Transition-metal Complexes containing Phosphorus Ligands. Part XIV.[1] *ortho*-Metallation Reactions involving Some Triaryl Phosphite Derivatives of Osmium

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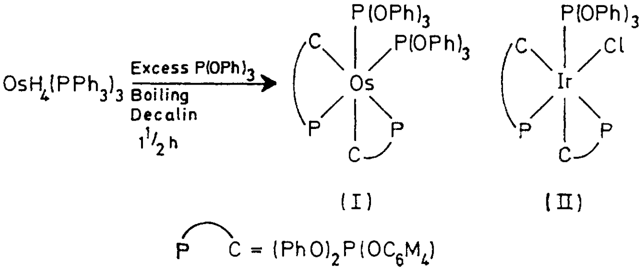
Osmium triphenylphosphine complexes, $[OsH_4(PPh_3)_3]$, $[OsH_2(CO)(PPh_3)_3]$, and $[OsHCl(CO)(PPh_3)_3]$ react with triphenyl phosphite in boiling organic solvents to yield triphenyl phosphite derivatives which subsequently undergo *ortho*-metallation. Products isolated and characterised include the substituted derivatives $[OsHCl(CO)(PPh_3)_2(p)]$ and $[OsHCl(CO)(PPh_3)(p)_2]$, the metallated species $[OsCl(pc)(CO)(PPh_3)(p)]$, $[OsCl(pc)(CO)(p)_2]$, $[OsH(pc)(CO)(PPh_3)(p)]$, and $[OsH(pc)(CO)(p)_2]$, and the dimetallated complexes $[Os(pc)_2(p)_2]$ and $[Os(pc)_2(CO)(p)]$ $[(p) = P(OPh)_3$; $(pc) = (PhO)_2P(OC_6H_4)]$.

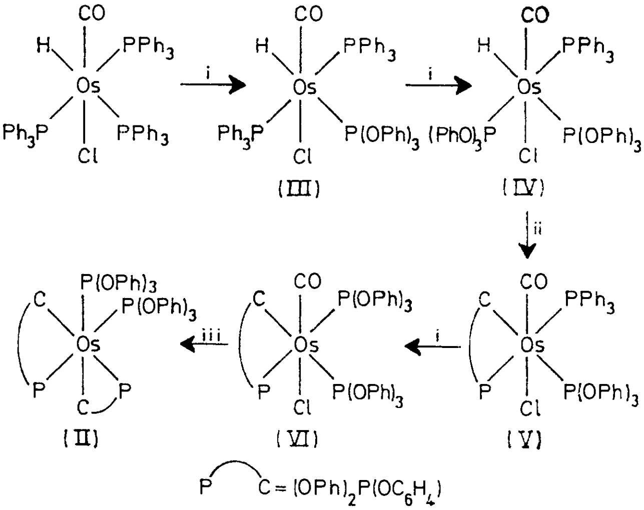
As part of our study of *cyclo*-metallation reactions we are investigating the *ortho*-metallation of triaryl phosphite ligands co-ordinated to platinum group metals. Earlier papers on this work have dealt with cyclo-metallated triaryl phosphite complexes of palladium,[2] platinum,[2] iridium,[3] and ruthenium;[4] in the present paper we discuss the preparation of the corresponding osmium derivatives.[5]

Although *cyclo*-metallation reactions are now known to feature extensively in the chemistry of the platinum group metals, few examples involving osmium complexes have been reported. While this paper was in preparation Douglas and Shaw reported [6] the *cyclo*-metallation of bulky dimethyl(1-naphthyl)phosphine ligands co-ordinated to osmium, and described products directly analogous to some of those discussed below. Deeming *et al.*, in their recent papers [7,8] on the fragmentation of organo-phosphine and -arsine ligands in trinuclear osmium carbonyl complexes have also described several metallated products. Finally, Parshall [9] has observed that the complexes $[OsH_2(CO)(PPh_3)_3]$ and $[OsHCl(CO)(PPh_3)_3]$ exchange their *ortho* hydrogen atoms with D_2 at 100 °C, but has not reported isolation of any metallated intermediates.

Osmium triphenyl phosphite complexes, suitable for use in the present work, were unknown and were therefore generated *in situ* by treatment of the appropriate triphenylphosphine derivatives, $[OsH_4(PPh_3)_3]$, $[OsH_2(CO)(PPh_3)_3]$, and $[OsHCl(CO)(PPh_3)_3]$, with an excess of triphenyl phosphite in boiling organic solvents. In several instances mixed phosphine/phosphite species, arising from the stepwise displacement of the triphenylphosphine ligands, were observed and isolated. However, in other cases *ortho*-metallation of the incoming triphenyl phosphite ligands occurred readily, and only the *ortho*-metallated products could be satisfactorily characterised. No evidence for the metallation of the residual triphenylphosphine ligands was found. The reactions observed are summarised in Schemes 1—3. Intermediates postulated but not isolated or characterised are given in brackets; all other species mentioned were fully characterised by i.r., proton and phosphorus n.m.r., and analytical data. The presence of *ortho*-metallated triphenyl phosphite ligands was confirmed using previously established [4] infrared criteria.



SCHEME 1



SCHEME 2 Excess of $P(OPh)_3$/boiling decalin. Steps: i, $+P(OPh)_3$ $(-PPh_3)$; ii, $-H_2$; iii, $+P(OPh)_3$ $(-HCl, -CO)$

The osmium(IV) tetrahydride, $[OsH_4(PPh_3)_3]$, reacts with excess of triphenyl phosphite in boiling decalin to afford the fully substituted, dimetallated, osmium(II) complex, $[Os(pc)_2(p)_2]$, which may be isolated as an air-stable white crystalline solid. The i.r. spectrum of this product clearly indicates the presence of metallated

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[1] Part XIII, D. A. Couch, S. D. Robinson, and J. N. Wingfield, *J.C.S. Dalton*, 1974, 1309.

[2] N. Ahmad, E. W. Ainscough, T. A. James, and S. D. Robinson, *J.C.S. Dalton*, 1973, 1151.

[3] E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc.* (*A*), 1971, 3413.

[4] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.

[5] E. W. Ainscough, T. A. James, S. D. Robinson, and J. N. Wingfield, *J. Organometallic Chem.*, 1973, **60**, C63.

[6] P. G. Douglas and B. L. Shaw, *J.C.S. Dalton*, 1973, 2078.

[7] A. J. Deeming, R. E. Kimber, and M. Underhill, *J.C.S. Dalton*, 1973, 2589 and references therein.

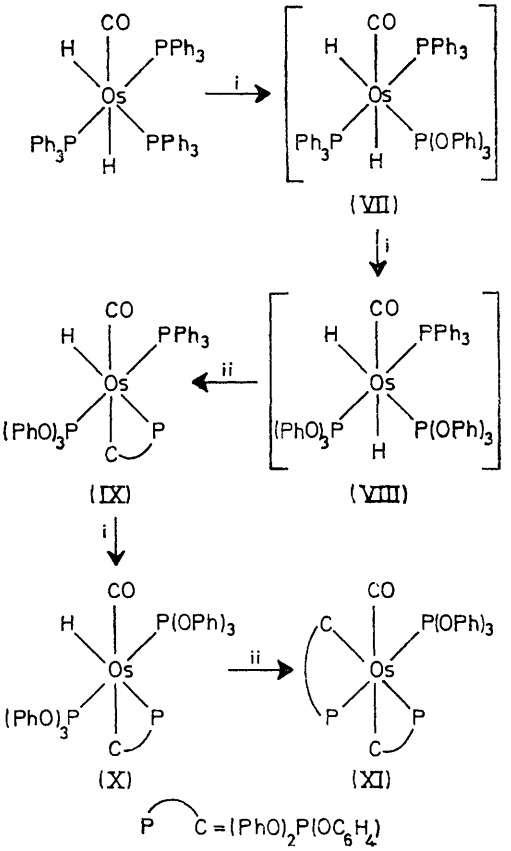
[8] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1973, 2727.

[9] G. W. Parshall, unpublished work referred to in *Accounts Chem. Res.*, 1970, **3**, 139.

triphenyl phosphite ligands (bands at 1100 and 800 cm^{-1}) and the absence of hydride or residual triphenylphosphine ligands. Proton n.m.r. spectra confirm the absence of hydrides. The proton-decoupled ^{31}P n.m.r. spectrum comprises four patterns of eight lines, indicative of four mutually coupled non-equivalent ^{31}P nuclei, and thus permits unambiguous assignment of stereochemistry (I) for this complex. The stereochemistry assigned to [Os(pc)$_2$(p)$_2$] is directly comparable with that found by X-ray diffraction [10] for the closely related, dimetallated, iridium species [Ir(pc)$_2$Cl(p)] [stereochemistry (II)]. All attempts to isolate and characterise partially substituted or monometallated intermediates from this reaction by employing shorter reaction times or lower reaction temperatures were unsuccessful. We are, therefore, unable to ascertain the reaction sequence which occurs in this system. However, osmium(IV) tetrahydrides, [OsH$_4$(PR$_3$)$_3$] are known [11] to react readily with donor ligands (L) to form osmium(II) dihydrides [OsH$_2$(PR$_3$)$_3$L], and it therefore seems probable that the initial step in the present reaction sequence involves addition of triphenyl phosphite (p) and elimination of one molecule of dihydrogen to afford [OsH$_2$(PPh$_3$)$_3$(p)]. The later steps in the reaction sequence are presumably similar to those established for the reaction of [OsH$_2$(CO)(PPh$_3$)$_3$] with triphenyl phosphite (Scheme 3). The prolonged treatment of [OsHCl(CO)(PPh$_3$)$_3$] with triphenyl phosphite in boiling decalin also affords the dimetallated complex [Os(pc)$_2$(p)$_2$] as the final product. This reaction is accompanied by elimination of HCl (1 mol), collected and estimated as AgCl, H$_2$ (1 mol), and CO (1 mol). The reaction sequence 2 was established for the process by the isolation and characterisation of the intermediate products (III) ⟶ (VI). Thus, treatment of [OsHCl(CO)(PPh$_3$)$_3$] with triphenyl phosphite in boiling benzene affords the monosubstituted product [OsHCl(CO)(PPh$_3$)$_2$(p)] which is assigned stereochemistry (III) on the basis of its high-field ^{1}H n.m.r. spectrum (Table 1). This assignment is in accord with the well known *trans*-labilising effect of the hydride ligand, and is supported by the high-field n.m.r. pattern [doublet $^2J(\mathrm{PH})_{trans}$ = 166 Hz] observed for the related complex [OsHCl(CO)(AsPh$_3$)$_2$(p)], prepared under similar conditions from [OsHCl(CO)(AsPh$_3$)$_3$]. With more vigorous conditions the disubstituted complex [OsHCl(CO)(PPh$_3$)(p)$_2$] was obtained. The high-field ^{1}H n.m.r. spectrum of this compound comprises a doublet of triplets, suggesting the presence of a symmetrical structure with the hydride *trans* to phosphine and *cis* to a pair of equivalent phosphite ligands. However, the ^{31}P n.m.r. spectrum reveals the presence of three non-equivalent phosphorus nuclei, and when taken in conjunction with the ^{1}H n.m.r. data is indicative of stereochemistry (IV). We therefore conclude that the couplings $^2J(\mathrm{PH})_{cis}$ arising from the phosphite and phosphine ligands are coincidently equivalent. Treatment of [OsHCl(CO)(PPh$_3$)$_3$] with triphenyl phosphite under more vigorous conditions gave a reaction mixture from which the *ortho*-metallated complex [OsCl(pc)(CO)(PPh$_3$)(p)] was isolated, thus suggesting that the metallation reaction takes precedent over the final substitution step. This observation accounts for our failure to obtain any evidence for the formation of the trisubstituted species, [OsHCl(CO)(p)$_3$], on treating [OsHCl(CO)(PPh$_3$)$_3$] or [OsHCl(CO)(AsPh$_3$)$_3$] with excess of triphenyl phosphite. The i.r. spectrum of [OsCl(pc)(CO)(PPh$_3$)(p)] shows bands attributable to carbonyl, triphenylphosphine, and *ortho*-metallated triphenyl phosphite ligands. The absence of hydride ligands was confirmed by n.m.r. and i.r. spectroscopy.

The final product, isolated in modest yield after a prolonged reaction in boiling decalin, was purified with difficulty and shown to be [Os(pc)$_2$(p)$_2$] identical with an authentic specimen prepared from [OsH$_4$(PPh$_3$)$_3$].

The vigorous conditions necessary to maintain [OsH$_2$(CO)(PPh$_3$)$_3$] in solution and induce reaction with triphenyl phosphite are sufficient to cause *ortho*-metallation of the incoming phosphite ligands; therefore no simple substitution products could be isolated. However the metallated intermediates (IX) and (X) were obtained, and their formation provides support for the reaction sequence proposed below (Scheme 3). Given the high *trans*-effect of the hydride ligand, an initial step involving



SCHEME 3 Excess of P(OPh)$_3$/boiling decalin. Steps: i, +P(OPh)$_3$ (−PPh$_3$); ii, −H$_2$

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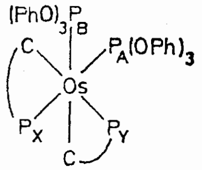
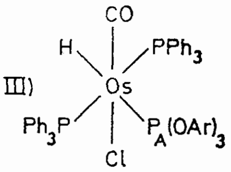
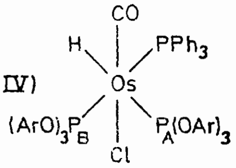
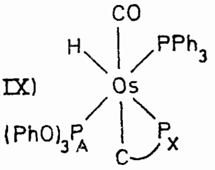
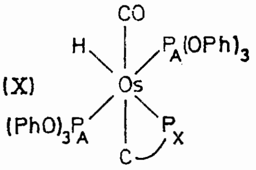
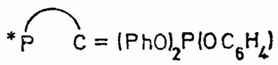
[10] J. M. Guss and R. Mason, *Chem. Comm.*, 1971, 58; *J.C.S. Dalton*, 1972, 2193.

[11] B. Bell, J. Chatt, and G. J. Leigh, *J.C.S. Dalton*, 1973, 997.

Some i.r. and n.m.r. data

Complex *		I.r. data [a]	^{1}H N.m.r. data [b]	^{31}P N.m.r. data [c]
(I) 		1100 800, 790 } (PhO)$_2$P(OC$_6$H$_4$)	τ 1·53 (m) τ 2·89—3·62 (m) τ 4·3 (m) } aromatic protons	−71·8 p.p.m. (8), P$_A$; −84·8 p.p.m. (8), P$_B$ −114·5 p.p.m. (8), P$_X$; −119·2 p.p.m. (8), P$_Y$ ^2J(P$_A$P$_B$) = 41·2 Hz; ^2J(P$_A$P$_X$) = 651·5 Hz; ^2J(P$_A$P$_Y$) = 35·3 Hz; ^2J(P$_B$P$_X$) = 27·9 Hz; ^2J(P$_B$P$_Y$) = 25 Hz; ^2J(P$_X$P$_Y$) = 38·3 Hz
(III) 	(a) Ar = Ph	2020 (m,br) ν(OsH) 1950 (s,br) ν(CO)	τ 2·35—3·53 (m) aromatic protons τ 15·28 (d of t) hydride ^2J(PH)$_{trans}$ = 161 Hz; ^2J(PH)$_{cis}$ = 23 Hz	−5·1 p.p.m. (d) PPh$_3$; −87·4 p.p.m. (t) P(OPh)$_3$ ^2J(P*P*$_A$) = 18 Hz −5·1 p.p.m. (broad peak) PPh$_3$ [d] −87·4 p.p.m. (d of t) P(OPh)$_3$ [d]
	(b) Ar = C$_6$H$_4$Me-*o*	2050 (m) ν(OsH) 1940 (s) ν(CO)	τ 2·05—3·6 (m) aromatic protons τ 7·77 (s) methyl protons τ 15·25 (d of t) hydride ^2J(PH)$_{trans}$ 167 Hz; ^2J(PH)$_{cis}$ = 25·8 Hz	
	(c) Ar = C$_6$H$_4$Me-*p*	2000 (m) ν(OsH) 1940 (s) ν(CO)	τ 2·0—3·04 (m) aromatic protons τ 8·0 (s) methyl protons τ 14·9 (d of t) hydride ^2J(PH)$_{trans}$ 160 Hz; ^2J(PH)$_{cis}$ 23 Hz	
(IV) 	(a) Ar = Ph	2040 (m) ν(OsH) 1950 (s) ν(CO)	τ 2·55—3·24 (m) aromatic protons τ 15·88 (d of t) hydride ^2J(PH)$_{trans}$ 152·2 Hz; ^2J(PH)$_{cis}$ 23 Hz	−4·0 p.p.m. (4) PPh$_3$ −88·2 p.p.m. (4), P$_B$; −88·3 p.p.m. (t), P$_A$ ^2J(PP$_A$) = 30 Hz; ^2J(PP$_B$) 423 Hz ^2J(P$_A$P$_B$) = 24 Hz
	(b) Ar = C$_6$H$_4$Me-*p*	2020 (m) ν(OsH) 1960 (s, br) ν(CO)	τ 2·08—3·28 (m) aromatic protons τ 7·96 (s) and 8·03 (s) methyl groups τ 15·36 (d of t) hydride ^2J(PH)$_{trans}$ 152 Hz; ^2J(PH)$_{cis}$ 23 Hz	
[OsHCl(CO)(AsPh$_3$)$_2${P(OPh)$_3$}]		1988 (m) ν(OsH) 1940 (s) ν(CO)	τ 2·1—3·2 (m) aromatic protons τ 14·93 (d) hydride ^2J(PH)$_{trans}$ 166 Hz	
(IX) 		1968 (m) ν(OsH) 1940 (s) ν(CO)	τ 2·67—3·73 (m) aromatic protons τ (17·38 (d of t) hydride ^2J(PH)$_{trans}$ 115 Hz; ^2J(PH)$_{cis}$ 25 Hz	−10·4 p.p.m. (4), PPh$_3$ −93·7 p.p.m. (4), P$_A$; −132·5 p.p.m. (4), P$_X$ ^2J(PP$_A$) 369 Hz; ^2J(PP$_X$) 23·8 Hz ^2J(P$_A$P$_X$) 17·9 Hz
(X) 		2000 (m) ν(OsH) 1970, 1940 (s) ν(CO) 1095, 800(PhO)$_2$P(OC$_6$H$_4^-$)	τ 2·5—3·24 (m) aromatic protons τ 17·76 (d of t) hydride ^2J(PH)$_{trans}$ 102·6 Hz; J^2(PH)$_{cis}$ 26·5 Hz	−82·3 p.p.m. (d) P$_A$ −131·2 p.p.m. (t) P$_X$ ^2J(P$_A$P$_X$) 23·8 Hz



* P C = (PhO)$_2$P(OC$_6$H$_4$)

[a] I.r. spectra (Nujol mull), s = strong; m = medium; br = broad. [b] ^{1}H N.m.r. recorded in deuteriochloroform at 90 MHz; s = singlet, d = doublet, t = triplet, m = multiplet. [c] ^{31}P N.m.r. recorded in chloroform at 36·43 MHz with all ^{1}H nuclei decoupled. Chemical shifts are given relative to 85% H$_3$PO$_4$ (±0·2 p.p.m.) in the sense that increasing field is positive. *J* Values ±1 Hz; numbers in parentheses indicate number of equal intensity lines in each resonance. [d] Protons not decoupled.

formation of the mono-substituted species $[OsH_2(CO)(PPh_3)_2(p)]$ [stereochemistry (VII)] seems entirely feasible. A further substitution, together with an *ortho*-metallation step, affords the first isolable product, $[OsH(pc)(CO)(PPh_3)(p)]$. This complex is assigned stereochemistry (IX) on the basis of spectroscopic data (Table). A subsequent product with very similar spectroscopic characteristics but devoid of triphenylphosphine is formulated as the fully substituted species $[OsH(pc)(CO)(p)_2]$ [stereochemistry (X)]. The final product, obtained in an impure state after the prolonged reaction of $[OsH_2(CO)(PPh_3)_3]$ with triphenyl phosphite in boiling decalin, was shown by i.r. and n.m.r. spectroscopy to contain carbonyl and metallated phosphite groups but no hydride ligands, and was therefore formulated as the dimetallated complex $[Os(pc)_2(CO)(p)]$ [stereochemistry (XI)]. Douglas and Shaw[6] have recently isolated a related complex $[Os(p'c)_2(CO)(p')]$ [p' = dimethyl(1-naphthyl)phosphine; p'c = metallated (p')] and suggested the participation of the hydride $[OsH(p'c)(CO)(p')_2]$ as a precursor, thus implying a reaction directly analogous to the conversion (X) $\longrightarrow$ (XI) proposed here (Scheme 3).

EXPERIMENTAL

Triphenylphosphineosmium complexes were prepared as previously described.[12] All reactions were performed under a dinitrogen atmosphere. I.r. spectra (4000—200 cm^{-1}) were recorded on a Perkin-Elmer 621 grating spectrometer using samples mulled in Nujol. ^1H and ^{31}P N.m.r. spectra were obtained using a Bruker HFX 90 spectrometer. M.p.s were determined in sealed tubes under dinitrogen.

Bis[triphenyl phosphito(C^2,P)]*bis(triphenyl phosphite)-osmium*(II) $[Os\{(PhO)_2P(OC_6H_4)\}_2\{P(OPh)_3\}_2]$. Triphenyl phosphite (0·9 g) and tetrahydridotris(triphenylphosphine)osmium (0·39 g) in decalin (5 ml) were heated together under reflux for 90 min. The solution was filtered hot, cooled to ambient temperature, diluted with n-hexane, and then cooled to −10 °C overnight. The white solid which deposited was filtered off, washed with methanol then n-hexane, and recrystallised from dichloromethane–methanol to yield *white crystals* (0·2 g, 35%), m.p. 172 °C (Found: C, 60·25; H, 4·45; P, 8·65. $C_{72}H_{58}O_{12}OsP_4$ requires C, 60·5; H, 4·1; P, 8·65%).

Carbonylchlorohydridobis(triphenylphosphine)(triphenyl phosphite)osmium(II) $[OsHCl(CO)(PPh_3)_2\{P(OPh)_3\}]$.—Triphenyl phosphite (0·22 g) and carbonylchlorohydridotris(triphenylphosphine)osmium (0·21 g) in benzene (10 ml) were heated together under reflux for 2½ h. The solution was cooled to ambient temperature, filtered, and then diluted with n-hexane (30 ml). The white solid which deposited was filtered off, washed with ethanol then n-hexane, and recrystallised from dichloromethane–methanol to yield *white crystals* (0·17 g, 80%), m.p. 192 °C (Found: C, 59·95; H, 4·6; P, 8·6. $C_{55}H_{46}ClO_4OsP_3$ requires C, 60·65; H, 4·25; P, 8·5%).

Similarly prepared using the appropriate triaryl phosphite were, *carbonylchlorohydridobis(triphenylphosphine)(tri-*o*-tolyl phosphite)osmium*(II) as white crystals (80%), m.p. 165 °C (Found: C, 62·1; H, 4·8; P, 7·8. $C_{58}H_{52}ClO_4OsP_3$ requires C, 61·55; H, 4·6; P, 8·2%), and *carbonylchlorohydridobis(triphenylphosphine)(tri-*p*-tolyl phosphite)osmium*(II) as white crystals (80%), m.p. 187 °C (Found: C, 61·3; H, 4·6; P, 8·1. $C_{58}H_{52}ClO_4OsP_3$ requires C, 61·55; H, 4·6; P, 8·2%).

Carbonylchlorohydridobis(triphenylarsine)(triphenyl phosphite)osmium(II) $[OsHCl(CO)(AsPh_3)_2\{P(OPh)_3\}]$. Triphenyl phosphite (0·3 g) and carbonylchlorohydridotris(triphenylarsine)osmium (0·23 g) in benzene (8 ml) were heated together under reflux for 45 min. The solvent was removed *in vacuo* and the resultant oil was recrystallised from dichloromethane–methanol to yield the required product as *white crystals* (0·15 g, 65%), m.p. 203 °C (Found: C, 55·6; H, 3·6; Cl, 3·6. $C_{55}H_{46}As_2ClO_4OsP$ requires C, 56·1; H, 3·95; Cl, 3·0%).

Carbonylchlorohydrido(triphenylphosphine)bis(triphenyl phosphite)osmium(II) $[OsHCl(CO)(PPh_3)\{P(OPh)_3\}_2]$.—Triphenyl phosphite (0·62 g) and carbonylchlorohydridotris(triphenylphosphine)osmium (0·52 g) in *m*-xylene (10 ml) were heated together under reflux for 30 min. The solution was cooled to ambient temperature, filtered, then diluted with n-hexane to yield a white precipitate. This was washed with ethanol then n-hexane, and recrystallised from dichloromethane–methanol to yield white crystals (0·2 g, 35%), m.p. 183—184 °C (Found: C, 57·7; H, 4·15. $C_{55}H_{46}ClO_7OsP_3$ requires C, 58·05; H, 4·05%).

Similarly prepared was *carbonylchlorohydrido(triphenylphosphine)bis(tri-*p*-tolyl phosphite)osmium*(II) as white crystals (49%) (Found: C, 59·95; H, 4·75; P, 7·6 $C_{61}H_{58}ClO_4OsP_3$ requires C, 59·5; H, 4·9; P, 7·35%).

Carbonylchloro[triphenyl phosphito(C^2,P)]*bis(triphenyl phosphite)osmium*(II) $[OsCl\{(PhO)_2P(OC_6H_4)\}(CO)\{P(OPh)_3\}_2]$.—Triphenyl phosphite (0·3 g) and carbonylchlorohydridotris(triphenylarsine)osmium (0·25 g) in decalin (5 ml) were heated together under reflux for 4 min. The solution was filtered, diluted with n-hexane, and then cooled to −10 °C. The resultant white precipitate was filtered off and washed with n-hexane (0·065 g, 25%) (Found: C, 56·2; H, 3·45; P, 8·0. $C_{55}H_{44}ClO_{10}OsP_3$ requires C, 55·8; H, 3·75; P, 7·85%).

Carbonylchloro(triphenylphosphine)[triphenyl phosphito-(C^2,P)]*(triphenyl phosphite)osmium*(II)*–0·5Dichloromethane* $[OsCl\{(PhO)_2P(OC_6H_4)\}(CO)(PPh_3)\{P(OPh)_3\}],0{\cdot}5CH_2Cl_2$.—Triphenylphosphine (0·25 g) and carbonylchlorohydrido(triphenylphosphine)bis(triphenyl phosphite)osmium (0·25 g) in decalin (5 ml) were heated together under reflux for 7 min. The solution was filtered, diluted with n-hexane, and then cooled to yield a white solid (0·1 g, 40%). Recrystallisation from dichloromethane–methanol produced white crystals of the required product as a dichloromethane adduct (Found: C, 56·4; H, 3·75; P, 8·1. $C_{55{\cdot}5}H_{45}Cl_2O_7OsP_3$ requires C, 56·6; H, 3·85; P, 7·9%). This compound may also be isolated from the mixture obtained on heating triphenyl phosphite with carbonylchlorohydridotris(triphenylphosphine)osmium in decalin under reflux for 9 min.

Bis[triphenyl phosphito(C^2,P)]*bis(triphenyl phosphite)-osmium*(II) $[Os\{(PhO)_2P(OC_6H_4)\}_2\{P(OPh)_3\}_2]$ (*Alternative Preparation*).—Triphenyl phosphite (0·3 g) and carbonylchlorohydridotris(triphenylphosphine)osmium (0·22 g) in decalin (4 ml) were heated together under reflux for 3 h. The solution was cooled to ambient temperature, filtered, then diluted with n-hexane to yield a white solid; this was filtered off, washed with n-hexane, and dried *in vacuo* (0·13 g, 40%) (Found: C, 60·25; H, 4·5; P, 8·55. $C_{72}H_{58}O_{12}OsP_4$ requires C, 60·5; H, 4·1; P, 8·65%).

Carbonylhydrido(triphenylphosphine)[triphenyl phosphito-(C^2,P)]*(triphenyl phosphite)osmium*(II) $[OsH\{(PhO)_2P(OC_6H_4)\}(CO)(PPh_3)\{P(OPh)_3\}]$.—Triphenyl phosphite (0·3

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[12] N. Ahmad, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1972, 843.

g) and carbonyldihydridotris(triphenylphosphine)osmium (0·2 g) in decalin (5 ml) were heated together under reflux for 5 min. The solution was cooled to ambient temperature, filtered, and then diluted with n-hexane. The resultant white precipitate was washed with n-hexane and then recrystallised from dichloromethane–methanol to give white crystals (0·14 g, 63%), m.p. 186—187 °C (Found: C, 60·2; H, 4·35; P, 8·85. $C_{55}H_{45}O_7OsP_3$ requires C, 60·0; H, 4·1; P, 8·45%).

Carbonylhydrido[*triphenyl phosphito*(C^2,P)]*bis*(*triphenyl phosphite*)*osmium*(II) $[OsH\{(PhO)_2P(OC_6H_4)\}(CO)\{P(OPh)_3\}_2]$.—Triphenyl phosphite (0·9 g) and carbonyldihydrotris(triphenylphosphine)osmium (0·5 g) in decalin (5 ml) were heated together under reflux for 1 h. The solution was filtered, diluted with n-hexane, and then cooled to −10 °C. The white solid which deposited was filtered off, washed with n-hexane, and then recrystallised from dichloromethane–methanol to give white crystals (0·25 g, 35%), m.p. 160—170 °C (Found: C, 57·65; H, 4·25; P, 7·85. $C_{55}H_{45}O_{10}OsP_3$ requires C, 57·5; H, 3·95; P, 8·1%).

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