F_N2 Reactions of Some Trinuclear Metal Carbonyl Clusters

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The metal carbonyl clusters $M_3(CO)_{12-n}(PBu^n_3)_n$ (M = Os, n = 0—1, M = Ru, n = 1—2) react with PBu^n_3 by bimolecular paths that involve fragmentation to mononuclear products, and that can be given the mechanistic designation F_N2.

The fragmentation of small metal carbonyl clusters must play a basic role in the synthesis of larger clusters by pyrolysis[1] and may play an important role in catalytic reactions.[2] In spite of this, very few kinetic studies of such reactions have been reported.[3] We have studied the reactions of PBu^n_3 with the clusters $M_3(CO)_{12-n}(PBu^n_3)_n$ (M = Os, Ru; n = 0—2)† and find that all but one of them react according to the rate equation shown in (1) where $k_{obs.}$ is the pseudo first order rate constant for loss of the reacting cluster.

$$k_{obs.} = k_1 + k_2[PBu^n_3] \qquad (1)$$

Examination of the dependence of the nature of the products on $[PBu^n_3]$ and the reaction temperature shows that the paths governed by k_1 lead only to substitution whereas the $k_2[PBu^n_3]$ paths can lead exclusively to fragmentation and formation of mononuclear products. Rate parameters are shown in Table 1. The activation parameters are such that reactions of PBu^n_3 with $Os_3(CO)_{12}$ at 170 °C and fairly low values of $[PBu^n_3]$ ($\leqslant 0.1$ M) occur exclusively *via* k_1 paths to form, successively, $Os_3(CO)_{11}(PBu^n_3)$, $Os_3(CO)_{10}(PBu^n_3)_2$, and finally, $Os_3(CO)_9(PBu^n_3)_3$ in essentially quantitative yield. At 70 °C, and with high concentrations of PBu^n_3 ($\geqslant 1$ M)

reaction occurs almost exclusively by the $k_2[PBu^n_3]$ path, and with formation only of mononuclear products.‡

Reaction of $Os_3(CO)_{11}(PBu^n_3)$ also leads only to $Os_3(CO)_{10}(PBu^n_3)_2$ and $Os_3(CO)_9(PBu^n_3)_3$ at high temperatures and low $[PBu^n_3]$, whereas only mononuclear products are formed at low temperatures and high $[PBu^n_3]$ when reaction occurs solely by the $k_2[PBu^n_3]$ path. When $[PBu^n_3]$ = 0.1 M, the mononuclear products are $Os(CO)_4(PBu^n_3)$ and $Os(CO)_3(PBu^n_3)_2$ in a concentration ratio *ca.* 2:1 and this ratio is constant over the whole course of the reaction. This contrasts with the concentration ratio observed for reaction of $Os_3(CO)_{12}$. In this case the initial ratio is $\geqslant 4:1$ which suggests that $Os_3(CO)_{12}$ undergoes an appreciable amount of direct fragmentation rather than substitution to form $Os_3(CO)_{11}$-(PBu^n_3) and fragmentation of this cluster.

Reaction of PBu^n_3 ($\leqslant 0.01$ M) with $Ru_3(CO)_{12}$ at $\geqslant 60$ °C leads to formation of $Ru_3(CO)_9(PBu^n_3)_3$ in $\geqslant 80\%$ yields (the remainder being mononuclear products) whereas reaction with $\geqslant 0.2$ M PBu^n_3 at 25 °C leads quantitatively to mononuclear products.§ Even under the former conditions $Ru_3(CO)_{12}$ reacts exclusively by the $k_2[PBu^n_3]$ path[4] and this shows that nucleophilic attack by PBu^n_3 on $Ru_3(CO)_{12}$ does not lead to more than small amounts of fragmentation. On the other hand, the data in Table 2 for reactions of $Ru_3(CO)_{11}(PBu^n_3)$ show that there is an excellent correlation between the relative yields of mononuclear and trinuclear products and the ratios

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† $Os_3(CO)_{11}(PBu^n_3)$ and $Os_3(CO)_{10}(PBu^n_3)_2$ were prepared *in situ* by addition of a known excess of PBu^n_3 to solutions of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ and the complexes characterized by the agreement of their i.r. spectra with those of the corresponding PEt_3 complexes (A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1970, 897). Kinetics of reactions of $Os_3(CO)_{12-n}(PBu^n_3)_n$ in decalin were followed by monitoring changes in the i.r. spectra. $Ru_3(CO)_{11}(PBu^n_3)$ and $Ru_3(CO)_{10}(PBu^n_3)_2$ were prepared by the method of Bruce *et al.* (M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Rieger, and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 442) and characterized by their i.r. spectra. Kinetics of their reactions in dodecane were followed by i.r. and/or u.v.-visible monitoring.

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‡ Bands at 2060(m), 1 980(m), and 1 935(s) cm^{-1} were assigned to $Os(CO)_4(PBu^n_3)$, and a band at 1 880 cm^{-1} was assigned to $Os(CO)_3(PBu^n_3)_2$, by analogy with spectra of $Os(CO)_4(PPh_3)$ and $Os(CO)_3(PPh_3)_2$ (F. L'Eplattinier and F. Calderazzo, *Inorg. Chem.*, 1968, 7, 1290). Relative molar absorbance coefficients of the two complexes were obtained in solution from intensity changes during the reaction $Os(CO)_4(PBu^n_3) + PBu^n_3 \rightarrow Os(CO)_3(PBu^n_3)_2 + CO$.

§ These were characterized as in ref. 4.

Table 1. Kinetic parameters for reactions of $M_3(CO)_{12-n}(PBu^n_3)_n$ with PBu^n_3.[a]

	n = 0		n = 1		n = 2	
	Ru	Os	Ru	Os	Ru	Os
$\Delta H_2^{\ddagger}$	12.1 ± 0.2^b	20.6 ± 0.2	7.9 ± 0.3	15.0 ± 1.4	17.3 ± 2.2	—
$\Delta S_2^{\ddagger}$	-27.5 ± 0.6^b	-22.7 ± 0.6	-38.7 ± 0.9	-35.0 ± 4.3	-19 ± 7	—
$10^5 k_2$ (100 °C)	6×10^4	6	5×10^4	25	4×10^3	—
$\Delta H_1^{\ddagger}$	31.8 ± 0.2^c	32.9 ± 0.3^d	22.1 ± 0.6	39.3 ± 1.2	26.5 ± 1.1	34.7 ± 0.2
$\Delta S_1^{\ddagger}$	20.2 ± 0.6^c	7.6 ± 0.9^d	-1.1 ± 1.8	23.1 ± 3.1	11.4 ± 3.4	20.2 ± 0.6
$10^5 k_1$ (100 °C)	5×10^3	2	5×10^4	1	6×10^4	0.5

[a] Units are: $\Delta H^{\ddagger}$, kcal mol^{-1}; $\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}; k_1, s^{-1}; k_2, 1 mol^{-1} s^{-1} (1 kcal = 4.184 kJ). Rate constants at 100 °C were calculated from the activation parameters. [b] Ref. 4. [c] Ref. 7. [d] These parameters are considerably different from those published recently (A. Shojaie and J. D. Atwood, *Organometallics*, 1985, **4**, 187). However, recalculation of the parameters using the data reported therein, leads to values in good agreement with, though considerably less precise than, those reported here.

Table 2. Kinetic parameters and relative yields of mononuclear and trinuclear products from $Ru_3(CO)_{11}(PBu^n_3)$.

T/°C	$[PBu^n_3]$/M	k_2/k_1/M^{-1}	$\dfrac{3[\text{Mononucl.}]}{[\text{Trinucl.}][PBu^n_3]}$ /M^{-1}[a]
26.5	0.014—0.40	129	129 ± 4^b
40.0	0.048	40.9	40.2^c
41.0	0.014—0.40	37.9	43.0 ± 2.5^b
50.0	0.008—0.01	19.9	$20.0 \pm 1.0^{c,d}$
50.0	0.014—0.40	19.9	22.1 ± 2.8^b

[a] [Mononucl.] = $[Ru(CO)_4(PBu^n_3)] + [Ru(CO)_3(PBu^n_3)_2]$; [Trinucl.] = $[Ru_3(CO)_9(PBu^n_3)_3]$. [b] Estimated from final absorbances and measured extinction coefficients at 465 nm for each product, and the ratio, 2:1, of $[Ru(CO)_4(PBu^n_3)]:[Ru(CO)_3(PBu^n_3)_2]$. Values are averages of three measurements and the uncertainties are mean deviations. [c] Estimated from intensities of i.r. bands of the products. [d] Average of two measurements.

$k_2[L]/k_1$, *i.e.* the $k_2[L]$ path for $Ru_3(CO)_{11}(PBu^n_3)$ leads to fragmentation and the k_1 path to substitution.¶ The rate equation for the cluster $Ru_3(CO)_{10}(PBu^n_3)_2$ shows only a small $k_2[L]$ contribution to the rate but the yields of mononuclear products correlate well with this term and the relative yields of $Ru(CO)_4(PBu^n_3)$ and $Ru(CO)_3(PBu^n_3)_2$ are 1:2. Reaction of $Os_3(CO)_{10}(PBu^n_3)_2$ proceeds to $Os_3(CO)_9(PBu^n_3)_3$ only by a k_1 term and no mononuclear products are detectable.

These results show that the bimolecular reaction of a nucleophile with several of the complexes examined can lead exclusively to fragmentation but that, in other cases, nucleophilic attack can lead to substitution. Preliminary studies suggest that similar nucleophile-induced fragmentation occurs in reaction of $P(OEt)_3$ with $Ru_3(CO)_{12}$,[5] and of PBu^n_3 and $P(OEt)_3$ with $Ru_3(CO)_{10}(dppm)$ (dppm = $Ph_2PCH_2PPh_2$).[6] The factors governing the susceptibility of such carbonyl clusters to bimolecular nucleophilic fragmentation, rather than substitution, remain to be investigated but it is obvious that this susceptibility represents the 'Achilles heel' of these otherwise very hard-to-fragment compounds. Weakly nucleophilic donors lead only to substitution[6,7] and quite extreme conditions are required to produce spontaneous fragmentation.[3a,c] Some structural data are obviously of relevance. The monosubstituted complexes $Ru_3(CO)_{11}L$ [L = PPh_3[8] or $P(C_6H_{11})_3$[9]] both show a general lengthening of the Ru–Ru bonds compared with $Ru_3(CO)_{12}$ and a specific and pronounced lengthening of the Ru–Ru bond *cis* to L. A

¶ This explanation of the formation of substitution products differs from, and is, we believe, much to be preferred over, that suggested in ref. 4.

similar but smaller effect is shown in $Os_3(CO)_{11}\{P(OMe)_3\}$[10] but not in $Ru_3(CO)_{10}\{P(OMe)_3\}_2$.[9] It appears, therefore, that the relatively very pronounced susceptibility of $M_3(CO)_{11}(P-Bu^n_3)$ (M = Ru or Os) to bimolecular nucleophilic fragmentation may originate in the expanded M_3 cluster and the greater length of one of the M–M bonds in particular.

$Fe_3(CO)_{11}(PPh_3)$ appears to undergo quite facile spontaneous fragmentation.[11] $Co_4(CO)_{12}$[3b] and $Rh_4(CO)_{12}$[12] undergo CO-induced fragmentation although the former seems to undergo S_N2 reactions with PPh_3 and other donor ligands,[3f] as does $Ir_4(CO)_{12}$.[13] However, nucleophile-induced fragmentations appear to be well enough established for them to be assigned the mechanistic designation F_N2.

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