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

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The kinetics of reactions of $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ with P- or As-donor ligands in *p*-xylene or toluene have been studied and shown to be characteristic of reversible dissociative processes. In both cases MeCN is *ca.* 10 times more nucleophilic towards the reactive intermediate than is PPh_3. Activation parameters confirm the weakness of the Os–NCMe bonds and suggest that loss of the first MeCN from $[Os_3(CO)_{10}(NCMe)_2]$ may be a concerted process in which a 'sideways on' bridging CO replaces the leaving MeCN. The strength of bridge bonding can be estimated to be $\geqslant 30$ kJ mol^{-1}.

The complexes $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{10}(NCMe)_2]$ are useful intermediates in the preparation of a wide variety of derivatives of the inert parent carbonyl cluster, $[Os_3(CO)_{12}]$.[1–3] Their usefulness lies in the facile replacement of the MeCN ligands and they represent a fairly large group of such 'lightly stabilized' complexes that can readily be formed by reaction of a parent carbonyl with trimethylamine oxide.[4–6] Although their crystallographic structures have been determined,[7] no kinetic studies have been carried out to confirm the presumed dissociative mechanisms for displacement of the MeCN ligands, or to quantify the actual strengths of the Os–NCMe bonds. We report here studies of substitution reactions of these complexes that do this and that also provide a measure of the effect of an MeCN, bonded to one Os atom, on the ease of displacement of another MeCN from a neighbouring Os atom in the cluster.

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[2] and characterized by their i.r. spectra,[1,2] measured in cyclohexane with a Perkin-Elmer 298 spectrophotometer. Triphenylphosphine (BDH) and triphenylarsine (Aldrich) were recrystallized from ethanol. Triphenyl phosphite (BDH) was used as received. *p*-Xylene and toluene (BDH, AnalaR grade) were dried over calcium chloride, distilled, and stored over molecular sieves.

Solutions for kinetic study were obtained by mixing pre-thermostatted solutions of complex and reacting ligand in 10-mm cuvettes placed in the thermostatted cell holder of a Cary 210 spectrophotometer. Slower reactions were followed by repetitive scanning of up to five reacting solutions at a time, and faster ones by following absorbance changes at a product maximum by using the time-drive mode. Cell temperatures were measured with an iron–Constantan thermocouple connected to a digital multimeter.

Results and Discussion

Reactions of $[Os_3(CO)_{11}(NCMe)]$.—The complex $[Os_3(CO)_{11}(NCMe)]$ shows an electronic spectrum with $\lambda_{max.} = 330$ nm and a shoulder at *ca.* 382 nm. Solutions obeyed Beer's law (ε 3.5×10^3 dm^3 mol^{-1} cm^{-1} at 382 nm). Reactions with PPh_3, $AsPh_3$, and $P(OPh)_3$ led to an increase of absorbance between 300 and 500 nm and the development of new maxima (or shoulders) [PPh_3, 345 (sh), 406 nm; $AsPh_3$, 342, 408 nm; $P(OPh)_3$, 330, 390 (sh) nm]. The absorbances of product solutions grew rapidly below 300 nm. Reactions of $[Os_3(CO)_{11}(NCMe)]$ with PPh_3, CO, and RNC are known to be quantitative,[2] and reactions with C_2H_4,[2] pyridine,[2] $PBu^n{}_3$,[8] and $Ph_2PCH_2PPh_2$ (dppm)[8] are also known simply to involve complete replacement of the NCMe ligand. There seems to be no reason why $P(OPh)_3$ or $AsPh_3$ should behave differently. Reactions were followed by monitoring the growth of product absorbance at *ca.* 400 nm. Plots of $\ln(A_\infty - A_t)$ *vs.* time were linear for at least two half-lives if $[L] \geqslant 0.01$ mol dm^{-3} ([complex] $= 1 \times 10^{-4}$ mol dm^{-3}) or 0.001 mol dm^{-3} ([complex] $= 1 \times 10^{-5}$ mol dm^{-3}) and rate constants were then independent of both the nature and concentration of the substituting ligand (Table 1). At lower [L] the gradients of the plots decreased slightly with time and lower rate constants were obtained. These results are characteristic of the simple dissociative mechanism shown in equations (1) and (2), the reverse of reaction (1) competing significantly with reaction (2) when [L]/[NCMe] is small enough. This was confirmed by carrying out reactions in the presence of various concentrations of added MeCN, the plots in Figure 1 being in excellent accord with rate equation (3). Separate plots of $1/k_{obs.}$ *vs.* [MeCN] at constant $[PPh_3]$, or $1/[PPh_3]$ at constant [MeCN] are also linear with closely similar intercepts and gradients. The ratio intercept:gradient gives $k_2/k_{-1} = 0.103 \pm 0.002$. This accounts for the slightly curved rate plots at low $[PPh_3]$ when no added MeCN is present. The value of $(k_{-1}/k_2)[\text{MeCN}]/[PPh_3]$ grows throughout the reaction and, when [complex] $= 1 \times 10^{-4}$ mol dm^{-3} and $[PPh_3] = 0.002$ mol dm^{-3}, for example, it reaches a significant value of 0.25 at 50% completion of reaction. The competition ratio is somewhat smaller than corresponding ratios for PPh_3 and CO reacting with other co-ordinatively unsaturated metal carbonyl clusters such as $[Ru_3(CO)_{11}]$[9] and $[(OC)_4Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$.[10] It confirms the relatively small selectivity and high reactivity of such intermediates and suggests a nucleophilicity order MeCN > CO > PPh_3 towards $[Os_3(CO)_{11}]$. The corresponding competition ratio for PPh_3 and cyclohexylamine towards $[Mo(CO)_5]$ is 1.2 ± 0.3[11]

$$[Os_3(CO)_{11}(NCMe)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Os_3(CO)_{11}] + \text{NCMe} \quad (1)$$

$$[Os_3(CO)_{11}] + \text{L} \xrightarrow{k_2} [Os_3(CO)_{11}\text{L}] \quad (2)$$

$$1/k_{obs.} = 1/k_1 + (k_{-1}/k_1k_2)[\text{MeCN}]/[PPh_3] \quad (3)$$

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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.

Table 1. Limiting first-order rate constants for reactions of $[Os_3(CO)_{11}(NCMe)]$ in *p*-xylene at 30 °C[a]

L	Number of measurements, N	$10^2k_{av.}/s^{-1}$	$\sigma(k_{obs.})^b/\%$
PPh_3	13[c]	1.45 ± 0.04	9.5
$AsPh_3$	13[c]	1.52 ± 0.04	8.1
$P(OPh)_3$	9[d]	1.59 ± 0.04	8.1
	35[e]	1.51 ± 0.02	8.6
	3[f]	1.76 ± 0.09[g]	

[a] Rate constants were obtained at 28.6—32.3 °C and were adjusted to 30.0 °C according to E_a = 115 kJ mol^{-1}. [b] Standard deviation (probable error) of a single measurement of $k_{obs.}$ estimated from $100[\Sigma(\Delta^2)/(N-1)]^{\frac{1}{2}}$, where $\Delta = (k_{obs.} - k_{av.})/k_{av.}$. [c] [Complex] = 1 × 10^{-4}, [L] = 0.01—0.50 mol dm^{-3}. [d] [Complex] = 1 × 10^{-4}, [L] = 0.015—0.38 mol dm^{-3}. [e] Average of values for all three ligands. [f] [Complex] = 1 × 10^{-5}, [L] = 0.001 mol dm^{-3}; average of one measurement for each of the three ligands. [g] Uncertainty estimated by assuming $\sigma(k_{obs.})$ = 8.6% as for all other runs.

Table 2. Limiting rate constants for the reaction of $[Os_3(CO)_{11}(NCMe)]$ with PPh_3 in toluene*

θ_c/°C	$10^4k_{obs.}/s^{-1}$			
6.40	3.23	3.57	3.29	4.20
11.0	8.62	9.07	8.99	8.70
15.6	18.4	17.3	17.7	17.6
19.9	37.2	38.2	39.2	38.3
24.9	72.8	77.8	78.9	77.2

* [Complex] = 1.1 × 10^{-4} mol dm^{-3}; the four rate constants at each temperature were measured, respectively, at $[PPh_3]$ = 0.025, 0.050, 0.075, and 0.10 mol dm^{-3}.

and this higher value might possibly be due to steric inhibition of $C_6H_{11}NH_2$ attack.

The temperature dependence of the reaction with PPh_3 was studied with toluene as solvent (Table 2) and the activation parameters are shown in Table 3. The much greater substitution lability of $[Os_3(CO)_{11}(NCMe)]$ compared with $[Os_3(CO)_{12}]$[8,12] results from a 25 kJ mol^{-1} more favourable value of $\Delta H^{\ddagger}$ and an 18 kJ mol^{-1} more favourable value of $T\Delta S^{\ddagger}$. Both of these probably originate from a much weaker Os–NCMe bond, the extent of bond breaking being significantly larger than for loss of CO. A closely similar relationship exists between $\Delta H^{\ddagger}$ for loss of $C_6H_{11}NH_2$ or CO from $[Mo(CO)_5L]$ although the values of $\Delta S^{\ddagger}$ for these two reactions are virtually identical.[11]

Reactions of $[Os_3(CO)_{10}(NCMe)_2]$.—Reaction with PPh_3 led to the development of a maximum at 428 nm (ε 7.0 × 10^3 dm^3 mol^{-1} cm^{-1}) without any evidence for formation of $[Os_3(CO)_{10}(PPh_3)(NCMe)]$ as an intermediate in the ultimate formation of $[Os_3(CO)_{10}(PPh_3)_2]$.[1,2] Reaction with $AsPh_3$ led to development of a maximum at 426 nm (ε 5.9 × 10^3 dm^3 mol^{-1} cm^{-1}), again without any evidence for intermediates. Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with PPh_3 is known to form $[Os_3(CO)_{10}(PPh_3)_2]$ quantitatively[2] and it also forms a very wide range of other simple disubstituted products in high isolated yield.[1,8] Again, there is no reason to believe that $AsPh_3$ should behave differently when added in large excess, and its kinetic behaviour is identical with that of PPh_3 (see below). Reactions were followed by monitoring the increasing absorbance at *ca.* 430 nm and excellent rate plots were obtained. Rate constants are independent of $[PPh_3]$, at least for $[PPh_3] \geqslant$ 0.02 mol dm^{-3} (Table 4), and the effect of free MeCN is also in accord with a dissociative mechanism. The competition ratio, analogous to k_2/k_{-1}, for reaction with PPh_3 is 0.099 ± 0.006 so that the replacement of a CO ligand in $[Os_3(CO)_{11}]$ by MeCN does not affect the relative nucleophilicities of MeCN and PPh_3 towards the reactive intermediates, in spite of possible structural differences in the intermediates (see below).

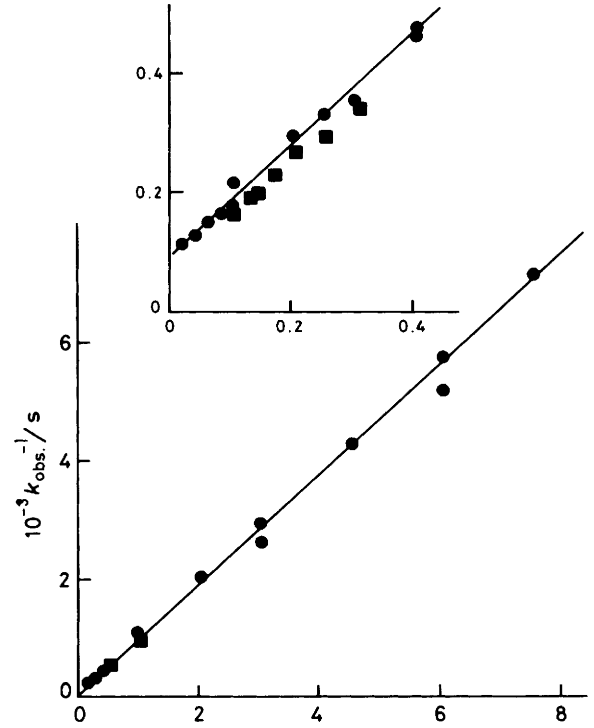
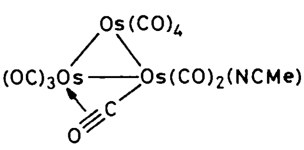
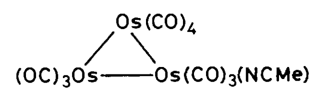


Figure 1. Dependence of $k_{obs.}^{-1}$ on $[MeCN]/[PPh_3]$ for reaction of $[Os_3(CO)_{11}(NCMe)]$: (●) $[PPh_3]$ = 0.0153, [MeCN] = 0—0.116 mol dm^{-3}; (■) [MeCN] = 0.001 54, $[PPh_3]$ = 0.0015—0.015 mol dm^{-3}. The lines drawn are based on the intercept (93.5 ± 1.4 s), and slope (906 ± 16 s) obtained from a linear least-squares analysis of all the data. Each value of $k_{obs.}$ was assumed to have a constant percentage uncertainty (probable error) which was shown by the analysis to be ±6.5%

The activation parameters (Table 3) for loss of MeCN from $[Os_3(CO)_{10}(NCMe)_2]$ are quite different from those for the monosubstituted complex. The enthalpy is much more favourable but this is just overcome by a much less favourable value of $T\Delta S^{\ddagger}$. This can be rationalized if $[Os_3(CO)_{10}(NCMe)]$ has a structure as in (**I**) with a bridging CO group of a type now well established.[13] The reaction, therefore, has some intramolecular S_N2 character, the bridge being formed as the Os–NCMe bond breaks. This would account for the low value of $\Delta H^{\ddagger}$ and the relatively unfavourable value of $\Delta S^{\ddagger}$.[8b]



(**I**)



(**II**)

The activation parameters for substitution contrast with those (Table 3) derived from a preliminary study of MeCN exchange at 50—75 °C.[1] However, Figure 2 shows an Eyring plot including both exchange and substitution data, and the two sets are clearly compatible. The curvature can easily be

Table 3. Activation parameters for [ligand]-independent substitution reactions of some Os_3 clusters[a]

Cluster	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}	$10^3k(25\ ^\circ C)$[b] / s^{-1}	$\sigma(k_{obs.})$ / %
$[Os_3(CO)_{11}(NCMe)]$[c]	112.4 ± 1.8	92.2 ± 6.4	80	8.1
$[Os_3(CO)_{10}(NCMe)_2]$[d]	91.3 ± 1.4	28.5 ± 4.6	19	8.3
$[Os_3(CO)_{10}(NCMe)_2]$[e]	121	117	9	
$[Os_3(CO)_{12}]$[f]	137.5 ± 1.2	31.8 ± 3.8	2×10^{-7}	

[a] All uncertainties are standard deviations derived as in ref. 8*a*. [b] Estimated from the activation parameters. [c] In toluene. [d] In *p*-xylene. [e] Quoted in ref. 1 for MeCN exchange at 50—75 °C. [f] From ref. 8*a*.

Table 4. Rate constants for reactions of $[Os_3(CO)_{10}(NCMe)_2]$ with L in *p*-xylene[a]

θ_c/°C	L	$10^3k_{obs.}$/s^{-1}					
15.0	PPh_3[b]	4.50	4.34	4.90	4.52		
15.5	PPh_3[c]	5.30	6.44	5.83	5.89	5.11	
20.2	PPh_3[c]	10.3	10.1	10.5	12.1	11.2	
24.9	PPh_3[c]	18.2	19.4	20.0	21.6	21.4	
25.5	$AsPh_3$[b]	20.0	19.5				
25.5	PPh_3[b]	18.8	18.5	18.3	19.3		
29.9	$AsPh_3$[b]	33.5	35.5	35.8			
29.9	PPh_3[b]	36.5	34.0	35.0			
34.3	PPh_3[c]	53.0	56.2	57.3	58.8	55.8	
34.5	$AsPh_3$[b]	63.0	64.0				
34.5	PPh_3[b]	60.5	63.0	66.9			
25.0	PPh_3[d]	19.3	7.08	5.49	3.19	2.14	1.72

[a] [Complex] = *ca.* 1×10^{-4} mol dm^{-3}. [b] [L] = 0.1 mol dm^{-3}. [c] $[PPh_3]$ = 0.0223, 0.0401, 0.0624, 0.0803, and 0.102 mol dm^{-3}, respectively. [d] $[PPh_3]$ = 0.01 mol dm^{-3} and $[MeCN]/[PPh_3]$ = 0, 0.125, 0.250, 0.50, 0.75, and 1.00, respectively.

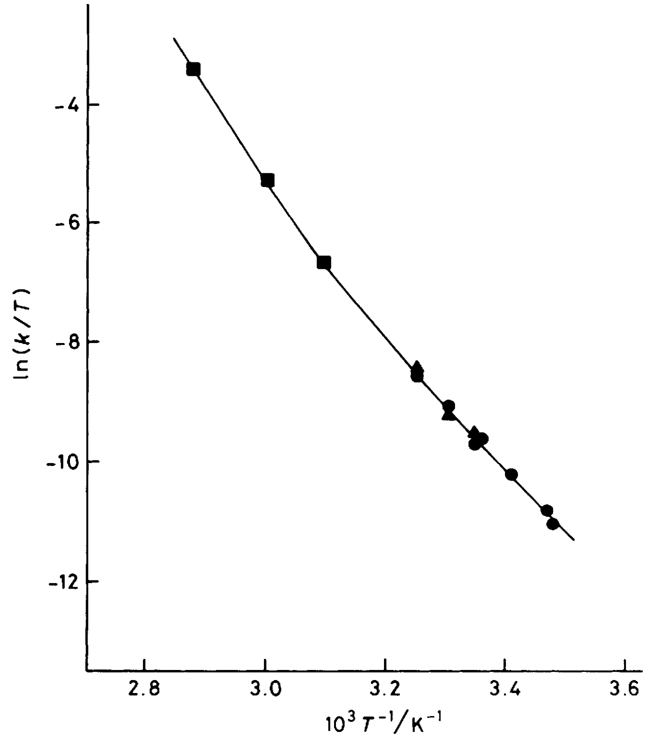


Figure 2. Eyring plot for reactions of $[Os_3(CO)_{10}(NCMe)_2]$ with PPh_3 (●) and with $AsPh_3$ (▲). (■) Values calculated from activation parameters, reported in ref. 1, for MeCN exchange at 50—75 °C. The rate constants calculated in this way were multiplied by 2.0 to allow for the fact that rate constants for exchange are based on the lifetime of ligated MeCN, *i.e.* the rate constants $k_{ex.}$ refer to the rate of breaking Os–NCMe bonds so that Rate = $k_{ex.}$[Os–NCMe] = $2k_{ex.}[Os_3(CO)_{10}(NCMe)_2]$

explained if a higher energy, non-concerted loss of NCMe can occur in parallel with the concerted path, the intermediate produced being the simple co-ordinatively unsaturated cluster (**II**).

This curvature implies that the two reaction paths occur simultaneously at 15—75 °C. The value of $\Delta H^\ddagger$ for formation of (**II**) is probably somewhat greater than 121 kJ mol^{-1}, and $\Delta H^\ddagger$ for formation of (**I**) is slightly less than 91 kJ mol^{-1}. The enthalpy difference between (**I**) and (**II**) will be given approximately by the difference in the values of $\Delta H^\ddagger$, *i.e.* $\geqslant 30$ kJ mol^{-1}, and this seems a perfectly reasonable value for the strength of attachment of the bridging CO to the otherwise co-ordinatively unsaturated Os atom. The entropy differences also reflect the tighter binding of the bridging ligand in (**I**).

The tendency for the reaction to form (**I**) may be related to the higher basicity of MeCN compared with CO. This would increase the electron density on the terminal CO ligands, make one of them a better nucleophile in the concerted displacement of the other MeCN, and strengthen the bridge when it is formed. The high value of $\Delta H^\ddagger$ for formation of (**II**) suggests that the presence of the second MeCN ligand actually stabilizes the complex towards the simple dissociative loss of MeCN to form a co-ordinatively unsaturated cluster in spite of the fact that the Os–NCMe bonds are appreciably longer in $[Os_3(CO)_{10}(NCMe)_2]$ compared with $[Os_3(CO)_{11}(NCMe)]$.[7] The reason for this is not obvious.

Finally, the fact that no $[Os_3(CO)_{10}L(NCMe)]$ is detected during formation of $[Os_3(CO)_{10}L_2]$ from $[Os_3(CO)_{10}(NCMe)_2]$ shows that, compared with MeCN, PPh_3 and $AsPh_3$ have a significant labilizing effect on the replacement of an MeCN ligand on another Os atom. This effect must be transmitted across the cluster. It cannot result from dissociation of a ligand from the Os atom to which the PPh_3 or $AsPh_3$ is attached, followed by transfer of the vacant co-ordination site to a neighbouring Os atom, as has been suggested for substituent effects on CO replacement in di- or poly-nuclear carbonyls.[14]

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