3174 *J. Am. Chem. Soc.* **1993,** *115,* 3174–3181

# Reaction Kinetics and Thermodynamics of the $(\mu_2\text{-H})_2Os_3(CO)_{10}$–CO System

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*Received June 15, 1992*

**Abstract:** The kinetics of the reversible addition of CO to the electronically unsaturated cluster $(\mu_2\text{-H})_2Os_3(CO)_{10}$ in decalin have been studied at 25.0–40.0 °C. The kinetic parameters for addition and loss of CO are $k_1(25.0\,°C) = 4.10(0.07) \times 10^{-2}\ M^{-1}\ s^{-1}$, $\Delta H_1^{\ddagger} = 15.7(0.4)$ kcal mol$^{-1}$, and $\Delta S_1^{\ddagger} = -12.1(1.3)$ cal K$^{-1}$ mol$^{-1}$ and $k_{-1}(25.0\,°C) = 7.0(0.8) \times 10^{-5}\ s^{-1}$, $\Delta H_{-1}^{\ddagger} = 25.9(0.4)$ kcal mol$^{-1}$, and $\Delta S_{-1}^{\ddagger} = +9.3(1.4)$ cal K$^{-1}$ mol$^{-1}$, respectively. The reactions are most probably simple concerted, one-step reactions. Equilibrium constants for addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ have been determined over the temperature range 25.0–90.0 °C and $K_1(25.0\,°C) = 5.9(0.7) \times 10^2\ M^{-1}$, $\Delta H_1° = -9.5(0.3)$ kcal mol$^{-1}$, and $\Delta S_1° = -19.2(0.9)$ cal K$^{-1}$ mol$^{-1}$. The kinetics of loss of $H_2$ from equilibrium mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ in the presence of CO to form $Os_3(CO)_{12}$ at 65.0–95.0 °C have also been studied. An unexpected feature of the reductive elimination of $H_2$ is that it can occur via a first-order reaction of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ ($\Delta H_3^{\ddagger} = 14.2(4.5)$ kcal mol$^{-1}$, $\Delta S_3^{\ddagger} = -35(13)$ cal K$^{-1}$ mol$^{-1}$, hence $k_3(25.0\,°C)$ = ca. $7 \times 10^{-6}\ s^{-1}$) as well as from $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ ($\Delta H_2^{\ddagger} = 27.7(2.3)$ kcal mol$^{-1}$, $\Delta S_2^{\ddagger} = +9.5(6.5)$ cal K$^{-1}$ mol$^{-1}$, and $k_2(25.0\,°C)$ = ca. $4 \times 10^{-6}\ s^{-1}$). Combination of these results with others reported earlier has enabled a complete energy profile to be obtained for the system $(\mu_2\text{-H})_2Os_3(CO)_{10} + 2CO \rightleftharpoons (\mu_2\text{-H})(H)Os_3(CO)_{11} + CO \rightleftharpoons H_2 + Os_3(CO)_{12}$ for which the overall parameters $K(25.0\,°C)$ = ca. $5 \times 10^7\ M^{-1}$, $\Delta H° = -19.1(2.4)$ kcal mol$^{-1}$, and $\Delta S° = -27.0(6.7)$ cal K$^{-1}$ mol$^{-1}$ apply. The standard heats of formation of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ are estimated to be 709 and 672 kcal mol$^{-1}$, respectively, and an estimate of the Os–H bond strengths in $(H)_2Os_3(CO)_{11}$ of ca. 62 kcal mol$^{-1}$ can be derived. This estimate is compared with other data for M–H bond strengths found in the literature, and the importance of effects due to the presence of different ligands and other metals attached to the metal in the M–H bond is emphasized.

## Introduction

The hydridocarbonyl compound $(\mu_2\text{-H})_2Os_3(CO)_{10}$ is a classical example of a formally electron deficient cluster and it has been known for some time to react with a wide variety of Lewis bases, L, to form the electron-precise adducts $(\mu_2\text{-H})(H)Os_3(CO)_{10}L$.[1] Addition of P-donors is quite fast at ambient temperatures,[2] but reaction with CO to form $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ is considerably slower. In the presence of CO loss of $H_2$ occurs at elevated temperatures with concomitant formation of $Os_3(CO)_{12}$.[1] Quantitative evaluation of the rates of adduct formation involving such an archetypical cluster has received no attention and kinetics studies of reductive elimination of $H_2$ from clusters are still relatively rare.[3] We have therefore studied the kinetics and equilibria of the reversible addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and the kinetics of displacement of $H_2$ from equilibrium mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ in the presence of CO. A combination of the results with those obtained for some reactions of $Os_3(CO)_{12}$[4] and $Os_3(CO)_{11}(NCMe)$[5] allows the construction of a complete energy profile for the transformation of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ into $Os_3(CO)_{12}$. Kinetic parameters for the unexpected direct loss of $H_2$ from $(\mu_2\text{-H})_2Os_3(CO)_{10}$ have also been obtained.

## Experimental Section

The clusters $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ were prepared from $Os_3(CO)_{12}$ (Strem Chemicals, Inc.) by published methods.[6] The clusters $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$ were made by reactions of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$, respectively, in 1,1-dichloroethane or decalin by bubbling $H_2$ through the solutions, and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ was also obtained by bubbling CO through pentane solutions of $(\mu_2\text{-H})_2Os_3(CO)_{10}$. In all cases the compounds were characterized by their well-known IR spectra.[6] Thus, for $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ in decalin $\nu_{CO}$ = 2136 (0.07), 2087 (0.52), 2064 (0.83), 2053 (1.00), 2027 (0.47), 2024 (0.47), 2016 (0.39), 1998 (0.39), and 1985 (0.25) cm$^{-1}$, and for $(\mu_2\text{-H})_2Os_3(CO)_{10}$ in decalin $\nu_{CO}$ = 2074 (0.77), 2061 (0.56), 2023 (1.00), 2008 (0.86), and 1986 (0.21) cm$^{-1}$. The numbers in parentheses following the wavenumbers are relative intensities of the bands as measured with a Nicolet 10DX FTIR spectrophotometer.

The gases $H_2$, CO, and $N_2$ and CO–$N_2$ mixtures of known composition were obtained from Canox Ltd., Matheson Canada Ltd., or Canlab. Acetonitrile (BDH) was stored over molecular sieves (Linde type 4A), and decalin (Aldrich) was dried over $MgSO_4$, distilled, and stored over molecular sieves.

Solutions of complex (ca. $4 \times 10^{-4}$ M) for kinetic studies were prepared by dissolving the complex in decalin in a Schlenk tube. This was sealed with a rubber septum cap and thermostated to ±0.2 °C by immersion in an oil bath (Lauda model NS-20) or water bath (Lauda Model RC 6). The solutions were purged with a stream of Argon and subsequently saturated with the appropriate gas. Samples were withdrawn periodically by syringe under a slight positive pressure of gas and transferred to capped phials, and the reactions were quenched by cooling the samples in an ice bath. IR spectra of the samples were recorded subsequently with Nicolet 10DX FTIR or Perkin Elmer 298 spectrophotometers. Concentrations of CO in decalin were interpolated or extrapolated (over a small

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**Table I.** Rate Constants for Reactions of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ or $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ To Form the Other or To Form Equilibrium Mixtures of the Two Clusters in Decalin ([complex] = ca. $4 \times 10^{-4}$ M)

| $T$, °C | $10^3$[CO], M ($10^4k_{obs}$, s$^{-1}$) |
|---|---|
| 25.0 | 5.87 (3.0, 3.3, 3.0, 2.9, 3.1), 2.34 (1.7), 0.29 (0.9), 0 (0.69, 0.70, 0.71) |
| 30.0 | 5.85 (5.4, 5.2, 5.3), 2.34 (3.0), 0 (1.5, 1.5) |
| 35.0 | 5.82 (9.0, 9.2, 8.9, 8.8, 9.0), 4.14 (7.3), 2.33 (5.3), 1.45 (4.5), 0.29 (3.4), 0 (3.1, 3.0, 3.2, 3.1) |
| 40.0 | 5.80 (15.0, 14.8, 15.2, 15.1, 15.0), 4.12 (12.4), 2.32 (9.5), 0.93 (7.5), 0.29 (6.4) |

temperature range) from solubilities measured[7] over the temperature range 20.0–70.0 °C,[8,9] and by application of Henry's law.

## Results

**Kinetics of Interconversion of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** Reactions of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ at 25.0–40.0 °C and under various partial pressures of CO led clearly to the formation of equilibrium mixtures of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$ according to eq 1. Reactions of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ at 25.0–40.0 °C and under Ar led to virtually complete formation of $(\mu_2\text{-H})_2Os_3(CO)_{10}$, but reactions under various small partial pressures of CO led to equilibrium mixtures of reactant and product. Values of $k_{obs}$ were determined by monitoring the decreasing absorbance of C–O stretching bands at 2023 cm$^{-1}$, when $(\mu_2\text{-H})_2Os_3(CO)_{10}$ was the initial cluster, or at 2087 cm$^{-1}$, when $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ was the initial cluster. Plots of $\ln(A_t - A_\infty)$ vs time were linear for at least 2 half-lives in both cases. The choice of starting cluster was made in such a way that maximum absorbance changes were observed. The values of $k_{obs}$ (Table I) depend on [CO] according to eq 2, irrespective of the direction of the reaction (Figure 1). The rate constants $k_1$ and $k_{-1}$ can be assigned to the addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and the reverse reaction, respectively, since $k_{obs}$ is generally the rate constant for approach to an equilibrium mixture. Linear least-squares analysis of the data was carried out with each value of $k_{obs}$ weighted according to a constant probable error, expressed as a percentage. Values of $k_1$ and $k_{-1}$ (and of $K_1 = k_1/k_{-1}$) are given in Table II, and the activation and thermodynamic parameters derived from them are shown in Table VI.

$$(\mu_2\text{-H})_2Os_3(CO)_{10} + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mu_2\text{-H})(H)Os_3(CO)_{11} \quad (1)$$

$$k_{obs} = k_{-1} + k_1[CO] \quad (2)$$

**Equilibrium Constants for Reaction 1 at Higher Temperatures.** Values of the equilibrium constants, $K_1$, were also obtained directly at 50.0–90.0 °C by using the expression $K_1 = C_{11}/C_{10}[CO]$, where $C_{11}$ and $C_{10}$ are equilibrium concentrations of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$, respectively. These concentrations were determined as follows.

**Table II.** Kinetic and Thermodynamic Parameters[a] for the Reactions $(\mu_2\text{-H})_2Os_3(CO)_{10} + CO \rightleftharpoons (\mu_2\text{-H})(H)Os_3(CO)_{11}$ in Decalin

| $T$, °C | $10^2k_1$, M$^{-1}$ s$^{-1}$ | $10^4k_{-1}$, s$^{-1}$ | $10^{-2}K_1$, M$^{-1}$ |
|---|---|---|---|
| 25.0 | 4.10(0.07) | 0.70(0.08) | 5.86(0.68) |
| 30.0 | 6.40(0.16) | 1.50(0.02) | 4.27(0.13) |
| 35.0 | 10.10(0.21) | 3.10(0.02) | 3.26(0.06) |
| 40.0 | 15.3(0.5) | 6.10(0.14) | 2.57(0.10) |

[a] Uncertainties, in parentheses, are estimates of the standard deviations based on $\sigma(k_{obs}) = \pm3.1\%$ obtained from the pooled variances of all the data.

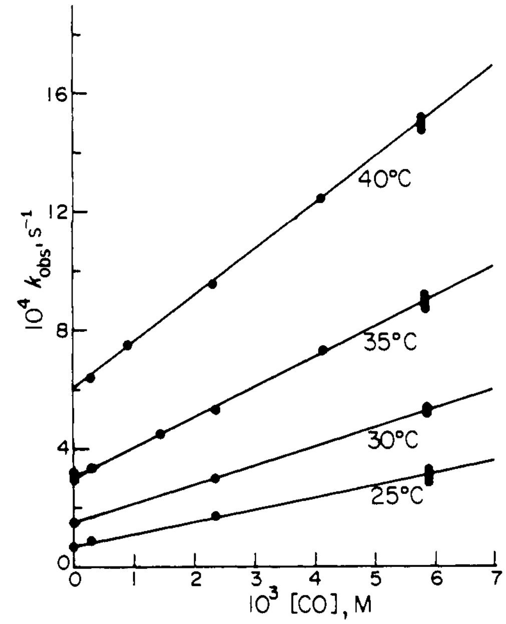

**Figure 1.** Dependence of $k_{obs}$ on [CO] for reactions of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ or $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ under CO to form the other cluster or equilibrium mixtures of the two clusters.

A known weight of the clusters $(\mu_2\text{-H})_2Os_3(CO)_{10}$, $Os_3(CO)_{12}$, or the freshly made $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ was dissolved in a known volume of decalin (CO saturated for the last cluster) and the FTIR spectrum of the solution was immediately measured. The effective molar absorbance coefficients, $\epsilon$, at the main absorption positions were obtained in units of M$^{-1}$ cm$^{-1}$ by dividing the absorbances by the concentration of the cluster and the path length of the cell (0.1 cm). The values, quoted in the text below, are averages of two quite independent measurements which agreed within ±1%. All spectra were recorded using the solvent subtraction routine and the observed absorbances were estimated by the two-point baseline calibration method.[10]

Solutions of known initial concentration, $C_o$, of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ were then prepared and transferred into test tubes through septum stoppers and the tubes were immersed in a thermostated bath. Once temperature equilibration was reached CO was bubbled through the solutions and a total pressure of 1 atm (CO plus solvent vapor) was maintained above the solutions. Sampling for FTIR monitoring commenced immediately after CO bubbling was started. When solutions were maintained at 50.0 and 60.0 °C samples were withdrawn by syringe, at regular intervals that were made as short as possible, and their FTIR spectra measured immediately. For solutions maintained at 70.0, 80.0, and 90.0 °C, samples were withdrawn repeatedly, at equal time intervals, and stored in capped phials in dry ice. The FTIR spectra of these samples were measured later together at one time.

The first two spectra of reactions at 50.0 and 60.0 °C showed the progressive formation of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and disap-

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(8) An important feature of these solubilities is that they vary with temperature only slightly and then mainly because of the varying partial pressures of the solvent rather than because of any significant heat of solvation. Thus, the solubilities under a partial pressure of 1 atm of CO are essentially independent of temperature (6.03(0.05) × $10^{-3}$ M) over the temperature range used.[7] Similar results were obtained by Angelici et al. for solubility of CO in 1,2-dichlorobutane.[9a] Grevels et al.[9b] took the solubility of CO in cyclohexane to be constant over the temperature range 22–42 °C, and Hoff et al.[9c] assert that heats of solvation of CO, $H_2$, $N_2$, and a number of liquid ligands are negligible compared to experimental errors in calorimetric measurements.

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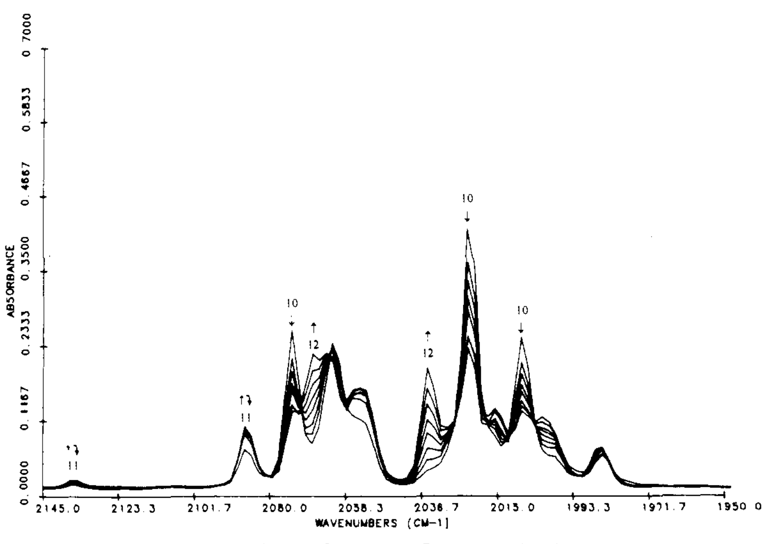


**Figure 2.** FTIR spectra recorded during studies of the $(\mu_2\text{-H})_2Os_3(CO)_{10} + CO \rightleftharpoons (\mu_2\text{-H})(H)Os_3(CO)_{11}$ equilibrium at 80.0 °C. The samples were withdrawn at constant time intervals of 0.5 min. Bands labeled 10, 11, and 12 correspond to $(\mu_2\text{-H})_2Os_3(CO)_{10}$, $(\mu_2\text{-H})(H)Os_3(CO)_{11}$, and $Os_3(CO)_{12}$, respectively. The arrows indicate the direction of the changes observed with increasing reaction time (see text).

**Table III.** Equilibrium Constants, $K_1$, for the Reaction $(\mu_2\text{-H})_2Os_3(CO)_{10} + CO \rightleftharpoons (\mu_2\text{-H})(H)Os_3(CO)_{11}$ in Decalin at Higher Temperatures

| $T$, °C | $10^5C_0$, M | $10^5C_{11}$, M | $10^5C_{12}$, M | $10^3[CO]$, M | $K_1$(exptl), $M^{-1}$ | $K_1$(extrap),[a] $M^{-1}$ |
|---|---|---|---|---|---|---|
| 50.0 | 63.3 | 32.9[b] | 0 | 5.74 | 190 | 152 ± 10 |
| 60.0 | 224 | 76.8[b] | 0 | 5.70 | 91.5 | 96 ± 10 |
| 70.0 | 26.7 | 7.85[c] | ca. 0 | 5.57 | 74.8 | 62 ± 9 |
| 80.0 | 26.7 | 5.01[c] | 0.76 | 5.50 | 43.5 | 41 ± 7 |
| 90.0 | 26.7 | 3.62[c] | 1.31 | 5.33 | 31.2 | 28 ± 6 |

[a] By extrapolation of $K_1$ values obtained from kinetic data at 25.0–40.0 °C. [b] From absorbance at 2136 $cm^{-1}$; $\epsilon = 1.30 \times 10^3$ $M^{-1}$ $cm^{-1}$. [c] From absorbance at 2087 $cm^{-1}$; $\epsilon = 1.70 \times 10^4$ $M^{-1}$ $cm^{-1}$.

pearance of $(\mu_2\text{-H})_2Os_3(CO)_{10}$. There was no evidence for the formation of $Os_3(CO)_{12}$, as indicated by the absence of any significant absorbance at 2035 $cm^{-1}$ where $Os_3(CO)_{12}$ has a strong ($\epsilon = 1.75 \times 10^4$ $M^{-1}$ $cm^{-1}$) and distinct absorption band.[6c] Subsequent spectra showed a slow growth of this absorbance as a developing shoulder on the side of the band at 2027 $cm^{-1}$ due to $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and a slow and much smaller concurrent decrease of absorptions due to $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$. Thus the second spectrum, which showed that a maximum amount of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ had been formed without any noticeable formation of $Os_3(CO)_{12}$, was used to calculate $C_{11}$, at both temperatures. This was done by using the $\epsilon$ value ($1.30 \times 10^3$ $M^{-1}$ $cm^{-1}$) of the band at 2136 $cm^{-1}$ due to $(\mu_2\text{-H})(H)Os_3(CO)_{11}$, which was quite strong and well-separated from any other bands. The value of $C_{10}$ was then obtained from $C_0 - C_{11}$.

The spectral changes recorded during the reactions at 70.0, 80.0, and 90.0 °C are exemplified by the set of eight spectra shown for reactions at 80.0 °C in Figure 2, where $C_0 = 2.67 \times 10^{-4}$ M. The main absorptions due to different complexes are simply labeled as 10 ($(\mu_2\text{-H})_2Os_3(CO)_{10}$), 11 ($(\mu_2\text{-H})(H)Os_3(CO)_{11}$), and 12 ($Os_3(CO)_{12}$). As indicated by the arrows in Figure 2 the intensities of the bands due to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ decrease and those due to $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ increase and then decrease throughout the reaction. Since the absorbances of the band at 2136 $cm^{-1}$ due to $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ were very weak at these temperatures, the absorbances of the band at 2087 $cm^{-1}$ ($\epsilon = 1.70 \times 10^4$ $M^{-1}$ $cm^{-1}$) due to $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ were used to monitor the change of the concentration of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$. These can be seen to increase rapidly and then decrease much more slowly. Thus the absorbance is already significant in the first spectrum measured which has the lowest intensity. The second spectrum measured is that giving the highest absorption at 2087 $cm^{-1}$, and subsequently the absorptions decrease slightly until the eighth and last spectrum measured, which shows the second-to-lowest absorbance. Clear isosbestic points were evident, especially for the second and subsequent spectra. This is shown most clearly by the spectra at $\gtrsim 2015$ $cm^{-1}$ where all but one, the first spectrum measured, pass through the same isosbestic point.

It is clear from the kinetics at lower temperatures that the equilibrium between $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ would have been fully established by the time that the second spectrum was measured and the subsequent decrease of absorbance at 2087 $cm^{-1}$ must be associated with the slow formation of $Os_3(CO)_{12}$ from the equilibrium mixture. The maximum absorbance at 2087 $cm^{-1}$ can therefore be used to give $C_{11} = 5.01 \times 10^{-5}$ M (at 80.0 °C) under these conditions. However, the absorbance at 2035 $cm^{-1}$ due to $Os_3(CO)_{12}$ has clearly become significant by the time the second spectrum was measured, but the small amount present, $C_{12}$, can be estimated to be $0.76 \times 10^{-5}$ M by using the measured value of $\epsilon$ at this wavenumber. Consequently $C_{10} = C_0 - C_{11} - C_{12}$ and the value of $K_1$ is therefore obtained as $5.01/\{26.7 - 5.01 - 0.76) \times 5.5 \times 10^{-3}\} = 43.5$ $M^{-1}$. The effect of the formation of $Os_3(CO)_{12}$ can be seen to be rather small, a 50% error in $C_{12}$ leading only to a 2% error in $K_1$. The values of $K_1$ at 70.0 and 90.0 °C were obtained in the same way. At 90.0 °C the correction for the $Os_3(CO)_{12}$ present was somewhat larger but at 70.0 °C it was negligible (Table III).

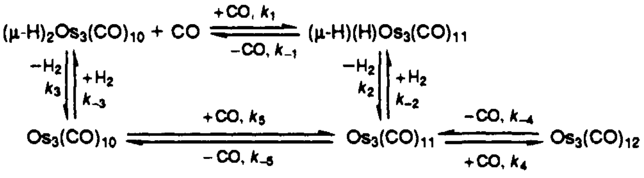
The values of $K_1$ so obtained at 50.0–90.0 °C are given in Table III together with those obtained by extrapolation of data at 25.0–40.0 °C. The extrapolated data are generally in good agreement with those measured directly, and the values of $\Delta H_1°$ and $\Delta S_1°$ obtained from the kinetics data at 25–40 °C alone and from the complete set of data from 25.0 to 90.0 °C are also in good agreement (Table VI). The more precise values obtained over the wider temperature range are taken as the best ones, the probable error in each measurement of $K_1$ being only ±9%.

**The Kinetics of Loss of $H_2$ from Equilibrium Mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** The kinetics of quantitative formation of $Os_3(CO)_{12}$ from equilibrium mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ under various partial

**Table IV.** Rate Constants for Reactions of CO with Equilibrium Mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ in Decalin To Form $Os_3(CO)_{12}$ ([complex] = ca. $4 \times 10^{-4}$ M)

| $T$, °C | $10^3$ [CO], M ($10^4 k_{obs}$, $s^{-1}$) |
|---|---|
| 65.0 | 0.90 (2.1), 1.41 (2.3), 2.26 (3.0), 4.00 (4.0), 5.64 (4.1) |
| 75.0 | 0.88 (3.5), 1.37 (4.5), 2.20 (6.7, 6.4), 3.90 (9.5, 9.0), 5.51 (11.1) |
| 85.0 | 0.86 (7.7), 1.35 (12.0), 2.16 (15.0), 3.79 (17.0), 5.39 (22.0) |
| 95.0 | 0.84 (13.0), 2.10 (25.0), 5.26 (51.0) |

**Scheme I**[a]



[a] The possible participation of solvent molecules in this scheme is ignored for simplicity.

pressures of CO were measured at 65.0–95.0 °C by monitoring the relatively strong band at 2023 $cm^{-1}$ due to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ which was the major constituent of the equilibrium mixtures under most conditions. The values of $k_{obs}$ showed a steady increase with [CO] but with a clear tendency to level off at higher [CO]. The analysis of these data (Table IV) will be described below.

## Discussion

**The Stoichiometric Mechanism for Interconversion of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** The data for the reactions shown in eq 1 are perfectly consistent with concerted addition or loss of CO in a simple single step with $k_1$ corresponding to the addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $k_{-1}$ corresponding to the loss of CO from $(\mu_2\text{-H})(H)Os_3(CO)_{11}$. However, the sequence of reactions shown in eq 3 is also consistent with the data, S being a solvent molecule. This scheme involves an initial,

$$(\mu_2\text{-H})_2Os_3(CO)_{10} \underset{-S}{\overset{+S}{\rightleftharpoons}} (\mu_2\text{-H})(H)Os_3(CO)_{10}S \underset{-CO,+S}{\overset{+CO,-S}{\rightleftharpoons}} (\mu_2\text{-H})(H)Os_3(CO)_{11} \quad (3)$$

highly reversible, bridged-to-terminal movement of one bridging hydride ligand that would almost certainly be accompanied by solvation of the vacant coordination site so created. The solvated species then undergoes replacement of S by CO in a second-order reaction. In this case the values of $k_{obs}$ for approach to equilibrium would be given by eq 4 or, if $K_{+CO}[CO] \ll k_{-S}$, by eq 5. This is of exactly the same form as eq 2 but with $k_1 = k_{+S}k_{+CO}/k_{-S}$ and $k_{-1} = k_{-CO}$. For both the forward and reverse reactions in

$$k_{obs} = k_{+S}(k_{+CO}/k_{-S})[CO]/\{1 + (k_{+CO}/k_{-S})[CO]\} + k_{-CO} \quad (4)$$

$$k_{obs} = (k_{+S}k_{+CO}/k_{-S})[CO] + k_{-CO} \quad (5)$$

eq 1 the transition state would include the $(\mu\text{-H})(H)Os_3(CO)_{10}$ moiety with S and CO molecules interchanging coordination sites at one Os atom.

Another alternative that is formally possible is shown by the reaction sequence in eq 6 in which CO addition to the doubly

$$(\mu_2\text{-H})_2Os_3(CO)_{10} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} (\mu_2\text{-H})_2Os_3(CO)_{11} \underset{k_{t\to br}}{\overset{k_{br\to t}}{\rightleftharpoons}} (\mu_2\text{-H})(H)Os_3(CO)_{11} \quad (6)$$

bridged cluster precedes the relatively slow bridged-to-terminal migration of one hydride ligand. In this case the values of $k_{obs}$ for approach to equilibrium are given by eq 7 so that $k_1$ in eq 2 corresponds to $k_{+CO}k_{br\to t}/(k_{-CO} + k_{br\to t})$ and $k_{-1}$ corresponds to $k_{t\to br}$.

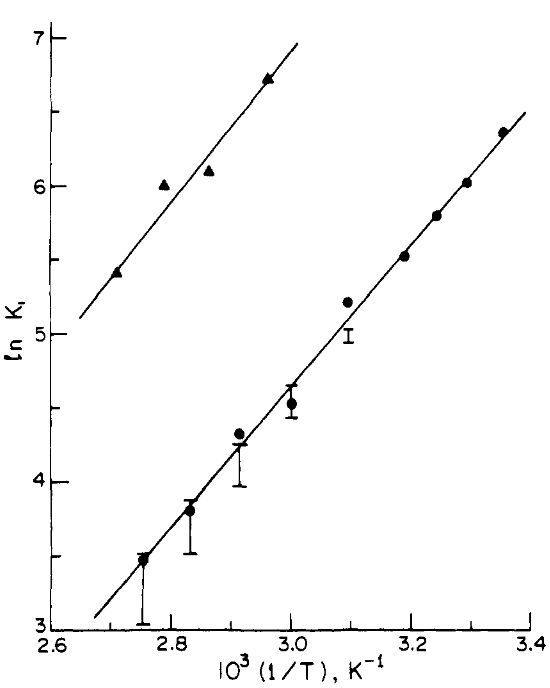


**Figure 3.** Temperature dependence of $K_1$. (●) Measured values (the four values at lower temperatures were obtained from the kinetics at 25–40 °C, and the values at higher temperatures were measured directly as described in the text). The values defined by error bars are extrapolated from values obtained at 25–40 °C. (▲) Values obtained by assuming that $k_3$ (in eq 8) = 0.

$$k_{obs} = \{k_{+CO}k_{br\to t}[CO]/(k_{-CO} + k_{br\to t})\} + k_{t\to br} \quad (7)$$

**The Stoichiometric Mechanism for Loss of $H_2$ from Equilibrium Mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** The values of $k_{obs}$ for reactions of equilibrium mixtures of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$ with CO at 65.0–95.0 °C (Table IV) vary with [CO] according to the rate equation shown in eq 8, where $k_2$ and $k_3$ can be assigned as shown in

$$k_{obs} = (k_2K_1[CO] + k_3)/(1 + K_1[CO]) \quad (8)$$

Scheme I. The values of $k_{-2}[H_2]$ and $k_{-3}[H_2]$ are negligible under the conditions of these reactions where $[CO] \gg [H_2]$, and $k_{-4}$ is also negligible.[4] The data can, in fact, be made to fit eq 8 with $k_3 = 0$ but the values of $K_1$ that are provided by this analysis are totally incompatible (Figure 3) with those found by direct study of the equilibrium or by extrapolation to higher temperatures of the values of $K_1$ found at 25.0–40.0 °C. The erroneous equilibrium constants are ca. 10 times higher than the directly measured extrapolated ones. The rate constant data for formation of $Os_3(CO)_{12}$ could not be studied over a sufficient range of [CO] and are not sufficiently numerous for the values of $k_2$, $k_3$, and $K_1$ all to be obtained independently but, since values of $K_1$ are known quite precisely, it is possible to derive the values of $k_2$ and $k_3$ from the data. Values of $K_1$ were calculated from the best values of $\Delta H_1°$ and $\Delta S_1°$ and plots of $k_{obs}(1 + K_1[CO])$ vs [CO] are shown in Figure 4 to be linear as expected from eq 8. Values of $k_3$ and $k_2K_1$ were obtained by a weighted least-squares analysis and were used to draw the continuous lines in Figure 4. These values are affected only slightly by any uncertainties in the $K_1$ values used. The temperature dependencies of the parameters $k_3$ and $k_2K_1$ were analyzed by a least-squares analysis, each value of ln $k_3/T$ or ln $k_2K_1/T$ being weighted according to their individual variances obtained from the standard deviations given in Table V. The activation parameters are given in Table VI. The values of $\Delta H_3^\ddagger$ and $\Delta S_3^\ddagger$ are not very precise because of the

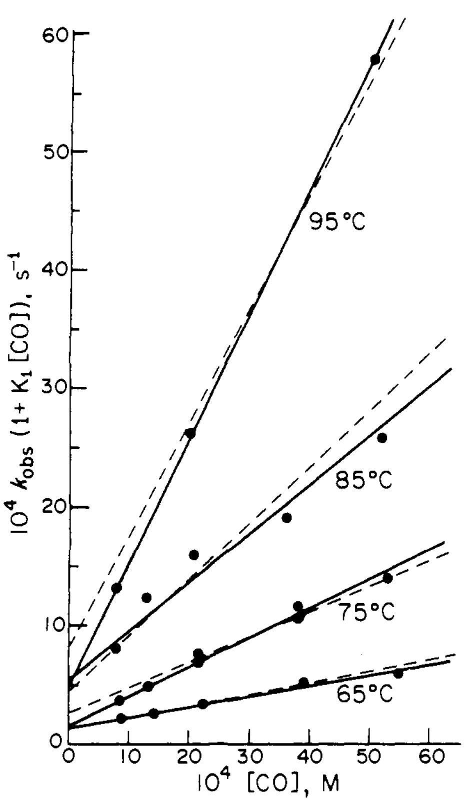


**Figure 4.** Dependence of $k = k_{obs}(1 + K_1[CO])$ on [CO] for the reactions of CO with equilibrium mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ to form $Os_3(CO)_{12}$. The continuous lines drawn are the least-squares lines obtained from each set of data separately (Table V) and the dashed lines are based on rate constants calculated from the derived activation parameters.

**Table V.** Kinetic Parameters[a] for Formation of $Os_3(CO)_{12}$ from Equilibrium Mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ in Decalin

| $T$, °C | $K_1$,[b] $M^{-1}$ | $10^3[CO]$, M | $10^4 k_3$, $s^{-1}$ | $10^2 k_2 K_1$, $M^{-1}\ s^{-1}$ | $\sigma(k)$,[c] % |
|---|---|---|---|---|---|
| 65.0 | 85.4(1.5) | 5.64 | 1.47(0.16) | 8.73(0.74) | 5.0 |
| 75.0 | 57.0(1.7) | 5.51 | 1.61(0.20) | 24.9(1.0) | 3.8 |
| 85.0 | 38.9(1.6) | 5.39 | 5.41(1.30) | 41.3(6.7) | 15.5 |
| 95.0 | 27.1(1.4) | 5.26 | 4.83(0.25) | 104.7(1.7) | 1.0 |

[a] Estimated standard deviations are given in parentheses. [b] Values of $K_1$ are estimated from the values of $\Delta H_1°$ and $\Delta S_1°$ obtained from the data at 25.0–90.0 °C (Table VI). [c] $k = k_{obs}(1 + K_1[CO])$ and $\sigma(k)$ values are the probable errors in $k$ estimated from the least-squares analysis.

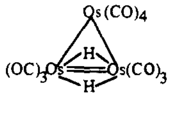
rather uncertain values of the intercepts of the plots in Figure 4. They will nevertheless be quite adequate for useful discussion of the intimate mechanisms (see below). The dashed lines in Figure 4 are drawn according to the calculated rate constants, $k_2$ and $k_3$, based on the activation parameters and show that there are some small but significant errors in the data which lead to erroneously low intercepts at 75.0 and 95.0 °C, a high intercept at 85.0 °C, but no significant error at 65.0 °C. These errors clearly do not vary systematically with temperature, and the calculated rate constants lead to a probable error for each of the 20 values of $k_{obs}$ (Table IV) measured over the range 65.0–95.0 °C that is only 11% (with maximum errors of 18%) which is quite a searching test of the overall analysis. The point to be emphasized strongly is that there are significant and reasonably precise values of the intercepts (Figure 4 and Table V).

**The Thermodynamics of Interconversion of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** The thermodynamics data for the addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ provide a basis for discussion of the possible intimate mechanisms of this reversible reaction. We prefer to discuss the results in terms of the simple structure **I**[1] for $(\mu_2\text{-H})_2Os_3(CO)_{10}$. This accounts for the very short doubly hydride bridged Os—Os bond[11] and is based on an electron precise $Os_3(CO)_{10}^{2-}$ moiety that contains one Os═Os double bond to which each of two $H^+$ ions can become symmetrically bonded.[12] The product, **II**, of CO addition to **I** is considered[1] to be based on an $(H)Os_3(CO)_{11}^-$ moiety that contains three single Os–Os bonds and a terminal $H^-$ ligand and that can be protonated to form an essentially symmetrical hydride bridge. These formulations provide simple pictorial rationalizations of the very short[11] doubly bridged Os–Os bond in $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and the much longer[13] singly bridged Os–Os bond in $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.

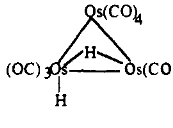
**Table VI.** Activation and Thermodynamic Parameters for the $(\mu_2\text{-H})_2Os_3(CO)_{10}$–CO System[a] in Decalin (See Scheme I for Numbering)

| | |
|---|---|
| $\Delta H_1^{\ddagger}$ [b] = 15.74(0.38) | $\Delta S_1^{\ddagger}$ = −12.1(1.3) |
| $\Delta H_{-1}^{\ddagger}$ [b] = 25.9(0.4) | $\Delta S_{-1}$ = +9.3(1.4) |
| $\Delta H_1°$ [b,c] = −10.1(0.8) | $\Delta S_1°$ = −21.2(2.7) |
| $\Delta H_1°$ [d] = −9.5(0.3) | $\Delta S_1°$ = −19.2(0.9) |
| $\Delta H_2^{\ddagger} + \Delta H_1°$ [b,e] = 18.2(2.3) | $\Delta S_2^{\ddagger} + \Delta S_1°$ = −9.7(6.4) |
| $\Delta H_2^{\ddagger}$ [f] = 27.7(2.3) | $\Delta S_2^{\ddagger}$ = +9.5(6.5) |
| $\Delta H_2^{\ddagger}$ [g] = 29.7(1.4) | $\Delta S_2^{\ddagger}$ = +35(5) |
| $\Delta H_3^{\ddagger}$ [b] = 14.2(4.5) | $\Delta S_3^{\ddagger}$ = −35(13) |
| $\Delta H_{-4}^{\ddagger}$ [h] = 32.9(0.3) | $\Delta S_{-4}^{\ddagger}$ = 7.6(0.9) |
| $\Delta H_{-4}^{\ddagger}$ [i] = 31.8(0.2) | $\Delta S_{-4}^{\ddagger}$ = +20.2(0.6) |
| $\Delta H_4^{\ddagger} - \Delta H_{-2}^{\ddagger}$ [j] = −3.8(0.2) | $\Delta S_4^{\ddagger} - \Delta S_{-2}^{\ddagger}$ = −9.7(0.8) |

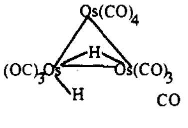
[a] Enthalpy values are in kcal $mol^{-1}$ and entropies are in cal $K^{-1}\ mol^{-1}$. Estimated standard deviations are given in parentheses. [b] Parameters were obtained from a linear least-squares analysis of ln $k/T$ or ln $K$ vs $1/T$, each value of ln $k/T$ or ln $K$ being weighted according to its individual uncertainty. [c] From $K_1$ values at 25–40 °C. [d] From unweighted analysis of ln $K$ vs $1/T$ at 25–90 °C. $\Delta G_1°$ (300K) = −3.7 kcal $mol^{-1}$. [e] From temperature dependence of $K_1k_2$. [f] From $(\Delta H_2^{\ddagger} + \Delta H_1°) - \Delta H_1°$ etc. [g] Parameters for loss of $H_2$ from $(\mu_2\text{-H})(H)Ru_3(CO)_{11}$ from ref 3b. [h] From ref 4. [i] Parameters for loss of CO from $Ru_3(CO)_{12}$ (Poë, A. J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860–1866). [j] From ref 5.



**I**



**II**



**III**

The value of $\Delta H_1°$ is −9.5 kcal $mol^{-1}$ and this means that the enthalpy required to convert the $(\mu_2\text{-H})_2Os_3(CO)_{10}$ to the $(\mu_2\text{-H})(H)Os_3(CO)_{10}$ moiety in the $(\mu_2\text{-H})(H)Os_3(CO)_{10}(CO)$ product must be ca. 10 kcal $mol^{-1}$ less than the strength of the additional Os–CO bond in the product. The strength of this bond is likely to be somewhat greater than that (45 kcal $mol^{-1}$)[14] estimated for the average Os–CO bond in $Os_3(CO)_{12}$ because the Os–CO bonds in $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ are generally a little shorter than those in $Os_3(CO)_{12}$.[13] Thus the energy required to rearrange the $(\mu_2\text{-H})_2Os_3(CO)_{10}$ is likely to be a little greater than 45 − 10 = 35 kcal $mol^{-1}$. This corresponds to the energy involved in lengthening the bridged Os–Os bond from 2.683 to 2.989 Å,[13,15] in converting one bridged hydride to a terminal one, and in bringing about any other changes to the $H_2Os_3(CO)_{10}$ moiety. This value will be important in considering the possible intimate mechanisms of the reactions in eq 1.

The value $\Delta S_1°$ = ca. −20 cal $K^{-1}\ mol^{-1}$ is much less negative than the −41.1 cal $K^{-1}\ mol^{-1}$ expected simply from the loss of translational and rotational entropy of the CO molecule.[16] This must be due to the greater intrinsic entropy of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ compared with $(\mu_2\text{-H})_2Os_3(CO)_{10}$. This results mainly from the looser bonding in the former due to the greater length and weaker strength of the singly bridged Os–Os bond and the presence of the more weakly bonded terminal Os–H bond which

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(11) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314–319.
(12) Churchill, M. R.; de Boer, B. G.; Rottella, F. J. *Inorg. Chem.* **1976**, *15*, 1843–1853.
(13) Churchill, M. R.; de Boer, B. G. *Inorg. Chem.* **1977**, *16*, 878–884.
(14) Connor, J. *Top. Curr. Chem.* **1977**, *71*, 71–110.
(15) The total of the three Os–Os bond lengths increases by 0.444 Å.[11,13]

replaces the more strongly bonded[3b] bridging hydride ligand. These changes evidently contribute ca. +20 cal $K^{-1}$ $mol^{-1}$ to the overall value of $\Delta S_1°$. A similar entropy increase is associated with the transformation of $CoRh(CO)_7$ to $CoRh(CO)_8$.[17]

**The Intimate Mechanisms of Interconversion of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** If these reactions involve a simple concerted addition or loss of a CO ligand then the transition state will have a structure resembling **III**. The value of 16 kcal $mol^{-1}$ for $\Delta H_1^{\ddagger}$ will be a measure of the difference between the heat required for partial rearrangement of the $(\mu_2\text{-H})_2Os_3(CO)_{10}$ moiety and that released by partial formation of the new Os–CO bond. The former will be some fraction, $x$, of the $\gtrsim$35 kcal $mol^{-1}$ required for complete rearrangement (see above) and the latter will be some fraction, $y$, of the $\gtrsim$45 kcal $mol^{-1}$ released by complete formation of the new Os–CO bond, i.e. $(\gtrsim 35x) - (\gtrsim 45y) = 16$. It must be remembered that the extent to which the total rearrangement energy exceeds 35 kcal $mol^{-1}$ is exactly the same as the extent to which the total strength of the new Os–CO bond exceeds 45 kcal $mol^{-1}$, and it is immediately obvious that $x$ must be considerably greater than $y$. At one extreme, if $x = 1$ then $y$ = ca. 0.4, but it would also theoretically be possible for $y$ to be zero and $x$ to be $\lesssim 0.5$. It seems more likely that some intermediate situation exists, e.g. $x$ = ca. 0.7 and $y$ = ca. 0.2, these estimates not being very sensitive to the extent to which the strength of the fully formed new Os–CO bond differs from 45 kcal $mol^{-1}$.

The values of $\Delta S_1^{\ddagger}$ and $\Delta S_1°$ also provide some insight into the changes in the cluster that would occur during concerted reactions. As in any transition state involving the loss of free CO by its incorporation into a transition state the loss of translational and rotational entropy of the CO will contribute ca. −40 cal $K^{-1}$ $mol^{-1}$ to $\Delta S_1^{\ddagger}$, irrespective of the extent of Os–CO bond formation.[16] The observed value $\Delta S_1^{\ddagger} = -12$ cal $K^{-1}$ $mol^{-1}$ shows that the transition state cluster has ca. +28 cal $K^{-1}$ $mol^{-1}$ more entropy than $(\mu_2\text{-H})_2Os_3(CO)_{10}$, but only +9 cal $K^{-1}$ $mol^{-1}$ more entropy than the product cluster $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ with its fully formed extra Os–CO bond ($\Delta S_{-1}^{\ddagger} = +9$ cal $K^{-1}$ $mol^{-1}$). As far as the clusters are concerned, therefore, the transition state is entropically much closer to the product than to the reactant cluster. This indicates, as did the enthalpy changes, that the $H_2Os_3(CO)_{10}$ moiety has undergone a major loosening on going from $(\mu_2\text{-H})_2Os_3(CO)_{10}$ to the transition state.

The total rearrangement enthalpy of $\gtrsim$35 kcal $mol^{-1}$ for converting the $H_2Os_3(CO)_{10}$ moiety in $(\mu_2\text{-H})_2Os_3(CO)_{10}$ to the corresponding one in $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ is important in considering whether solvation can be an intermediate step in the overall addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ as in the sequence of reactions shown in eq 3. If the extent of rearrangement required to form the $(\mu_2\text{-H})(H)Os_3(CO)_{10}S$ intermediate is the same as that for formation of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$, and if the Os–S (S = decalin) bond strength can be considered to be close to that in $(OC)_5W(C_6H_{12})$, i.e. ca. 12 kcal $mol^{-1}$,[18] then $\Delta H°$ for formation of $(\mu_2\text{-H})(H)Os_3(CO)_{10}S$ will be $\gtrsim 35 - 12 = \gtrsim 23$ kcal $mol^{-1}$. This would seem to provide convincing evidence against the scheme in eq 3 since the enthalpy required to form the solvated intermediate is significantly greater, by $\gtrsim$7 kcal $mol^{-1}$, than the observed value of $\Delta H_1^{\ddagger}$. The assumptions made in arriving at this estimate do not seem unreasonable and would have to be quantitatively in considerable error for the scheme in eq 3 to be at all possible.

**Table VII.** Activation Parameters for Bimolecular Reactions of CO with Some Metal Carbonyl Clusters

| cluster | $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | $\Delta S^{\ddagger}$, cal $K^{-1}$ $mol^{-1}$ |
|---|---|---|
| $(\mu_2\text{-H})_2Os_3(CO)_{10}$[a] | 15.74(0.38) | −12.1(1.3) |
| $Ru_3(CO)_{10}(\mu\text{-CO})(\mu\text{-H})^-$ [b] | 14.1(0.5) | −8.00(1.73) |
| $Os_3(CO)_{10}(\mu\text{-CO})(\mu\text{-H})^-$ [b] | 20(3) | −10(3) |
| *cis*-$Rh_2Fe_4(CO)_{16}B^-$ [c] | 17 | −7 |
| $Co_2Rh_2(CO)_{12}$[d] | 12.7(1.6) | −15.4(5.6) |
| $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$[e] | 8.3(1.4) | −35(4) |

[a] This work. [b] For $^{12}CO/^{13}CO$ exchange of the $PPh_4^+$ salts in THF (Payne, M. W.; Leussing, D. L.; Shore, S. G. *Organometallics* **1991**, *10*, 574–580). [c] For CO induced isomerization of the $Na^+$ salt to *trans*-$Rh_2Fe_4(CO)_{16}B^-$ in THF (Bandyopadhyay, A. K.; Khattar, R.; Fehlner, T. P. *Inorg. Chem.* **1989**, *28*, 4434–4436). [d] For eventual fragmentation to form $CoRh(CO)_7$ in *n*-hexane (Garland, M.; Pino, P. *Organometallics* **1991**, *10*, 2643–2647). [e] For fragmentation in decalin to form $Os(CO)_5$ and, initially, $Os_2(CO)_5(\mu\text{-}C_4Ph_4)$.[6c]

Finally, the reaction sequence in eq 6 can also be considered unlikely since it seems unreasonable for $(\mu_2\text{-H})_2Os_3(CO)_{10}$ (which is an electron precise cluster if the Os=Os double bond is allowed for) to add a ligand completely without there being any adjustment at all of the bonding within the $(\mu_2\text{-H})_2Os_3(CO)_{10}$ moiety.[19] It does, on the other hand, seem perfectly reasonable for the $(\mu_2\text{-H})_2Os_3(CO)_{10}$ molecule to rearrange toward the form it would be taking up in the final product anyway, as the Os···CO bond-making process occurs. We therefore believe that the reaction is best described by a simple concerted CO addition and $(\mu_2\text{-H})_2Os_3(CO)_{10}$ rearrangement, with a transition state approximately as indicated by **III**. The relative amount of bond making and rearrangement in the transition state is not well-defined although the extent of rearrangement has to be *greater* than the extent of Os–CO bond making when the "extent" is defined in energetic terms as was described above.

Kinetic data for second-order reactions of CO with metal carbonyl clusters are relatively rare but some examples are given in Table VII. In general the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ do not vary much considering the wide variety of solvent, reaction types, and metal in the clusters that are involved. Generally these reactions are believed to involve an opening up of the clusters and the consequent weakening of the cluster bonding in the transition state, and this leads to relatively small negative values of $\Delta S^{\ddagger}$. However, the data for the reaction of $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ are distinctive, and this reaction appears to involve the concerted removal of the $Os(CO)_4$ moiety from the cluster as $Os(CO)_5$ and the generation of the intermediate $Os_2(CO)_5(\mu\text{-}C_4Ph_4)$ which then reacts rapidly to form $Os_2(CO)_6(\mu\text{-}C_4Ph_4)$.[6c] The very negative value of $\Delta S^{\ddagger}$ and the exceptionally low value of $\Delta H^{\ddagger}$ could both be ascribed to the concerted tightening up of the $Os_2(CO)_5(\mu\text{-}C_4Ph_4)$ moiety that can occur due to *development* of an Os=Os double bond (or formation of a 4-electron donor bridging carbonyl as is found in $Mn_2(CO)_8(\mu\text{-CO})$ etc.)[20] that is required to maintain electronic saturation of the bonding in this moiety.

**The Intimate Mechanisms for Elimination of $H_2$ from Equilibrium Mixtures of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.** The observation of a process involving first-order reaction of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ to form $Os_3(CO)_{12}$ in the presence of CO was an unexpected but unambiguous result of these studies. Although the activation parameters are rather uncertain they do show that the reaction has a low activation enthalpy and very

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[16] (a) The standard entropy of CO in the gas phase at 1 atm of pressure is 47.3 cal $K^{-1}$ $mol^{-1}$ [16b] and this can be converted to 41.1 cal $K^{-1}$ $mol^{-1}$ for a standard state of 1 M. These gas-phase data are likely to be applicable also to decalin solutions in view of the negligible heat of solution of CO in decalin.[8] The value of 41.1 cal $K^{-1}$ $mol^{-1}$ is consistent with the general values derived by Page[16c] for more or less any bimolecular reaction. (b) *National Bureau of Standards Tables of Chemical Thermodynamic Properties*, National Bureau of Standards: Washington, DC; 1982. (c) Page, M. I. *Angew. Chem., Intl. Ed.* **1977**, *16*, 449–459.

[17] Garland, M.; Horváth, I. T.; Bor, G.; Pino, P. *Organometallics* **1991**, *10*, 559–567.

[18] Brown, C. E.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 2530–2536.

[19] These conclusions do not seem likely to be affected appreciably by the fact that the species $(\mu_2\text{-H})_2Os_3(CO)_{11}$ is analogous to the $(\mu_2\text{-H})_2Os_3(CO)_{10}(PPh_3)$ proposed to occur during the fluxional interchange of the hydrides in $(\mu_2\text{-H})(H)Os_3(CO)_{10}(PPh_3)$ (Keister, J. B.; Frey, U.; Zbinden, D.; Merbach, A. E. *Organometallics* **1991**, *10*, 1497–1501).

[20] Dunkin, I. R.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248–7249. Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785–786.

negative activation entropy for a first-order process. Such processes can be accepted as dissociative in nature provided the residual moiety, left behind after the dissociation, can reasonably be conceived to have a low intrinsic entropy and correspondingly low enthalpy.[21] This could be envisaged here if the $Os_3(CO)_{10}$ moiety remaining after the dissociation contains an Os≡Os triple bond between the two Os atoms with three CO ligands attached, the strength of bonding within the cluster being enhanced in this way and the transition state being "tighter", and therefore of low entropy, as a result. Alternatively a similar outcome could be obtained if there were two strongly bridging CO ligands in the $Os_3(CO)_{10}$, each of which is a 4-electron donor,[20] or if there were strong solvent participation in the transition state with each apparently unsaturated $Os(CO)_3$ unit bonding to an entering solvent molecule. Two bridging CO ligands could decrease the entropy by as much as 40 cal $K^{-1}$ $mol^{-1}$,[17] and concerted entry of two solvent molecules to maintain the 18-electron count for these two Os atoms cannot be ruled out in view of the immediate availability of the necessary solvent molecules in the vicinity of the departing $H_2$ molecule.

Other first-order mechanisms can be envisaged. Initial fragmentation into $Os(CO)_4$ and $(\mu_2\text{-H})_2Os_2(CO)_6$ (where the latter would require solvation, CO bridging, or the presence of an Os≡Os triple bond in order to maintain the 18-electron count for each Os atom) would probably lead to $Os(CO)_5$ and the very stable $(H)_2Os_2(CO)_8$[22] in the presence of CO, and these were not observed. $F_N1$ fragmentations of metal clusters are rather rare[3a] and unlikely for an $Os_3$ cluster with its strong Os–Os bonds. Initial rate-determining CO dissociation, followed by a series of reactions, including $H_2$ loss and subsequent CO uptake, also seems unlikely in the presence of CO. We therefore believe that rate-determining dissociative loss of $H_2$ from the $(\mu_2\text{-H})_2Os_3(CO)_{10}$ is the most likely mechanism.

The first-order loss of $H_2$ from $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ can reasonably be considered to involve a sequence of reactions as shown in eqs 9–12. The conversion of one bridged to one terminal hydride, as in reaction 9, would probably require $\Delta H^{\ddagger}$ = ca. 11 kcal $mol^{-1}$,[3b] leaving ca. 17 kcal $mol^{-1}$ for loss of the two hydrides as $H_2$ from $(H)_2Os_3(CO)_{11}$. The $\Delta H^{\ddagger}$ value of ca. 17 kcal $mol^{-1}$ is very low compared with that for loss of $H_2$ from $(H)_2Os(CO)_4$ for which $k(126\,°C) < 6 \times 10^{-5}\ s^{-1}$ and $\Delta H^{\ddagger} > 34$ kcal $mol^{-1}$, CO dissociation being preferred to $H_2$ elimination.[22] It is indeed rather close to the enthalpy difference of ca. 15 kcal $mol^{-1}$ between $(Cy_3P)_2(OC)_3W(H)_2$ and $(Cy_3P)_2(OC)_3W\cdots(H_2)$ (Cy = $C_6H_{11}$), the latter being the transition state for loss of molecular hydrogen from $(Cy_3P)_2(OC)_3W(\eta^2\text{-}H_2)$, a reaction that is probably assisted by agostic bond formation involving a hydrogen atom from one Cy group.[23] The loss of $H_2$ from $(H)_2Os_3(CO)_{11}$ could also be assisted to some extent, either by incipient solvation in a developing $Os_3(CO)_{11}S$ molecule or by partial formation of a bridging CO ligand, acting as a 4-electron donor, if the latter is the way that $Os_3(CO)_{11}$ relieves itself of its coordinative unsaturation. An indication that the $Os_3(CO)_{11}$ moiety is stabilized in some such a way is provided by the rather low positive value of $\Delta S^{\ddagger}$ for dissociative loss of CO from $Os_3(CO)_{12}$ ($\Delta S_4^{\ddagger}$ in Table VI). However, it can reasonably be maintained that the stabilization of the transition state for loss of $H_2$ from $(H)_2Os_3(CO)_{11}$ will be smaller than that for loss of CO from $Os_3(CO)_{12}$. This is because the space occupied by the departing $H_2$ molecule in a 3-center transition state,[3b] or in an $Os\cdots(H_2)$ transition state in which the $H_2$ molecule is still partially $\eta^2$-bonded to the Os atom, will be greater than that occupied by the departing, end-on bonded, CO molecule as it leaves $Os_3(CO)_{12}$. There will therefore be less room for approach of a solvent molecule or a bridging CO ligand toward the coordination site that is being vacated by the $H_2$ molecule. The fact that the value of $\Delta H^{\ddagger}$ for attack of $H_2$ on $Os_3(CO)_{11}$ (which is probably in the form $Os_3(CO)_{11}S$ (S = 1,2-dichloroethane)[5] or $Os_3(CO)_{10}(\mu\text{-CO})$) is 3.8 kcal $mol^{-1}$ greater than that for attack by CO (Table VI) may be, at least in part, a reflection of this feature.

$$(\mu\text{-H})(H)Os_3(CO)_{11} \rightleftharpoons (H)_2Os_3(CO)_{11} \qquad (9)$$

$$(H)_2Os_3(CO)_{11} \rightleftharpoons (H_2)Os_3(CO)_{11} \qquad (10)$$

$$(H_2)Os_3(CO)_{11} \rightleftharpoons H_2 + Os_3(CO)_{11} \qquad (11)$$

$$Os_3(CO)_{11} + CO \rightleftharpoons Os_3(CO)_{12} \qquad (12)$$

The difference between the values of $\Delta G^{\ddagger}$ for loss of $H_2$ from $(\mu\text{-H})(H)M_3(CO)_{11}$ (M = Ru and Os) was discussed in Keister, Maher, et al. in terms of different ground state stabilizations but with the two three-centered transition states having similar energies.[3b] Now that better values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are available[24] for comparison (Table VI) it can be seen that the much greater inertness of the Os cluster is a result of entropic effects, the enthalpy of activation being, if anything, slightly more favorable. A similar effect can be seen in the relative ease of loss of CO from $M_3(CO)_{12}$ (M = Ru vs Os); the values of $\Delta H^{\ddagger}$ are comparable, and the much greater lability of the Ru cluster is mainly due to a more favorable value of $\Delta S^{\ddagger}$ (Table VI). These effects are consistent with greater solvation or CO-bridging effects when M = Os, and/or with a much tighter $Os\cdots(\eta^2\text{-}H_2)$ transition state, as compared with less solvation etc. and a much looser 3-centered transition state for loss of $H_2$ from the $Ru_3$ cluster.

Again, other mechanisms for the overall, first-order loss of $H_2$ might be envisaged but rate-determining loss of $H_2$ seems to be the most likely one. $Os_3(CO)_{11}(NCMe)$ reacts by what appears to be a first-order dissociation of NCMe to form an $Os_3(CO)_{11}$ moiety which reacts with $H_2$,[5] and $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ can also be formed from $Os_3(CO)_{12}$ by what is almost certainly a CO dissociative process.[4] Microreversibility would therefore require $H_2$ loss from $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ to involve a rate-determining $H_2$ dissociative process.

**The Thermodynamics of Formation of $Os_3(CO)_{12}$ from $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and the Os–H Bond Energies.** The kinetic data can now be combined with some relevant published data to construct a full enthalpy profile for the conversion of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ to $Os_3(CO)_{12}$ as shown in Figure 5. The key additional values needed are $\Delta H_{-2}^{\ddagger} - \Delta H_4^{\ddagger} = 3.8 \pm 0.2$ kcal $mol^{-1}$ for attack of $H_2$ and CO on $Os_3(CO)_{11}$[5] and $\Delta H_{-4}^{\ddagger} = 32.9 \pm 0.3$ kcal $mol^{-1}$ for dissociative loss of CO from $Os_3(CO)_{12}$[4] (see Scheme I). The profile is not dependent on the intimate mechanism of the loss of $H_2$ from $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and it is therefore possible to calculate the enthalpy change for reaction of this cluster to form $Os_3(CO)_{12}$, viz. $\Delta H° = (27.7 \pm 2.3) - (3.8 \pm 0.2) - (32.9 \pm 0.3) = -9.0 \pm 2.3$ kcal $mol^{-1}$. The entropy change can be obtained in a similar way ($\Delta S° = -7.8 \pm 6.6$ cal $K^{-1}$ $mol^{-1}$) and $\Delta G°(300K) = -6.7 \pm 0.3$ kcal $mol^{-1}$.

Since we also know the enthalpy of addition of CO to $(\mu_2\text{-H})_2Os_3(CO)_{10}$ and the heats of formation of $Os_3(CO)_{12}$ (637 kcal $mol^{-1}$)[14] and CO (−26.4 kcal $mol^{-1}$)[16b] we can estimate the heats of formation of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ and $(\mu_2\text{-H})_2Os_3(CO)_{10}$ to be 672 and 709 kcal $mol^{-1}$, respectively.

Another feature of importance that can be obtained from the data is an estimate of the average Os–H bond energies in $(H)_2Os_3(CO)_{11}$. Essentially what is needed for this is the difference between the enthalpy changes accompanying the

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[23] Zhang, K.; Gonzalez, A. A.; Hoff, C. D. *J. Am. Chem. Soc.* **1989**, *111*, 3627–3632.

[24] The values available to Keister et al. were estimates made before it was realized that $k_1$ was an important term in eq 8 and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were both erroneously low.

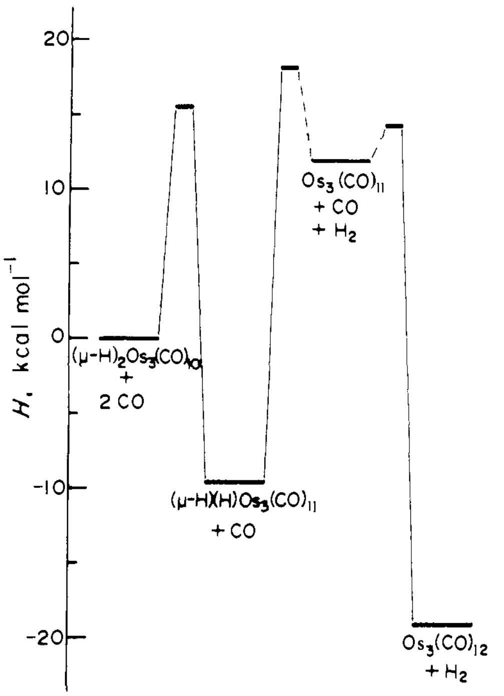

**Figure 5.** Enthalpy profile for the reaction of $(\mu_2\text{-H})_2Os_3(CO)_{10}$ with CO to form $Os_3(CO)_{12}$. The $Os_3(CO)_{11}$ intermediate is probably stabilized by solvation or by formation of CO bridges.

processes shown in eqs 13 and 14, i.e. the enthalpy for the reaction shown in eq 15, *where the* $[Os_3(CO)_{11}]$ *moieties are all identical geometrically and energetically.*[25] This means that the $[Os_3(CO)_{11}]$ moiety, whether in the $(H_2)\cdots[Os_3(CO)_{11}]$ transition state or as formed when the $H_2$ has completely left, is not stabilized by the solvation or CO bridging (and any other bonding changes) that occur in formation of the real transition state but maintains the configuration characteristic of that in the complex $(H)_2Os_3(CO)_{11}$. This ensures that the $\Delta H$ for reaction 16 does indeed correspond to the sum of the strengths of the Os–H bonds in $(H)_2Os_3(CO)_{11}$ provided general solvation of the species is ignored as seems reasonable in the case of these neutral carbonyls in a nonpolar solvent such as decalin. The value of $\Delta H$ for reaction 14 can only be guessed at. However, it can be guessed at quite precisely since $[Os_3(CO)_{11}]$ has by definition a nonsolvated open coordination site, not blocked by CO bridging, and so the value is not likely to be appreciably more than ca. 2 kcal mol$^{-1}$. The value of $\Delta H$ for reaction 15 can therefore be estimated as 27.7 ± 2.3 kcal mol$^{-1}$ ($\Delta H_2^{*}$ in Table VI), *less* the enthalpy required to convert the bridging hydride in $(\mu_2\text{-H})(H)Os_3(CO)_{11}$ to the terminal form (ca. 11 kcal mol$^{-1}$),[3b] *plus* any stabilization enthalpy due to solvation or CO bridging etc. that occurs in the real transition states $(H_2)\cdots Os_3(CO)_{11}$, *less* the 2 kcal mol$^{-1}$ change estimated for reaction 14. Stabilization due to solvation can be considered in the light of the strength of the W-$(C_6H_{12})$ bond in $(OC)_5W(C_6H_{12})$ which has been measured to be 11.6 ± 3 kcal mol$^{-1}$ in the gas phase.[18] Alternatively stabilization due to solvation or CO bridging etc. can be considered in the light of the ca. 12 kcal mol$^{-1}$ lower value of $\Delta H_{-4}^{*}$ compared with the average value (45 kcal mol$^{-1}$) estimated[14] for the Os–CO bond strength in $Os_3(CO)_{12}$. We can estimate, therefore, that the stabilization of the $(H_2)\cdots Os_3(CO)_{11}$ transition state probably amounts to roughly 5 kcal mol$^{-1}$. Since the H–H bond energy is 104 kcal mol$^{-1}$,[16b] the enthalpy change for the reaction shown in eq 16 can be estimated to be 28 – 11 + 5 – 2 + 104 = 124 kcal mol$^{-1}$ so that each Os–H bond in $(H)_2Os_3(CO)_{11}$ has a strength of ca. 62 kcal mol$^{-1}$. The uncertainty in this value is difficult to estimate objectively mainly because of the uncertainty in the value of 5 kcal mol$^{-1}$ chosen for the stabilization due to solvation etc. of the $(H_2)\cdots Os_3(CO)_{11}$ transition state, but it is probably good to ca. ±3 kcal mol$^{-1}$. (This allows for a ±6 kcal mol$^{-1}$ accumulated error in the 124 kcal mol$^{-1}$ enthalpy for reaction 16. Note that if $\Delta H$ for reaction 14 is greater than the 2 kcal mol$^{-1}$ assumed, the Os–H bond strength will be *reduced.*) The estimate of 62 ± 3 kcal mol$^{-1}$ is close to the 67 kcal mol$^{-1}$ estimated by Keister et al.[3b] by adding ca. 10% to another estimated value (60 kcal mol$^{-1}$) for the Ru–H bond energy. Halpern[26] suggested that M–H bond strengths do not increase appreciably from second- to third-row transition metals but Simhões et al.[27] had obtained values of 60 and 73 kcal mol$^{-1}$, respectively, for the Mo–H and W–H bonds in $(\eta^5\text{-}C_5H_5)_2M(H)_2$, and Pearson[28] believes that third-row transition metals do have stronger M–H bonds than second-row metals. The Ir–H bond in $(\eta^5\text{-}C_5H_5)(Me_3P)(Cy)IrH$ has been estimated rather precisely to be 74 kcal mol$^{-1}$.[29] The value of >34 kcal mol$^{-1}$ for $\Delta H^{*}$ for dissociation of $H_2$ from $(H)_2Os(CO)_4$[22] suggests a value of *at least* 68 kcal mol$^{-1}$ for the Os–H bonds, ignoring any stabilization of the $Os(CO)_4$ moiety in the transition state due to solvation etc., and this approaches the value of ≥74 kcal mol$^{-1}$ offered by Calderazzo[30] for the same system. It seems necessary to accept the not unreasonable view that M–H bond strengths will depend on not only the metal and its oxidation state but also the other ligands present and, where appropriate, any other metal atoms attached to the metal in the M–H bond. In the $(H)_2Os_3(CO)_{11}$ cluster it appears that the $Os_2(CO)_8$ unit has a perceptible weakening effect on the Os–H bonds involving the third Os atom. Such influences clearly require further study.

$$(H)_2[Os_3(CO)_{11}] \rightarrow (H)_2\cdots[Os_3(CO)_{11}] \qquad (13)$$

$$H_2 + [Os_3(CO)_{11}] \rightarrow (H)_2\cdots[Os_3(CO)_{11}] \qquad (14)$$

$$(H)_2[Os_3(CO)_{11}] \rightarrow H_2 + [Os_3(CO)_{11}] \qquad (15)$$

$$(H)_2[Os_3(CO)_{11}] \rightarrow 2H^{\bullet} + [Os_3(CO)_{11}] \qquad (16)$$

**Acknowledgment.** We are grateful to the reviewers for offering perceptive and constructive criticism of the original version of this paper, and we thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Science and Engineering Research Council, Ottawa, for partial support. One of us (Y.Z.) is grateful for the award of a University of Toronto Open Fellowship.

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