Transition-metal Complexes containing Phosphorus Ligands. Part XV.[1] *ortho*-Metallation Reactions involving some Triphenyl Phosphite Derivatives of Ruthenium and Rhodium

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The complexes $[Ru(CO)(Cl)H(PPh_3)_3]$, $[Ru(CO)H_2(PPh_3)_3]$, $[Ru(CO)_3(PPh_3)_2]$, and $[RuH_2(PPh_3)_4]$ react with triphenyl phosphite in hydrocarbon solvents to yield triphenyl phosphite derivatives which subsequently undergo *ortho*-metallation. Products which have been isolated and/or characterised include the substituted species $[Ru(CO)(Cl)H(PPh_3)_2\{P(OPh)_3\}]$ and $[Ru(CO)(Cl)H(PPh_3)\{P(OPh)_3\}_2]$, and the metallated derivatives $[Ru(CO)(Cl)\{P(OPh)_3\}_2(pc)]$, $[Ru(CO)H(PPh_3)\{P(OPh)_3\}(pc)]$, $[Ru(CO)H\{P(OPh)_3\}_2(pc)]$, and $[Ru\{P(OPh)_3\}_2(pc)_2]$ [pc = $P(OPh)_2(OC_6H_4)$]. Attempts to reverse the metallation process by addition of hydrogen chloride or hydrogen to $[Ru\{P(OPh)_3\}_2(pc)_2]$ under mild conditions have been unsuccessful; however, this complex undergoes demetallation in the presence of perfluorocarboxylic acids, R_FCO_2H, to yield the species *trans*-$[Ru(O_2CR_F)_2\{P(OPh)_3\}_4]\cdot R_FCO_2H$ ($R_F = CF_3$ or C_2F_5). The rhodium complex $[RhH\{P(OPh)_3\}_4]$ in boiling n-heptane loses hydrogen to yield the metallated product $[Rh\{P(OPh)_3\}_3(pc)]$.

HAVING previously described reactions involving triphenyl phosphite ligands bound to ruthenium,[2] osmium,[1,3] iridium,[4] palladium,[5] and platinum[5] we now conclude this aspect of our work by reporting some further examples of analogous reactions for triphenyl phosphite complexes of ruthenium and rhodium. Previous work on the *ortho*-metallation reactions of triphenyl

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[1] Part XIV, E. W. Ainscough, T. A. James, S. D. Robinson, and J. N. Wingfield, *J.C.S. Dalton*, 1974, 2384.

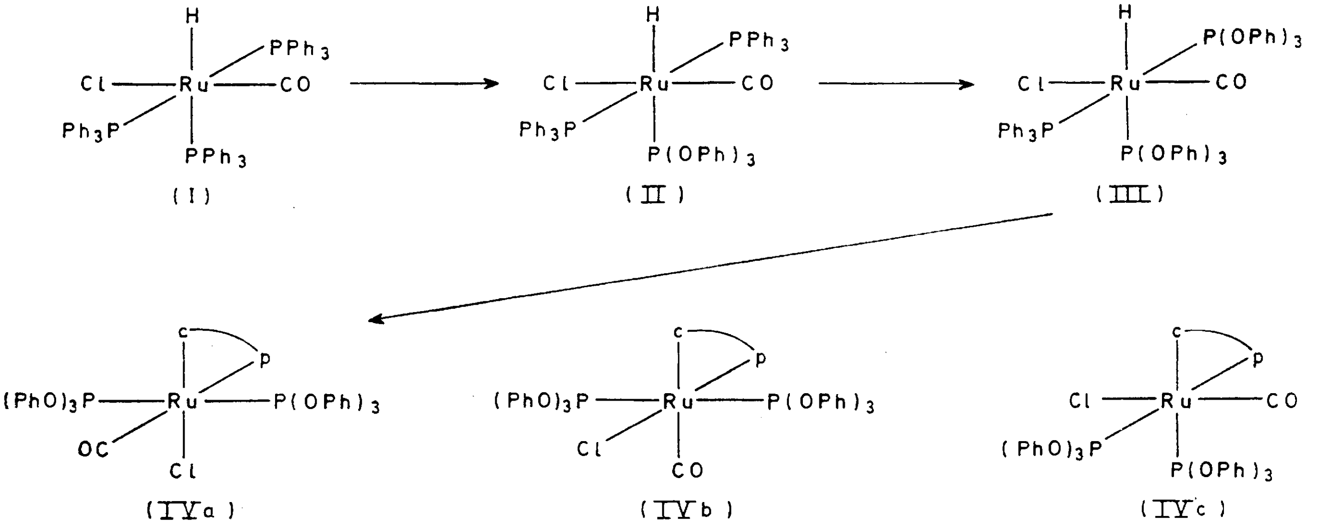
[2] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.

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

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

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

phosphite complexes of ruthenium includes two accounts of the formation of [$RuCl\{P(OPh)_3\}_3(pc)$] [pc = triphenyl phosphito(C^2P), $P(OPh)_2(OC_6H_4)$],[2,6] together with descriptions of [$Ru(C_8H_{12})(pc)_2$][7] and several *ortho*-metallated carbonyl derivatives obtained on treating [$Ru_3(CO)_{12}$] with triphenyl phosphite.[8] In addition cyclometallation reactions have been reported for a variety of sulphur,[9] nitrogen,[10] phosphorus,[11-13] and arsenic donor ligands[11] bound to ruthenium. Results published by Parshall and his co-workers[6,14] together with those described here provide the only examples of cyclometallation reactions involving triaryl phosphite complexes of rhodium.



SCHEME 1 pc = $P(OPh)_2(OC_6H_4)$

RESULTS AND DISCUSSION

Procedures for the isolation of the (triphenyl phosphite)-ruthenium derivatives required in this work had not been developed, therefore the complexes were generated *in situ* by treating the triphenylphosphine complexes [$Ru(CO)(Cl)H(PPh_3)_3$], [$Ru(CO)H_2(PPh_3)_3$], [$Ru(CO)_3(PPh_3)_2$], and [$RuH_2(PPh_3)_4$] with triphenyl phosphite in hydrocarbon solvents. Two simple substitution products [$Ru(CO)(Cl)H(PPh_3)_2\{P(OPh)_3\}$] and [$Ru(CO)(Cl)H(PPh_3)\{P(OPh)_3\}_2$] were characterised; all other isolable species contained at least one *ortho*-metallated triphenyl phosphite ligand and it appears that, in all cases investigated, the introduction of a triphenyl phosphite ligand *cis* to hydride in a non-metallated complex leads to rapid metallation. No evidence for the cyclometallation of the residual triphenylphosphine ligands was detected. The reactions observed are summarised in Schemes 1—3; intermediates postulated but not isolated or characterised are given in parentheses, all other products being fully characterised by i.r., ^1H and ^{31}P n.m.r. spectroscopy and, with one exception, analytical data. The presence of *ortho*-metallated triphenyl phosphite ligands was monitored by observation of C–H deformation bands at *ca.* 1 100 and 800 cm^{-1}. Poor yields recorded in several instances reflect the difficulty experienced in crystallising rather intractable products.

The reaction of [$Ru(CO)(Cl)H(PPh_3)_3$] with $P(OPh)_3$ in cold benzene gave the monosubstituted complex [$Ru(CO)(Cl)H(PPh_3)_2\{P(OPh)_3\}$], (II); in boiling benzene the disubstituted species [$Ru(CO)(Cl)H(PPh_3)\{P(OPh)_3\}_2$], (III), was formed. Under more vigorous conditions, metallation accompanied by complete displacement of PPh_3 occurred leading to formation of [$Ru(CO)(Cl)\{P(OPh)_3\}_2(pc)$] (IVa) or (IVb) (Scheme 1). The monosubstituted product is expected to possess stereochemistry (II),[15] and this expectation is confirmed by the high-field ^1H n.m.r. pattern (doublet of triplets) and the proton-decoupled ^{31}P n.m.r. spectrum (doublet and triplet; relative intensities 2 : 1). The disubstituted product [$Ru(CO)(Cl)H(PPh_3)\{P(OPh)_3\}_2$] displayed second-order ^{31}P and high-field ^1H n.m.r. spectra which may be attributed to the ABC and X parts respectively of an ABCX spin system. Computer simulation of the experimental spectra followed by an iterative refinement procedure afforded data (Table) which are indicative of stereochemistry (III). Signs of the couplings in these and other second-order spectra are based on the assump-

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[6] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **91**, 4990.

[7] J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

[8] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 1667.

[9] H. Alper and A. S. K. Chan, *J. Organometallic Chem.*, 1973, **61**, C59.

[10] M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J. Organometallic Chem.*, 1973, **60**, 343 and refs. therein.

[11] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2094.

[12] B. R. James, L. D. Markham, and D. K. W. Wang, *J.C.S. Chem. Comm.*, 1974, 439.

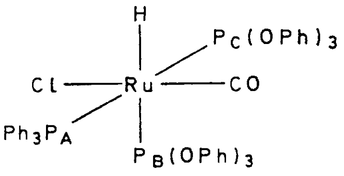
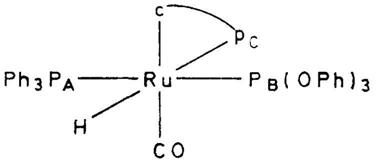
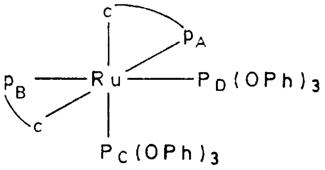
[13] P. G. Douglas and B. L. Shaw, *J.C.S. Dalton*, 1973, 2078.

[14] E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, 1972, **11**, 964.

[15] J. J. Levison and S. D. Robinson, *Chem. Comm.*, 1968, 1405.

tion that ^2J(PP′)(*trans*) and ^2J(PH)(*trans*) are positive.[16] The ^{31}P n.m.r. spectrum of the *ortho*-metallated product [Ru(CO)(Cl){P(OPh)$_3$}$_2$(pc)] comprised a doublet and a triplet (relative intensities 2 : 1) indicative of stereochemistry (IVa) or (IVb) rather than the expected (IVc), and thereby implies that the metallation is accompanied by a stereochemical rearrangement. The high value of ν(CO) observed for [Ru(CO)(Cl){P(OPh)$_3$}$_2$(pc)] is indicative of carbonyl *trans* to a phosphorus ligand and thus favours stereochemistry (IVa). Attempts to isolate other intermediates from this reaction or to induce a further *ortho*-metallation step involving elimination of hydrogen chloride were unsuccessful.

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

Complex	ν(CO)	[a] High-field ^{1}H n.m.r.[b]	^{31}P n.m.r.[c]
[Ru(CO)(Cl)H(PPh$_3$)$_2${P(OPh)$_3$}] (II)	1 960	15.36 (d of t) ^2J(PH) (*trans*) 200, ^2J(PH) (*cis*) 22.3	−122.1 (t), −39.5 (d) ^2J(PP) 27
 (III)	1 970	15.61 (second order) ^2J(P$_A$H) −20.9, ^2J(P$_B$H) +194.5, ^2J(P$_C$H) −18.1	−36.5 (P$_A$) −122.5 (P$_B$) −129 (P$_C$) } second order ^2J(P$_A$P$_B$) −34.4, ^2J(P$_A$P$_C$) +463, ^2J(P$_B$P$_C$) −36.8
[Ru(CO)(Cl){P(OPh)$_3$}$_2$(pc)](IV)	2 020		−159 (t), −114.7 (d) ^2J(PP)(*cis*) 53.7
[Ru(CO)H(PPh$_3$)$_2$(pc)] (VII)		16.67 (d of t) ^2J(PH) (*trans*) 132, ^2J(PH) (*cis*) 23	
 (VIII)	1 958	15.93 (d of t) ^2J(PH) (*trans*) 142, ^2J(PH) (*cis*) 21.5	−45.1 (d of d) (P$_A$), −137.5 (d of d) (P$_B$), −165.2 (d of d) (P$_C$) ^2J(P$_A$P$_B$) 390, ^2J(P$_A$P$_C$) 26.8, ^2J(P$_B$P$_C$) 32.75
[Ru(CO)H{P(OPh)$_3$}$_2$(pc)] (IX)	1 980	15.32 (d of t) ^2J(PH) (*trans*) 150; ^2J(PH)(*cis*) 23.5	−164.3 (t), −136.3 (d) ^2J(PP) (*cis*) 35.75
 (XI)			−155.8 (P$_A$) −152.9 (P$_B$) −127.8 (P$_C$) −120.6 (P$_D$) } second order ^2J(P$_A$P$_B$) −53.7, ^2J(P$_A$P$_C$) −34.5, ^2J(P$_A$P$_D$) −52, ^2J(P$_B$P$_C$) −44.1, ^2J(P$_B$P$_D$) +685, ^2J(P$_C$P$_D$) −54.3
[Ru(O$_2$CCF$_3$)$_2${P(OPh)$_3$}$_4$]			−119.0 (s)
[Ru(O$_2$CC$_2$F$_5$)$_2${P(OPh)$_3$}$_4$]			−118.7 (s)
[RhH{P(OPh)$_3$}$_4$]		20.15 (q of d) ^2J(PH) 45, ^1J(RhH) 7	
[RhH{P(OC$_6$H$_4$Me-*p*)$_3$}$_4$]		20.32 (q of d) ^2J(PH) 45, ^1J(RhH) 8	

[a] ν(MH) vibrations were either too weak to be detected or were masked by ν(CO). [b] In τ, recorded in deuteriochloroform at 90 MHz, s = singlet, d = doublet, t = triplet, q = quintet. [c] Recorded in chloroform at 36.43 MHz with all ^{1}H nuclei decoupled. Chemical shifts are given relative to 85% H_3PO_4 (±0.2 p.p.m.) in the sense that increasing field is positive; J ±1 Hz.

The ruthenium dihydride [Ru(CO)H$_2$(PPh$_3$)$_3$], (V), reacts readily with P(OPh)$_3$ in boiling benzene to afford [Ru(CO)H(PPh$_3$){P(OPh)$_3$}(pc)], (VIII), and in boiling xylene to yield a mixture of (VIII) and [Ru(CO)H{P(OPh)$_3$}$_2$(pc)], (IX), as the only characterisable products. All attempts to obtain simple substitution intermediates [Ru(CO)H$_2$(PPh$_3$)$_{3-n}${P(OPh)$_3$}$_n$] (n = 1—3) or dimetallated products were unsuccessful. Assuming that the first step involves displacement of a labile triphenylphosphine ligand *trans* to hydride, it is possible to advance a plausible reaction scheme, 2, involving successive formation of species (VI)—(IX). The high-field ^{1}H n.m.r. spectrum of the product [Ru(CO)H{P(OPh)$_3$}$_2$(pc)] comprised a doublet of triplets consistent with the favoured symmetrical stereochemistry (IX). The immediate precursor [Ru(CO)H(PPh$_3$){P(OPh)$_3$}(pc)], which displayed a similar high-field ^{1}H n.m.r. pattern, is assigned the corresponding stereochemistry (VIII). The coincidental equivalence of ^2J(PH)(*cis*) for hydride coupled to mutually *trans* PPh$_3$ and P(OPh)$_3$ ligands, which is implied by this assignment, is confirmed by the ^{31}P n.m.r. spectra in which the triphenylphosphine resonance, identified by the presence of PH (aromatic) couplings, appeared as a doublet of doublets in the ^{1}H decoupled spectrum.

The ruthenium tricarbonyl [Ru(CO)$_3$(PPh$_3$)$_2$] undergoes substitution and oxidative-addition reactions with

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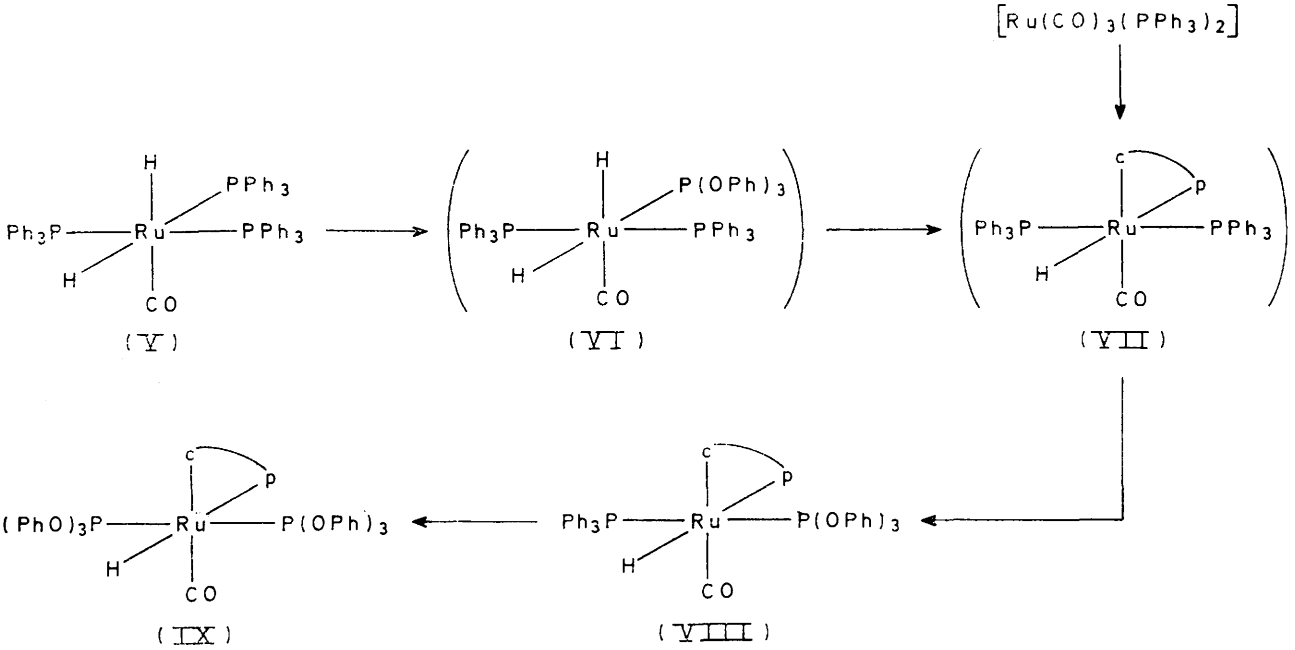
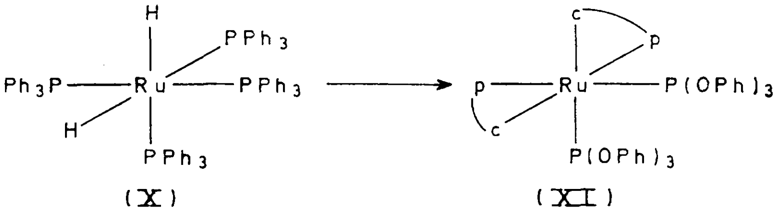
[16] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345 and refs. therein.

$P(OPh)_3$ in boiling xylene leading to successive formation of the metallated species $[Ru(CO)H(PPh_3)_2(pc)]$, (VII), $[Ru(CO)H(PPh_3)\{P(OPh)_3\}(pc)]$ (VIII), and $[Ru(CO)H\{P(OPh)_3\}_2(pc)]$ (IX). The intermediate product (VII) was identified in solution by high-field n.m.r. (Table); products (VIII) and (IX) were obtained as a mixture and were shown to have ^{31}P and high-field ^1H n.m.r. spectra identical with those of authentic samples obtained from (V).

The ruthenium dihydride $[RuH_2(PPh_3)_4]$, (X), on treatment with $P(OPh)_3$ in boiling xylene affords the dimetallated product $[Ru\{P(OPh)_3\}_2(pc)_2]$, (XI), the ruthenium analogue of the previously reported osmium complex $[Os\{P(OPh)_3\}_2(pc)_2]$.[1] The ruthenium complex displayed a second-order ^{31}P n.m.r. spectrum consistent with the presence of four non-equivalent ^{31}P nuclei, and is therefore assigned stereochemistry (XI), analogous to that previously established for $[Os\{P(OPh)_3\}_2(pc)_2]$. Computer simulation of an ABCD spin system using the data given in the Table gave a resonance pattern in excellent agreement with that obtained experimentally. The signs of the couplings are given assuming $J(PP')$ (*trans*) is positive.[16] These data do not necessarily correspond to the best possible fit.



SCHEME 2 pc = $P(OPh)_2(OC_6H_4)$



SCHEME 3 pc = $P(OPh)_2(OC_6H_4)$

Attempts to achieve demetallation of $[Ru\{P(OPh)_3\}_2(pc)_2]$ using hydrogen chloride or hydrogen under mild conditions were unsuccessful, unchanged complex only being recovered. This result is rather surprising in view of the relative ease with which many other cyclometallation reactions involving triphenyl phosphite complexes of ruthenium,[6] rhodium,[14] and palladium [5] are reversed. However, $[Ru\{P(OPh)_3\}_2(pc)_2]$ did react with perfluorocarboxylic acids, R_FCO_2H, to yield products of stoicheiometry $[Ru(O_2CR_F)_2\{P(OPh)_3\}_4]\cdot R_FCO_2H$ ($R_F = CF_3$ or C_2F_5). The complexes $[Ru(O_2CR_F)_2\{P(OPh)_3\}_4]\cdot R_FCO_2H$ have a singlet resonance in their ^{31}P n.m.r. spectra and are therefore formulated as *trans* derivatives. The ^{19}F n.m.r. pattern of the trifluoroacetate was a singlet while that of the pentafluoropropionate comprised two rather broad resonances with relative intensities 2 : 3 attributable to CF_2 and CF_3 groups respectively. To account for the presence of a singlet ^{19}F resonance common to the trifluoroacetate ligands and the trifluoroacetic acid in the complex $[Ru(O_2CCF_3)_2\{P(OPh)_3\}_4]\cdot CF_3CO_2H$ we suggest that rapid exchange of the trifluoroacetate groups is occurring. The absence of $^3J(^{19}F^{19}F)$ coupling in the spectrum of the pentafluoropropionato-complex, and the lack of a second ^{19}F signal when excess of trifluoroacetic acid is added to a solution of $[Ru(O_2CCF_3)_2\{P(OPh)_3\}_4]\cdot CF_3CO_2H$, support this conclusion. However, attempts to freeze out this exchange process at low temperatures (178 K) were unsuccessful. Our work on the metallation of triphenyl phosphite complexes of rhodium included the first synthesis of $[RhH\{P(OPh)_3\}_4]$ and its tri-*p*-tolyl phosphite analogue,[15] and the formation of the metallated species $[Rh\{P(OPh)_3\}_3(pc)]$. However, these complexes have been fully described elsewhere[6] and are, therefore, not discussed further. Attempts to obtain other metallated triphenyl phosphite derivatives of rhodium were unsuccessful.

EXPERIMENTAL

Triphenylphosphine complexes of ruthenium and rhodium were prepared as previously described.[17] All reactions were made under a nitrogen atmosphere. I.r. spectra (200—4 000 cm^{-1}) were recorded on a Perkin-Elmer 621 grating spectrometer using samples mulled in Nujol. Hydrogen-1 and ^{31}P n.m.r. spectra were obtained using a Bruker HFX 90 spectrometer. M.p.s were determined in sealed tubes under nitrogen.

Unless otherwise indicated, products were obtained as oils by evaporating the reaction solutions under reduced pressure at ambient temperature, and were washed with n-hexane before being recrystallised from dichloromethane–methanol.

Carbonylchlorohydridobis(triphenylphosphine)(triphenyl phosphite)ruthenium(II)*–Dichloromethane*(1/1), $[Ru(CO)(Cl)H(PPh_3)_2\{P(OPh)_3\}]\cdot CH_2Cl_2$ (II).—Triphenyl phosphite (0.75 g) and carbonylchlorohydridotris(triphenylphosphine)ruthenium, (I) (0.5 g), were mixed in cold benzene (15 cm^3) and allowed to stand overnight. The $[Ru(CO)(Cl)H(PPh_3)_3]$ slowly dissolved to give a colourless solution. Using the method given above the product was obtained as white crystals (0.52 g, 100%), m.p. 147—149 °C, τ 4.72(s) (solvated CH_2Cl_2) [Found: C, 61.25; H, 4.55. $C_{55}H_{46}ClO_4P_3Ru$ requires C, 65.75; H, 5.05. $C_{56}H_{48}Cl_3O_4P_3Ru$ (1 mol of CH_2Cl_2) requires C, 61.75; H, 4.8%].

Carbonylchlorohydrido(triphenylphosphine)bis(triphenyl phosphite)ruthenium(II), $[Ru(CO)(Cl)H(PPh_3)\{P(OPh)_3\}_2]$ (III).—Triphenyl phosphite (0.47 g) and complex (I) (0.3 g) were heated together under reflux in benzene (5 cm^3) for 1 h. Using the method given above the product was obtained as white microcrystals (0.13 g, 40%), m.p. 183 °C (Found: C, 62.75; H, 4.4; P, 9.15. $C_{55}H_{46}ClO_7P_3Ru$ requires C, 63.0; H, 4.45; P, 8.85%).

Carbonylchlorobis(triphenyl phosphite){*triphenyl phosphito*(C^2P)}*ruthenium*(II), $[Ru(CO)(Cl)\{P(OPh)_3\}_2(pc)]$ (IV).—Triphenyl phosphite (1.4 g) and complex (I) (0.91 g) were heated together under reflux in xylene (15 cm^3) for 1 h. Using the above technique the product was obtained as white crystals (0.12 g, 12%), m.p. 163—165 °C (Found: C, 60.45; H, 4.1; Cl, 4.1; P, 9.35. $C_{55}H_{44}ClO_{10}P_3Ru$ requires C, 60.35; H, 4.05; Cl, 3.25; P, 8.5%).

Carbonylhydrido(triphenylphosphine)(triphenyl phosphite){*triphenyl phosphito*(C^2P)}*ruthenium*(II), $[Ru(CO)H(PPh_3)\{P(OPh)_3\}(pc)]$ (VIII).—Triphenyl phosphite (0.7 g) and carbonyldihydridotris(triphenylphosphine)ruthenium (V), (0.46 g) were heated together under reflux in benzene (15 cm^3) for 1 h. Using the above technique the product was obtained as white crystals (0.13 g, 26%), m.p. 174—176 °C (Found: C, 65.0; H, 4.5; P, 8.05. $C_{55}H_{45}O_7P_3Ru$ requires C, 65.25; H, 4.5; P, 9.2%).

A Mixture of Complex (VIII) *and Carbonylhydridobis(triphenyl phosphite)*{*triphenyl phosphito*(C^2P)}*ruthenium*(II), $[Ru(CO)H\{P(OPh)_3\}_2(pc)]$ (IX).—Triphenyl phosphite (0.7 g) and complex (V) (0.46 g) were heated together under reflux in xylene (20 cm^3) for 1 h. Using the above technique the mixture was obtained as white crystals (0.21 g, *ca.* 40%) (Found: C, 63.0; H, 4.4; P, 8.85. $C_{55}H_{45}O_7P_3Ru$ requires C, 65.25; H, 4.5; P, 9.2. $C_{55}H_{45}O_{10}P_3Ru$ requires C, 62.3; H, 4.3; P, 8.75%).

Alternative preparation. The above mixture could be prepared in a similar fashion from $P(OPh)_3$ (0.7 g) and tricarbonylbis(triphenylphosphine)ruthenium (0.34 g) in xylene (20 cm^3) (0.14 g, *ca.* 28%) (Found: C, 63.1; H, 4.4%).

Bis(triphenyl phosphite)bis{*triphenyl phosphito*(C^2P)}*ruthenium*(II)*–Dichloromethane* (1/1), $[Ru\{P(OPh)_3\}_2(pc)_2]\cdot CH_2Cl_2$ (XI).—Triphenyl phosphite (0.5 g) and dihydridotetrakis(triphenylphosphine)ruthenium, (X) (0.38 g), were heated together under reflux in xylene (15 cm^3) for 1 h. Using the above method the dichloromethane-solvated product was obtained as white crystals (0.11 g, 25%), m.p. 250 °C, τ 4.72(s) (solvated CH_2Cl_2) [Found: C, 61.65; H, 4.25; Cl, 5.3; P, 9.05. $C_{72}H_{58}O_{12}P_4Ru$ requires C, 64.5; H, 4.35; P, 9.25. $C_{73}H_{60}Cl_2O_{12}P_4Ru$ (1 mol CH_2Cl_2) requires C, 61.5; H, 4.25; Cl, 5.0; P, 8.7%].

Bis(trifluoroacetato)tetrakis(triphenyl phosphite)ruthenium(II)*–Trifluoroacetic Acid* (1/1), $[Ru(O_2CCF_3)_2\{P(OPh)_3\}_4]\cdot CF_3CO_2H$.—Trifluoroacetic acid (0.5 cm^3) and complex (XI) (0.3 g) were heated together under reflux in benzene (18 cm^3) for 2 h. Using the above method the product was obtained as white crystals (0.11 g, 29%), m.p. 179 °C (Found: C, 55.3, 54.95; H, 4.0, 3.75; P, 7.3, 7.5. $C_{78}H_{61}F_9O_{18}P_4Ru$ requires C, 55.7; H, 3.65; P, 7.35%). Similarly prepared using pentafluoropropionic acid was bis(pentafluoropropionato)tetrakis(triphenyl phosphite)ruthenium(II)–pentafluoropropionic acid (1/1) as white crystals (39%), m.p. 178—180 °C (Found: C, 51.9; H, 3.4; P, 6.8. $C_{81}H_{61}F_{15}O_{18}P_4Ru$ requires C, 53.1; H, 3.35; P, 6.75%).

Attempted Demetallation of Complex (XI) *by Hydrogen.*—Complex (XI) (0.15 g) was dissolved in cold benzene (10 cm^3). The cold solution was flushed with hydrogen for 15 min. The solution was heated under reflux for 1 h, then cooled to ambient temperature with a stream of hydrogen passing through it, and the solvent was removed under reduced pressure. Unchanged complex (XI) was recrystallised from the resulting oil (0.12 g, 80%).

Attempted Demetallation of Complex (XI) *by Hydrogen Chloride.*—Complex (XI) was treated in a similar manner with hydrogen chloride instead of hydrogen. However, only the unchanged complex was recovered.

Hydridotetrakis(triphenyl phosphite)rhodium(I), $[RhH\{P(OPh)_3\}_4]$.—Triphenyl phosphite (1.55 g) and carbonylhydridotris(triphenylphosphine)rhodium (0.90 g) were heated together under reflux in ethanol (30 cm^3) to give a pale yellow solution which was then filtered, cooled slowly to ambient temperature, and kept overnight at 5 °C. The required product which separated as a pale yellow solid was filtered off, washed with ethanol and n-hexane, recrystallised from dichloromethane–methanol as air-sensitive creamy yellow crystals, and dried *in vacuo* (0.60 g, 45%), m.p. 155—165 °C (decomp.) (Found: C, 63.65; H, 4.50; P, 9.05. $C_{72}H_{61}O_{12}P_4Rh$ requires C, 64.3; H, 4.50; P, 9.25%).

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

Similarly prepared was hydridotetrakis(tri-*p*-tolyl phosphite)rhodium(I) as air-sensitive white *microcrystals* (62%) (Found: C, 66.9; H, 5.75; P, 8.50. $C_{84}H_{85}O_{12}P_4Rh$ requires C, 66.65; H, 5.70; P, 8.20%).

Tris(triphenyl phosphite){triphenyl phosphito(C^2P)}-*rhodium*(I), [Rh{P(OPh)$_3$}$_3$(pc)].—Triphenyl phosphite (0.9 g) and [Rh(CO)H(PPh$_3$)$_3$] (0.5 g) were heated together under reflux in n-heptane (15 cm^3) for 15 min. The yellow amorphous powder which deposited on cooling was filtered off, washed with n-hexane, and dried *in vacuo* (0.42 g, 57%) (Found: C, 64.75; H, 4.60; P, 8.65. $C_{72}H_{59}O_{12}P_4Rh$ requires C, 64.4; H, 4.45; P, 9.20%).

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