Ditertiary Alkylphosphine Derivatives of the Group VI Metal Carbonyls and their Oxidation with Iodine

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The preparation and characterisation of the complexes *fac,fac*-[$M_2(CO)_6$(dmpe)$_3$] (M = Cr, Mo, W; dmpe is $Me_2PCH_2CH_2PMe_2$) and *cis*-[$M(CO)_2$(dmpe)$_2$] is reported. The oxidation of *cis*-[$M(CO)_4$(dmpe)] with iodine gives [$M(CO)_4$(dmpe)I]I which can be converted into [$M(CO)_3$(dmpe)I_2] (M = Mo, W). Iodine oxidation of *fac,fac*-[$M_2(CO)_6$(dmpe)$_3$] gives [$M_2(CO)_4$(dmpe)$_3I_4$] (M = Mo, W), which are also obtained from the reaction of [$M(CO)_3$(dmpe)I_2] with dmpe. Oxidation of *cis*-[$M(CO)_2$(dmpe)$_2$] gives [$M(CO)_2$(dmpe)$_2$I]I (M = Mo, W) which are also obtained in the reaction of [$M_2(CO)_4$(dmpe)$_3I_4$] with dmpe. The products of these oxidation reactions have been characterised by i.r. and n.m.r. (^1H and ^{31}P) spectroscopy. The cations [$M(CO)_2$(dmpe)$_2$I]$^+$ are shown to be fluxional in the temperature range 220—320 K and a monocapped trigonal prismatic structure is indicated for the low-temperature form. Comparisons are made with analogous complexes containing $Ph_2PCH_2CH_2PPh_2$ (dpe) and differences in their behaviour on oxidation are explained in terms of the steric effect of the substituents (methyl, phenyl) at phosphorus.

MANY carbonyl complexes of molybdenum(II) and tungsten(II) containing the ditertiary arylphosphines $Ph_2PCH_2PPh_2$ (dpm) and dpe have been reported. These complexes belong to the general types described by the formulae [$M(CO)_3LX_2$], [$M_2(CO)_4L_3X_2$], [$M(CO)_2L_2X_2$], and [$M(CO)_2L_2X$]X (M = Mo, W; L = dpm, dpe; and X = Cl, Br, I). The metal(II) derivatives are usually prepared either by halogen oxidation of the appropriate substituted metal(0) complex or by direct reaction between the ligand L and the appropriate metal(II) carbonyl halide.[1] There are very few examples known where chelating ditertiary alkylphosphine ligands have been employed in the preparation of Group VI metal(II) carbonyl complexes, the only examples of which we are aware are *cis*-[Mo(η-C_5H_5)Cl(CO)(dmpe)] and [{Mo(η-C_5H_5)$(CO)_2$COR}$_2$(dmpe)] which were reported recently.[2]

We have prepared two new series of metal(0) complexes and studied their oxidation by iodine to give dmpe complexes of molybdenum(II) and tungsten(II). The results illustrate some new features in this type of chemistry which indicate that multidentate alkylphosphine ligands may be used to advantage in other systems.

RESULTS

Preparation of [$M_2(CO)_6$(dmpe)$_3$] *and* [$M(CO)_2$(dmpe)$_2$] *Complexes.*—Reaction between dmpe in ether and [Mo(η-cycloheptatriene)$(CO)_3$][3] in hexane at room temperature led to rapid precipitation of [$Mo_2(CO)_6$(dmpe)$_3$] as a pale yellow solid. A similar reaction with [Cr(η-cycloheptatriene)$(CO)_3$][3] produced yellow [$Cr_2(CO)_6$(dmpe)$_3$] but the substitution process was very much slower in this case. When applied to [W(η-cycloheptatriene)$(CO)_3$] the substitution by dmpe was too slow for practical purposes; instead [$W_2(CO)_6$(dmpe)$_3$] was prepared by heating [$W(CO)_3(NCMe)_3$][4] in an excess of pure dmpe at 410 K for 3 h.

The i.r. spectra of the [$M_2(CO)_6$(dmpe)$_3$] complexes in solution show two carbonyl bands [M = Cr, 1920s and 1820m,br; M = Mo, 1932s and 1830m,br; M = W, 1925s and 1820m,br cm^{-1} (CH_2Cl_2)]. The mass spectra show molecular ions accompanied by the expected fragmentation through loss of carbonyl ligands. The n.m.r. spectra of these compounds establish that they are properly represented as *fac,fac*-[$M_2(CO)_6$(dmpe)$_3$] (M = Cr, Mo, W). Thus, taking the molybdenum compound as an example, the ^{31}P spectrum contains two signals at +2·5 and −24·4 p.p.m. (w.r.t. H_3PO_4). These values are to be compared with those found for the co-ordinated phosphorus atoms in [$Mo(CO)_5$(dmpe)] (+2·2 p.p.m.)[5] and in *cis*-[$Mo(CO)_4$(dmpe)] (−26·7 p.p.m.)[5] and suggest, respectively, that the [$Mo_2(CO)_6$(dmpe)$_3$] molecule contains both a bridging dmpe ligand with phosphorus *trans*-to CO and a chelating dmpe ligand with both phosphorus atoms *cis* to CO. We were unable to resolve any P–P coupling between the chelate and the bridging phosphorus. The proton n.m.r. spectrum confirms that there is no unco-ordinated phosphorus in the complex. The two methylene proton resonances can be assigned to the bridging (δ 1·72, 4H) and chelating (δ 1·88, 8H) dmpe ligands respectively. The methyl proton resonances appear as three doublets (δ, p.p.m.; *N*, Hz) (1·50, 6·6; 1·36, 5·2; 1·31, 4·6) which cannot be assigned with certainty.

When *fac,fac*-[$Mo_2(CO)_6$(dmpe)$_3$] is heated with dmpe (1 : 1) in a sealed tube at *ca.* 470 K for 16 h the complex *cis*-[$Mo(CO)_2$(dmpe)$_2$] is formed in high yield. However, a more direct route to this compound is provided by heating $Mo(CO)_6$ with dmpe (1 : 2) in an evacuated sealed tube at 470—490 K for 18—24 h. The tungsten analogue is most readily obtained by treating the bis-diene complex *cis*-[W(η-cyclohexa-1,3-diene)$_2(CO)_2$][6] with dmpe (1 : 2) in boiling hexane. The reaction is complete in 30—50 h. The chromium complex, *cis*-[$Cr(CO)_2$(dmpe)$_2$], was obtained by irradiating a mixture of $Cr(CO)_6$ and dmpe (1 : 2) in acetonitrile solution (*ca.* 1%

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[1] R. Colton, *Co-ordination Chem. Rev.*, 1971, **6**, 269.

[2] R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, 1969, **8**, 1792, and references therein.

[3] E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 1958, 4559.

[4] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

[5] J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J.C.S. Dalton*, 1973, 347.

[6] R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

w/v) with radiation from a medium-pressure mercury lamp at ambient temperature for 18 h.

The racemic complexes *cis*-$[M(CO)_2(dmpe)_2]$ are all readily soluble in methylene chloride and more polar solvents. They are characterised by two intense carbonyl bands in the i.r. region [M = Cr, 1856 and 1798; M = Mo, 1873 and 1815; M = W, 1867 and 1810 cm^{-1} (hexane)]. Each compound gives a molecular ion of medium intensity which fragments in the usual manner by loss of carbonyl groups. The ^{31}P n.m.r. spectra confirm the *cis*-stereochemistry of the complexes thus, taking the molybdenum complex as an example, there are two resonances at −23·6 and −42·2 p.p.m. (w.r.t. H_3PO_4), of which the former is assigned to the two phosphorus atoms *trans* to CO and the latter is assigned to the two phosphorus atoms which are *trans* to each other. The proton n.m.r. spectra of the *cis*-$[M(CO)_2(dmpe)_2]$ complexes are very complicated. The spectrum of *cis*-$[Mo(CO)_2(dmpe)_2]$ in $[^2H_6]$benzene, for example, consists of four apparent triplets (δ p.p.m., N Hz) (1·67, 6·1; 1·33, 5·1; 1·24, 4·0; 0·86, 4·1). Double-irradiation experiments showed that each of these resonances is coupled to two others. No further interpretation is possible at this time.

Tetracarbonylmetal(II) *Complexes*.—The reaction between $[W(CO)_4I_2]_2$ and dmpe (1 : 1) in methylene chloride solution at 273 K gives $[W(CO)_3(dmpe)I_2]$ in only moderate yield together with *cis*-$[W(CO)_4(dmpe)]$, indicating that dmpe functions both as a nucleophile and as a reducing agent in this reaction. The reaction products also suggest that nucleophilic attack by the unco-ordinated phosphine in the seven-co-ordinate intermediate complex $[W(CO)_4(dmpe)I_2]$ displaces CO rather than iodide ion. The aryl phosphines dpm and dpe react with $[W(CO)_4I_2]_2$ to give only the substitution product $[W(CO)_3LI_2]$; reduction was not observed.[1]

Iodine reacts with *cis*-$[M(CO)_4(dmpe)]$ (M = Mo, W) in methylene chloride solution at 260 K to give $[M(CO)_4(dmpe)I]I$ in high yield. The solid complex $[W(CO)_4(dmpe)I]I$ exists in two modifications, A and B, which differ in their solubility properties and in their solid-state i.r. spectra. One form, A, dissolved easily in CH_2Cl_2 and in acetone and has carbonyl stretching vibrations (Nujol and KBr) at 2100w, 2095w, 2020s,br, 1980m, and 1965s cm^{-1}. The other form, B, is only slightly soluble in the same solvents and has carbonyl stretching vibrations (Nujol and KBr) at 2092s, 2033s, 2002s, and 1972s cm^{-1}. The i.r. spectra of both A and B in chloroform solution are identical (2094w, 2036s, 2009s, 1981s, 1902m,sh, 1885m,br, and 1868m,sh cm^{-1}). Form B cannot be recovered from solution, being converted into form A. The molybdenum analogue, $[Mo(CO)_4(dmpe)I]$ does not exhibit this behaviour and exists only in the A form, both in the solid state and in solution.

The i.r. spectra of $[M(CO)_4(dmpe)I]I$ (M = Mo, W) in solution are readily explained as a composite of both *cis*-$[M(CO)_4(dmpe)]$ [M = W, 2011m, 1906m,sh, 1887, and 1869m,sh cm^{-1} (CH_2Cl_2)] and $[M(CO)_4(dmpe)I]^+$ which are related by the equilibrium:

$$[M(CO)_4(dmpe)I]I \rightleftharpoons cis\text{-}[M(CO)_4(dmpe)] + I_2 \quad (1)$$

The spectrum of $[M(CO)_4(dmpe)I]I$ is further complicated by the fairly rapid loss of CO from the cation in solution to give $[Mo(CO)_3(dmpe)I_2]$, the final product of the reaction. This is consistent with the decrease in the M–CO bond strength from M = W to M = Mo.[7]

Spectrophotometric examination of the equilibrium [equation (1)] (M = W) in CH_2Cl_2 and in acetone solution failed to detect the presence of free iodine (λ 505 nm, log ε 2·94), so that a further equilibrium must be taken into account which involves the tri-iodide ion:

$$I^- + I_2 \rightleftharpoons I_3^- \quad (2)$$

Independent measurements showed $K_2 > 10^5$ (*cf.* $K_2 \sim 10^7$ l mol^{-1} in MeCN [8]). Combining the equilibria shown in equations (1) and (2) with the assumption that the concentrations of $[W(CO)_4(dmpe)]$ and I_3^- are approximately equal enables the equilibrium constant K_3 ($= K_1K_2$) for the oxidation reaction equilibrium to be

$$[W(CO)_4(dmpe)I]^+ + 2I^- \rightleftharpoons [W(CO)_4(dmpe)] + I_3^- \quad (3)$$

measured. The values of K_3 obtained in this way are 15 ± 2 in CH_3Cl_2 and 1500 ± 200 l mol^{-1} in acetone solution. These values suggested that the pure metal(II) cation might be isolated as the tri-iodide salt.

Addition of iodine to a solution of $[M(CO)_4(dmpe)I]I$ (M = Mo, W) (1 : 1) in CH_2Cl_2 cooled in ice gave the corresponding $[M(CO)_4(dmpe)I]I_3$ in each case. The i.r. spectra in solution of the rust brown crystalline solids isolated from the reaction show only four carbonyl bands [M = Mo, 2098m, 2045m, 2020s, and 1991s; M = W, 2096m, 2037m, 2008s, and 1983s cm^{-1} (CH_2Cl_2)], indicating that the equilibrium represented by equation (1) is completely suppressed. Identical solution spectra were observed for $[M(CO)_4(dmpe)I]BPh_4$ (M = Mo, W), prepared as pale yellow solids by metathesis of the iodide with $NaBPh_4$ in ice cold methylene chloride. The addition of Et_4NI to a solution containing $[M(CO)_4(dmpe)I]BPh_4$ (M = Mo, W) causes reduction to give the metal(0) complex $[M(CO)_4(dmpe)]$ [*cf.* equation (3)], which is also formed quantitatively when $[W(CO)_4(dmpe)I]I$ in methylene chloride is shaken with an excess of aqueous thiosulphate solution.

The solid complexes $[M(CO)_4(dmpe)I]I$ (M = Mo, W) can be stored without deterioration over long periods in the dark at 240 K. At room temperature in daylight the solid salts decompose to give $[M(CO)_3(dmpe)I_2]$, the process being more rapid when M is molybdenum (days) than when M is tungsten (weeks). The spontaneous decomposition is accelerated in solution at ambient temperature (M = Mo, minutes; M = W, hours). The decarbonylation is irreversible, thus $[M(CO)_3(dmpe)I_2]$

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[7] A. Cartner, B. Robinson, and P. J. Gardner, *J.C.S. Chem. Comm.*, 1973, 317.

[8] *Chem. Soc. Special Publ.* No. 17, 1964, p. 343.

(M = Mo, W) treated with CO (200 atm, 300 K, 100 h, CH_2Cl_2) did not give any trace of $[M(CO)_4(dmpe)I]I$.

The oxidation of $[M(CO)_4(dmpe)]$ (M = Mo, W) with iodine shows certain features which have not previously been observed for ditertiary phosphine complexes of this type and which may indicate some similarity between dmpe and the bidentate ditertiary arsine ligand, diars. Oxidation of $[W(CO)_4(diars)]$ with iodine produces $[W(CO)_4(diars)I]I$ which does not suffer decarbonylation in boiling chloroform whereas $[W(CO)_3(triars)I]I$ is readily converted into $[W(CO)_2(triars)I_2]$ under the same conditions.[9] By analogy with these findings the iodine oxidation of $[W(CO)_4(dpe)]$ to give $[W(CO)_3(dpe)I_2]$ was presumed to involve $[W(CO)_4(dpe)I]I$ as an intermediate which could not be isolated.[10]

Tricarbonylmetal(II) *Complexes*.—The yellow molybdenum(II) complex $[Mo(CO)_3(dmpe)I_2]$ is sensitive to aerial oxidation even in the solid state, giving a maroon solid which may be the molybdenum(V) complex $[MoOI_3(dmpe)]$. The bright yellow tungsten(II) analogue $[W(CO)_3(dmpe)I_2]$ is much more resistant to oxidation by air both in the solid state and in solution. As with other ditertiary phosphine complexes, $[M(CO)_3LI_2]$ (M = Mo, W; L = dpm, dpe),[11] the dmpe complexes do not undergo decarbonylation when heated in solution; this is in contrast to bis(tertiaryphosphine) complexes $[M(CO)_3L_2I_2]$ (M = Mo, W; L = PPh_3,[12] PEt_3 [13]) which give $[M(CO)_2L_2I_2]$ under such conditions.

The i.r. spectra of the $[M(CO)_3(dmpe)I_2]$ (M = Mo, W) complexes in solution show three carbonyl bands as expected [M = Mo, 2043m, 1969s, and 1910m; M = W, 2037m, 1962s, and 1906m cm^{-1} (CH_2Cl_2)]. In the solid state, the two higher frequency bands in each case appear as well resolved doublets [M = Mo, 2044s, 2032s, 1967s, 1953s, and 1910s; M = W, 2033s, 2020s, 1952s, 1941s, and 1900s cm^{-1} (Nujol)].

Proton N.m.r. Spectra of Tetracarbonyl and Tricarbonylmetal(II) *Compounds*.—The increase in acidity of the metal when it is oxidised is reflected in the value of the coupling constant, $^2J_{PH}$, which increases from *ca.* 7 Hz in $[M(CO)_4(dmpe)]$ [5] to *ca.* 10·5 Hz in $[M(CO)_3(dmpe)I_2]$ and *ca.* 12 Hz in $[M(CO)_4(dmpe)I]I$. This change is similar in direction but smaller in magnitude to that which occurs when dmpe ($^2J_{PH}$ 2·5 Hz) is quaternised giving $[Me_2dmpe](BF_4)_2$ ($^2J_{PH}$ 14·4 Hz). Oxidation also causes a general shift to low field which is greater for methylene protons than for methyl protons. None of the n.m.r. spectra of the metal(II) complexes show any evidence for dmpe functioning as a unidentate ligand. Lack of solubility precludes the measurement of n.m.r. spectra of analogous compounds containing dpm, dpe, and diars as ligands so that comparison is not possible.

Neutral Dicarbonylmetal(II) *Complexes*.—The tricarbonyl complexes $[M(CO)_3(dmpe)I_2]$ (M = Mo, W) react with dmpe (2 : 1) in acetone solution at room temperature to form the dimeric dicarbonyl complexes which are formulated as $[M_2(CO)_4(dmpe)_3I_4]$ on the basis of satisfactory microanalysis. These latter compounds are slowly deposited from the reaction as canary yellow powders which are only sparingly soluble in chloroform, benzene, and acetone. The i.r. spectra of the complexes in solution show only two carbonyl bands [M = Mo, 1935s and 1850m; M = W, 1930s and 1839m cm^{-1} (CH_2Cl_2)]. The same complexes are also prepared by iodine oxidation of the corresponding *fac,fac*-$[M_2(CO)_6(dmpe)_3]$ compound.

Carbon monoxide does not react with $[M_2(CO)_4(dmpe)_3I_4]$ (M = Mo, W) (200 atm, 100 h, 300 and 370 K, CH_2Cl_2 solution), in contrast to the analogous dpe complexes which give both $[M(CO)_3(dpe)I_2]$ and $[M(CO)_2(dpe)_2I]I$ (M = Mo, W) with carbon monoxide under ambient conditions.[11] We suggest that the greater steric demands of the diphenylphosphino-group compared to the dimethylphosphino-group are at least partially responsible for this difference.

Ionic Dicarbonylmetal(II) *Complexes*.—Reaction of the dimeric complexes $[M_2(CO)_4(dmpe)_3I_4]$ (M = Mo, W) with dmpe (2 : 1·2) in boiling acetone leads to the isolation of slightly air-sensitive compounds having the molecular formula corresponding to $[M(CO)_2(dmpe)_2I_2]$. Measurements of the conductivity of these compounds show they are 1 : 1 electrolytes in solution (CH_2Cl_2–acetone, 2 : 3 v/v), and this, together with their i.r. spectra in solution which exhibit two carbonyl bands (M = Mo, 1952s and 1886m; M = W, 1948s and 1881m cm^{-1} (CH_2Cl_2)], indicates that the compounds should be reformulated as *cis*-$[M(CO)_2(dmpe)_2I]I$, where *cis* refers to the relative orientation of the carbonyl ligands in the cation. The same ionic complexes are obtained when the metal(0) complexes *cis*-$[M(CO)_2(dmpe)_2]$ are oxidised with iodine (1 : 1) in methylene chloride solution.

The i.r. spectra of *cis*-$[M(CO)_2(dmpe)_2I]I$ (M = Mo, W) in the solid state show the same doubling of the two bands as was noticed in the tricarbonyl complexes, $[M(CO)_3(dmpe)I_2]$. The crystal structure of $[W(CO)_2(dmpe)_2I]I$ shows two distinct species in the unit cell [14] so that it is reasonable to suggest that the doubling arises from differences in the site symmetry in the solid state [M = Mo, 1956s, 1948s, 1878m, and 1856s; M = W, 1951s, 1943s, 1870m, and 1851m cm^{-1} (Nujol)].

The ^1H n.m.r. spectra of both $[M(CO)_2(dmpe)_2I]^+$ cations show that they are fluxional in the temperature range 220—320 K. At room temperature the spectrum consists of an apparent quintet (δ p.p.m., *N* Hz) (M = Mo, 1·88, 2; M = W, 1·95, 2) due to the methyl protons and a broad signal (M = Mo, 2·37; M = W, 2·28) produced by the methylene protons. When ^{31}P is decoupled the methyl proton absorbance appears as a

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[9] R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 6570; J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *ibid.*, 1964, 3009; J. Lewis, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *ibid.*, 1963, 3600; H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *ibid.*, 1960, 1803, 1806.

[10] J. Lewis and R. Whyman, *J. Chem. Soc.*, 1965, 5486.

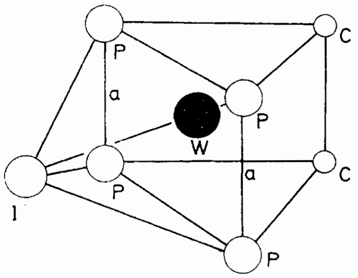
[11] M. W. Anker, R. Colton, C. J. Rix, and I. B. Tomkins, *Austral. J. Chem.*, 1969, **22**, 1341.

[12] R. Colton and C. J. Rix, *Austral. J. Chem.*, 1969, **22**, 305.

[13] J. R. Moss and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 595.

[14] M. G. B. Drew, unpublished work.

single sharp signal and the methylene signal sharpens substantially. This indicates that all eight methyl groups in the cation are equivalent on the n.m.r. time-scale at room temperature and also equally coupled to each of the four phosphorus atoms. At temperatures below 240 K, the p.m.r. spectrum consists of a doublet of triplets (Δ 21 Hz) for the methyl protons, the doublet being symmetrical about the centre of the high-temperature quintet. The doublet splitting is a chemical-shift effect (60 and 100 MHz spectra) with the triplets (*N* 3·5 Hz) arising from P–H coupling as shown by ^{31}P decoupling which gave two sharp signals in the methyl proton region. Thus, at low temperatures the cations *cis*-$[M(CO)_2(dmpe)_2I]^+$ (M = Mo, W) may contain two different types of methyl group each of which is equally coupled to two phosphorus nuclei. It is also possible that the triplets arise by virtual coupling; this would not imply equal coupling to two phosphorus nuclei. The methylene protons give two signals (Δ 48 Hz) at low temperature which are centred about the high-temperature mean. Poor resolution and lack of definition prevented any further clarification except to demonstrate that these methylene protons are also coupled to phosphorus.



The co-ordination sphere of $[W(CO)_2(dmpe)_2I]^+$ with metal–ligand bonds omitted. The dmpe ligand occupies bites *a*

These spectra can be interpreted in terms of a seven-co-ordinate capped trigonal prismatic (C_{2v}) structure with iodine in the capping position above the $[P_4]$ face (see Figure). This conclusion is supported by an *X*-ray molecular structure determination of $[W(CO)_2(dmpe)_2I]I$, with which the molybdenum(II) analogue is isomorphous.[14] The same type of geometry has recently been found in $[Mo(CNBu^t)_6I]I$ [15] and in $[Mo(CO)_2(diars)_2Cl]I_3$.[16] At low temperatures there will be a different magnetic environment on each side of the $[P_4]$ plane face, so that the methyl groups on one side of the plane have a different chemical shift to those on the other side. The same argument may apply to the methylene protons and to this must be added the effects of conformations of the chelate ring. The high-temperature spectrum can be explained by a polytopal rearrangement which leads to an averaging of the two types of magnetic environment experienced by the methyl groups, possibly by rapid migration of the iodine over all five faces of the $[P_4C_2]$ trigonal prism.

The n.m.r. spectrum of *cis*-$[W(CO)_2(dpm)_2I]I$ in $[^2H_6]$dimethyl sulphoxide solution showed that the cation contained six-co-ordinate tungsten(II); one dpm is bidentate and the other is unidentate.[17] The n.m.r. spectra of the seven-co-ordinate ditertiary arsine complexes $[M(CO)_2(dam)_2X_2]$ (M = Mo, W; X = Cl, Br, I) show that they too exhibit mixed co-ordination but, in addition, there is rapid intramolecular ligand exchange at room temperature whereby the uni- and bi-dentate dam ligands are rapidly exchanging their modes of co-ordination.[18] The former possibility is excluded in the present instance by the observation that the methyl resonances are in the ratio 1 : 1 rather than 3 : 1. The latter type of behaviour cannot be rigorously excluded in the present instance although, on the evidence available, we regard it as most implausible. The ^{31}P n.m.r. spectrum of $[Mo(CO)_2(dmpe)_2I]I$ showed that all the phosphorus atoms are equivalent (δ ^{31}P −28 p.p.m. w.r.t. H_3PO_4) at room temperature and attempts to measure the ^{13}C n.m.r. spectra (which might have provided an unambiguous answer) were frustrated by lack of solubility of the compounds ($\ngtr 0·2$ g cm^{-3} MeCN).

The dicarbonyl salts, $[M(CO)_2(dmpe)_2I]I$ (M = Mo, W), do not undergo decarbonylation even in refluxing xylene (10 h) to give $[M(CO)(dmpe)_2I_2]$ in contrast to the behaviour of $[M(CO)_4(dmpe)I]I$ which was mentioned earlier.

Whereas $[M(CO)_2(dpe)_2]$ (M = Mo, W) reacts with iodine to give the metal(I) cation $[M(CO)_2(dpe)_2]I_3$,[10] the metal(II) cation $[M(CO)_2(dpe)_2I]^+$, which may be six-co-ordinate, is unstable with respect to $[M_2(CO)_4(dpe)_3I_4]$,[18] and cannot be isolated from the oxidation reaction. The metal(I) complexes containing dmpe, $[M(CO)_2(dmpe)_2]^+$, can be obtained from $[M(CO)_2(dmpe)_2]$ by oxidation with a stoicheiometric amount of a silver salt.[19]

CONCLUSIONS

The reactions described in this paper are represented diagrammatically in the Scheme. These indicate a reasonable mechanism for the synthesis of *cis*-$[M(CO)_2(dmpe)_2]$ from $M(CO)_6$. It has been shown that $[M(CO)_4(dmpe)]$ is formed by chelation of $[M(CO)_5(dmpe)]$.[5] Subsequent reaction of the mono-chelate complex with dmpe proceeds by way of *fac,fac*-$[M_2(CO)_6(dmpe)_3]$ to give the bis-chelate complex. Our attempts to prepare $[M(CO)(dmpe)_3]$ or, more likely, $[M_2(CO)_2(dmpe)_5]$, the missing member in the series of complexes leading to $[M(dmpe)_3]$,[20] have been unsuccessful so far.

The consequences of using dmpe in place of dpe upon

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[15] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.

[16] M. G. B. Drew and J. C. Wilkins, *J.C.S. Dalton*, 1973, 2664.

[17] C. J. Rix, Ph.D. Thesis, Melbourne University, 1971.

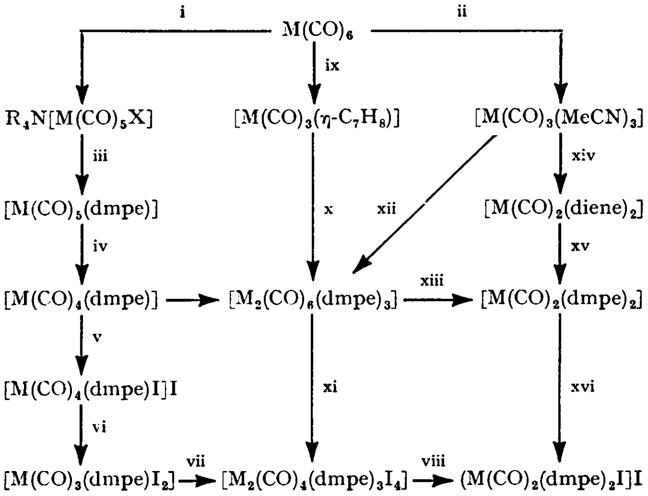
[18] M. W. Anker, R. Colton, and C. J. Rix, *Austral. J. Chem.*, 1971, **24**, 1157.

[19] J. A. Connor, G. K. McEwen, and C. J. Rix, in Proceedings of the International Conference on the Chemistry and Uses of Molybdenum, Reading, 1973, to be published.

[20] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1962, 4982.

the oxidation of the complexes which they form have already been referred to. There are many differences both in the stability and in the reactivity of comparable compounds. In particular, it would appear that the presence of dmpe causes a stabilisation of cationic metal(II) derivatives relative to the dpe analogues. This is further reflected in the fact that the ability of dpe complexes to act as carbon monoxide carriers [1] is suppressed in the dmpe system.

Comparison of the electronic effects of phosphorus substituent groups show that, regardless both of the oxidation state and of the substituents at the phosphorus atom, these groups are π-electron acceptors which enter into direct polar conjugation with an electron-donor centre. In particular, there is no significant difference in the electronic effects of the diphenylphosphino- and dimethylphosphino-groups.[21] Measurements of the oxidative one-electron transfer reactions of the complexes described here and many closely related metal(0) compounds have shown that the value of the potential, $E_{\frac{1}{2}}$, is influenced by steric effects, especially where bidentate ligands are present.[22] There is no compelling evidence to suggest that in strictly comparable systems the M–P bond length to trialkylphosphines is shorter than that to triarylphosphines. We suggest that the dmpe complexes are more easily oxidised than their dpe counterparts because the methyl groups in the former are less able to protect the metal from attack by the oxidising agent than the larger phenyl groups in the latter, which because of their size are better able to afford some hindrance to the electron transfer process.



SCHEME Reagents and conditions: i, R_4NX, diglyme, reflux; ii, MeCN, reflux; iii, dmpe, $AgBF_4$,CH_2Cl_2; iv, heat; v, I_2, CH_2Cl_2, 260 K; vi, reflux, CH_2Cl_2; vii, dmpe, acetone, RT, 4 h; viii, dmpe, acetone, reflux, 25 h; ix, C_7H_8, reflux; x, dmpe, RT, hexane (M = Mo); xi, I_2, acetone, RT; xii, dmpe, 410 K, 3 h (M = W); xiii, dmpe, 470 K, 16 h; xiv, cyclohexa-1,3-diene, reflux (M = W); xv, dmpe, hexane, reflux; xvi, I_2, CH_2Cl_2, RT

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 thoroughly purged with nitrogen before use. I.r. spectra were obtained in hexane or methylene chloride solutions or Nujol mulls or KBr discs as appropriate and measured with a P.E.257 grating spectrometer, calibrating with polystyrene. Mass spectra were recorded on an A.E.I. 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 in a variety of solvents. Conductance measurements were made on a Phillips PR 9500/01 bridge in acetone or in acetone–CH_2Cl (3 : 2 v/v) solutions. Microanalyses were carried out by Mr. M. Hart and his staff, Manchester University. The following starting materials were purchased as reagent grade materials, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (all from Strem Chemicals, Danvers, Mass. U.S.A.), and the following were prepared by literature methods: $[M(CO)_4(dmpe)]$ (M = Mo, W),[5] $[M(CO)_3(\eta\text{-}C_7H_8)]$ (M = Cr, Mo),[3] $[W(CO)_3(MeCN)_3]$,[4] $[W(\eta\text{-}C_6H_8)_2(CO)_2]$,[6] and dmpe.[23]

Preparation of Metal(0) *Compounds*.—*Hexacarbonyl*[*tris*(*ethylenebis*{*dimethylphosphine*})]*dimolybdenum*. The ligand dmpe (1·42 cm³, 1·1 g, 7·4 mmol) dissolved in ether (20 cm³) was added slowly to a stirred solution of $[Mo(\eta\text{-}C_7H_8)(CO)_3]$ (1·0 g, 3·7 mmol) in hexane (50 cm³) at room temperature. The bright orange-red hexane solution immediately became cloudy as a pale yellow precipitate of the complex formed. When addition of the ligand was complete the precipitated solid was filtered off, washed with hexane, and reprecipitated from CH_2Cl_2 by ether. Finally the complex was isolated, washed with ether, and dried *in vacuo* to give a dull fawn-yellow solid (1·1 g, 1·4 mmol; 76% based on Mo), m.p. 165° (dec) (Found: C, 35·6; H, 6·4; P, 22·7. $C_{24}H_{48}Mo_2O_6P_6$ requires C, 35·6; H, 5·9; P, 22·3%).

Hexacarbonyl[*tris*(*ethylenebis*{*dimethylphosphine*})]*dichromium*. This compound was prepared in an analogous manner and isolated as a yellow powder (65%) (Found: C, 39·2; H, 6·7; Cr, 14·7. $C_{24}H_{48}Cr_2O_6P_6$ requires C, 39·8; H, 6·6; Cr, 14·4%); δ(^{1}H) 1·88 (8H), 1·72 (4H), 1·26—1·55 (36H) p.p.m.; δ(^{31}P) −13·4 and −48·8 p.p.m,; *m*/*e* (*I*, %) 722 (22, M^+), 707 (1) ,694 (1), 638 (4), 623 (2), 610 (56), 595 (6), 582 (4), 554 (1), 488 (16), 436 (14), 404 (41), and 352 (100).

Hexacarbonyl[*tris*(*ethylenebis*{*dimethylphosphine*})]*ditungsten*. This compound was obtained when $[W(CO)_3(MeCN)_3]$ (1·2 g, 3·2 mmol) was heated with dmpe (1·2 cm³, 6·2 mmol) at 410 K for 3 h. The resulting yellow oil was mixed with CH_2Cl_2 (10 cm³) and precipitated by addition of ether. The complex was obtained as a yellow powder (0·30 g, 20%) (Found: C, 29·0; H, 5·3; P, 19·4. $C_{24}H_{48}O_6P_6W_2$ requires C, 29·2; H, 4·9; P, 18·9%); δ(^{1}H) 1·97 (8H), 1·82 (4H), 1·62 (d, *N* 7·4), 1·52 (d, *N* 4·0), and 1·44 (d, *N* 6·0) (36H) p.p.m.; *m*/*e* 986 (100%, M^+). The *molybdenum* complex was also prepared in the following way. Hexacarbonylmolybdenum (1·0 g, 3·8 mmol) in hexane solution (120 cm³) containing a slight stoicheiometric excess of dmpe (1·15 g, 7·5 mmol) was irradiated with a medium-pressure u.v. lamp

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[21] E. N. Tsvestkov, M. M. Makhamatkhanov, D. L. Lobanov, and M. I. Kabachnik, *Zhur. obshchei. Khim.*, 1972, **42**, 769.

[22] M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwen, *J.C.S. Dalton*, 1973, 1743.

[23] G. W. Parshall, *J. Inorg. Nuclear Chem.*, 1960, **14**, 291.

(100 W Hanovia) for 6 h during which time the complex was formed as a buff coloured precipitate. The complex was purified in the usual manner (0·21 g, 15%).

Dicarbonyl[bis(ethylenebis{dimethylphosphine})]molybdenum. Hexacarbonylmolybdenum (2·6 g, 10 mmol) and dmpe (3·8 cm^3, 20 mmol) were sealed in an evacuated Carius tube (volume *ca.* 50 cm^3). The tube was heated at 470—490 K for *ca.* 18 h, and then allowed to cool to room temperature overnight. The tube was opened and the volatile contents removed. The canary yellow residue was dissolved in CH_2Cl_2. This solution was diluted with ether (1 : 1 v/v) and cooled to 195 K whereupon yellow crystals were deposited. Recrystallisation gave pale yellow crystals of the complex (3 g, 6·6 mmol). The yield was not optimised (Found: C, 37·1; H, 7·3; P, 26·1. $C_{14}H_{32}MoO_2P_4$ requires C, 37·2; H, 7·1; P, 27·4%); ν(CO) 1858s, 1794s (CS_2), 1838s, 1766s (CH_2Cl_2) cm^{-1}; *m/e* (*I*, %) 454 (53, M^+), 439 (2), 426 (100), and 396 (32); *M* (cryoscopic in benzene) 438.

Dicarbonyl[bis(ethylenebis{dimethylphosphine})]tungsten. [$W(\eta$-$C_6H_8)_2(CO)_2$] (4·0 g, 10 mmol) and dmpe (3·8 cm^3, 20 mmol) were heated in hexane (50 cm^3) for 42 h. The hot solution was filtered and evaporated to dryness giving a pale yellow powder which was washed with cold pentane and reprecipitated from CH_2Cl_2–hexane (4·5 g, 8·3 mmol) (Found: C, 30·7; H, 5·9; P, 23·6. $C_{14}H_{32}O_2P_4W$ requires C, 31·1; H, 5·9; P, 23·0%); *m/e* (*I*, %) 540 (100, M^+), 525 (9), 512 (80), and 484 (65).

Dicarbonyl[bis(ethylenebis{dimethylphosphine})]chromium. Hexacarbonyl chromium (1 g, 4·5 mmol) and dmpe (1·7 cm^3, 9 mmol) in acetonitrile solution (120 cm^3) were irradiated for 18 h in an inert atmosphere. The green solution was evaporated to dryness and the residue extracted with CH_2Cl_2. Pentane was added to the extract and the complex was isolated as pale yellow crystals at 240 K (Found: C, 40·4; H, 7·9; Cr, 12·1; P, 30·8. $C_{14}H_{32}CrO_2P_4$ requires C, 41·2; H, 7·8; Cr, 12·8; P, 30·4%); *m/e* (*I*, %) 408 (30, M^+), 393 (2), 380 (3), 352 (100), 337 (12), 263 (10), and 202 (84); *M* (cryoscopic in benzene) 414.

Preparation of Metal(II) *Complexes.*—The preparations of analogous molybdenum(II) and tungsten(II) complexes were similar and so only those for molybdenum will be described. Analytical and spectroscopic data for the tungsten compounds are included as appropriate.

Tetracarbonyliodo(ethylenebis{dimethylphosphine})molybdenum(II) *iodide.* Iodine (0·64 g, 2·5 mmol) in CH_2Cl_2 (40 cm^3) was added slowly to a solution of [$Mo(CO)_4$(dmpe)] (0·91 g, 2·5 mmol) in CH_2Cl_2 (35 cm^3) in the dark at ice-salt temperature. An orange solid was deposited from the mixture. When the addition of iodine was complete the solvent was removed by distillation under reduced pressure from the reaction held at ice–salt temperature (*ca.* 260 K), leaving the complex as an orange powder (1·38 g, 2·25 mmol) (Found: C, 19·4; H, 2·8; I, 41·9; P, 10·0. $C_{10}H_{16}I_2MoO_4P_2$ requires C, 19·6; H, 2·5; I, 41·4; P, 10·1%). Conductance (10^{-3}M-acetone solution 295 K) 59 A cm^2 V^{-1} mol^{-1}.

The two forms of the *tungsten* analogue were separated by extraction of the mixture with a small quantity of *cold* CH_2Cl_2. The insoluble material (form B) contained C, 17·6; H, 2·4; I, 36·0; P, 8·7; while the soluble material (form A) contained C, 17·2; H, 2·3; I, 35·9; P, 8·9. $C_{10}H_{16}I_2O_4P_2W$ requires C, 17·2; H, 2·3; I, 36·3; P, 8·9%. Conductance (10^{-3}M-acetone solution 295 K) 88·3 (form A), 87·8 (form B) A cm^2 V^{-1} mol^{-1}.

Tetracarbonyliodo(ethylenebis{dimethylphosphine})molybdenum(II) *tri-iodide.* Iodine (0·054 g, 0·21 mmol) in CH_2Cl_2 (5 cm^3) was added to an ice-cold solution of [$Mo(CO)_4$(dmpe)I]I (0·13 g, 0·21 mmol) in CH_2Cl_2 (40 cm^3). The mixture was then diluted with heptane (15 cm^3) and evaporated to dryness by distillation under reduced pressure at ice temperature leaving the complex salt as a rust brown solid. The solid was washed twice with cold pentane and dried *in vacuo* (0·16 g, 0·19 mmol) (Found: C, 13·9; H, 2·0; I, 58·6; P, 7·4. $C_{10}H_{16}I_4MoO_4P_2$ requires C, 13·9; H, 1·9; I, 58·7; P, 7·2%). Conductance (10^{-3}M-acetone solution 298 K) 134 A cm^2 V^{-1} mol^{-1}; δ (CD_3OD) 2·12 (3H, *J* 12 Hz) and 2·60 (1H, *J* 21 Hz) p.p.m. For the *tungsten* analogue (Found: C, 12·5; H, 2·1; I, 53·3. $C_{10}H_{16}I_4O_4P_2W$ requires C, 12·5; H, 1·7; I, 53·2%). Conductance 142 A cm^2 V^{-1} mol^{-1}; δ (CD_3OD) 1·60 (3H, *J* 12 Hz), 2·12 (1H, *J* 20 Hz) p.p.m.

Tricarbonyldi-iodo(ethylenebis{dimethylphosphine})molybdenum(II). The complex [$Mo(CO)_4$(dmpe)I]I (0·10 g, 0·16 mmol) was dissolved in CH_2Cl_2 (60 cm^3) and the solution refluxed for *ca.* 1 h, to give a yellow-brown solution. Addition of heptane to the cooled solution and slow evaporation of the solvent under reduced pressure resulted in the deposition of yellow crystals which were washed with pentane and dried *in vacuo* (0·07 g, 0·12 mmol) (Found: C, 18·4; H, 2·9; I, 44·3; P, 11·2. $C_9H_{16}I_2MoO_3P_2$ requires C, 18·6; H, 2·7; I, 43·6; P, 10·6%). δ ($CDCl_3$) 1·94 (3H, *J* 10·6 Hz) and 2·32 (1H, *J* 15 Hz) p.p.m. The *tungsten* analogue (reflux for 3 h) (Found: C, 16·2; H, 2·4; I, 37·5; P, 9·2. $C_9H_{16}I_2O_3P_2W$ requires C, 16·1; H, 2·4; I, 37·7; P, 9·2%); δ ($CDCl_3$) 2·01 (3H, *J* 10·6 Hz) and 2·28 (1H, *J* 14 Hz) p.p.m.

Tetracarbonyltetraiodotris(ethylenebis{dimethylphosphine})-dimolybdenum(II). A solution of dmpe (0·03 g, 0·2 mmol) in acetone (30 cm^3) was added slowly to [$Mo(CO)_3$(dmpe)I_2] (0·235 g, 0·4 mmol) in acetone (35 cm^3). The mixture was stirred at room temperature for 4 h during which time a solid was slowly deposited. The solid was isolated by decantation, washed with acetone–hexane (1 : 1 v/v) and dried *in vacuo* (0·20 g, 0·16 mmol). Alternatively, iodine (0·043 g, 0·17 mmol) in acetone (30 cm^3) was added slowly to [$Mo_2(CO)_6$(dmpe)$_3$] (0·068 g, 0·17 mmol) in acetone (30 cm^3). Addition of heptane (30 cm^3) and concentration gave the complex as a yellow precipitate (0·13 g, 0·11 mmol) (Found: C, 21·2; H, 3·8; I, 40·4; P, 14·6. $C_{22}H_{48}I_4Mo_2O_4P_6$ requires C, 20·9; H, 3·9; I, 40·3; P, 14·8%). The *tungsten* analogue was isolated from CH_2Cl_2 solution as a solvate adduct (Found: C, 18·3; H, 3·3; Cl, 5·9; I, 32·4; P, 12·0. $C_{22}H_{48}I_4O_4P_6W_2$,4/3CH_2Cl_2 requires C, 18·1; H, 3·3; Cl, 6·0; I, 32·9; P, 12·0%).

Dicarbonyliodobis(ethylenebis{dimethylphosphine})molybdenum(II) *iodide. Method* (*A*). A mixture of dmpe (0·08 g, 0·53 mmol) and [$Mo_2(CO)_4$(dmpe)$_3I_4$] (0·115 g, 0·091 mmol) in acetone (50 cm^3) was heated at reflux for 25 h. The pale yellow solution was cooled, diluted with heptane to the point of turbidity, filtered, and then concentrated to produce a pale yellow precipitate of the ionic dicarbonyl complex. The solid was isolated by decantation, washed with pentane and dried *in vacuo* (0·064 g, 0·09 mmol).

Method (*B*). Iodine (0·112 g, 0·44 mmol) in CH_2Cl_2 (25 cm^3) was added slowly to [$Mo(CO)_2$(dmpe)$_2$] (0·20 g, 0·44 mmol) in CH_2Cl_2 (30 cm^3). The pale yellow solution was worked-up in the manner described in method (A), to give the complex (0·235 g, 0·33 mmol) (Found: C, 23·9; H, 4·4; I, 35·6; P, 18·0. $C_{14}H_{32}I_2MoO_2P_4$ requires C, 23·8;

H, 4·5; I, 36·0; P, 17·6%). Conductance [10^{-3}M-acetone–CH_2Cl_2 (3 : 2 v/v) solution 295 K] 91 A cm^2 V^{-1} mol^{-1} (under identical conditions the conductance of Pr^n_4NI is 92 A cm^2 V^{-1} mol^{-1}. The *tungsten* analogue, Found: C, 21·8; H, 4·1; I, 30·9; P, 15·4. $C_{14}H_{32}I_2O_2P_4W$ requires C, 21·2; H, 4·0; I, 32·0; P, 15·6%. Conductance [10^{-3} acetone–CH_2Cl_2 (3 : 2 v/v) solution, 295 K] 97 A cm^2 V^{-1} mol^{-1}.

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