Preparation and Some Reactions of Group VI Metal Monodentate Bisphosphine Carbonyl Complexes. Mechanistic Aspects of Chelate-ring Formation

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A series of complexes $LM(CO)_5$ [M = Cr, Mo, or W; L = $Me_2PCH_2CH_2PMe_2$ (dmpe), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dpp), or $Ph_2PCH_2CH_2AsPh_2$ (ape)] has been prepared and characterised by analysis, and i.r., mass, and n.m.r. spectroscopy. The complexes can be methylated with Me_3OBF_4 to give $[(MeL)M(CO)_5]BF_4$. The acid-assisted nucleophilic substitution reaction used in the formation of the complexes can also be applied to their conversion into bridged complexes, $L[M(CO)_5]_2$. Variations in geminal coupling constants $^2J_{PCH}$ and aromatic solvent induced shifts for the series of complexes $(dmpe)M(CO)_n$ (M = Cr, Mo, or W; n = 4 or 5) are discussed and compared with those in $(Me_2PXCH_2)_2$ (X = O or S) and $[(Me_3PCH_2)_2](BF_4)_2$, whose syntheses are also reported. Changes in the ^{31}P chemical shift are used to demonstrate that the chelation shift is comparable to the co-ordination shift. Kinetic studies of the rate of the chelation reaction, $LM(CO)_5 \longrightarrow LM(CO)_4 + CO$, have been used to elucidate details of its mechanism. The reaction follows first-order kinetics, as required for the intramolecular process. The magnitude of the enthalpy of activation (*ca.* 140 kJ mol^{-1}) and the similarity in rate between phosphorus and arsenic nucleophiles, suggest a large dissociative component in the activation. The positive entropy of activation and particularly its large variation (+6 to +71 J K^{-1} mol^{-1}) suggest a concerted process in the transition state. The smaller the potential chelate ring, the faster the reaction in the series L = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, or 3); this appears to be largely an entropy effect.

BIDENTATE ligands containing tertiary atoms of Group V elements linked by a flexible hydrocarbon chain will usually chelate to a transition metal or, more rarely, serve as a bridge between two such metals. In the case of Group VI metal hexacarbonyl complexes the product of chelation is usually *cis*-$LM(CO)_4$, where L represents a ligand such as *o*-phenylenebis(dimethylarsine) (diars) [1] or tetraphenyldiphosphinoethane (dpe).[2] Recently it has been shown that the ligand bis(diphenylarsino)methane (dam) [3] and its antimony analogue (dpsm) [4] will react with Group VI metal carbonyl complexes at high temperature over many hours to give monosubstituted complexes in which the ligand is monodentate, that is, of the type $LM(CO)_5$. The reaction between the aniline complex $PhNH_2W(CO)_5$ and dpe or bis(diphenylphosphino)methane (dpm) at room temperature over several hours produces $(dpe)W(CO)_5$ and $(dpm)W(CO)_5$ respectively. When the former complex is treated with benzyl bromide quaternisation of the free phosphorus atom occurs slowly.[5]

Complexes of the type $LM(CO)_5$ may be prepared in high yield from the reaction between the ligand L, the halogenopentacarbonylmetallate $[XM(CO)_5]^-$, and a Lewis acid. This reaction, which is very rapid, has been applied to the specific synthesis of complexes containing neutral monodentate ligands, *e.g.* $PH_3Cr(CO)_5$.[6] We report an extension of this Lewis acid-assisted nucleophilic substitution procedure to systems in which the ligand, L, is potentially chelating and bidentate, together with some studies of the reactions of such complexes.

RESULTS AND DISCUSSION

The complexes reported here were all prepared in moderate to very good yields from reactions between equimolar proportions of the salts $Me_4N[XM(CO)_5]$ [X = Cl or I; M = Cr, Mo, or W], the ligands $R_2E(CH_2)_nPR_2$ (R = Ph, E = P, n = 1—3; R = Ph, E = As, n = 2; R = Me, E = P, n = 2) and Et_3OBF_4 in methylene chloride solution at room temperature. Analytical data are presented in Table 1.

By applying the same procedure to the monodentate phosphine product of the above reaction, it was possible to prepare the bridged complexes $(CO)_5MR_2E(CH_2)_nPR_2M(CO)_5$. When R = Me, E = P, and n = 2, the bridged product appears to decompose in solution very easily as we were unable to isolate the solid complex, but when the tetraphenyl analogue (R = Ph) was used, the solid 2 : 1 (M : L) adduct [7] was readily isolated.

When $Ph_2PCH_2CH_2AsPh_2$ (ape) was used as the ligand L, the product contained the ligand bonded through the phosphorus atom only; this was clearly demonstrated by the ^{31}P n.m.r. spectrum. This result indicates the superior nucleophilicity of the phosphorus atom donor site in a strictly competitive situation where consequences of steric effects are minimised.

When the chelating ligand lacks flexibility in the carbon skeleton connecting the two donor atoms, as in *o*-phenanthroline (*o*-phen), no monodentate product was formed and the sole product was the well known (*o*-phen)$Cr(CO)_4$.[8] This is to be compared with *NNN′N′*-tetramethylethylenediamine (tmen) which gives (tmen)$Cr(CO)_5$ under similar conditions.[6]

The uncomplexed phosphorus atom in these complexes was very readily quaternised by trimethyloxonium tetrafluoroborate, $(dmpe)Cr(CO)_5$ (dmpe =

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[1] H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1960, 1803.

[2] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1961, 4980.

[3] R. Colton and C. J. Rix, *Austral. J. Chem.*, 1971, **24**, 2461.

[4] T. Fukumoto, Y. Matsumura, and R. Okawara, *J. Organometallic Chem.*, 1972, **37**, 113.

[5] R. L. Keiter and D. P. Shah, *Inorg. Chem.*, 1972, **11**, 191.

[6] J. A. Connor, E. M. Jones, and G. K. McEwen, *J. Organometallic Chem.*, 1972, **43**, 357.

[7] H. Werner, R. Prinz, E. Bundschuh, and K. Deckelmann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 606.

[8] W. Hieber and F. Mühlbauer, *Z. anorg. Chem.*, 1935, **221**, 337.

$Me_2PCH_2CH_2PMe_2$) and (dpe)$Cr(CO)_5$ giving the salts [(Medmpe)$Cr(CO)_5$]BF_4 and [(Medpe)$Cr(CO)_5$]BF_4 respectively. An attempt was made to phenylate (dpe)$Cr(CO)_5$ using Ph_3SBF_4 as the phenylating reagent,[9] but this was not successful.

I.r. Spectra.—In the region 2200—1600 cm^{-1}, the monodentate phosphine complexes $LM(CO)_5$ showed the pattern of bands expected for a compound of pseudo-C_{4v} symmetry.[10] The frequencies of the carbonyl stretching vibrations are listed in Table 2, which also includes those for *cis*-$LM(CO)_4$ compounds. From the lack of variation, within experimental error, in the frequencies of this series of complexes it is apparent that care should be exercised in making deductions about the π-acceptor–σ-donor properties of similar ligands on the basis of carbonyl stretching-frequency data alone. Thus there is no significant difference, based on this criterion, between the ligands dpe and dmpe or between the atoms chromium and tungsten. Quaternisation of the non-bonded phosphorus atom in $LCr(CO)_5$ (L = dmpe or dpe) did not result in any observable change in the carbonyl stretching frequencies of the neutral complex.

TABLE 1

Analyses, melting points, yields, and appearances of $LM(CO)_{6-x}$ complexes and other compounds

				Analysis found (required)/%					Yield	
L	M	*x*	Formula	C	H	M	P	M.p./°C	%	Appearance
dmpe	Cr	1	$C_{11}H_{16}CrO_5P_2$	38·3 (38·6)	4·9 (4·7)	14·7 (15·2)		122—123	72	White powder
		2	$C_{10}H_{16}CrO_4P_2$	37·8 (38·2)	5·1 (5·1)		19·6 (19·7)	146—150	70	Pale yellow powder
	Mo	1	$C_{11}H_{16}MoO_5P_2$	34·0 (34·2)	4·2 (4·2)		16·0 (16·1)		75	Oil
		2	$C_{10}H_{16}MoO_4P_2$	32·7 (33·5)	4·6 (4·5)		16·4 (17·3)	150—152	90	Yellow crystals
	W	1	$C_{11}H_{16}O_5P_2W$	27·4 (27·8)	3·5 (3·4)		13·0 (13·1)		70	Oil
		2	$C_{10}H_{16}O_4P_2W$	26·8 (26·9)	3·6 (3·6)		13·9 (13·9)	189—191	88	Yellow crystals
dpm	Cr	1	$C_{30}H_{22}CrO_5P_2$	63·8 (62·1)	4·6 (3·8)	8·9 (9·0)		93—94	87	Pale yellow powder
dpe	Cr	1	$C_{31}H_{24}CrO_5P_2$	63·6 (63·2)	4·6 (4·1)	7·3 (8·8)		95—97	89	Pale yellow powder
dpp	Cr	1	$C_{32}H_{26}CrO_5P_2$	64·1 (63·8)	4·5 (4·3)	9·8 (8·6)		170—172	91	Pale yellow crystals
ape	Cr	1	$C_{31}H_{24}AsCrO_5P$	58·2 (58·6)	4·0 (4·2)	7·2 (8·2)		67—70	87	Yellow powder
$Medmpe^+BF_4^-$	Cr	1	$C_{12}H_{19}BCrF_4O_5P_2$	31·0 (32·4)	4·2 (4·3)	11·0 (11·7)		157—158	78	Colourless needles
$Medpe^+BF_4^-$	Cr	1	$C_{32}H_{27}BCrF_4O_5P_2$	53·0 (55·3)	4·6 (3·9)	7·1 (7·5)		228—230	91	Colourless needles
$[Me_3PCH_2CH_2PMe_3](BF_4)_2$			$C_8H_{22}B_2F_8P_2$	27·2 (27·1)	6·4 (6·2)				85	Colourless crystals
$Me_2POCH_2CH_2POMe_2$			$C_6H_{16}O_2P_2$	39·5 (39·6)	8·8 (8·8)			222—224	68	Colourless crystals

TABLE 2

I.r. spectra of the complexes $LM(CO)_{6-n}$ in the range 2200—1600 cm^{-1}

<table>
<tr><th><i>n</i></th><th>M</th><th>L</th><th>A_1''</th><th>B_1</th><th>A_1'</th><th>E</th><th>Solvent</th></tr>
<tr><td>5</td><td>Cr</td><td>dmpe</td><td>2063w</td><td></td><td>1950m</td><td>1938vs</td><td><i>a</i></td></tr>
<tr><td>5</td><td>Cr</td><td>Medmpe+</td><td>2066w</td><td></td><td colspan="2">1938vs</td><td><i>b</i></td></tr>
<tr><td>5</td><td>Mo</td><td>dmpe</td><td>2073w</td><td>1984vw</td><td>1955m</td><td>1947vs</td><td><i>a</i></td></tr>
<tr><td>5</td><td>W</td><td>dmpe</td><td>2071w</td><td>1975vw</td><td>1949m</td><td>1939s</td><td><i>a</i></td></tr>
<tr><td>5</td><td>Cr</td><td>dpm</td><td>2064w</td><td>1983vw</td><td colspan="2">1946vs</td><td><i>a</i></td></tr>
<tr><td>5</td><td>Cr</td><td>dpe</td><td>2065m</td><td>1985w</td><td>1953m</td><td>1943s</td><td><i>a</i></td></tr>
<tr><td>5</td><td>Cr</td><td>Medpe+</td><td>2068m</td><td>1989vw</td><td colspan="2">1941s</td><td><i>b</i></td></tr>
<tr><td>5</td><td>W</td><td>dpe</td><td>2072w</td><td>1982w</td><td>1948m</td><td>1940s</td><td><i>c</i></td></tr>
<tr><td>5</td><td>Cr</td><td>(dpe)Cr(CO)$_5$</td><td>2065w</td><td>1986vw</td><td>1955s</td><td>1942s</td><td><i>a</i></td></tr>
<tr><td>5</td><td>Cr</td><td>dpp</td><td>2065m</td><td>1985w</td><td>1952m</td><td>1941s</td><td><i>a</i></td></tr>
<tr><td>5</td><td>Cr</td><td>ape</td><td>2065w</td><td>1988vw</td><td>1953m</td><td>1941s</td><td><i>a</i></td></tr>
<tr><td></td><td></td><td></td><td>A_1</td><td>A_2</td><td>B_1</td><td>B_2</td><td></td></tr>
<tr><td>4</td><td>Cr</td><td>dmpe</td><td>2009m</td><td>1921m</td><td>1900s</td><td>1894vs</td><td><i>a</i></td></tr>
<tr><td>4</td><td>Mo</td><td>dmpe</td><td>2020m</td><td>1929m</td><td>1909s</td><td>1903vs</td><td><i>a</i></td></tr>
<tr><td>4</td><td>W</td><td>dmpe</td><td>2017m</td><td>1922m</td><td>1902s</td><td>1897vs</td><td><i>a</i></td></tr>
<tr><td>4</td><td>Cr</td><td>dpm</td><td>2015m</td><td>1930m</td><td>1911s</td><td>1898s</td><td><i>c</i></td></tr>
<tr><td>4</td><td>Cr</td><td>dpe</td><td>2013m</td><td>1926m</td><td>1911s</td><td>1899s</td><td><i>a</i></td></tr>
<tr><td>4</td><td>W</td><td>dpe</td><td>2021m</td><td>1925m</td><td>1910vs</td><td>1899s</td><td><i>c</i></td></tr>
<tr><td>4</td><td>Cr</td><td>dpp</td><td>2010m</td><td>1929m</td><td>1908s</td><td>1890s</td><td><i>c</i></td></tr>
<tr><td>4</td><td>Cr</td><td>ape</td><td>2014m</td><td>1926m</td><td>1909s</td><td>1897s</td><td><i>c</i></td></tr>
</table>

[a] Hexane. [b] CH_2Cl_2. [c] n-Octane.

Mass Spectra.—Contrary to expectation,[11] none of the monodentate phosphine complexes, $LM(CO)_5$, showed a molecular ion in its mass spectrum. The spectrum observed initially corresponded to that of $LM(CO)_4$, followed by successive loss of four CO groups to give LM^+. Even at the lowest source temperature attainable

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[9] A. N. Nesmeyanov, Y. A. Chapovsky, I. V. Polovyanyuk, and L. G. Makarova, *J. Organometallic Chem.*, 1967, **7**, 329.

[10] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[11] J. Müller and J. A. Connor, *Chem. Ber.*, 1969, **102**, 1148.

in our spectrometer it was not possible to observe the molecular ion $LM(CO)_5^+$. As we shall show, the conversion of $LM(CO)_5$ into $LM(CO)_4$ is fairly rapid in solution at *ca.* 100 °C, so that at 50—70 °C (the source temperature usually used) a substantial contribution to the energy required to rupture the M–CO bond must come from the electron beam.

Where L is a phenyl-substituted ligand, the results (Table **3**) indicate that the ion $LCr(CO)_3^+$ is either absent or in very low abundance in the mass spectra of the complexes. Similar behaviour has been observed previously with the carbene complexes $(CO)_5CrC(XPh)C_4H_3O$ ($X = O$ or S)[12] and the aryl isocyanide complexes $(CO)_{6-x}Cr(CNR)_x$ ($x = 2$ or 3; R = aryl),[13] and in each case it has been explained by the formation of π-arene complexes. The formation of these π-arene complexes, *e.g.* $(CO)_2CrC(XPh)C_4H_3O$ and $(CO)_2Cr(CNR)_2$, in the mass spectrometer has received strong support from the finding that (dam)$Cr(CO)_5$ is converted to (dam)$Cr(CO)_2$ on heating (in the latter compound one arsenic atom is bonded to chromium in the normal manner while the other end of the ligand is bonded to chromium through a π-bonded phenyl ring [14]).[3] Following these precedents, it is a simple matter to rationalise the absence of the $LCr(CO)_3^+$ ion in terms of the preferred loss of two carbonyl groups from $LCr(CO)_4^+$ to give $LCr(CO)_2^+$, which might have the structure shown below. As Table **3** also shows, this process does not occur in the tungsten complex (dpe)$W(CO)_5$, the mass spectrum of which contains the ion (dpe)$W(CO)_3^+$ of moderate abundance. This would suggest that the increased size of the tungsten atom prevents the internal rearrangement from taking place. In this context it is significant that when (dam)$W(CO)_5$ is heated the π-arene compound (dam)$W(CO)_2$ is not formed.[3]

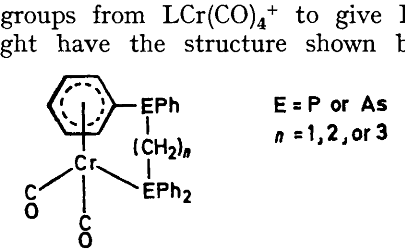

TABLE 3

Relative abundances of some ions in the mass spectra of the complexes $LM(CO)_5$

L M	dpm Cr	dpe Cr	ape Cr	dpp Cr	dpe W	$(dpe)Cr(CO)_5$ Cr	dmpe Cr	dmpe Mo	dmpe W
LM^+	100	100	100	100	100	100	100	100	100
$LM(CO)^+$	4·8	29	3	15	176	22	14	92	82
$LM(CO)_2^+$	0·6	5	0·6	0·3	91	3	5	77	110
$LM(CO)_3^+$		0·2			19	0·3	2	45	53
$LM(CO)_4^+$		11	5	5	96	8	19	83	63
LM_2^+	3·8	0·4	2	4	6	6		4	
$LM_2(CO)^+$	0·5	0·1		0·4	9	1		3	
$LM_2(CO)_2^+$	0·4		0·6	1	8	0·3		4	
$LM_2(CO)_3^+$	0·1	0·1	0·6	0·4	5	1		3	
$LM_2(CO)_4^+$	0·1	0·2	0·2	1	17	1		6	
$LM_2(CO)_5^+$		0·3	0·4	2	5	5		6	
$LM_2(CO)_6^+$					8	0·4		1	
$LM_2(CO)_7^+$	0·1	0·1		0·3	13	1		2	
$LM_2(CO)_8^+$								1	
$LM_2(CO)_9^+$					4	0·3		0·6	
$LM_2(CO)_{10}^+$		0·1			10	2		3	
$Ph_2P(CH_2)_nEPh_2^+$	2·1	55	40	4	128	7			
$Ph_3P(CH_2)_nE^+$	0·4		147	36	30				
Ph_3PE^+			119		33				
$Ph_2PEPh_2^+$		26	14		109				
$MPPh_2EPh_2^+$	0·2	29	57	13	96	96			
$MAsPh_2^+$			190						
$MPPh_2^+$	9·4	13	358	17	328				

If the complex $LM(CO)_5$ was heated in the source region of the mass spectrometer and the spectrum rerun after a few minutes it was found that the abundances of ions corresponding to the fragmentation of the bridged complex $LM_2(CO)_{10}$, which are very weak in the original spectrum, had increased considerably while those of the $LM(CO)_n^+$ ($n < 4$) ions had decreased. In this way the final spectrum obtained for pure (dpe)-$Cr(CO)_5$ was almost identical to that obtained initially for pure (dpe)$Cr_2(CO)_{10}$, showing successive loss of all ten carbonyl groups. Similar observations have also been made for the complexes (dpm)$Cr(CO)_5$, (dpp)-$Cr(CO)_5$ (dpp = $Ph_2PCH_2CH_2CH_2PPh_2$), and (dpe)-$W(CO)_5$. In the case of (ape)$Cr(CO)_5$, the ions corresponding to (ape)$Cr_2(CO)_x^+$ ($x = 6$—10) were not observed. Neither of the complexes (dmpe)$M(CO)_5$ (M = Cr or W) showed any ions arising from the formation of (dmpe)$M_2(CO)_{10}$ in the spectrometer, which is consistent with our inability to isolate the solid complexes by chemical synthesis; however the complete range of (dmpe)$Mo_2(CO)_x^+$ ($x = 1$—10) ions was observed. It is not clear why dmpe should not form a bridge between $M(CO)_5$ (M = Cr or W) fragments either in the mass spectrometer or by designed synthesis, especially as the complexes $(CO)_5MMe_2EE'Me_2M'(CO)_5$ (M,M' = Cr or W; E,E' = P or As) have recently been

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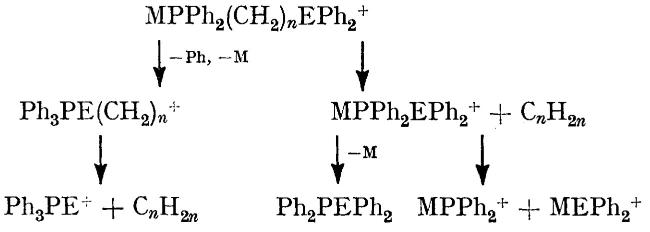
[12] J. A. Connor and E. M. Jones, *J. Chem. Soc.* (*A*), 1971, 3368.

[13] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J.C.S. Dalton*, 1972, 1246.

[14] G. B. Robertson, P. O. Whimp, R. Colton, and C. J. Rix, *Chem. Comm.*, 1971, 573.

shown to be relatively stable.[15] Nothing is known of the path by which $LM_2(CO)_{10}^+$ [L = (dpm), (dpe), or (dpp); M = Cr or W] is formed in the mass spectrometer but an ion–molecule reaction between $M(CO)_6$ and $LM(CO)_4^+$ appears reasonable.

The fragmentation pattern of the ion ML^+ has been established with the help of metastable transitions. In the case of the complexes $LM(CO)_5$ [L = (dpm), (dpe), (dpp), or (ape), M = Cr; L = (dpe), M = W] this is shown below. Abundance ratios of the ions produced in these reactions are listed in Table 3.



N.m.r. Spectra.—Results of the proton n.m.r. spectra are tabulated in Table 4. The spectrum of pure dmpe fell in the category of ' deceptively simple,' that is, in which both the CH_3 and the CH_2 protons each appear as a sharp doublet with a broad central envelope. The difference between the two sharp outer lines is equal to N, where $N = |^2J_{PH} + {}^5J_{PH}|$ and $|^2J_{PH} + {}^3J_{PH}|$ respectively. If the reasonable assumption that $^5J_{PH}$ is zero, or very small when compared to $^2J_{PH}$, is made, then it is possible to measure $^2J_{PH}$ directly. Similar reasoning applies to the salt $[Me_3PC_2H_4PMe_3](BF_4)_2$. The spectra of the complexes $(dmpe)M(CO)_4$ (M = Cr, Mo, or W) appeared as two sharp doublets in the ratio 3 : 2. The fact that the central envelope was absent suggests that the value of $^3J_{PP}$ is much smaller in the complexes than in the free ligand. The assumption that $^5J_{PH}$ is zero is substantiated by the observation that the two different phosphorus atoms in the monodentate phosphine complexes, $(dmpe)M(CO)_5$, gave rise to a pair of sharp doublets due to the two distinct pairs of P-methyl groups. If long range P–H coupling were present a pair of double doublets would be expected.

In the monodentate phosphine complexes, the lower-field doublet is attributed to that end of the molecule which is bonded to the metal ($^2J_{PCH_3}$ *ca.* 7·6 Hz), while the doublet at higher field ($^2J_{PCH_3}$ *ca.* 2·5 Hz) corresponds to the non-bonded end of the molecule. These two coupling constants are in close agreement with those found for $(dmpe)M(CO)_4$ and pure dmpe respectively. The spectrum of the salt $[(Medmpe)Cr(CO)_5]BF_4$ was similar, but now the doublet (^2J 7·8 Hz) due to the methyl groups of the metal-bonded phosphorus atom was to higher field of that produced by those of the free, quaternised phosphorus atom. The coupling constants of the methyl-quaternised phosphorus ($^2J_{P+CH_3}$ 14·2 Hz) are very close to that in $[Me_2dmpe](BF_4)_2$ (14·4 Hz). The increase in the absolute value of $^2J_{PCH}$ in the order dmpe < $(dmpe)M(CO)_4$ < X_2dmpe (X = O or S) < Me_2dmpe^{2+}, which parallels the increasing deshielding of the methyl groups, reflects the increasing electronegativity of the group attached to the phosphorus atom. As the *s* character of the phosphorus atomic orbitals bonding to carbon increases, it has been shown that the geminal coupling constant in the P–C–H fragment becomes less positive (more negative). There is also strong evidence that the absolute sign of $^2J_{PCH}$ is positive in Me_3P and Et_3P and negative in phosphonium salts and trialkylphosphine chalcogenides.[16] Dmpe and its derivatives fit well with these arguments which also suggest that the sign of $^2J_{PCH}$ in the metal carbonyl complexes $(dmpe)M(CO)_n$ (n = 4 or 5) is also negative.

The spectra of the complexes containing phenyl-

TABLE 4

Proton n.m.r. chemical shifts δ/p.p.m. and solvent shifts Δ

	Free Me			Bound Me			CH$_2$			Ph	
	δ [a]	Δ [b]	$^2J_{PCH}$	δ [a]	Δ [b]	$^2J_{PCH}$	δ [a]	Δ [b]	N [c]	δ [a]	Δ [b]
dmpe	1·00	0·16	2·5				1·42	0·11	7·5		
$(dmpe)Cr(CO)_5$	1·06	0·27	2·3	1·47	0·60	7·2	1·60	0·30	*d*		
$(dmpe)Mo(CO)_5$	0·98	0·17	2·3	1·41	0·49	6·8	1·70	0·40	*d*		
$(dmpe)W(CO)_5$	0·98	0·18	2·2	1·54	0·53	7·2	1·50	0·20	*d*		
$[Me_2dmpe](BF_4)_2$	1·89 [e]		14·4				2·46		6·8		
$[MedmpeCr(CO)_5]BF_4$	1·82 [e]		14·2	1·53		7·8	2·23		7·0		
cis-$(dmpe)Cr(CO)_4$				1·48	0·50	7·8	1·70	0·80	16·2		
cis-$(dmpe)Mo(CO)_4$				1·46	0·51	7·2	1·67	0·77	16·4		
cis-$(dmpe)W(CO)_4$				1·61	0·55	7·3	1·72	0·84	15·8		
dpe							2·10	−0·10		7·27	−0·07
$(dpe)Cr(CO)_5$							2·20	−0·07		7·37	0·35
$[MedpeCr(CO)_5]BF_4$	2·55 [e]		13·5				2·29			7·55	
$dpe[Cr(CO)_5]_2$							2·38 [f]			7·03	
$(dpe)W(CO)_5$							2·48 [g]			7·42	
ape						P–CH$_2$	2·13	−0·09		7·28	
						As–CH$_2$	2·07	−0·07			
$(ape)Cr(CO)_5$							2·25			7·34	
$(Me_2PO)_2C_2H_4$	1·57		12·7				2·02		2·3		
$(Me_2PS)_2C_2H_4$	1·93 [h]		13·0				2·43		2·3		

[a] $CDCl_3$ solution. [b] $\Delta = \delta(CDCl_3) - \delta(C_6D_6)$. [c] $N = |^2J_{PH} + {}^3J_{PH}|$. [d] Broad multiplet. [e] CD_3CN. [f] C_6D_6 only. [g] d_6-Acetone. [h] CF_3COOH.

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substituted ligands showed no distinction (at 100 MHz) between the two types of CH_2 groups in, for example, the complex (dpe)$Cr(CO)_5$. Two methylene proton resonances, separated by 6 Hz, were observed in the spectrum of pure ape, but this distinction disappeared completely in the complex (ape)$Cr(CO)_5$. In general, therefore, the n.m.r. spectra of $LM(CO)_n$ [L = (dpm), (dpe), (dpp), or (ape); $n = 4$ or 5] complexes provide very little information of value, in contrast to (dmpe)$M(CO)_n$ ($n = 4$ or 5) complexes.

Table 4 also contains information about aromatic solvent induced shift (ASIS) effects in the n.m.r. spectra of these complexes. These effects were particularly marked in the complexes of dmpe. It has been established that benzene solvent molecules interact preferentially with centres of positive charge in the solute, which will show a larger ASIS as a consequence.[17] The ASIS, defined by $\Delta = \delta(CDCl_3) - \delta(C_6D_6)$, of the methyl groups attached to the co-ordinated phosphorus atom in (dmpe)$M(CO)_n$ ($n = 4$ or 5) is approximately three times as large as that of those attached to the free phosphorus atom in (dmpe)$M(CO)_5$ or in pure dmpe. This confirms the increase in the positive charge at the phosphorus atom as a result of complex formation. The ASIS of the methylene protons in the complex (dmpe)$M(CO)_5$ (*ca.* 30 Hz) is also greater than that of the methylene protons in pure dmpe (11 Hz), but increases still more in (dmpe)-$M(CO)_4$ (*ca.* 80 Hz) suggesting that steric factors also contribute to the magnitude of Δ (see also the discussion of ^{31}P shifts).

Our study of the ^{31}P n.m.r. spectra of the compounds described here was limited by their solubility. We have succeeded in obtaining spectra for ape and dmpe and their derivatives. Results are collected in Table 5.

TABLE 5

^{31}P Chemical shifts (δ p.p.m.) relative to 85% H_3PO_4 [a]

	$\delta(\pm 0{\cdot}5)$	Δ_{CS} [b]	Solvent [d]
$\mathrm{Me_2PCH_2CH_2PMe_2}$	$+48{\cdot}5$		Neat
$(\mathrm{Me_2PCH_2CH_2}\mathit{P}\mathrm{Me_2})\mathrm{Cr(CO)_5}$	$-18{\cdot}5$	$-67{\cdot}0$	1
$(\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2PMe_2})\mathrm{Cr(CO)_5}$	$+47{\cdot}3$	$-1{\cdot}2$	1
$(\mathrm{Me_2PCH_2CH_2}\mathit{P}\mathrm{Me_2})\mathrm{Mo(CO)_5}$	$+2{\cdot}2$	$-46{\cdot}3$	2
$(\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2PMe_2})\mathrm{Mo(CO)_5}$	$+45{\cdot}9$ [c]	$-2{\cdot}6$	2
$(\mathrm{Me_2PCH_2CH_2}\mathit{P}\mathrm{Me_2})\mathrm{W(CO)_5}$	$+22{\cdot}8$	$-25{\cdot}7$	2
$(\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2PMe_2})\mathrm{W(CO)_5}$	$+46{\cdot}0$ [c]	$-2{\cdot}5$	2
cis-$(\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2}\mathit{P}\mathrm{Me_2})\mathrm{Cr(CO)_4}$	$-55{\cdot}7$	$-104{\cdot}2$	1
cis-$(\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2}\mathit{P}\mathrm{Me_2})\mathrm{Mo(CO)_4}$	$-26{\cdot}7$	$-75{\cdot}2$	1
cis-$(\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2}\mathit{P}\mathrm{Me_2})\mathrm{W(CO)_4}$	$-11{\cdot}5$	$-60{\cdot}0$	1
$[\mathrm{Me_2}\mathit{P}\mathrm{CH_2CH_2}\mathit{P}\mathrm{Me_3}](\mathrm{BF_4})_2$	$-31{\cdot}0$	$-79{\cdot}5$	3
$\mathrm{Me_2}\mathit{P}\mathrm{OCH_2CH_2}\mathit{P}\mathrm{OMe_2}$	$-60{\cdot}8$	$-109{\cdot}3$	4
$\mathrm{Me_2}\mathit{P}\mathrm{SCH_2CH_2}\mathit{P}\mathrm{SMe_2}$	$-44{\cdot}2$	$-92{\cdot}7$	4
$\mathrm{Ph_2AsCH_2CH_2PPh_2}$	$+12{\cdot}6$		2
$(\mathrm{Ph_2AsCH_2CH_2}\mathit{P}\mathrm{Ph_2})\mathrm{Cr(CO)_5}$	$-50{\cdot}2$	$-62{\cdot}8$	2

[a] Positive shifts taken as upfield of 85% H_3PO_4. [b] Δ_{CS} Is the co-ordination chemical shift defined as $\delta_{complex} - \delta_{ligand}$, where $\delta_{complex}$ is the chemical shift of the italicised phosphorus atom and δ_{ligand} is that of the free ligand. [c] Doublet $|^3J_{PP}| = 26$ Hz. [d] Solvent: 1, d_6-acetone; 2, $CDCl_3$; 3, CD_3CN; 4, CF_3COOH.

The ^{31}P spectra of the monodentate phosphine (dmpe)$M(CO)_5$ (M = Cr, Mo, or W) complexes demonstrate conclusively that the potentially bidentate phosphine ligand is co-ordinated to the metal atom through only one of its phosphorus atoms, and that rapid intramolecular exchange between the two phosphorus atoms of the ligand does not occur. The spectra showed two phosphorus resonances in each case, the higher field resonance having a chemical shift very similar to that of pure dmpe and is therefore assigned to the free phosphorus atom in the complex. The lower-field resonance is assigned to the phosphorus atom co-ordinated to the metal atom. This downfield resonance appeared as a broad singlet and the co-ordination shift, Δ_{CS} (see Table 5), decreases in the expected order Cr > Mo > W.[18] These co-ordination shifts are in very close agreement with those calculated from the equations given by Mann *et al.*[19] In the molybdenum and tungsten complexes the upfield resonance due to the free phosphorus atom could be resolved into a doublet with $^3J_{PP} = |26\ \mathrm{Hz}|$ in each case. This feature could not be resolved in the case of the complex (dmpe)$Cr(CO)_5$.

The series of complexes (dmpe)$M(CO)_4$ (M = Cr, Mo, or W) also show co-ordination shifts in the expected order described above. Of particular interest here is the change in the ^{31}P chemical shift in going from the mono- [(dmpe)$M(CO)_5$] to the bi-dentate[(dmpe)$M(CO)_4$] phosphine complex which we will describe as the chelation shift. Table 5 shows that this shift, which is downfield from the complex (dmpe)$M(CO)_5$, follows the descending order Cr (37·2) > W (34·3) > Mo (28·9). It is generally agreed that three factors determine ^{31}P chemical shifts in principle; these are, briefly, electronegativity differences among the substituents, the occupancy of *d* orbitals on the phosphorus atom by ($p \longrightarrow$ or $d \longrightarrow d$) π-bonding, and changes in the bond angles at the phosphorus atom.[20] From this we conclude that the chelation shift can be attributed principally to those constraints in the chelate ring which lead to an increase in the bond angle at phosphorus in the complex (dmpe)$M(CO)_4$. It is to be noted that, in the case of the tungsten complex, the chelation shift is rather larger than the co-ordination shift. Further evidence in favour of the influence of chelation upon the ^{31}P shift comes from a comparison of the complexes $Me_3PCr(CO)_5$ and *cis*-$(Me_3P)_2Cr(CO)_4$ in which the shifts remain almost identical at $-6{\cdot}5$ and $-6{\cdot}7$ p.p.m. respectively.[21]

^{31}P N.m.r. spectroscopy was also used to distinguish the form of complexation in (ape)$Cr(CO)_5$. It was found that the phosphorus resonance shifted downfield by 62·8 p.p.m. in going from the free ligand to the complex, thus establishing the mode of co-ordination as being through the phosphorus atom; no evidence was found of bonding through the arsenic atom in this complex.

Kinetic Studies.—The preparation of $LM(CO)_4$ complexes is usually carried out by heating the ligand, L,

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with $M(CO)_6$ either simply or else in the presence of a catalyst, such as the tetrahydroborate ion.[22] When the ligand is a chelating diphosphine the presumed intermediate $LM(CO)_5$ has not been isolated. It has been suggested [23] that under the conditions of the reaction the complex $LM(CO)_5$, once formed, loses carbon monoxide to give $LM(CO)_4$ as the only product. Exceptions to this rule, and their further reactions, have already been mentioned.

The availability of a wide range of complexes $LM(CO)_5$ as the products of the specific syntheses described here enabled us to observe the kinetics of the chelation step by which the complexes $LM(CO)_4$ are formed. We have followed the reactions by i.r. spectrophotometry and they obey the first-order equation (1). The derived rate

$$-\mathrm{d}[LM(CO)_5]/\mathrm{d}t = \mathrm{d}[LM(CO)_4]/\mathrm{d}t = k[LM(CO)_5] \quad (1)$$

constants and, in some cases, activation parameters are given in Table 6.

TABLE 6

(*a*) Rate constants for the reaction $LM(CO)_5 \longrightarrow LM(CO)_4 + CO$ at various temperatures

L	M	t/°C	10^5k/s^{-1}	t/°C	10^5k/s^{-1}	t/°C	10^5k/s^{-1}	Solvent
dmpe	Cr	83	0·0656	109	1·27	124	7·5	*a*
	Mo					124	14·5	*a*
	W					124	0·353	*b*
dpe	Cr	83	0·27	109	6·0	124	34·0	*a*
	W	123	0·447	134	1·03	150	9·0	*b*
dpm	Cr	99	2·35	109	10·2	124	55·0	*a*
dpp	Cr					124	26·0	*a*
ape	Cr					124	39·0	*a*
$(dpe)Cr(CO)_5$	Cr					124	5·5	*a*

[a] n-Octane. [b] n-Nonane.

(*b*) Activation parameters derived from the results in (*a*)

L	M	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$T\Delta S^‡$/kJ mol^{-1} (124 °C)
dmpe	Cr	132	6	2·4
dpm	Cr	141	71	28
dpe	Cr	135	27	11
dpe	W	155	40	16

The mechanism of the chelation process presumably involves nucleophilic attack on the metal atom by the 'free' end of the bidentate ligand, with the displacement of a carbonyl group. As usual, two mechanistic extremes may be envisaged,[24a] dissociative and associative (corresponding to the S_N1 and S_N2-extreme mechanisms envisaged for monodentate ligand substitution). It is to be expected that the enthalpy of activation ($\Delta H^‡$) would approach the M–CO bond energy for a primarily dissociative process and be rather independent of the nature of the incoming nucleophile, whilst for the associative process $\Delta H^‡$ is expected to be rather smaller than the M–CO bond energy and to vary with the nature of the nucleophile. A number of investigations have shown [23] that the reaction between the complex $M(CO)_6$ and a monodentate ligand involves a rate-determining dissociative step and the enthalpy of activation has been found to correlate with the mean M–CO bond energy.

In the present case, the observed first-order kinetics are inherent to the *intra*molecular process and do not help to elucidate the mechanism. More subtly, the variation in rate constant with incoming nucleophile does not usually establish an associative process, for the potential *cis*- or *trans*-effect of the already co-ordinated donor atom of L could effect the rates, whatever the mechanism. However, comparing the rates at 124 °C for the analogous systems $(ape)Cr(CO)_5$ and $(dpe)Cr(CO)_5$, we find that the change in incoming nucleophile (As or P respectively) causes little change in rate constant. Any potential *cis*- or *trans*-effect is presumably the same in each case, and the conclusion must be that most of the enthalpy of activation for the process [$(dpe)Cr(CO)_5$; $\Delta H^‡ = 135$ kJ mol^{-1}] arises from Cr–CO bond rupture [mean Cr–CO bond energy [25] in $Cr(CO)_6$; $\Delta H° = 107·4$ kJ mol^{-1}]. This result agrees with the finding that substitutions of the complex $Cr(CO)_6$ by Ph_3P and Ph_3As occur at similar rates.[23] Again, the effect of changing the metal from chromium to tungsten was to produce a marked decrease in the rate of chelation, by a factor of 85 in the case of the complexes $(dpe)M(CO)_5$ (M = Cr or W at 124 °C). This difference is due primarily to the greater enthalpy of activation in the case of the tungsten complex [$(dpe)W(CO)_5$; $\Delta H^‡ = 155$ kJ mol^{-1}], for which the mean W–CO bond energy is probably considerably greater [mean W–CO bond energy [26] in $W(CO)_6$; $\Delta H° = 176·2$ kJ mol^{-1}].

In comparing the chelation reactions of the other ligands, L, we noted considerable variation in rate constants (compared especially at 124 °C) and in activation parameters in some cases. [In Table 6(*b*), variations in $T\Delta S^‡$ at 124 °C are to be compared with $\Delta H^‡$ when considering the underlying reasons for the variation in k at this temperature.] In the series L =

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$Ph_2P(CH_2)_nPPh_2Cr(CO)_5$ (n = 1—3) the rate of chelation decreased as the chain length increased. This result implies that the formation of the four-membered chelate ring occurs more easily than that of five- or six-membered rings. Comparison of the enthalpies of activation for the reactions of the compounds where n = 1 and 2 (dpm and dpe respectively) shows a slight decrease in $\Delta H^‡$ with chain length (6 kJ mol^{-1}), perhaps reflecting less ' strain ' in forming the five-membered ring. However, the difference in entropies of activation gives rise to a much larger effect (17 kJ mol^{-1} at 124 °C) in the *opposite* sense. This perhaps reflects the higher ' effective concentration,' or statistical advantage,[24b] of the second ligand atom in the shorter chelate chain. [This result may also help to explain the formation of the *cis*-$Me_4P_2Cr(CO)_4$ complex from the reaction between $Cr(CO)_6$ and P_2Me_4.[27] The complex contains a three-membered chelate ring, the formation of which must be considered to be favoured by the entropy contribution to the free energy of activation.]

When the effect of the substituents at the phosphorus donor atom are considered, we observed that the chelation of the methyl-substituted ligand, dmpe, is slower than that of its phenyl-substituted analogue, dpe, by a factor of *ca.* 5 at 124 °C. The alkyl phosphine is a stronger σ-donor. However, the enthalpies of activation are rather similar (132 and 135 kJ mol^{-1} respectively). We deduce from this that an *enthalpy* contribution from partial bond formation between the incoming phosphorus and the chromium atoms is not required in the transition state. This agrees with our observations above (comparing ape and dpe). Nor is a potential *cis*- or *trans*-effect important, at least in this instance. The difference in *entropies* of activation, however, is more important and accounts for most of the difference in rate constant (difference in $T\Delta S^‡ = 8{\cdot}6$ kJ mol^{-1}). It is surprising that the presumably more sterically hindered dpe should have a more favourable entropy of activation. However it is again an *entropy* factor which is the more important.

When the bridged binuclear complex $(dpe)[Cr(CO)_5]_2$ is heated in n-octane solution it decomposes to give the complexes $(dpe)Cr(CO)_4$ [7] and $Cr(CO)_6$. The rate of this reaction is much slower than that of chelation of $(dpe)Cr(CO)_5$, showing that before ring closure can occur additional energy is required to break one of the Cr–P bonds in the bridged binuclear complex. These observations compare with the mass-spectral results, which show that the bridged complex is rather more stable than the monodentate phosphine complex, at least in the gas phase.

We have also compared the rate of chelation for the three complexes $(dmpe)M(CO)_5$ (M = Cr, Mo, or W) and find that the rate decreases in the order Mo > Cr > W in the approximate ratio 40 : 20 : 1. It has been observed [24c] that the rates of CO-exchange with the metal hexacarbonyl complexes follow this pattern, presumably with an M–CO dissociation as the rate-determining step. Again our result is in keeping with a dissociative-type mechanism.

In summary our view of the mechanism is as follows. The principal *enthalpy* requirement for activation is M–CO bond stretching, although ' strain ' in the ' bending ' of the chelate ring contributes, especially in the formation of small rings. Possible *cis*- or *trans*-activating effects, and the σ-donor capacity of the incoming ligand, do not appear to contribute. The principal *entropy* contribution to activation appears to be the statistical advantage enjoyed by the donor atom at the ' free ' end of a short chelate chain, although steric effects also contribute here. The mechanism is to be thought of as *concerted*, in that the stretching of a M–CO bond must be accompanied by the ' appearance ' of an incoming donor atom in the right orientation. Factors which increase the probability of this occurrence increase the rate of the chelation reaction.

EXPERIMENTAL

All preparations and reactions were carried out in an atmosphere of oxygen-free nitrogen. Solvents and liquid reagents were purified and dried in the usual manner and then carefully purged with nitrogen before use. Melting points were recorded on a Koffler heating block and are uncorrected.

I.r. spectra were obtained in hexane, octane, nonane, or methylene chloride solutions on a PE 257 grating spectrometer using 0·5-mm cells. Mass spectra were recorded on an AEI MS 12 instrument with a nominal beam energy of 70 eV. N.m.r. spectra were recorded on P.E R12 (60 MHz, protons only) and Varian HA 100 (100 MHz, protons; 40·5 MHz, phosphorus) instruments using a variety of solvents (Tables 5 and 6). Microanalyses were carried out by Mr. M. Hart and his staff, Manchester University.

The starting materials $Et_4N[(CO)_5MI]$ (M = Cr, Mo, or W),[28] R_3OBF_4 (R = Me [29] or Et [30]), and dmpe [31] were prepared by literature methods. The preparations of the complexes $LM(CO)_5$ [L = (dpm), (dpe), $(dpe)M(CO)_5$, (dmpe), (dpp), and (ape), M = Cr; L = (dmpe), M = Mo; L = (dmpe), (dpe), M = W] were carried out in a similar manner in each case; that of $(dpe)Cr(CO)_5$ may be taken as an example.

Pentacarbonyl[ethylenebis(diphenylphosphine)]chromium, $(dpe)Cr(CO)_5$.—The ligand dpe (0·93 g, 2·33 mmol) dissolved in CH_2Cl_2 (15 cm^3) was added to the salt $Et_4N[(CO)_5CrI]$ (1·05 g, 2·33 mmol) dissolved in CH_2Cl_2 (50 cm^3) at room temperature. A solution of Et_3OBF_4 (0·44 g, 2·33 mmol) in CH_2Cl_2 (10 cm^3) was added to the stirred mixture immediately, after which an orange colour appeared. The latter disappeared within a few seconds leaving a pale yellow solution. Volatile components (CH_2Cl_2, EtCl) were removed by distillation under reduced pressure and the residue was extracted with ether to give, eventually, a yellow powder which was recrystallised at −20 °C using ether–hexane (3 : 1 v/v) as solvent. The product was obtained as pale yellow *crystals* (Table 1).

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Methylation of the unco-ordinated donor atom in these complexes is illustrated in the case of (dpe)Cr(CO)$_5$, the same procedure being used in each instance.

Pentacarbonyl[(*2-diphenylphosphinoethyl*)*diphenylmethylphosphonium*]*chromium Tetrafluoroborate*, [(Medpe)Cr(CO)$_5$]-BF$_4$.—A slight excess of Me$_3$OBF$_4$ (0·025 g, 0·18 mmol) dissolved in acetonitrile (5 cm^3) was added to a stirred solution of the complex (dpe)Cr(CO)$_5$ (0·10 g, 0·17 mmol) in acetonitrile (5 cm^3). The mixture was stirred for 0·5 h, after which the solvent was removed by distillation under reduced pressure. The residue was extracted with CH$_2$Cl$_2$ (in which any excess of Me$_3$OBF$_4$ is insoluble) and crystallisation at -20 °C gave the complex salt as colourless *crystals* (Table 1).

Tetracarbonyl[*ethylenebis*(*dimethylphosphine*)]*chromium*, (dmpe)Cr(CO)$_4$.—*Method A*. Equimolar amounts of the complex Cr(CO)$_6$ and dmpe were placed in a thick-walled glass tube which was then evacuated and sealed. The mixture was then heated at 180 °C (oil bath) for 12 h. The yellow oil remaining when the tube had been opened was mixed with a small amount of absolute ethanol. On cooling this solution to *ca.* -45 °C the complex was obtained as pale yellow *crystals*.

Method B. Equimolar quantities of the complex Cr(CO)$_6$ and pure dmpe were mixed in absolute ethanol. A small amount of NaBH$_4$ (*ca.* 20 mg) was added[22] to the solution which was then heated at reflux for 18 h. Purification was accomplished as in Method A.

Ethylenebis(*trimethylphosphonium*) *Di*(*tetrafluoroborate*), [Me$_2$dmpe](BF$_4$)$_2$.—Pure dmpe (0·54 g, 3·6 mmol) was added to a solution containing Me$_3$OBF$_4$ (1·0 g, 7·25 mmol) in acetonitrile (25 cm^3). The volume of the solution was reduced to *ca.* 10 cm^3 and then cooled in ice, whereupon white crystals of the salt were slowly deposited. These were isolated by filtration and then dried under high vacuum.

Ethylenebis(*dimethylphosphine oxide*).—Hydrogen peroxide (1 cm^3, 30 vol. %) was added slowly to a stirred solution of dmpe (0·25 g, 1·7 mmol) in absolute ethanol (20 cm^3). After 1 h a large volume of diethyl ether was added to the mixture, causing a white solid to precipitate from the solution. This was isolated by filtration and then purified by sublimation under vacuum at 130—140 °C (oil bath).

Kinetic Measurements.—Reactions in which the LM(CO)$_5$ complexes are converted to LM(CO)$_4$ were monitored by observing the decrease in absorbance of the A_1'' and E carbonyl stretching modes of the former and the increase in absorbance of the A_1 and B_2 carbonyl stretching modes of the latter. Where the latter was rather insoluble, it was not possible to monitor its formation beyond the early stages of the reaction. The solvents used were n-octane [for LCr(CO)$_5$] and n-nonane [for LW(CO)$_5$] supplied by B.D.H. The purity of these materials was monitored by both g.l.c. and u.v. spectroscopy.

Rate constants were obtained from plots of $\log_{10} (D_t - D_\infty)$ against time t, where D_t is the i.r. absorbance at time t and D_∞ is the absorbance at infinite time. In each case the plot was reasonably linear for 75% completion of the reaction. Activation parameters were calculated, from standard equations,[32] by the method of least squares using our FORTRAN program ARRHENIUS-4 on the ICL 1906A computer at the University of Manchester Regional Computer Centre. The probable error in $\Delta H^\ddagger$ is *ca.* 2 kJ mol^{-1} and that in $\Delta S^\ddagger$ *ca.* 10 J K^{-1} mol^{-1}.

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