Kinetics and mechanism of ligand substitution in [Cr(π-ligand)(CO)$_3$] complexes (ligand = naphthalene, pyrene, thiophene, 2,6-dimethylpyridine, or cycloheptatriene) and of *fac*/*mer* isomerization in [M(CO)$_3$L$_3$] (M = Cr, Mo or W; L = phosphite, phosphine or isocyanide)†

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Kinetic studies of the reaction [Cr(π-ligand)(CO)$_3$] + 3L $\longrightarrow$ [Cr(CO)$_3$L$_3$] + π-ligand revealed a second-order rate law with the π-ligand lability decreasing in the order naphthalene > thiophene > cycloheptatriene > 2,5-dimethylpyridine. In terms of the entering ligand, the rates increased in the order PrCN < P(OMe)$_3$ < PBu$_3$. Rates of intramolecular exchange in the [M(CO)$_{6-x}${P(OMe)$_3$}$_x$] series increased in the order x = 3 < 1 < 2 and M = Mo < W < Cr. These results are consistent with molecular modelling of the trigonal twist pathway for [Cr(CO)$_{6-x}$(PR$_3$)$_x$] complexes (x = 1–3, R = H or Me).

The chromium group metals form a rich variety of [M(π-ligand)(CO)$_3$] (ligand = mono or polycyclic arene, heteroarene, triene) and [M(π-diene)(CO)$_4$] complexes which, in addition to their synthetic utility in organic synthesis,[1] also function as transfer reagents or catalyst precursors for a variety of transformations. For example, the easily prepared [Cr(C$_{10}$H$_8$)(CO)$_3$] (C$_{10}$H$_8$ = naphthalene) has been used both as a stoichiometric reagent for arene exchange[2] and as a precursor for metal-catalysed isomerization, cycloaddition, hydrogenation and halogenoalkane addition reactions.[3] There has thus been a considerable interest in the kinetic lability[4–6] and relative ordering of thermodynamic stability[7] of such complexes as aids for systematic synthesis and for the design of homogeneous catalytic processes.

We have previously reported a kinetic study of uncatalysed arene exchange in labile Cr(π-ligand)(CO)$_3$ complexes,[5a] and present here our results on the kinetics and mechanism of ligand displacement in this same series by phosphine, phosphite and cyanide donor ligands. During preparation of this manuscript a study which includes the kinetics and thermodynamics of the reaction of certain of these substrates with PBu$_3$ was reported.[6j] The initial products of these reactions are predominantly the *fac*-[Cr(CO)$_3$L$_3$] complexes, and in view of the recent interest in intramolecular isomerization of octahedral metal complexes,[8] we present also our kinetic and computational results regarding the *fac*/*mer* isomerization in the [M(CO)$_3$L$_3$] series (M = Cr, Mo or W; L = phosphine, phosphite or isocyanide).

Results and Discussion

Substitution reactions

The reactions in Scheme 1 were monitored in decalin by UV/VIS spectroscopy using the disappearance of the red-orange substrate (see Experimental section). For reactions studied at less than 50 °C (naphthalene, thiophene, cycloheptatriene), the rate of *fac* $\longrightarrow$ *mer* isomerization of the product [Cr(CO)$_3$L$_3$] complex is slow, and the small amounts of *mer* isomer observed are derived directly from the substitution reaction (see below); calibration with pure *fac*-[Cr(CO)$_3${P(OMe)$_3$}] shows a yield of >90% *fac* isomer in all cases. For complexes requiring temperatures greater than 50 °C, *fac* $\longrightarrow$ *mer* isomerization proceeds at a rate which is significant compared to the rate of substitution, and at t_∞, *fac*–*mer* mixtures which are at or close to thermodynamic equilibrium are obtained. This does not interfere with monitoring of the substitution reaction, except in the case of the reaction of [Cr(dmpy)(CO)$_3$] with PBu$_3$ where changes in the UV/VIS spectrum due to isomerization overlap with changes associated with the disappearance of the yellow substrate. The rate of substitution of this complex by PBu$_3$ at 70 °C is about 50 times slower than the reaction of [Cr(C$_7$H$_8$)(CO)$_3$] with PBu$_3$. The corresponding complexes of styrene and octamethylnaphthalene are inert towards phosphite substitution at temperatures up to 90 °C.

$$[\mathrm{Cr}(\pi\text{-ligand})(\mathrm{CO})_3] + 3\mathrm{L} \longrightarrow [\mathrm{Cr}(\mathrm{CO})_3\mathrm{L}_3] + \text{ligand}$$

Scheme 1 Ligand = pyrene, naphthalene, thiophene or 2,5-dimethylthiophene, L = P(OMe)$_3$; ligand = cyclohepta-1,3,5-triene, L = P(OMe)$_3$, PBu$_3$ or PrCN; ligand = 2,6-dimethylpyridine (dmpy), L = PBu$_3$

The product [Cr(CO)$_3${P(OMe)$_3$}$_3$] has been characterized by reaction on a synthetic scale. While infrared spectra of reaction solutions clearly indicate the presence of *fac*-[Cr(CO)$_3$(PBu$_3$)$_3$] {ν_{CO} 1930, 1842 cm^{-1} (decalin); *cf.* [Cr(CO)$_3$(PMe$_3$)$_3$] 1923, 1821 cm^{-1} (CHCl$_3$)[9]}, attempts at isolation are frustrated by instability in the absence of an excess of PBu$_3$. Though the lower homologues [Cr(CO)$_3$(PR$_3$)$_3$] (R = H, Me or Et) have been characterized,[9–11] use of more sterically demanding ligands such P(C$_6$H$_{11}$)$_3$ permits isolation of 16e$^-$[Cr(CO)$_3${P(C$_6$H$_{11}$)$_3$}$_2$] which in solution adds two-electron ligands to provide 18e$^-$[Cr(CO)$_3$] complexes with low activation energies.[12] We thus attribute the instability of [Cr(CO)$_3$(PBu$_3$)$_3$] to facile phosphine dissociation. The complex [Cr(CO)$_3$(PrCN)$_3$] was identified *in situ* by the strong ν_{CO} absorption at 1938 cm^{-1} (decalin) {*cf.* [Cr(CO)$_3$(EtCN)$_3$] 1919, 1794 cm^{-1} (EtCN)[13]}. The lower homologues (MeCN, EtCN) were unsuitable for the kinetic work due to the immiscibility of the free cyanides with decalin.

Under pseudo-first-order conditions, all the above reactions proceed to completion with the exception of that of [Cr(C$_7$H$_8$)(CO)$_3$] with PrCN, where an equilibrium constant of 7.7×10^{-3} dm^6 mol^{-2} at 110 °C may be measured by UV/VIS spectroscopy. The equilibrium is confirmed by infrared studies (Fig. 1) which show an appropriate response to increasing [PrCN] at t_∞. Reaction of PrCN with [Cr-

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† *Supplementary data available* (No. SUP 57164, 4 pp.): first-order rate constants for substitution reactions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Non-SI units employed: mmHg ≈ 133 Pa, psi ≈ 6895 Pa, dyn = 10^{-5} N.

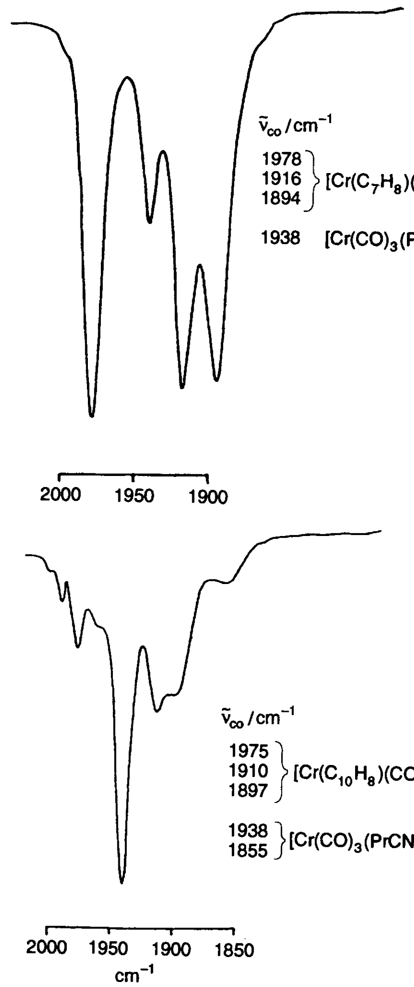


Fig. 1 Infrared spectra of equilibrium mixtures formed on reaction of $[Cr(C_7H_8)(CO)_3]$ and $[Cr(C_{10}H_8)(CO)_3]$ with PrCN (decalin, 110 °C, $[PrCN] = 0.2$ mol dm^{-3})

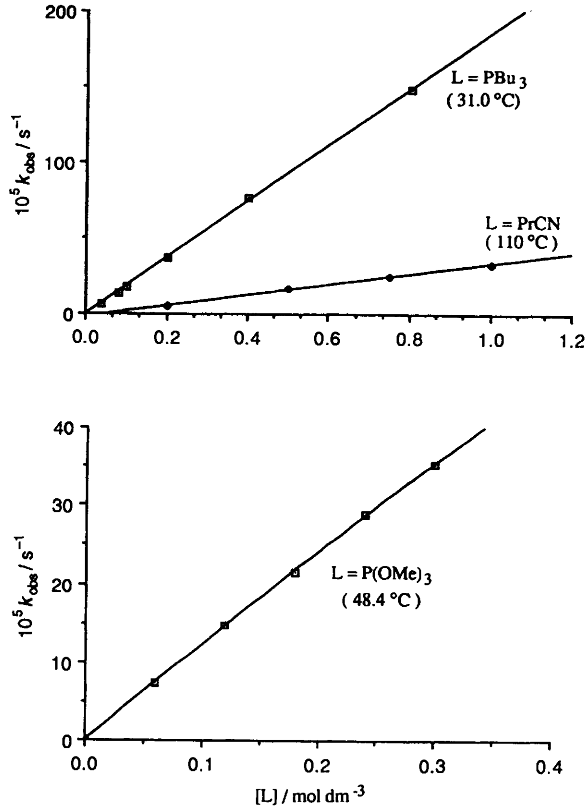
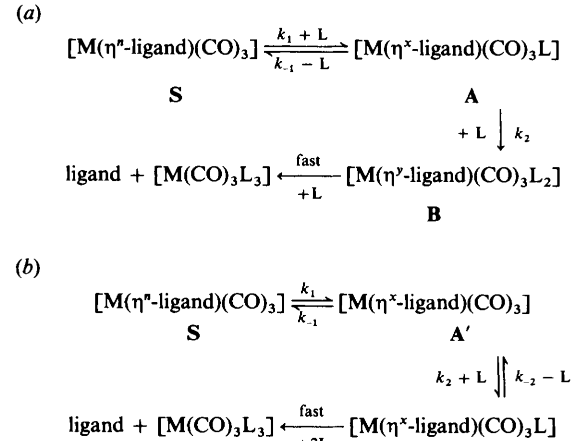


Fig. 2 Plots of k_{obs} against [L] for the reactions $[Cr(C_7H_8)(CO)_3] + 3L \longrightarrow [Cr(CO)_3L_3] + C_7H_8$ where L = $P(OMe)_3$, PBu_3 or PrCN

$(C_{10}H_8)(CO)_3]$ also yields an equilibrium which is displaced much more substantially to the right (Fig. 1). A similar equilibrium is established in the reaction of this complex with tetrahydrofuran.[3a,h] These results are consistent with thermochemical data[14] which show that $[Cr(CO)_3L_3]$ complexes are more stable than $[Cr(C_7H_8)(CO)_3]$ in the order MeCN (17.6 kJ mol^{-1}) < PEt_3 (148) ≈ $P(OMe)_3$ (157) and that $[Cr(C_7H_8)(CO)_3]$ is more stable than $[Cr(C_{10}H_8)(CO)_3]$ by 53.5 kJ mol^{-1}. In our hands, reaction of $[Cr(C_7H_8)(CO)_3]$ with PrCN in dichloroethane proceeds with complete consumption of starting material; examination of the infrared spectrum at t_∞ shows only the presence of $[Cr(CO)_6]$, indicative of substitution followed by a chlorination/decomposition which drives the reaction to completion. Such an instability of zerovalent Group 6 complexes in dichloroethane has been noted previously.[6g] In toluene as solvent, a quantitative yield of $[Cr(C_6H_5Me)(CO)_3]$ is observed, indicative of rate-determining initial substitution to give $[Cr(CO)_3(PrCN)_3]$ followed by rapid exchange with solvent.[15] Though it has been shown that $[Mo(C_6H_5Me)(CO)_3]$ is 29.7 kJ mol^{-1} less stable than $[Mo(C_7H_8)(CO)_3]$,[16] the high toluene concentration used in this study forces the reaction to completion.



Scheme 2

$$\frac{-d[S]}{dt} = \frac{k_1k_2[S][L]^2}{k_{-1} + k_2[L]} \qquad (1)$$

$$-d[S]/dt = k_1[S][L] \qquad (2)$$

Plots of k_{obs} against [L] for the reaction of $[Cr(C_7H_8)(CO)_3]$ with $P(OMe)_3$, PBu_3 and PrCN are shown in Fig. 2 and are consistent with the rate-determining associative process shown in Scheme 2(*a*). Application of the steady-state approximation to intermediate **A** yields the rate equation (1) which if $k_2[L] \gg k_{-1}$ reduces to (2). There is no spectroscopic evidence for detectable concentrations of any intermediates, but to maintain an 18e$^-$ configuration at the metal values of $x = 4$ and $y = 2$ are required for η^6-donors and $x = 3$ and $y = 1$ for the η^5-donor thiophene.

The plot for the reaction of $[Cr(C_7H_8)(CO)_3]$ with $P(OMe)_3$ exhibits some negative curvature with increasing phosphite concentration, as do all plots of k_{obs} against $[P(OMe)_3]$ for the other $[Cr(\pi\text{-ligand})(CO)_3]$ complexes studied. This might be taken as confirmatory evidence for an alternative mechanism [Scheme 2(*b*)] in which ring slippage *without* M–L bond formation yields the initial intermediate A′. Application of the steady-state approximation to A′ yields the rate law (3).

Table 1 Derived rate constants and activation parameters for the substitution reaction $[Cr(\pi\text{-ligand})(CO)_3] + 3L \longrightarrow [Cr(CO)_3L_3] + \text{ligand}$

Ligand	L	T/°C	10^3k_1/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
Cycloheptatriene	P(OMe)$_3$	31.2	0.247 (0.008)	70.3 (2.4)	−114 (8)
		37.1	0.436 (0.03)		
		48.4	1.16 (0.03)		
	PBu$_3$	31.0	1.26 (0.02)	66.1 (2.6)	−117 (8)
		40.6	4.13 (0.03)		
		50.4	8.70 (0.07)		
	PrCN	88.5	0.0713 (0.0009)	81.6 (2.4)	−78 (6)
		100.0	0.172 (0.006)		
		110.0	0.344 (0.007)		
Naphthalene	P(OMe)$_3$	23.5	0.674 (0.02)	67.8 (6.6) [41.4]	−120 (22) [−140]
		31.2	1.33 (0.06)		
		37.1	2.37 (0.03)		
Pyrene	P(OMe)$_3$	56.6	0.239 (0.04)	86.9 (3.6) [56.4]	−146 (10) [−123]
		68.7	0.735 (0.04)		
		78.0	1.77 (0.05)		
Thiophene	P(OMe)$_3$	37.1	0.969 (0.04)	68.2 (3.0) [46.4]	−114 (10) [−120]
		47.0	2.34 (0.04)		
		56.6	4.93 (0.20)		
2,5-Dimethylthiophene	P(OMe)$_3$	37.1	0.228 (0.04)	81.3 (8.0) [57.7]	−145 (28) [−111]
		47.0	0.684 (0.03)		
		56.6	1.52 (0.02)		

Refers to k_1 of Scheme 2(*a*); two standard derivations in parentheses. Values for reaction with PBu$_3$ from ref. 6(*j*) are in square brackets.

$$\frac{-\mathrm{d}[S]}{\mathrm{d}t} = \frac{k_1k_2[S][L]}{k_{-1} + k_2[L]} \qquad (3)$$

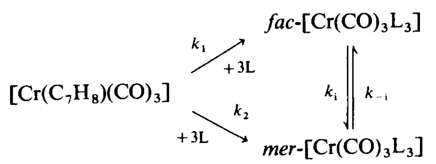
The implication of the kinetic results is that both limiting conditions ($k_{-1} \gg k_2[L]$ and $k_2[L] \gg k_{-1}$) can be attained over the ligand concentration used. We believe, however, that such an interpretation is in error; for $[Cr(C_{10}H_8)(CO)_3]$, putative values of the limiting rate constant (*ca.* 5×10^{-3} s^{-1} at 37.1 °C) differ considerably from the rate constants for what should be the same ligand-independent slippage pathway which mainly carries the arene-exchange reaction of $[Cr(C_{10}H_8)(CO)_3]$ (*ca.* 1×10^{-5} s^{-1} at 160 °C). The origin of the curvature is not known, but may be due to an increase in relative permittivity with increasing [P(OMe)$_3$], as suggested in a previous study of this reaction.[6f] For the P(OMe)$_3$ reactions, the derived second-order rate constants (Table 1) were calculated from the linear portion of plots of k_{obs} against [L]. Activation parameters are also reported. Such parameters have previously been reported for the reaction of $[Cr(C_7H_8)(CO)_3]$ with P(OMe)$_3$ in cyclohexane[6f] and with MeCN in dichloromethane.[6d] Included for comparison in square brackets are recently reported values for reaction of these substrates with PBu$_3$.[6j]

Several points of interest may be noted.

(*a*) For the reaction of $[Cr(C_7H_8)(CO)_3]$ with PBu$_3$, P(OMe)$_3$ and PrCN, $\Delta H^\ddagger$ values increase with decreasing basicity of the ligand. The substantially negative $\Delta S^\ddagger$ values for all the reactions are consistent with an associative process. It is of interest that while other $\Delta H^\ddagger$ values for the P(OMe)$_3$ and PBu$_3$ reactions differ by 20–30 kJ mol^{-1} for reactions of the aromatic π-donor complexes, those of the conjugated cycloheptatriene complex differ by only about 4 kJ mol^{-1}.

(*b*) The decreased lability of the 2,5-dimethylthiophene and thiophene complexes is primarily enthalpy controlled. This may reflect the greater thermodynamic stability of the dimethyl complex (12.5 kJ mol^{-1}).[6j] In the [Mo(arene)(CO)$_3$] series, methyl disubstitution also increases thermodynamic stability by approximately 12 kJ mol^{-1},[15] and decreases kinetic lability.[6a]

(*c*) The relative ordering of π-ligand lability established for ligand *exchange* (2,6-dimethylpyridine > pyrene > 2,5-dimethylthiophene > naphthalene > cycloheptatriene) is different from the ordering for the ligand *substitution* reactions described herein (naphthalene > thiophene > cycloheptatriene > 2,5-dimethylthiophene > pyrene > 2,6-dimethylpyridine). The $\Delta H^\ddagger$ values for the exchange process, which is essentially unimolecular in character, are substantially higher {117 kJ mol^{-1} for exchange[5a] *versus* 68 kJ mol^{-1} for substitution in the case of $[Cr(C_{10}H_8)(CO)_3]$}. Such differences in order are not surprising. Recent results[6j] on the associative substitution of polycyclic [Cr(arene)(CO)$_3$] complexes with PBu$_3$ show a clear correlation of decreasing rate of reaction with increasing loss of resonance energy on formation of the presumed 18e$^-$ $[Cr(\eta^4\text{-arene})(CO)_3(PBu_3)]$ intermediate. In contrast, computational results on dissociative ring slippage (which carries the greater part of the arene-exchange reaction) show a discrete minimum not at η^4 but at η^2 in the case of $[Cr(C_{10}H_8)(CO)_3]$ and predict $\eta^6 \longrightarrow \eta^3 \longrightarrow \eta^1$ slippage to be preferred for the pyrene and pyridine complexes.[5a]



Scheme 3

Finally, the reaction between $[Cr(C_7H_8)(CO)_3]$ and P(OMe)$_3$ (1 : 10 mole ratio) in toluene has been monitored by ^{31}P NMR spectroscopy at 31 °C, a temperature where *mer* $\rightleftharpoons$ *fac* isomerization [$k_i + k_{-i}$ (Scheme 3) = 1.7×10^{-5} s^{-1}] is an order of magnitude slower than the rate of substitution [$k_1 + k_2$ (Scheme 3) = 24.7×10^{-5} s^{-1}]. In the early stages of the reaction (up to 10% conversion), approximately 15% of the product is the *mer* isomer, indicating a direct formation from $[Cr(C_7H_8)(CO)_3]$. Change of ligand to naphthalene or 2,5-dimethylthiophene reduces this to about 5%, as does a change of metal from chromium to molybdenum or tungsten. Such a stereochemical leakage is not surprising. The final stage of displacement of ligand from the $[M(\eta^y\text{-ligand})(CO)_3L_2]$ intermediate **B** in Scheme 2 is likely to be dissociative in character, yielding a fluxional, 16e$^-$ $[M(CO)_3L_2]$ intermediate.

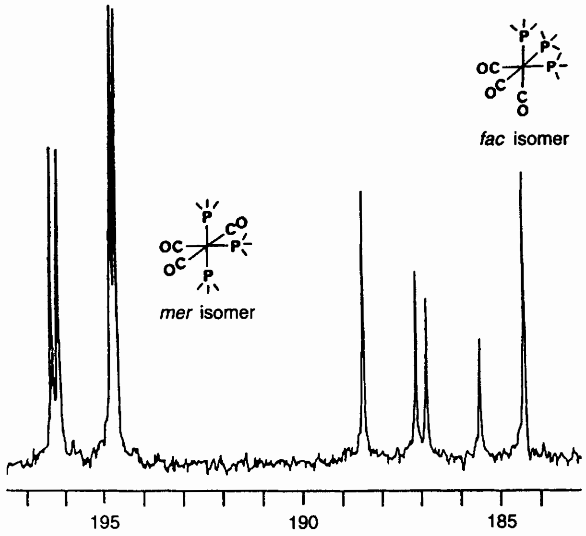


Fig. 3 The ^{31}P NMR spectrum of the equilibrium *mer*/*fac*-$[Cr(CO)_3\{P(OMe)_3\}_3]$ mixture (toluene)

mer/*fac* Isomerization

The *fac* isomers were obtained by reaction of the free pro-ligand with $[M(C_7H_8)(CO)_3]$ [L = $P(OMe)_3$, M = Cr, Mo or W; L = MeNC, M = Cr]. For the phosphite complexes, rate constants for isomerization were measured in decalin by UV/VIS spectroscopy. Equilibrium constants were measured by ^{31}P NMR analysis of equilibrated solutions. The spectrum at equilibrium of $[Cr(CO)_3\{P(OMe)_3\}_3]$ is illustrated in Fig. 3; in all cases, the *mer* isomer exhibits an A_2B spectrum from which $^2J_{P-P}$ values were extracted by computer simulation (see Experimental section). The complex *fac*-$[Cr(CO)_3(PBu_3)_3]$ was generated in toluene *in situ* and *fac*/*mer* isomerization monitored by ^{31}P NMR spectroscopy in the presence of an excess of PBu_3. In contrast to the phosphite complexes, the ^{31}P spectrum of *mer*-$[Cr(CO)_3(PBu_3)_3]$ is first order. The *fac*/*mer* isomerization of $[Cr(CO)_3(CNMe)_3]$ proceeds with considerable decomposition in decalin, but smoothly in toluene and was monitored by ^1H NMR spectroscopy. Rate and equilibrium constants and activation parameters for the phosphite complexes are collected in Table 2. Data for the chromium compound are consistent with those reported previously.[16] Equilibrium constants are independent of temperature in the range studied. Rate constants are independent of the concentration of added pro-ligand, indicating an intramolecular mechanism proceeding through either a trigonal prism or bicapped tetrahedron. Recent two-dimensional NMR work on $[Cr(CO)_2(CX)\{P(OMe)_3\}_3]$ (X = S or Se)[16a] complexes has provided convincing evidence for a trigonal-prismatic intermediate or transition state.

Several features may be noted which are also common to the $[Cr(CO)_4L_2]$ series.[4b]

(*a*) The position of equilibrium is depedent primarily on steric factors; the decrease in K in the order $PBu_3 > P(OMe)_3 >$ CNMe parallels the decreasing cone angle of these ligands (132 > 128 > 95°).[17] In terms of the metal, values of K for a given ligand (Cr $\gg$ Mo $\approx$ W) parallel the increase in radius between first- and second/third-row metals[18] though an electronic contribution may also be important. Calculations on $[Cr(CO)_4(PH_3)_2]$ indicate a slightly greater stability of the *cis* isomer (< 5 kJ mol^{-1}) which increases to 37 kJ mol^{-1} for $[Mo(CO)_4(PH_3)_2]$;[8d,e] *fac*-$[Mo(CO)_3(PH_3)_3]$ is calculated to be 69 kJ mol^{-1} more stable than the *mer* isomer.[8g]

(*b*) The complex $[Cr(CO)_3(PBu_3)_3]$ isomerizes at approximately 10 times the rate of $[Cr(CO)_3\{P(OMe)_3\}_3]$. It has been shown previously[19a,b] that the rate of *cis*/*trans* isomerization of $[Mo(CO)_4(PR_3)_2]$ complexes increases in the order R = Me $\ll$ Bu $\approx$ Et which parallels the order of increasing cone angle. Structural examination of these three complexes and other *cis*-$[Mo(CO)_4L_2]$ complexes[19b] shows generally an increasing distortion from octahedral co-ordination with increasing cone angle. Thus, the observed rate acceleration is consistent with increasing relief of interligand steric strain in the trigonal-prismatic transition state.

(*c*) The rate of isomerization increases in the order Mo < W < Cr. The much more substantial negative entropy value for the tungsten complex may be noted. This has been observed previously in a study of ^{13}CO scrambling in $[M(CO)_4(^{13}CO)(PEt_3)]$ (M = Cr or W)[20] and has been attributed to a highly sterically strained intermediate with little lengthening of the W–P bond compared to considerable lengthening in the Cr–P case. The data here indicate that molybdenum is more similar to chromium, with the higher activation enthalpy reflecting the greater Mo–P bond enthalpy.

Combined with data on ^{13}CO scrambling in $[W(CO)_4(^{13}CO)\{P(OMe)_3\}]$[20] and *cis*/*trans* isomerization in $[W(CO)_4\{P(OMe)_3\}_2]$,[4b] the present results indicate that the rate of intramolecular isomerization in the $[W(CO)_{6-x}\{P(OMe)_3\}_x]$ series increases in the order $x = 3 < 1 < 2$.

A qualitative angular-overlap analysis of the octahedral $\longrightarrow$ trigonal prismatic transition[4b] suggests that in terms of electronic factors the barrier is determined primarily by loss of σ stabilization and might therefore be expected to increase in the order $x = 1 < 2 < 3$. The discontinuous nature of the experimentally observed trend may thus indicate the importance of steric factors. This possibility has been investigated by molecular mechanics methods, using as a basis the published structures of $[Cr(CO)_5(PH_3)]$,[21] *cis*-$[Cr(CO)_4(PH_3)_2]$[22] and *fac*-$[Cr(CO)_3(PH_3)_3]$.[21] The analogous PMe_3 complexes were

Table 2 Data for *fac* $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ *mer* isomerization

Complex	T/°C	10^5k_1/s^{-1}	10^5k_{-1}/s^{-1}	K[a]	$\Delta H_1^{\ddagger}$[b]	$\Delta S_1^{\ddagger}$	$\Delta H_{-1}^{\ddagger}$	$\Delta S_{-1}^{\ddagger}$
$[Cr(CO)_3\{P(OMe)_3\}_3]$	52.5	8.08	1.13	7.2	87.2 (10.4)	−55 (30)	87.0 (9.2)	−72 (72)
	64.0	30.6	4.20	7.3				
	75.0	81.8	11.4	7.2				
	87.2	198	27.0	7.3				
$[Cr(CO)_3(PBu_3)_3]$	60.0	251	20.2	12.4	—	—	—	—
$[Cr(CO)_3(CNMe)_3]$	75.0	12.7	76.2	0.17	—	—	—	—
$[Mo(CO)_3\{P(OMe)_3\}_3]$	100.0	2.50	0.83	3.0	99.0 (10.0)	−70.0 (25)	99.0 (9.4)	−79 (25)
	110.0	5.26	1.76	3.0				
	120.0	13.9	4.62	3.0				
	130.0	27.6	9.20	3.0				
$[W(CO)_3\{P(OMe)_3\}_3]$	80.0	3.87	0.92	4.2	69.1 (7.0)	−134 (21)	69.3 (8.4)	−146 (23)
	90.0	8.80	2.10	4.2				
	100.0	14.9	3.60	4.1				
	110.0	27.5	6.60	4.2				

[a] K = [*mer*]/[*fac*]. [b] $\Delta H^{\ddagger}$ in kJ mol^{-1}, $\Delta S^{\ddagger}$ in J K^{-1} mol^{-1} with standard deviations in parentheses.

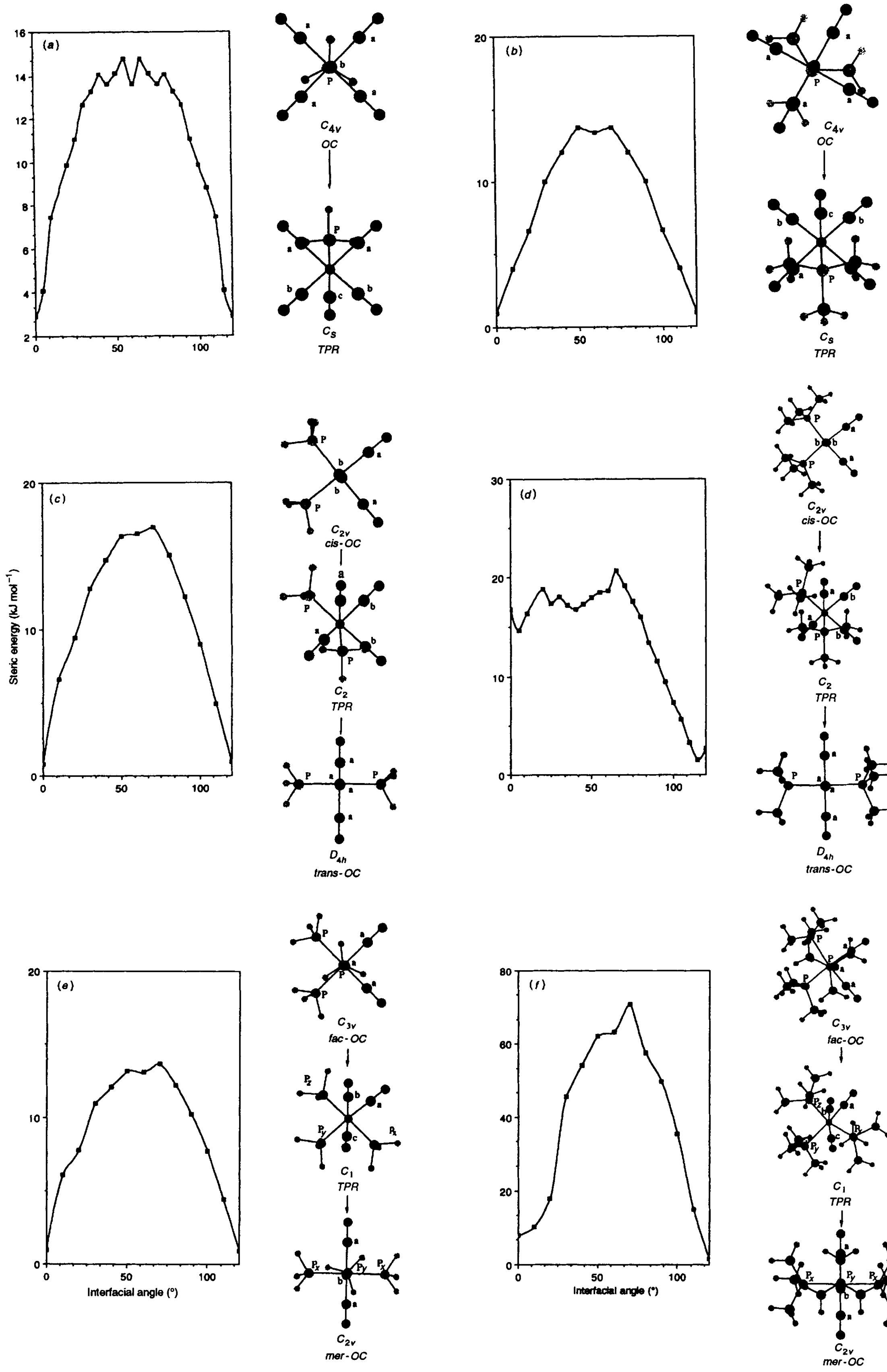
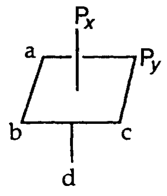


Fig. 4 Rotational profiles for (*a*) [Cr(CO)$_5$(PH$_3$)], (*b*) [Cr(CO)$_5$(PMe$_3$)], (*c*) [Cr(CO)$_4$(PH$_3$)$_2$], (*d*) [Cr(CO)$_4$(PMe$_3$)$_2$], (*e*) [Cr(CO)$_3$(PH$_3$)$_3$] and (*f*) [Cr(CO)$_3$(PMe$_3$)$_3$]

generated from these by replacement of hydrogen by methyl. Owing to the increased degrees of freedom associated with variation of the M–P–O–C dihedral angle,[23] we have not at this stage investigated modelling of the P(OMe)$_3$ derivatives.

Ground-state structures were minimized in energy using the MM2 program (see Experimental section). For the PH$_3$ complexes, these reproduce very closely the observed structural parameters. The structure of [Cr(CO)$_5$(PMe$_3$)] generated in this way agrees closely with previous modelling and X-ray studies.[24] The octahedral $\longrightarrow$ trigonal prismatic energy



profiles shown in Fig. 4 were generated by driving of the dihedral angle between appropriate triangular faces. For example, productive *cis* ⟶ *trans* isomerization in the [Cr(CO)$_4$L$_2$] derivative can be accomplished either by rotation of (P$_x$, CO$_a$, CO$_b$) relative to (P$_y$, CO$_c$, CO$_d$) or (P$_x$, CO$_b$, CO$_c$) relative to (P$_y$, CO$_a$, CO$_d$). Though these faces are rendered non-equivalent in the ground state due to the orientation of the PR$_3$ ligands, the rotational-energy profile is independent of the choice of face pairs. Similar comments apply to the [Cr(CO)$_3$L$_3$] and [Cr(CO)$_5$L] complexes.

The change in symmetry on rotation to the trigonal-prismatic structure may be noted, and is reflected in the differing degeneracies of CO and PR$_3$ ligands between ground and transition states. Important geometrical data for ground-state octahedral and transition-state trigonal-prismatic structures are given in Table 3. Parameters such as M–CO linearity, M–C and C–O bond lengths, H–P–H/C–P–C angles and {with the exception of the [Cr(CO)$_3$(PMe$_3$)$_3$] complex} M–P bond lengths change little on face rotation. Geometrical changes are primarily subsumed within compression of octahedral angles in the rotated faces and changes in the tilting of the PR$_3$ ligand as a whole, shown as M–P–Z in Table 3 where Z is the centroid of the face defined by the three non-metal phosphorus substituents. Several points of interest may be noted.

(*a*) All trigonal-prismatic structures are characterized by a compression of the average interligand angles within the eclipsed faces to 84–86° from average octahedral values of 90°. Similar differences are observed between the ground-state structures of [ZrMe$_6$]$^{2-}$ (trigonal prismatic)[25] and [MnMe$_6$]$^{2-}$ and [ErMe$_6$]$^{3-}$ (octahedral).[26] There is some indication in the rotational profiles of the monosubstituted complexes for a small energy minimum at the trigonal-prismatic configuration.

(*b*) Geometrical distortion and phosphine tilting in both the ground and transition states is generally more pronounced in the PMe$_3$ series, consistent with the sterically more demanding nature of the ligand. This is reflected also in the relative energies of the *cis*/*trans*-[Cr(CO)$_4$L$_2$] and *mer*/*fac*-[Cr(CO)$_3$L$_3$] isomer pairs. Whereas isomers of the PH$_3$ complexes differ insignificantly in energy, calculations on the PMe$_3$ complexes reproduce the observed *trans* > *cis* and *mer* > *fac* stability ordering observed for the P(OMe)$_3$ complexes. The relatively greater stability of *trans* over *cis* (13.8 kJ) as opposed to *mer* over *fac* (6.27 kJ) is also consistent with data on [Cr(CO)$_4$(PBu$_3$)$_2$] (K = [*trans*]/[*cis*] = 48.3 at 28 °C, ΔG = 9.61 kJ mol^{-1})[4b] and [Cr(CO)$_3$(PBu$_3$)$_3$] (K = [*mer*]/[*fac*] = 12.4 at 60 °C, ΔG = 7.11 kJ mol^{-1}).

(*c*) For the PMe$_3$ series, calculations reproduce the experimentally observed ordering of the barriers to trigonal twist of $x = 2 < 1 < 3$. The substantial increase for the $x = 3$ complex is consistent with the need to eclipse phosphine ligands in the trigonal-prismatic transition state. Of particular interest is the relatively small barrier for *cis* ⟶ *trans* isomerization which may be attributed to steric acceleration resulting from decreased steric interactions between phosphine ligands in *both* the trigonal-prismatic transition state and ground-state *trans* product structures. This is most evident in the M–P–Z tilt angle, which in contrast to the cases of the [Cr(CO)$_5$L] and [Cr(CO)$_3$L$_3$] molecules, decreases along the whole of the rotational profile.

Table 3 Energies and geometries of octahedral and trigonal-prismatic [Cr(CO)$_{6-x}$L$_x$] structures (x = 1–3, L = PH$_3$ or PMe$_3$)*

		L	
Complex		PH$_3$	PMe$_3$
[Cr(CO)$_5$L]	ΔE (*OC* ⟶ *TPR*)/kJ	11.7	13.0
	OC		
	M–P	2.29	2.25
	P–M–CO$_a$	90	91
	P–M–CO$_b$	180	179
	CO$_a$–M–CO$_a$	90	90
	CO$_a$–M–CO$_b$	90	89
	M–P–Z	10	6
	TPR		
	M–P	2.29	2.24
	P–M–CO$_c$	86	87
	CO$_c$–M–CO$_c$	86	88
	CO$_a$–M–CO$_b$	86	84
	CO$_b$–M–CO$_b$	86	86
	M–P–Z	9	48
[Cr(CO)$_4$L$_2$]	ΔE (*cis* ⟶ *trans*)/kJ	0.12	−13.8
	(*cis* ⟶ *TPR*)	16.3	3.76
	cis		
	M–P	2.30	2.26
	P–M–CO$_a$	90	91
	P–M–P	91	96
	P–M–CO$_b$	90	89
	CO$_a$–M–CO$_a$	90	86
	CO$_b$–M–CO$_b$	180	178
	M–P–Z	7	40
	TPR		
	M–P	2.30	2.26
	P–M–CO$_b$	86	87
	P–M–CO$_a$	81	82
	CO$_a$–M–CO$_b$	86	86
	M–P–Z	9	29
	trans		
	M–P	2.30	2.26
	P–M–P	179	178
	P–M–CO$_a$	90	90
	CO$_a$–M–CO$_a$	90	90
	M–P–Z	9	6
[Cr(CO)$_3$L$_3$]	ΔE (*fac* ⟶ *mer*)/kJ	−0.08	−6.27
	(*fac* ⟶ *TPR*)	12.7	62.7
	fac		
	M–P	2.29	2.36
	P–M–P	90	98
	CO–M–CO	90	86
	M–P–Z	25	24
	TPR		
	M–P(average)	2.30	2.40
	P$_x$–M–P$_y$	86	94
	P$_x$–M–CO$_c$	86	87
	P$_y$–M–CO$_c$	86	84
	P$_z$–M–CO$_a$	85	76
	P$_z$–M–CO$_b$	86	83
	CO$_a$–M–CO$_b$	86	88
	M–P$_x$–Z	12	22
	M–P$_y$–Z	69	48
	M–P$_z$–Z	30	53
	mer		
	M–P(average)	2.29	2.40
	P$_x$–M–P$_y$	90	94
	P$_x$–M–P$_x$	180	178
	CO$_a$–M–CO$_b$	90	89
	M–P$_x$–Z	31	18
	M–P$_y$–Z	37	23

* Bond lengths in Å, angles in °.

The modelling results thus provide a satisfactory rationale for the observed kinetic and thermodynamic data and indicate the importance of steric effects in such phosphine complexes.

Experimental

The NMR and infrared spectra were recorded on JEOL FX-100 and Perkin-Elmer 257 spectrometers respectively; NMR chemical shifts in ppm are relative to $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P). The UV/VIS spectra were recorded on a Perkin-Elmer 402 spectrometer. The $[M(\pi\text{-ligand})(CO)_3]$ complexes were prepared using literature methods from $[Cr(CO)_3(NH_3)_3]$[27] (styrene, 2,6-dimethylpyridine), $[W(CO)_3(MeCN)_3]$ (cycloheptatriene)[28] or $[M(CO)_6]$ (the rest).[29] Methyl isocyanide was prepared by a literature procedure.[30]

(*a*) Kinetics

(*i*) **Substitution reactions.** Substrate samples of analytical purity were used in the kinetic work. Decalin was purified by stirring over concentrated H_2SO_4 for 4 h, followed by washing with water, aqueous Na_2CO_3 and again with water. After drying over $CaSO_4$, the solvent was passed down an alumina column, distilled under vacuum (15 mmHg) from sodium, and stored under argon. Tributylphosphine was refluxed over CaH_2 and distilled, $P(OMe)_3$ was refluxed and distilled from sodium; PrCN was heated with concentrated HCl, dried over K_2CO_3 and distilled.

An appropriate amount of substrate (sufficient to give a 2×10^{-3} mol dm^{-3} solution) was dissolved in a decalin–proligand mixture of the required composition and transferred under nitrogen (commercial grade, oxygen free) in the absence of light to a sealed 1 cm glass cell of minimum dead volume equipped with a Teflon stopcock. After degassing for 15 min, the cell was sealed under a positive pressure of nitrogen (5 psi) and placed in the constant-temperature jacket (± 0.2 °C) of the spectrometer.

All studies were carried out under pseudo-first-order conditions ($[L] \geqslant 2 \times 10^{-2}$ mol dm^{-3}) and monitored by the disappearance of the substrate over not less than three half-lives. A monitoring wavelength of 510 nm was used for all the $Cr(CO)_3$ complexes except that of (pyrene) (560 nm). Values of k_{obs} were obtained from linear plots of $\ln(A_t - A_\infty)$ against time, using a minimum of ten absorbance/time pairs. All plots gave correlation coefficients greater than 0.9995. Duplicate runs generally showed a reproducibility of better than $\pm 5\%$. A full table of rate data is contained in SUP 57164.

(*ii*) **Isomerization reactions.** Solutions of *fac*-$[M(CO)_3\{P(OMe)_3\}_3]$ (5×10^{-4} mol dm^{-3} in decalin) were placed in the 1 cm cell described above, degassed with argon (oxygen free) and sealed under a positive pressure of argon (5 psi). The chromium complex was monitored *in situ* in the constant-temperature jacket of the spectrometer (± 0.2 °C), while the less labile molybdenum and tungsten complexes were immersed in a constant-temperature oil-bath (± 0.2 °C) and removed periodically for monitoring. Rate constants ($k_1 + k_{-1}$) were obtained from plots of $\ln(A_t - A_\infty)$ against time using the change in absorbance at 310 mm (Mo and W) and 320 nm (Cr). All plots had correlation coefficients of greater than 0.998.

The ^{31}P NMR monitoring of *fac*/*mer* isomerization was conducted *in situ* using 0.1 mol dm^{-3} solutions of *fac*-$[M(CO)_3\{P(OMe)_3\}_3]$ in $[^2H_8]$toluene degassed with nitrogen. Values of $k_1 + k_{-1}$ were obtained from plots of $\ln[(P_\infty - P_t)/(P_t + 1)]$ against time where P is the integrated *mer*/*fac* ratio. The isomerizations of $[Cr(CO)_3(CNR)_3]$ (R = Me or Bu^t) were studied similarly by ^1H NMR spectroscopy. The substitution reactions in $[^2H_8]$toluene were conducted using 0.2 mol cm^{-3} solutions of $[Cr(C_7H_8)(CO)_3]$ containing a 10-fold excess of $P(OMe)_3$. The rate of substitution was monitored from the relative integral of free phosphite to that of the (*mer* + *fac*) product.

(*b*) Preparations

The complex $[Cr(C_7H_8(CO)_3]$ (0.3 g, 1.3 mmol) was added to a mixture of $P(OMe)_3$ (2.0 g, 6 mmol) in hexane (10 cm^3). After degassing with nitrogen the red solution was left to stand overnight. After removal of solvent under vacuum, the residue was recrystallized from hexane to give *fac*-$[Cr(CO)_3\{P(OMe)_3\}_3]$ (0.4 g, 65%) [Found (Calc.): C, 28.4 (28.4); H, 5.35 (5.30)%]. Infrared (decalin): 1962, 1888 and 1874 cm^{-1}. ^{31}P NMR (toluene): δ 184.6. Other *fac*-$[M(CO)_3L_3]$ complexes were prepared in the same way: *fac*-$[Mo(CO)_3\{P(OMe)_3\}_3]$ [Found (Calc.): C, 26.4 (26.1); H, 5.15 (4.90)%]; infrared (decalin) 1974, 1898 and 1884 cm^{-1}; ^{31}P NMR (toluene) δ 168.7; *fac*-$[W(CO)_3\{P(OMe)_3\}_3]$ [Found (Calc.): C, 22.4 (22.5); H, 4.25 (4.20)%]; infrared (decalin) 1970, 1893 and 1878 cm^{-1}; ^{31}P NMR (toluene) δ 151.5 ($J_{W-P} = 381$ Hz); *fac*-$[Cr(CO)_3(CNMe)_3]$ [Found (Calc.): C, 41.9 (41.7); H, 3.20 (3.45); N, 16.3 (16.2)%]; infrared (CH_2Cl_2) 2175, 2131, 1941 and 1859 cm^{-1}; ^1H NMR ($CDCl_3$), δ 3.28 (s); *fac*-$[Cr(CO)_3(PBu_3)_3]$ only *in situ*; infrared (decalin) 1930 and 1842 cm^{-1}; ^{31}P NMR (toluene) δ 21.4.

Samples of *mer* isomers were obtained by heating the *fac* isomers [light petroleum (b.p. 60–80 °C) for phosphite complexes and toluene for isocyanide complexes] at 75–85 °C for several hours under nitrogen. Solvent evaporation and subsequent separation by Chromatotron {ethyl acetate–light petroleum (b.p. 40–60 °C) (1 : 4) for phosphite complexes and diethyl ether for $[Cr(CO)_3(CNMe)_3]$} gave the *mer*- and *fac*-$[Cr(CO)_3L_3]$ complexes in order of elution, except for $[W(CO)_3\{P(OMe)_3\}_3]$ where the order of elution was reversed. The complexes *mer*/*fac*-$[Cr(CO)_3(CNBu^t)_3]$ could not be separated by chromatography. Recrystallization from light petroleum (b.p. 40–60 °C) gave the pure *mer* isomers, except for *mer*-$[Mo(CO)_3\{P(OMe)_3\}_3]$ which proved difficult to crystallize: *mer*-$[Cr(CO)_3\{P(OMe)_3\}_3]$ [Found (Calc.): C, 27.7 (28.4); H, 5.55 (5.30)%]; infrared (decalin) 1975w, 1890w and 1875s cm^{-1}; ^{31}P NMR (toluene) δ 187.2 (m, P_{trans}) and 195.4 (m, $2P_{cis}$) ($J_{P-P} = 63$ Hz); *mer*-$[Mo(CO)_3\{P(OMe)_3\}_3]$, infrared (decalin) 2000w, 1987w and 1885s cm^{-1}; ^{31}P NMR (toluene) δ 170.6 (m, P_{trans}) and 177.7 (m, $2P_{cis}$) ($J_{P-P} = 45$ Hz); *mer*-$[W(CO)_3\{P(OMe)_3\}_3]$ [Found (Calc.): C, 22.4 (22.5); H, 4.25 (4.20)%]; infrared (decalin) 1970w, 1893w and 1878s cm^{-1}; ^{31}P NMR (toluene) δ 151.8 (m, P_{trans}) and 156.0 (m, $2P_{cis}$) ($J_{P-P} = 32$, $J_{W-Pcis} = 371$, $J_{W-Ptrans} = 427$ Hz); *mer*-$[Cr(CO)_3(MeNC)_3]$ [Found (Calc.): C, 42.0 (41.5); H, 3.40 (3.45); N, 16.4 (16.2)%]; infrared (CH_2Cl_2) 2171w, 2099s, 1963w and 1879s; ^1H NMR ($[^2H_8]$toluene) δ 2.07 (Me_{trans}, s) and 2.17 ($2Me_{cis}$, s); *mer*-$[Cr(CO)_3(PBu_3)_3]$ only *in situ*; ^{31}P NMR (toluene) δ 29.5 (P_{trans}, t) and 42.0 ($2P_{cis}$, d) ($J_{P-P} = 21.9$ Hz).

(*c*) Computations

Molecular mechanics calculations were performed using a modified version[31] of the MM2 program[32] which allowed inclusion of atoms having a co-ordination number up to six. Parameters involving chromium were taken from ref. 23 and the remainder from the program itself. In order to calculate the rotational profiles, the angle-bending force constants involving chromium were set to an artificially high value of 9.999 mdyn Å rad^{-2}, and ideal angles were calculated for each step of 10° in the rotation of the triangular faces.

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