Reactions of Carbon Dioxide with Electron-rich Trimethylphosphine Compounds of Rhenium and Tungsten: Crystal Structure of $[W(PMe_3)_4H_2(CO_3)]$†

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The new compounds *trans*-$[Re(PMe_3)_4(CO)(O_2CH\text{-}O)]$, *cis*-$[Re(PMe_3)_4(CO)H]$, *trans*-$[Re(PMe_3)_4(CO)I]$, *trans*-$[Re(PMe_3)_4(CO)Cl]$, *trans*-$[Re(PMe_3)_4\{\eta^2\text{-}SC(O)\}H]$, $[Re(PMe_3)_5H_2][BF_4]$, $[Re(PMe_3)_4(CO)H_2][BF_4]$, $[Re(PMe_3)_5I]$, $[W(PMe_3)_4H_2(CO_3)]$, and $[Ru(PMe_3)_3(CO)(CO_3\text{-}OO')]$ are described. The crystal structure of $[W(PMe_3)_4H_2(CO_3)]$ has been determined.

Carbon dioxide reacts readily with nucleophilic metal centres.[1–22] The insertion of carbon dioxide into transition metal–hydrogen bonds forming uni- or bi-dentate formato derivatives is also well known.[23–34] The co-ordination chemistry of the CO_2 ligand has been reviewed.[11,35–37] Here we describe the reactions of carbon dioxide with $[Re(PMe_3)_5H]$ and $[W(PMe_3)_3H_6]$, and related studies.

Results and Discussion

The compound $[Re(PMe_3)_5H]$ (**1**) has been previously described.[38,39] One preparative route entails the reduction of rhenium pentachloride in neat trimethylphosphine, as a reactive solvent, giving a yield of 20%. In our modified method, when rhenium pentachloride in neat trimethylphosphine is reduced by sodium sand, under 2 atm of hydrogen, the yield of $[Re(PMe_3)_5H]$ rises to *ca.* 60%. There is also a second product, namely $[Re(PMe_3)_4H_3]$, isolated in 10% yield. When the reaction was carried out under an atmosphere of dideuterium rather than dihydrogen, the ^1H and ^2H n.m.r. spectra show the formation of the deuterium derivatives $[Re(PMe_3)_5D]$ (**1-^{2}H**) and $[Re(PMe_3)_4D_3]$ together with the hydrogen analogues. The integration data show the ratio of (**1**) to (**1-^{2}H**) to be *ca* 1 : 1. The n.m.r. data also show the presence of a trace amount of deuteriated PMe_3. These observations show that the presence of a dihydrogen atmosphere greatly improves the yield of $[Re(PMe_3)_5H]$ but does not prevent the solvent from acting as a source of hydrogen.

The photoelectron spectrum of $[Re(PMe_3)_5H]$ has been recorded.[40] The first ionisation energy of 5.93 eV can be assigned to the d^6 electrons, which indicates that (**1**) has a highly electron-rich metal centre.

Treatment of $[Re(PMe_3)_5H]$ at 70 °C with carbon dioxide (3 atm), gives white crystals of *trans*-$[Re(PMe_3)_4(CO)(O_2CH)]$, (**2**), containing unidentate formate. The analytical and spectroscopic data for this compound and for the other new compounds described below are given in Table 1 and only selected data will be discussed in the text.

In the ^1H n.m.r. spectrum of (**2**) the resonance at δ 8.66 may be assigned to the hydrogen of the formato group by analogy with *trans*-$[Pt\{P(C_6H_{11})_3\}(O_2CH)]$ (δ 9.19),[41] *trans*-$[Pt(PEt_3)_2H(O_2CH)]$ (δ 9.36),[42] $[Mo(PMe_3)_4H(O_2CH\text{-}OO')]$ (δ 8.05),[43] and $[W(PMe_3)_3H_2(O_2CH\text{-}OO')(O_2CH\text{-}O)]$ (δ 9.05).[44] The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows a singlet at δ 167.5 and a weak resonance at 201.0 p.p.m., with poorly resolved carbon–phosphorus coupling, which can be assigned to a terminally bound carbonyl ligand. In the gated decoupled ^{13}C n.m.r. spectrum the former is a doublet [(J(C–H) 190.5 Hz] and may be assigned to the formato carbon. The corresponding values for the formato group of $[Re(dppe)_2(O_2CH)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[45] are δ 171.9 p.p.m. and J(C–H) 202.0 Hz.

The i.r. spectrum shows the three bands expected[41,46–48] for an unidentate formato ligand, ν(C–H) at 2 760w, ν_{asym}(OCO) at 1 634s, and ν_{sym}(OCO) at 1 318m cm^{-1}. The intense band at 1800 cm^{-1} may be assigned to ν(C=O).

The ^1H and ^2H n.m.r. spectra of the products obtained by treatment of the 1:1 mixture of (**1**) and (**1-^{2}H**) with carbon dioxide showed the presence of a 1:1 mixture of *trans*-$[Re(PMe_3)_4(CO)(O_2CH)]$ (**2**) and *trans*-$[Re(PMe_3)_4(CO)(O_2CD)]$ (**2-^{2}H**). The ^2H n.m.r. spectrum of the latter showed a broad singlet at δ 8.65 assignable to the O_2CD ligand, and the i.r. spectrum showed a weak band at 1 998 cm^{-1}, assignable to ν(C–D). The reaction between $[Re(PMe_3)_5H]$ and carbon dioxide (2 atm) in $[^2H_5]$benzene was monitored by ^1H n.m.r. spectroscopy. The initial spectrum (1 h) showed the presence of a resonance at δ 8.66 assignable to (**2**), as well as a second multiplet centred at δ 8.53, also assignable to a formato ligand. After 1 d the intensity of the resonance at δ 8.66 had increased significantly relative to that at δ 8.53. The resonance at δ 8.53 has the appearance of a symmetrical, twelve-line multiplet; however, upon broad-band phosphorus decoupling this multiplet simplified to two singlet resonances and these suggest the presence of two intermediate formato moieties. The presence of these two additional formate ligands was supported by the ^{13}C n.m.r. spectra, which showed two singlets at δ *ca.* 163.0 and 167.0 p.p.m. The $[^2H_6]$benzene was removed from the n.m.r. solution *in vacuo* and the resultant solids redissolved in $[^2H_6]$benzene. The multiplet at δ 8.53, assigned to the intermediate species, had now disappeared but the hydride resonance associated with $[Re(PMe_3)_5H]$ had reappeared and the resonances due to *trans*-$[Re(PMe_3)_4(CO)(O_2CH)]$ were still present. The solution i.r. spectrum of a benzene solution of $[Re(PMe_3)_5H]$ saturated with carbon dioxide showed a band at 1620 cm^{-1} assignable to co-ordinated formate. It can be concluded from these observations that there are intermediate formate compounds which readily revert to $[Re(PMe_3)_5H]$.

Treatment of complex (**1**) with carbon monoxide at 70 °C gave very soluble white crystals of *cis*-$[Re(PMe_3)_4(CO)H]$ (**3**).

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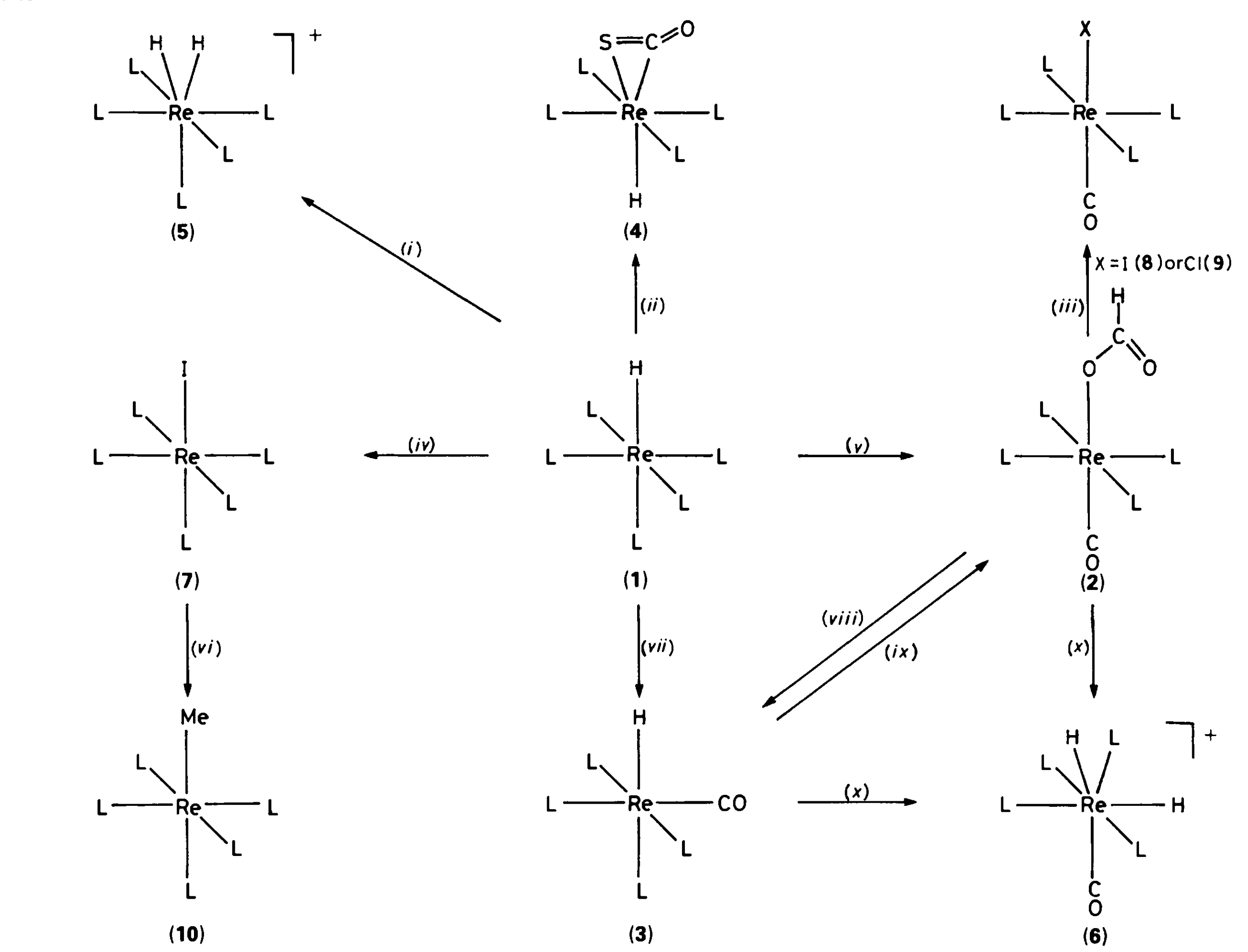
† (Carbonato-*OO′*) dihydridotetrakis(trimethylphosphine)tungsten.

Supplementary data available: see Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1990. Issue 1, pp. xix—xxii.

Non-S.I. units employed: atm = 101 325 Pa, bar = 10^5 Pa, eV = 1.60×10^{-19} J.



Scheme 1. L = PMe$_3$. (*i*) HBF$_4$ in Et$_2$O, yield 90%; (*ii*) COS at r.t. for 24 h, 45%; (*iii*) X = I, MeI at r.t. for 24 h, 70%; X = Cl, CHCl$_3$, or CCl$_4$ at r.t for 1d, 60%; (*iv*) MeI at r.t. for 3 h, 60%; (*v*) CO$_2$ (2.5 atm) at 70 °C for 4 d, 75%; (*vi*) Methyl-lithium at r.t. for 7 h, 70%; (*vii*) CO (2.5 atm) at 70 °C for 3 d, 82%; (*viii*) Warm to 70 °C for 2 d, >90%; (*ix*) CO$_2$ (3 atm) at 70 °C for 4 d, 73%; (*x*) HBF$_4$ in Et$_2$O at r.t. for 30 min, 85%

The ^{1}H n.m.r. spectrum shows the presence of three distinct co-ordinated phosphine environments with relative intensities of 2:1:1, and an eight-line pattern centred at δ −7.04 assignable to a metal-bound hydrogen moiety. The eight-line spectrum may be assigned as an overlapping doublet of doublet of triplets [J(P$_a$–H) 25.1, J(P$_c$–H) 25.2, J(P$_b$–H) 7.4 Hz]. The 202.4 MHz ^{31}P-{^{1}H} n.m.r. spectrum of (**3**) showed three clearly resolved resonances with relative integrated intensities of 2:1:1, at δ −46.9, −50.1, and −51.0 p.p.m. respectively. The presence of a Re–H moiety was also supported by the presence of a band in the i.r. spectrum, at 1 917 cm^{-1}. The strong band at 1 849 cm^{-1} is assignable to a terminally bound carbonyl ligand. The data indicates that complex (**3**) has a *cis* geometry, *i.e.* *cis*-[Re(PMe$_3$)$_4$(CO)H].

Treatment of (**3**) with excess of carbon dioxide at 70 °C gives the metalloformato complex, *trans*-[Re(PMe$_3$)$_4$(CO)(O$_2$CH)] (**2**). This reaction is reversible, warming solutions of (**2**) to 70 °C causes the slow evolution of carbon dioxide over several days giving (**3**) quantitatively. Similarly, attempts to sublime (**2**) *in vacuo* gave pure (**3**). Compound (**2**) is thus a reversible carrier for carbon dioxide.

Treatment of complex (**1**) with COS gave, after fractional crystallisation, white crystals of trimethylphosphine sulphide and, in modest yield, white crystals of *trans*-[Re(PMe$_3$)$_4${η^2-SC(O)}H] (**4**). The ^{1}H n.m.r. spectrum shows one environment for the PMe$_3$, at δ 1.42, and a binomial quintet at δ −3.10 assignable to Re–H. The i.r. spectrum shows bands at 1 935w and 1 791s cm^{-1}. The former may be assigned to ν(Re–H) and the latter to ν(C=O) of the η^2-bound COS ligand.[49] There are previous examples of the insertion of carbonyl sulphide into metal–hydrogen bonds giving monothioformates,[49] and loss of sulphur from COS is well known.[50,51]

Protonation of complex (**1**) with 1 equivalent of tetrafluoroboric acid, gave white microcrystalline [Re(PMe$_3$)$_5$H$_2$][BF$_4$] (**5**). The ^{1}H n.m.r. spectrum shows only one resonance assignable to co-ordinated phosphine, at δ 1.72, and a binomial sextet at δ −7.47 which can be attributed to two metal-bound hydrogen atoms coupling to five apparently equivalent phosphine ligands. This latter observation suggests the molecule to be fluxional at room temperature. The room temperature ^{31}P-{^{1}H} n.m.r. spectrum also indicates the fluxionality of the species since there is only a single resonance at δ − 50.2 p.p.m.

Protonation of complex (**2**) in diethyl ether with 1 equivalent of tetrafluoroboric acid gave white crystals of [Re(PMe$_3$)$_4$(CO)-H$_2$][BF$_4$] (**6**), (see below). There was no evidence for the presumed intermediate cation [Re(PMe$_3$)$_4$(CO)(HO$_2$CH)]$^+$.

Protonation of complex (**3**) with tetrafluoroboric acid gave white microcrystalline [Re(PMe$_3$)$_4$(CO)H$_2$][BF$_4$] (**6**). The ^{1}H n.m.r. spectra show broad resonances assignable to bound trimethylphosphine which resolved to three doublets upon cooling to −40 °C, at δ 1.58, 1.80, and 1.91, with relative integrated intensities of 1:2:1. The rhenium-hydride resonance appeared as a second-order quintet centred at δ −5.75 at 20 °C, and as a symmetrical eight-line multiplet upon cooling to the low-temperature limit of −65 °C; even at this temperature the multiplet is still second order and not fully resolved, precluding the calculation of any hydride–phosphorus coupling constants. However, from the relative intensities it can be deduced that there are two hydrogen ligands present. The fluxional nature of the molecule at room temperature is also evident in the ^{31}P-{^{1}H} n.m.r. spectrum which exhibits only two broad resonances at 20 °C, but at −40 °C there are three resonances, still broadened, at δ −25.5, −48.9, and −55.6 p.p.m., with relative integrated intensities of 1:2:1. The data are consistent with the structure of **(6)** shown in Scheme 1.

Table 1. Analytical and spectroscopic data[a]

Compound	N.m.r. data
(1-^{2}H)	^{2}H (in benzene, 38.4 MHz): −8.60 [1 D, m (6 lines), br, Re–D]
(2)[b] C, 30.0 (29.6); H, 7.0 (6.6)	^{1}H: 1.39 [36 H, t, *J*(P–H) 2.9, 4PMe$_3$], 8.66 [1 H, qnt *J*(P–H) 1.1, O$_2$CH] ^{31}P: −33.4 [m, br, 4PMe$_3$] ^{13}C: 21.7 [q, *J*(C–H) 127, 4PMe$_3$], 167.5 [d, *J*(C–H) 190.5, O$_2$CH], 201.0 (br s, CO)
(2-^{2}H)[c]	^{2}H: 1.38 [36 D, br, 4PMe$_3$], 8.65 [1 D, br, O$_2$CD]
(3)[d] C, 29.8 (30.0); H, 6.9 (7.1)	^{1}H: −7.04 [1 H, m (8 lines), J_t (P–H) 25.2, J_d(P–H) 25.1, J'_d(P–H) 7.4, Re–H], 1.20 [9 H, d, *J*(P–H) 5.8, PMe$_3$], 1.42 [9 H, d, *J* (P–H) 5.8, PMe$_3$], 1.55 [18 H, t, *J*(P–H) 2.8, 2PMe$_3$] ^{31}P: −46.9 [2 P, d, *J*(P–P) 25.6, 2PMe$_3$], −50.1 [1 P, q, *J*(P–P) 25.6, PMe$_3$], −51.0 [1 P, m, br, PMe$_3$]
(4)[e] C, 28.8 (28.3); H, 6.6 (6.7)	^{1}H: −3.10 [1 H, qnt, *J*(P–H) 7.6, Re–H], 1.42 [36 H, c, 4PMe$_3$] ^{31}P: −43.2 (br, 4PMe) ^{13}C: 22.3 (c, 4PMe$_3$), 198.7 [qnt, *J*(P–C) 5.5, COS]
(5)[f] C, 27.7 (27.5); H, 7.5 (7.2)	^{1}H in CD$_3$OD: −7.47 [2 H, sxt, *J*(P–H) 28.5, 2Re–H], 1.72 [45 H, d, *J*(P–H) 7.4, 5PMe$_3$] ^{31}P in CD$_3$OD: −50.2 (s, 5PMe$_3$)
(6)[g] C, 25.9 (25.7); H, 6.3 (6.3)	^{1}H in CD$_3$OD$_2$ at 20 °C: −5.75 (2 H, c, 5 lines, 2 Re–H), 1.80 (36 H, c, br, 4PMe$_3$), at −65 °C, −5.75 (2 H, c, 8 lines, 2Re–H), 1.58 [9 H, d, *J*(P–H) 7.5, PMe$_3$], 1.80 [18 H, d, *J*(P–H) 8.4, 2PMe$_3$], 1.91 [9 H, d, *J*(P–H) 10.5, PMe$_3$] ^{31}P-{^{1}H} in CD$_3$OD at 20 °C: −56.2 (s, br), −49.5 (s, br); at −40 °C, −55.6 (1 P, m, br, PMe$_3$), −48.9 (2 P, br, 2PMe$_3$), −25.5 (1 P, br, PMe$_3$)
(7)[h] C 25.8 (25.9); H, 6.0 (6.5)	^{1}H: 1.25 [9 H, d, *J*(P–H) 6.4, PMe$_3$], 1.59 [36 H, t, *J*(P–H) 2.3, 4 PMe] ^{31}P-{^{1}H}: −56.9 [4 P, d, br, *J*(P–P) 9.7, 4 PMe$_3$], −51.0 (1 P, s, br, PMe$_3$)
(8)[i] C, 24.4 (24.1); H, 5.5 (5.6)	^{1}H: 1.52 [t, *J*(P–H) 2.3, 4PMe$_3$] ^{31}P: −49.0 (br, 4PMe$_3$)
(9)[j] C, 28.0 (28.1); H, 6.0 (6.5)	^{1}H: 1.42 [t, J_{ap} (P–H) 8.4, 4PMe$_3$] ^{31}P: −36.8 (s, br, 4PMe$_3$)
(11)[k] C, 28.6 (28.4); H 7.0 (6.9)	^{1}H in (CD$_3$)$_2$CO: −1.67 [2 H, ddt, J_t(P–H) 46.0, J_d(P–H) 40.9, J_d(P–H) 36.8, 2W–H], 1.42 [18 H, t, *J*(P–H) 3.2, 2PMe$_3$], 1.60 [18 H, vt, J_{ap}(P–H) 4.0, 2PMe$_3$] ^{31}P in (CD$_3$)$_2$CO: −15.0 [2 P, t, *J*(P–P) 7.6, 2PMe$_3$], −21.8 [2 P, t, *J*(P–P) 7.6, 2PMe$_3$] ^{13}C in (CD$_3$)$_2$CO: 18.2 (m, 2PMe$_3$), 25.3 (m, 2PMe$_3$), 163.5 (s, CO$_3$)
(17)[l] C, 31.3 (31.6); H, 6.9 (6.5)	^{1}H in (CD$_3$)$_2$SO: 1.36 [18 H, t, *J*(P–H), 3.7, 2PMe$_3$], 1.47 [9 H, d, *J*(P–H) 10.0, PMe$_3$] ^{31}P in (CD$_3$)$_2$SO: 11.6 [1 P, t, *J*(P–P) 26.0, PMe$_3$], −1.4 [2 P, d, *J*(P–P) 26.0, 2PMe$_3$] ^{13}C in (CD$_3$)$_2$SO: 14.2 (t, 2PMe$_3$), 18.9 (d, PMe$_3$), 166.2 (s, CO$_3$), 203.2 [q, *J*(P–C) 14.0, CO]

[a] Unless otherwise stated the n.m.r. solvent is C$_6$D$_6$, ^{1}H at 300 MHz, ^{31}P at 101.2 MHz, ^{13}C at 62.8 MHz; δ values, *J* in Hz. *J′* refers to the separation of the outer lines in virtually coupled multiplets. Analytical data given as: Found (Calc.), %. I.r. data for Nujol mulls. [b] I.r. data (cm^{-1}): 1 318m, 1 634s, 1 800s, and 2 760w, see text. F.d. mass spectrum: *m/z* 564 (^{187}Re), *P*$^+$. [c] I.r. data (cm^{-1}) (Nujol mull, CsI plates): 1 319m, 1 634s, 1 798s, and 1 998w. [d] I.r. data (cm^{-1}): ν(C=O), 1 849s, and ν(Re–H) 1 917m. Mass spectrum: *m/z* 520 (^{187}Re), *P*$^+$. [e] I.r data (cm^{-1}): 1 298m, 1 791vs, and 1 935w. Mass spectrum: *m/z* 551 (^{187}Re), [P$^+$ −H]. [f] ν(Re–H) 2 023s cm^{-1}. [g] ν(Re–H or C=O) 1 806m and 1 860s cm^{-1}. [h] I, 18.3 (18.3)%. [i] ν(C=O) 1 803s cm^{-1}; Cl, 6.7 (6.4)%. [j] ν(C=O), 1 803s cm^{-1}; Br, 20.3 (19.7)%. [k] I.r. data (cm^{-1}): 951s, 1 013m, 1 235m, 1 276m, 1 283m, 1 299m, 1 617s, and 1 868w, br. F.a.b. mass spectrum: *m/z* 550 (^{184}W), *P*$^+$. [l] I.r. data (cm^{-1}) 1 289m, 1 302m, 1 600vs, and 1 935vs. F.a.b. mass spectrum: *m/z* 419 (^{102}Ru), *P* + H$^+$.

Treatment of complex **(1)** with methyl iodide gave yellow crystals of [Re(PMe$_3$)$_5$I] **(7)** in high yield. The analogous chloro compound, [Re(PMe$_3$)$_5$Cl], has been prepared by the sodium amalgam reduction of a mixture of [ReCl$_4$(thf)$_2$] and trimethylphosphine in tetrahydrofuran (thf).[38]

Addition to complex **(2)** of an excess of methyl iodide gave pale yellow crystals of *trans*-[Re(PMe$_3$)$_4$(CO)I] **(8)**. This showed a strong band for ν(C=O) at 1803 cm^{-1}. When the reaction was monitored by ^{1}H n.m.r. spectroscopy a singlet resonance assignable to methane was observed at δ 0.26. Treatment of **(2)** with chloroform or carbon tetrachloride gave white crystals of *trans*-[Re(PMe$_3$)$_4$(CO)Cl] **(9)**, in high yield.

The methylation of [Re(PMe$_3$)$_5$Cl] by methyl-lithium to form [Re(PMe$_3$)$_5$Me] **(10)** has been previously reported.[38] Treatment of **(7)** with 1 equivalent of methyl-lithium also gave **(10)**.

Treatment of [W(PMe$_3$)$_3$H$_6$] at 70 °C with carbon dioxide (2.5 atm) gave yellow crystalline [W(PMe$_3$)$_4$H$_2$(CO$_3$)] **(11)** which is soluble in toluene, thf, and acetone, together with the compound *cis*-[W(PMe$_3$)$_4$(CO)$_2$] which was isolated from the light petroleum soluble fraction of the reaction products. The i.r. spectrum of **(11)** shows two strong absorbances at 1617 and 1 235 cm^{-1} consistent with the presence of a bidentate carbonate ligand, the chelating nature of the ligand being inferred by the large splitting between these two bands.[53] There is a further medium-intensity band at 1 013 cm^{-1} assignable to a carbonate ligand, and these values correspond closely to the i.r. spectrum of the complex [Fe(PMe$_3$)$_3$(CO)(CO$_3$-*OO′*)] which contains a bidentate carbonate ligand [ν(C–O) 1604, ν$_{asym}$(C–O) 1293, and ν$_{sym}$(C–O) 1013 cm^{-1}]. The weak, broad band at 1868 cm^{-1} in the i.r. spectrum of **(11)** can be assigned to ν(W–H). The ^{13}C n.m.r. spectrum of complex **(11)** shows the two multiplets expected for the two sets of inequivalent phosphine ligands as well as a weak singlet at δ 163.5 p.p.m. Organic carbonates show resonances in the ^{13}C n.m.r. spectra between δ 150 and 160 p.p.m.,[55] and the complex Na[Co(pren)(CO$_3$-*OO′*)] [pren = 1,1′-ethylenebis(pyrrolidine-2-carboxylate) (2−)] shows a band at δ 168.7 p.p.m. assigned to the CO$_3$ group.[56]

The crystal structure of complex **(11)** has been determined. The molecular structure is shown in the Figure[57] with bond lengths and angles in Table 2. Each molecule has crystallographic *m*2*m* symmetry which forces the carbonate ligand to be planar and symmetrically bound. The C(5)–O(2) bond retains marked double bond character [1.214(6)Å)] and C(5)–O(1) must also have some multiple bond nature [1.318(4)Å] compared with a typical single C–O bond of 1.43Å. The dimensions of the carbonate ligand lie within the expected range as observed for other bidentate carbonates.[58] The two hydrides were not located by difference Fourier methods, but are presumed to lie on average in the plane defined by P(2), W(1), and P(2^{II}) and on the opposite side of the four phosphine ligands from the carbonate. This results in the co-ordination geometry being described as distorted dodecahedral with a tetrahedron defined by the phosphine ligands intersecting with that defined by the carbonate and the two missing hydrides. Examination of the molecular packing shows no unusually short intermolecular contacts.

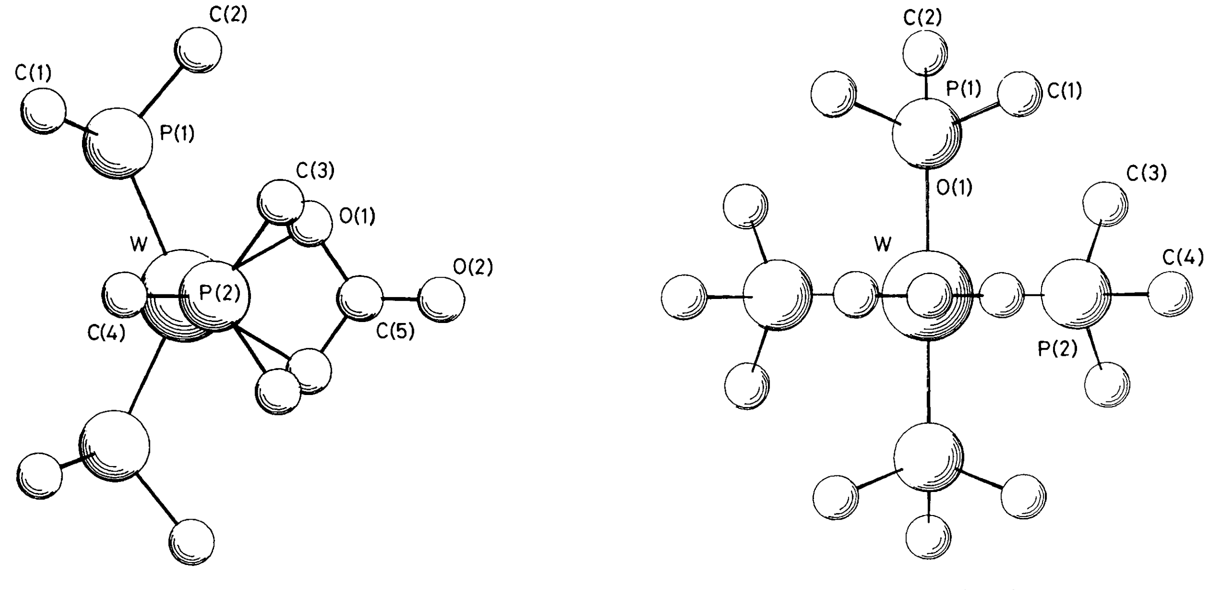


Figure. Molecular structure of complex (**11**). Two orthogonal views are given (ref. 58) and hydrogen atoms are omitted for clarity

Table 2. Selected bond lengths (Å) and angles (°) for complex (**11**)

W(1)–P(1)	2.444(1)	P(1)–W(1)–P(1^{I})	130.5(4)
W(1)–P(2)	2.492(1)	P(1)–W(1)–P(2)	94.27(1)
W(1)–O(1)	2.164(2)	P(2)–W(1)–P(2^{II})	159.54(4)
		O(1)–W(1)–O(1^{I})	60.21(13)
		P(1)–W(1)–O(1)	84.67(7)
		P(1)–W(1)–O(1^{I})	144.88(7)
		P(2)–W(1)–O(1)	81.16(2)
P(1)–C(1)	1.830(3)	W(1)–P(1)–C(1)	118.90(11)
P(1)–C(2)	1.821(4)	W(1)–P(1)–C(2)	115.20(15)
		C(1)–P(1)–C(1^{III})	97.4(2)
		C(1)–P(1)–C(2)	101.60(15)
P(2)–C(3)	1.807(3)	W(1)–P(2)–C(3)	115.36(12)
P(2)–C(4)	1.814(4)	W(1)–P(2)–C(4)	122.06(17)
		C(3)–P(2)–C(3^{I})	100.6(3)
		C(3)–P(2)–C(4)	100.0(2)
O(1)–C(5)	1.318(4)	W(1)–O(1)–C(5)	94.5(2)
C(5)–O(2)	1.214(6)	O(1)–C(5)–O(1^{I})	110.9(4)
		O(1)–C(5)–O(2)	124.6(2)

Superscripts denote atoms generated from the asymmetric unit by the symmetry operators: I $-x,y,z$; II $-x,y,\frac{1}{2}-z$; III $x,y,\frac{1}{2}-z$.

Recently Lyons and Wilkinson[24] showed that treatment of $[W(PMe_3)_3H_6]$ with carbon dioxide under mild conditions gave the compound $[W(PMe_3)_3H_2(O_2CH\text{-}OO')(O_2CH\text{-}O)]$. Treatment of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with carbon dioxide (3 atm) at room temperature gave the known compound *cis*-$[W(PMe_3)_4(CO)_2]$[59] and, as the toluene soluble extract, the compound $[W(PMe_3)_4H_2(CO_3\text{-}OO')]$, (**11**).

We have also carried out a study of the reduction of anhydrous transition-metal halides in PMe_3 as solvent under an atmosphere of carbon dioxide. Treatment of anhydrous chromium trichloride in excess of pure trimethylphosphine under an atmosphere of CO_2 with sodium sand gave the known[60] compound *cis*-$[Cr(PMe_3)_4(CO)_2]$ (**12**). Reduction using sodium sand of a mixture of molybdenum pentachloride in pure PMe_3 under CO_2 gave a mixture of $[Mo(PMe_3)_5(CO)]$ (**13**) and *cis*-$[Mo(PMe_3)_4(CO)_2]$ (**14**). These compounds have been described previously.[59] When the molybdenum pentachloride was replaced by tungsten hexachloride the major product is the previously reported monocarbonyl $[W(PMe_3)_5(CO)]$ (**15**).[53,60] Treatment of anhydrous iron dichloride in pure PMe_3 under CO_2 with sodium sand gave the known *trans*-$[Fe(PMe_3)_3(CO)_2]$ (**16**).[61] Treatment of ruthenium trichloride in excess of trimethylphosphine with sodium sand gave $[Ru(PMe_3)_4Cl_2]$. Further reduction of $[Ru(PMe_3)_4Cl_2]$ using sodium sand amalgam under an atmosphere of carbon dioxide gave $[Ru(PMe_3)_3(CO)(\eta^2\text{-}CO_3\text{-}OO')]$ (**17**).

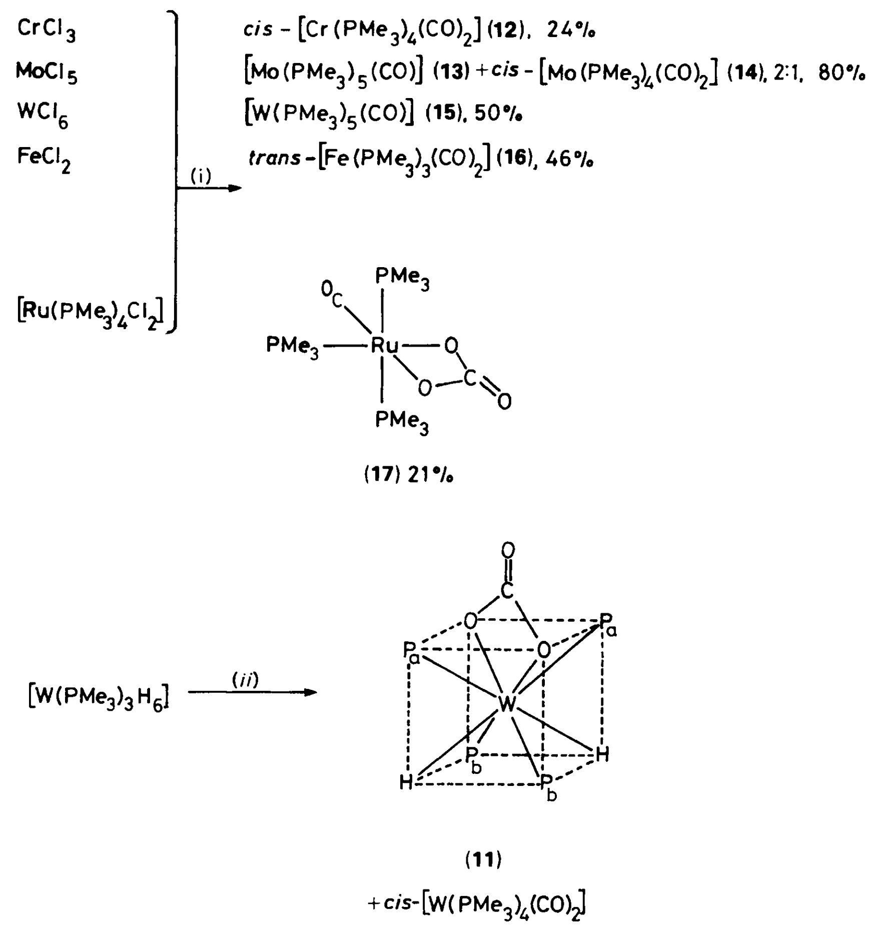
An exploratory study of the reaction between ruthenium atoms and methyl formate was made. A large excess of methyl formate was co-condensed with ruthenium atoms at −195 °C in a metal vapour synthesis apparatus.[62] After warming the reaction mixture to room temperature a deep red solid could be washed from the wall of the reaction vessel using hot thf. The extract was filtered and removal of the thf from the filtrate gave a red powder. This proved to be highly insoluble and resisted characterisation. However, treatment of the red powder with PMe_3 gave colourless crystals of complex (**17**). The ^1H n.m.r. spectrum showed two resonances assignable to co-ordinated PMe_3, a doublet at δ 1.47 and a virtually coupled triplet at δ 1.36, with relative intensities of 1:2. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consisted of a triplet resonance at δ 11.6 [*J*(P–P) 26.0 Hz] and a doublet resonance at δ −1.4 p.p.m. with relative intensities of 1:2. The i.r. spectrum showed strong bands at 1 600 and 1 935 cm^{-1}. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed two features apart from those due to the co-ordinated phosphine ligands; a singlet at δ 166.2 and a quartet at 203.2 p.p.m. The former can be assigned to a bidentate CO_2 ligand and the latter to a Ru-CO moiety in which the carbon atom couples equally to the three phosphine ligands [*J*(C–P) 14.0 Hz]. The data are consistent with the structure for (**17**) shown in Scheme 2.

The reactions and structures proposed for the new compounds are shown in the Schemes. The reduction of carbon dioxide to give transition-metal carbonyl compounds has been long known. Here we have demonstrated the use of this reaction to synthesise both new and known electron-rich transition-metal trimethylphosphine compounds.

Experimental

All preparations and reactions described were carried out under an argon atmosphere using standard vacuum-line and Schlenk-tube techniques, or in an inert-atmosphere dry-box.

Unless stated otherwise, all solvents were pre-dried over molecular sieves and subsequently distilled from potassium [for light petroleum (b.p. 100—120 °C), toluene, benzene, tetrahydrofuran, and cyclohexane], sodium–potassium alloy [for



Scheme 2. (*i*) In liquid PMe_3 as solvent, reduction with sodium sand under an atmosphere of carbon dioxide; (*ii*) carbon dioxide (2.5 atm) at 70 °C for 4 d, yield 60%

pentane, light petroleum (b.p. 40—60 °C), and diethyl ether] or phosphorus pentoxide (for dichloromethane), under dinitrogen. Deuteriated solvents for n.m.r. solutions were stored over molecular sieves and were transferred by vacuum distillation. Carbon dioxide was of research grade supplied by Air Products plc.

N.m.r. spectra were recorded using the following instruments: ^1H 250 MHz, Bruker AM-250; 300 MHz, Bruker WH-300; ^{31}P, 101.2 MHz, Bruker AM-250; 202.4 MHz, Bruker AM-500; ^{13}C, 62.8 MHz, Bruker AM-250; 125.6 MHz, Bruker AM-500; ^2H, 38.4 MHz, Bruker AM-250. Proton and ^{13}C spectra were referenced internally with respect to tetramethylsilane ($\delta = 0$) using the residual protio-solvent resonance (^1H) and the solvent resonance (^{13}C), ^{31}P spectra externally with respect to trimethyl phosphate in D_2O. All heteronuclear n.m.r. experiments were recorded with broad-band proton decoupling unless stated otherwise. All chemical shifts are quoted in δ and coupling constants in Hz. Abbreviations used are: s = singlet; d = doublet; t = triplet; q = quartet; qnt = quintet; sxt = sextet; m = multiplet; vt = virtual triplet; c = complex; br = broad; J_{ap} = apparent coupling constant for virtually coupled multiplet.

Infrared spectra were recorded on either a Perkin-Elmer 457 grating spectrophotometer, a Philips Scientific SP2000 grating spectrophotometer, or a Perkin-Elmer 1710 FT spectrophotometer.

Elemental microanalyses were carried out by the Analysis Department in this laboratory, or in the case of very air-sensitive materials, by Alfred Bernhardt Ltd., West Germany.

Low resolution mass spectra were recorded on an AE MS 902 mass spectrometer, or in the case of fast atom bombardment (f.a.b.) and field desorption (f.d.) spectra on a Micromass ZAB-IF spectrometer. Photoelectron spectra were recorded on a PES Laboratories 0078 spectrometer using a heated inlet system. The spectrometer was calibrated using the ionisation potentials of He, Xe, and N_2.[40]

Hydridopentakis(trimethylphosphine)rhenium, (**1**).—Sodium sand (5.5 g) and PMe_3 (40 cm^3) at 77 K were treated with $ReCl_5$ (6.0 g, 16.5 mmol). The mixture was warmed to room temperature (r.t.). The ampoule was then charged with hydrogen (2.5 atm) and stirred at r.t. for 4 d. The volatile components were removed *in vacuo* and the resultant solids extracted into light petroleum (b.p. 40—60 °C, 200 cm^3) giving a green solution which was filtered. The filtrate was concentrated under reduced pressure to 5 cm^3 and cooled to −80 °C, giving green crystals. The ^1H n.m.r. spectrum identified the product as a 7:1 mixture of $[Re(PMe_3)_5H]$ and $[Re(PMe_3)_4H_3]$, by comparison with authentic data.[38] Yield of $[Re(PMe_3)_5H]$ *ca* 5.7 g, 60.0%.

Deuteriopentakis(trimethylphosphine)rhenium, (**1-^{2}H**).—The procedure was exactly as described for complex (**1**) using $ReCl_5$ (2.0 g, 5.5 mmol), sodium sand (3.0 g), PMe_3 (30 cm^3), and D_2 (*ca.* 2 atm). The ^1H and ^2H n.m.r. spectra showed the product to contain an approximately 1:1 mixture of $[Re(PMe_3)_5H]$ and $[Re(PMe_3)_5D]$. Total yield 2.1 g, *ca.* 67.0%.

trans-*Carbonyl(formato-*O*)tetrakis(trimethylphosphine)rhenium*, (**2**).—The compound $[Re(PMe_3)_5H]$ (1.5 g, 2.6 mmol) in light petroleum (b.p. 100–120 °C, 50 cm^3) was treated with carbon dioxide (2.5 atm). The mixture was stirred at 70 °C for 4 d and the volatile materials removed under reduced pressure. The solid products were extracted into light petroleum (b.p. 40—60 °C, 3 × 100 cm^3), the resultant colourless solution filtered, concentrated to 100 cm^3, and cooled to -20 °C, giving a white precipitate. Yield 1.1 g, 75.0%.

trans-*Carbonyl*([^2H]*formato*-O)*tetrakis*(*trimethylphosphine*)*rhenium*, (**2**-^{2}**H**).—The procedure was as described above but using a mixture of [$Re(PMe_3)_5H$] and [$Re(PMe_3)_5D$] (1.7 g, 3.0 mmol). Yield 1.2 g, 71%. The ^1H and ^2H n.m.r. spectra revealed the product to be an approximately 1:1 mixture of *trans*-[$Re(PMe_3)_4(CO)(O_2CH)$] and *trans*-[$Re(PMe_3)_4(CO)(O_2CD)$].

cis-*Carbonylhydridotetrakis*(*trimethylphosphine*)*rhenium*, (**3**).—The compound [$Re(PMe_3)_5H$] (0.2 g, 0.35 mmol) in light petroleum (b.p. 100—120 °C, 50 cm^3) was heated at 70 °C for 3 d under carbon monoxide (2.5 atm). The solvent was removed under reduced pressure and the solid products extracted into light petroleum (b.p. 40—60 °C, 150 cm^3) giving a colourless solution. This was filtered, concentrated to 5 cm^3, and cooled to -80 °C, producing white crystals. Yield 0.15 g, 82%.

Reaction of Complex (**3**) *with Carbon Dioxide*.—The compound *cis*-[$Re(PMe_3)_4(CO)H$] (0.2 g, 0.38 mmol) in light petroleum (b.p. 100—120 °C, 50 cm^3) was heated at 70 °C for 4 d under carbon dioxide (3 atm). The solvent was removed under reduced pressure and the solid products extracted into light petroleum (b.p. 40—60 °C, 2 × 100 cm^3), the resultant solution was filtered, concentrated to 50 cm^3, and cooled to -20 °C, producing a white precipitate. Yield 0.16 g, 73%. The ^1H n.m.r. spectrum identified the product as *trans*-[$Re(PMe_3)_4(CO)(O_2CH)$].

trans-(*Carbonyl sulphide*)*hydridotetrakis*(*trimethylphosphine*)*rhenium*, (**4**).—The compound [$Re(PMe_3)_5H$] (1.1 g. 1.94 mmol) in light petroleum (b.p. 40—60 °C, 50 cm^3) was stirred under COS (1 atm) for 1 d at r.t. The volatile materials were removed under reduced pressure and the solid products extracted into light petroleum (b.p. 40—60 °C, 200 cm^3), the resultant colourless solution was filtered, concentrated (to 80 cm^3), and cooled to -20 °C, producing colourless crystals. These were identified as trimethylphosphine sulphide from proton n.m.r. and microanalytical data.

The supernatant was filtered, concentrated to 20 cm^3, and cooled to -80 °C producing a colourless solid. This was purified by sublimation onto a liquid-nitrogen-cooled probe at 120 °C and 10^{-5} mbar. The white sublimate was the compound *trans*-[$Re(PMe_3)_4(COS)H$]. Yield 0.48 g, 45%.

Those solids found to be insoluble in light petroleum (b.p. 40—60 °C) were extracted into thf (100 cm^3) and the resultant solution filtered, concentrated to 10 cm^3, and cooled to -20 °C producing colourless crystals. The ^1H n.m.r. spectrum revealed the presence of the cation [$Re(PMe_3)_5H_2$]$^+$.

Dihydridopentakis(*trimethylphosphine*)*rhenium Tetrafluoroborate*, (**5**).—The compound [$Re(PMe_3)_5H$] (0.41 g, 0.72 mmol) in diethyl ether (30 cm^3) was stirred at r.t. and $HBF_4 \cdot Et_2O$ in diethyl ether (4.5 cm^3, 0.16 mol dm^3, 0.72 mmol) was added in a dropwise manner. The mixture was allowed to stir at r.t. for 30 min and the colourless solution filtered from a white precipitate, which was then washed with diethyl ether (2 × 10 cm^3). The solid was dissolved in methanol (10 cm^3) and diethyl ether added until solid began to appear (50 cm^3). The solution was filtered and cooled to -80 °C to produce colourless crystals. The supernatant was filtered and cooled to -80 °C to produce more crystals. Total yield 0.42 g, 90.0%.

Carbonyldihydridotetrakis(*trimethylphosphine*)*rhenium Tetrafluoroborate*, (**6**).—*Method A*. The compound *trans*-[$Re(PMe_3)_4(CO)(O_2CH$-*OO′*)] (0.68 g, 1.20 mmol) was partially dissolved in diethyl ether (80 cm^3) and the slurry was stirred at r.t. To this was slowly added $HBF_4 \cdot Et_2O$ in diethyl ether (8.5 cm^3, 0.16 mol dm^{-3}, 1.36 mmol). The mixture was stirred for a further 30 min and the colourless solution filtered from a white precipitate. This was washed with diethyl ether (2 × 10 cm^3) and dissolved in methanol (30 cm^3). Diethyl ether (*ca.* 100 cm^3) was added until a precipitate began to appear, the solution filtered and cooled to -80 °C to produce colourless crystals. The supernatant was filtered and cooled to -80 °C to produce a second batch of crystals. The product was identified as [$Re(PMe_3)_4(CO)H_2$][BF_4] by the ^1H n.m.r. and i.r. spectra. Yield 0.62 g, 85.0%.

Method B. The compound *cis*-[$Re(PMe_3)_4(CO)H$] (0.45 g, 0.87 mmol) in diethyl ether (50 cm^3) was stirred at r.t. and a solution of $HBF_4 \cdot Et_2O$ in diethyl ether (5.5 cm^3, 0.16 mol dm^{-3}, 0.88 mmol) was added in a dropwise manner. The mixture was stirred at r.t. for 30 min and the colourless solution was filtered from a white precipitate. The solid was washed with diethyl ether (2 × 10 cm^3), dissolved in methanol (20 cm^3), and diethyl ether added until solid began to appear (80 cm^3). The solution was filtered and cooled to -80 °C to produce colourless crystals. The supernatant was filtered and cooled to -80 °C to produce more crystals. Total yield 0.46 g, 87%.

Iodopentakis(*trimethylphosphine*)*rhenium*, (**7**).—The compound [$Re(PMe_3)_5H$] (1.10 g, 1.94 mmol) in diethyl ether (50 cm^3) was stirred at r.t. and methyl iodide (0.34 g, 2.4 mmol) in diethyl ether (10 cm^3) was added. The mixture was stirred at r.t. for 3 h. The volatile materials were removed under reduced pressure and the resultant solids were extracted into light petroleum (b.p. 40—60 °C, 100 cm^3). The extract was filtered, concentrated (to 10 cm^3) under reduced pressure, and cooled to -80 °C giving yellow crystals. Yield 0.81 g, 60%.

trans-*Carbonyliodotetrakis*(*trimethylphosphine*)*rhenium*, (**8**).—The compound *trans*-[$Re(PMe_3)_4(CO)(O_2CH)$] (30 mg, 0.05 mmol) and methyl iodide (1.0 cm^3) in benzene (25 cm^3) *in vacuo*, in a sealed glass tube, were allowed to stand for 24 h at r.t. The solvent was removed under reduced pressure and the residue extracted with light petroleum (b.p. 40—60 °C, 50 cm^3). The resultant colourless solution was filtered, concentrated to 5 cm^3, and cooled to -20 °C, producing an off-white precipitate. Yield 20 mg, 70%.

trans-*Carbonylchlorotetrakis*(*trimethylphosphine*)*rhenium*, (**9**).—The compound *trans*-[$Re(PMe_3)_4(CO)(O_2CH)$] (0.1 g, 0.18 mmol) in chloroform (30 cm^3) was allowed to stand at r.t. for 1 d. The volatile materials were then removed under reduced pressure and the resultant solids were extracted into light petroleum (b.p. 40—60 °C, 100 cm^3). The colourless solution was filtered, concentrated (to 10 cm^3), and cooled to -20 °C, producing a white precipitate. This was collected and dried *in vacuo*. Yield 0.07 g, 65%. The same procedure using carbon tetrachloride rather than chloroform gave complex (**5**) in 60% yield.

Methylpentakis(*trimethylphosphine*)*rhenium*, (**10**).—The compound [$Re(PMe_3)_5I$] (0.39 g, 0.56 mmol) in diethyl ether (30 cm^3) was stirred at r.t. and methyl-lithium in diethyl ether (0.47 cm^3, 1.3 mol dm^{-3}, 0.61 mmol) was added slowly. The mixture was stirred at r.t. for 7 h, after which the initial yellow colour of the solution had been discharged. The volatile materials were removed under reduced pressure and the resultant solids extracted into light petroleum (b.p. 40—60 °C, 100 cm^3). The extract was filtered and the volatile materials were removed under reduced pressure to give a yellow solid identified as [Re(PMe$_3$)$_5$Me] by comparison of the ^{1}H n.m.r. data with literature values.[38] Yield *ca.* 70%.

(Carbonato-OO′)dihydridotetrakis(trimethylphosphine)tungsten, **(11)**.—The compound [W(PMe$_3$)$_3$H$_6$] (0.7 g, 1.67 mmol) in light petroleum (b.p. 100—120 °C, 60 cm^3) was heated at 70 °C for 4 d under carbon dioxide (2.5 atm). A yellow solid precipitated which was separated by filtration. The precipitate was washed with toluene (2 × 10 cm^3), dissolved in acetone (50 cm^3), the resultant yellow solution was filtered, the filtrate was concentrated to 20 cm^3 and cooled to 0 °C, producing yellow crystals. Yield 0.55 g, 60%. Examination of the soluble products of the reaction mixture showed them to contain the known compound *cis*-[W(PMe$_3$)$_2$(CO)$_2$] which is soluble in light petroleum.

Reaction between [W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H] *and* CO$_2$: *Synthesis of* [W(PMe$_3$)$_4$H$_2$(CO$_3$)], **(11)**, *and* cis-[W(PMe$_3$)$_4$(CO)$_2$].—The compound [W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H] (0.3 g, 0.53 mmol) in thf (70 cm^3) was stirred at r.t. for 3 d under carbon dioxide (3 atm) producing a red solution. The volatile materials were removed under reduced pressure and the resultant yellow solid extracted into light petroleum (b.p. 40—60 °C, 150 cm^3). The extract was filtered, concentrated to 40 cm^3, and cooled to −20 °C, producing a small amount of yellow solid which was identified as [W(PMe$_3$)$_4$H$_2$(CO$_3$)] by the ^{1}H n.m.r. spectrum. The supernatant solution was concentrated to 5 cm^3 and cooled to −80 °C, producing an orange solid identified as *cis*-[W(PMe$_3$)$_4$(CO)$_2$]. Yield 0.09 g, 33%. A second extraction of the reaction products with toluene separated a small quantity of [W(PMe$_3$)$_4$H$_2$(CO$_3$)]. Yield 0.1 g, 34%.

cis-*Dicarbonyltetrakis(trimethylphosphine)chromium*, **(12)**.—Sodium sand (2.5 g) and PMe$_3$ (30 cm^3) at 77 K were treated with anhydrous CrCl$_3$ (2.1 g, 13.2 mmol). The mixture was warmed to r.t. and treated with carbon dioxide (2 atm). After stirring for 1 h at r.t. the solution became blue and after 24 h this had changed to a deep orange. After 4 d the volatile materials were removed *in vacuo* and the residue was extracted into light petroleum (b.p. 40—60 °C, 200 cm^3) giving a yellow solution which was filtered, concentrated to 10 cm^3, and cooled to —20 °C producing yellow crystals. The product was characterised by ^{1}H n.m.r. and i.r. spectroscopy and microanalysis. Yield 1.3 g, 24%.

Synthesis of [Mo(PMe$_3$)$_5$(CO)] **(13)** *and* cis-(Mo(PMe$_3$)$_4$(CO)$_2$] **(14)**.—Sodium sand (2.2 g) and PMe$_3$ (40 cm^3) at 77 K were treated with MoCl$_5$ (2.1 g, 7.7 mmol). The mixture was warmed to r.t. and carbon dioxide (2 atm) was added. The mixture was stirred at r.t. and the solution developed a red colour after 5 d, having passed through purple and green stages. The excess of trimethylphosphine was removed under reduced pressure and the solid products were extracted into light petroleum (b.p. 40—60 °C, 200 cm^3) giving a deep orange solution. This was filtered, concentrated to 30 cm^3, and cooled to −20 °C, producing yellow-brown crystals. The supernatant was separated, concentrated to 10 cm^3, and cooled to −80 °C, producing more crystals. The two batches of crystals were combined and dissolved in pentane (30 cm^3). The solution was concentrated to 10 cm^3 and cooled to −80 °C, giving yellow crystals. These were found to be a 2:1 mixture of [Mo(PMe$_3$)$_5$(CO)] and *cis*-[Mo(PMe$_3$)$_4$(CO)$_2$] and were identified by comparison of spectroscopic data with those of authentic samples.[59] The combined yield was *ca.* 80%. Both products could be sublimed onto a liquid-nitrogen-cooled probe at 120 °C and 10^{-2} mbar. A sample of the mixture was chromatographed on deactivated alumina (6% w/w water). Elution with diethyl ether gave *cis*-[Mo(PMe$_3$)$_4$(CO)$_2$] whilst [Mo(PMe$_3$)$_5$(CO)] did not pass through the column.

Carbonylpentakis(trimethylphosphine)tungsten, **(15)**.—Sodium sand (5.0 g) and PMe$_3$ (40 cm^3) at 77 K were treated with tungsten hexachloride (4.70 g, 11.8 mmol) and the mixture was warmed to r.t. under carbon dioxide (2.3 atm). After stirring at r.t. for 5 d the solution was yellow. The volatile materials were removed under reduced pressure and the residue was extracted into light petroleum (b.p. 40—60 °C, 200 cm^3). The yellow extract was filtered and the solvent was removed under reduced pressure. The yellow-brown residue was extracted into pentane (30 cm^3), and the solution was filtered. The solvent was removed from the filtrate under reduced pressure to yield a yellow-brown solid. Yield 3.5 g, 50%. The product was identified by ^{1}H n.m.r. and i.r. spectroscopy and analytical data.[53,60]

trans-*Dicarbonyltris(trimethylphosphine)iron*, **(16)**.—Sodium sand (2.5 g) and PMe$_3$ (30 cm^3) at 77 K was treated with anhydrous FeCl$_2$ (2.5 g, 19.7 mmol). The mixture was warmed to r.t. and carbon dioxide (2 atm) was added. The reaction mixture was stirred at r.t. for 6 d after which the solution was green. The volatile materials were removed under reduced pressure and the residue was extracted into light petroleum (b.p. 40—60 °C, 200 cm^3). The resultant green solution was filtered, concentrated to 100 cm^3, and cooled to —80 °C, producing green crystals. The supernatant was further concentrated to 50 cm^3 and cooled to −80 °C, producing a second batch of green crystals. Total yield 3.1 g, 46%. The product was characterised by ^{1}H n.m.r. and i.r. spectroscopy and microanalytical data.[61]

(Carbonato-OO′)carbonyltris(trimethylphosphine)ruthenium, **(17)**.—*Method A*. The compound [Ru(PMe$_3$)$_4$Cl$_2$] (1.9 g, 4.0 mmol) was dissolved in thf (70 cm^3) and transferred onto sodium amalgam (1% w/w Na). The mixture was charged with carbon dioxide (2.5 atm) and shaken at r.t. for 1 d. The resulting yellow solution was filtered and the volatile materials removed under reduced pressure giving a yellow oily solid which was extracted into light petroleum (b.p. 40—60 °C, 150 cm^3). The yellow extract was filtered and the solvent was removed under reduced pressure giving a yellow oily solid from which a white solid was sublimed at 70 °C and 10^{-4} mbar onto a probe cooled by liquid dinitrogen. The sublimate was warmed to r.t. and dissolved in thf (30 cm^3) giving a colourless solution from which the solvent was removed *in vacuo*. The resultant white solid was washed with light petroleum ether (b.p. 40—60 °C, 2 × 10 cm^3) and dissolved in thf (75 cm^3). The solution was filtered, concentrated to 30 cm^3, and cooled to −20 °C, producing white crystals. Yield 0.35 g, 21%.

Method B. Ruthenium atoms (0.55 g, 5.4 mmol), evaporated from one hearth of a 3.5 kW double-hearth reactor, were co-condensed with methyl formate (40 cm^3) over a period of 4 h during which the power was maintained at 4.2 kV and 200 mA. The walls of the glass jar were washed with hot thf (700 cm^3) giving a red solution containing a red solid. The solution was concentrated to 300 cm^3, filtered through a bed of Celite, and the solvent was removed under reduced pressure producing a red solid. Total yield of red solid 0.71 g. Trimethylphosphine (3 cm^3) was distilled *in vacuo* onto a suspension of the red solid (0.1 g) in thf (200 cm^3). The mixture was stirred at r.t. for 1 d, after which the initial deep red colour had been discharged. The volatile materials were removed under reduced pressure and the resultant white solid was washed with toluene (2 × 10 cm^3) and dissolved in hot thf (150 cm^3). The colourless solution was filtered, concentrated to 100 cm^3, and cooled to −20 °C, producing white crystals. Yield 0.12 g.

Table 3. Atomic co-ordinates for complex (**11**)

Atom	x/a	y/b	z/c
W(1)	0.0000	0.228 40(1)	0.2500
P(1)	0.168 60(6)	0.144 79(7)	0.2500
P(2)	0.0000	0.264 53(7)	0.430 17(6)
C(1)	0.203 4(2)	0.053 5(3)	0.351 0(2)
C(2)	0.274 5(3)	0.240 4(4)	0.2500
C(3)	0.105 6(3)	0.344 6(4)	0.474 9(3)
C(4)	0.0000	0.155 0(4)	0.519 9(3)
C(5)	0.0000	0.442 3(4)	0.2500
O(1)	0.082 5(2)	0.381 3(2)	0.2500
O(2)	0.0000	0.541 5(3)	0.2500
H(1)	0.273 9(2)	0.025 3(3)	0.340 8(2)
H(2)	0.200 8(2)	0.997 3(3)	0.413 0(2)
H(3)	0.155 1(2)	−0.009 3(3)	0.356 0(2)
H(4)	0.342 4(3)	0.203 6(4)	0.2500
H(5)	0.268 0(3)	0.287 0(4)	0.3100
H(6)	0.101 6(3)	0.355 6(4)	0.547 6(3)
H(7)	0.102 7(3)	0.417 0(4)	0.441 2(3)
H(8)	0.171 9(3)	0.307 3(4)	0.458 2(3)
H(9)	0.0620	0.109 3(4)	0.509 4(3)
H(10)	0.0000	0.184 3(4)	0.588 4(3)

Crystal Structure Determination.—Crystal data. $C_{13}H_{38}O_3P_4W$, $M = 550.2$, orthorhombic, $a = 13.162(3)$, $b = 12.248(3)$, $c = 13.611(3)$ Å, $U = 2\,194.2$ Å^3, space group *Cmcm*, $Z = 4$, $D_c = 1.67$ Mg m^{-3}, $F(000) = 1\,096$, $\lambda(\text{Mo-}K_{\alpha 1}) = 0.709\,30$ Å, $\mu(\text{Mo-K}_\alpha) = 56.72$ cm^{-1}, crystal dimensions $0.6 \times 0.55 \times 0.45$ mm, yellow tablet.

Data collection and processing. A crystal of complex (**11**) was sealed under dinitrogen in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer, the cell dimensions being obtained by least squares from the positions of 25 carefully centred reflections. Data collection was in the ω—2θ mode with scan width $(0.95 + 0.35 \tan\theta)°$. 7 886 Reflections were measured ($1 < \theta < 30.0°$), giving, after application of an absorption correction[63] and merging of equivalents [minimum, maximum corrections 1.0, 2.1; R (merge) = 0.028], 1 569 observed [$I > 3\sigma(I)$] to be used in structure solution and refinement.

Structure analysis and refinement. Solution was in the non-centric space group *Cmc*2, using the heavy-atom method. Refinement by full-matrix least squares with all non-hydrogen atoms anisotropic. Examination of packing revealed the true space group to be *Cmcm*. Many hydrogens were located but were included in calculated positions. They were allowed to refine riding on their parent carbon with an overall U_{iso} which refined to 0.100(7) Å^2. Corrections were made for anomalous dispersion[64] and isotropic extinction.[65] A modified Chebyshev weighting scheme was applied[66] with coefficients 11.44, −9.50, and 8.41 to give satisfactory agreement analyses. At convergence $R = 0.019$, $R' = 0.022$.

Solution and refinement used the Oxford CRYSTALS system[67] on the VAX 11/750 computer of the Chemical Crystallography Laboratory, Oxford University. Scattering factors were taken from ref 68. Fractional co-ordinates are given in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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