

# Complex Kinetics of “Simple” Substitution Reactions of $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$ with Smaller P-Donor Nucleophiles

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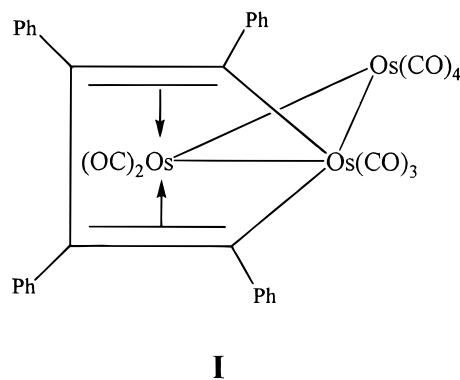
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The osmacyclopentadiene ring in the triangular  $\text{Os}_3$  cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  bridges two of the Os atoms and is found to activate associative attack at the third Os atom (which is in an  $\text{Os}(\text{CO})_4$  moiety) by a factor of  $\sim 10^9$  compared with reactions of the parent cluster  $\text{Os}_3(\text{CO})_{12}$ . The overall reactions in heptane of 17 P-donor nucleophiles with Tolman cone angles  $\theta \leq 143^\circ$  lead to substitution at the  $\text{Os}(\text{CO})_4$  center in three rapid but kinetically observable stages: (i) reversible attack by a nucleophile to form an adduct in which an Os–Os bond in the cluster has been broken, (ii) loss of CO and formation of a new closed  $\text{Os}_3$  cluster, and, usually, (iii) isomerization of the initially formed cluster to form the final substituted product. The dependence of the rates on the  $\sigma$ -basicity and size of the nucleophiles shows that the standard reactivity toward adduct formation is very high, only high nuclearity clusters that contain encapsulated C atoms being known to react faster. Nucleophiles with  $\theta \leq 120 \pm 4^\circ$  react at rates that are independent of their size and that increase substantially with their  $\sigma$ -basicity. When the cone angles are larger, steric retardation is observed. Equilibrium constants for adduct formation by 14 of the nucleophiles were obtained from the rates of adduct formation and loss of L from the  $\text{Os}_3(\text{CO})_9\text{L}(\mu\text{-C}_4\text{Ph}_4)$  adducts and by two other methods. Loss of CO or L from the adducts becomes slower the greater the net donicity of the ligands but is essentially independent of ligand size. Rates of isomerization of the initial product are not very precise and are not appreciably sensitive to the nature of the ligands. Activation parameters were obtained for reactions involving five of the nucleophiles, and these, together with the magnitudes of the electronic and steric effects, can lead to estimates of the contributions of bond making and bond breaking in the transition states.

## Introduction

The interaction of alkyne substrates with transition metal carbonyl clusters has attracted a great deal of interest over the past two decades.<sup>1</sup> One of the major reasons has been the desire to use cluster-bound substrates as model systems to gain an understanding of reactions between unsaturated organic absorbates on catalytic metal surfaces.<sup>2</sup> Alkyne substrates show a wide variety of bonding modes toward dinuclear complexes or small metal carbonyl clusters,<sup>2,3</sup> and reactions of  $\text{C}_2\text{-Ph}_2$  with  $\text{Os}_3(\text{CO})_{12}$  lead to several of these.<sup>3–5</sup> Thus,  $\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{Ph}_2)$  is formed initially,<sup>5</sup> followed by  $\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_2\text{Ph}_2)$ <sup>4a,5</sup> and then  $\text{Os}_3(\text{CO})_9(\eta^2\text{-C}_2\text{Ph}_2)(\mu\text{-C}_2\text{Ph}_2)$ <sup>5</sup> in which the two  $\text{C}_2\text{Ph}_2$  ligands rapidly couple to form  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$ .<sup>4b</sup> The structure is shown

schematically as **I**, which contains an osmacyclopentadienyl ring. Loss of CO and uptake of a third  $\text{C}_2\text{Ph}_2$



molecule lead to  $\text{Os}_3(\text{CO})_8(\eta^2\text{-C}_2\text{Ph}_2)(\mu\text{-C}_4\text{Ph}_4)$  and then  $\text{C}_6\text{Ph}_6$ .<sup>4c,5</sup> On the other hand, reaction with CO leads to facile fragmentation of cluster **I**<sup>5</sup> to form  $\text{Os}_2(\text{CO})_6(\mu\text{-$

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$\text{C}_4\text{Ph}_4$ )<sup>4d,e</sup> and  $\text{Os}(\text{CO})_5$ .<sup>4f</sup> Thus, reactions of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{C}_2\text{Ph}_2$  not only lead to products with a wide variety of types of cluster–alkyne bonding but also illustrate the facility with which C–C coupling can occur at metal “nanosurfaces”. The cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  is a crucial exemplary intermediate in this series of reactions in that C–C coupling has been involved in its formation and further C–C coupling occurs after substitution of another  $\text{C}_2\text{Ph}_2$  molecule. Its substitution reactions are therefore of interest mechanistically, and also kinetically in being capable of showing the quantitative effect of the osmacyclopentadiene moiety on the reactivity at one of the Os atoms.

The main reactions known to be undergone by this cluster comprised, until recently,<sup>6</sup> slow CO dissociation to form  $\text{Os}_3(\text{CO})_8(\mu\text{-C}_4\text{Ph}_4)$ <sup>4c</sup> and associative fragmentation by CO or  $\text{PPh}_3$  to form mixtures of binuclear and mononuclear products.<sup>5</sup> For substitution to be accomplished via the CO dissociative path the  $\text{Os}_3(\text{CO})_8(\mu\text{-C}_4\text{Ph}_4)$  had to be formed first and the substituting ligand added afterward so as to avoid the much more rapid direct associative fragmentation of the  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  by  $\text{PPh}_3$  or similar ligands.<sup>5,6</sup> However, it has been reported<sup>6</sup> that rapid associative substitution by P-donor ligands can occur directly into  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  provided that the Tolman cone angles,  $\theta$ , of the P-donors are  $\leq 143^\circ$ .<sup>6</sup> The products of reactions with  $\text{P}(\text{OCH}_2)_3\text{CEt}$  (etpb) and  $\text{P}(\text{OPh})_3$  were shown crystallographically<sup>6</sup> to result from substitution at the  $\text{Os}(\text{CO})_4$  moiety, and the other 16  $\text{Os}_3(\text{CO})_8\text{L}(\mu\text{-C}_4\text{Ph}_4)$  clusters isolated can be concluded to have similar structures.<sup>6</sup> Qualitative observation of the course of these reactions suggested that rapid formation of  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)\text{-L}$  adducts occurred before CO loss to form the substituted products. Similarly rapid formation of adducts with  $\text{M}_5\text{C}(\text{CO})_{15}$  ( $\text{M} = \text{Ru}, \text{Fe}$ ) has been observed,<sup>7,8</sup> and we report here a detailed kinetics study of the reactions of 17 P-donor nucleophiles with  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$ , which turn out frequently to occur in three rather than two observable stages. Rate constants for the initial formation of the adducts show a clear and quantitatively resolvable dependence on the  $\sigma$ -basicity and size of the nucleophiles, and the rates of other reactions are also found to vary systematically with the nature of the ligands involved. The osmacyclopentadienyl moiety is found to activate associative substitution reactions with P–n-Bu<sub>3</sub> by a dramatic factor of  $10^9$  compared with those of the parent cluster  $\text{Os}_3(\text{CO})_{12}$ .

## Experimental Section

The sources and treatment of reagents and the synthesis of  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  were exactly as described elsewhere.<sup>6</sup> Solvents were bubbled with Ar for 1 h after distillation and stored under Ar or were degassed by means of at least three freeze–pump–thaw cycles after distillation and before use. Infrared spectra were measured on a Nicolet 10DX FTIR spectrophotometer. UV–vis spectroscopy and monitoring of slower reac-

tions were carried out with a Hewlett-Packard 8452 diode array spectrophotometer equipped with a cell holder thermostated by a water bath ( $\pm 0.1^\circ\text{C}$ ). Faster reactions were monitored by stopped-flow measurements with a Hi-Tech SF-51 instrument that was equipped with an SU-40 spectrophotometer interfaced with a Hewlett-Packard Series 300 computer. Solutions were prepared as described elsewhere.<sup>7</sup> Concentrations of complex were  $\sim 10^{-4}$  M, and nucleophiles were always in pseudo-first-order excess. Rate constants for slower reactions that showed simple one-stage first-order dependence on [complex] were analyzed by means of a modified<sup>9</sup> KORE program,<sup>10</sup> and slower reactions that occurred via two successive first-order steps were analyzed by use of an Enzfite program. Stopped-flow data were processed by using a Hi-Tech HS-1 Technical Datapro software suite, which provides a package for complete data acquisition, presentation, and analysis. A single or double exponential analysis with a fluctuating end point was successfully used to obtain the pseudo-first-order rate constants.

## Results

**The Rate Constants.** The cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  shows a fairly sharp absorbance maximum at 420 nm ( $\epsilon \approx 8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a broad maximum at ca. 570 nm ( $\epsilon \approx 3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). At 420 nm the absorbance always decreased rapidly during the first stage of reaction and less rapidly during subsequent stages. However, at  $\sim 570$  nm the initial rapid decrease in absorbance was followed by an increase to a final value comparable with the initial absorbance, and this sequence of absorbance changes, and their magnitudes, made it more convenient to monitor the reactions at this wavelength. The absorbance bands of the substituted products were virtually the same as those of the unsubstituted cluster. The rates of the first steps were generally sufficiently fast, compared with those of any subsequent ones, for their observed rate constants ( $k(1)$ ) to be obtainable by simple first-order analysis of the absorbance decrease. The subsequent absorbance increase almost always occurred in two stages, and in cases where the third stage was relatively quite slow and its absorbance change quite small, single-exponential analysis of the second stage was possible to give  $k(2)$ . However, when the rates of the second and third steps were more comparable, double-exponential analysis of the data was necessary and provided values of both  $k(2)$  and  $k(3)$ . Figure 1a shows an example of the decreasing absorbance during the first stage of a reaction, and b and c show how a double-exponential analysis is sometimes needed for the absorbance growth during the second and third stages. The rate constant  $k(3)$  for the third step is sometimes hard to determine accurately (especially when the absorbance changes are small) because of the uncertainty of the final absorbance value. However, the existence of that step is quite clear, and the double-exponential analysis provides precise values for the rate constant of the second step. Rate constants for reactions with etpb are given in Table 1.

There is an inherent ambiguity<sup>11</sup> in the analysis of kinetic data in terms of two successive exponential changes in the time-dependent absorbance,  $A_t$ , and this has to be considered. The rate equation when any

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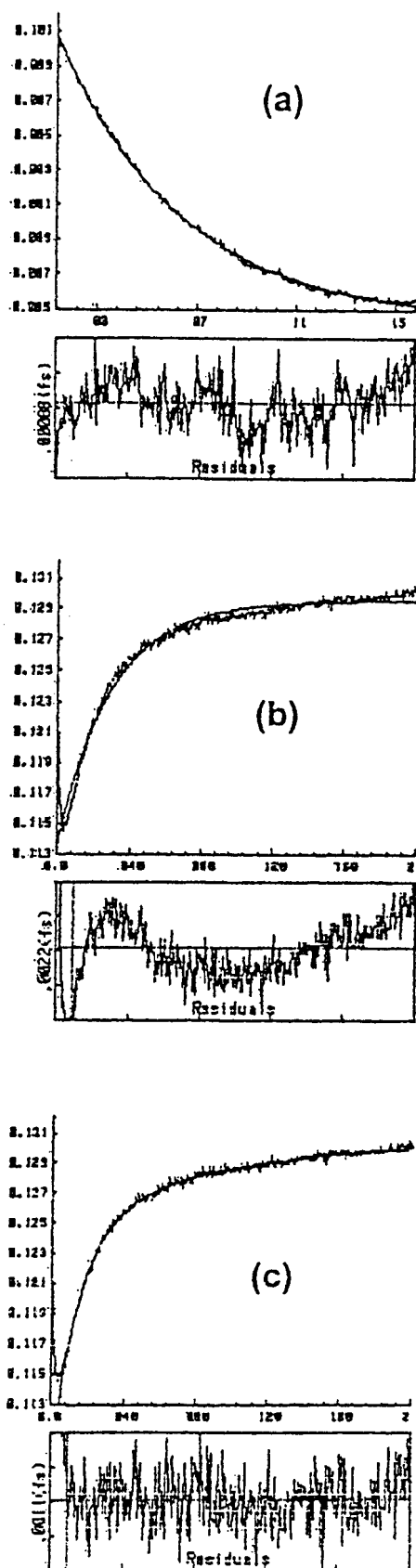
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**Figure 1.** (a) Stopped-flow trace of reaction of P(OMe)<sub>3</sub> at 13.6 °C (single-exponential analysis; absorbance change ( $\Delta A$ ) = 0.006). (b) Stopped-flow trace of reaction with etpb at 22.0 °C (single-exponential analysis;  $\Delta A$  = 0.018). (c) Same as b but with double-exponential analysis. (These traces have been scanned in directly from the stopped-flow printout.)

**Table 1. Rate Constants for the Reactions of Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -C<sub>4</sub>Ph<sub>4</sub>) with Etpb in Heptane<sup>a</sup>**

<i>T</i> , °C	[L], mM	<i>k</i> (1), s <sup>-1</sup>	10 <sup>4</sup> <i>k</i> (2), s <sup>-1</sup>	10 <sup>4</sup> <i>k</i> (3), s <sup>-1</sup>
7.3	1.23	0.217	220	
7.3 <sup>b</sup>	1.39		201	33
7.3 <sup>b</sup>	2.08		221	21
7.3 <sup>b</sup>	2.78		318	32
7.3	2.87	0.219	322	
7.3 <sup>b</sup>	3.47		376	30
7.3 <sup>b</sup>	4.16		348	25
7.3	4.95	0.257		
7.3 <sup>b</sup>	5.56		485	39
7.3	6.45	0.284	617	
7.3 <sup>b</sup>	6.94		501	31
7.3	8.13	0.308		
7.3	12.1	0.355		
7.3	15.1	0.393		
13.6 <sup>b</sup>	1.22		360	93
13.6 <sup>b</sup>	2.04		378	66
13.6	2.04	0.379	345	92
13.6 <sup>b</sup>	2.76		510	85
13.6	2.76	0.407	460	89
13.6	3.74	0.423	599	65
13.6	5.14	0.458	754	86
13.6	6.46	0.481	883	62
13.6	8.23	0.537	994	68
13.6	9.76	0.58	1130	63
13.6	11.5	0.597	1200	37
13.6	12.6	0.633	1340	33
22.0	2.17	0.812	502	108
22.0	2.87	0.835	670	88
22.0	4.95	0.90	1000	80
22.0	6.45	0.97	1250	72
22.0	8.13	1.05	1600	88
22.0	12.1	1.19	1320	82
22.0	15.1	1.29	1690	77

<sup>a</sup> Reactions monitored by stopped-flow techniques at 572 nm unless otherwise indicated. <sup>b</sup> Reactions monitored with the H.P. UV-vis spectrophotometer.

species A (which has an absorbance  $A_A = A_0$  when only A is present) changes to species B (absorbance  $A_B$  if only pure B is present) and then C (absorbance  $A_C = A_\infty$ ) is shown in eq 1.

$$A_\infty - A_t = \alpha \exp(-k(2)t) + \beta \exp(-k(3)t) \quad (1)$$

where

$$\alpha = \{(A_B - A_A)k(2) + (A_A - A_0)k(3)\}/(k(3) - k(2)) \quad (2)$$

and

$$\beta = (A_C - A_B)k(2)/(k(3) - k(2)) \quad (3)$$

The two exponential changes that are being considered here correspond to the second and third of the three steps involved in the overall reaction so the two rate constants are designated as  $k(2)$  and  $k(3)$ . It turns out<sup>11</sup> that there are two possible solutions to eq 1, and one cannot, in the first instance, distinguish which of the rate constants,  $k(2)$  and  $k(3)$ , actually corresponds to which stage of the reaction. However, there are tests that can sometimes be applied<sup>11</sup> that enable a distinction to be made, and these show that the first of the two exponential increases does indeed correspond to the second stage in the overall process. The tests can be demonstrated by making use of eq 4 to calculate the relative absorbances of B and C.

$$A_B/A_C = 1 - (k(3) - k(2))\beta/A_\infty k(2) \quad (4)$$

All the terms on the right-hand side are provided by the initial solution to eq 1. If the values of  $k(2)$  vary with  $[\text{L}]$  (as do the values of  $k(2)$  in Table 1), the ratios  $A_B/A_C$  must still be constant at all values of  $[\text{L}]$  if the rate constants  $k(2)$  and  $k(3)$  are correctly assigned to the formation of B and C, respectively. If those rate constants are not properly assigned, then the ratio will show a pronounced dependence on  $[\text{L}]$ . In that case eq 5 will provide the correct absorbance ( $A_{B'}$ ) for the

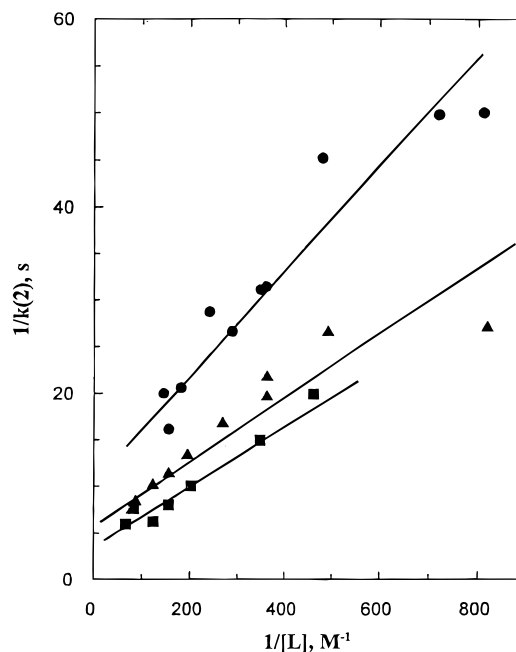
$$A_{B'} = A_A + (A_B - A_A)k(2)/k(3) \quad (5)$$

intermediate B'.  $A_B$  and  $A_{B'}$  cannot both be constant with varying  $[\text{L}]$ . Thus the data in Table 1 for the reactions with etpb at 13.6 °C and  $[\text{etpb}] = 1.221$  and 12.58 mM ( $k(2)/k(3) = 4.0$  and 40.6, respectively) show values of  $A_B/A_C = 0.93$  and 0.94. At 22.0 °C and  $[\text{etpb}] = 2.171, 4.947, 8.129,$  and 15.11 mM (values of  $k(2)/k(3) = 4.6, 12.5, 18.2,$  and 21.9, respectively) the values of  $A_B/A_C$  are all constant at 0.96, and the values of  $A_{B'}$  are not at all constant. This shows that the values of  $k(2)$  for etpb in Table 1 are genuinely applicable to the second stage of the overall reaction.

Even if neither of the rate constants is dependent on  $[\text{L}]$ , an assignment can be made on the basis of estimates of  $A_B$  and  $A_{B'}$  and an evaluation of which is the more reasonable.<sup>11</sup> For  $\text{L} = \text{etpb}$ , where we know that the assignment is correct, and in the region of  $[\text{L}]$  where  $k(2)$  is constant, the absorbance increases typically from A to B by ~80% of the overall increase from A to C. On the other hand the values derived for  $A_{B'}$  show that the absorbance would increase by a factor of more than 10 from A to B' and decrease by almost as much from B' to C. For  $\text{L} = \text{P}(\text{O}-i\text{-Pr})_3$ , where the dependence of  $k(2)$  on  $[\text{L}]$  is not nearly as pronounced as for  $\text{L} = \text{etpb}$ , the absorbance increase from A to B is 75% of the overall change, whereas the increase from A to B' would be twice the overall increase, with a large decrease on formation of C. For  $\text{L} = \text{PEt}_3$ , where  $k(2)$  does not change at all with  $[\text{L}]$ , the absorbance increase from A to B is about 30% of the total change, whereas for A to B' the absorbance would increase by a factor of 2.5 compared to the overall change and decrease by a factor of 1.5 from B' to C. The results are almost identical for  $\text{L} = \text{P}-n\text{-Bu}_3$  and  $\text{PCy}_2\text{H}$ . We can therefore conclude again that the original assignment of the intermediate to B rather than B' is correct, and we take this to be generally true for all these reactions.

The rate constants  $k(1)$ ,  $k(2)$ , and (where available)  $k(3)$  are tabulated in Table 1 and in tables of the Supplementary Information, and they can be assigned unambiguously to three successive stages of reaction beginning with  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  and ending with  $\text{Os}_3(\text{CO})_8\text{L}(\mu\text{-C}_4\text{Ph}_4)$ .<sup>6</sup>

All but two of the nucleophiles studied behave in the way described above, but  $\text{P}(\text{OPh})_3$  and  $\text{PPh}_2\text{H}$  behave differently. At 13.6 and 21.6 °C and with values of  $[\text{P}(\text{OPh})_3]$  below ~20 mM, a double-exponential analysis for the first rapid decrease in absorbance is required and the rate constants obtained are rather erratic. However, at higher values of  $[\text{P}(\text{OPh})_3]$  and at all three temperatures, single-exponential absorbance decreases are found as for all the other nucleophiles (see below). Another complication that is unique to this nucleophile is that what appear to be reliable values for  $k(3)$  are



**Figure 2.** Plots of  $1/k(2)$  against  $1/[\text{L}]$  for reactions with  $\text{L} = \text{etpb}$  at 7.3 (●), 13.6 (▲), and 22.0 (■) °C.

obtained at 7.6 °C, but unlike the situation with all other values of  $k(3)$ , these show a dependence on  $[\text{P}(\text{OPh})_3]$ . Apart from these unusual features, which have not been explored further, the systematic variations of the values of  $k(1)$  are in accord with the systematic variations shown by the other nucleophiles (see below). With  $\text{PPh}_2\text{H}$  the initial decrease in absorbance gives very precise values for  $k(1)$ . However, this decrease is followed by a further decrease that leads to rate constants showing a complex dependence on  $[\text{PPh}_2\text{H}]$  that is probably due to the observed partial decomposition of this nucleophile. This decomposition does not affect the eventual formation of the substituted product,<sup>6</sup> but it does affect the kinetics.

The values of  $k(1)$  always increase linearly with  $[\text{L}]$  according to eq 6 and values of  $k(1)_a$  and  $k(1)_b$  were

$$k(1) = k(1)_a + k(1)_b[\text{L}] \quad (6)$$

obtained by a weighted linear least-squares analysis<sup>7,12</sup> and are shown in Table 2. Values of  $k(2)$  are also frequently dependent on  $[\text{L}]$ , but in the way shown in eq 7.

$$k(2) = ak(2)_{\text{lim}}[\text{L}]/\{1 + a[\text{L}]\} \quad (7)$$

Values of  $k(2)_{\text{lim}}$  can be estimated by a weighted linear least-squares analysis of the dependence of  $1/k(2)$  on  $1/[\text{L}]$  (Figure 2) and are also shown in Table 2. Values of  $k(3)$  (Table 2) are always independent of  $[\text{L}]$  within the precision of their determination. Rate constants obtained by monitoring at 382 nm were in quite good agreement with those based on 570 nm monitoring apart from the value of  $k(1)_a$  for  $\text{P}(\text{OMe})\text{Ph}_2$ , which is very high. When the rate constants for the second stage were of the right magnitude, it was possible to obtain values from both Hewlett-Packard and stopped-flow measurements and the agreement was also good. The

**Table 2. Kinetic Data for the Reactions of Os<sub>3</sub>(CO)<sub>9</sub>(μ-C<sub>4</sub>Ph<sub>4</sub>) with L in Heptane, at 13.6 °C and Monitored at 570 nm (unless otherwise indicated)**

no. <sup>a</sup>	L	pK <sub>a</sub> ' <sup>b</sup>	θ <sup>c</sup> (deg)	k(1) <sub>b</sub> (M <sup>-1</sup> s <sup>-1</sup> )	10 <sup>3</sup> k(1) <sub>a</sub> (s <sup>-1</sup> )	σ(k(1)) <sup>d</sup> (%)	10 <sup>3</sup> k(2) <sub>lim</sub> (s <sup>-1</sup> )	σ(k(2)) <sup>d</sup> (%)	10 <sup>4</sup> k(3) (s <sup>-1</sup> )	σ(k(3)) <sup>d</sup> (%)
1	etpb	-0.30	101	13.5 ± 0.8 <sup>e</sup>	192 ± 6	3.2(7)	97 ± 17	12.6(10)	30.1 ± 2.2	19(7)
				22.8 ± 0.7	338 ± 5	1.6(9)	141 ± 5	11.3(8)		
				37.9 ± 1.0 <sup>f</sup>	726 ± 7	1.1(7)	240 ± 16	3.7(9)		
2	P(OMe) <sub>3</sub>	0.83	107	20.0 ± 0.7	173 ± 8	6.1(11)	202 ± 38	17(12)	175 ± 7	11(8)
				32.3 ± 0.4	120 ± 4	3.3(14)	71.3 ± 2.9	10.5(12)	40 ± 2	16(10)
3	P(OEt) <sub>3</sub>	1.64	109	24.0 ± 0.5 <sup>e</sup>	67 ± 5	4.3(8)	39 ± 2	9.9(10)	40 ± 2	16(10)
				44.6 ± 1.3 <sup>g</sup>	219 ± 14	5.9(8)	167 ± 5	3.6(6)	204 ± 11	11(4)
4	P(OMe) <sub>2</sub> Ph	1.48	120	18.9 ± 0.5 <sup>h</sup>	49 ± 4	7.5(13)	26.0 ± 0.66	5.2(12)	117 ± 10	26(9)
				21.7 ± 0.7	81 ± 5	6.8(12)	51 ± 1	3.8(12)	115 ± 8	28(12)
				29.8 ± 0.8 <sup>f</sup>	205 ± 9	4.9(11)	160 ± 19	14(8)	270 ± 9	10(9)
5	P(OEt) <sub>2</sub> Ph	1.99	121	25.3 ± 0.4	71 ± 3	4.2(12)	39 ± 2	8.2(10)	95 ± 6	19(10)
6	PMe <sub>2</sub> Ph	5.07	122	141 ± 2	41 ± 10	4.8(13)	38.5 ± 0.2	1.4(7)		
7	PPh <sub>2</sub> H	0.52	126	33.4 ± 1.2	440 ± 20	5.7(13)				
8	P(OPh) <sub>3</sub>	-2.79	128	1.84 ± 0.07 <sup>i</sup>	86 ± 4	4.8(7)	34.1 ± 2.4	5.3(6)		
				2.64 ± 0.1	104 ± 5	4.7(10)	35 ± 5	23(11)		
				3.98 ± 0.26 <sup>j</sup>	193 ± 20	5.4(5)	78 ± 25	23(10)		
9	P(O-i-Pr) <sub>3</sub>	3.38	130	31.3 ± 0.5	70 ± 3	3.6(13)	31.3 ± 0.4	3.0(13)	108 ± 4	12(11)
10	P(OMe)Ph <sub>2</sub>	2.09	132	11.5 ± 0.7	21 ± 3	11.1(10)	114 ± 3	8.7(9)	~50	
				13.4 ± 0.7 <sup>k</sup>	113 ± 5 <sup>k</sup>	6.3(11)	106 ± 3 <sup>k</sup>	7.6(10)		
11	PEt <sub>3</sub>	7.96	132	92.4 ± 4.1	~0	12.0(9)	9 ± 1	24(7)	15 ± 1	17(8)
12	P(n-Pr) <sub>3</sub>	8.57	132	40.1 ± 1.2	~0	9.6(6)	4.2 ± 0.4	24(6)	20 ± 1	8(8)
13	P(n-Bu) <sub>3</sub>	8.67	132	45.3 ± 1.2	~0	6.9(13)	17.5 ± 2.0	15(5)	11 ± 1	19(6)
14	P(OEt)Ph <sub>2</sub>	2.35	133	10.2 ± 0.1	22.4 ± 1.0	2.6(10)	10.0 ± 0.2 <sup>l</sup>	5.1(7)		
				68.2 ± 1.4 <sup>j</sup>	88.5 ± 6.6	4.7(9)	14 ± 1	17(9)	~5	
15	PMePh <sub>2</sub>	4.06	136	40.5 ± 1.6 <sup>n</sup>	17.8 ± 1.6	13.2(12)	2.7 ± 0.1	10(5)	~0.1	
				49.5 ± 1.4	38 ± 6	7.6(14)	5.5 ± 0.2	13(28)	~0.4	
				21.8 ± 1.1	13 ± 4	11.0(10)	24.0 ± 0.8 <sup>l</sup>	14.2(17)		
16	PEtPh <sub>2</sub>	4.60	140	21.8 ± 1.1	13 ± 4	11.0(10)	31.1 ± 0.9 <sup>m</sup>	8.0(7)		
							~15		14.2 ± 1.1	23(9)
17	PCy <sub>2</sub> H	6.08	143	15.8 ± 0.8	6 ± 4	13.0(8)				

<sup>a</sup> Nucleophile number. <sup>b</sup> The pK<sub>a</sub>' values are taken from ref 14e. <sup>c</sup> Tolman cone angles. <sup>d</sup> Estimated standard error of measurement of *k* (numbers of different concentrations of L are given in parentheses). <sup>e</sup> At 7.3 °C. <sup>f</sup> At 22.0 °C. <sup>g</sup> At 21.3 °C. <sup>h</sup> At 7.6 °C. <sup>i</sup> At 7.9 °C. <sup>j</sup> At 21.6 °C. <sup>k</sup> Monitored at 382 nm. <sup>l</sup> Monitored with the Hewlett-Packard spectrophotometer. <sup>m</sup> Monitored with the stopped-flow equipment. <sup>n</sup> At 7.5 °C.<sup>l</sup>

**Table 3. Activation and Thermodynamic Parameters<sup>a</sup>**

	etpb	P(OEt) <sub>3</sub>	P(OMe) <sub>2</sub> Ph	P(OPh) <sub>3</sub>	PMePh <sub>2</sub>
ΔH <sub>‡L</sub> <sup>†</sup>	10.0 ± 1.4	6.7 ± 0.4	4.68 ± 0.65	8.83 ± 0.88	5.7 ± 0.5
ΔS <sub>‡L</sub> <sup>†</sup>	-15.4 ± 4.7	-28.1 ± 1.4	-36.0 ± 2.3	-26 ± 3	-30.9 ± 1.6
ΔH <sub>‡L</sub> <sup>‡</sup>	14.3 ± 0.4	13.1 ± 1.1	16.4 ± 1.3	7.8 ± 2.7	18.1 ± 1.4
ΔS <sub>‡L</sub> <sup>‡</sup>	-9.4 ± 1.2	-17.0 ± 3.9	-6.1 ± 4.6	-36 ± 10	-1.9 ± 4.7
ΔH <sub>‡L</sub> <sup>°</sup>	-4.3 ± 1.5	-6.4 ± 1.2	-11.7 ± 1.5	1.0 ± 2.8	-12.4 ± 1.4
ΔS <sub>‡L</sub> <sup>°</sup>	-6.0 ± 4.9	-11.1 ± 4.1	-29.9 ± 5.1	10 ± 10	-29.0 ± 5.0
ΔH <sub>‡CO</sub> <sup>†</sup>	10.7 ± 3.1	17.1 ± 1.0	22.7 ± 2.1	4.8 ± 4.8	
ΔS <sub>‡CO</sub> <sup>†</sup>	-24 ± 11	-3.9 ± 3.3	14.7 ± 7.5	-48 ± 17	
ΔH <sub>‡</sub> <sup>†</sup>	9.5 ± 7.0	18.5 ± 1.2	11.2 ± 4.0		
ΔS <sub>‡</sub> <sup>†</sup>	-36 ± 24	-3.4 ± 4.3	-28 ± 14		

<sup>a</sup> Enthalpies in kcal mol<sup>-1</sup> and entropies in cal K<sup>-1</sup> mol<sup>-1</sup>.

tabulated standard errors of measurement show that the values of *k*(1) are generally very precise, those of *k*(2) are somewhat less so, and those of *k*(3) are often of relatively poor precision. Reactions of five of the nucleophiles were followed over a range of temperatures, and activation parameters of good precision were obtained by a weighted least-squares analysis<sup>12</sup> and are reported in Table 3.

**Equilibrium Constants for the First Stage of Reaction.** It is very clear that the values of *k*(1)<sub>a</sub> are not constant as would be expected if they corresponded to rate constants for CO dissociation or rate-determining isomerization of the cluster to form a reactive intermediate.<sup>7,8</sup> The form of the absorbance changes observed here for the substitution reactions of Os<sub>3</sub>(CO)<sub>9</sub>(μ-C<sub>4</sub>Ph<sub>4</sub>) is similar to those observed for substitution reactions of M<sub>5</sub>C(CO)<sub>15</sub> (M = Ru<sup>7</sup> and Fe<sup>8</sup>). In those cases the first

step is also accompanied by a substantial decrease in absorbance of the band in the visible–near-UV region of the electronic spectra. This absorbance decrease is ascribed to reaction of the P-donor ligand, L, with the cluster to form an adduct, and for reasons identical with those adduced for the M<sub>5</sub>C(CO)<sub>15</sub> clusters,<sup>7,8</sup> we conclude that the first stage of reaction here is also adduct formation. The rate equation, shown in eq 6, shows that adduct formation is reversible so that the values of *k*(1)<sub>b</sub> in Table 2 can be assigned to the adduct formation reaction (and be renamed *k*<sub>+L</sub>), while *k*(1)<sub>a</sub> can be assigned to the loss of L from the adduct and reformation of the starting cluster, so that it can be renamed *k*<sub>-L</sub>. The adduct formation reactions of Ru<sub>5</sub>C(CO)<sub>15</sub> show a detectable, but not very precise, value of *k*<sub>-L</sub> only when L = etpb or P(OPh)<sub>3</sub>.<sup>7</sup> For Fe<sub>5</sub>C(CO)<sub>15</sub>, in addition to etpb and P(OPh)<sub>3</sub>, the nucleophiles P(OMe)<sub>3</sub> and PPh-

**Table 4. Equilibrium Constants ( $M^{-1}$ ) for Adduct Formation at 13.6 °C (unless otherwise indicated)**

no. <sup>a</sup>	L	$K_{+L}$	$K_{+L}'$	$K_{+L}''$ ( $100A_{\text{adduct}}/A_{\text{initial}}$ )
1	etpb	$70 \pm 7^b$	$188 \pm 55^b$	$287 \pm 43$ ( $59 \pm 20$ ) <sup>b</sup>
			$104 \pm 50^{b,c}$	
		$68 \pm 4$	$167 \pm 43$	$143 \pm 14$ ( $46 \pm 12$ )
2	P(OMe) <sub>3</sub>	$50 \pm 2^d$	$116 \pm 42^d$	$177 \pm 24$ ( $76 \pm 22$ ) <sup>c</sup>
		$116 \pm 9$	$48 \pm 14$	$167 \pm 19$ ( $17 \pm 8$ )
			$91 \pm 9^{b,c}$	
3	P(OEt) <sub>3</sub>	$360 \pm 35^b$	$513 \pm 90^b$	$413 \pm 31$ ( $2 \pm 1$ ) <sup>b</sup>
		$215 \pm 20$	$440 \pm 45$	$497 \pm 46$ ( $28 \pm 7$ )
		$205 \pm 20^e$	$320 \pm 35^e$	$410 \pm 43$ ( $29 \pm 8$ ) <sup>e</sup>
4	P(OMe) <sub>2</sub> Ph	$354 \pm 40^f$	$470 \pm 110^f$	$443 \pm 21$ ( $4-8$ ) <sup>f</sup>
		$268 \pm 20$	$230 \pm 13$	$371 \pm 25$ ( $1.5-6.5$ )
		$145 \pm 10^d$	$158 \pm 42^d$	$261 \pm 15$ ( $21 \pm 4$ ) <sup>d</sup>
5	P(OEt) <sub>2</sub> Ph	$360 \pm 80$	$362 \pm 54$	$661 \pm 9$ ( $16 \pm 1$ )
6	PMe <sub>2</sub> Ph	$3700 \pm 1000$		
7	PPh <sub>2</sub> H	$76 \pm 6$		
8	P(OPh) <sub>3</sub>	$21.4 \pm 1.8^g$	$11 \pm 1^g$	$26.3 \pm 1.5$ ( $1-5$ ) <sup>g</sup>
		$25.5 \pm 1.3$	$16.8 \pm 4.1$	$14.2 \pm 0.8$ ( $0-6$ )
		$21.0 \pm 3.6^h$	$11 \pm 5^h$	$12.1 \pm 1.4$ ( $21 \pm 10$ ) <sup>h</sup>
9	P(O-i-Pr) <sub>3</sub>	$448 \pm 26$	$647 \pm 37$	$823 \pm 10$ ( $16 \pm 1$ )
10	P(OMe)Ph <sub>2</sub>	$564 \pm 114$		$630 \pm 12$ ( $11 \pm 1$ )
11	PEt <sub>3</sub>	v. large		
12	P(n-Pr) <sub>3</sub>	v. large		
13	P(n-Bu) <sub>3</sub>	v. large		
14	P(OEt)Ph <sub>2</sub>	$458 \pm 26$		$791 \pm 38$ ( $11 \pm 2$ )
15	PMePh <sub>2</sub>	$2300 \pm 300^i$		$3400 \pm 340$ ( $9 \pm 1$ ) <sup>i</sup>
		$1340 \pm 250$		$2700 \pm 770$ ( $12 \pm 4$ )
		$775 \pm 75^h$		$1300 \pm 160$ ( $25 \pm 2$ ) <sup>h</sup>
16	PEtPh <sub>2</sub>	$1900 \pm 650$		$1540 \pm 110$ ( $6 \pm 1$ )
17	PCy <sub>2</sub> H	$5000 \pm 3000$		$3300 \pm 450$ ( $9 \pm 1$ )

<sup>a</sup> Nucleophile number. <sup>b</sup> At 7.3 °C. <sup>c</sup> These values were obtained by analysis with omission of data at low [L]. <sup>d</sup> At 22.0 °C. <sup>e</sup> At 21.3 °C. <sup>f</sup> At 7.6 °C. <sup>g</sup> At 7.9 °C. <sup>h</sup> At 21.6 °C. <sup>i</sup> At 7.5 °C.

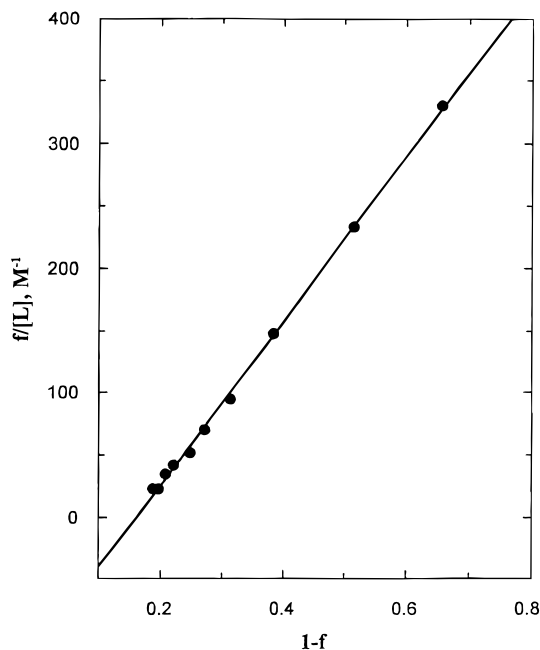
(OMe)<sub>2</sub> show significant values of  $k_{-L}$  as well, although they are not at all precise either.<sup>8</sup> In the reactions described here, quite precise values of  $k_{-L}$  are known for virtually all the adduct formation reactions. The ratios  $k_{+L}/k_{-L}$  therefore provide values that can be assigned to the equilibrium constants,  $K_{+L}$ , for formation of the adducts, and these are reported in Table 4.

The equilibrium constants can also be obtained<sup>8</sup> from the dependence on [L] of the rate constants,  $k(2)$ , for the second stage of the overall reaction according to eq 7. Because the second-stage reactions are generally much slower than the first, the reacting species during the second stages are equilibrium mixtures containing  $Os_3(CO)_9(\mu-C_4Ph_4)$  and the adducts  $Os_3(CO)_9L(\mu-C_4Ph_4)$ . It follows<sup>8</sup> that the values of  $a$  in eq 7 should be equal to the equilibrium constants for adduct formation, and they are listed as  $K_{+L}'$  in Table 4.

A third way of estimating the equilibrium constants is available from the dependence on [L] of the absorbance changes during adduct formation. The computer output of the analysis of absorbance changes by the stopped-flow equipment provides values of  $A_0$ , the absorbance of the initial cluster  $Os_3(CO)_9(\mu-C_4Ph_4)$ , and  $A_{\text{eq}}$ , the absorbance of the equilibrium mixtures of the original cluster and the adducts  $Os_3(CO)_9L(\mu-C_4Ph_4)$ . It can easily be shown that, in the simplest case, the decrease in absorbance during this first stage should depend on [L] according to eq 8, where  $K_{+L}''$  is the

$$(A_0 - A_{\text{eq}})/A_0[L] = -K_{+L}''A_{\infty}/A_0 + K_{+L}''A_{\text{eq}}/A_0 \quad (8)$$

equilibrium constant derived in this way and  $A_{\infty}$  is the unknown absorbance when [L] is very large and all the



**Figure 3.** Plot of  $f/[L]$  against  $1 - f$  for  $L = P(OEt)_2Ph$ , where  $f = (A_0 - A_{\text{eq}})/A_0$  as in eq 8.

cluster exists in the form of the adduct. Plots of  $(A_0 - A_{\text{eq}})/A_0[L]$  against  $A_{\text{eq}}/A_0$  are found to be linear (e.g., Figure 3), so that values of  $K_{+L}''$  and  $A_{\infty}/A_0$  can be obtained from the gradients and the ratio intercepts/gradients, respectively. Their values are given in Table 4.

**Systematic Dependence of the Rate Constants on the Electronic and Steric Properties of the Nucleophiles. The Kinetics of Adduct Formation.** Systematic studies of adduct formation by P-donor ligands with metal carbonyl clusters are quite rare.<sup>7,8,13</sup> However, data for a large number of associative reactions of metal carbonyl clusters are available,<sup>14</sup> and it has been concluded<sup>7,14a,c</sup> that adduct formation could be an initial step in these reactions but that further reaction of the adducts is too fast for them to be observable. All the data for these reactions are successfully analyzable according to eq 9<sup>13,14c,e</sup> or related equations.<sup>15</sup> These partition the rates between electronic

$$\log k_{+L} = \alpha + \beta(pK_a' + 4) + \gamma(\theta_{\text{th}} - \theta)\lambda \quad (9)$$

effects due to different nucleophile  $\sigma$ -basicities and steric effects due to different nucleophile sizes. In eq 9 the  $\sigma$ -basicity parameter  $pK_a'$  is related either to  $pK_a$  values<sup>16</sup> or to Bartik's  $\chi$  values<sup>17</sup> depending on whether

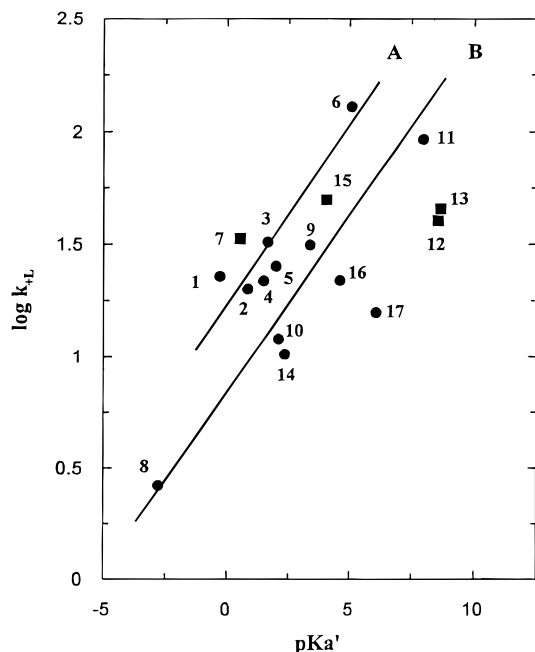
(13) (a) Hudson, R. H. E.; Poë, A. J. *Organometallics* **1995**, *14*, 3238–3248. (b) Neubrand, A.; Poë, A. J.; van Eldik, R. *Organometallics* **1995**, *14*, 3249–3258.

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(17) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29–41.



**Figure 4.** Dependence of  $\log k_{+L}$  on  $pK'_a$ . Line A is drawn through data for nucleophiles 1–6 with  $\theta \leq 122^\circ$ . Line B is drawn through data for nucleophiles 8–11 and 14 with cone angles close to  $130^\circ$ . To draw the line, the data were corrected for the small differences of the cone angles from  $130^\circ$  by using  $\gamma = -0.04 \text{ deg}^{-1}$  (see text). The data denominated by ■ were not used in any of the analyses.

the latter include an unwanted  $\pi$ -acidity contribution or not. The parameter  $\theta$  is simply Tolman's ligand cone angle,<sup>18</sup> while  $\theta_{th}$  is a cone angle above which steric effects become significant and  $\lambda$ , the switching factor, becomes unity instead of zero.<sup>15</sup> The value of  $\alpha$  is a measure of a standard reactivity (SR) chosen as the  $\log k$  value for a nucleophile with  $\theta < \theta_{th}$  and  $pK'_a = -4$ .<sup>13a,14e</sup> No significant contributions to the rates by aryl effects,<sup>19</sup> or due to nucleophile  $\pi$ -acidity,<sup>20</sup> have been detected so far.

The values of  $k_{+L}$  at  $13.6^\circ\text{C}$  in Table 2 have been successfully fitted to eq 9 as follows. Figure 4 shows the dependence of  $\log k_{+L}$  on  $pK'_a$ , and it is possible to group the nucleophiles into four categories.

(i) Nucleophiles 1–6 have cone angles that vary from  $101^\circ$  to  $123^\circ$  and form a group where  $\log k_{+L}$  depends linearly on  $pK'_a$  irrespective of the cone angles (line A). The gradient,  $\beta$ , is found to be  $0.160 \pm 0.037$  from an unweighted linear least-squares analysis (rmsd<sup>22</sup> = 0.121 and  $R^2 = 0.823$ ).

(ii) Nucleophiles 8–11 and 14 all have cone angles close to  $130^\circ$ , and their values of  $\log k_{+L}$  fall on another straight line, B, after small adjustments are made to a common cone angle of  $130^\circ$  according to the value of  $\gamma$  ( $-0.04 \text{ deg}^{-1}$ ) obtained subsequently. The gradient of line B is  $0.160 \pm 0.013$  (rmsd = 0.074 and  $R^2 = 0.982$ ),

(18) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

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(20) Giering et al.<sup>21</sup> believe they can quantify  $\pi$ -acidity effects when the P-donors are present as *ligands*, but when applied to these reactions involving P-donors as nucleophiles, their analysis suggests that  $\pi$ -acidity *weakens* nucleophile strength. This is contrary to the reasonable expectation that  $\pi$ -acidity would strengthen the bonding in such transition states.

(21) Giering, W. P. Personal communication.

(22) rmsd = root-mean-square deviation.

which is essentially identical with the value obtained from nucleophiles 1–6. However, line B lies  $0.40 \pm 0.04$  below line A.

(iii) Nucleophiles 16 and 17 ( $\theta = 140^\circ$  and  $143^\circ$ ) lie clearly below line B, and these results indicate that there is a steric threshold between  $122^\circ$  and  $130^\circ$ , above which steric effects are operative.

(iv) There is a final group of points that do not fit with the trends shown by the other groups and that have to be considered. The nucleophiles P-*n*-Pr<sub>3</sub> and P-*n*-Bu<sub>3</sub> (both with Tolman cone angles of  $132^\circ$ ) lie well below line B, their rate constants being a factor of  $\sim 2$  lower than that for the isosteric nucleophile PEt<sub>3</sub>, which fits well to that line. Inspection of the kinetic data for these nucleophiles does not suggest that experimental error is the cause of this discrepancy, and we do not believe that minor variations in the cone angles could account for it. Further, ligand 15 (PMePh<sub>2</sub>) has a rate constant  $\sim 2$  times higher than would be expected compared with that for the almost identical nucleophile 16 (PEtPh<sub>2</sub>), a nucleophile that lies below line B, as it should with its cone angle of  $140^\circ$ . We are therefore forced to omit these sets of data from further analysis. Finally, the nucleophile PPh<sub>2</sub>H lies significantly above line A, whereas its Tolman cone angle of  $126^\circ$  suggests that, if anything, it should lie below it. This deviation will be considered later.

Analysis of the fit to eq 9 of the set of data for the 13 remaining nucleophiles was carried out according to the procedure described previously,<sup>13a,14c</sup> and the results are shown in Table 5. The value of  $\beta$  is essentially the same as those found separately from either the group of small nucleophiles or the group of near-isosteric nucleophiles ( $\theta \approx 130^\circ$ ) and the goodness of fit, and the uncertainties in the derived parameters are distinctly better than those reported for other clusters.<sup>8,13a</sup> Even when data for all the 17 nucleophiles are included in the analysis, the fit is reasonable, the effects of the three or four deviant nucleophiles being largely damped by those of the 13 conforming ones. The values of  $\theta_{th}$  and  $\gamma$  remain the same, but  $\beta$  is reduced slightly to  $0.11 \pm 0.02$ ,  $R^2$  decreases to 0.669, and the rmsd increases to 0.203. However, these relatively small changes leave unaltered any of the chemical conclusions that can be drawn.

One problem with the method of analysis used is that it gives no measure of the uncertainty in the steric threshold since the best set of parameters is obtained by variation of  $\theta_{th}$  until  $R^2$  is maximized and the rmsd is minimized.<sup>14c</sup> An alternative method is to treat the data for the smaller ( $\theta \leq 122^\circ$ ) and larger ( $\theta \geq 128^\circ$ ) nucleophiles separately. The smaller nucleophiles give a value of  $\beta = 0.160$  (see above) and  $\log k_{+L} - \beta(pK'_a + 4) = \alpha = 0.58 \pm 0.05$  at  $13.6^\circ\text{C}$ . When plotted against  $\theta$ , the intersection,  $\theta_{th} = 121^\circ$ , of this horizontal part of the steric profile with the sloping part obtained from the fit of the larger nucleophiles to eq 10 can be

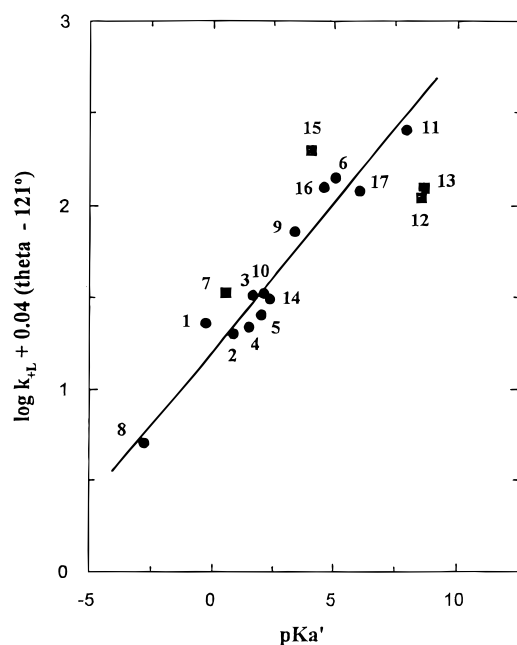
$$\log k_{+L} = \alpha + \beta(pK'_a + 4) + \gamma\theta \quad (10)$$

obtained, and its uncertainty of  $\sim \pm 4^\circ$  can be obtained as well by allowing appropriately for the covariance in the uncertainties of the horizontal and sloping parts of the steric profile. An important point to note here is that the average adjustment of  $\theta$  that is required to produce a perfect fit to the sloping part of the steric profile is

**Table 5. Electronic and Steric Parameters for Reactions of  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  at 13.6 °C (unless otherwise indicated)**

rate constant	$N^a$	$\theta_{\text{th}}$ (deg)	SR <sup>b,c</sup>	$\beta$	$\gamma$ (deg <sup>-1</sup> )	rmsd ( $R^2$ )
$k_{+L}$	13	122	0.95(9)	+0.152(15)	-0.042(6)	0.109 (0.920)
$k_{+L}^d$	13	121(4)	0.90(22) <sup>e</sup>	+0.160(37) <sup>e</sup>		0.121 (0.823)
				+0.160 <sup>f</sup>	-0.040(8) <sup>f</sup>	0.009 (0.904)
$k_{-L}$	11	$\leq 101$	-	-0.57(7)	0 <sup>g</sup>	0.169 (0.869)
				(-0.10) <sup>h</sup>		
$k_{-\text{CO}}$	15	$\leq 101$	-	-0.44(9)	0 <sup>i</sup>	0.303 (0.637)
				(-0.084) <sup>h</sup>		
$k_{-\text{CO}}$	15	$\leq 101$		0.31(15)	-0.013(11) <sup>j</sup>	0.287 (0.674)
				(0.062) <sup>h</sup>		

<sup>a</sup> Number of ligands used in analysis. <sup>b</sup> The value of the standard reactivity has been adjusted to 25 °C by using the activation enthalpy for etpb (Table 3), i.e., by adding 0.31. <sup>c</sup> Numbers in parentheses for SR and the other parameters are standard deviations. <sup>d</sup> This analysis was carried out in two separate steps, i.e., for six nucleophiles with  $\theta \leq 122^\circ$  eq 9 was used with  $\lambda = 0$ , and for seven nucleophiles with  $\theta \geq 128^\circ$ , eq 9 was used with  $\lambda = 1$  and  $\theta_{\text{th}} = 0$  (see text). <sup>e</sup> From data for the smaller nucleophiles. <sup>f</sup> From data for the larger nucleophiles; value of  $\beta$  taken as the same as from data for smaller nucleophiles. <sup>g</sup> Set to zero. No improvement in the analysis is observed when the term in  $\gamma$  is included. <sup>h</sup> The italicized numbers in parentheses are dimensionless values of  $\beta$  obtained by using the relationship between  $\delta$  and  $pK_a''$ . The corresponding nonitalicized numbers have units of ppm<sup>-1</sup> (see text). <sup>i</sup> Set to zero. <sup>j</sup> This analysis allowed for the term  $\gamma\theta$  in eq 9.



**Figure 5.** Electronic profile for adduct formation, i.e., dependence of  $\log k_{+L} - 0.04(\theta - 121)$  on  $pK_a'$  ( $R^2 = 0.944$ ). The data denominated by  $\blacksquare$  were not used in the analysis of the fit.

only  $\pm 1.4^\circ$  and this shows the very satisfactory nature of the cone angles involved.

The complete data can be represented by the electronic profile shown in Figure 5, where the values of  $\log k_{+L}$  have been adjusted by adding the small correction  $0.40(\theta_{\text{th}} - 121^\circ)$  to allow for the steric effects of the larger nucleophiles. The values  $\beta = 0.159 \pm 0.012$ , rmsd = 0.104, and  $R^2 = 0.944$  show that the data are very well represented by this analysis, only ca. 6% of the variation in the values of  $\log k_{+L}$  remaining unaccountable for on the basis of these simple electronic and steric effects. Inevitably, nucleophiles 12, 13, and 15 still do not fit the profile, but the data for  $\text{PPh}_2\text{H}$  (point 7) lie as close to the line as those for several other nucleophiles when no correction is made for its size; that is, its cone angle can be concluded to be closer to  $121^\circ$  than to  $126^\circ$ . This is not a large adjustment for a P-donor containing the very polarizable H atom. The overall fit of 14 of the 17 nucleophiles to eq 9 is therefore excellent.

A difficulty in assessing analyses such as these obviously has to do with the appropriateness of the Tolman cone angles as a measure of relative nucleophile size. Although adjustments to Tolman cone angles are sometimes made in order to improve fits of specific sets of kinetic and thermodynamic data,<sup>23</sup> either the adjustments are unjustified<sup>24</sup> or their effects are insignificant. The modest increase proposed<sup>23</sup> for the cone angle of  $\text{PEt}_3$  to  $136^\circ$  is not enough to alter the results appreciably, while the enormous proposed increases<sup>23</sup> of  $21^\circ$  and  $25^\circ$  in the cone angles of  $\text{P(OMe)}_3$  and  $\text{P(OEt)}_3$ , respectively, are not supported by analysis<sup>24</sup> of a wide range of data. Analysis of some published data in the way described here does suggest<sup>24</sup> that cone angles for these phosphites could justifiably be increased by  $10^\circ$ , but that would not bring them up above the steric threshold observed in this study.

Apart from these and other spasmodic cone angle modifications, a major choice that is available is between Tolman's cone angles and the ligand repulsion energies,  $E_R$ , derived by Brown et al. by molecular mechanics calculations on  $\text{Cr(CO)}_5\text{L}$ , etc.<sup>25</sup> As found with analyses of other sets of data,<sup>7,8,13a,14c</sup> use of  $E_R$  values leads to a fit that is significantly inferior to that found above.

**Loss of L from the Adduct.** These reactions involve the loss of the P-donor ligands from the adducts, and since the adducts have fully formed Os–P bonds with probable contributions from ligand  $\pi$ -acidity, an electronic parameter that expresses that contribution should be involved in any analysis of the systematics. Unfortunately no parameters that provide an independent measure of the  $\pi$ -acidity for individual P-donor ligands are available so one has to make do with parameters such as  $\delta$ , the  $^{13}\text{C}$  chemical shifts in  $\text{Ni(CO)}_3\text{L}$  relative to that in  $\text{Ni(CO)}_4$ ,<sup>26</sup> or  $\chi$ .<sup>17</sup> Both of these are affected by  $\pi$ -acidity, although to slightly different extents, and their use as electronic parameters assumes that any measured rate constants have the same sensitivity to the relative contributions of  $\sigma$ -basicity and  $\pi$ -acidity as

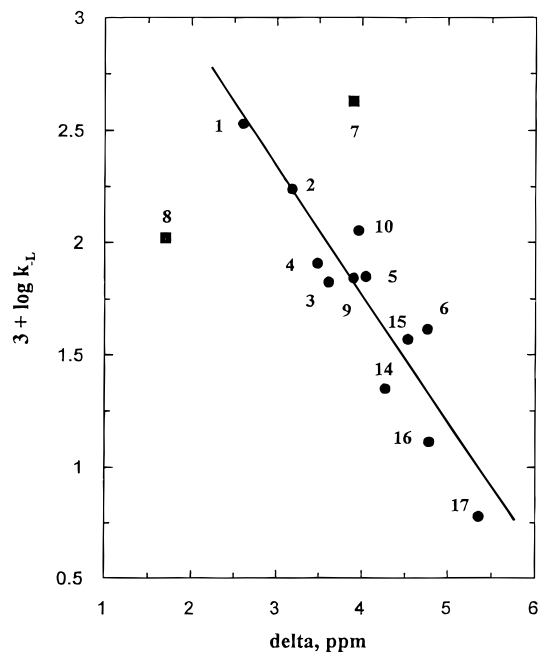
(23) For example: Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5656–5680.

(24) Chen, L. Ph.D. Thesis, University of Toronto, Canada, 1991.

(25) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286–1294. Choi, M.-G.; Brown, T. L. *Inorg. Chem.* **1993**, *32*, 5603–5610. Brown, T. L.; Lee, K. *J. Coord. Chem. Rev.* **1993**, *128*, 89–116.

(26) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951–1958.





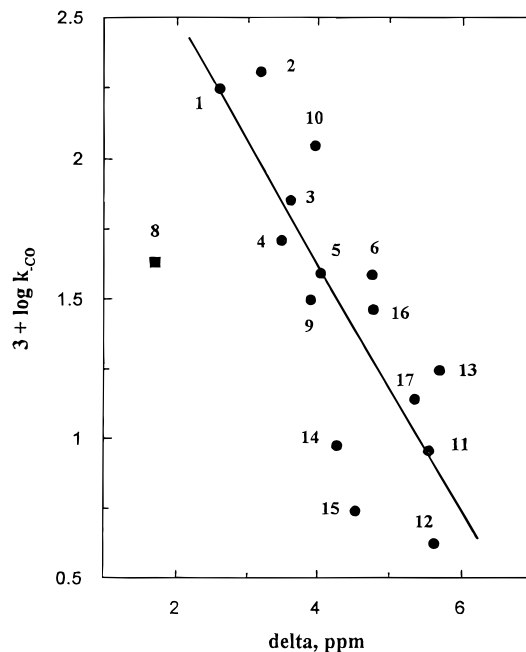
**Figure 6.** Dependence of  $\log k_{-L}$  on the net donor capacity of L as given by  $\delta(^{13}\text{CO})$  ( $R^2 = 0.87$ ). The data denominated by ■ were not used in the analysis of the fit.

$\delta$  or  $\chi$ . Any major deviations from this assumption would show up in deviant behavior by the  $\pi$ -acids compared with those that are  $\sigma$ -bases only. Figure 6 shows the dependence of  $\log k_{-L}$  on  $\delta$ , and it can be seen that, with the exception of data for two ligands  $\text{PPh}_2\text{H}$  and  $\text{P(OPh)}_3$  (no. 8), the values of  $\log k_{-L}$  decrease linearly with increasing  $\delta$ , no evidence for any steric effects being evident. The great majority of the data are therefore in accord with eq 11<sup>27</sup> with  $\gamma = 0$ . No advantage is gained

$$\log k_{-L} = \alpha + \beta\delta + \gamma\theta \quad (11)$$

by including the possibility of a steric effect in the analysis, and the values of  $\beta$  and the "goodness of fit" parameters are shown in Table 5. The value of  $\beta$  has units of  $\text{ppm}^{-1}$  and is not immediately comparable with the values of  $\beta$  obtained for adduct formation, when  $\text{p}K_a'$  is used as the  $\sigma$ -donor electronic parameter and  $\beta$  is dimensionless. However, the values of  $\delta$  and  $\text{p}K_a''$  for the relevant ligands correlate moderately well ( $R^2 = 0.764$ ). Values of  $\text{p}K_a''$  for  $\pi$ -acid ligands as well as for pure  $\sigma$ -donors can be obtained from  $\chi$  in exactly the same way as  $\text{p}K_a'$  values.<sup>13a,14c</sup> ( $\text{p}K_a'$  and  $\text{p}K_a''$  values are identical for pure  $\sigma$ -donors.) They are therefore equivalent to  $\chi$  but lead to dimensionless values of  $\beta$  when used as the electronic parameter. They could therefore be used in the analysis of the  $\log k_{-L}$  data, but the fit is not as good as when  $\delta$  is used. Nevertheless, the dimensionless value of  $\beta$  that is obtained (Table 5) can be compared with corresponding values for the other reactions.

**Loss of CO from the Adduct.** The absorbance changes during the second stage of the reactions are closely similar to those that have been ascribed to loss of CO from the adducts  $\text{M}_5\text{C}(\text{CO})_{15}\text{L}$  ( $\text{M} = \text{Ru}$  or  $\text{Fe}$ ).<sup>7,12</sup> We therefore ascribe them to the loss of CO from the



**Figure 7.** Dependence of  $\log k_{-CO}$  on the net donor capacity of L as given by  $\delta(^{13}\text{CO})$  ( $R^2 = 0.64$ ). The data denominated by ■ were not used in the analysis of the fit.

adducts  $\text{Os}_3(\text{CO})_9\text{L}(\mu\text{-C}_4\text{Ph}_4)$  so that  $k(2)$  can be renamed  $k_{-CO}$ . The values of  $\log k_{-CO}$ , like those of  $\log k_{-L}$ , show a linear decrease with increasing  $\delta$  (Figure 7), though the scatter is quite pronounced. Nevertheless, the data can be fitted to eq 11 moderately well (Table 5) provided the data for the one distinctly deviant ligand ( $\text{P(OPh)}_3$ ) are omitted. The value of  $\gamma$  is only marginally significant, but the goodness of fit is not improved when it is set to zero, although the precision of  $\beta$  (in units of  $\text{ppm}^{-1}$ ) is improved. Examination of the correlation between the values of  $\delta$  and  $\text{p}K_a''$  ( $R^2 = 0.968$ ) for the ligands involved in these reactions allows a dimensionless value of  $\beta$  to be obtained for comparative purposes.

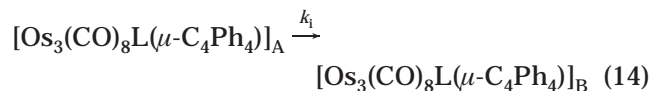
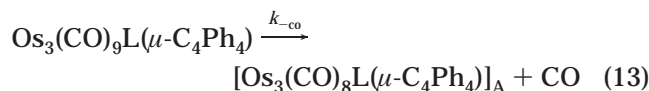
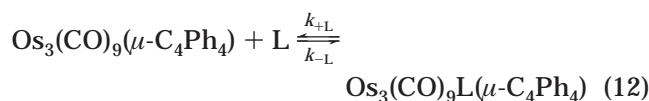
**The Final Stage.** The third stages of the reactions are not kinetically so well-defined. The rather approximate values of  $\log k(3)$  are constant at  $\sim 2.01$  ( $\text{rmsd} = 0.12$ ) for six ligands with  $\theta \leq 130^\circ$ . No values of  $k(3)$  were obtained for ligands with cone angles of  $122^\circ$ ,  $126^\circ$ , and  $128^\circ$ , but this could have been due more to the absence of sufficiently large absorbance changes than to genuinely small (or large) rate constants. When  $\theta > 130^\circ$ , the rate constants seem to be significantly lower, but no regular trend is observable. As shall be seen below, this final stage can be assigned to an isomerization of the initial, kinetic product of CO loss and  $\text{Os}_3$  ring closure. The rate constants  $k(3)$  can therefore be renamed  $k_i$ .

## Discussion

**(1) The Stoichiometric Mechanisms.** The reactions studied here lead eventually to the monosubstituted clusters  $\text{Os}_3(\text{CO})_8\text{L}(\mu\text{-C}_4\text{Ph}_4)$ , where the 17 P-donor ligands all have  $\theta \leq 143^\circ$ . The crystallographic structures of two of the products ( $\text{L} = \text{etpb}$  and  $\text{P(OPh)}_3$ ) show<sup>6</sup> that the P-donor substituent has displaced a CO ligand from the  $\text{Os}(\text{CO})_4$  moiety in the cluster and that it is in a position trans to the Os atom in the osmacyclopentadiene ring. The close similarity of the FTIR

(27) Hudson, R. H. E.; Poè, A. J. *Inorg. Chim. Acta* **1997**, *259*, 257–263.

spectra of the other 15 products to those of the two crystallographically characterized ones strongly suggests that their structures are the same. The formation of these products, however, does not proceed via a simple single step but via at least two kinetically detectable steps as shown by eqs 12–14.



**Adduct Formation (Eq 12).** The fact that  $k(1)_a$  in eq 6 is not constant for all the nucleophiles shows that this rate constant cannot be assigned to a CO-dissociative process or to rate-determining isomerization.<sup>7,8</sup> Rather it has to be assigned to the loss of L from an adduct  $\text{Os}_3(\text{CO})_9\text{L}(\mu\text{-C}_4\text{Ph}_4)$  formed by reversible addition of L to the original cluster. Thus  $k(1)_a$  can be designated as  $k_{-L}$ , and the addition process is characterized by  $k(1)_b = k_{+L}$ . The significant contribution to  $k(1)$  of the terms  $k(1)_a$  contrasts with the behavior observed with the clusters  $\text{M}_5\text{C}(\text{CO})_{15}$  ( $\text{M} = \text{Ru}^7$  and  $\text{Fe}^8$ ). The reactions of the carbonyls  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  with  $\text{P}(\text{OPh})_3^{13a}$  and  $\text{Fe}_2(\text{CO})_6(\text{NO})(\mu\text{-AsMe}_2)$  with  $\text{SbPh}_3^{28}$  also show detectable rate constants for loss of ligand from the adduct, but they are exceptional among the larger group of ligands studied.<sup>29</sup> The cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  is unique, therefore, in forming weak enough adducts for the rate constants for loss of the added ligand to be determined with considerable precision for a wide range of P-donors.

The equilibrium constants,  $K_{+L}$ , for adduct formation can be obtained quite precisely from the ratios  $k_{+L}/k_{-L}$ , values of which are given in Table 4. However, values of the equilibrium constants can also be obtained from the extent of the decrease in the absorbance, during the first step of the substitution, as a function of [L] and are given as  $K_{+L}'$  in Table 4. This method also leads to ratios of the molar absorbances of reactant cluster and adduct. A third way of obtaining the equilibrium constants is from the dependence of  $k(2)$  on [L] over a time scale where the adduct formation equilibrium is set up relatively rapidly, and these values are given as  $K_{+L}'$  in Table 4.

The precision of the values of  $K_{+L}$  is often quite good, but it inevitably decreases as the intercept of the plot of  $k(1)$  against [L] (eq 6) becomes smaller and less well-defined and as  $K_{+L}$  becomes larger. The precision of  $K_{+L}'$  is usually fairly low and depends very much on how many values of  $k(2)$  were obtained at low [L] where  $k(2)$  was much less than  $k(2)_{\text{lim}}$ . Sometimes the values of  $K_{+L}'$  depend very strongly on one or two points at low [L] so that any error in that point has a large systematic effect.

(28) Jackson, R. A.; Kanluen, R.; Poë, A. J. *Inorg. Chem.* **1984**, *23*, 523–527.

(29) The cluster  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  undergoes reversible adduct formation with CO, and precise rate constants for the reverse reaction have been obtained.<sup>30</sup>

(See, for example, Table 2 and Figure 2.) Perhaps related to this is the fact that even a small contribution to  $k_{+L}$  by a unimolecular path (not dependent on [L]) can reduce  $K_{+L}'$  substantially. Thus, for reactions with etpb at 13.6 °C, if a path such as this has a rate constant of only 0.01 s<sup>-1</sup> (i.e., ~25% of the lowest measured value of  $k(2)$ ), the data are consistent with  $K_{+L} = K_{+L}' = 70 \text{ M}^{-1}$ .<sup>31</sup> This contribution should occur independently of which ligand is involved, but this does not seem to be the case and cannot be so when  $K_{+L}' < K_{+L}$ . The values of  $K_{+L}''$  depend quite strongly on the term  $A_0 - A_{\text{eq}}$  in eq 8. This can be quite imprecise at low values of [L] either because the difference is small or because there are systematic errors in  $A_0$ . The values of  $A_{\infty}/A_0$  that are given by this method are usually quite small, but they also vary randomly even for the same reaction at different temperatures. Since this is unlikely to be a real effect, it seems that there must indeed be systematic errors in this method. However, these cannot account for all the values of  $K_{+L}''$  that are higher than the others because  $A_{\infty}/A_0$  must always be  $\geq 0$ . Thus, for reaction with  $\text{P}(\text{OEt})_3$  at 13.6 °C, even if  $A_{\infty}/A_0 = 0$ ,  $K_{+L}''$  would still be  $\geq 320 \text{ M}^{-1}$ . On balance we believe that the values of  $K_{+L}$  are the best estimates of the equilibrium constants for adduct formation.

However, the values of  $A_{\infty}/A_0$ , even if only approximate, are important for another reason. In the case of the reactions of the clusters  $\text{M}_5\text{C}(\text{CO})_{15}$  ( $\text{M} = \text{Ru}$  and  $\text{Fe}$ ),<sup>7,8</sup> supporting evidence for the formation of adducts in the first stage of reaction was the substantial decrease in absorbance of the bands characteristic of metal–metal interactions and the existence of known and isolated adducts. Adduct formation is able to occur without violation of electron counting rules because it is accompanied by opening up of the closed cluster by breaking one M–M linkage, and it was assumed that this was the explanation for the decrease in absorbance. The systems studied here provide a quantitative measurement of the extent of such an absorbance decrease, and Table 5 shows that the decrease is generally quite large and the final absorbance is often negligible.<sup>32</sup>

**The Second and Third Steps (Eqs 13 and 14).** The second step involves a virtually complete recovery of the absorbance in most cases. This supports the conclusion, based on the kinetics, that this step involves dissociative loss of CO and re-formation of the closed cluster that now contains a P-donor substituent.<sup>34</sup>

The isolated and well-characterized final products have the same stoichiometry as the products of CO dissociation. For this reason the third observed step (eq 14) has to be assigned to an isomerization process in which the kinetically formed substituted cluster product rearranges to what must be the most stable form as

(30) Poë, A. J.; Sampson, C. N.; Smith, R. T.; Zheng, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3174–3181.

(31) A much more important and unexpected unimolecular path has been detected by this sort of discrepancy.<sup>30</sup>

(32) This evidence relates to another explanation for adduct formation. This involves some form of “slippage” of the osmacyclopentadiene moiety, analogous to that first proposed for cyclopentadiene complexes.<sup>33</sup> However, this process would not account for the substantial absorbance decrease in the way that cluster opening does since all that would happen during adduct formation would be the replacement of one donor electron pair from the diene unit by another from the nucleophile.

(33) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663. Basolo, F. *Polyhedron* **1990**, *9*, 1503–1535.

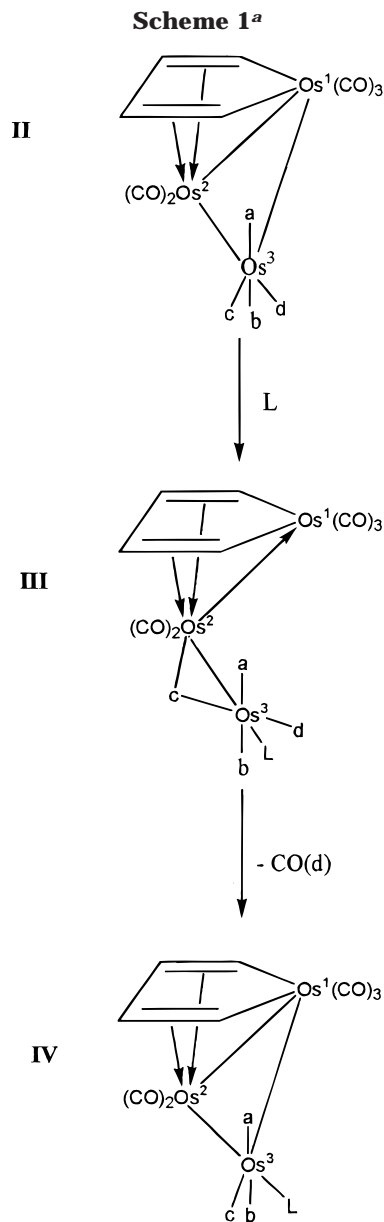
given by the crystallographic studies. Although there is no evidence as to how this occurs in this system, the small absorbance change generally observed is quite consistent with isomerization. Similar processes that involve small absorbance changes in the electronic spectra have been postulated for reactions of the adducts  $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}\text{L}$  initially formed from  $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}$ .<sup>13b</sup> Detailed NMR studies have shown that such adducts exist in several different forms.<sup>35</sup> Axial–equatorial isomerization processes have also been shown to occur with kinetically formed  $(\mu\text{-H})_3\text{Re}_3(\text{CO})_{11}\text{L}$  clusters.<sup>36</sup>

**(2) The Intimate Mechanisms.** The details of the stoichiometric processes described in eq 12–14 can most simply be discussed in terms of Scheme 1. The structure of  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$ <sup>4b,6</sup> can be represented by **II**. The carbonyl ligands on Os(3) are arranged so as to complete an approximately octahedral coordination when the Os–Os bonds are included, and they are represented simply by letters for convenience.

The Os(1)–Os(3) bond is the longest of the three Os–Os bonds<sup>4b</sup> and is 0.06 Å longer than the average Os–Os bond distance in  $\text{Os}_3(\text{CO})_{12}$ .<sup>37</sup> The Os(1)–Os(2)–Os(3) angle is also the largest, and it seems reasonable to conclude that it is the Os(1)–Os(3) bond that breaks when the adduct is formed. To create an empty coordination site on Os(3), the Os(1)–Os(3) bond has to break heterolytically with the electron pair moving to Os(1). However, this simple charge separation is unlikely to occur in the nonpolar heptane solvent used here, and some way of dissipating the charge has to be envisaged. In the case of associative substitution of  $\text{Os}_3(\text{CO})_{12}$  it is believed to be accomplished by transformation of two terminal CO ligands into bridging ones.<sup>39</sup>

Inspection of the  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  structure<sup>4b,6</sup> suggests, however, that although bridge formation between Os(3) and Os(2) is sterically quite possible, the region between Os(2) and Os(1) is very congested. Instead of Os(2)–Os(1) bridging, the dissipation of charge could be brought about by means of a structure represented by **III** in Scheme 1. This suggestion is supported by the fact that several closely analogous structures are known that contain Os→Os bonds where formal donation of a lone pair occurs from an otherwise six-coordinate d<sup>6</sup> Os atom, or from a five-coordinate d<sup>8</sup> Os atom, to another Os atom.<sup>4a,c,38</sup>

As shown, the scheme implies that the nucleophile approaches Os(3) in the plane of the  $\text{Os}_3$  cluster and between CO ligands (c) and (d), and it is CO(c) that has been forced into a bridging position. Exact reversal of this process will obviously lead to the known reformation of the original cluster, but loss of CO(d) will allow the reaction to proceed. CO(c) resumes its position trans to the re-formed Os(3)–Os(1) bond, but L ends up trans to Os(2). This is not the final structure of the



<sup>a</sup> For convenience the Os atoms are numbered here with superscripts, in contrast with the numbering Os(1), etc., in the text.

product, so isomerization is necessary to enable the final position of L to be trans to Os(1).

Although speculative, this scheme has the virtue of explaining the essential features of the reactions in a simple and reasonable way. More complex versions could be offered that might explain more detailed aspects of the data. Thus, other “flight paths” along which the nucleophile can approach the  $\text{Os}(\text{CO})_4$  moiety are possible, and these could lead to various different isomers of the adduct. There is also a real possibility that isomerization of the adduct would occur before CO loss. Intervention of one or more processes of that sort could provide a mechanistic explanation for the differences between the equilibrium constants  $K_{+L}$  and  $K_{+L'}$ . If adduct formation does not occur in a single step, then eq 8 would be an oversimplification of the situation. There would be more than one equilibrium constant involved, as well as extra molar extinction coefficients, and different apparent equilibrium constants would inevitably result.

(34) The question of whether this CO dissociation is reversible or not cannot be answered with certainty. The presence of CO leads to a competing direct reaction with the starting complex, and the effect of CO on the rates of the reaction in eq 13 would be difficult to study.

(35) Aime, S.; Gobetto, R.; Valls, E. *Inorg. Chim. Acta* **1998**, 275–276, 521–527.

(36) Beringhelli, T.; D'Alfonso, G.; Monoja, A. P.; Freni, M. *Inorg. Chem.* **1991**, 30, 2757–2763.

(37) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, 16, 878–884.

(38) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K. *Organometallics* **1989**, 8, 1030–1039, and references therein.

**Energetics of the Reactions.** The most dramatic feature of the energetics of these reactions is the fact that the value of  $k_{\text{+L}}$  for reaction with  $\text{P-n-Bu}_3$  at 13.6 °C is over  $10^9$  times faster than the associative reaction of  $\text{P-n-Bu}_3$  with the parent cluster  $\text{Os}_3(\text{CO})_{12}$  at that temperature.<sup>39</sup> The  $\mu\text{-C}_4\text{Ph}_4$  moiety clearly has an enormously labilizing effect that is transmitted to the  $\text{Os}(\text{CO})_4$  unit from which the CO is displaced. This can be related to the length of the  $\text{Os}(1)\text{--Os}(3)$  bond and the openness of the  $\text{Os}(1)\text{--Os}(2)\text{--Os}(3)$  bond angle, as discussed above, but some of the lability might be ascribable to electronic effects induced by the osmacyclopentadiene moiety. These might facilitate the electron redistribution that must accompany adduct formation. However, what the osmacyclopentadiene moiety almost certainly does *not* do is labilize the CO ligands on  $\text{Os}(1)$  and  $\text{Os}(2)$  since we have shown that  $\text{Os}_2(\text{CO})_6(\mu\text{-C}_4\text{Ph}_4)$  is exceedingly inert to substitution.

Beyond this singular behavior lies the fact that the systematic dependence of rates of various reactions on the electronic and steric properties of the nucleophiles is important because it can provide insight into the intimate energetic natures of the reactions. The parameters in Table 5 quantify that dependence for the reactions discussed here. Not all the ligands involved conform quantitatively to the simple systematics defined by the relevant equations, but despite a lack of ready explanations for the deviants, the systematic behavior is followed by the great majority of ligands and is, we believe, significant and useful.

As far as adduct formation is concerned, the standard reactivity (SR; given by  $\alpha$  in eq 9) for  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  puts it near the top of the ranking of metal carbonyl clusters. Only  $\text{Ru}_5\text{C}(\text{CO})_{15}$  (SR =  $2.86 \pm 0.18$ )<sup>7,13a</sup> and  $\text{Ru}_6\text{C}(\text{CO})_{17}$  (SR =  $1.51 \pm 0.26$ )<sup>13a,14c</sup> show appreciably higher values, and these are distinguished by the presence of the encapsulated C atoms. It is slightly larger than that of  $\text{Rh}_4(\text{CO})_9(\mu\text{-HC}(\text{PPh}_2)_3)$  ( $0.64 \pm 0.01$ ),<sup>14e</sup> where the tripod ligand presumably introduces steric strain into the cluster, and it is considerably larger than that of the still very labile, coordinatively unsaturated  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  ( $-0.53 \pm 0.13$ ).<sup>13a</sup> The distinguishing features noted are important because many "undistinguished" clusters such as  $\text{Rh}_6(\text{CO})_{16}$  or  $\text{Os}_6(\text{CO})_{18}$ , for instance, are not particularly labile. Beyond that, these labile clusters are too different for any detailed conclusions to be drawn, and functionalization (by introduction of substituents into the clusters, for example<sup>40</sup>) is obviously needed to provide sets of data that can be more meaningfully compared.

The electronic selectivity, as defined by  $\beta$  in eq 9, is quite low.<sup>14e,40</sup> Values of  $\beta$  can be related to the degree of bond making as well as to other bonding changes in the transition states.<sup>13b,14c,e</sup> The latter may be discouraged by increased nucleophile basicity and so lead to lower  $\beta$  values, but it is also possible that the low selectivity is simply the result of the very high intrinsic reactivity of this cluster and that  $\beta$  is mainly a function of bond making.<sup>14e</sup> The greater the intrinsic ability of the cluster to open out spontaneously, the less it will require the assistance of bond making by the nucleo-

phile to reach the transition state and the less selective the cluster will be.

Similarly, the onset of steric effects occurs at a rather intermediate cone angle,<sup>14e,40</sup> indicating that ligand–ligand repulsions in the transition states are only moderate, as would be expected if metal–nucleophile bond making itself is only moderate. The flexibility of the transition state, when the steric threshold is exceeded, is also quite high,<sup>14e,40</sup> as indicated by the fact that  $\gamma$  has quite a small negative value. All this gives the picture of a rather loose transition state with substantial Os–Os bond breaking but relatively little Os–P bond making, a picture that indicates considerable internal stress in the ground-state cluster itself.

The data for loss of the P-donors (eq 13) from the adducts are unique, only scattered and imprecise data having been reported elsewhere.<sup>7,8,13a</sup> The concept of standard reactivity is not applicable to dissociative reactions such as these, but the actual rate constants are very high, matching those of adduct formation. Apart from this, the loss of L is characterized simply by a negative value of  $\beta$ , as expected, since Os–L bond breaking is likely to become more difficult the greater the basicity of L and the greater the strength of the Os–L bond. This effect must overcome any effect due to the increasing electrophilicity of the Os atom as L leaves, an increase that would favor re-formation of the Os–Os bond as the cluster closes up again; that is, Os–L bond breaking is more important than Os–Os bond making. The absence of any detectable steric effects is also as expected if steric acceleration, due to increasing ligand size, is balanced by steric problems associated with the re-formation of the Os–Os bond. Inverse steric effects are sometimes seen when formation, or strengthening, of metal–metal bonds is more important than metal–ligand bond breaking.<sup>12</sup>

Because of the use of  $\delta$  as the electronic parameter, the units of  $\beta$  for loss of L are  $\text{ppm}^{-1}$ . However, when  $\beta$  is made dimensionless (as described above and reported in Table 5), it is about as negative as the value of  $\beta$  for adduct formation is positive. In other words, the energetic advantages enjoyed by the more basic ligands on going to the transition state for adduct formation is about the same as those experienced on going from the partially formed Os–P bond in the transition state to the fully formed Os–P bond in the adduct. In this sense the transition states are energetically about halfway between the reactants and the adduct products.

As is the case for loss of L, the rate constants for loss of CO are very large, and the absolute reactivity is therefore very high. Although the data in Figure 7 are quite badly scattered,<sup>42</sup> the value of  $\beta$  is clearly negative, as is that for CO loss from the adducts  $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}\text{L}$ .<sup>27</sup> These negative values contrast with the positive values (up to  $0.61 \text{ ppm}^{-1}$ ) found for  $\text{Ru}_3(\text{CO})_{12-n}\text{L}_n$  ( $n = 1\text{--}3$ )<sup>41</sup> and which indicate transition-state stabilization by better donors, rather than the ground-state stabilization expected because of stronger Ru–CO bond

(41) Brodie, N. M. H.; Poë, A. J. *Can. J. Chem.* **1995**, *73*, 1187–1195.

(42) This can be ascribed to the problem, already alluded to, in analyzing the data in terms of eq 7. Not only can the values of  $\text{p}K_{\text{a}}'$  be strongly affected by data at low [L] (Table 4) but so can the values of  $k(2)_{\text{lim}}$  (i.e.,  $k\text{-CO}$ ) (Table 2). These data can be affected because at low [L] the first step will be slower and can overlap with the second.

(39) Poë, A. J.; Sekhar, V. *Inorg. Chem.* **1985**, *24*, 4376–4380.

(40) Farrar, D. H.; Hao, J.; Mourad, O.; Poë, A. J. *Organometallics* **1997**, *16*, 5015–5022.

strengths; that is, the stronger electron donors in some way compensate the cluster for the loss of the CO ligand and/or the metal–P bonds become shorter and stronger because of the release of steric strain. However, when CO loss is accompanied by metal–metal bond formation, as in the reactions of the adducts, electronic destabilization of the transition state may occur because the re-formation of the metal–metal bond is inhibited by a greater electron density on the metal to which the P-donor is attached and which acts as an electrophile.

The almost complete absence of any steric effects on the loss of CO shows, as is the case for loss of L, that relief of steric strain as a ligand leaves is balanced by repulsions experienced during Os–Os bond re-formation.

The absence of any substantial ligand dependence of the rates of isomerization in the final stage of substitution also suggests that any effects must be small and/or must balance out in some relatively simple way.

The activation parameters in Table 3 for adduct formation do not show any particularly obvious trends with  $pK_a'$  or  $\theta$  but they all show the low values of  $\Delta H_{+L}^\ddagger$  and negative  $\Delta S_{+L}^\ddagger$  expected for bimolecular reactions. They also show a rough compensation effect<sup>43</sup> when  $\Delta H_{+L}^\ddagger$  is plotted against  $\Delta S_{+L}^\ddagger$ , but the data are not precise enough to determine if a true isokinetic temperature exists.<sup>43</sup> The values of  $\Delta H_{-L}^\ddagger$  are also quite low, and this probably reflects the significant contribution of Os–Os bond making that offsets the enthalpy required for bond breaking. All the entropies are negative, but they become increasingly so as  $\Delta H_{-L}^\ddagger$  increases, probably because of the steadily decreasing importance of Os–Os bond making that occurs coincidentally with loss of L. Combination of the activation parameters for addition and loss of L provide thermodynamic parameters for the adduct formation equilibria. Most of the equilibria are favored by enthalpy and opposed by entropy effects, as expected from the stoichiometry, but  $P(O\text{Ph})_3$  is exceptional, as it is in some of the linear free energy relationships discussed above. The activation parameters for loss of CO do not show any perceptibly regular relationship to those for loss of L, and one of the pairs shows a high enthalpy and quite favorable entropy, suggestive of low contribution from Os–Os bond making. The isomerization reactions vary from having quite a high and unfavorable enthalpy, with a compensatingly favorable entropy, to having a low enthalpy and very unfavorable entropy.

### Summary

(i) The cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-C}_4\text{Ph}_4)$  (**I**) undergoes very rapid substitution at the  $\text{Os}(\text{CO})_4$  moiety, and the kinetics of reaction with 17 smaller P-donor nucleophiles ( $\theta \leq 143^\circ$ ) have been monitored mainly by stopped-flow methods.

(ii) Reactions occur in at least two stages, and the absorbance changes and the kinetics of the first stage indicate that it involves formation of an adduct,  $\text{Os}_3(\text{CO})_9\text{L}(\mu\text{-C}_4\text{Ph}_4)$ . The structures of the parent cluster and of two of the final products suggest that it is the

Os–Os bond between the Os atom in the osmacyclopentadiene ring and in the  $\text{Os}(\text{CO})_4$  group that breaks. Reversible addition of the nucleophile to the  $\text{Os}(\text{CO})_4$  unit is followed by CO dissociation from that unit with concomitant re-formation of the Os–Os bond. The kinetic product is usually an unstable isomer of the final product so that isomerization is frequently a third kinetically observable step.

(iii) Equilibrium constants for adduct formation can be obtained from the kinetic data for both the first and second stages and from the extent of absorbance change in the first stage as a function of [L]. The values obtained by the different methods are not always the same. This may be due to experimental problems, but it is also possible that undetected isomerization of the adducts before CO loss in the second stage could contribute to this.

(iv) The diene unit in the cluster exerts an enormous labilizing effect on substitution at the  $\text{Os}(\text{CO})_4$  moiety, as shown by the  $10^9$  greater rate of substitution by  $P\text{-n-Bu}_3$  into this cluster compared with  $\text{Os}_3(\text{CO})_{12}$ .

(v) The systematic dependence of the rates of adduct formation on the  $\sigma$ -donicity and size of 14 of the nucleophiles fit closely to the well-established equation  $\log k_{+L} = \alpha + \beta(pK_a' + 4) + \gamma(\theta_{\text{th}} - \theta)\lambda$ .<sup>14c,e</sup> Size effects do not become apparent (i.e.,  $\lambda = 0$ ) until  $\theta = \theta_{\text{th}} = 120 \pm 4^\circ$ . The steric effect at larger cone angles (when  $\lambda = 1$ ) and the always exerted electronic effect are both moderately small and indicate that the cluster is intrinsically very reactive. The standard reactivity,  $\text{SR} = \alpha$ , is only exceeded by that of  $\text{Ru}_6\text{C}(\text{CO})_{17}$  and  $\text{Ru}_5\text{C}(\text{CO})_{15}$ .

(vi) The dissociative loss of L and CO from the adducts is essentially independent of the size of L but is retarded by greater net donicity of L. The final isomerization step is little affected by the size or basicity of L.

(vii) The quantitative sensitivity of the rates to the donicity and, where appropriate, the size of L allows consideration of the contributions of bond making and bond breaking in the transition states, and this can be supplemented by evidence from the activation parameters obtained for five of the ligands. It can be concluded, for example, that Os–P bond making and Os–Os bond breaking are both significant in the transition states for adduct formation and that bond breaking and Os–Os bond making are both significant in the transition states for dissociative loss of L or CO from the adducts. It is also possible to show that the formation of the transition states on the way to the adducts is as sensitive to the nature of the nucleophiles as is the subsequent completion of Os–P bond formation. In that sense the transition states for adduct formation can be considered to be approximately halfway from reactant to product.

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**Supporting Information Available:** Tables of  $k(1)$ ,  $k(2)$ , and  $k(3)$  at various values of [L] and temperature are given in Tables 6–21. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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