Transition-metal Complexes Containing Phosphorus Ligands. Part VII.[1] New and Improved Syntheses of Some Triphenylphosphine Complexes of Rhodium, Iridium, Ruthenium, and Osmium

By **N. Ahmad, S. D. Robinson,* and M. F. Uttley**, Department of Chemistry, King's College, Strand, London WC2R 2LS

Previously reported, convenient, single-stage syntheses for important hydride, carbonyl, and nitrosyl containing triphenylphosphine complexes of the platinum group metals have been further improved by use of ethanolic potassium hydroxide or triethylamine in place of sodium borohydride as basic reducing agent. The technique has also been extended to include convenient new syntheses for the ruthenium and osmium triphenylphosphine derivatives. *cis*-$RuCl_2(CO)_2(PPh_3)_2$, $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$. The stereochemistry of these last-named complexes is discussed. Attempts to extend this mode of synthesis to include derivatives of other triarylphosphines are described. New complexes synthesised include $Rh(NO)L_3$[L = $P(p\text{-}C_6H_4Cl)_3$ and $P(p\text{-}C_6H_4Me)_3$] and $Ru(CO)_3L_2$ [L = $P(p\text{-}C_6H_4Me)_3$ and $P(p\text{-}C_6H_4OMe)_3$].

In a previous publication [2] we described a technique for the convenient, single-stage synthesis of numerous triphenylphosphine derivatives of the platinum metals containing carbonyl, nitrosyl, or hydride ligands. We now report improvements and extensions to these syntheses; in particular we describe alternative, more convenient and efficient reagents capable of replacing sodium borohydride in these reactions. The efficiency of a series of base–alcohol reducing systems involving sodium carbonate, sodium formate, triethylamine and potassium hydroxide was examined. Potassium hydroxide–alcohol was found to be a particularly effective reducing system and its use permitted extension of our general technique to include simple, convenient syntheses of several important osmium carbonyl hydride derivatives, previously accessible only by much more tedious routes. We also sought extension of the syntheses to include preparation of platinum group metal complexes containing other triarylphosphine ligands. Only a small proportion of the large number of syntheses attempted using these latter phosphines gave the desired products in satisfactory yield and purity. The remaining syntheses were unsatisfactory for a variety of reasons including poor yields, irreproducibility, and formation of impure or mixed products. No single reason can be cited for these failures; however, solubility differences, arising from changes in the triarylphosphine employed, are expected to influence the course of these solubility-controlled reactions and are therefore probably a major contributory factor.

Synthesis.—The literature relating to previous syntheses of *cis*-$RuCl_2(CO)_2(PPh_3)_2$, $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$ is summarised below; similarly surveys for other complexes mentioned in this work were provided in our earlier paper [2] on synthesis technique and are, therefore, not repeated here.

The *cis*-isomer of $RuCl_2(CO)_2(PPh_3)_2$ synthesised in this work has previously been prepared by reaction of various ruthenium carbonyl halide species including $[RuCl_2(CO)_2]_n$,[3] $[RuCl_4(CO)_2]^{2-}$,[4] and $RuCl_2(CO)_3$(tetrahydrofuran) [5] with triphenylphosphine. The same complex has also been obtained by carbonylation of $RuCl_2(PPh_3)_4$.[6] Several other *cis*- and *trans*-isomers have also

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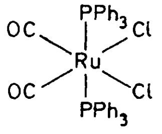
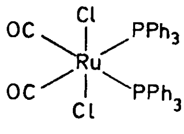
been reported. The new single-step synthesis, which involves formation of $Ru(CO)_3(PPh_3)_2$ and subsequent reaction *in situ* with carbon tetrachloride, affords the required complex in high yield and purity. The osmium triphenylphosphine derivatives discussed in this paper have all been characterised previously. $OsHCl(CO)(PPh_3)_3$ was first prepared by Vaska [7,8] and was subsequently correctly formulated as a carbonyl hydride derivative of osmium(II).[9,10] Synthesis was first achieved by prolonged reaction of ammonium chloro-osmate(IV) and triphenylphosphine in a high-boiling alcoholic solvent, and this technique is in current use.[11] The carbonyl dihydride, $OsH_2(CO)(PPh_3)_3$, has previously been obtained by a two-step process involving treatment of the hydridochloride, $OsHCl(CO)(PPh_3)_3$, with alcoholic base.[12] The dicarbonyldihydride, $OsH_2(CO)_2(PPh_3)_2$, has previously been prepared [13] by reacting preformed $OsH_2(CO)_4$ with triphenylphosphine in refluxing tetrahydrofuran for 12 hours; it has also been obtained [13] in 50% yield by high-pressure hydrogenation of $Os(CO)_3(PPh_3)_2$. The new syntheses described below offer a substantial improvement in speed and efficiency over those currently available. In each case solutions of sodium chloro-osmate, formaldehyde, and, if required, potassium hydroxide are added to a vigorously stirred, boiling solution of triphenylphosphine in 2-methoxyethanol. The syntheses of $OsH_2(CO)(PPh_3)_3$ and $OsH_2(CO)_2(PPh_3)_2$ are performed under very similar conditions; use of a large excess of triphenylphosphine suppresses carbonylation and affords the former, while the latter is prepared in the presence of excess of aqueous formaldehyde and a deficiency of phosphine. The synthesis of $Ru(NO)_2(PPh_3)_2$ by the single-step technique affords the best results when triethylamine rather than potassium hydroxide is used in place of sodium borohydride. Many of the other syntheses described in this paper will also proceed, though usually somewhat less efficiently, when potassium hydroxide is replaced by sodium carbonate, sodium formate, or triethylamine. The apparatus and general technique employed in these syntheses are essentially identical with those described in our previous publication.[2] Minor modifications leading to improved yield or purity for certain products are given in the Experimental section. Once again we stress the importance of achieving and maintaining homogeneous reaction conditions wherever possible by efficient stirring and rapid, successive addition of reagents.

Structural features.—Evidence concerning structure and stereochemistry of the ruthenium derivatives, *cis*-$RuCl_2(CO)_2(PPh_3)_2$, and the osmium derivatives $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$ is discussed below; similar discussion relating to other complexes mentioned in this work was given in our previous paper [2] and is, therefore, not repeated here.

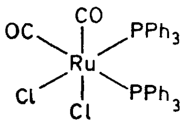
The ruthenium dicarbonyl complex, $RuCl_2(CO)_2(PPh_3)_2$ may exist in five stereoisomeric forms; three of these (IA)—(IC) possess a pair of *cis*-carbonyl ligands. The isomer prepared in our synthesis [ν(CO) 2065(s) 1998(s) cm^{-1}] has previously been assigned structures (IA),[6] and (IB),[3] on the basis of circumstantial evidence derived from dipole moment and proton n.m.r. data.



(IA)



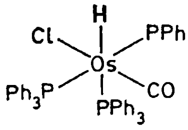
(IB)



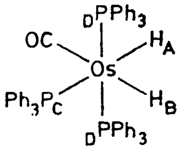
(IC)

However a more recent paper [14] assigns stereochemistry (IA) to a new *cis*-dicarbonyl isomer, $RuCl_2(CO)_2(PPh_3)_2$ [ν(CO) 2043 and 1979 cm^{-1} (CH_2Cl_2)], and proposes stereochemistry (IB) or (IC) for the isomer identical with that prepared in the present study.

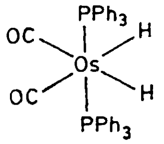
The high-field n.m.r. spectrum of the osmium complex, $OsHCl(CO)(PPh_3)_3$, recorded here for the first time, shows a doublet of triplets [$J(P_tH) = 87{\cdot}0$ Hz; $J(P_cH) = 24{\cdot}5$ Hz] centred at τ 16·27; this data confirms for $OsHCl(CO)(PPh_3)_3$ in solution, a structure (II) similar to that found [15] by *X*-ray crystallography for the related bromo-derivative in the solid state.

(II)


The high-field n.m.r. spectrum of $OsH_2(CO)(PPh_3)_3$ comprises two first-order patterns of 12 lines each and confirms the stereochemistry (III) previously suggested on the basis of i.r. data alone.[12] The structure (IV) has previously been proposed for $OsH_2(CO)_2(PPh_3)_2$ on the basis of high-field n.m.r. data [triplet τ 17·65, $J(PH) = 23$ Hz].[13] Our n.m.r. data for this complex [triplet τ

(III)


H_A τ 18·91: $J(P_CH_A)$ 69·5 Hz
$J(P_DH_A)$ 28·5 Hz
$J(H_AH_B)$ 4·7 Hz
H_B τ 17·34; $J(P_CH_B)$ 16·5 Hz
$J(P_DH_B)$ 28·5 Hz



(IV)

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17·08, J(PH) = 22·75 Hz] differ slightly from those previously recorded but confirm the stereochemistry suggested.

EXPERIMENTAL

Microanalyses were performed by Dr. Strauss at Oxford and Dr. Bernhardt at Mulheim, Germany. I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 457 grating spectrometer and calibrated using polystyrene film. N.m.r. spectra were recorded on a Varian HA 100 spectrometer. Melting points were all accompanied by a degree of decomposition and were measured in air (Kofler hot stage) and in a sealed capillary under nitrogen (Buchi melting point apparatus). Platinum metal salts were purchased from Johnson Matthey; hydrated ruthenium trichloride was used as purchased and may have contained appreciable amounts of ruthenium(IV) species. Other reagents and solvents were purchased from B.D.H. and used without further purification.

All reactions were performed under oxygen-free nitrogen.

Preparation of Complexes.—General observations. The success of the following preparations depends, in almost every instance, upon the maintenance of essentially homogeneous reaction conditions until precipitation of product occurs and reaction is complete. This requires the addition of the various reagent solutions *rapidly* and *successively* to the vigorously boiling reaction mixture, and failure to observe this precaution leads to precipitation of insoluble intermediates which may fail to react further, and thus contaminate the product. The reactions are conveniently performed in a 250 ml conical flask fitted with a condenser, a nitrogen inlet, and a port for introduction of reagent solutions. The reaction solutions are stirred magnetically. The products were frequently deposited in an analytically and spectroscopically pure state, and were merely washed; further purification was achieved where necessary by application of literature methods. The use of these reactions for large-scale syntheses has not been investigated; difficulties in achieving and maintaining homogeneous reaction conditions may be encountered when attempting to scale up the preparations.

Rhodium Complexes.—Hydridotetrakis(triphenylphosphine)rhodium. Solutions of hydrated rhodium trichloride (0·26 g, 1·0 mmol) in warm ethanol (20 ml) and potassium hydroxide (0·4 g) in warm ethanol (20 ml) were added in rapid succession to a vigorously stirred solution of triphenylphosphine (2·62 g, 10 mmol) in boiling ethanol (80 ml). The mixture was heated under reflux for 10 min, cooled to 30°, filtered, and the precipitate washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give the required product as yellow microcrystals (0·88 g, 77%), m.p. 145—147° in air, 154—156° under nitrogen (Found: C, 74·7; H, 5·3; P, 10·5. Calc. for $C_{72}H_{61}P_4Rh$: C, 75·0; H, 5·35; P, 10·75%).

Hydridocarbonyltris(triphenylphosphine)rhodium. A solution of hydrated rhodium trichloride (0·26 g, 1·0 mmol) in ethanol (10 ml) was added to a vigorously stirred solution of triphenylphosphine (2·62 g, 10 mmol) in boiling ethanol (100 ml). After a delay of 15—20 s, aqueous formaldehyde (10 ml, 40% w/v soln.) and a solution of potassium hydroxide (0·8 g) in ethanol (20 ml) were added rapidly and successively to the vigorously stirred, boiling reaction mixture and the whole was heated under reflux for 10 min; it was then allowed to cool to 30°. The crystalline product was filtered off and washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give yellow microcrystals (0·85 g, 94%), m.p. 120—122° in air, and 172—174° under nitrogen (Found: C, 72·1; H, 5·15; P, 9·85. Calc. for $C_{55}H_{46}OP_3Rh$: C, 71·9; H, 5·05; P, 10·1%).

Nitrosyltris(triphenylphosphine)rhodium. Solutions of hydrated rhodium trichloride (0·13 g, 0·5 mmol) in ethanol (10 ml) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·2 g) in ethanol (50 ml) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylphosphine (1·31 g, 5 mmol) in ethanol (40 ml). The mixture was boiled for a further 2 min, cooled to 30°, filtered, and the precipitate washed with ethanol, water, ethanol and finally n-hexane; it was then dried *in vacuo* to give the required product as red crystals (0·43 g, 95%), m.p. 160° in air, 205—206° under nitrogen (Found: C, 70·6; H, 4·7; P, 10·35; N, 1·5. Calc. for $C_{54}H_{45}NOP_3Rh$: C, 70·45; H, 4·75; P, 9·85; N, 1·4%.

*Nitrosyltris(tri-*p*-tolylphosphine)rhodium.* This complex was similarly prepared using tri-*p*-tolylphosphine; after evaporation of the reaction solution to small volume under nitrogen it deposited the compound as dark red microprisms (60%), ν(NO) 1602 cm^{-1}, m.p. 140—143° in air, 208—209° under nitrogen (Found: C, 72·1; H, 6·2; N, 1·55; P, 8·6. $C_{63}H_{63}NOP_3Rh$ requires C, 72·35; H, 6·05; N, 1·35; P, 8·9%).

*Nitrosyltris(tri-*p*-chlorophenylphosphine)rhodium.* This complex was similarly prepared using tri-*p*-chlorophenylphosphine; it was deposited from the reaction solution as red-brown *microcrystals* (80%) ν(NO) 1598 cm^{-1}, m.p. 100—106° in air (Found: C, 52·45; H, 3·15; N, 1·3;. $C_{54}H_{36}Cl_9NOP_3Ph$ requires C, 52·61; H, 2·95; N, 1·15%).

Iridium Complexes mer- *and* fac-*Trihydridotris(triphenylphosphine)iridium.*—Sodium hexachloroiridate (1·68 g, 3·0 mmol) was dissolved in ethanol (30 ml) with gentle warming; the solution was then filtered. The filtrate and a solution of sodium borohydride (0·6 g) in ethanol (60 ml) were added in rapid succession to a boiling solution of triphenylphosphine (6·3 g, 24 mmol) in ethanol (240 ml). *There was much frothing and evolution of hydrogen on addition of the sodium borohydride solution.* The mixture was heated under reflux for 15 min and then allowed to cool to 55°; it was immediately filtered. The filtrate was retained for subsequent isolation of the *fac*-isomer.

The precipitated, impure *mer*-isomer was washed with ethanol (55°), water, ethanol, and finally n-hexane and then dried *in vacuo*. Traces of *fac*-isomer were removed by boiling the complex in a small volume of ethanol and filtering the suspension at the boiling point. Microcrystals of pure *mer*-isomer were dried *in vacuo* (1·04 g, 36%), m.p. 192—193° in air 228—230° sealed under nitrogen (Found: C, 65·9; H, 5·1; P, 9·3. Calc. for $C_{54}H_{48}IrP_3$: C, 66·05; H, 4·95; P, 9·45%). *mer*-Trihydridotris(triphenylphosphine)iridium may be further recrystallised from benzene–methanol when it forms a 1 : 1 benzene adduct (Found: C, 67·8; H, 5·15; P, 8·3. Calc. for $C_{60}H_{54}IrP_3$: C, 67·95; H, 5·15; P, 8·75%).

The filtrate retained from the synthesis of *mer*-$IrH_3(PPh_3)_3$ was concentrated under reduced pressure to obtain the *fac*-isomer. The crude material thus deposited was washed with ethanol, water, and ethanol then, repeatedly, with hot n-hexane; it was finally dried *in vacuo* to afford *fac*-$IrH_3(PPh_3)_3$, practically free from *mer*-isomer (yield 1·31 g, 45%). Recrystallisation from benzene–methanol yielded pure *fac*-trihydridotris(triphenylphosphine)iridium as white microcrystals, m.p. 168—171° in air, 208—218° sealed under nitrogen (Found: C, 65·85; H, 4·9; P, 9·05. Calc. for $C_{54}H_{48}IrP_3$: C, 66·05; H, 4·95; P, 9·45%).

Hydridocarbonyltris(triphenylphosphine)iridium. Solutions of sodium hexachloroiridate (0·84 g, 1·5 mmol) in warm 2-methoxyethanol (30 ml), aqueous formaldehyde (15 ml, 40% w/v soln.), and potassium hydroxide (0·5 g) in 2-methoxyethanol (30 ml) were added in rapid succession to a vigorously stirred, boiling solution of triphenylphosphine (2·37 g, 9·0 mmol) in 2-methoxyethanol (90 ml). The solution was heated under reflux for 15 min, allowed to cool, and then diluted with methanol (20 ml). The crystalline product was filtered off, washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* (1·35 g, 95%), m.p. 166—167° in air, 216—218° sealed under nitrogen (Found: C, 65·6; H, 4·75; P, 9·05. Calc. for $C_{55}H_{46}IrOP_3$: C, 65·53; H, 4·6; P, 9·2%).

*Hydridocarbonyltris(tri-*p*-tolylphosphine)iridium.* This complex was similarly prepared using tri-*p*-tolylphosphine and was induced to crystallise from the reaction solution by addition of a small volume of water. The precipitated product was washed with water followed by minimal volumes of ethanol and n-hexane; it was then dried *in vacuo* to give yellow microcrystals (50%); ν(IrH) 2060m and ν(CO) 1925vs cm^{-1}; m.p. 141—142° in air 162—163° under nitrogen (Found: C, 68·35; H, 5·9; P, 8·0. $C_{64}H_{64}IrOP_3$ requires C, 67·75; H, 5·7; P, 8·2%).

Ruthenium Complexes.—Dichlorodicarbonylbis(triphenylphosphine)ruthenium (*cis*-carbonyl ligands). To a boiling solution of triphenylphosphine (0·78 g, 3·0 mmol) in 2-methoxyethanol (20 ml) were added successively a solution of hydrated ruthenium trichloride (0·13 g, 0·5 mmol) in 2-methoxyethanol (10 ml), aqueous formaldehyde (5 ml, 40% w/v soln.), potassium hydroxide (0·2 g) in 2-methoxyethanol (10 ml) and, finally, neat carbon tetrachloride (5 ml). The mixture was heated under reflux for 30 min, cooled, and diluted with methanol (30 ml). The precipitated product was washed with ethanol, water, and ethanol, and then recrystallised from dichloromethane–methanol to give white crystals (0·255 g, 68%), m.p. 233—236° in air (Found: C, 60·65; H, 4·25; P, 8·2. Calc. for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60·65; H, 4·0; P, 8·25%).

Dihydridocarbonyltris(triphenylphosphine)ruthenium. Method a. Solutions of hydrated ruthenium trichloride (0·13 g, 0·5 mmol) in ethanol (10 ml), aqueous formaldehyde (5 ml, 40% w/v soln.), and potassium hydroxide (0·2 g) in ethanol (10 ml) were added successively to a boiling solution of triphenylphosphine (0·78 g, 3 mmol) in ethanol (30 ml). The mixture was heated under reflux for 5 min, cooled and the precipitated product washed with ethanol, water, ethanol, and finally n-hexane. Recrystallisation from benzene–n-hexane gave white crystals (0·34 g, 74%), m.p. 160—162° in air, 213—215° sealed under nitrogen (Found: C, 72·4; H, 5·15. Calc. for $C_{55}H_{47}OP_3Ru$: C, 71·95; H, 5·15%).

Method b. Solutions of hydrated ruthenium trichloride (0·13 g, 0·5 mmol) in 2-methoxyethanol (10 ml), aqueous formaldehyde (5 ml, 40% w/v soln.), and potassium hydroxide (0·2 g) in water (5 ml) were added in rapid succession to a solution of triphenylphosphine (0·78 g, 3 mmol) in boiling 2-methoxyethanol (40 ml). The mixture was heated under reflux, cooled to 30°, and the precipitated product washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give white crystals (0·34 g, 74%) (Found: C, 71·85; H, 4·8. Calc. for $C_{55}H_{47}OP_3Ru$: C, 71·95; H, 5·15%). Dihydridocarbonyltris(triphenylphosphine)ruthenium was also prepared by Method a, using triethylamine (5 ml) or sodium carbonate (0·2 g) in place of potassium hydroxide; yields were 76 and 72% respectively.

Tricarbonylbis(triphenylphosphine)ruthenium. Solutions of hydrated ruthenium trichloride (0·39 g, 1·5 mmol) in 2-methoxyethanol (30 ml), aqueous formaldehyde (30 ml, 40% w/v soln.), and potassium hydroxide (0·6 g) in 2-methoxyethanol (30 ml) were added in rapid succession to a well stirred boiling solution of triphenylphosphine (2·37 g, 9 mmol) in 2-methoxyethanol (90 ml). The reaction solution was heated under reflux for 1 h and then cooled to room temperature. The resultant pale yellow microcrystalline precipitate was washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* (0·95 g, 89%), m.p. 170—173° in air and 262—266° sealed under nitrogen (Found: C, 66·3; H, 4·5; 4·2; P, 8·85. Calc. for $C_{39}H_{30}O_3P_2Ru$: C, 66·0; H, 4·25; P, 8·75%).

Tricarbonylbis(triphenylphosphine)ruthenium was similarly prepared as pale yellow crystals using triethylamine (15 ml) or sodium carbonate (0·6 g) in place of potassium hydroxide; yields were 65 and 88% respectively.

*Tricarbonylbis(tri-*p*-tolylphosphine)ruthenium.* This complex was similarly prepared using tri-*p*-tolylphosphine and recrystallised from dichloromethane–methanol as white microcrystals (70%); ν(CO) 1890vs cm^{-1}; m.p. 178—181° in air (Found: C, 67·55; H, 5·2; P, 7·45. $C_{45}H_{42}O_3P_2Ru$ requires C, 68·1; H, 5·35; P, 7·8%.

*Tricarbonylbis(tri-*p*-methoxyphenylphosphine)ruthenium.* This complex was similarly prepared using tri-*p*-methoxyphenylphosphine and recrystallised from dichloromethane–methanol as pale yellow microcrystals (50%); ν(CO) 1870, 1890 cm^{-1}; m.p. 152—158° in air (Found: C, 59·8; H, 4·6; P, 6·65. $C_{45}H_{42}O_9P_2Ru$ requires C, 59·55; H, 4·65; P, 6·85%).

Dinitrosylbis(triphenylphosphine)ruthenium. A solution of hydrated ruthenium trichloride (0·26 g, 1·0 mmol) in ethanol (10 ml) was added to a stirred solution of triphenylphosphine (1·56 g, 6·0 mmol) in boiling ethanol (60 ml). Triethylamine (*ca.* 4 ml) was rapidly added until a dark purple colour developed; *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·4 g) in ethanol (20 ml) and triethylamine (6 ml) were then added immediately. The mixture was heated under reflux for 5 min and then allowed to cool. The precipitate was filtered off, washed successively with ethanol, water, ethanol and n-hexane, and then dried *in vacuo* to give the required product as red microneedles (0·55 g, 82%); ν(NO) 1665 and 1619 cm^{-1}; m.p. 144—145° in air and 185—186° under nitrogen (Found: C, 62·15; H, 4·15; N, 4·05; P, 8·25. Calc. for $C_{36}H_{30}N_2O_2Ru$: C, 63·05; H, 4·4; N, 4·1; P, 9·05%).

Osmium Complexes.—Hydridochlorocarbonyltris(triphenylphosphine)osmium. Solutions of sodium hexachloro-osmate (0·673 g, 1·2 mmol) in 2-methoxyethanol (35 ml), and aqueous formaldehyde (15 ml, 40% w/v soln.) were added in rapid succession to a vigorously stirred, boiling solution of triphenylphosphine (1·97 g, 7·5 mmol) in 2-methoxyethanol (75 ml). The reaction mixture was heated under reflux for 30 min, during which time the colour changed from brown-red to yellow; it was then allowed to cool to room temperature. The precipitated product was washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give white microcrystals (1·2 g, 95%), m.p.

179—183° in air, 289—290° sealed under nitrogen (Found: C, 63·55; H, 4·7; P, 8·5. Calc. for $C_{55}H_{46}ClOOsP_3$: C, 63·4; H, 4·45; P, 8·9%).

Dihydridocarbonyltris(triphenylphosphine)osmium. Solutions of sodium hexachloro-osmate (0·84 g, 1·5 mmol) in 2-methoxyethanol (30 ml), aqueous formaldehyde (12 ml, 40% w/v soln.), and potassium hydroxide (0·84 g) in 2-methoxyethanol (15 ml) were added in rapid succession to a vigorously stirred boiling solution of triphenylphosphine (4·72 g, 18 mmol) in 2-methoxyethanol (75 ml). The mixture was heated under reflux for 30 min, during which time the colour changed to pale yellow and a white precipitate separated; it was then allowed to cool to room temperature. The precipitate was washed with ethanol, water, ethanol, and finally n-hexane to give white micro-crystals (1·14 g, 73%), m.p. 202—204° in air, 245—246° under nitrogen (Found: C, 65·85, 65·35; H, 4·65, 5·0; P, 9·5. Calc. for $C_{55}H_{47}OOsP_3$: C, 65·6; H, 4·7; P, 9·25%).

Dihydridodicarbonylbis(triphenylphosphine)osmium. Solutions of sodium hexachloro-osmate (1·18 g, 2·0 mmol) in 2-methoxyethanol (30 ml), aqueous formaldehyde (55 ml, 40% w/v soln.), and potassium hydroxide (2·0 g) in 2-methoxyethanol (20 ml) were added in rapid succession to a vigorously stirred, boiling solution of triphenylphosphine (0·92 g, 3·5 mmol) in 2-methoxyethanol (100 ml). The very dark reaction solution was heated under reflux for 30 min during which time it slowly lightened in colour; it was then allowed to cool to room temperature. The precipitated product was washed with ethanol, water, ethanol, and finally n-hexane and then dried *in vacuo* to give creamy white microcrystals (0·93 g, 57%), m.p. 243—244° in air, 257—258° sealed under nitrogen (Found: C, 59·15; H, 4·5; P, 8·25. Calc. for $C_{38}H_{32}O_2OsP_2$: C, 59·05; H, 4·15; P, 8·0%).

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