Contribution from the Inorganic Chemistry Laboratory
University of Oxford, United Kingdom

Molybdenum and Tungsten Complexes with Terdentate and Quadridentate Phosphorus Ligands

I.V. Howell[1] and L.M. Venanzi[2]

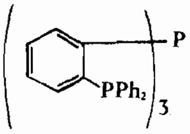
Received October 8, 1968

*The potentially quadridentate ligand, tris(*o*-diphenylphosphinophenyl)phosphine (QP), reacts with molybdenum and tungsten hexacarbonyls to give the complexes* $[M(CO)_3(QP)]$ *(M=Mo, W) in which QP acts as a terdentate ligand . These can be converted into the complexes* $[M(CO)_2(QP)]$ *in which QP acts as a quadridentate ligand. Oxidation of* $[W(CO)_2(QP)]$ *yields the seven-coordinate divalent species* $[WX(CO)_2(QP)]^+$ *(X=Cl, Br, I), which can be converted into the complexes* $[WX_2(CO)(QP)]$ *(X=Cl, Br, I). Oxidation of* $[Mo(CO)_2(QP)]$ *proceeds similarly but yields less stable products. The ligand bis(*o*-diphenylphosphinophenyl)phenylphosphine (TP) reacts with molybdenum and tungsten hexacarbonyls to yield the complexes* $[M(CO)_3(TP)]$ *(M=Mo, W). Mild oxidation of* $[W(CO)_3(TP)]$ *yields the species* $[WX(CO)_3(TP)]^+$ *(X=Br, I) or* $[WI_2(CO)_2(TP)]$ *depending on conditions used.* $[MoI_2(CO)_2(TP)]$ *was obtained from oxidation of* $[Mo(CO)_3(TP)]$*.*

Introduction

The substitution products of Group VI metal carbonyls (*i.e.* $[M(CO)_n(L)_{6-n}]$, M=Cr, Mo, W) have been widely studied.[3] Many complexes containing multidentate phosphorus and arsenic ligands have been isolated, and have been shown to give rise to a variety of products on mild oxidation. The following generalisations can be made: (1) Most of the oxidation products are seven-coordinate M^{II} species; (2) all the M^{I} species produced maintain the coordination number of the parent carbonyl compound; (3) complexes *cis*-$[M(CO)_2(diphos)_2]$ (M=Cr, Mo, W; diphos=$Ph_2PC_2H_4PPh_2$) give *trans*-$[M(CO)_2(diphos)_2]$[4] (4) chromium forms seven-coordinate complexes less readily than molybdenum and tungsten; (5) molybdenum complexes are more stable than their tungsten analogues.

The investigation of the oxidation reactions of complexes of chromium(0) with the multidentate ligands tris(*o*-diphenylphosphinophenyl)phosphine (QP), **1**, and bis(*o*-diphenylphosphinophenyl)phenylphosphine, (TP), **2**, showed that the mild oxidation of the complex $[Cr(CO)_2(QP)]$ gave six-coordinate chromium(I) derivatives of the type $[Cr(CO)_2(QP)]^+$.[5] It has also been reported that complexes *cis*-$[M(CO)_2(diphos)_2]$ (M=Cr, Mo, W) gave products of the type *trans*-$[M(CO)_2(diphos)_2]$. This contrasts the reaction of the analogous complexes with the chelating diarsine *o*-$(Me_2As)_2C_6H_4$ which on oxidation gives seven-coordinate M(II) derivatives of the type $[MX(CO)_2(diars)_2]^+$.[6]



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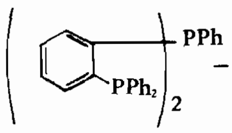

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As the complexes $[M(CO)_2(QP)]$ (M=Mo, W) cannot give, on oxidation, products of *trans*-configuration, it was of interest to study the products obtained from their oxidation.

Results and Discussion

The ligands QP and TP react with molybdenum and tungsten hexacarbonyls to give complexes of the type $[M(CO)_3(ligand)]$ (M=Mo, W; ligand=QP, TP). Complexes $[M(CO)_2(QP)]$ are obtained from the tricarbonyl derivatives by heating at *ca.* 240°C/0.1 mm. Some of the physical properties of the above complexes are given in Table I.

The reaction of $[W(CO)_2(QP)]$ with two equivalents of a suitable oxidizing agent gives seven-coordinate complexes $[WX(CO)_2(QP)]^+$ (X=Br from N-bromosuccinimide, X=I from iodine), which were isolated as their tetraphenylborates. Four equivalents of iodine yielded the complex $[WI(CO)_2(QP)]I_3$. Oxidation of $[W(CO)_2(QP)]$ with antimony pentachloride gave $[WCl(CO)_2(QP)]^+$ which, however, could not be obtained analytically pure. The physical properties of these compounds, supporting the above formulation, are given in Table I.

Treatment of $[WI(CO)_2(QP)]^+$ with sodium borohydride gives back $[W(CO)_2(QP)]$.

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(1) Present address: The British Petroleum Company Limited, B. P. Research Centre, Sunbury-on-Thames, Middlesex, England.
(2) Present address: The State University of New York at Albany, Albany, New York, 12203.
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Table I. Some Physical Properties of Molybdenum and Tungsten Complexes Containing QP and TP

Compound	Colour	Λ_M [a]	$\chi_{M(\text{corr})}$ [b]	CO stretches [c]
$[W(CO)_3(TP)]$	yellow	0.3	13	1940,1855, 1845
$[W(CO)_3(QP)]$	yellow	0.2	1	1945,1855 (sh) 1850
$[W(CO)_2(QP)]$	orange-red	0.25 [d]	−11	1860,1805
$[WBr(CO)_3(TP)][BPh_4]$	yellow	15.8	73	2050,1975, 1950
$[WI(CO)_3(TP)][BPh_4]$	orange	13.8	30	2045,1995, 1950
$[WI_2(CO)_2(TP)]$	brown	6.5	122	1935,1860
$[WBr(CO)_2(QP)][BPh_4]$	orange	16.0	22	2015,1960 [e]
$[WI(CO)_2(QP)][BPh_4]$	orange	15.4	38	2000,1950
$[WI(CO)_2(QP)]I_3$ [f]	yellow-brown	25.9	80	2000,1945
$[WCl_2(CO)(QP)]$	orange	7.5 [g]	75	1880 [e]
$[WBr_2(CO)(QP)]$	orange	5.0 [h]	110	1880 [e]
$[WI_2(CO)(QP)]$	orange-brown	25.4 [i]	154	1880 [e]
$[Mo(CO)_3(TP)]$	yellow	0.0	13	1960,1870, 1860 (sh)
$[Mo(CO)_3(QP)]$	yellow	0.6	8	1935,1870 (sh) 1860
$[Mo(CO)_2(QP)]$	orange	0.9 [d]	12	1875,1820
$[MoI_2(CO)_2(TP)]$	yellow	6.8	332	1940,1870
$[MoI(CO)_2(QP)][BPh_4]$	orange	14.8	47	2010,1965

[a] For 10^{-3} M nitrobenzene solutions at 20°C (mho. cm^2). [b] 10^6 χ_M (c.g.s. units) at room temperature. [c] In dichloromethane solution; sh = shoulder; in cm^{-1} units. [d] Slowly oxidised by the solvent with consequent increase of Λ_M with time. [e] In Nujol mulls. [f] Presence of tri-iodide ion confirmed by absorption maxima at 27,000 and 34,000 cm^{-1}. [g] For 0.36×10^{-3} M solution at 20°C; reading extrapolated to zero time. [h] For 0.66×10^{-3} M solution at 20°C; reading extrapolated to zero time. [i] Gives blue-green solution immediately, which turns yellow in *ca.* 20 min without significant change in conductivity.

Complexes of the type $[WX_2(CO)(QP)]$ can be prepared either by heating the compounds $[WX)CO)_2(QP)]X$ (X = Br, I) in vacuo at 130°C for 15 hr or by refluxing the compounds $[WX(CO)_2(QP)][BPh_4]$ (X = Cl, Br) with an excess of the appropriate lithium halide in diglyme. These complexes are less stable in solution than the corresponding dicarbonyl derivatives and, when dissolved in solvents such as dichloromethane and chloroform, undergo marked chemical changes as indicated by their infrared spectra in the carbonyl region. Thus, the complex $[WCl_2(CO)(QP)]$ dissolves in chloroform to give a yellow-orange solution with a band at 1895 cm^{-1} but this band is replaced over *ca.* 4 hr by two bands at 2015 and 1965 cm^{-1}. The bromo-complex dissolves in chloroform to give a yellow-brown solution with three bands at 2015, 1955, and 1905 cm^{-1}. The 1905 band vanishes over 10 to 15 min. The iodocomplex dissolves to give a deep blue solution with a single sharp peak at 1930 cm^{-1}. Over about 1 hr, the blue colour fades to leave a yellow solution with bands at 2005 and 1950 cm^{-1}. The positions of the new bands in chloroform solutions suggest that species of the type $[WX(CO)_2(QP)]X$ (X = Cl, Br, I) are formed together with materials containing no carbonyl groups (see experimental section). It has not proved possible as yet to elucidate fully the nature of these reactions. Other physical properties of the complexes $[WX_2(CO)(QP)]$ are given in Table I.

It is thus seen that the oxidation of the compounds yields seven-coordinate compounds and not six-coordinate species as isolated from the oxidation of $[W(CO)_2(diphos)_2]$. As in this compound, as well as in the corresponding QP derivative, the four phosphorus atoms occupy *cis*-positions, it appears likely that the different behaviour between the complexes of diphos and QP is due to the ability of the former to give rise to *trans*-$[W(CO)_2(diphos)_2]$. The rigid structure of the QP ligand prevents such a rearrangement in its complexes. However, the reason for the oxidative stability of *trans*-$[W(CO)_2(diphos)_2]$ is, as yet, not clear.

Molybdenum hexacarbonyl reacts with QP giving $[Mo(CO)_3(QP)]$, from which $[Mo(CO)_2(QP)]$ has been isolated. Oxidation of the latter product, as described for the tungsten analogues, gives seven-coordinate complexes $[MoX(CO)_2(QP)]^+$ from which products of the type $[MoX_2(CO)(QP)]$ have been obtained. The products characterised are given in Table I. The molybdenum complexes are very much less stable than their tungsten analogues and, it did not prove possible to isolate and characterise fully an extensive series of compounds.

The results obtained, however, confirm the expected full analogy in behaviour between molybdenum and tungsten.

The molybdenum and tungsten hexacarbonyls react with the terdentate ligand bis(*o*-diphenylphosphinophenyl)phenylphosphine, TP, to give $[Mo(CO)_3(TP)]$ (M = Mo, W). Some of their physical properties are listed in Table I. Their geometry, as well as that of the $[M(CO)_3(QP)]$ species, could not be established using infrared measurements for the reasons given elsewhere.[5] Electronic and steric considerations, however, suggest that they might have *cis*-configurations.

The oxidation of $[W(CO)_3(TP)]$ by iodine is critically dependent on the solvent used and the temperature conditions. In solution in dichloromethane-ethanol or in suspension in ethanol at 20°C, the complex is oxidised to the cation $[WI(CO)_3(TP)]^+$, which was isolated and characterised as the tetraphenylborate (see Table I). If, however, the reaction is carried out in benzene at 20°C, the reaction is slow, and $[WI_2(CO)_2(TP)]$ is obtained (see Table I). A Nujol mull of this species has two carbonyl bands in the infrared at 1935 and 1860 cm^{-1}, but, in chloroform or other polar solvents, two additional new peaks appear at 1975 and 1895 cm^{-1}, which do not alter in intensity over several hours. If the oxidation is carried out in ethanol at 50°C, these four peaks are again obtained. This evidence would seem to best be explained in terms of the formation of an equilibrium mixture of two isomers of the complex [$WI_2(CO)_2(TP)$] in polar solvents.

The bromination reaction is also critically dependent on the conditions used. If the complex in solution in dichloromethane or in suspension in ethanol is treated with two equivalents of N-bromosuccinimide in acetone at 0°C and sodium tetraphenylborate in ethanol is added to the solution obtained, a yellow precipitate of [$WBr(CO)_3(TP)$][BPh_4] is obtained. (No precipitate is formed if the reaction is carried out at room temperature or at –20°C). If the oxidation is effected using bromine in toluene at 0°C, a yellow precipitate is formed. The infrared spectrum indicates that this species could be [$WBr(CO)_3(TP)$]Br, but all attempts to convert this to the complex [$WBr_2(CO)_2(TP)$] resulted in decomposition.

As noted with the QP complexes, the molybdenum compounds are considerably less stable than their tungsten analogues. The only derivative which could be isolated was [$MoI_2(CO)_2(TP)$], which has very similar properties to its tungsten counterpart. When isolated from benzene solution, this complex has one molecule of benzene of recrystallization associated with it, but this can be removed by heating the sample at 130 °C in vacuo. The heating is, however, accompanied by some decomposition to yield small amounts of a green paramagnetic species, as indicated by magnetic data.

Experimental Section

The phosphorus ligands were prepared as described elsewhere.[7]

Tricarbonylbis (o-*diphenylphosphinophenyl*) *phenylphosphinetungsten*(0). TP (0.95 g) and resublimed tungsten hexacarbonyl (0.56 g) were irradiated in refluxing di-*n*-butyl ether (50 ml) under nitrogen for 12 hr. The solvent was removed by rotary evaporation, and the product recrystallized from benzene–heptane as yellow crystals (1.23 g), which were dried *in vacuo* at 175°C. (Calcd. for $C_{45}H_{33}O_3P_3W$: C, 60.15; H, 3.7%. Mol. Wt. 899. Found: C, 60.35; H, 3.8%. Mol. Wt. in benzene 920).

Tricarbonyltris(o-*diphenylphosphinophenyl*)*phosphinetungsten*(0). QP (1.63 g) and resublimed tungsten hexacarbonyl (0.96 g) were irradiated in refluxing di-*n*-butyl ether (50 ml) under nitrogen for 15 hr. The solvent was removed by rotary evaporation, and the product dissolved in benzene (100 ml) and filtered. The solution was reduced to 20 ml, and added to a chromatographic column of silica gel (55 cm x 2.5 cm diameter). The required product was eluted with benzene, and recrystallized from benzene—heptane as yellow crystals, (1.78 g), which were dried *in vacuo* at 175°C. (Calcd. for $C_{57}H_{42}O_3P_4W$: C, 63.2; H, 4.0%. Mol. Wt. 1083. Found: C, 63.15; H, 3.9%. Mol. Wt. in benzene 1118).

Dicarbonyltris(o-*diphenylphosphinophenyl*)*phosphinetungsten*(0). The complex [$W(CO)_3(QP)$] (1.6 g) was heated at 245°C/0.05 mm for 72 hr. The product was recrystallized from benzene—heptane as orange-red crystals (1.0 g), and dried *in vacuo* at 200°C. (Calcd. for $C_{56}H_{42}O_2P_4W$: C, 63.8; H, 4.0%. Mol. Wt. 1055. Found: C, 63.9; H, 4.2%. Mol. Wt. in benzene 1097).

Bromotricarbonylbis(o-*diphenylphosphinophenyl*)*phenylphosphinetungsten*(*II*) *Tetraphenylborate*. The complex [$W(CO)_3(TP)$] (0.30 g) suspended in ethanol (30 ml) was treated with N-bromosuccinimide (0.12 g) in acetone (10 ml) and ethanol (20 ml) under nitrogen with vigorous stirring for 1 hr at 0°C. The resulting yellow solution was filtered, and a filtered solution of sodium tetraphenylborate (0.50 g) in ethanol (20 ml) was added with vigorous stirring. The yellow precipitate (0.30 g) was filtered off, washed well with ethanol, and dried *in vacuo*. (Calcd. for $C_{69}H_{53}BBrO_3P_3W$: C, 63.9; H, 4.1; Br, 6.15%. Found: C, 63.7; H, 4.1; Br, 6.3%).

Iodotricarbonylbis(o-*diphenylphosphinophenyl*)*phenylphosphinetungsten*(*II*) *Tetraphenylborate*. The complex [$W(CO)_3(TP)$] (0.225 g) in dichloromethane (15 ml) was treated with iodine (0.063 g) in ethanol (25 ml) with vigorous stirring under nitrogen for 30 min. Sodium tetraphenylborate (0.50 g) in ethanol (25 ml) was added with rapid stirring, and a further 15 ml of ethanol added. The precipitate was filtered off, recrystallized from dichloromethane—ethanol as a fine orange powder, and dried *in vacuo*. Yield 0.15 g. (Calcd. for $C_{69}H_{53}BIO_3P_3W$: C, 61.6; H, 4.0; I, 9.45%. Found: C, 61.45; H, 4.0; I, 9.6%).

Di-iododicarbonylbis(o-*diphenylphosphinophenyl*)*phenylphosphinetungsten*(*II*) *Tetraphenylborate*. To a vigorously stirred solution of [$W(CO)_3(TP)$] (0.225 g) in benzene (50 ml), a solution of iodine (0.063 g) in benzene (40 ml) was added under nitrogen over 1 hr at room temperature. The red-orange solution was stirred for 24 hr, and the yellow-orange precipitate filtered off, washed with heptane, and dried *in vacuo* at 130°C. Yield 0.21 g. During drying, the complex lost benzene of recrystallization and turned brown. (Calcd. for $C_{44}H_{33}I_2O_2P_3W$: C, 47.0; H, 2.95; I, 22.6%. Found: C, 47.0; H, 3.2; I, 22.4%).

Bromodicarbonyltris(o-*diphenylphosphinophenyl*)*phosphinetungsten*(*II*) *Tetraphenylborate*. The complex [$W(CO)_2(QP)$] (0.20 g) suspended in ethanol (20 ml) was treated with a solution of N-bromosuccinimide (0.070 g) in acetone (10 ml) with vigorous stirring at room temperature over 10 min. The solution was filtered, and a solution of sodium tetraphenylborate (0.50 g) in ethanol (15 ml) added with vigorous stirring. The orange precipitate was recrystallized from dichloromethane-ethanol as orange crystals, and dried *in vacuo*. Yield 0.19 g. (Calcd. for $C_{80}H_{62}BBrO_2P_4W$: C, 66.1; H, 4.3; Br, 5.5%. Found: C, 66.3; H, 4.3; Br, 5.8%).

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*Iododicarbonyltris(*o*-diphenylphosphinophenyl)phosphinetungsten(II) Tetraphenylborate.* The complex $[W(CO)_2(QP)]$ (0.20 g) in dichloromethane (10 ml) was treated with a solution of iodine (0.048 g) in ethanol (30 ml) over 10 min with good stirring. Sodium tetraphenylborate (0.50 g) in ethanol (10 ml) was added with vigorous stirring, and the orange precipitate filtered off, recrystallized from dichloromethane—ethanol as orange crystals (0.19 g), and dried *in vacuo.* (Calcd. for $C_{80}H_{62}BIO_2P_4W$: C, 64.0; H, 4.2; I, 8.45%. Found: C. 63.9; H, 4.15; I, 8.6%).

*Iododicarbonyltris(*o*-diphenylphosphinophenyl)phosphinetungsten(II) Tri-iodide.* (A suspension of $[W(CO)_2(QP)]$ (0.21 g) in ethanol (10 ml) was treated with iodine (0.11 g) in ethanol (20 ml) with vigorous stirring under nitrogen for 15 min at room temperature. A clear solution was formed from which a yellow-brown solid precipitated. This was filtered off, washed with a little ethanol, and dried *in vacuo* at 110°C. Yield 0.22 g. During drying, the compound turned green and lost a little iodine. The yellow-brown colour returned over 24 hr. (Calcd. for $C_{56}H_{42}I_4O_2P_4W$: C, 43.05; H, 2.7; I, 32.6. Found: C, 43.0; H, 2.9; I, 32.4%).

*Dichlorocarbonyltris(*o*-diphenylphosphinophenyl)phosphinetungsten(II).* The complex $[W(CO)_2(QP)]$ (0.50 g) in chloroform (10 ml) was treated with a solution of antimony pentachloride in chloroform (10 ml of 0.047 *M*) with vigorous stirring at room temperature over 10 min. The solution was stirred for a further 20 min, and then ethanol (50 ml) was added, and stirring continued for a further 30 min. The solution was filtered, and sodium tetraphenylborate (1.0 g) in ethanol (10 ml) added. The orange-yellow precipitate was filtered off and recrystallized from dichloromethane—ethanol. The product (0.27 g) was refluxed in dry diglyme (30 ml) with anhydrous lithium chloride (2.7 g) with vigorous stirring under nitrogen for 4 hr. The red solution was evaporated to dryness by rotary evaporation, and the residue extracted with benzene. The product (0.095 g) was obtained as an orange powder after addition of heptane, and was dried *in vacuo* at 130°C. (Calcd. for $C_{55}H_{42}Cl_2OP_4W$: C, 60.2; H, 3.9; Cl, 6.45%. Found: C, 60.0; H, 3.9; Cl, 6.25%).

*Dibromocarbonyltris(*o*-diphenylphosphinophenyl)phosphinetungsten(II).* The complex $[W(CO)_2(QP)]$ (0.21 g) in dichloromethane (10 ml) was treated with N-bromosuccinimide (0.071 g) in acetone (10 ml) with vigorous stirring at room temperature over 10 min. The solvents were removed by rotary evaporation, and the residue extracted with warm ethanol, from which it was precipitated after addition of heptane as an orange powder (0.15 g). The product was heated *in vacuo* at 130°C for 16 hr, which resulted in the loss of one mole of carbon monoxide. (Calcd. for $C_{55}H_{42}Br_2OP_4W$: C, 55.7; H, 3.6; Br, 13.5%. Found: C, 55.4; H, 3.8; Br, 13.8%).

The complex $[WBr_2(CO)(QP)]$ (0.05 g) was dissolved in bromoform (10 ml) and the solution allowed to stand for 1 hr. The carbonyl peak at 1895 cm^{-1} was replaced by two new bands at 2010 and 1955 cm^{-1}. The solvent was evaporated to dryness, and the solid (which, in a Nujol mull, had carbonyl peaks at 2005 and 1945 cm^{-1} together with some $P=O$ and $W=O$ bands) was extracted with acetone and precipitated with heptane. The yellow precipitate was heated *in vacuo* at 130°C for 6 hr. The infrared spectrum of the product now had a single carbonyl peak at 1890 cm^{-1}. A chloroform solution of this material rapidly developed two bands at 2010 and 1955 cm^{-1} to replace that at 1895 cm^{-1}. It seems likely that the species $[WBr_2(CO)(QP)]$ disproportionates in solution to give $[WBr(CO)_2(QP)]Br$, which on heating is reconverted to $[WBr_2(CO)(QP)]$, together with some material containing no carbonyl groups.

*Di-iodocarbonyltris(*o*-diphenylphosphinophenyl)phophosphinetungsten(II).* A suspension of the complex $[W(CO)_2(QP)]$ (0.21 g) in ethanol (30 ml) was treated with iodine (0.050 g) in ethanol (30 ml) with vigorous stirring over 30 min at room temperature. The mixture was warmed to 50°C, filtered, and the product obtained as a pale orange powder (0.14 g) after the addition of heptane, and was dried *in vacuo* at 130°C for 16 hr. The product darkened during heating and lost one mole of carbon monoxide. (Calcd. for $C_{55}H_{42}I_2OP_4W$: C, 51.6; H, 3.3; I, 19.8%. Found: C, 51.45; H, 3.4; I, 19.65%).

*Tricarbonylbis(*o*-diphenylphosphinophenyl)phenylphosphinemolybdenum(0).* TP (0.95 g) and resublimed molybdenum hexacarbonyl (0.41 g) were refluxed in dry di-*n*-butyl ether (50 ml) under nitrogen for 3½ hr. The solvent was removed by rotary evaporation, and the product recrystallized from benzene—heptane as golden-yellow crystals (0.92 g), and dried *in vacuo* at 175°C. (Calcd. for $C_{45}H_{33}MoO_3P_3$: C, 66.7; H, 4.1; P, 11.5%. Found: C, 67.0; H, 4.3; P, 11.4%).

*Tricarbonyltris(*o*-diphenylphosphinophenyl)phosphinemolybdenum(0).* QP (0.41 g) and resublimed molybdenum hexacarbonyl (0.14 g) were refluxed in dry di-*n*-butyl ether (50 ml) under nitrogen for 3 hr. The solvent was removed by rotary evaporation, and the product recrystallized from benzene—heptane as a yellow powder (0.40 g), which was dried *in vacuo* at 130°C. (Calcd. for $C_{57}H_{42}MoO_3P_4$: C, 68.8; H, 4.25; P, 12.45%. Found: C, 68.4; H, 4.45; P, 12.35%).

*Dicarbonyltris(*o*-diphenylphosphinophenyl)phosphinemolybdenum(0).* The complex $[Mo(CO)_3(QP)]$ (1.8 g) was heated at 235°C/0.05 mm for 15 hr, and the product recrystallized from benzene—heptane as orange-red crystals (1.1 g), which were dried *in vacuo* at 200°C. Calcd. for $C_{56}H_{42}MoO_2P_4$: C, 69.4; H, 4.4; P, 12.8. Found: C, 69.15; H, 4.4; P, 12.7%).

*Di-iododicarbonylbis(*o*-diphenylphosphinophenyl)phenylphosphinemolybdenum(II).* To a vigorously stirred solution of $[Mo(CO)_3(TP)]$ (0.27 g) in benzene (50 ml), a solution of iodine (0.085 g) in benzene (40 ml) was added over 14 min under nitrogen at room temperature. A deep red solution was formed, and this soon darkened to an intense brown. Stirring was continued for a further 15 hr, and the yellow-orange precipitate was filtered off, washed with benzene (10 ml), and dried *in vacuo* at room temperature. Yield 0.20 g Calcd. for $C_{50}H_{39}I_2MoO_2P_3$ ($[MoI_2(CO)_2(TP)] . C_6H_6$): C, 53.8; H, 3.5; I, 22.8;

P, 8.35%. Found: C, 53.5; H, 3.5; I, 21.5; P, 8.35%). When this material was heated *in vacuo* at 130°C, it lost weight and turned green, but the original yellow colour returned over a few hr in air. (Calcd. for $C_{44}H_{33}I_2MoO_2P_3$: C, 51.0; H, 3.2; I, 24.5;, P, 9.0%. Found: C, 51.1; H, 3.35; I, 23.7; P, 8.85%).

*Iododicarbonyltris(*o*-diphenylphosphinophenyl)phosphinemolybdenum(II) Tetraphenylborate.* Since analytical data on the product obtained by the same method as that used for the analogous tungsten complex suggested that the final product coprecipitated with sodium iodide, the following modified procedure was adopted. The complex [$Mo(CO)_2(QP)$] (0.30 g) in suspension in ethanol (30 ml) was treated with a solution of iodine (0.076 g) in ethanol (20 ml) over 10 min, with good stirring, under nitrogen at room temperature. Acetone (10 ml) was added to aid solution of the product, and then silver nitrate (0.060 g) in water (1 ml) and ethanol (20 ml) were added with good stirring over 10 min. The silver iodide precipitate was filtered off, and a solution of sodium tetraphenylborate (0.50 g) in ethanol (20 ml) added to the filtrate with vigorous stirring. The precipitate was filtered off, extracted with acetone, filtered through a fine filter paper, and obtained as an orange-yellow powder by concentrating the solution by rotary evaporation after the addition of ethanol. The complex (0.16 g) was filtered off, washed with ethanol, and dried *in vacuo* at room temperature. (Calcd. for $C_{80}H_{56}BIMoO_2P_4$: C, 68.0; H, 4.4; I, 9.0; P, 8.8%. Found: C, 67.8; H, 4.5; I, 8.8; P, 8.65%). During drying, the complex turned green, but returned to its original orange-yellow colour over 24 hr.

Analyses and Physical Measurements. These were performed as described elsewhere.[8]

Acknowledgements. The authors thank the Royal Society for a grant-in-aid for the purchase of chemicals and the British Petroleum Company Limited for a studentship (to I.V.H.).

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