The Mechanism of Displacement of Diene from $[M(\eta^4\text{-diene})(CO)_4]$ (M = Cr, Mo, or W, diene = norbornadiene; M = Mo, diene = cyclo-octa-1,5-diene) and the *cis* $\rightleftharpoons$ *trans* Isomerization of $[M(CO)_4L_2]$ Complexes [L = PBu_3, $P(OMe)_3$, or $P(OPh)_3$]

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Kinetic studies are reported of the displacement of the diene from $[M(\eta^4\text{-diene})(CO)_4]$ [diene = norbornadiene, M = Cr, Mo, or W; diene = cyclo-octa-1,5-diene (cod), M = Mo] by phosphorus ligands [L = PBu_3, $P(OMe)_3$, or $P(OPh)_3$] to give complexes $[M(CO)_4L_2]$. With the exception of $[Mo(cod)(CO)_4]$, all reactions exhibit a bimolecular rate law of the type $-d[A]/dt = k_{obs.}[A][L]$, where A = $[M(diene)(CO)_4]$ which is interpreted mechanistically as a stepwise ligand-assisted dechelation of the diene; $k_{obs.}$ may be seen to increase in the order $Cr < W \ll Mo$, while the ordering in terms of ligand $[P(OPh)_3 < P(OMe)_3 < PBu_3]$ reflects the increasing order of ligand nucleophilicity. *cis–trans* Isomerization of $[M(CO)_4L_2]$ (L = PBu_3, $P(OMe)_3$, or $P(OPh)_3$; M = Cr, Mo, or W) has also been studied kinetically. With the exception of $[Mo(CO)_4\{P(OPh)_3\}_2]$, all isomerizations are intramolecular. Rates of isomerization increase in the order $Mo < W < Cr$ and in the order $P(OPh)_3 < P(OMe)_3 < PBu_3$, while K_{eq} (=[*trans*]/[*cis*]) increases in the order $W \approx Mo \ll Cr$ and in the order $P(OPh)_3 < P(OMe)_3 < PBu_3$. These results are interpreted in terms of both steric and electronic factors.

In a previous article,[1] we presented kinetic studies of both the diolefin exchange reaction $[Cr(\eta^4\text{-diene})(CO)_4] + \text{diene}' \longrightarrow [Cr(\eta^4\text{-diene}')(CO)_4] + \text{diene}$ [diene = buta-1,3-diene or *trans,trans*-hexa-2,4-diene; diene′ = norbornadiene (nbd) or cyclo-octa-1,5-diene (cod)] and the substitution reaction of (η^4-buta-1,3-diene)tetracarbonylchromium with $P(OR)_3$ (R = Me or Ph) to give $[Cr(CO)_4\{P(OR)_3\}_2]$. Athough displacement of diene from $[M(\eta^4\text{-diene})(CO)_4]$ complexes has been used synthetically to prepare a variety of $[M(CO)_4L_2]$ (L = phosphine or phosphite) complexes, only one other kinetic study of diene displacement has been described,[2] namely the reaction of $[Mo(cod)(CO)_4]$ with phosphine ligands (L) to give *cis*-$[Mo(CO)_4L_2]$. In addition, as catalytic transformations of dienes using $[M(CO)_6]$ proceed through the intermediacy of $[M(\eta^4\text{-diene})(CO)_4]$ complexes,[3] information relevant to the lability of co-ordinated dienes is of interest. We report here a comparative kinetic study of the displacement of diene from $[M(nbd)(CO)_4]$ (M = Cr, Mo, or W) and from $[Mo(cod)(CO)_4]$ by phosphine and phosphite ligands, together with an investigation of the rates and mechanism of the *cis* $\rightleftharpoons$ *trans* isomerization of the $[M(CO)_4L_2]$ products so formed.

Results and Discussion

(*A*) *Diene Displacement.*—Kinetically monitored reactions between $[M(nbd)(CO)_4]$ (M = Cr, Mo, or W) or $[Mo(cod)(CO)_4]$ and the phosphine or phosphite ligands PBu_3, $P(OMe)_3$, or $P(OPh)_3$ were carried out in n-heptane at the temperatures given in Tables 1—3 using at least a ten-fold excess of ligand to ensure first-order conditions. Reactions of $[Mo(nbd)(CO)_4]$ with $P(OMe)_3$ or PBu_3 were effectively complete within the time of mixing at room temperature. Reaction of $[W(nbd)(CO)_4]$ with PBu_3 was too fast to be measured at 46.5 °C and was therefore measured at 30.4 °C.

The substrates are light yellow complexes showing a weak absorption in the visible region together with a much stronger absorption in the near ultraviolet. Reactions with phosphites and of $[Mo(nbd)(CO)_4]$ with PBu_3 were continuously monitored at the wavelengths given in the Experimental section where the product complexes $[M(CO)_4L_2]$ are effectively transparent. Reactions of $[M(nbd)(CO)_4]$ (M = Cr or W) with PBu_3 were monitored by i.r. sampling using the disappearance of the highest frequency CO absorption of $[M(nbd)(CO)_4]$ as these reactions produce quantities of the yellow *trans*-$[M(CO)_4(PBu_3)_2]$ complex.

Table 1. Rate data for the reaction of $[Cr(nbd)(CO)_4]$ with L in n-heptane

θ_c/°C	Entering group	[L]/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
46.5	$P(OMe)_3$ [a]	0.044	0.56
		0.066	0.93
		0.088	1.25
		0.11	1.55
		0.132	1.60
		0.154	2.11
		0.176	2.18
		0.220	2.93
46.5	$P(OPh)_3$ [a]	0.066	0.106
		0.088	0.142
		0.110	0.169
		0.132	0.200
		0.156	0.234
		0.176	0.253
		0.198	0.286
		0.220	0.320
46.5	PBu_3 [b]	0.005	2.878
		0.010	4.641
		0.015	7.203
		0.020	9.129
		0.025	11.44
		0.030	13.57
		0.035	16.16

[a] $[Cr(nbd)(CO)_4] = 2.2 \times 10^{-3}$ mol dm^{-3}. [b] $[Cr(nbd)(CO)_4] = 5 \times 10^{-4}$ mol dm^{-3}.

Values of $k_{obs.}$ are given in Tables 1—3. With the exception of the reaction of $[W(nbd)(CO)_4]$ with PBu_3, a linear least-squares fitting of plots of $k_{obs.}$ against [L] yielded slopes (k_a of Table 4) whose standard deviations approximate the standard deviations of the differences between the duplicate runs for the $k_{obs.}$ values (±5%). The higher standard deviation for the reaction of $[W(nbd)(CO)_4]$ with PBu_3 reflects the poorer reproducibility of the duplicate runs (±10%) rather than a

Table 2. Rate data for the reaction of $[Mo(diene)(CO)_4]$ (diene = nbd or cod) (1.10×10^{-3} mol dm^{-3}) with L

θ_c/°C	Solvent	Leaving group	Entering group	[L]/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
46.5	n-Heptane	nbd	$P(OPh)_3$	0.011	8.04
				0.0165	13.82
				0.022	17.17
				0.033	26.29
				0.044	32.72
46.5	n-Heptane	cod	$P(OPh)_3$	0.011	1.766
				0.0165	1.866
				0.022	2.427
				0.033	3.671
				0.044	4.338
				0.055	5.065
				0.066	5.395
				0.077	6.526
				0.088	7.278
				0.099	8.111
33.2	n-Heptane	nbd	$P(OPh)_3$	0.011	5.277
				0.022	9.438
				0.033	13.32
				0.044	17.82
				0.055	22.72
28.3	n-Heptane	nbd	$P(OPh)_3$	0.011	3.131
				0.033	9.505
				0.044	12.80
				0.055	16.12
46.5	Benzene	nbd	$P(OPh)_3$	0.011	5.013
				0.022	9.445
				0.033	13.24
				0.044	17.44
				0.055	22.01
				0.066	26.78
46.5	Chloroform	nbd	$P(OPh)_3$	0.011	4.745
				0.022	9.161
				0.033	13.16
				0.044	16.47
				0.055	21.42
				0.066	24.84
				0.077	28.85

Table 3. Rate data for the reaction of $[W(nbd)(CO)_4]$ with L in n-heptane

θ_c/°C	Entering group	[L]/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
46.5	$P(OMe)_3$ [a]	0.07	4.96
		0.14	10.13
		0.21	15.15
		0.28	20.08
		0.35	25.20
		0.42	31.03
		0.49	40.63
		0.56	54.01
46.5	$P(OPh)_3$ [a]	0.07	0.511
		0.14	1.028
		0.21	1.382
		0.28	2.001
		0.35	2.128
		0.42	2.555
		0.49	3.111
		0.56	3.535
30.4	PBu_3 [b]	0.005	3.49
		0.01	4.33
		0.015	6.59
		0.02	6.04
		0.025	8.33
		0.03	7.89
		0.035	9.14
		0.04	10.15

[a] $[W(nbd)(CO)_4] = 7.0 \times 10^{-3}$ mol dm^{-3}. [b] $[W(nbd)(CO_4)] = 5 \times 10^{-4}$ mol dm^{-3}; i.r. monitoring by following disappearance of peak at 1 960 cm^{-1}.

poorer linear least-squares fit.* In all reactions of $[M(nbd)(CO)_4]$ complexes, the intercept of $k_{obs.}$ against [L] (k_1 of Table 4) lies within 2—3σ of zero; in the reaction of $[Mo(cod)(CO)_4]$ with $P(OPh)_3$, however, a positive, non-zero intercept is well defined.

Several chemically reasonable mechanisms may be associated with this first-order dependence of $k_{obs.}$ on [L]. In particular, as the reaction involves displacement of a bidentate ligand, mechanisms involving rapid pre-equilibrium formation of an intermediate containing a η^2-diene must be considered: (*a*) rapid associative pre-equilibrium followed by rate-determining dissociative formation of products, equations (1) and (2), where A is $[M(\eta^4\text{-diene})(CO)_4]$, B is $[M(\eta^2\text{-diene})(CO)_4L]$, C is the co-ordinatively unsaturated $[M(CO)_4L]$, D is $[M(CO)_4L_2]$, and K_{eq} is given by equation (3). For this mechanism, $k_{obs.}$ is given by equation (4), which reduces

$$A + L \xrightleftharpoons{K_{eq}} B \qquad (1)$$

$$B \xrightarrow{k'} \text{diene} + C \xrightarrow{+L} D \qquad (2)$$

$$K_{eq} = [B]/[A][L] \qquad (3)$$

$$k_{obs.} = k'K_{eq}[L]/(1 + K_{eq}[L]) \qquad (4)$$

to $k_{obs.} = k'K_{eq}[L]$ if $K_{eq}[L] \ll 1$. With respect to the ligand concentrations used here (10^{-1}—10^{-2} mol dm^{-3}), this qualitatively requires $K_{eq} < 0.1$ dm^3 mol^{-1}. This condition is almost certainly satisfied, since i.r. monitoring reveals no detectable absorbances assignable to B. Complexes such as *cis*-$[W(C_2H_4)(CO)_4(PPr^i{}_3)]$ have been prepared, and exhibit i.r. absorptions at 2 029, 1 933, 1 916, and 1 905 cm^{-1}.[5a] For this mechanism, the measured activation parameters will be associated with $K_{eq}k'$ ($\Delta H_{eq} + \Delta H^\ddagger$, $\Delta S_{eq} + \Delta S^\ddagger$). However, if, as is often the case, $\Delta H_{eq} \ll \Delta H^\ddagger$ and $\Delta S_{eq} \ll \Delta S^\ddagger$, then the measured activation parameters are expected to reflect the nature of the rate-determining step associated with k', and the strongly negative activation entropy (Table 4) is not consistent with a reaction which is dissociative in nature.

(*b*) Another alternative is a rapid associative pre-equilibrium followed by rate-determining associative formation of products, equations (5) and (6), where A, B, D, and K_{eq} are defined as in (*a*). Treatment in the same way shows that $k_{obs.}$ is given by equation (7), which reduces to $k_{obs.} = k'[L]$ when $K_{eq}[L] \gg 1$. In the concentration range employed here, this qualitatively requires that $K_{eq} > 10^3$ dm^3 mol^{-1}. Again, there is no spectroscopic evidence for B, and in addition, kinetic studies of the substitution of olefin by phosphine in *cis*-

$$A + L \xrightleftharpoons{K_{eq}} B \qquad (5)$$

$$B + L \xrightarrow{k'} D + \text{diene} \qquad (6)$$

$$k_{obs.} = k'K_{eq}[L]^2/(1 + K_{eq}[L]) \qquad (7)$$

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* There is a brief report [4] that this reaction attains a limiting rate at high phosphine concentration. We find no evidence for this over the range of phosphine concentrations used in this study.

Table 4. Derived rate constants for substitution of $[M(\eta^4\text{-diene})(CO)_4]$

Complex	Ligand	Solvent	θ_c/°C	10^4k_1 [a]/s^{-1}	10^4k_a [a]/dm^3 mol^{-1} s^{-1}
$[Cr(nbd)(CO)_4]$	$P(OMe)_3$	n-Heptane	46.5	—	12.78(0.66)
	$P(OPh)_3$	n-Heptane	46.5	—	1.37(0.03)
	PBu_3	n-Heptane	46.5	—	442.4(7.9)
$[Mo(nbd)(CO)_4]$ [b]	$P(OPh)_3$	n-Heptane	46.5	—	742.4(37.6)
	$P(OPh)_3$	n-Heptane	33.2	—	393.9(7.4)
	$P(OPh)_3$	n-Heptane	28.3	—	294.9(2.2)
	$P(OPh)_3$	Benzene	46.5	—	390.4(6.5)
	$P(OPh)_3$	Chloroform	46.5	—	365.2(6.8)
$[Mo(cod)(CO)_4]$ [c]	$P(OPh)_3$	n-Heptane	46.5	0.95(0.13)	72.2(2.3)
$[W(nbd)(CO)_4]$	$P(OMe)_3$	n-Heptane	46.5	—	80.5(3.6)
	$P(OPh)_3$	n-Heptane	46.5	—	5.74(0.24)
	PBu_3	n-Heptane	30.4	—	190.9(17.4)
$[Cr(\eta^4\text{-}CH_2CHCHCH_2)(CO)_4]$	$P(OMe)_3$	n-Heptane	26.5	19.0(2.6)	376(30) [d]

[a] Standard deviations are given in parentheses. [b] Determined activation parameters are $\Delta H^\ddagger = 36.80 \pm 7.8$ kJ mol^{-1} and $\Delta S^\ddagger = -151 \pm 25$ J K^{-1} mol^{-1}. [c] Reported activation parameters for k_a in benzene using PPh_3 are $\Delta H^\ddagger = 87.7$ kJ mol^{-1} and $\Delta S^\ddagger = -13$ J K^{-1} mol^{-1} [ref. 2*a*]. [d] Data from ref. 1.

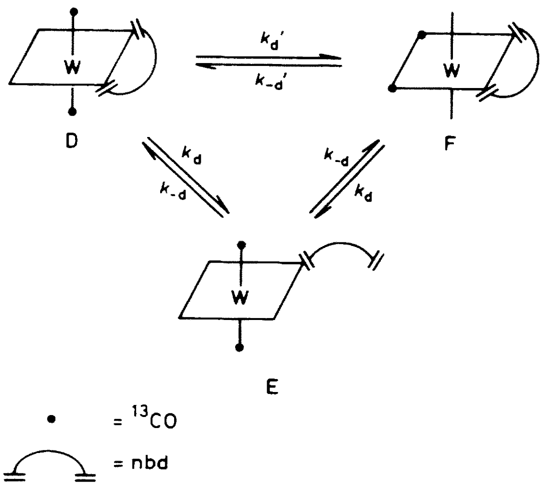
$[M(\eta^2\text{-olefin})(CO)_4(PR_3)]$ [5b] and $[M(\eta^2\text{-olefin})(CO)_3(P\text{–}P)]$ (P–P = bidentate phosphine) [5c] complexes show that the reaction proceeds through dissociative loss of olefin, with measured positive entropies of activation.

(*c*) A rapid dissociative pre-equilibrium followed by rate-determining associative formation of products is also possible, equations (8) and (9), where **B** now represents a co-ordinatively unsaturated $[M(\eta^2\text{-diene})(CO)_4]$ intermediate and $K_{eq} = [B]/[A]$. Thus, it may be shown that $k_{obs.}$ is given by equation (10). Experiments in the literature, however, indicate that such a dissociation is not established as a rapid pre-equilibrium. The thermal isomerization of the ^{13}CO-dilabelled species **D** to give exclusively **F** most likely proceeds *via* rate-determining chelate opening to give **E**, followed by a rapid pseudo rotation and ring closure (see below); a simple trigonal twist mechanism does not give this result.[4] Assuming that ring closure is much faster than ring opening ($k_{-d} \gg k_d$), it can be shown that $k_d = 2k_d'$. For the above isomerization at 40 °C, $k_d = 0.48 \times 10^{-4}$ s^{-1}. Although a k_d value cannot be extracted from the kinetic study of the substitution of $[W(nbd)(CO)_4]$ reported here (plots of $k_{obs.}$ against [L] have zero intercepts), the analogous k_1 value for ring opening of $[Mo(cod)(CO)_4]$ derived from substitution data (Table 4) is 0.95×10^{-4} s^{-1} at 46.5 °C. Thus, it seems unlikely that ring opening is established as a rapid pre-equilibrium.

$$A \underset{}{\overset{K_{eq}}{\rightleftharpoons}} B \qquad (8)$$

$$B + L \xrightarrow{k'} [M(\eta^2\text{-diene})(CO)_4L] \xrightarrow[\text{fast}]{+L} \text{diene} + [M(CO)_4L_2] \qquad (9)$$

$$k_{obs.} = k'K_{eq}[L]/(1 + K_{eq}) \qquad (10)$$



Perhaps the most satisfactory explanation of these results can be obtained from a steady state treatment of equations (11) and (12), where **A** is $[M(\eta^4\text{-diene})(CO)_4]$, **B** is $[M(\eta^2\text{-diene})(CO)_4L]$, and **C** is $[M(CO)_4L_2]$. Application of the steady state hypothesis to **B** yields equation (13), which assuming that $k_2[L] \gg k_{-a}$, reduces to equation (14).

$$A + L \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} B \qquad (11)$$

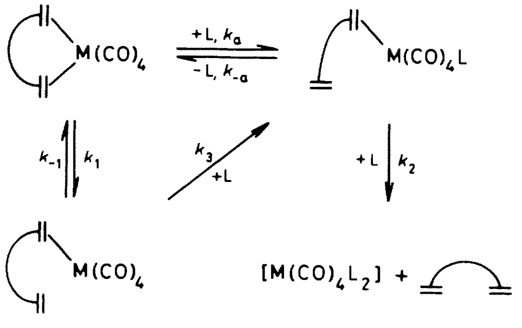
$$B \xrightarrow[+L]{k_2} C + \text{diene} \qquad (12)$$

$$k_{obs.} = k_a k_2[L]^2/(k_{-a} + k_2[L]) \qquad (13)$$

$$k_{obs.} = k_a[L] \qquad (14)$$

A similar rate law and interpretation have been reported for displacement of the polyene ligand from $[M(\eta^6\text{-polyene})(CO)_3]$ complexes (polyene = arene, cycloheptatriene, or borazine) by phosphorus donor ligands.[6]

Reported investigations of the displacement of buta-1,3-biene from (η^4-buta-1,3-diene)tetracarbonylchromium by $P(OMe)_3$[1] and of cod from $[Mo(cod)(CO)_4]$ by phosphorus and nitrogen ligands [2] have yielded plots of $k_{obs.}$ against [L] which are linear, but which do not pass through the origin. We have interpreted these results as arising from competing associative and dissociative pathways shown below.



Steady state treatment of this mechanism yields equation (15),

$$k_{\text{obs.}} = \frac{k_1k_3[\text{L}]}{k_{-1} + k_3[\text{L}]} + \frac{k_ak_2[\text{L}]^2}{k_{-a} + k_2[\text{L}]} \qquad (15)$$

which on the assumptions that $k_2[\text{L}] \gg k_{-a}$ and $k_3[\text{L}] \gg k_{-1}$, reduces to equation (16). Thus, on the basis of this scheme,

$$k_{\text{obs.}} = k_1 + k_a[\text{L}] \qquad (16)$$

the results involving displacement of nbd described here imply that k_1 is too small to be defined within the precision of the available data.

Several points may be noted: (*a*) the greater lability of nbd as opposed to cod in the reaction of $[\text{Mo}(\eta^4\text{-diene})(\text{CO})_4]$ (diene = nbd or cod) with P(OPh)_3 may be associated almost entirely with the great increase in k_a rather than any change in k_1. Examination of the activation parameters (Table 4) shows that this greater lability is due primarily to the decreased enthalpy of activation. The implications of this are not clear without a study of a wider range of 1,4- and 1,5-diene complexes, and it must be emphasized that caution must be used in relating ground-state bond enthalpy values to the rates of bimolecular reactions. Thus, recent low-temperature calorimetric and kinetic data show that the lability of the polyene in the series $[\text{Cr(cycloheptatriene)(CO)}_3] > [\text{Cr(benzene)(CO)}_3] \approx [\text{Cr(toluene)(CO)}_3] > [\text{Cr(mesitylene)(CO)}_3]$ is not paralleled exactly by the trend in chromium–polyene bond enthalpy contributions, which are in the order mesitylene > cycloheptatriene > toluene > benzene.[7]* Although within the series of arene complexes, ligand lability does follow the ordering of increasing chromium–arene bond enthalpy contribution, steric effects may also be important, and it has been shown that within a series of alkyl-substituted borazinetricarbonylchromium complexes, the lability of the borazine is more easily associated with steric factors.[6e]

In contrast, the greater lability of the diolefin in (η^4-buta-1,3-diene)tetracarbonylchromium as compared to $[\text{Cr(nbd)(CO)}_4]$ may be associated with *both* an increased k_1 and k_a value (Table 4); *i.e.*, both dissociative and associative ring-opening pathways have significantly lower activation enthalpies. The preference of a Cr(CO)_4 fragment for a non-conjugated as opposed to a conjugated diene has been discussed by Hoffmann and Elian,[8] and the much lower activation energy observed for site exchange in (η^4-buta-1,3-diene)tetracarbonylchromium as opposed to $[\text{Cr(cod)(CO)}_4]$ may reflect the lower activation enthalpy for this ring opening.[9]

There exists a parallel in $[\text{Fe}(\eta^4\text{-diene})(\text{CO})_3]$ chemistry, where displacement of ligand from labile $[\text{Fe}(\eta^4\text{-dienone})(\text{CO})_3]$ complexes proceeds *via* competing dissociative and associative pathways,[10] whereas less labile conjugated $[\text{Fe}(\eta^4\text{-1,3-diene})(\text{CO})_3]$ complexes undergo substitution exclusively *via* the bimolecular pathway.[11]

(*b*) The ordering of rate in terms of the metal observed here (Mo ≫ W > Cr) has a parallel in the displacement of cycloheptatriene from tricarbonyl(η^6-cycloheptatriene)metal complexes by phosphorus [6d] and nitrile [12] ligands. Again, this trend is not reflected in the ground-state bond enthalpy contributions [W–cycloheptatriene (311 kJ mol^{-1}) > Mo (264) > Cr (150)] or in the less precise data available for $[\text{M(nbd)(CO)}_4]$ [Mo–nbd (187 kJ mol^{-1}) > Cr (80)].[13]

(*c*) The dependence of rate on solvent and the nature of the ligand are also consistent with an associative displacement. A dramatic decrease in k_a with increasing solvent polarity may be noted (Table 4); this has been associated with an increased substrate solvation which is sufficient to diminish substantially the concentration of reactants within the solvent cage. Although increasing solvent polarity has been shown to increase dissociative rate constants, plots of $k_{\text{obs.}}$ against [L] for all the reactions of $[\text{Mo(nbd)(CO)}_4]$ pass effectively through the origin.

For a given donor atom, k_a may be seen to be dependent on the basicity or polarizability of the ligand, as measured by Δhnp, the half neutralization potential of the ligand with respect to 1,3-diphenylguanidine in nitromethane.[14] For the phosphite reactions, plots of log k_a against Δhnp show the values for chromium and tungsten at 46.5 °C to lie on lines which are approximately parallel, and extrapolation of a line parallel to the tungsten line from the single point available from the reaction of $[\text{Mo(nbd)(CO)}_4]$ with P(OPh)_3 yields a value of k_a (*ca.* 3 640 dm^3 mol^{-1} s^{-1}) for the reaction of $[\text{Mo(nbd)(CO)}_4]$ with P(OMe)_3 which is consistent with the very rapid rate observed even at room temperature.

(*d*) Finally, the contrast in mechanism between exchange or substitution reactions of η^2-mono-olefin ML_5 and η^4-diene ML_4 complexes may be noted. The former react exclusively *via* rate-determining dissociation of olefin,[5a,5b,15] while the latter react mainly by a bimolecular pathway. Although ground-state metal–polyene bond enthalpies would appear to be simple multiples of metal–olefin bond strengths (to a first approximation),[13] it seems unlikely that this would be equally partitioned between the two steps of a sequential dissociation of a diolefin ligand or the three steps of a sequential dissociation of an arene or triene ligand. For a rigid chelated diene, dechelation will most likely result in substantial weakening of the remaining metal–olefin bond, and a ligand-assisted bimolecular mechanism may therefore represent a pathway of lower activation energy, although the exact mode of ligand assistance still remains unclear. Similarly in iron chemistry, $[\text{Fe(olefin)(CO)}_4]$ complexes react exclusively by rate-determining olefin dissociation,[16] whereas $[\text{Fe}(\eta^4\text{-diene})(\text{CO})_3]$ complexes react *via* predominantly bimolecular pathways.[10,11]

(*B*) cis $\rightleftharpoons$ trans *Isomerization of* $[\text{M(CO)}_4\text{L}_2]$ *Complexes.*—Examination of the i.r. spectra recorded during the displacement of nbd or cod shows that for all the ligands used, molybdenum yields only the *cis*-$[\text{M(CO)}_4\text{L}_2]$ isomer, whereas in the case of chromium, an equilibrium *cis–trans* mixture is formed from the start of the displacement. The behaviour of tungsten is intermediate, yielding only the *cis* isomer on displacement by phosphite, while PBu_3 yields initially the *cis* isomer which isomerizes under the reaction conditions to a *cis–trans* mixture. In order to investigate this isomerization more quantitatively, we have isolated either the pure *cis* or *trans* isomers and studied their isomerization using ^{31}P n.m.r. Although there are several qualitative observations of such isomerizations in the literature,[17] quantitative studies have only recently been reported on the *cis* $\rightleftharpoons$ *trans* isomerization of $[\text{Mo(CO)}_4(\text{PR}_3)_2]$ (R = Me, Et, Bu, or Ph) complexes.[18] The PPh_3 complex isomerizes *via* phosphine dissociation, whereas the others are intramolecular and are assumed to proceed by the trigonal twist or related mechanisms.

The *cis* and *trans* isomers listed in Table 5 were prepared as described in the Experimental section and their isomeric purity established by i.r. and ^{31}P and ^{13}C n.m.r. spectroscopy. The *cis*-$[\text{M(CO)}_4\text{L}_2]$ complexes show characteristically the four allowed i.r. carbonyl vibrations ($2a_1 + b_1 + b_2$) although in some cases the two bands of lowest wavenumber are unresolved. The *trans*-$[\text{M(CO)}_4\text{L}_2]$ complexes show a strong band due to the single allowed e_u vibration, together with

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* Note that high-temperature decomposition and iodination studies place the chromium–polyene bond enthalpy contributions in the order mesitylene > toluene ≈ benzene > cycloheptatriene (F. A. Adeji, D. L. S. Brown, J. A. Connor, M. L. Leung, I. M. Paz-Andrade, and H. A. Skinner, *J. Organomet. Chem.*, 1975, **97**, 221).

Table 5. Spectroscopic data for *cis*- and *trans*-$[M(CO)_4L_2]$ complexes

		cis Isomer			*trans* Isomer		
		Infrared [a]	^{31}P [b]	^{13}C [c]	Infrared [a]	^{31}P [b]	^{13}C [c]
M = Cr [d]	L = PBu_3	*e*	32.8	—	1 844vw, 1 877vs	48.4	224.2 (12.7)
	L = $P(OMe)_3$	2 023, 1 940, 1 933, 1 912	184.6	—	1 958vw, 1 912vs	192.9	218.3 (20.2)
	L = $P(OPh)_3$	2 034, 1 954, 1 933	170.9	—	1 980vw, 1 930vs	180.4	215.8 (20.0)
M = Mo [f]	L = PBu_3	2 010w, 1 912m, 1 896m, 1 884s	14.3	210.7 (9.8) 215.1 (7.5)	1 884	26.0	—
	L = $P(OMe)_3$	2 034m, 1 952m, 1 944m, 1 922s	170.4	207.3 (13.8) 211.4 (13.0)	1 970vw, 1 923vs	178.5	—
	L = $P(OPh)_3$	2 045m, 1 962m, 1 944s,br	150.4	204.8 (13.4) 208.8 (17.0)	1 980vw, 1 944vs	159.1	—
M = W	L = PBu_3 [d]	2 004m, 1 901m, 1 885m, 1 875m	−6.03 (226.2)	—	1 900vw, 1 876vs, 1 846vw	2.24 (270.4)	203.7 (5.9)
	L = $P(OMe)_3$ [f]	2 032m, 1 946m, 1 938m, 1 917s	137.7 (379.6)	198.4 (10.3) 201.4 (12.2)	1 960vw, 1 916vs	142.5 (428.8)	—
	L = $P(OPh)_3$ [f]	2 043m, 1 958m, 1 938s,br	133.3 (412.6)	196.2 (10.1) 198.7 (18.3)	1 972vw, 1 936vs	136.5 (454.1)	—

[a] Values in cm^{-1}; in n-heptane. [b] Values in p.p.m. from 85% H_3PO_4; toluene solution; $J(W-P)/Hz$ in parentheses. [c] Values in p.p.m. from $SiMe_4$; $CDCl_3$ solution; $J(P-C)/Hz$ in parentheses. [d] *trans* Isomer isolated pure; values for *cis* from isomerization. [e] *cis* Isomer not detected in i.r. spectrum. [f] *cis* Isomer isolated pure; values for *trans* from isomerization.

Table 6. Rate and equilibrium constants for *cis* $\rightleftharpoons$ *trans* isomerization of $[M(CO)_4L_2]$ complexes

		$\theta_c/°C$	K_{eq}	$10^4(k_1 + k_{-1})$ [a]$/s^{-1}$	$10^4k_{-1}/s^{-1}$	$10^4k_1/s^{-1}$
M = Cr [b]	L = PBu_3	28	48.3	—	—	—
	L = $P(OMe)_3$	28	4.78	12.7 (1.6)	2.19	10.5
	L = $P(OPh)_3$	28	14.2	—	—	—
M = Mo [c]	L = PBu_3	74	3.56	4.41 (0.16)	0.969	3.45
		86	3.56	17.1 (0.05)	3.73	13.3
	L = $P(OMe)_3$	93	0.991	1.45 (0.04)	0.728	0.722
	L = $P(OPh)_3$	93	3.14	0.364 (0.04)	0.087	0.276
M = W	L = PBu_3 [b]	46	8.93	3.45 (0.37)	0.35	3.10
	L = $P(OMe)_3$ [c]	65	1.02	2.81 (0.05)	1.39	1.42
	L = $P(OPh)_3$ [c]	93.5	3.48	3.24 (0.11)	0.72	2.52

[a] Standard deviations are given in parentheses. [b] Determined from *trans* → *cis* isomerization. [c] Determined from *cis* → *trans* isomerization.

either one or two very weak bands. These weak bands, which vary in number and position in the literature, have been attributed to the Raman active a_{1g} and b_{1g} modes and to ^{13}C bands,[19] and in some cases are undoubtedly due to small amounts of contaminating *cis* isomer.[20] Carbon-13 spectra of *trans*-$[M(CO)_4L_2]$ show a single triplet, whereas the *cis* isomers show a triplet at smaller chemical shift due to the *trans*-$(CO)_2$ pair and an apparent triplet at higher chemical shift due to the *cis*-$(CO)_2$ pair for which the coupling constant is $^2J[C-M-P(cis) + C-M-P(trans)]$. Where available, literature data are in agreement with those reported here.

Isomerizations (either *cis* → *trans* or *trans* → *cis*) have been followed qualitatively by i.r. and quantitatively by ^{31}P n.m.r. (see Experimental section), since *cis* and *trans* ^{31}P resonances are well separated with the *trans* isomer being characteristically at higher chemical shift. For a reaction of the type (17), equation (18) can be derived, where $\rho_\infty = [trans]/[cis]$ and is equivalent to the ratio of the intensities of the *trans* and *cis* ^{31}P resonances. Thus, plots of $\ln[(\rho_\infty - \rho_t)/(\rho_t + 1)]$ against time yield values of $k_1 + k_{-1}$, and since $\rho_\infty = K_{eq} = k_1/k_{-1}$, values of k_1 and k_{-1} may be determined. Values are presented in Table 6, and those obtained for $[Mo(CO)_4(PBu_3)_2]$ at 74 °C agree well with those determined using i.r. spectroscopy ($k_1 + k_{-1} = 5.11 \times 10^{-4}\ s^{-1}$, $K_{eq} = 5.3$, 74.1 °C, heptane).[18b] Rate constants for $[Cr(CO)_4L_2]$ [L = PBu_3 or $P(OPh)_3$] could not be obtained due to the low abundance of the *cis* isomer in the equilibrium mixture and to the rapidity of the isomerization. The value obtained for $[Cr(CO)_4\{P(OMe)_3\}_2]$ is much less precise than other values in Table 6 for the same reasons. Values of K_{eq} show no significant temperature dependence.

$$cis\text{-}[M(CO)_4L_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[M(CO)_4L_2] \qquad (17)$$

$$-(k_1 + k_{-1})t = \ln\left[\frac{\rho_\infty - \rho_t}{\rho_t + 1}\right] + \ln\left[\frac{\rho_0 + 1}{\rho_\infty - \rho_0}\right] \qquad (18)$$

Of the reactions listed, only the isomerization of $[Mo(CO)_4\{P(OPh)_3\}_2]$ appears to proceed *via* a ligand-dissociative mechanism, as judged by the formation of $[Mo(CO)_5\{P(OPh)_3\}]$ (ν_{CO} at 2 083, 1 975, and 1 963 cm^{-1})[17c] when the complex is heated at the temperature of isomerization under an atmosphere of CO. All other complexes show no detectable formation of $[M(CO)_5L]$ under analogous conditions.

The position of equilibrium may be seen to be dependent primarily on steric factors. For all three metals, the decrease in K_{eq} in the order $PBu_3 > P(OPh)_3 > P(OMe)_3$ parallels the decreasing cone angle of these ligands (132 > 128 > 107°).[21]

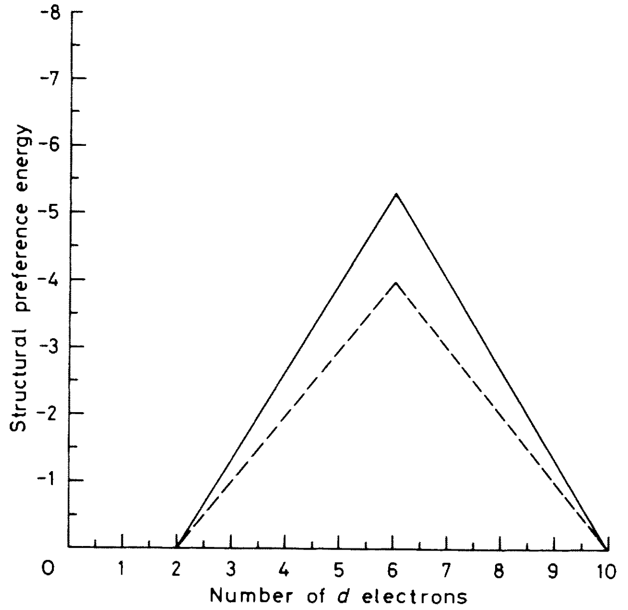
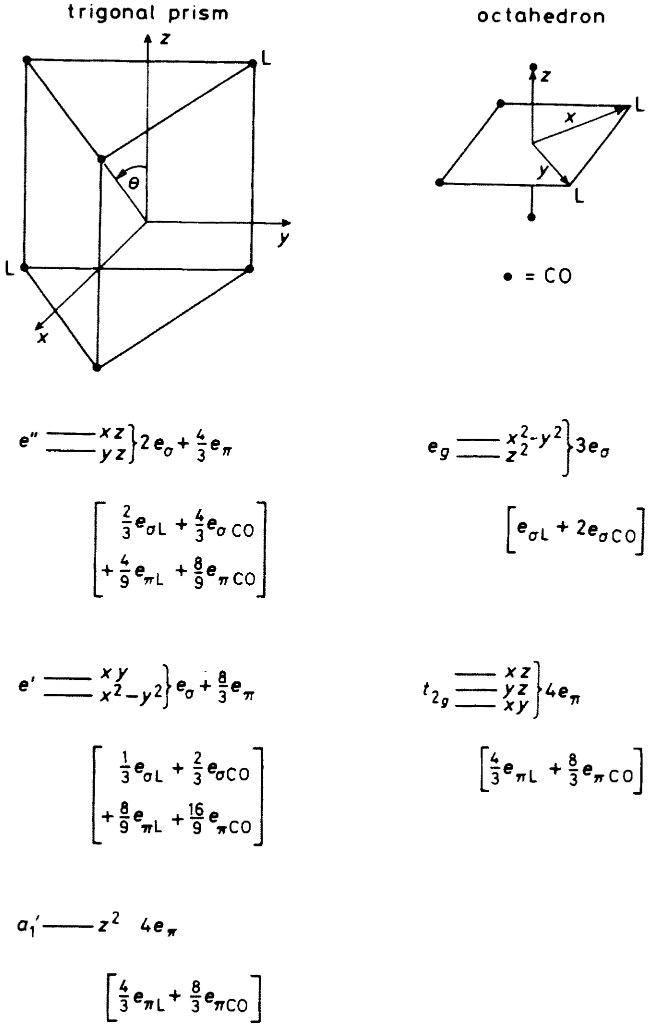


Figure 1. Plot of structural preference energy (arbitrary units) e_π (———) and e_σ (- - -) (low-spin only) against *d*-electron configuration; negative energy values indicate a greater stabilization of the octahedron relative to the trigonal prism

In terms of metal, the values of K_{eq} for a given ligand (Cr $\gg$ Mo $\sim$ W) parallel the increase in covalent radius between first and second/third row metals [Mo (1.62) > Cr (1.48 Å)].[22] A smaller electronic effect which favours the minimized mutually *trans* CO interactions of the *cis* isomer may, however, be masked. Thus, whereas K_{eq} for $[Mo(CO)_4(PBu_3)_2]$ is 3.56, K_{eq} for the oxidized $[Mo(CO)_4(PBu_3)_2]^+$ cation is 33.[23] The increased value of K_{eq} seems best interpreted in terms of the decreased π back-bonding requirements of the metal in the 17-electron species.

Steric and electronic effects also influence the relative rates of intramolecular isomerization. Thus, the rates of *cis* $\rightleftharpoons$ *trans* isomerization of $[Mo(CO)_4(PR_3)_2]$ increase in the order R = Me $\ll$ Bu $\approx$ Et which parallels the order of increasing cone angle [Me (118) < Et (132) = Bu (132°)].[18b] *X*-Ray structural examinations of these three complexes and other *cis*-$[M(CO)_4L_2]$ derivatives[24] show generally an increasing distortion from octahedral symmetry (principally an increased P–M–P angle) with increasing cone angle. Thus, the observed acceleration of rate with increasing cone angle reflects the increasing relief of interligand steric strain in the trigonal prismatic intermediate or transition state.

Our work, however, indicates the additional importance of electronic contributions. For all metals, values of k_1 are in the order $PBu_3 > P(OMe)_3 > P(OPh)_3$. Even though $P(OPh)_3$ and PBu_3 differ by only 4° in cone angle, large differences in k_1 are observed, while the relative rates for the phosphite complexes are the reverse of their order of cone angle. On the assumption that the isomerization proceeds *via* a trigonal prismatic intermediate or transition state, an angular overlap comparison of octahedral and trigonal prismatic geometries is instructive. For a simple face twisting in which M–L and M–C bond lengths and the angle remain constant [$\sin\theta = \sqrt{\tfrac{2}{3}}$, $\cos\theta = \sqrt{\tfrac{1}{3}}$, $\theta = 54°44'$], the energy level diagrams shown below may be derived.[25]



The structural preference energy plot shown in Figure 1 indicates that the transition to the trigonal prism is accompanied by a loss of both σ- and π-stabilization (assuming a π stabilization of the *occupied* orbitals since the ligands are *π acceptors*), although the loss of σ stabilization is *proportionately* greater. In electronic terms, lower barriers to isomerization would be expected in complexes for which this loss is minimized. Several points may be noted: (*a*) the structural preference energy for d^5 is less than that for d^6. Although accurate rates are not available, it is clear that the *cis* $\rightleftharpoons$ *trans* isomerization of $[Mo(CO)_4(PBu_3)_2]^+$ is several orders of magnitude faster than that of its neutral $[Mo(CO)_4(PBu_3)_2]$ analogue.[23]

(*b*) For the ligands studied here, variations in rate constants for a given metal cover only a range of one order of magnitude, and thus electronic changes are of a smaller degree than in (*a*). Although admittedly few, photoelectron spectroscopic results for $[Mo(CO)_4L_2]$ complexes[26] suggest that as the σ/π donor : acceptor ratio of the ligand increases, so does the electron density at the metal centre. Thus, as the donor : acceptor ratio for the ligand series changes in the order $P(OPh)_3 < P(OMe)_3 < PBu_3$, the ratio of e_σ to e_π for the metal centre is expected to change in the same order. Note that in the diagram above, the orbital degeneracies are maintained strictly only when L = CO. When L $\neq$ CO, the e' and e'' sets of the trigonal prism and the e_g set of the octahedron are split, whereas the t_{2g} set is divided into *xy* and a degenerate (*xz*, *yz*) pair. The quantities in square brackets indicate an average interaction per electron of the non-degenerate set. Through this ligand series, e_σ would appear to increase (and therefore increase the barrier to isomerization),

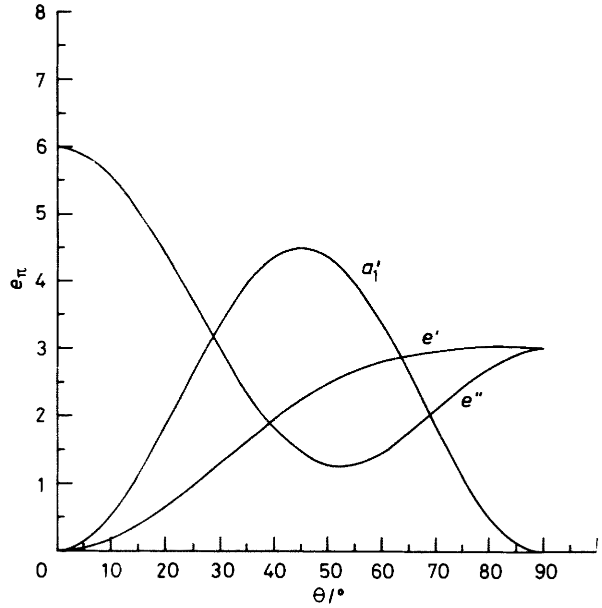


Figure 2. Plot of π stabilization energy, e_π (arbitrary units), against θ

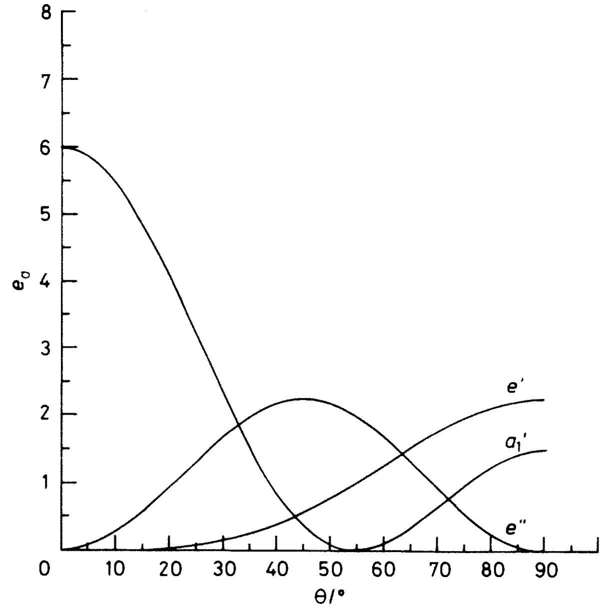


Figure 3. Plot of σ stabilization energy, e_σ (arbitrary units), against θ

whereas e_π would appear to decrease (and therefore decrease the barrier to isomerization). The important factor in determining the *relative* rates of isomerization will be the *relative* rate of change of e_σ compared to e_π. This may be expressed in more quantitative terms as follows. Figure 1 shows that for low-spin d^6, the difference in energy between the octahedral and trigonal prismatic geometries is given by $\Delta E = 4e_\sigma + \frac{16}{3}e_\pi$, and thus $d(\Delta E)/dL = d(e_\sigma)/dL + \frac{4}{3}d(e_\pi)/dL$, where the derivatives represent the rate of change of the given quantities through the ligand series $P(OPh)_3$, $P(OMe)_3$, and PBu_3. If ΔE is a reasonable measure of the barrier to, and therefore the rate of, isomerization, then the experimental data indicate that $d(\Delta E)/dL < 0$ [an increasing rate of isomerization in the order $P(OPh)_3 < P(OMe)_3 < PBu_3$]. This condition can be satisfied only if $-\frac{4}{3}d(e_\pi)/dL > d(e_\sigma)/dL$. The common problem of the separate estimation of e_σ and e_π in low-valent complexes is encountered here, but if the above interpretation is correct, the results would indicate that the increasing rate of isomerization [$P(OPh)_3 < P(OMe)_3 < PBu_3$] is due to the faster *rate of change* of e_π, even though in absolute terms, $e_\sigma > e_\pi$.

(*c*) For a given ligand, the rate of isomerization increases in the order Mo < W < Cr. Although comparative crystallographic data are not available, it seems reasonable to suppose that increased interligand repulsions in the smaller chromium complex may provide a steric acceleration of the type previously described. In addition, an electronic factor may also make a contribution. Compared to a first-row metal, second- and third-row metals show larger values of e_σ and e_π, although e_σ is enhanced to a greater extent than e_π. In the above interpretation, a relative increase in e_σ compared to e_π should result in a decrease in the rate of isomerization, as observed. Electronic factors must be mainly responsible for the differences in rate observed between Mo and W. Unfortunately, no useful data exist which would allow a comparison of e_σ and e_π for these second- and third-row elements. A similar ordering in terms of metal is found in the rate of scrambling of the label in *cis*-$[M(CO)_4(^{13}CO)\{P(OMe)_3\}]$.[27]

(*d*) The octahedral value of θ maximizes neither the σ- nor π-stabilization in the trigonal prism. Figures 2 and 3 show the changes in stabilization energy as a function of θ. Solution of the appropriate equations shows that for low-spin d^6, σ overlap is maximized at θ = 45°, while π overlap is maximised at θ = 52°14′. Assuming that $4e_\pi = e_\sigma$, the total stabilization is maximized at θ = 46°48′. Thus, the degree of distortion of the octahedron at the intermediate or transition state is likely to be a function of the σ/π donor : acceptor ratio of the ligand.

Finally, it may be noted that whereas all the present evidence points towards the formation of *cis*-$[M(CO)_4L_2]$ as the kinetic product of nbd or cod displacement, this is not a *necessary* requirement of the stepwise displacement of a *cis* chelating ligand. Several examples have been reported where *cis–trans* mixtures of $[M(CO)_4L_2]$ complexes are formed from $[M(CO)_4(E{-}E)]$ [E–E = $R_2N(CH_2)_nNR_2$ or $RS(CH_2)_nSR$] [28] under conditions where *cis* $\rightleftharpoons$ *trans* isomerization is not occurring. As the reactions proceed *via* both $[M(CO)_4(\eta^2\text{-}E{-}E)]$ and $[M(CO)_4L]$ intermediates, the geometry of the final product will reflect the site preference and fluxionality of these intermediates. In contrast, the isomeric mixtures of $[M(CO)_4L_2]$ isolated from non-catalysed reactions of $[M(CO)_6]$ with phosphine and phosphite ligands are thermodynamic *cis–trans* equilibrium mixtures, since the temperatures required for disubstitution are greater than the temperatures required for the *cis* $\rightleftharpoons$ *trans* isomerizations studied here.

Experimental

Infrared and u.v.-visible spectra were recorded on Perkin-Elmer 257 and Perkin-Elmer 402 instruments respectively. Carbon-13 and ^{31}P n.m.r. spectra were recorded on a JEOL FX 100 spectrometer; $[Cr(acac)_3]$ (acac = acetylacetonate) was used as relaxation agent for the ^{13}C spectra. Phosphine and phosphite ligands were distilled from sodium and degassed before use; heptane and other solvents used in the kinetic runs were distilled and degassed.

The complexes $[Cr(nbd)(CO)_4]$ (ν_{CO} at 2 029, 1 952, 1 944, and 1 915 cm^{-1}), $[Mo(nbd)(CO)_4]$ (ν_{CO} at 2 038, 1 956, and 1 912 cm^{-1}), and $[Mo(cod)(CO)_4]$ (ν_{CO} at 2 039, 1 951, and 1 907 cm^{-1}) were prepared from $[M(CO)_6]$ and nbd or cod.[29] $[W(nbd)(CO)_4]$ was prepared from $[W(pip)_2(CO)_4]$ (pip = piperidine) and nbd as described below; this reaction provides better yields than that reported using $[W(CO)_3(MeCN)_3]$.[30] All the $[M(diene)(CO)_4]$ complexes gave satisfactory microanalyses.

Table 7. Conditions for the preparation of $[M(CO)_4L_2]$ complexes

Complex	Reaction time/h	θ_c/°C	Isomer isolated	Colour
$[Cr(CO)_4L_2]$				
L = $P(OMe)_3$	2	60	*trans*	White
$P(OPh)_3$	4	80	*trans*	White
PBu_3	2	40	*trans*	Yellow
$[Mo(CO)_4L_2]$				
L = $P(OMe)_3$	3	40	*cis*	White
$P(OPh)_3$	1	60	*cis*	White
PBu_3	1	25	*cis*	White
$[W(CO)_4L_2]$				
L = $P(OMe)_3$	1	30	*cis*	White
$P(OPh)_3$	4	45	*cis*	White
PBu_3	3	30	*trans*	Yellow

Preparation of $[W(nbd)(CO)_4]$.—$[W(pip)_2(CO)_4]$ (1.8 g, 4 mmol)[31] and nbd (5 cm^3, 46 mmol) were refluxed in light petroleum (b.p. 60—80 °C, 100 cm^3) for 8 h under nitrogen. The reaction mixture was cooled in an ice-bath and the precipitated polymer removed by filtration. The filtrate was reduced in volume and cooled to −78 °C, yielding 1.1 g (71%) of $[W(nbd)(CO)_4]$ (ν_{CO} at 2 045, 1 960, and 1 912 cm^{-1}).

Preparation of $[M(CO)_4L_2]$ *Complexes*.—$[M(nbd)(CO)_4]$ (2 mmol) and a 40-fold excess of phosphine or phosphite were stirred in heptane under the conditions given in Table 7 until the i.r. spectrum indicated complete consumption of starting material. Solvent and excess ligand were removed under vacuum, and the crude products were crystallized from light petroleum (b.p. 60—80 °C) for the phosphite complexes and methanol for the phosphine complexes. All products gave satisfactory microanalyses.

Kinetics.—Complex and ligand solutions were prepared and mixed in the absence of light and degassed using argon. For reactions followed by u.v.-visible spectroscopy, the mixed solution was flushed under argon into a thermostatted silica cell (10-mm pathlength) and the reaction was monitored directly at 400, 340, and 420 nm for $[M(nbd)(CO)_4]$ (M = Cr, Mo, or W) respectively, and at 340 nm for $[Mo(cod)(CO)_4]$. For reactions followed by i.r., samples were withdrawn periodically from the thermostatted solution by syringe and measured using 1-mm NaCl cells at room temperature. A ligand–solvent blank was used in all cases, and the temperature was controlled to ±0.01 °C.

Reactions were followed to completion, yielding an average of 15 absorbance/time data pairs. Values of $k_{obs.}$ were obtained from a linear least-squares plot of $\ln [(A_0 - A_\infty)/(A_t - A_\infty)]$ *versus* time; all plots gave correlation coefficients greater than 0.9995. Reactions were performed in duplicate, and the values used in Tables 1—3 represent the average of duplicate runs.

cis $\rightleftharpoons$ *trans* Isomerizations of $[M(CO)_4L_2]$ complexes were followed by direct ^{31}P monitoring of toluene solutions (*ca.* 0.1 mol dm^{-3}) placed in the constant temperature n.m.r. probe (±1 °C) at the temperatures given in Table 6. At these temperatures, the time required for signal accumulation (*ca.* 5 s) was not significant.

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