Kinetics of Reactions of Hydrogen with $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$†

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The kinetics of reactions of $[Os_3(CO)_{11}(NCMe)]$ with H_2 and CO, and of $[Os_3(CO)_{10}(NCMe)_2]$ with H_2, have been studied in the presence of free MeCN. The reactions involve slow dissociation of MeCN from the clusters and subsequent competition between MeCN and H_2 or CO for the vacant co-ordination site on the intermediate cluster. Rate constants for nucleophilic attack on $[Os_3(CO)_{11}]$ are in the order MeCN > PPh_3 ≈ CO > H_2 and temperature-dependence studies provide activation enthalpy and entropy differences. These, together with a value of 1.34 ± 0.03 for the deuterium kinetic isotope effect, are consistent with a simple three-centre transition state for reaction of $[Os_3(CO)_{11}]$ with H_2. The cluster $[Os_3H_2(CO)_{10}]$ reacts with MeCN to form $[Os_3H_2(CO)_{10}(NCMe)]$ and equilibrium data for this reaction have been obtained.

Activation of H_2 by transition-metal centres is a fundamental process in catalytic hydrogenation reactions.[1] Reactions of this type usually lead to the 'oxidative' addition of H_2 to the metal centre to form a *cis* dihydrido product, although examples of η^2 (sideways bonded) dihydrogen are becoming increasingly common.[2]

In an attempt to elucidate the intimate mechanism of reaction of this important process the rates of oxidative addition of H_2 to three- and four-co-ordinate d^8 metal complexes have been studied in some detail[1–3] and a mechanism involving a three-centre transition state has become widely accepted. The kinetics of oxidative addition to metal centres in metal carbonyl clusters have received considerably less attention and little is known about the intimate mechanisms of such reactions. Reactions that have been studied kinetically are the addition of H_2 to the M_3 cluster in $[M_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ (M = Ru,[4a] Os,[4b] or mixed Ru, Os[4c]) but no direct measurements of oxidative-addition rates were obtained. Reactions of $[Ru_3(CO)_{11}(CO_2Me)]^-$ with H_2 have also been studied.[4d] The proposed mechanism for all these reactions involves slow dissociation of CO prior to oxidative addition of hydrogen to the co-ordinatively unsaturated intermediate.

A number of other examples of facile oxidative-addition reactions of H_2 with metal carbonyl clusters are known,[5,6] but no kinetic studies for these reactions have been reported. One such cluster is $[Os_3(CO)_{12}]$ which reacts at temperatures above 100 °C with H_2 at atmospheric pressure to form the synthetically useful and structurally interesting compound $[Os_3H_2(CO)_{10}]$.[6] However, this reaction is not entirely clean and a much more convenient synthesis of $[Os_3H_2(CO)_{10}]$ involves the reaction of H_2 with $[Os_3(CO)_{10}(NCMe)_2]$,[7] which occurs very cleanly at ambient temperatures. In view of the simplicity and synthetic importance of this reaction, and the paucity of kinetic studies of reactions of H_2 with transition-metal carbonyl clusters, we have studied the kinetics of the reaction of H_2 with this cluster and with the closely related complex $[Os_3(CO)_{11}(NCMe)]$.

Experimental

The complexes $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ were prepared from $[Os_3(CO)_{12}]$ (Strem Chemicals) by published methods[7,8] and characterised by their i.r. spectra. The gases H_2, CO, H_2–N_2 mixtures of known composition, and D_2 were obtained from Canox Ltd., Matheson Canada Ltd., or Canlab. Acetonitrile (BDH) was stored over molecular sieves (Linde Type 4A), triphenylphosphine (BDH) was recrystallised from ethanol, and 1,2-dichloroethane (Baker) was dried over $MgSO_4$, distilled, and stored over molecular sieves.

Solutions of complex (*ca.* 4×10^{-4} mol dm^{-3}) for kinetic studies were prepared by dissolving the complex, together with a known amount of MeCN where required, in 1,2-dichloroethane in a Schlenk tube which was subsequently sealed with a rubber septum cap and thermostatted to ±0.2 °C by immersion in an oil-bath (Lauda model NS-20). The solutions were purged with a stream of argon and then saturated, if required, with the appropriate gas. Samples were withdrawn periodically by syringe under a slight positive pressure of gas, and the reaction was quenched by cooling in an ice-bath and purging with argon. I.r. spectra of the samples were recorded on a Nicolet 10DX FTIR or Perkin-Elmer 298 spectrophotometer.

Reactions were followed by monitoring the decrease in absorbance of carbonyl stretching bands at 2 040 cm^{-1} for $[Os_3(CO)_{11}(NCMe)]$ and at 1 982 cm^{-1} for $[Os_3(CO)_{10}(NCMe_2)]$, over the temperature ranges 35—55 and 25—45 °C, respectively. These bands were reasonably distinct from those of any products and values of A_∞ were generally <20% of initial absorbance. The spectroscopic changes were very clean as illustrated by the set of spectra, shown in Figure 1, for the reaction of $[Os_3(CO)_{11}(NCMe)]$ with H_2. The sharpness of the isosbestic points is evident. Plots of $\ln(A_t - A_\infty)$ *vs.* time were linear for at least two half-lives.

Solutions for equilibrium studies of formation of the adduct $[Os_3H_2(CO)_{10}(NCMe)]$ were obtained by mixing pre-thermostatted solutions of $[Os_3H_2(CO)_{10}]$ (*ca.* 1×10^{-4} mol dm^{-3}) and MeCN (0—6.28 mol dm^{-3}) in 1,2-dichloroethane or pure MeCN in 10-mm cuvettes. Reactions were allowed to proceed to completion in the thermostatted cell holder of a Cary 210 spectrophotometer and the decrease in absorbance of a band at 370 nm was monitored, the final apparent molar absorption coefficients being obtained from the ratio of the absorbance to the total complex concentration over the temperature range 25.5—39.5 °C.

Concentrations of H_2 and CO in 1,2-dichloroethane were estimated by using the method of Wilhelm and Battino.[9] The solubility of H_2 at 25 °C in 1,2-dichloroethane was taken to be the same as that in 1,1,2,2-tetrachloroethane, and CO was

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† Undecacarbonyl(methyl cyanide)-*triangulo*-triosmium and 1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-bis(methyl cyanide)-*triangulo*-triosmium.

Non-S.I. unit employed: atm = 101 325 Pa.

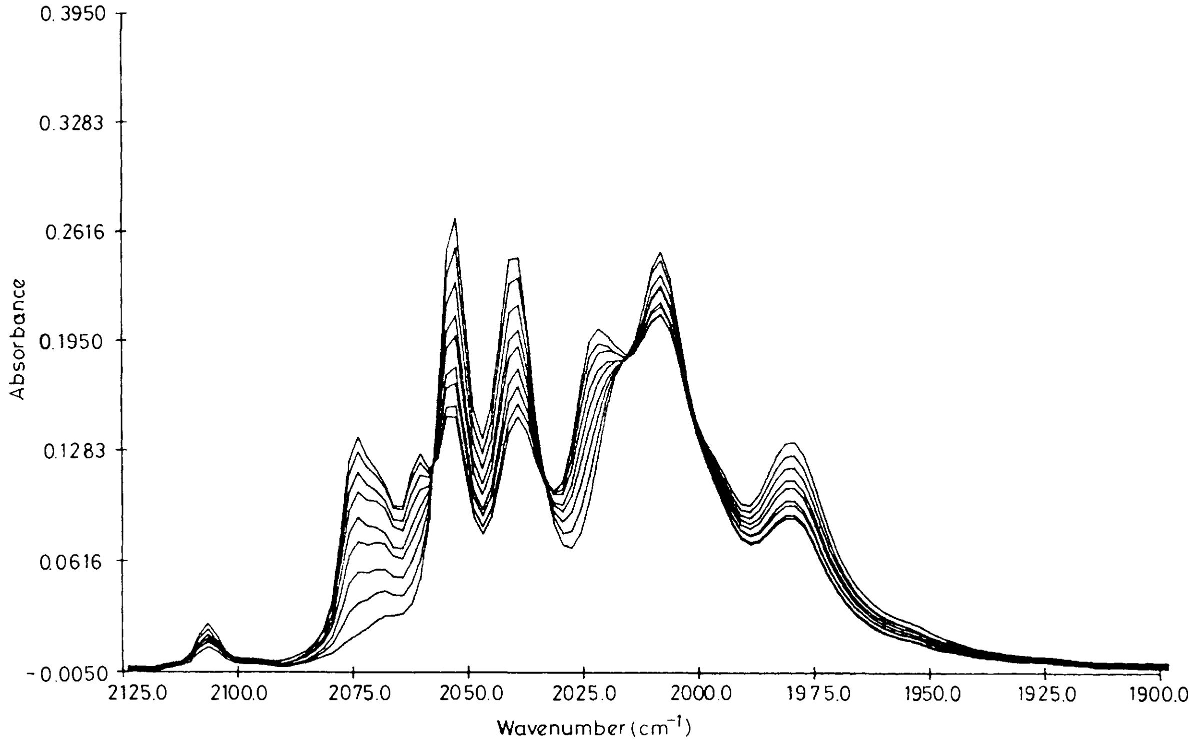

Figure 1. Original i.r. spectra taken during reaction of [$Os_3(CO)_{11}(NCMe)$] with H_2 in 1,2-dichloroethane at 35 °C

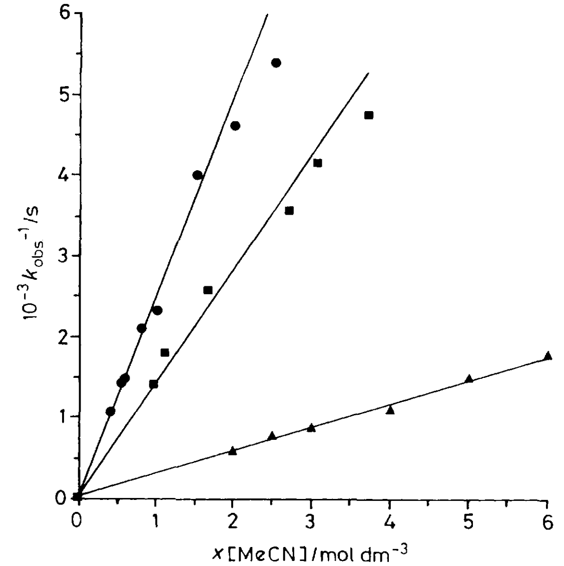

Figure 2. Dependence of $k_{obs.}^{-1}$ on [MeCN] for reactions of [$Os_3(CO)_{12-n}(NCMe)_n$] with L at 35 °C: (▲) $n = 1$, L = CO, $x = 10^2$; (●) $n = 1$, L = H_2, $x = 10$; (■) $n = 2$, L = H_2, $x = 10^2$

taken to be 2.53 times more soluble than H_2, in accordance with data for a number of chlorinated hydrocarbons.[9] Vapour pressures of 1,2-dichloroethane were estimated by extrapolation of published values.[10]

Activation parameters were estimated from unweighted least-squares analysis of the dependence of ln(k/T) on $1/T$. The probable errors, $\sigma(k)$, of individual measurements of k were estimated from the residuals. Allowance was made for the numbers of degrees of freedom involved in the analysis so that 95% confidence limits for the parameters can be obtained by doubling the quoted uncertainties.[11]

Results

Reactions of [$Os_3(CO)_{11}(NCMe)$] and [$Os_3(CO)_{10}(NCMe)_2$] in 1,2-dichloroethane under 1 atm of hydrogen and with various values of [MeCN] led cleanly to the formation of [$Os_3H_2(CO)_{11}$] and [$Os_3H_2(CO)_{10}$], respectively, as indicated by i.r. spectroscopy. No spectroscopic evidence for formation of any other products was observed. The values of $k_{obs.}$ for both reactions were reduced as [MeCN] was increased. Data conform to rate equation (1) and plots of $1/k_{obs.}$ *vs.* [MeCN] for reactions at 35 °C are shown in Figure 2.

$$1/k_{obs.} = a + b[\mathrm{MeCN}]/[\mathrm{H_2}] \qquad (1)$$

The reaction of hydrogen with [$Os_3(CO)_{11}(NCMe)$] at 35 °C was also followed at constant [MeCN] and under various partial pressures of hydrogen in H_2—N_2 mixtures. A plot of $1/k_{obs.}$ *vs.* $1/[H_2]$ for reactions at 30 °C is shown in Figure 3.

Reactions of D_2 with [$Os_3(CO)_{11}(NCMe)$] at 35 °C were also followed and values of $k_{obs.}$ are reported in Table 1 together with values for the reaction with H_2 obtained at the same time under otherwise identical conditions.

Reactions of CO with [$Os_3(CO)_{11}(NCMe)$] at various values of [MeCN] and under 1 atm of CO led cleanly to [$Os_3(CO)_{12}$]. The values of $k_{obs.}$ were also in accordance with equation (1) but with H_2 replaced by CO (Figure 2).

Reactions of PPh_3 with [$Os_3(CO)_{11}(NCMe)$] in toluene have been previously studied kinetically.[12] We have repeated these studies, but with 1,2-dichloroethane as solvent and in the temperature range 10—25 °C. As shown by the earlier studies,[12] $k_{obs.}$ is independent of [PPh_3] in the absence of free MeCN, and the results are shown in Table 2 together with the activation parameters derived from the temperature dependence.

Addition of MeCN to [$Os_3H_2(CO)_{10}$] was also investigated. Rapid formation of [$Os_3H_2(CO)_{10}(NCMe)$] was observed to occur when MeCN was $\geqslant 0.27$ mol dm^{-3}, as indicated by i.r. spectroscopy. New CO stretching bands were observed at

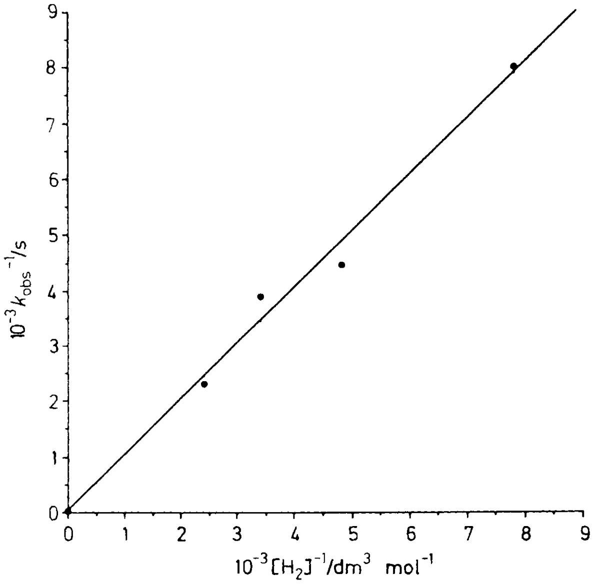

Figure 3. Dependence of $k_{obs.}^{-1}$ on $[H_2]^{-1}$ for the reaction of $[Os_3(CO)_{11}(NCMe)]$ with H_2 at [MeCN] = 0.02 mol dm^{-3} in 1,2-dichloroethane at 35 °C

Table 1. Rate data for reaction of $[Os_3(CO)_{12-n}(NCMe)_n]$ with H_2 or D_2[a] at 35 °C

[MeCN] mol dm^{-3}	n	$10^4 k_{obs.}(H_2)$ s^{-1}	$10^4 k_{obs.}^{b}(D_2)$ s^{-1}	$k_3(H_2)/k_3(D_2)$
0.006	1	8.75	5.29	1.28
0.008	1	4.79	3.45	1.39
0.014	1	2.94[b]	2.31	1.27
0.015	1	2.70	2.07	1.37
0.016	1	2.57[b]	1.87	1.31
0.020	1	2.16	1.55	1.40
				Av. = 1.34 ± 0.03
0.065	2	12.1	6.89	1.76 ± 0.09[c]

[a] $[H_2] = [D_2] = 4.14 \times 10^{-3}$ mol dm^{-3}. [b] From dependence of $k_{obs.}^{-1}$ on [MeCN]. [c] Uncertainty assumed to be the same (5%) as that for a single measurement of the ratio when $n = 1$.

Table 2. Temperature dependence of $k_{obs.}$ for reaction of $[Os_3(CO)_{11}(NCMe)]$ with PPh_3 in 1,2-dichloroethane

θ_c °C	$[PPh_3]$ mol dm^{-3}	$10^4 k_{obs.}$ s^{-1}
10	0.04	13.3
15	0.04	28.6
15	0.03	27.5
15	0.02	28.3
20	0.04	56.7
25	0.04	111

$\Delta H^{\ddagger} = 96.60 \pm 1.09$ kJ mol^{-1}, $\Delta S^{\ddagger} = 42.0 \pm 3.7$ J K^{-1} mol^{-1}, $\sigma(k_{obs.}) = 1.8\%$*

* Probable error for an individual measurement of $k_{obs.}$

2 104w, 2 069vs, 2 049s, 2 021vs, 2 013(sh),br, 1 980m, and 1 961w cm^{-1}. These bands are essentially identical with those observed for $[Os_3H_2(CO)_{10}(PhCN)]$ [2 103w, 2 067vs, 2 049s, 2 024vs, 2 008(sh),br, 1 985m, and 1 966w cm^{-1}].[13] Equilibrium data were obtained from molar absorption coefficients of the band at 370 nm. These decrease according to equation (2) as

$$\varepsilon_{obs.} = (1/K)\{(\varepsilon_{obs.} - \varepsilon_{complex})/[MeCN]\} + \varepsilon_{adduct} \quad (2)$$

expected for simple adduct formation and the values are shown in Table 3. Plots of $\varepsilon_{obs.}$ *vs.* $(\varepsilon_{obs.} - \varepsilon_{complex})/[MeCN]$ were linear and provided values for the equilibrium constant, K, for adduct formation as well as the value of the molar absorption coefficient of the adduct at 370 nm.

Discussion

The formation of $[Os_3H_2(CO)_{11}]$ and $[Os_3H_2(CO)_{10}]$ from the reactions of hydrogen with $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$, respectively, is consistent with reactions of PPh_3,[12] CO,[12] $AsPh_3$,[12] $P(OPh)_3$,[12] RNC,[7a] C_2H_4,[7a] pyridine,[7a] $PBu^n{}_3$,[14] and $Ph_2PCH_2PPh_2$[14] with these complexes all of which involve complete replacement of the MeCN ligand by simple rate-determining dissociative processes.

The reduction of the rate of reaction of $[Os_3(CO)_{11}(NCMe)]$ with increasing [MeCN] at constant $[H_2]$, and with decreasing $[H_2]$ at constant [MeCN], is also consistent with the simple dissociative mechanism shown in equations (3) and (4). Reduction in the rate of reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with increasing [MeCN] at constant $[H_2]$ is also consistent with the similar mechanism for reaction of $[Os_3(CO)_{10}(NCMe)_2]$ shown in equations (5)—(7). Since no spectroscopic indication of the $[Os_3H_2(CO)_{10}(NCMe)]$ adduct was obtained during reactions in the presence of the relatively low [MeCN] used, we conclude that reaction (7) is fast and complete as written (see below).

$$[Os_3(CO)_{11}(NCMe)] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Os_3(CO)_{11}] + MeCN \quad (3)$$

$$[Os_3(CO)_{11}] + H_2 \xrightarrow{k_4} [Os_3H_2(CO)_{11}] \quad (4)$$

$$[Os_3(CO)_{10}(NCMe)_2] \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Os_3(CO)_{10}(NCMe)] + MeCN \quad (5)$$

$$[Os_3(CO)_{10}(NCMe)] + H_2 \xrightarrow{k_6} [Os_3H_2(CO)_{10}(NCMe)] \quad (6)$$

$$[Os_3H_2(CO)_{10}(NCMe)] \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [Os_3H_2(CO)_{10}] + MeCN \quad (7)$$

The rate equations corresponding to these mechanisms are shown in equations (8) and (9) and are of the same form as equation (1). The values of $1/k_3$ or $1/k_5$ are equal to a in

$$1/k_{obs.} = 1/k_3 + (k_{-3}/k_3k_4)[MeCN]/[H_2] \quad (8)$$

$$1/k_{obs.} = 1/k_5 + (k_{-5}/k_5k_6)[MeCN]/[H_2] \quad (9)$$

equation (1) and to the respective intercepts in Figure 2, but they are only very imprecisely given by linear least-squares analysis. However, values of k_3 have been obtained from the reaction of $[Os_3(CO)_{11}(NCMe)]$ with PPh_3 in 1,2-dichloroethane (Table 2) and values of k_5 can be obtained from data for reactions of $[Os_3(CO)_{10}(NCMe)_2]$ in *p*-xylene with PPh_3 since no solvent effect was observed for this reaction.[12] Values of k_3 and k_5 at any required temperature can be calculated from the activation parameters (Table 2 and ref. 12).

We can therefore obtain values of $b = k_{-3}/k_3k_4$ or k_{-5}/k_5k_6 from each value of $(1/k_{obs.} - 1/k_3)[H_2]/[MeCN]$ and $(1/k_{obs.} - 1/k_5)[H_2]/[MeCN]$, respectively, and multiplication by k_3 or k_5 will give the competition ratios k_{-3}/k_4 and k_{-5}/k_6. Average values of b are shown in Table 4 together with values of k_4/k_{-3} and k_6/k_{-5}. The temperature dependences of the competi-

Table 3. Molar absorption coefficients and equilibrium data for addition of MeCN to $[Os_3H_2(CO)_{10}]$ in 1,2-dichloroethane

[MeCN]	25.5 °C		30.0 °C		35.5 °C		39.5 °C	
mol dm^{-3}	ε^a	K^b	ε^a	K^b	ε^a	K^b	ε^a	K^b
0.00	1 461		1 478		1 489		1 499	
0.27	2 439	2.08	2 354	1.86	2 281	1.72	2 245	1.66
0.56	2 910	2.03	2 786	1.78	2 688	1.64	2 620	1.56
1.07	3 391	2.27	3 267	2.01	3 156	1.87	3 132	1.97
3.04	3 744	1.71	3 638	1.54	3 521	1.43	3 430	1.34
4.09	3 898	2.08	3 802	1.91	3 858	1.61	3 560	1.46
5.21	3 928	1.85	3 814	1.57	3 707	1.52	3 616	1.41
6.28	4 049	3.05	3 952	2.66	3 780	1.76	3 690	1.62
ε_{adduct}	4 184^c		4 100^c		3 987^c		3 905^c	
K^d	2.15 ± 0.16		1.90 ± 0.14		1.65 ± 0.08		1.57 ± 0.08	
K^e	2.08 ± 0.06		1.85 ± 0.06		1.71 ± 0.08		1.64 ± 0.09	

^{f} $\Delta H^{\ominus} = -15.37 \pm 1.40$ kJ mol^{-1}; $\Delta S^{\ominus} = -45.35 \pm 4.56$ J K^{-1} mol^{-1}; $\sigma(K) = 2.7\%$

[a] In dm^3 mol^{-1} cm^{-1}. [b] In dm^3 mol^{-1}. [c] ε_{adduct} obtained from intercepts of plots of $\varepsilon_{obs.}$ *vs.* $(\varepsilon_{obs.} - \varepsilon_{complex})$/[MeCN], as shown by equation (2). [d] $K_{av.}$ calculated from individual points and ε_{adduct}. N.B. The absence of any significant trends in the values of K with increasing [MeCN] suggests that the equilibrium is not very solvent dependent in spite of the rather large changes in the mole ratios of 1,2-dichloroethane and MeCN. [e] Obtained from gradients of plots described in footnote *c*. [f] Calculated by using all values of K obtained as in footnotes *d* and *e*.

Table 4. Kinetic parameters for reactions of $[Os_3(CO)_{12-n}(NCMe)_n]$

θ_C/°C	n	N^a	Reactant^b	$10^2\ b$/s	$10^2 k_y/k_{-x}$	$\sigma(k_{obs.})^c$/%
35	1	11	H_2	10.0 ± 0.45	2.42 ± 0.11^d	7.1
45	1	5	H_2	2.56 ± 0.07	2.79 ± 0.07^d	
55	1	3	H_2	0.706 ± 0.031	3.23 ± 0.14^d	
25	2	3	H_2	2.85 ± 0.17	18.1 ± 1.00^e	8.2
35	2	6	H_2	0.58 ± 0.021	26.2 ± 0.80^e	
45	2	3	H_2	0.706 ± 0.031	36.8 ± 1.60^e	
25	1	4	CO	9.84 ± 0.18	9.01 ± 0.16^f	5.2
35	1	8	CO	2.81 ± 0.05	8.62 ± 0.15^f	
45	1	7	CO	0.873 ± 0.02	8.20 ± 0.20^f	

[a] Number of individual measurements of $k_{obs.}$ [b] $10^3[H_2] = 4.44, 4.14, 3.68$, and 3.09 mol dm^{-3} at 25, 35, 45, and 55 °C, respectively; 10^3[CO] = 11.1, 10.4, and 9.21 mol dm^{-3} at 25, 35, and 45 °C, respectively. [c] Probable errors of individual measurements of $k_{obs.}$ estimated by the method of pooled variance applied to the data at all temperatures. [d] $x = 3, y = 4$. [e] $x = 5, y = 6$. [f] $x = 3, y = 10$.

Table 5. Activation parameters for addition reactions of $[Os_3(CO)_{12-n}(NCMe)_{n-1}]$

y	x	n	Reactants	$(\Delta H_y^{\ddagger} - \Delta H_{-x}^{\ddagger})$/ kJ mol^{-1}	$(\Delta S_y^{\ddagger} - \Delta S_{-x}^{\ddagger})$/ J K^{-1} mol^{-1}	$\sigma(k_y/k_{-x})$/%
4	3	1	H_2/MeCN	11.87 ± 0.60	7.65 ± 1.42	7.9
10	3	1	CO/MeCN	−3.89 ± 1.30	−33.02 ± 4.64	8.4
10	4	1	H_2/CO	−15.76 ± 0.92*	−40.67 ± 3.18	6.1
6	5	2	H_2/MeCN	27.92 ± 2.30	79.42 ± 7.48	8.4

* Obtained from the ratios of b (for reaction with H_2) to b (for reaction with CO). In this way the values of k_{-3} cancel and the uncertainties are less than those obtained simply from the differences $(\Delta H_4^{\ddagger} - \Delta H_{-3}^{\ddagger}) - (\Delta H_{10}^{\ddagger} - \Delta H_{-3}^{\ddagger})$, *etc.*

tion ratios were obtained by linear least-squares analyses of $\ln(k_4/k_{-3})$ or $\ln(k_6/k_{-5})$ *vs.* $1/T$ and the activation parameter differences are shown in Table 5.

Reactions with CO must proceed *via* the mechanism shown in equations (3) and (10) and a similar analysis of the data

$$[Os_3(CO)_{11}] + CO \xrightarrow{k_{10}} [Os_3(CO)_{12}] \qquad (10)$$

leads to the values of b and k_{-10}/k_{-3} shown in Table 4, and values of $(\Delta H_{10}^{\ddagger} - \Delta H_{-3}^{\ddagger})$ and $(\Delta S_{10}^{\ddagger} - \Delta S_{-3}^{\ddagger})$ are given in Table 5. The values of the competition parameters for reactions of $[Os_3(CO)_{11}]$ with MeCN, H_2, and CO can be combined with that for reaction of PPh_3[12] to give the sequence MeCN > PPh_3 ≈ CO > H_2 for the rate constants for nucleophilic attack on this unsaturated cluster. The sequence covers a range of 30—40 depending on the temperature. The relatively high nucleophilicity of MeCN shows that the unsaturated cluster is more susceptible to attack by hard nucleophiles and the small range covered by the other softer nucleophiles suggests a high absolute reactivity and low discriminating power for $[Os_3(CO)_{11}]$. The approximate equality of the rates of nucleophilic attack by PPh_3 and CO* contrasts somewhat with data for $[Ru_3(CO)_{11}]$ where CO is *ca.* 5 times more nucleophilic than PPh_3.[15]

The similar rate constants for attack by CO and H_2 contrast with the very small value of $k(H_2)/k(CO)$ = *ca.*

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* It was previously assumed,[12] on the basis of the $[Ru_3(CO)_{11}]$ data, that CO would be more nucleophilic than PPh_3 towards $[Os_3(CO)_{11}]$.

1×10^{-3} found for reactions of $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_9]$.[4a] Rather special reasons have been adduced for this.[4a,c] An even smaller value, 4×10^{-5} at 25 °C, has been obtained for reactions with $[Ru_3(CO)_{10}(CO_2Me)]^-$.[4d] A value of 1.4×10^{-3} at 23 ± 1 °C for $k(H_2)/k(CO)$ has been reported[3a] for reactions of the co-ordinatively unsaturated complex $[RhCl(PPh_3)_2]$ while a value of $< 2.4 \times 10^{-5}$ has been obtained for $[RhCl(PPh_3)_3]$ at the same temperature.* For $[Co(CO)_3(CO_2Et)]$ the ratio is 7×10^{-3} at 25 °C.[3d] It is evident that relative rates of oxidative addition of H_2 and simple addition of CO to co-ordinatively unsaturated metal centres vary over a very wide range depending on the degree of unsaturation and, presumably, on the nature of the metal centre. However, the temperature dependence of the competition ratios should also be of interest but is only available for the intermediates studied here. Although H_2 is only 2—4 times less reactive than CO towards $[Os_3(CO)_{11}]$ in terms of rate constants this is the result of a 16 kJ mol^{-1} higher value for $\Delta H^{\ddagger}$ for attack by H_2 that is almost offset by a 41 J K^{-1} mol^{-1} less negative value of $\Delta S^{\ddagger}$, *i.e.* the reaction with H_2 is quite strongly disfavoured enthalpically but favoured entropically. These results can be explained by formation of a three-centred transition state for reaction of H_2 with $[Os_3(CO)_{11}]$ similar to those proposed for reactions at other metal centres.[3,4]

Thus, the balance between the energy required to weaken the strong H–H bond and the energy gained by partial formation of the two quite strong Os–H bonds must evidently be such that attack by H_2 is enthalpically more difficult than attack by CO. On the other hand, formation of the rather flexible three-centre $Os(\eta^2\text{-}H \cdots H)$ transition state leads to a significantly higher entropy for this transition state than for that involved in CO attack. The value of 1.34 ± 0.03 for $k_3(H_2)/k_3(D_2)$ is very similar to the kinetic isotope effects found for reactions of mononuclear complexes such as $[Ir(CO)Cl(PPh_3)_2]$[3e] and $[RhCl(PPh_3)_2]$[3a] and for the formally unsaturated cluster $[Ru_3(CO)_{10}(CO_2Me)]^-$[4d] for which three-centred transition states have been proposed. No detectable isotope effect was observed, however, for reactions of $[Co(CO)_3(CO_2Et)]$ and no explanation was offered.[3d]

The competition between H_2 and MeCN for attack on $[Os_3(CO)_{10}(NCMe)]$ is relatively less unfavourable to H_2 than that for attack at $[Os_3(CO)_{11}]$ in terms of relative rate constants. However, this is the result of a less favourable value of $(\Delta H_6^{\ddagger} - \Delta H_{-5}^{\ddagger})$ that is overcome by a considerably more favourable difference $(\Delta S_6^{\ddagger} - \Delta S_{-5}^{\ddagger})$. This may be due to the fact that $[Os_3(CO)_{10}(NCMe)]$ appears to be stabilised at lower temperatures by a form of CO bridging that relieves the co-ordinative unsaturation on the Os atom that has lost an MeCN ligand.[12] This would decrease the reactivity of the $[Os_3(CO)_{10}(NCMe)]$ intermediate and make formation of the transition state more difficult. In order for any bond making to occur, the CO bridging in this cluster intermediate will have to open up and full opening would require as much as 30 kJ mol^{-1}.[12] Formation of the three-centre OsH_2 transition state by a sideways approach of the H_2 molecule must require more opening up than the partial formation of the new Os–NCMe bond and this could account for a major part of the 16 kJ mol^{-1} difference between $(\Delta H_6^{\ddagger} - \Delta H_{-5}^{\ddagger})$ and $(\Delta H_4^{\ddagger} - \Delta H_{-3}^{\ddagger})$. Some of this difference could also originate in differences in the OsH_2 interactions themselves. However, the not very different isotope effects for reactions of H_2 with $[Os_3(CO)_{11}]$ and $[Os_3(CO)_{10}(NCMe)]$ (Table 1) suggests that this may not be a very large contribution and it would be somewhat difficult to quantify. The greater opening up involved in reaction of H_2 with $[Os_3(CO)_{11}(NCMe)]$ also has to be invoked to account for the large difference between $(\Delta S_6^{\ddagger} - \Delta S_{-5}^{\ddagger})$ and $(\Delta S_4^{\ddagger} - \Delta S_{-3}^{\ddagger})$ although the quantitative aspect of this contribution is virtually impossible to evaluate. A similar argument might be advanced for the very low value of $k(H_2)/k(CO)$ found for $[Ru_3(CO)_{10}(CO_2Me)]^-$[4c] where bridging by the CO_2Me group might be quite important.

Finally, the equilibrium data for formation of $[Os_3H_2(CO)_{10}(NCMe)]$ from $[Os_3H_2(CO)_{10}]$ show that the equilibrium constants are quite small. It is for this reason that $[Os_3H_2(CO)_{10}(NCMe)]$ is not seen as a product of the reaction of H_2 with $[Os_3(CO)_{10}(NCMe)_2]$ in the presence of the relatively low concentrations of MeCN used in the kinetic study. The small equilibrium constants are due to an approximate balance between a reasonably substantial favourable value of $\Delta H^{\ominus}$ and a correspondingly unfavourable value of $T\Delta S^{\ominus}$. No other data of this sort appear to be available for comparison although the adduct has been isolated.[7b]

Acknowledgements

We thank the Natural Science and Engineering Research Council, Ottawa and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

1 J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, 1987, ch. 5; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 5th edn., Wiley-Interscience, New York, 1988, ch. 30; B. R. James, 'Homogeneous Hydrogenation,' Wiley, New York, 1973, ch. 12; G. W. Parshall, 'Homogeneous Catalysis,' Wiley-Interscience, New York, 1980, ch. 3 and 5; B. R. James, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, New York, 1982, vol. 8, ch. 51.

2 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **108**, 451; M. Bautista, K. A. Earl, R. H. Morris, and A. Sella, *ibid.*, 1987, **109**, 3780 and refs. therein.

3 (*a*) D. A. Wink and P. C. Ford, *J. Am. Chem. Soc.*, 1987, **109**, 438; (*b*) C. E. Johnson and R. Eisenberg, *ibid.*, 1985, **107**, 3148; (*c*) J. Halpern, *Inorg. Chim. Acta*, 1981, **50**, 11 and refs. therein; (*d*) F. Ungváry and L. Markó, *Organometallics*, 1983, **2**, 1608; (*e*) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, 1966, **88**, 3511; (*f*) P. Zhou, A. A. Vitale, J. S. San Filippo, jun., and W. H. Saunders, jun., *J. Am. Chem. Soc.*, 1985, **107**, 8049.

4 (*a*) L. M. Bavaro, P. Montangero, and J. B. Keister, *J. Am. Chem. Soc.*, 1983, **105**, 4977; (*b*) L. M. Bavaro and J. B. Keister, *J. Organomet. Chem.*, 1985, **287**, 357; (*c*) L. M. Bavaro and J. B. Keister, personal communication; (*d*) D. J. Taube, A. Rokicki, M. Anstock, and P. C. Ford, *Inorg. Chem.*, 1987, **26**, 526.

5 A. P. Humphries and H. D. Kaesz, *Prog. Inorg. Chem.*, 1979, **25**, 145; J. Bamford, Z. Dawoodi, K. Henrich, and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1982, 554; M. H. Chisholm, *ACS Symp. Ser.*, 1981, **155**, 17; M. D. Curtis, L. Messerle, N. A. Fotinos, and R. F. Gerlach, *ibid.*, p. 221; G. L. Geoffroy and R. A. Epstein, *Inorg. Chem.*, 1977, **16**, 2795.

6 J. W. Koepe, M. A. Andrews, S. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.

7 (*a*) B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407; (*b*) J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. de Boer, *J. Am. Chem. Soc.*, 1975, **97**, 4145.

8 A. J. Poë, C. N. Sampson, and R. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 5459.

9 E. Wilhelm and R. Battino, *Chem. Rev.*, 1973, **73**, 1.

10 R. C. Weast (ed.), 'Handbook of Chemistry and Physics,' 53rd edn., Chemical Rubber Co., Cleveland, 1972.

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* Reaction of CO with $[RhCl(PPh_3)_3]$ leads to displacement of one of the PPh_3 ligands and the rate of addition of CO to this complex must be at least as high as the rate of displacement of the PPh_3.

11 M. A. Cobb, B. Hungate, and A. J. Poë, *J. Chem. Soc., Dalton Trans.*, 1976, 2226; J. Mandel, 'Statistical Analysis of Experimental Data,' Interscience, New York, 1964.
12 K. Dahlinger, A. J. Poë, P. K. Sayal, and V. C. Sekhar, *J. Chem. Soc., Dalton Trans.*, 1986, 2145.
13 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1975, **88**, C21.
14 A. J. Poë and V. C. Sekhar, *Inorg. Chem.*, 1985, **24**, 4376; *J. Am. Chem. Soc.*, 1984, **106**, 5034.
15 A. J. Poë and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1974, 1860.

Received 21*st December* 1988; *Paper* 8/04984J