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Exceptional substitutional lability of the 'raft' cluster $Os_6(CO)_{20}NCMe$[1]

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Abstract

The kinetics of reactions of the planar 'raft' cluster $Os_6(CO)_{20}(NCMe)$ with a wide variety of P-donor ligands, L, in toluene have been studied. Replacement of NCMe by L proceeds via initial, very rapid and reversible formation of the adducts $Os_6(CO)_{20}(NCMe)L$ in a pre-equilibrium step which is followed by relatively slow disssociation of the NCMe ligand. The equilibrium and rate constants vary systematically with the electronic and steric natures of the ligands, L, in a way that suggests that bond making by the P-donors in the adducts is comparable with the increase of bond making during the dissociation of NCMe, and that the bonding in the adducts is therefore quite weak. The susceptibility of $Os_6(CO)_{20}(NCMe)$ to nucleophilic attack by the P-donors is at least 10^5 times greater than that of $Os_3(CO)_{11}(NCMe)$ while the dissociative lability of the NCMe is less by at least a factor of 100. © 1999 Elsevier Science S.A. All rights reserved.

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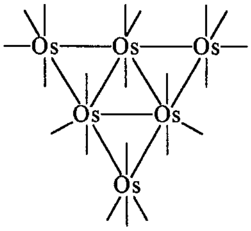
1. Introduction

The so-called raft cluster $Os_6(CO)_{21}$ and its substituted derivatives [1] are all believed to exist as a planar array of Os atoms with ligands distributed as shown schematically in I



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. They have an electron count of 90 [2] which allows each Os atom to attain the 18 electron configuration, and $Os_6(CO)_{21}$ can be regarded as having an $Os_3(CO)_9$ core to which are attached three bridging $Os(CO)_4$ moieties. In this it resembles the hypothetical isomeric form of $Os_3(CO)_{12}$ with one bridging CO group on each side of the Os_3 triangle, and the known cluster $Os_3(CO)_9(\mu\text{-}CO)(\mu\text{-}CNCF_3)_2$ [3]. It is extremely insoluble and crystallographic structure determination and study of its reactions in homogeneous solution have not proved to be possible. However, a number of substituted derivatives are known that are sufficiently soluble for crystals to be isolated ([1]d-e) and for their reactions in solution to be studied ([1]c-f). These substituted clusters show low energy electron transitions at approimately 600 nm that are consistent with there being low lying non bonding or slightly anti bonding molecular orbitals as predicted theoretically ([2]b). These facilitate two-electron reduction ([1]c) and suggest possible high susceptibility to nucleophilic attack by Lewis bases. Even the high nuclearity carbonyl cluster (HNCC) $Ru_6C(CO)_{17}$, which has two electrons more than the 18 electron rule would allow, is very susceptible to attack by P-donor nucleophiles ([5]d) so it seemed worthwhile

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[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday in recognition of his outstanding contribution to organometallic and inorganic chemistry.

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Table 1
IR data for the raft clusters $Os_6(CO)_{20}L$ in toluene

L	ν(CO) cm^{-1}							
NCMe	2023(w)	2088(s)	2071(s)	2036(s)	2021(s)	2003(m)	1995(m)	1961(m)
NCMe[a]	2108(w)	2070(s)	2061(m,sh)	2021(s)	2014(m, sh)	1998(m)	1988(m,sh)	1950(w)
$P(OMe)_3$[b]	2127(vw)	2091(s)	2075(m)	2041(vs)	2022(s)	2000(w)	1959(w)	
$P(OPh)_3$	2121(w)	2088(s)	2077(m)	2039(vs)	2023(s)	1995(w)	1959(w)	
$P(p\text{-}C_6H_4Cl)_3$	2126(w)	2093(s)	2069(m)	2042(vs)	2029(s)	2001(w)	1963(w)	
$P(p\text{-}C_6H_4CF)_3$	2127(vw)	2095(s)	2069(m)	2043(vs)	2029(s)	2002(w)	1956(w)	
$P(p\text{-}C_6H_4F)_3$	2125(vw)	2092(s)	2068(m)	2042(vs)	2029(s)	2001(w)	1960(w)	

[a] For $Os_6(CO)_{19}(NCMe)_2$.
[b] In CH_2Cl_2, from ([1]c).

to undertake a kinetic study of some substitution reactions of soluble substituted derivatives of the parent $Os_6(CO)_{21}$. In contrast to the enormous body of knowledge about the synthetic and structural aspects of HNCCs ([2]a [4]), systematic kinetic studies of HNCCs in general are still quite rare [5] and the ones of raft clusters are non existent in the current literature. We report here the results of kinetic studies of $Os_6(CO)_{20}NCMe$ with a variety of P-donor ligands and these show that this raft cluster is indeed very susceptible to nucleophillic substitution.

2. Experimental and results

2.1. Chemicals

$Os_3(CO)_{12}$ and P-donor ligands were obtained and purified if necessary exactly as described elsewhere ([5]c,d [6]). The compounds $Os_6(CO)_{21-n}(NCMe)_n$ ($n=$ 1 or 2) were prepared by the published method ([1]c,f) which leads to mixtures of these two products in high yields. In a typical preparation, $Os_3(CO)_{10}(NCMe)_2$ (0.1 g, 0.11 mmol) dissolved in CH_2Cl_2 (50 ml) was treated with a small, catalytic amount of $PdCl_2$ (0.01 g). After stirring for 3 h, the dark blue solution was filtered, concentrated and separated by chromatography on silica t.l.c. plates, and eluted with CCl_4 (75%), $CHCl_3$ (20%) and MeCN (5%) mixtures. The major products $Os_6(CO)_{20}(NCMe)$ (40% yield, blue) and $Os_6(CO)_{19}(NCMe)_2$ (30% yield, purple) are the bottom two bands on the TLC plates. The products $Os_6(CO)_{21-n}$ $(NCMe)_n$ ($n=1$ or 2) were characterized by their IR spectra (Table 1). The UV-vis spectra of the products showed a major absorbance band at 602 nm ($\varepsilon = 3.9 \times 10^3$ M^{-1} cm^{-1}.) for $n=1$ and a broad band ($\varepsilon = 3.5 \times 10^3$ M^{-1} cm^{-1}) at the same wavelength (with a shoulder on its low energy side) for $n=2$. Solid $Os_6(CO)_{20}(NCMe)$ is moderately unstable and this necessitated the frequent and tedious repetitive isolation of this product in relatively small amounts.

2.2. The course of the reactions

The starting cluster $Os_6(CO)_{20}(NCMe)$ has not so far been fully characterized by crystallography and it is not even known for certain where the NCMe substituent is. We take it, as a working hypothesis, that the NCMe ligand is on an 'outer' Os atom (as with all other substituted derivatives of $Os_6(CO)_{21}$) ([1]c,e,f) and most probably in an axial position. These assumptions do not affect the conclusions reached from the kinetic studies and, at the very least, the kinetic studies described below add materially to what we know about this cluster whatever its detailed structure may be. In those cases where subsequent reactions were slow enough to give time for FTIR spectroscopic measurements, the spectra of the initial products (Table 1) of the reactions of $Os_6(CO)_{20}(NCMe)$ with the P-donors (L) were shown to be $Os_6(CO)_{20}L$, with the new ligand in an equatorial position on one of the outer Os atoms ([1]f). The replacement of NCMe from $Os_6(CO)_{20}(NCMe)$ by L is accompanied by a shift of the band at 600 nm to slightly higher wavelengths and quite sharp isosbestic points are observed when any subsequent stages of reaction do not overlap appreciably.

2.3. Kinetics

Faster reactions were monitored by stopped flow techniques, and slower ones by making use of a Hewlett Packard diode array spectrophotometer, exactly as described elsewhere [5]. Reactions were followed by monitoring the decrease in absorbance of the band at approximately 600 nm. Dilute solutions ($5-10 \times 10^{-5}$ M) of cluster were used and the absorbance decreases during substitution varied from approximately 0.03 to as low as 0.003. In spite of this, the sensitivity of the Hi Tech stopped flow equipment was sufficient to give excellent traces of absorbance versus time and rate constants precise to 2–3%, while the data from the Hewlett Packard spectrophotometer were only slightly less precise.

Table 2
Pseudo first order rate constants for reactions of $Os_6(CO)_{20}(NCMe)$ with nucleophiles, L, in toluene at 25°C ([complex] = $(5–10)\times10^{-5}$ M)

10[etpb] (mM)	10^2k_{obs} (s^{-1})	10[P(OMe)$_2$Ph] (mM)	10^2k_{obs} (s^{-1})	10[P(p-F$_3$CC$_6$H$_4$)$_3$] (mM)	10^4k_{obs} (s^{-1})
1.37	16.0	1.26	12.2	3.32	2.59
2.73	19.7	1.89	12.9	12.1	6.70
4.10	22.3	2.52	13.6	14.1	9.50
5.47	24.3	3.78	14.9	28.0	22.2
6.84	25.7	6.30	16.0	53.6	26.5
12.3	25.8	12.6	16.0	102	38.8
17.8	25.5	25.2	16.0	207	69.9
10[P(OMe)$_3$] (mM)	10^2k_{obs} (s^{-1})	10[P(OEt)Ph$_2$] (mM)	10^2k_{obs} (s^{-1})	10[P(p-FC$_6$H$_4$)$_3$] (mM)	10^3k_{obs} (s^{-1})
2.54	11.2	0.926	11.1	15.9	16.2
3.39	12.1	1.85	15.4	25.7	25.8
5.08	13.8	2.78	18.4	51.0	42.9
6.78	14.4	4.63	19.9	65.0	54.4
11.1	14.7	13.9	21.9	94.9	71.9
13.6	15.1	18.5	21.9	129	81.3
17.0	16.0	23.2	22.2	161	86.1
42.4	17.0	46.3	21.6		
84.8	17.0				
170	17.3				
10[P(p-ClC$_6$H$_4$)$_3$] (mM)	10^3k_{obs} (s^{-1})	10[PPh$_3$] (mM)	10^3k_{obs} (s^{-1})	10[PPhCy$_2$] (mM)	10^3k_{obs} (s^{-1})
3.28	7.55	2.97	9.2	2.71	378
5.47	8.04	4.46	11.9	3.52	437
8.20	8.86	5.94	14.1	6.63	489
13.5	13.9	11.9	27.1	10.9	510
131	15.9	20.0	46.2	24.0	533
197	19.1	38.2	69.5		
328	21.0	74.2	80.4		
459	22.9				
10[P(p-MeOC$_6$H$_4$)$_3$] (mM)	10^3k_{obs} (s^{-1})		10[PPh$_2$(p-OMe)] (mM)	10^3k_{obs} (s^{-1})	
16.8	158		32.0	37.6	
33.8	180		62.9	55.2	
57.4	183		95.9	73.6	
86.1	190		189	87.2	
142	182				
284	179				

2.4. Kinetic data

The absorbance changes detected by the stopped flow instrument were analyzed by the instrument's own Data Pro software to give rate constants. Occasionally the changes had to be analyzed according to a double exponential absorbance change. Data from the Hewlett Packard spectrophotometer were transferred to a PC and analyzed by the modified [7] non linear least squares programme KORE [8], or the Enzfit programme that allowed for double exponential analysis. The rate constants are shown in Table 2.

3. Discussion

3.1. The stoichiometric mechanisms

The rate constants obtained from the initial decrease in absorbance at 602 nm (which corresponds to the formation of the monosubstituted cluster $Os_6(CO)_{20}L$) all increase with [L] to a limiting value as suggested by the data in Table 2. These increases each give an excellent fit to

$$K_{obs} = ab[L]/\{1 + b[L]\} \tag{1}$$

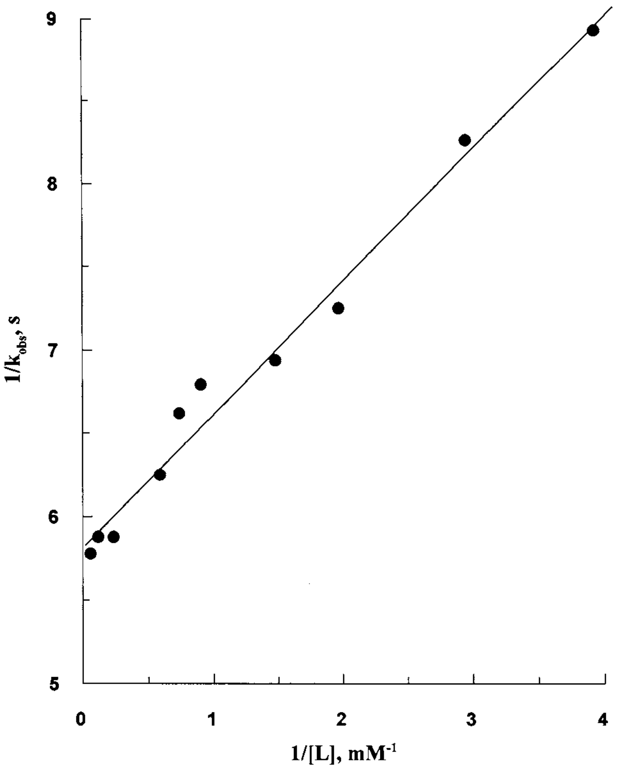

Fig. 1. 'Double inverse' plot of the data for $L = P(OMe)_3$.

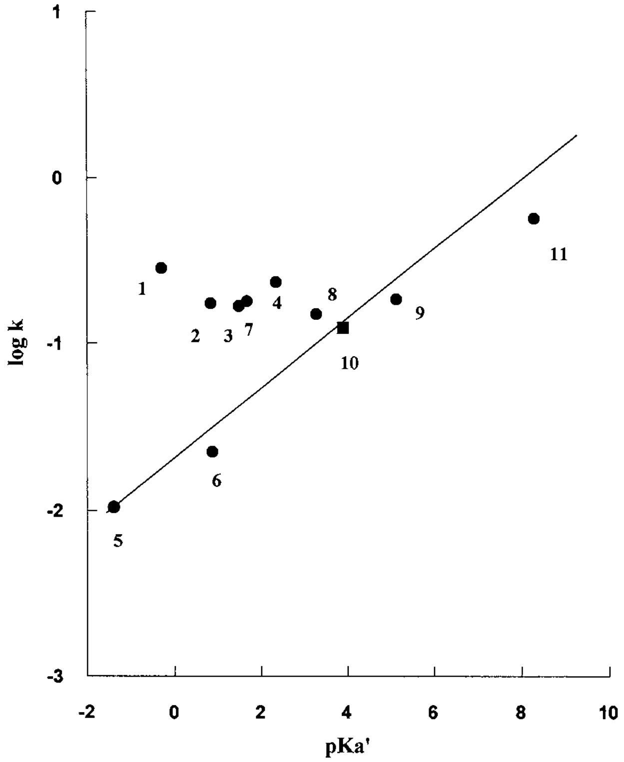

Fig. 2. Electronic profile for dissociation of NCMe from $Os_6(CO)_{20}(NCMe)L$. Ligand numbers are given in Table 3. The line is drawn through the data for the isosteric ligands with $\theta = 145°$ (ignoring those for $L = P(p\text{-}FC_6H_4)_3$ (**7**) which are clearly deviant).

where a and b are constants. Conventional 'double reciprocal' plots of $1/k_{obs}$ against $1/[L]$ are linear, as exemplified by the data for $P(OMe)_3$ in Fig. 1, and the intercepts and gradients lead to values of a and b as shown in Table 3. The values of a (the limiting rate constants at high enough values of [L] for $b[L]$ to be much greater than unity) are very dependent on the nature of the ligand L. It is therefore not possible to

Table 3
Rate and equilibrium constants for the reactions of $Os_6(CO)_{20}(NCMe)$ with nucleophiles, L, in toluene at 25°C[a]

Ligand	θ (deg)[b]	δ (ppm)[c]	pK'_a[d]	$10^3 a$ (s^{-1})[e]	$10^{-2} b$ (M^{-1})[f]	$10^{-2} ab$ (M^{-1} s^{-1})[f]	$\sigma(k_{obs})$ (%)[g]
Etpb (**1**)	101	2.60	−0.30	282(25)	96.5(11.3)	26.9(2.5)	3.5
$P(OMe)_3$ (**2**)	107	3.18	0.83	172(2)	71.7(4.7)	123.0(0.7)	2.2
$P(OMe)_2Ph$ (**3**)	120	3.48	1.48	166(3)	204.4(24.0)	34.0(3.3)	2.6
$P(OEt)Ph_2$ (**4**)	133	4.27	2.35	232(5)	108.0(10.0)	24.9(1.8)	3.8
$P(p\text{-}F_3CC_6H_4)_3$ (**5**)	145	3.10[h]	−1.39	10.5(2.4)	0.80(0.25)	0.0081(0009)	15.7
$P(p\text{-}ClC_6H_4)_3$ (**6**)	145	3.54	0.87	22.4(2.3)	12.9(3.8)	0.273(0.053)	21.4
$P(p\text{-}FC_6H_4)_3$ (**7**)	145	3.77	1.67	178(14)	0.65(0.08)	0.116(0.005)	4.3
PPh_3 (**8**)	145	4.30	3.28	150(30)	2.06(0.60)	0.307(0.025)	12.3
$P(p\text{-}MeOC_6H_4)_3$ (**9**)	145	4.43	5.13	180(50)			6.1
$PPh_2(o\text{-}MeOC_6H_4)$ (**10**)	~150[i]	~5.65[j]	~3.9[j]	123(9)[k]	1.40(0.20)[k]	0.169(0.013)	4.4
$PPhCy_2$ (**11**)	162	5.64	8.3	568(17)	81.9(13)	46.5(5.8)	3.2

[a] [complex] = $(5\text{–}10) \times 10^{-5}$ M; numbers in parentheses are estimated standard deviations for the preceding number.

[b] Tolman cone angles [14].

[c] C^{13} chemical shift in $Ni(CO)_3L$ relative to $Ni(CO)_4$ [13].

[d] Sigma basicity parameter [11].

[e] $a = k$ in Eq. (3).

[f] $b = K$ in Eq. (2).

[g] Standard error for determination of a rate constant.

[h] Value obtained from correlation of δ with pK'_a for other ligands used here.

[i] Approximate value estimated by interpolation between θ values for PPh_3 and $P(o\text{-}MeC_6H_4)_3$. Data not used in analysis using Eq. (4) but they are plotted in Fig. 3.

[j] Approximate value estimated by interpolation between PPh_3 and $P(p\text{-}MeOC_6H_4)_3$. Data not used in analysis using Eq. (4) but they are plotted in Fig. 2.

explain the rate equation by the slow formation of an isomeric form of the cluster in a steady state which can either rapidly revert to the stable form of the cluster or react with L to form the product. The rate equation for this sequence would be identical in form with Eq. (1) but the value of *a* would correspond to the rate of isomerization and would therefore be independent of the nature of L. Still less can the rate equation be explained by reversible dissociation of the NCMe ligand, followed by attack by L on the vacant coordination site so created. In this case *a* would correspond to the rate constant for dissociation of the NCMe and would again be independent of the nature of L. Moreover, the less-than-limiting rate constants would result from the reverse of the NCMe dissociation. The rate of this process would increase during the progress of the reaction as more and more NCMe is released and the rate plots would not follow the good first order behaviour that is actually observed. The only sequence of events that would provide the observed rate equation, and have values of a that depend on the nature of L, is shown in Eqs. (2) and (3):

$$Os_6(CO)_{20}(NCMe) + L \overset{K}{\rightleftharpoons} Os_6(CO)_{20}(NCMe)\ L \qquad (2)$$

$$Os_6(CO)_{20}(NCMe)L \xrightarrow{k} Os_6(CO)_{20}L + NCMe \qquad (3)$$

Eq. (2) describes the rapid formation of an equilibrium mixture of the reactants and an adduct containing the incoming nucleophile, and Eq. (3) involves dissociative loss of the NCMe ligand from the adduct. This sequence of reactions implies that the values of *b* obtained by fitting the data to Eq. (1) are equal to the equilibrium constants, *K*, for the reaction shown in Eq. (2), and the values of *a* are equal to the values of the limiting rate constants, *k*, for the reactions shown in Eq. (3). The values of both *a* and *b* will therefore depend on the nature of L, as observed, and *ab* will provide values of *kK*. Attempts to measure the rates of formation of the adducts $Os_6(CO)_{20}(NCMe)L$ by monitoring the absorbance changes over short time periods did not provide convincing evidence of such processes. Absorbance changes were sometimes observed but they were very small and the rate constants that were derived from them were not reproducible and did not vary with [L] in the way expected. It is possible that these observations were due to the presence of small amounts of impurities. We cannot, therefore, say anything about the rates of formation of the adducts except that they are very fast.

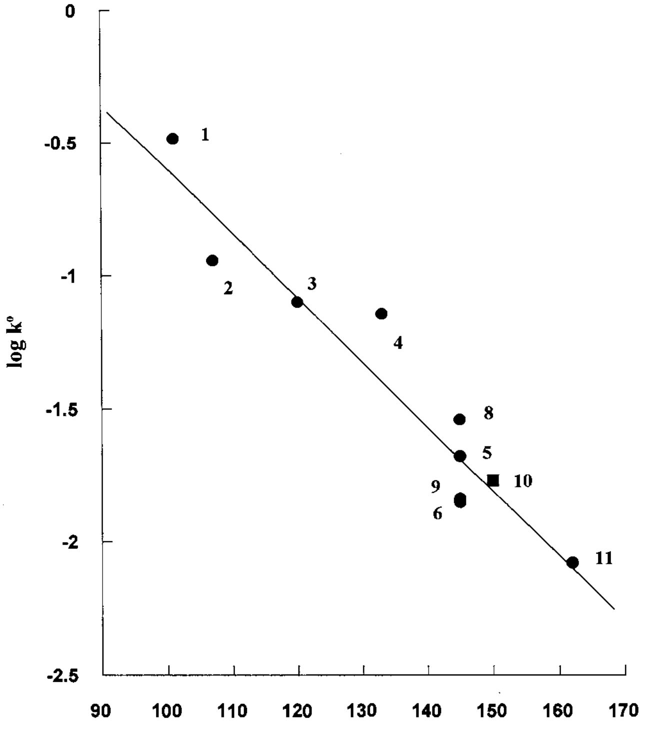

Fig. 3. Steric profile for dissociation of NCMe from $Os_6(CO)_{20}(NCMe)L$. $\log k° = \log k - \beta pK'_a$ with $\beta = 0.22$.

This proposed mechanism is similar to those deduced for the displacement of CO from $M_5C(CO)_{15}$ (M = Ru and Fe) by smaller nucleophiles ([5]b,c) apart from the important facts that, in those cases, the approach to the equilibrium mixture analogous to Eq. (2) is slow enough to be measured and the rates of loss of CO from the adducts are slow enough for ligand dissociation from the adducts to be quite distinguishable from their formation. The displacement of the NCMe ligand to form $Os_6(CO)_{20}L$ as in Eq. (3) is followed, in several cases, by a slower reaction, details of which will be reported elsewhere.

The mechanism for NCMe displacement from the $Os_6(CO)_{20}(NCMe)$ raft complex is unique, dissociative displacement being the usual mechanism in the few carbonyl cluster complexes studied. The rate constants that have been observed at 25°C for $Rh_6(CO)_{15}(NCMe)$ ([5]a), $(\mu\text{-}H)_3Re_3(CO)_{11}(NCMe)$ [9], and $Os_3(CO)_{11}(NCMe)$ [10] are 0.1, 2×10^{-4} and 8×10^{-3} s^{-1}, respectively. The high rate constant for the Rh_6 cluster must be associated with Rh being a second row transition metal and the rate for $Os_3(CO)_{11}(NCMe)$ is clearly the one most relevant to those for the raft cluster. The lowest pseudo first order rate constant observed for the raft cluster is 2.6×10^{-4} s^{-1} for its reaction with 3.3×10^{-4} M $P(p\text{-}F_3CC_6H_4)_3$. This could be as much as ten times larger than the value for NCMe dissociation, i.e. the process that is not followed, so that the rate constant for the raft cluster reacting via the dissociative path must be less than approximately 5×10^{-5} s^{-1}. This is about two orders of magnitude lower than that for $Os_3(CO)_{11}(NCMe)$ so the lability of the NCMe ligand is fairly strongly reduced by the presence of the extra three osmium atoms present in the raft cluster. On the other hand it can be estimated that the rate constant for the (non observed) associative displacement of NCMe by PPh_3 from

Table 4
Kinetic parameters obtained by application of Eq. (4) to substitution reactions of $Os_6(CO)_{20}(NCMe)$ by P-donor ligands at 25°C

Measured constant	Electronic parameter for L	log K (or k) for etpb[a]	β	γ (deg^{-1})	R^2[b]	RMSD[c]
K[d]	δ	3.96	$+1.11(0.36)$ ppm^{-1}	$-0.062(0.017)$	0.70	0.510
K[d]	pK'_a	4.13	$+0.28(0.10)$	$-0.067(0.018)$	0.67	0.540
Kk[d]	δ	3.43	$+1.89(0.32)$ ppm^{-1}	$-0.094(0.015)$	0.88	0.45
Kk[d]	pK'_a	3.46	$+0.49(0.09)$	$-0.068(0.012)$	0.87	0.472
k[e]	δ	-0.812	$+0.89(0.10)$ ppm^{-1}	$-0.037(0.005)$	0.93	0.139
k[e]	p$K_{a'}$	-0.678	$+0.22(0.03)$	$-0.024(0.004)$	0.92	0.144

[a] The parameter α in Eq. (4) has no particular meaning in these cases so the values of log K or log k for the smallest ligand used are given instead.
[b] R is the multiple correlation coefficient.
[c] RMSD is the root mean square deviation.
[d] Data for all ten ligands **1–9** and **11** were used.
[e] Data for $P(p\text{-}FC_6H_4)_3$ was clearly the only significantly deviant ligand (Fig. 2) and these data were therefore omitted from the analyses.

$Os_3(CO)_{11}(NCMe)$ must be $< \sim 10^{-2}$ M^{-1} s^{-1} whereas that for formation of the $Os_6(CO)_{20}(NCMe)(PPh_3)$ adduct must be $> \sim 10^3$ M^{-1} s^{-1}. The raft cluster is therefore at least 10^5 times more labile than $Os_3(CO)_{11}(NCMe)$ towards nucleophilic attack by P-donors.

3.2. Dependence of rates on the electronic and steric natures of the nucleophiles, L

The large number of ligands used in this study, and the wide variation in their electronic and steric properties, makes possible a separation of the contributions of their electronic and steric effects to the rate or equilibrium constants by application of the now well known and successfully applied Eq. (4) ([5]b-d) [11,12]. The parameters pK'_a ([5]d [11]) and δ [13] are,

$$\log k(\text{or } K) = \alpha + \beta\delta(\text{or } pK'_a) + \gamma(\theta - \theta_{th}) \tag{4}$$

respectively, measures of the electronic properties of the P-donors in terms of σ donicity alone, or the net electron donicity resulting from opposing σ-basicity and π-acidity. The parameter is the ligand cone angle [14] which provides a quantitative estimate of the relative ligand sizes while θ_{th} is the value of the steric threshold below which no steric effects are evident [11,12]. In the cases to be considered here, steric effects are evident for all the ligands and the value of θ_{th} is therefore always $\geq 101°$, the cone angle of the smallest ligand (etpb). The choice of which electronic parameter to use depends on the extent to which the π-acidities of the ligands contribute to the strengths of the bonds involving the P-donors. In general, if the P-donor is involved in nucleophilic attack, π-bonding is not important [11] and pK'_a is the appropriate parameter to use. However, when the P-donor is present as a fully bonded ligand in the complexes whose rates are being considered, then δ is more appropriate ([11]b). The only significant difference in the results (Table 4) lies in the values of the electronic coefficients, β, which are dimensionless when pK'_a is used but which have units of ppm^{-1} when δ is used. This results from the quite good correlation ($R^2 = 0.90$) between pK'_a and δ for the particular set of ligands used here.

The fit of the values of K to Eq. (4) is quite poor and this can be traced to values of log K for PPh_3, $P(p\text{-}ClC_6H_4)_3$ and $P(p\text{-}FC_6H_4)_3$ which deviate by ≥ 0.7 from the trend set by the other ligands. The absorbance changes in obtaining the data for these ligands are quite small and this is reflected in the values of $\sigma(k_{obs})$ (Table 3) and the uncertainties in K. However, the latter are not large enough to account for all the deviations and the reasons for their magnitude are not clear. The fit of the values of k to Eq. (4) are, by contrast, very good and this must be related to the good precision of the limiting rates that results from the relatively large number of k_{obs} values that go to determine them. Only the value of log k for $P(p\text{-}FC_6H_4)_3$ is deviant (by 0.54) and the fit, and the uncertainties (though not the values) of the derived parameters, improves significantly when data for this ligand are ignored.

3.3. The intimate mechanisms

The parameters derived by application of Eq. (4) to the equilibrium and kinetic data reported here allow consideration of the intimate details of the processes involved in the displacement of the NCMe ligand. Substitution reactions of CO by P-donors in some other high nuclearity carbonyl clusters also occur via initial formation of adducts ([5]b,c). This is believed to be accompanied by breaking of one metal-metal bond in the cluster and formation of a new metal–L bond, followed by loss of a CO ligand from the adduct and reformation of the broken metal–metal bond. Adducts of this sort have been characterized spectroscopically and even crystallographically for $M_5C(CO)_{15}$ (M = Ru and Os) [15].

The situation here is unique in that the ligand displaced from the adduct is NCMe and not CO, and it is convenient to look first at the parameters obtained for the loss of NCMe from the adduct. Values of β for dissociative loss of CO from mononuclear carbonyls are generally positive but quite small ($< \sim 0.1$ ppm^{-1}) [16]. This must arise because the electron density on the metal decreases only slightly as the CO ligand leaves, the loss of σ-donated electrons being largely offset by the recovery of electrons removed by back donation. In the clusters $Ru_5C(CO)_{15}L$ ([5]c) and (μ-H)(H)$Os_3(CO)_{10}L$ ([11]b) the values for CO loss are actually substantially negative (-0.2 and -0.09 ppm^{-1}, respectively) and this was accounted for by the way in which reformation of metal–metal bonds accompanied the loss of CO. By contrast the value of β for loss of NCMe from $Os_6(CO)_{20}(NCMe)L$ is fairly large and positive. In this case the loss of electron density that had been σ-donated to the metal is not offset by regaining electrons that had been removed by back donation since no such back donation occurs in metal–NCMe bonds. Increasing basicity of the P-donor ligands can therefore be taken advantage of by increasing strengths of the Os–P bonds. Any contribution from renewed Os–Os bonding would have acted in the opposite direction, and this suggests that the adduct does not contain a fully broken Os–Os bond that reforms as the NCMe leaves.

Steric effects of substituents on the loss of NCMe would not be expected to be very different from those for loss of CO, and values of γ for the latter are generally positive for mononuclear carbonyls as is reasonable. For the adducts of the metal carbonyl clusters $M_5C(CO)_{15}L$ (M = Ru and Fe) ([5]b,c) the values of are appreciably negative (-0.04 and -0.06 deg^{-1}, respectively) because of the occurrence of renewed metal–metal bonding as the CO leaves. The value of γ for loss of NCMe from $Os_6(CO)_{20}(NCMe)L$ is also negative (-0.04 deg^{-1}) but this could be ascribed to the shortening of the Os–P bonds, and the growing interligand repulsion as they grow stronger, rather than to Os–Os bond formation.

Turning now to the parameters for initial formation of the adducts, we note that no systematic measurements of equilibrium constants for formation of adducts between P-donors and metal carbonyl clusters have been reported elsewhere. It would be more usual to use δ as the electronic parameter describing the electronic nature of the P-donor ligand in such reactions because of the contribution of π-acidity in completely formed bonds. However, the value of β obtained by using pK'_a as the electronic parameter is useful because it can be compared with β values obtained from rate constants for related associative reactions. The value of β (0.28) obtained in this way for complete formation of the adduct is comparable to the values for the partial formation of metal–P bonds in the transition states for adduct formation by $M_5C(CO)_{15}$ (M = Ru and Fe, 0.2 and 0.3, respectively) ([5]b,c). We therefore conclude that the bonding of the P-donors in the adducts is quite weak and that it is most unlikely that complete Os–P bond formation has occurred or, as a consequence, that Os–Os bond breaking is complete either. It also follows that π-acidity could be negligible in the adducts so that the use of pK'_a as the electronic parameter was appropriate after all.

Coupled with the very fast rates of adduct formation, and the small absorbance changes that accompany it, this leads to the view that the adducts in this case are quite different from those previously observed for HNCCs ([5]b,c [16]). It may be that electrons from the P-donor ligands are donated into an empty low lying molecular orbital ([2]b) extending over the Os_6 'surface'. This can act as a site of attachment of the incoming ligand, preparatory to NCMe dissociation, so that it is suitably positioned to replace the NCMe ligand when the latter leaves. Even this weak attachment has to involve some distortion of the ligands on the Os_6 surface since the value of γ for adduct formation is appreciably negative.

4. Conclusions

Reactions of the unusual raft cluster $Os_6(CO)_{20}(NCMe)$ with P-donor ligands, L, are unique in both their stoichiometric mechanisms and their very high rates.

The displacement of NCMe from $Os_6(CO)_{20}(NCMe)$ by P-donor ligands occurs via very rapid and reversible initial formation of adducts between the cluster and the P-donor. The dependence of the equilibrium constants on the electronic and steric natures of the P-donors suggests that complete formation of an Os–P bond and compensating breaking of an Os–Os bond does not occur on forming these adducts. Some sort of weaker interaction, possibly involving donation into an empty molecular orbital, delocalized over the 'Os_6 surface', might be occurring instead.

The rates of formation of the adducts show that this raft cluster is over 10^5 more susceptible to nucleophilic attack by P-donor nucleophiles, but at least 100 times less susceptible to NCMe dissociation, than $Os_3(CO)_{11}(NCMe)$.

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