-η^3-EtSCCMeCMe)(CO)$_9$ and (μH)Ru$_3$(μ_3-η^3-BuSCCEtCEt)(CO)$_9$

(μ-H)Ru$_3$(μ_3-η^3-EtSCCMeCMe)(CO)$_9$ (20.0 mg, 0.0293 mmol), (μ-H)Ru$_3$(μ_3-η^3-BuSCCEtCEt)(CO)$_9$ (15.5 mg, 0.0210 mmol) and decane (5 mL) were placed in a 10-mL flask under nitrogen. The mixture was heated to 60 °C for 10 h. At intervals samples were removed for IR analysis. After 10 h, solvent was removed by vacuum transfer. A portion of the residue was submitted for MS FAB analysis and ^{1}H NMR analysis. The remainder was separated by TLC on silica gel, eluting with hexanes. Three bands were observed, in order of elution; narrow yellow band, 6.0 mg, $Ru_3(\mu\text{-}SBu)(\mu_3\text{-}\eta^3\text{-}CCEtCHEt)(CO)_9$; narrow yellow band, 7.8 mg, $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$; broad orange band, very small amount, unanalyzed. Identification of $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$ was made by comparison of IR, ^1H NMR and mass spectra with the data reported in the literature.[3] Analysis of the mixture was essentially identical to the combination of the features of the analyses of the two isolated products.

$Ru_3(\mu\text{-}SBu)(\mu_3\text{-}\eta^3\text{-}CCEtCHEt)(CO)_9$. IR(hexanes): 2081 w, 2058 s, 2042 s, 2025 w, 1009 s, 2000 s, 1994 m, 1982 w cm^{-1}. ^1H NMR ($CDCl_3$, 25°C): 2.70 (m, $2H_{a,a'}$), 2.40 (q, $2H_{b,b'}$), 2.03 (m, $1H_c$), 1.77 (m, $2H_{d,d'}$), 1.64 (m, $2H_{e,e'}$), 1.44 (m, $2H_{f,f}$) 1.37 (t, $3H_g$), 1.22 (t, $3H_h$), 0.93 (t, $3H_i$) ppm, J_{cf} 3.4 Hz, J_{cf} 9.6 Hz, J_{fh} 6.8 Hz, $J_{dg} = J_{ab} = J_{ei}$ = 7.0 Hz. MS (EI): m/z 742 ($^{102}Ru_3$).

RESULTS

As previously reported, the reaction of an alkyne RCCR′ with $H_3Ru_3(\mu_3\text{-}CSR)(CO)_9$ produces 1 equiv of the corresponding cis-alkene, $HRu_3(\mu_3\text{-}\eta^3\text{-}RSCCR'CR')(CO)_9$ and $Ru_3(\mu\text{-}SR)(\mu_3\text{-}\eta^3\text{-}CCR'CHR')(CO)_9$.[3] Structures of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$[7] and $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCPhCHPh)(CO)_9$[3] have been determined. At 25° C the isolated yields of $HRu_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$ and $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$ are 44% and 10%, respectively. The relative yields are consistent with initial formation of $HRu_3(\mu_3\text{-}\eta^2\text{-}EtSCCMeCMe)(CO)_9$ and then isomerization to $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$.

As previously reported,[3] the rearrangement of $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$ to $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$ is a clean and quantitative reaction. The IR spectra of samples taken during the reaction display isosbestic points, indicating a quantitative reaction with no measurable build-up of an intermediate. The linearity of the plot of ln(absorbance) *vs.* time indicates a rate law which is first-order in cluster concentration.[3] The rate constant is unaffected by a CO atmosphere (at 60°C, $7.9(0.5) \times 10^{-5}$ s^{-1} under 1 atm nitrogen *vs.* $8.2(0.2) \times 10^{-5}$ s^{-1} under 1 atm of CO).[3] We were unable to determine the deuterium kinetic isotope effect because the deuteriated derivative could not be synthesized due to H/D exchange during chromatography. The nature of the hydrocarbyl substituents has a small effect upon the rate, as isomerization of $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta^3\text{-}EtSCCRCR)(CO)_9$ to $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCRCHR)(CO)_9$ is about 1.4 times faster for R = Ph (at 60.0°C, $k = 1.12(0.02) \times 10^{-4}$ s^{-1}) than for R = Me.[3]

As these results did not provide much information concerning the elementary steps in the mechanisms, additional experiments were undertaken.

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A cross-over experiment was undertaken to establish the intramolecular nature of the C—SR bond cleavage. The only significant products isolated from isomerization of a mixture of $HRu_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$ and $HRu_3(\mu_3\text{-}\eta^3\text{-BuSCCEtCEt})(CO)_9$ were $Ru_3(\mu\text{-SEt})(\mu_3\text{-}\eta^3\text{-CCMeCHMe})(CO)_9$ and $Ru_3(\mu\text{-SBu})(\mu_3\text{-}\eta^3\text{-CCEtCHEt})(CO)_9$. This result shows that inter-cluster exchange of the thiolate and hydrocarbyl fragments does not occur and homolytic C—SR cleavage to produce free radicals is unlikely.

The rate constants for the rearrangement measured at barometric pressure and temperatures of 40.0–70.0°C are listed in Table I. The Eyring plot of all experimental data (13 measurements) gives values of $\Delta H^{\ddagger}$ = 127(3) kJ/mol (30.3(0.8) kcal/mol) and $\Delta S^{\ddagger}$ = +56(11) J/mol-K (+13.4(2.6) eu).

The rate constants for this rearrangement measured at pressures in the 500–30,000 psi (3 – 207 MPa) range are listed in Table II. The IR spectra during the course of the reaction in a typical run (103.4 MPa) are shown on Figure 2. The IR spectra and kinetic data confirm that the system is still well-behaved under these conditions and, more importantly, there are no leaks from/to the reaction solution in the apparatus. A plot of ln (A_0/A) for the absorbance at 2095.5 cm^{-1} *vs.* time for a single run is shown on Figure 3. The observed leveling of the curve in the plot is due to the final absorbance not being zero. This seriously affects linearity of the plot at long times. Due to experimental difficulties and the long time required to determine the final absorbance required for a $\ln(A\text{-}A_\infty)$ plot, it was decided to use the initial rate constant derived from the first 5–6 data points recorded during the first half-life of a run. The errors of the rate constants correspond to the 95% confidence limit of a linear regression analysis including consideration of Student's t values.

TABLE I Rate constants at 1 atm pressure for the rearrangement of $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$ to $Ru_3(\mu\text{-SEt})(\mu_3\text{-}\eta^3\text{-CCMeCHMe})(CO)_9$ in decane solution

T(°C)	*k (10^{-5} s^{-1})*
70.0	35 ± 2
60.0	7.9 ± 0.6
50.0	2.0 ± 0.1
40.0	0.44 ± 0.02

TABLE II Variable pressure kinetic data at 48.0°C for the rearrangement of $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$ to $Ru_3(\mu\text{-SEt})(\mu_3\text{-}\eta^3\text{-CCMeCHMe})(CO)_9$ in decane solution

pressure (Mpa)	*k (10^{-5} s^{-1})*
3.4	1.08 ± 0.07
6.9	1.060 ± 0.013
13.8	1.039 ± 0.011
34.5	0.937 ± 0.017
51.7	0.87 ± 0.03

TABLE II (*Continued*)

pressure (Mpa)	*k (10^{-5} s^{-1})*
69.0	0.819 ± 0.013
103.4	0.70 ± 0.04
127.6	0.682 ± 0.017
155.2	0.625 ± 0.011
206.9	0.55 ± 0.03

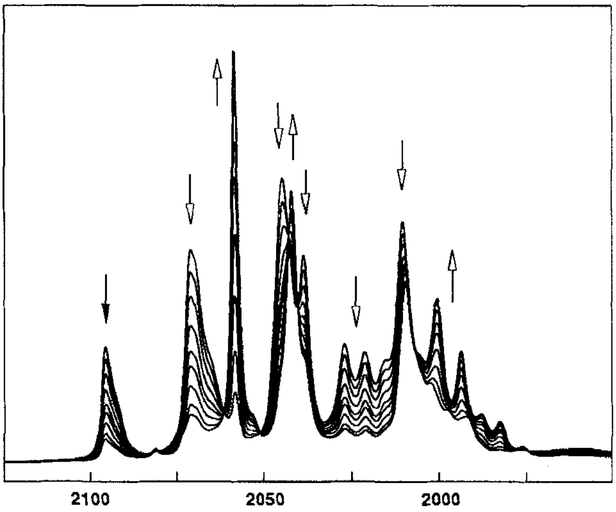

FIGURE 2 IR spectra monitoring of the progress of the rearrangement from a run at 103.4 MPa.

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A number of treatments of the dependence of rate constant upon pressure have been proposed[6]. The most common approach is the linear relationship: ln k = a + bP with the slope of $-\Delta V^{\ddagger}/RT$. Quite often, however, curvature is observed due to the limits of compressibility at high pressure. Several equations have been employed to account for deviations from linearity, but the most commonly used is the parabolic function in Equation (1). The term $\Delta V^{\ddagger}_0$ is the difference in volume, extrapolated to 0 pressure, between the transition state and the ground state. The coefficient $\Delta\beta^{\ddagger}$ is the compressibility coefficient of activation. It has been suggested that solvent effects are responsible for non-zero values of $\Delta\beta^{\ddagger}$. Single measurements were made at 10 different pressures to determine curvature of the ln (k_{obs}) *vs.* pressure (P) relationship. The plot of ln k *vs.* P is shown on Figure 4. A polynomial fit of the plot in Figure 4 according to Equation (1) gives $\Delta V^{\ddagger}_0 = +12.7(1.1)$ cm^3/mol and $\Delta\beta = +0.037(0.012)$ cm^3/(mol-MPa) (+3.7(1.2) cm^3/(mol-kbar)).

$$\ln k = \ln k_0 + (-\Delta V_0^{\ddagger}/RT)P + (\Delta\beta^{\ddagger}/2RT)P^2 \quad (1)$$

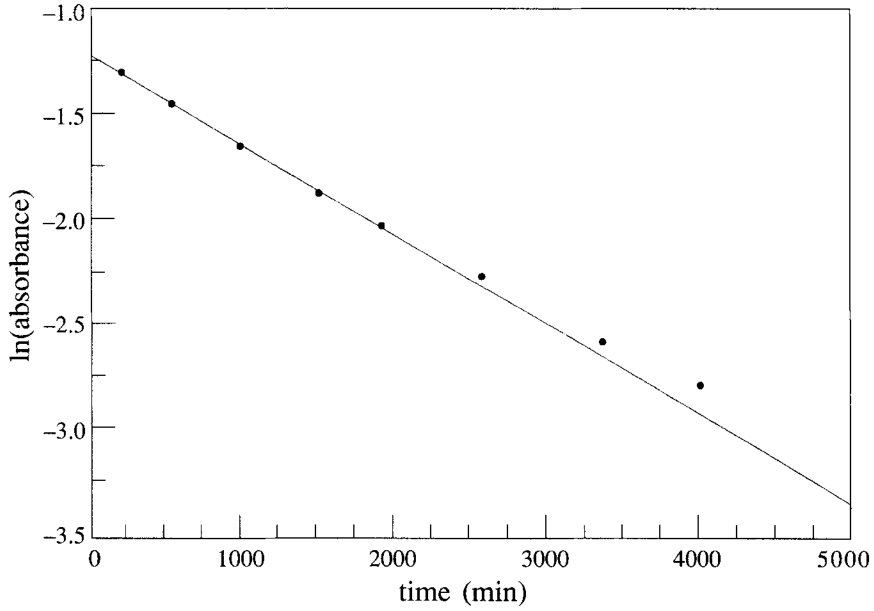

FIGURE 3 Plot of ln(absorbance) *vs.* time at 103.4 MPa and 48.0°C.

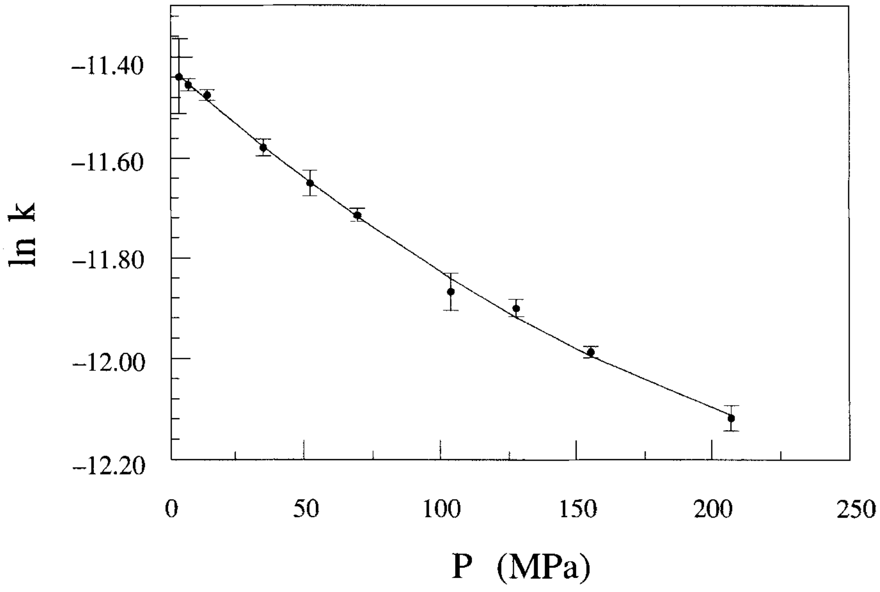

FIGURE 4 Plot of ln k *vs* P and the fit calculated according to Equation (1).

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DISCUSSION

Activation volumes and volume profiles have been determined for a wide variety of inorganic and organic reactions.[6] Recently these parameters have been determined for some reactions of metal clusters. One might expect larger volume changes associated with cluster reactions due to more severe steric interactions of ligands across the cluster framework and the possible involvement of metal-metal bond cleavage and formation. Ligand additions to $H_2Os_3(CO)_{10}$ display $\Delta V^\ddagger_0$ of -8 to -32 cm^3/mol, with the value related to the cone angle of the ligand and the steric threshold for addition.[8] Ligand substitutions involving a CO dissociation typically display values of *ca.* +20 cm^3/mol (for example, substitution on $[PPN][HRu_3(CO)_{11}]$ (+21.2 cm^3/mol) and $Ru_3(CO)_{10}(P(OMe)_3)(CO_2Me)^-$ (+24 cm^3/mol)[9]), but the smaller than expected $\Delta V^\ddagger_0$ for CO dissociation from (μ-H) $Ru_3(\mu\text{-}COMe)(CO)_{10}$ (+9.6cm^3/mol) was rationalized in terms of a μ-COMe to $\mu_3\text{-}\eta^2$-COMe rearrangement accompanying CO dissociation.[10] Reductive elimination of hydrogen from $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ also shows a significantly positive value, +20 cm^3/mol.[10] On the other hand, examples of hydride fluxionality display $\Delta V_0^\ddagger$ near zero (+4 cm^3/mol for $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CHCO_2Me)(CO)_9$;[11] -0.8 cm^3/mol for $H(\mu\text{-}H)Os(CO)_{10}(PPh_3)$);[11] Another example involving C-H elimination, the isomerization of $H_3Ru_3(\mu_3\text{-}CCO_2Me)(CO)_9$ to $H_2Ru_3(\mu\text{-}_3\text{-}\eta^2\text{-}CHCO_2Me)(CO)_9$, displays $\Delta V^\ddagger_0$ of $-0.27(0.14)$ cm^3 mol^{-1}.[12] Other relevant intramolecular processes which have been reported are carbonyl fluxionality on $Ru_3(CO)_7L$(trithiane) (+13.1 and +14.1 cm^3/mol)[13] and $Ir_4(CO)_9$(trithiane) ($\Delta V^\ddagger_0$ +8.3 cm^3/mol, ΔV +15.4 cm^3/mol)[14] and fluxional isomerization of $Fe(CO)_2(PPh_3)$(1,3-cyclo-ocatadiene) (+0.5 cm^3/mol) and $Fe(CO)_2(PPh_3)$(7,7-dimethoxybicyclo[2.2.1]heptene (+5.3 cm^3/mol).[15] These studies suggest that variable pressure kinetic studies of cluster rearrangements can differentiate between intramolecular rate-determining steps such as metal-metal bond cleavage *vs.* C—H elimination or hydride migration.

During the course of isomerization of $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$ to $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$, significant changes occur within the molecule: the Ru_3 framework is opened by cleavage of one Ru-Ru bond, reductive elimination of a C—H bond occurs, the C—SEt bond is broken, a Ru-SEt-Ru bridge is formed and, in addition, the connectivity of carbon atoms to metal centers is changed (Figure 1). It was previously reported that the reaction was first-order in cluster concentration and independent of CO concentration; the lack of CO inhibition proves that *reversible* CO dissociation does not precede the rate-determining step, but does not rule out rate-determining CO dissociation. This work was undertaken in the expectation that the values of $\Delta V^\ddagger_0$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$,

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would provide insight into the mechanism of this novel isomerization, in particular the involvement of hydride migration, metal-metal bond cleavage and metal-sulfur bond formation. Prior work suggests that $\Delta V^{\ddagger}_0$ values should decrease in the following order: metal-CO bond cleavage (*ca.* +20 cm^3/mol), C—C bond cleavage (+10 cm^3/mol), bridge-terminal CO migration (+5 cm^3/mol for full isomerization, +2 cm^{3}mol for $\Delta V^{\ddagger}_0$), hydride migration (±5 cm^3/mol), ligand association (–10 to –20 cm^3/mol); no examples of activation volumes for metal-metal bond cleavage have been reported, but the value is expected to be larger than that for C—C cleavage.

The overall change in partial molar volume $\Delta\bar{V}$ for the isomerization $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$ to $Ru_3(\mu\text{-SEt})(\mu_3\text{-}\eta^3\text{-CMeCHMe})(CO)_9$ has not been experimentally determined. However, crystal structures for $HRu_3(EtSCCMeCMe)(CO)_9$[7] and $Ru_3(SEt)(CCPhCPhH)(CO)_9$[3] have been reported. From the solid state molar volumes (325.3 cm^3/mol and 431.9 cm^3/mol, respectively) and the estimated difference in the volume contribution for the phenyl substituent compared to the methyl substituent (*ca.* +45 cm^3/mol, derived from comparisons of organic compounds), we can estimate that $\Delta\bar{V}$ for the isomerization is *ca.* +20 cm^3/mol.

The activation volume, $\Delta V^{\ddagger}_0$, is the difference in partial molar volumes between the ground state and the transition state at 0 pressure and is the sum of the intrinsic and solvation contributions. The instrinsic volume contains the volume changes associated with changes in bond lengths and angles of the reacting species and is the quantity of primary mechanistic interest. Since the reactants and product are uncharged, we believe that the volume change associated with solvation is small. Indeed, the rate constant for isomerization is virtually unchanged in THF solution (2.5(0.1) × 10^{-4} s^{-1} at 66.6°C) compared with decane solution (2.1 × 10^{-4} s^{-1}, interpolated from an Eyring plot). The activation volume may be greater or less than the change in volume for the overall reaction, $\Delta\bar{V}$.

The activation volume of +12.7 cm^3/mol for the transformation of $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$ to $Ru_3(\mu\text{-SEt})(\mu_3\text{-}\eta^3\text{-CCMeCHMe})(CO)_9$ indicates significant bond breaking in the transition state, roughly half of the total volume change expected for the reaction. The positive value for $\Delta S^{\ddagger}$ (+56 J/K-mol) also suggests this. Although the trends in $\Delta V_0^{\ddagger}$ and $\Delta S^{\ddagger}$ for a given reaction type are frequently correlated, cases of opposite signs for $\Delta V_0^{\ddagger}$ and $\Delta S^{\ddagger}$ have been noted. In particular, intramolecular rearrangements occurring with minimal bond stretching, *e.g.* a trigonal twist isomerization of octahedral complexes, have been associated with large and negative $\Delta S^{\ddagger}$ and near-zero $\Delta V_0^{\ddagger}$.[16] This has also been found to be true for hydride fluxionality ($\Delta V_0^{\ddagger}$ = +4 cm^3/mol and $\Delta S^{\ddagger}$ = –40(3) J/K-mol for $(\mu\text{-H})_2Ru_3(\mu_3\text{-CHCO}_2\text{Me})(CO)_9$[10] $\Delta V_0^{\ddagger}$ = –0.8 cm^3/mol and $\Delta S^{\ddagger}$ = –54(6) J/K-mol

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for $H(\mu\text{-}H)Os(CO)_{10}(PPh_3)$[10]). The activation volume for this cluster isomerization is smaller than found for most examples of CO dissociation, suggesting that CO dissociation is not rate-limiting and with the lack of rate dependence upon CO, dissociation is not involved in or prior to the rate-determining step. Either C—SEt bond cleavage or cluster opening by Ru—Ru or Ru—C bond cleavage, or a combination of these could give rise to the observed $\Delta V_0^{\ddagger}$; C—H elimination (at least the one example we have measured thus far) and hydride fluxionality display small volumes of activation and so may also be involved. Although we are unaware of examples of activation volumes for homolytic C—S bond cleavage, a value comparable to that for carbon-carbon bond cleavage, *ca.* +10 cm^3/mol, would be expected.[6a] Metal-metal bond cleavage is expected to exhibit a significantly positive activation volume. It has been previously noted that $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta^3\text{-}EtOCCMeCMe)(CO)_9$ does not isomerize under comparable conditions, but C—OMe bond cleavage and C—H elimination proceed at significantly higher temperatures under a hydrogen atmosphere, forming $H_3Ru_3(\mu_3\text{-}CCHMeCH_2Me)(CO)_9$.[2] This strongly suggests that C—SEt bond cleavage is involved in the rate-determining step of isomerization of $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$ to $Ru_3(\mu\text{-}SEt)(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$. Results of the cross-over experiment show that any C—SR bond cleavage must be accompanied by Ru—SR bond formation to account for the lack of scrambling of the SR moiety. As this bond formation would be expected to reduce $\Delta V_0^{\ddagger}$ from the value of *ca.* +10 cm^3/mol for C—S cleavage, opening of the cluster must also accompany cleavage of the C—S bond.

A reasonable mechanism is shown in Figure 5. We assume that C—H elimination is facile but reversible (step a). This step probably would contribute little to

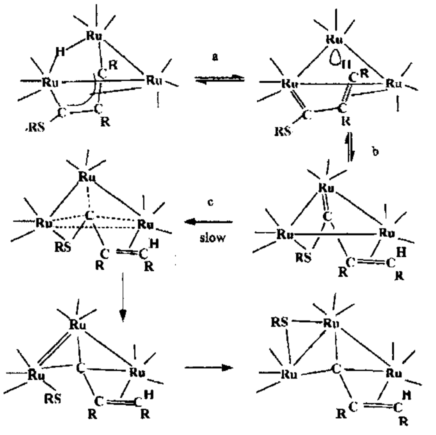

FIGURE 5 Proposed mechanism for isomerization of $(\mu\text{-}H)Ru_3(\mu^3\text{-}\eta^3\text{-}EtSCCMeCMe)(CO)_9$ to $Ru_3(\mu_3\text{-}\eta^3\text{-}CCMeCHMe)(CO)_9$.

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the activation volume. This elimination generates a vacant coordination site, but one not geometrically favorable for sulfur coordination. By cleavage of the Ru—Ru bond and migration of the EtSCCRCHR ligand as shown (step b), the unsaturation is transferred to the Ru atom which can coordinate to sulfur, thus creating a saturated cluster. Oxidative addition of the C—SEt bond then occurs as the rate-determining step (step c). These steps would also be possible for $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-MeOCCMeCMe})(CO)_9$ and other alkoxy substituted analogs. The lower reactivity for $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-MeOCCMeCMe})(CO)_9$, as compared with $(\mu\text{-H})Ru_3(\mu_3\text{-}\eta^3\text{-EtSCCMeCMe})(CO)_9$, is explained by the stronger C—OMe *vs.* C—SEt bond and the weaker Ru—OMe *vs.* Ru—SEt bond.

Acknowledgments

This work was supported by the National Science Foundation through grant CHE9213695. We thank Professors Rudi van Eldik (University of Erlangen-Nürnberg) and André Merbach (Lausanne) for valuable collaborations which taught JBK the utility of high pressure measurements.

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