Reaction of Di-μ-diethylphosphido-bis(tetracarbonylmolybdenum) (*Mo–Mo*) with Tri-n-butylphosphine: Kinetics and Mechanism of a Reaction involving Seven-co-ordinate Complexes

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In the absence of light, di-μ-diethylphosphido-bis(tetracarbonylmolybdenum) (*Mo–Mo*), (I), undergoes a two-step carbonyl substitution reaction with tri-n-butylphosphine in decalin, giving $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4]$, (II), and $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)]$, (III). The substitution reaction does not go to completion in the presence of carbon monoxide and the kinetics of the forward and reverse reaction for each step have been studied. All the substitutions occur by a dissociative mechanism involving the reactive intermediate $[L(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3]$ (L = CO or PBu_3) which has a co-ordinatively unsaturated six-co-ordinate molybdenum atom. Values of the competition ratio k_{CO}/k_{PBu_3} for bimolecular attack on this intermediate, at 80 °C, range from 67.0 for L = CO to 2.62×10^4 for L = PBu_3. Thus the co-ordinatively unsaturated metal centre shows an unexpected high sensitivity to the nature of the incoming ligand and to steric and/or electronic variations on the adjacent metal atom. The substitution of one CO group by PBu_3 in (I) does not affect the rate of dissociation of CO, whereas (II) has a different rate of dissociation of PBu_3 compared to (III). Activation parameters for the rate constants and competition ratios, together with equilibrium data, for these reactions are reported.

DI-μ-DIETHYLPHOSPHIDO-BIS(TETRACARBONYLMOLYBDENUM) (*Mo–Mo*), (I), is a metal–metal bonded carbonyl with two diethylphosphido-bridges. An *X*-ray study has shown [1] that its structure is characterised by a planar $\overline{M-P-M-P}$ ring. Each metal atom is at the centre of a seven-co-ordinate structure, which can be seen as resulting from distorsion of a *cis*-$Mo(CO)_4P_2$ unit to allow metal–metal bond formation. The Mo–Mo bond distance is 3.057 Å, and the Mo–P–Mo and P–Mo–P angles are 75.4 and 104.6°, respectively. The dimethylphosphido-analogue is known to react at room temperature with triphenyl- and triethyl-phosphine in benzene under visible light to give only bis(phosphine) derivatives.[2] On this basis, complex (I) offers the opportunity of studying the behaviour of a seven-co-ordinate metal atom towards substitution.

The scarcity of mechanistic data,[3,4] together with my interest in the general field of bridged binuclear carbonyl complexes,[5] prompted a study of the thermal reaction of (I) with tri-n-butylphosphine. Both the mono- and the bis-substituted products of this reaction can be isolated, and this paper reports a detailed kinetic and mechanistic study of reactions (1) and (2) in decalin as solvent.

$$[(OC)_4\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] + CO \quad (1)$$

$$[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)] + CO \quad (2)$$

EXPERIMENTAL

The complex $[(OC)_4\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4]$, (I), was prepared following Hayter's method for the dimethylphosphido-analogue.[6] The i.r. spectrum in decalin showed peaks at 2 027s, 1 972m, and 1 958vs cm^{-1} (*cf.* in chloroform: 2 019s and 1 948vs, br cm^{-1}).[7] The complex $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4]$, (II), was prepared by reaction of (I) (1.2 g, 2 mmol) with PBu_3 (1.25 g, 6.25 mmol) in carefully deoxygenated methylcyclohexane (23 cm^3) at 80 °C under 1 atm of carbon monoxide.† After 2 h, solvent was removed under reduced pressure to yield orange-red crystals, which were washed with methanol and recrystallised from n-hexane–ethanol, yield ⩾60% [Found: C, 41.8; H, 6.2%; *M* (in $CHCl_3$) 720. Calc.: C, 42.2; H, 6.2%; *M* 768]. I.r. spectrum in decalin: 2 039m, 1 990m—s, 1 946sh, 1 936vs, 1 921m, and 1 883m cm^{-1}. The complex $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)]$, (III), was prepared by reaction of (I) (0.9 g, 1.5 mmol) with PBu_3 (1.5 g, 7.5 mmol) in carefully deoxygenated decalin (10 cm^3) at 110 °C under a 5% CO–Ar mixture. (The reaction could be carried out under Ar at 90 °C.) After 3 h, solvent was removed under reduced pressure and the resulting red oil was treated with methanol to give yellow-orange microcrystals. These were filtered off, washed with methanol, and recrystallised from n-hexane–ethanol, yield ⩾45% (Found: C, 48.3; H, 8.3. Calc.: C, 48.4, H, 7.9%). I.r. spectrum in decalin: 1 965w and 1 901s cm^{-1} {*cf.* spectrum in cyclohexane of $[(Et_3P)(OC)_3\overline{Mo(\mu\text{-}PMe_2)_2Mo}(CO)_3(PEt_3)]$, (IV),: 1 968 and 1 906 [1 901 (sh)] cm^{-1}}.[8] The close similarity between the i.r. spectrum of (III) and that reported for (IV) indicates the two complexes have a similar centrosymmetric structure, in which, in the solid state, each of the phosphine ligands is *trans* to a different phosphido-bridge.[9] Tri-n-butylphosphine (Baker) was distilled under reduced pressure and kept under Ar. Decalin (R.P.E.C. Erba) was distilled under reduced pressure and stored over molecular sieves. Argon and carbon monoxide were high-purity SIO products.

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† 1 atm = 101 325 Pa, 1 cal = 4.184 J.

[1] M. H. Linck and L. R. Nassimbeni, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1105.

[2] D. T. Thompson, *J. Organometallic Chem.*, 1965, **4**, 74.

[3] C. White and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 261.

[4] A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 441.

[5] Marino Basato, *J.C.S. Dalton*, 1975, 911 and refs. therein.

[6] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.

[7] J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1964, 1005.

[8] P. S. Braterman and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 1454.

[9] R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1967, 1735.

Certified Ar–CO mixtures were provided by SIAD, relative errors in their analysed contents being always less than 0.5%.

Procedure.—Solutions were prepared and deoxygenated, kinetic runs carried out, and concentrations of carbon monoxide determined, as previously described.[5] Most reactions were in a Slenk tube under Ar and/or CO, but in some cases a steady flow of argon through the solutions was maintained, the flow rate being monitored in an oil bubbler. Samples were ejected by temporarily closing the exit to build up pressure before inserting a stainless-steel sample-ejection tube. Samples were ejected directly into i.r. cells and spectra recorded immediately in the C–O stretching region on a Perkin-Elmer 457 spectrophotometer, reference cells being filled with matching PBu^n_3 when appropriate.

RESULTS

The reaction proceeds in two distinct stages, the first being characterised by growth of the i.r. bands of $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4]$, (II), and the second by decay of these bands and growth of those characteristic of $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)]$, (III). The rather different CO effect on the rates of the two substitutions, together with favourable equilibrium positions, allowed a detailed kinetic study of the forward and reverse reactions for both substitutions.

The forward reaction of the first stage gave, both under Ar and under CO, quantitative formation of (II). The reaction was monitored by following the decreasing intensity of the band at 2 027 cm^{-1}. Under pseudo-first-order conditions, plots of log $|A_t - A_\infty|$ against time were linear over three half-lives. The observed rate constants ($=k_f$) decreased with increasing CO pressure, and were almost constant under Ar for $[PBu_3] \geqslant 0.234$ mol dm^{-3}. At a given phosphine concentration below this value, the reaction rate increased on application of a stream of argon, indicating that the lower k_f values observed under ' static ' argon are consistent with retardation caused by carbon monoxide released during the substitution. The forward reaction of the first stage obeyed the rate equation $k_f = a/\{1 + (b[CO]/[PBu_3])\}$.

The reverse reaction of the first stage was studied at various CO pressures in the absence of added phosphine by following the peak due to (II) at 2 039 cm^{-1}. An equilibrium was attained in all cases between (I), CO, (II), and PBu_3 released during the reaction. The kinetic data were treated in accordance with the reaction being of the type (3) for

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B + C \qquad (3)$$

which k (equal to k_r, the observed rate constant for the reverse reaction of the first stage) could be determined, assuming the initial concentration of B and C to be zero, by using equation (4). Here A_0 is the initial absorbance,

$$\ln \frac{A_0^2 - A_eA_t}{(A_t - A_e)A_0} = \left(\frac{A_0 + A_e}{A_0 - A_e}\right) \cdot kt \qquad (4)$$

A_t is the absorbance at time t, and A_e is the absorbance of (II) at equilibrium. The latter was determined by graphical extrapolation since a slow successive reaction took place which prevented a simple direct measurement. Rate plots based on equation (4) showed good linearity in each case. The rate constant k_r was independent of CO pressure, *i.e.* $k_r = c$. All rate data for the first stage, together with the equilibrium constants, are collated in Table 1.

TABLE 1

Rate and equilibrium data for the reaction $[(OC)_4\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] + CO$ in decalin. [Complex] = 5×10^{-4}—2×10^{-3} mol dm^{-3}

θ_c/°C	$10^3[PBu_3]$/mol dm^{-3}	p_{CO}/atm	$10^3[CO]$/mol dm^{-3}	10^5k_f/s^{-1}	10^5k_r/s^{-1}	K
60.0	18.8	0.00	0.00	6.83		
	18.8	0.00 [a]	0.00 [a]	7.17		
	112	0.00	0.00	6.85		
	112	1.10	6.25	3.08		
	270	0.00	0.00	7.26		
	270	1.10	6.25	4.94		
	504	0.00	0.00	7.70		
	504	1.10	6.25	6.14		
	654	0.00	0.00	7.26		
	654	1.10	6.25	6.40		
70.0	110	0.00	0.00	30.1		
	110	1.10	6.12	9.78		
	221	0.00	0.00	29.2		
	221	1.10	6.12	15.4		
	381	0.00	0.00	32.5		
	381	1.10	6.12	22.2		
	536	0.00	0.00	29.9		
	536	1.10	6.12	25.0		
	663	0.00	0.00	33.0		
	663	1.10	6.12	26.8		
80.0	18.5	0.00	0.00	*ca.* 77		
	18.5	0.00 [a]	0.00 [a]	119		
	39.8	1.10	5.98	15.9		
	73.4	0.00	0.00	111		
	73.4	1.10	5.98	26.2		
	109	0.00	0.00	116		
	109	0.55	2.99	51.4		
	109	1.10	5.98	31.5		
	234	0.00	0.00	125		
	234	1.10	5.98	62.0		
	363	0.00	0.00	113		
	363	1.10	5.98	75.5		
	550	0.00	0.00	134		
	550	1.10	5.98	98.1		
	673	0.00	0.00	134		
	673	1.10	5.98	106		
110.0	0.62 [b]	0.55	2.70		2.33	*ca.* 12
	0.82 [b]	1.10	5.40		2.16	*ca.* 12
120.0	0.41 [b]	0.276	1.28		6.50	*ca.* 6
	0.67 [b]	1.10	5.10		7.13	*ca.* 5
130.0	0.38 [b]	0.276	1.20		19.6	*ca.* 5
	0.69 [b]	1.10	4.76		18.0	*ca.* 4

[a] Bubbling Ar. [b] Approximate final concentration at equilibrium.

The forward reaction of the second stage under Ar gave quantitative formation of (III). In the presence of CO, however, an equilibrium mixture of (II) and (III) was obtained. The reaction was monitored by following the change in absorbance of the peaks at 2 039 and/or 1 901 cm^{-1}. Under pseudo-first-order conditions, plots of log $|A_t - A_\infty|$ against time were linear for over three half-lives. The observed rate constants, $k_{obs.}$, then represent, under bubbling Ar, the observed rate constant of the forward reaction [$= k_{f(Ar)}$], and under CO, where $A_\infty = A_e$, the sum of the observed rate constants of the forward and reverse reactions [$= k_{f(CO)} + k_r$].[10] In the latter case the two terms were separated by introducing the spectrophotometrically determined concentration ratio, at equilibrium, of complexes (II) and (III). Consistent results were obtained by following either the forward or reverse reaction of the second stage. Rate plots for reactions under ' static ' Ar were non-linear because k_f is extremely sensitive to CO. Vigorous bubbling of Ar through the solution was necessary in order to remove

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[10] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, Tokyo, 1961, p. 186.

TABLE 2

Rate and equilibrium data for the reaction $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] + PBu_3 \rightleftharpoons [(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)] + CO$ in decalin. $[\text{Complex}]^a = 2 \times 10^{-4}$—$1 \times 10^{-3}$ mol dm^{-3}

$\frac{\theta_c}{°C}$	$\frac{10^3[PBu_3]}{\text{mol dm}^{-3}}$	$\frac{p_{CO}}{\text{atm}}$	$\frac{10^3[CO]}{\text{mol dm}^{-3}}$	$\frac{10^5(k_f + k_r)}{s^{-1}}$	$\frac{[(III)]_e}{[(II)]_e}$	$\frac{10^5 k_f}{s^{-1}}$	$\frac{10^5 k_r}{s^{-1}}$	$10^2 K$
60.0	272	0.00 [b]	0.00 [b]			11.1		
	607	0.00 [b]	0.00 [b]			10.7		
70.0	270	0.00	0.00			*ca.* 17.7		
	270	0.00 [b]	0.00 [b]			44.5		
	603	0.00 [b]	0.00 [b]			39.8		
80.0	295	0.00 [b]	0.00 [b]			112 [c]		
	758	0.00 [b]	0.00 [b]			144 [c]		
	1 140	0.00 [b]	0.00 [b]			178		
100.0	89.7	0.106	0.54	8.37	2.83	6.18	2.19	
	269	0.106	0.54	19.9	9.19	17.9	1.95	
	444	0.106	0.54	33.9	14.3	31.7	2.22	
	647	0.106	0.54	39.4	23.6	37.8	1.60	
110.0	<0.18	1.10	5.4				4.98 [d]	
	<0.24	0.106	0.52				5.01 [d]	
	93	1.10	5.4	6.60 [d]	0.337 [d]	1.66 [d]	4.94 [d]	
	103	0.106	0.52	21.8	4.41	17.8	4.03	1.75 [e]
	178	0.106	0.52	31.2	6.19	26.9	4.34	
	356	0.106	0.52	58.7	12.7	54.4	4.28	
	456	0.106	0.52	71.3	13.5	66.4	4.92	
	456	0.276	1.35	34.0	5.67	28.9	5.10	
	456	0.55	2.7	18.9	3.51	14.7	4.19	
120.0	<0.16	0.276	1.28				13.4 [d]	
	<0.16	0.55	2.6				12.4 [d]	
	<0.16	1.10	5.1				12.7 [d]	1.69 [e]
	105	0.106	0.49	44.4	4.17	35.8	8.59	
	176	0.106	0.49	72.1	7.85	64.0	8.14	
	272	0.106	0.49	121	12.1	112	9.24	
	357	0.106	0.49	152	21.2	145	6.85	
130.0	<0.21	0.276	1.20				30.0 [d]	1.53 [e]
	<0.26	1.10	4.8				30.1 [d]	

[a] Starting from $[(OC)_4\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)]$, (II), or from $[(Bu_3P)(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)]$, (III). [b] Bubbling Ar. [c] Low approximate values (see text). [d] Starting from (III); all other runs started from (II). [e] See text: $\Delta H^{\ominus} = -9$ kJ mol^{-1} (-2 kcal mol^{-1}), $\Delta S^{\ominus} = -56$ J K^{-1} mol^{-1} (-13 cal K^{-1} mol^{-1}).

the carbon monoxide released during the reaction. This removal proved difficult at 80.0 °C due to the fast rate of CO production, and for two runs the k_f values were based on the first half-life of the increasingly curved rate plot. The forward reaction of the second stage follows, under Ar, the rate equation $k_{f(Ar)} = d$, and under CO, $k_{f(CO)} = e[PBu_3]/[CO]$.

The observed rate of the reverse reaction was almost constant under all conditions of [CO] and [PBu$_3$], corresponding to the rate equation $k_r = f$. The [CO] dependence of the reverse reaction was also studied by following the disappearance of complex (III) at various partial CO pressures in the absence of added PBu$_3$. Complex (III) completely disappeared forming (II), which in turn reacted further to give an equilibrium mixture of (II) and (I). Consistent kinetic results were obtained.

All the rate data for the second stage, together with the equilibrium constants, are collated in Table 2. The variation of the equilibrium constant with temperature was determined by measuring equilibrium concentrations in three samples of the same solution at three different temperatures. The values so obtained are consistent with those determined from kinetic data.

DISCUSSION

The kinetic data are consistent with all the substitutions occurring through a dissociative mechanism according to reactions (5) and (6) (L = CO for the first stage and PBu$_3$ for the second). The rate equation is given by (7), where the two terms represent respectively the observed rate constants of the forward and reverse

$$[L(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_4] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [L(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3] + CO \quad (5)$$

$$[L(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3] + PBu_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [L(OC)_3\overline{Mo(\mu\text{-}PEt_2)_2Mo}(CO)_3(PBu_3)] + CO \quad (6)$$

$$k_{obs.} = k_f + k_r = (k_1/\{1 + (k_{-1}[CO]/k_2[PBu_3])\}) + (k_{-2}/\{1 + (k_2[PBu_3]/k_{-1}[CO])\}) \quad (7)$$

reactions. This rate equation is seen to be consistent with the experimentally derived ones as follows.

Equation (7) applied to the forward reaction of the first stage reduces under Ar to $k_{obs.} = k_{f(Ar)} = k_1$ and under CO, on rearrangement, takes the form $1/k_{f(CO)} = (1/k_1) + (k_{-1}[CO]/k_1k_2[PBu_3])$. This equation predicts linear plots of $1/k_{f(CO)}$ against $1/[PBu_3]$ from which the values of k_1 and k_{-1}/k_2 can be derived. Good linear plots were indeed obtained. It is worth noting that the $k_{f(CO)}$ value observed in a run under 0.55 atm CO gave the consistent value of 81.2 for k_{-1}/k_2 (*cf.* $k_{-1}/k_2 = 67.0 \pm 11.2$ under 1.1 atm CO), assuming k_1 is independent of CO pressure. The values found for k_1 and k_{-1}/k_2 also justify *a posteriori* the kinetic treatment [equation (4)] of the reverse reaction of the first stage under various constant CO pressures and absence of added phosphine. In fact under these experimental conditions the term $k_2[\mathrm{PBu_3}]/k_{-1}[\mathrm{CO}]$ is always $\leqslant 1$, and consequently the rate of disappearance of (II) to give an equilibrium mixture of (II), (I), and $\mathrm{PBu_3}$ is given by $-d[(\mathrm{II})]/dt = k_{-2}[(\mathrm{II})] - (k_1k_2/k_{-1}[\mathrm{CO}])[(\mathrm{I})][\mathrm{PBu_3}]$. At constant [CO] this equation reduced to the form valid for a reaction of the type $\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{C}$ as given in equation (4).

Equation (7) is also consistent with the experimental rate equations for the second stage. In fact the observed constancy of k_r even at the high $[\mathrm{PBu_3}]/[\mathrm{CO}]$ ratio employed ($\leqslant 1.2 \times 10^3$) indicates that $k_2[\mathrm{PBu_3}]/k_{-1}[\mathrm{CO}]$ is always $\leqslant 1$, and as a consequence equation (7) reduces to $k_{f(\mathrm{Ar})} = k_1$, $k_{f(\mathrm{CO})} = k_1k_2[\mathrm{PBu_3}]/k_{-1}[\mathrm{CO}]$, and $k_r = k_{-2}$. It is worth noting that a consistent value of 8.21×10^{-7} s^{-1} is found for k_1k_2/k_{-1} by studying the dependence of k_f on P_{CO}, compared with a value of 8.02×10^{-7} s^{-1} obtained from the $[\mathrm{PBu_3}]$ dependence.

All the reported kinetic parameters for both stages (the first in Tables 3 and 4 and the second in Table 5) were obtained by a least-squares analysis of the data. For a particular set of data, the same percentage standard deviation in $k_{\mathrm{obs.}}$ was generally assumed at all the temperatures. Only for the dependence of $k_{f(\mathrm{CO})}$ on $[\mathrm{PBu_3}]$ was each $k_{f(\mathrm{CO})}$ value weighted assuming the same percentage standard deviation at a given temperature.[5] All the tabulated uncertainties are standard deviations corrected for the number of degrees of freedom, so that estimates of 95% confidence limits can be made by doubling the uncertainties.

TABLE 3

Kinetic parameters [a] of the first stage obtained from the rate equations $k_{f(\mathrm{Ar})} = k_1{}^b$ and $k_r = k_{-2}$ for the reaction $[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\mathrm{PEt_2})_2\mathrm{Mo(CO)_4}] + \mathrm{PBu_3} \rightleftharpoons [(\mathrm{Bu_3P})(\mathrm{OC})_3\mathrm{Mo}(\mu\text{-}\mathrm{PEt_2})_2\mathrm{Mo(CO)_4}] + \mathrm{CO}$

θ_c/°C	10^5k_1/s^{-1}	10^5k_{-2}/s^{-1}
60.0	7.41	
70.0	31.8	
80.0	126	
110.0		2.24
120.0		6.81
130.0		18.8

$\Delta H_1^\ddagger$ = 136 ± 3 kJ mol^{-1} (32.5 ± 0.6 kcal mol^{-1})
$\Delta S_1^\ddagger$ = 83 ± 7 J K^{-1} mol^{-1} (20 ± 2 cal K^{-1} mol^{-1})
$\sigma[k_{f(\mathrm{Ar})}] = 7.1\%$
$\Delta H_{-2}^\ddagger$ = 133 ± 5 kJ mol^{-1} (31.8 ± 1.2 kcal mol^{-1})
$\Delta S_{-2}^\ddagger$ = 12 ± 12 J K^{-1} mol^{-1} (3 ± 3 cal K^{-1} mol^{-1}) $\sigma(k_r) = 7.8\%$

[a] Uncertainties are standard deviations (see text). [b] For $[\mathrm{PBu_3}] \geqslant 0.234$ mol dm^{-3}.

Values of $\Delta S_1^\ddagger$ for the first and second stages, together with the nature of the retardation of the rate by carbon monoxide, are in good agreement with reversible CO-dissociative mechanisms. Furthermore the close similarity of the two values of $\Delta H_1^\ddagger$ shows that phosphine introduced in the first stage has only a small effect on the dissociation of carbon monoxide from the other molybdenum atom in the second stage. Values of *ca.* 33 kcal mol^{-1} for $\Delta H^\ddagger$ and 20 cal K^{-1} mol^{-1} for $\Delta S^\ddagger$ have been reported for the CO-dissociative paths in substitution reactions of $[\mathrm{L(OC)_2Co}(\mu\text{-}\mathrm{C_2Ph_2})\mathrm{Co(CO)_3}]$ (L = CO or $\mathrm{PBu_3}$),[11] $[\mathrm{L(OC)_3Co}(\mu\text{-}\mathrm{GePh_2})\mathrm{Co(CO)_4}]$ (L = CO or $\mathrm{PPh_3}$),[12] and $[(\mathrm{Ph_3P})(\mathrm{OC})_2\mathrm{Fe}(\mu\text{-}\mathrm{SPh})_2\mathrm{Fe(CO)_3}]$.[5] These observations suggest that in binuclear complexes the rate of dissociation of CO from a given metal atom is to some extent independent of electronic and steric variations at the other metal centre, even in the presence of a metal–metal bond.

TABLE 4

Kinetic parameters [a] of the first stage obtained from the rate equation $1/k_{f(\mathrm{CO})} = (1/k_1) + (k_{-1}[\mathrm{CO}]/k_1k_2[\mathrm{PBu_3}])^b$ for the reaction $[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\mathrm{PEt_2})_2\mathrm{Mo(CO)_4}] + \mathrm{PBu_3} \rightleftharpoons [(\mathrm{Bu_3P})(\mathrm{OC})_3\mathrm{Mo}(\mu\text{-}\mathrm{PEt_2})_2\mathrm{Mo(CO)_4}] + \mathrm{CO}$

θ_c/°C	10^5k_1/s^{-1}	k_{-1}/k_2	$\sigma[k_{f(\mathrm{CO})}]$/ %
60.0	8.39 ± 0.31	30.7 ± 2.8	2.8
70.0	42.2 ± 3.0	59.9 ± 8.1	4.3
80.0	166 ± 17	67.0 ± 11.2	8.1

$\Delta H_1^\ddagger$ = 145 ± 4 kJ mol^{-1} (34.7 ± 1.1 kcal mol^{-1})
$\Delta S_1^\ddagger$ = 112 ± 13 J K^{-1} mol^{-1} (27 ± 3 cal K^{-1} mol^{-1})
$\Delta H_{-1}^\ddagger - \Delta H_2^\ddagger$ = 43 ± 8 kJ mol^{-1} (10.2 ± 2.0 kcal mol^{-1})
$\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger$ = 157 ± 25 J K^{-1} mol^{-1} (37 ± 6 cal K^{-1} mol^{-1})

[a] Uncertainties are standard deviations (see text); the standard deviations take into account the covariance of the parameters $1/k_1$ and k_{-1}/k_1k_2 obtained from least-squares analysis according to equation (7). [b] $p_{\mathrm{CO}} = 1.1$ atm.

TABLE 5

Kinetic parameters [a] of the second stage obtained from the rate equations $k_{f(\mathrm{Ar})} = k_1$,[b] $k_{f(\mathrm{CO})} = (k_1k_2/k_{-1}[\mathrm{CO}])[\mathrm{PBu_3}]$,[c] and $k_r = k_{-2}{}^d$ for the reaction $[(\mathrm{Bu_3P})(\mathrm{OC})_3\mathrm{Mo}(\mu\text{-}\mathrm{PEt_2})_2\mathrm{Mo(CO)_4}] + \mathrm{PBu_3} \rightleftharpoons [(\mathrm{Bu_3P})(\mathrm{OC})_3\mathrm{Mo}(\mu\text{-}\mathrm{PEt_2})_3\mathrm{Mo(CO)_3(PBu_3)}] + \mathrm{CO}$

θ_c/°C	10^5k_1/s^{-1}	$10^7(k_1k_2/k_{-1})$/s^{-1}	$10^{-4}(k_{-1}/k_2)$	10^5k_{-2}/s^{-1}
60.0	10.9		1.27 [e]	
70.0	42.1		1.84 [e]	
80.0	178		2.62 [e]	
100.0		3.54		
110.0		8.02		4.99
120.0		18.4		12.8
130.0				30.0

$\Delta H_1^\ddagger$ = 132 ± 7 kJ mol^{-1} (31.7 ± 1.6 kcal mol^{-1})
$\Delta S_1^\ddagger$ = 76 ± 20 J K^{-1} mol^{-1} (18 ± 5 cal K^{-1} mol^{-1})
$\sigma[k_{f(\mathrm{Ar})}] = 12.3\%$
$\Delta H_1^\ddagger + \Delta H_2^\ddagger - \Delta H_{-1}^\ddagger$ = 97 ± 4 kJ mol^{-1} (23.3 ± 1.0 kcal mol^{-1})
$\Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger$ = −109 ± 11 J K^{-1} mol^{-1} (−26 ± 3 cal K^{-1} mol^{-1}) $\sigma[k_{f(\mathrm{CO})}] = 9.8\%$
$\Delta H_{-1}^\ddagger - \Delta H_2^\ddagger$ = 35 ± 8 kJ mol^{-1} (8.4 ± 1.9 kcal mol^{-1})
$\Delta S_{-1}^\ddagger - \Delta S_2^\ddagger$ = 185 ± 23 J K^{-1} mol^{-1} (44 ± 6 cal K^{-1} mol^{-1})
$\Delta H_{-2}^\ddagger$ = 112 ± 2 kJ mol^{-1} (26.8 ± 0.6 kcal mol^{-1})
$\Delta S_{-2}^\ddagger$ = −37 ± 6 J K^{-1} mol^{-1} (−9 ± 1 cal K^{-1} mol^{-1})
$\sigma(k_r) = 3.8\%$

[a] Uncertainties are standard deviations (see text). [b] Under bubbling Ar. [c] $p_{\mathrm{CO}} = 0.106$ atm. [d] Using the more accurate values obtained in the runs, which, starting from (III), went to completion. [e] From the estimated activation parameters.

A marked difference between the first and second stages emerges on considering the competition ratio k_{-1}/k_2 for bimolecular attack on the six-co-ordinate intermediate $[\mathrm{L(OC)_3Mo}(\mu\text{-}\mathrm{PEt_2})_2\mathrm{Mo(CO)_3}]$ (L = CO or $\mathrm{PBu_3}$) formed by loss of a CO ligand. The value of this ratio ranges, at 80 °C, from 67.0 for $L = CO$ to 2.62×10^4 for $L = PBu_3$. These values indicate that the molybdenum atom exercises a high preference for nucleophilic attack by CO rather than PBu_3, and that this preference is markedly enhanced by substitution on the adjacent metal of one CO ligand by a phosphine group. A competition ratio of 67.0 for bimolecular attack on a co-ordinatively unsaturated complex is high compared with those previously found in other binuclear bridged complexes of cobalt and iron,[11,12,5] and for bimolecular attack on $[Mo(CO)_4(PPh_3)]$,[13] $[Ru(CO)_3L]$ ($L = PPh_3$ or PBu_3),[14,15] and $[Ni(CO)_3]$.[16] In fact in all these cases ratios of *ca.* unity are found. Nevertheless some discrimination in favour of attack by the smaller CO group was not unexpected, in view of the trend observed in passing from less to more crowded structures. Consideration of the activation parameters shows that the higher activation enthalpy ($\Delta H_{-1}^{\ddagger} - \Delta H_2^{\ddagger} = 10.2$ kcal mol^{-1}) for CO attack is dominated by a much more positive (or less negative) activation entropy ($\Delta S_{-1}^{\ddagger} - \Delta S_2^{\ddagger} = 37$ cal K^{-1} mol^{-1}). Values of these parameters for the second stage reveal that the large increase in k_{CO}/k_{PBu_3} is a combined effect of a smaller difference in $\Delta H^{\ddagger}$ ($\delta\Delta H^{\ddagger} = 8.4$ kcal mol^{-1}) and a more positive difference in $\Delta S^{\ddagger}$ ($\delta\Delta S^{\ddagger} = 44$ cal K^{-1} mol^{-1}).

The kinetic behaviour observed in this study contrasts greatly with that observed for the intermediate $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2]$ ($L = CO$ or PBu_3) where k_{CO}/k_{PBu_3} is almost insensitive to changing L. In fact the behaviour illustrated here by co-ordinatively unsaturated intermediates is more comparable with that generally observed in bimolecular substitution on co-ordinatively saturated complexes. Some examples will serve to illustrate this point. For the complex $[L(OC)_2Co(\mu\text{-}CO)(\mu\text{-}GePh_2)Co(CO)_3]$ ($L = CO$ or PBu_3), where bimolecular attack is postulated to occur, k_{CO}/k_{PPh_3} increases by a factor of $\geqslant 1\,000$ on changing L from CO to PPh_3.[12] For S_N2 attack by PBu_3 on the complex $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ ($L = CO$ or PBu_3) the rate decreases by a factor of $\geqslant$*ca.* 100 on changing L from CO to PBu_3.[11] In the reaction of $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3]$ with PPh_3 the first substitution of CO occurs *via* S_N2 attack at room temperature, whereas the second substitution at the adjacent metal centre occurs by a dissociative mechanism at *ca.* 100 °C.[5] It is also interesting to note that bimolecular attack by PBu_3 on $[L(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$ ($L = CO$ or PBu_3) is little affected by changing L.[12] All these observations suggest that the co-ordinatively unsaturated metal in $[L(OC)_3Mo(\mu\text{-}PEt_2)_2Mo(CO)_3]$ behaves very like a saturated centre. One might therefore conclude that the poor discrimination normally exhibited by co-ordinatively unsaturated complexes is to a great extent associated with their 'open' structures.

Turning to a consideration of the effect of changing L on the competition ratio k_{CO}/k_{PBu_3}, it appears this may arise due to both steric and electronic factors. In the case of $[L(OC)_2CO(\mu\text{-}C_2Ph_2)Co(CO)_3]$ ($L = CO$ or PBu_3),[11] the large difference in k_{PBu_3} terms has been partly attributed to the electronic flexibility of the C_2Ph_2 bridge, which is capable of transmitting electronic variations from one metal to another. This flexibility seems absent for PEt_2 bridges, but possible electronic effects could well be transmitted through the metal–metal bond. If electronic effects were predominant, it is not clear why these variations are not reflected in the rate of dissociation of CO. In the absence of further data it seems reasonable to assume that steric effects are predominant, especially as the importance of steric effects in bimolecular substitutions of metal carbonyls is well established.[5] Replacing a small CO group with a large phosphine ligand would be expected to make approach to the adjacent metal relatively more difficult for PBu_3 than for CO.

The values of the activation parameters for the reverse reaction are consistent for both stages with a reversible PBu_3-dissociative mechanism. The lower activation enthalpy and the less favourable activation entropy for the reverse reaction of the second stage ($\Delta H^{\ddagger} = 26.8$ against 31.8 kcal mol^{-1}, $\Delta S^{\ddagger} = -9$ against 3 cal K^{-1} mol^{-1}) imply that complex (III) is destabilised compared to (II) probably as a result of steric effects, which serve to lower the $\Delta H^{\ddagger}$ for Mo–PBu_3 bond breaking. The same steric effects may also explain the negative value of $\Delta S^{\ddagger}$, which implies that there is some steric restriction to PBu_3 removal in the transition state.

The value of the equilibrium constant at 120 °C for the first substitution is *ca.* 6, which changes to a value of 1.69×10^{-2} for the second. This means that complex (II) is *ca.* 350 times more stable with respect to (I) than is (III) with respect to (II). This variation is mainly due to a more favourable enthalpy variation for the first substitution. In fact, by combining the activation parameters, one obtains $\Delta H^{\ominus} = -6.9 \pm 1.6$ kcal mol^{-1} and $\Delta S^{\ominus} = -13 \pm 4$ cal K^{-1} mol^{-1} for the first stage, and $\Delta H^{\ominus} = -3.5 \pm 1.2$ kcal mol^{-1} and $\Delta S^{\ominus} = -17 \pm 3$ cal K^{-1} mol^{-1} for the second. It is worth noting that similar destabilisation has been observed in PPh_3 substitution of the di-iron complex $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3]$.[5] In this case, the destabilisation is attributable to a less favourable entropy variation for the second stage.

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