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Transition-metal Complexes containing Phosphorus Ligands. Part II.¹ Triaryl Phosphite Derivatives of Ruthenium and Osmium

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Simple metathetical replacement reactions have been utilised to synthesise some triaryl phosphite complexes $MX_2[P(OR)_3]_4$ (M = Ru or Os; X = Cl, Br, or I) from the corresponding triphenylphosphine derivatives $MX_2(PPh_3)_x$ (x = 3 or 4). Carbonyl and nitrosyl derivatives $MX_2(CO)[P(OR)_3]_3$, $MX_2(CO)_2[P(OR)_3]_2$, and $MX_3(NO)[P(OR)_3]_2$ have also been prepared. The complexes $RuHX(PPh_3)_3$ (X = Cl or Br) have been shown to undergo metathetical exchange to form triaryl phosphite complexes which react further, with elimination of a molecule of hydrogen, to yield organo-ruthenium(II) species. Structures containing a σ -bond between the central ruthenium atom and an *ortho*-carbon atom of one of the aryl rings are proposed for these latter derivatives and supporting spectroscopic evidence is discussed.

DURING a study of the ligand properties of triaryl phosphites ¹ we have prepared an extensive series of their derivatives of ruthenium(II) and osmium(II) halides, together with some novel ruthenium(II) phosphite complexes in which the ruthenium atom is σ -bonded to one of the *ortho*-carbon atoms of a co-ordinated triaryl phosphite ligand. We now describe the syntheses and physical characteristics of the new triaryl phosphite complexes. Additional physical measurements and an ¹ Part I, J. J. Levison and S. D Robinson, J. Chem. Soc. (A), 1970, 96.

investigation of the stereochemistry of these and some other triaryl phosphite derivatives will be reported elsewhere.

No simple triaryl phosphite complexes of ruthenium had been reported previously and examples of analogous osmium derivatives were confined to the dicarbonyl complexes $OsX_2(CO)_2[P(OPh)_3]_2$.² After our preliminary report, other workers mentioned their independent

² L. A. W. Hales and R. J. Irving, J. Chem. Soc. (A), 1967, 1932; W. Hieber, V. Frey, and P. John, Chem. Ber., 1967, 100, 1961.

preparation of dichlorotetrakis(triphenyl phosphite)ruthenium(II) and discussed its catalytic properties.³ The novel reaction of RuHCl(PPh3)3 with triaryl phosphites, which we first reported 4 and now discuss in detail was published independently by Knoth et al.⁵ while this paper was in preparation: our conclusions on the structures of the complexes support their findings.

Dihalogenotetrakis(triaryl phosphite)-ruthenium and -osmium Complexes, $MX_2[P(OR)_3]_4$.—Triphenylphosphine complexes $MX_2(PPh_3)_x$ (x = 3 or 4)⁶ react readily with an excess of triaryl phosphite in warm organic solvents to yield the corresponding triaryl phosphite derivatives $MX_2[P(OR)_3]_4$. The reactions may be carried out with n-hexane or ethanol solutions, when the product precipitates directly, or in benzene or dichloromethane solution when the complex is precipitated by the addition of n-hexane or ethanol. The tetrakis(triaryl phosphite) complexes are pale yellow or white crystalline solids and, in common with the other triaryl phosphite complexes reported in this paper, are very soluble in benzene and chlorinated hydrocarbon solvents. Molecular-weight values obtained for these and other triaryl phosphite derivatives described are up to 50% less than those required for monomeric species. Similar anomalous molecular-weight data have been reported ⁷ for other triaryl phosphite complexes of the platinum metals and for the triphenylphosphineruthenium(II) complexes RuX₂(PPh₃)₄.⁶ Pending further investigation we are reluctant to attribute our results to dissociation of the complexes.

Monocarbonyl Derivatives, MX₂(CO)[P(OR)₃]₃.—The ruthenium monocarbonyl complexes are readily prepared by treatment of the corresponding tetrakis(triary) phosphite) complexes with carbon monoxide at 25° in dichloromethane solution. Attempts to prepare the related osmium complexes gave carbonyl-containing species with consistently low carbon analyses; these were not characterised further.

Dicarbonyl Derivatives, $MX_2(CO)_2[P(OR)_3]_2$.--Prolonged carbonylation of the corresponding dihalogenotetrakis(triaryl phosphite)ruthenium complexes at high temperature (ca. 100°) leads to some formation of dicarbonyl derivatives. However the ruthenium dicarbonyl complexes RuX₂(CO)₂[P(OR)₃]₂ are more readily prepared by treatment of the polymeric dicarbonyl species $[RuX_2(CO)_2]_n^8$ with triaryl phosphites in boiling n-heptane. The synthesis of the corresponding dicarbonyl osmium derivatives OsX₂(CO)₂[P(OPh)₃]₂ from the complexes $[OsX_2(CO)_3]_2$ has previously been reported.² We find that triaryl phosphite complexes of this stoicheiometry may also be prepared by carbonylation of sodium hexachlorosmate in boiling diethylene

glycol followed by treatment of the resulting solution with triaryl phosphite. The presence of two strong bands attributable to v(CO) in the i.r. spectra of these dicarbonyl products indicates a *cis*-configuration of the carbonyl ligands.

Nitrosyl Derivatives, RuCl₃(NO)[P(OR)₃]₂.--Treatment of the complexes RuCl₂[P(OR)₃]₄ with nitrosyl chloride in dichloromethane leads to rapid formation of the complexes $RuCl_3(NO)[P(OR)_3]_2$ as pale yellow-green air-stable crystalline solids; these are the first nitrosylcontaining triaryl phosphite complexes of ruthenium to be reported. The nitrosyl stretching frequencies $\nu(NO)$ of these complexes lie within the range recorded 9 for a series of ruthenium(II) complexes RuX₃(NO)L₂ containing NO⁺ ligands; we therefore regard the new complexes as formal derivatives of ruthenium(II).

Trialkyl Phosphite Derivatives.—Trialkyl phosphites displace triphenylphosphine from the complexes MX₂(PPh₃)₄ but the resultant trialkyl phosphite derivatives are extremely soluble and difficult to isolate. However the presence of chlorine atoms in tris-2-chloroethyl phosphite renders its derivatives somewhat less soluble and we have thus isolated the complex $RuCl_2[P(OC_2H_4Cl)_3]_4$ in modest yield.

Hydrogen Elimination Reactions: Formation of Ruthenium-Carbon Bonds.-The complexes RuHX(PPh₃)₃ (X = Cl or Br) react with an excess of triphenyl phosphite in suspension in hot n-hexane with ready elimination of a molecule of hydrogen to form the organoruthenium complexes $RuX[P(OC_6H_4)(OPh)_2][P(OPh)_3]_3$ (I; a, b). Similar reactions in benzene at 25° have provided evidence for the intermediate formation of the hydride complexes RuHX[P(OPh)₃]₄ in these reactions.⁵ Treatment of the organo-ruthenium complexes with carbon monoxide in boiling benzene yields the monocarbonyl derivatives RuX(CO)[P(OC₆H₄)(OPh)₂][P(OPh)₃]₂.² The corresponding complexes derived from tri-p-tolyl phosphite have similarly been prepared. Attempts to isolate the related osmium derivatives were frustrated by lack of a suitable route to the precursors OsHX(PPh₂)₃. The organo-ruthenium complexes are white, air stable, crystalline solids; osmometric molecular-weight studies in benzene at 35° suggest that they are monomeric. However the significance of the molecular-weight results is doubtful in view of our findings for other triaryl phosphite derivatives. The structures which we suggest for the organo-ruthenium complexes [(I) and (II)] are supported by spectroscopic and analytical data and agree with those deduced by Knoth et al., on the basis of 220 MHz n.m.r. and deuteriation studies.⁵ The loss of the hydride ligand on formation of these organoruthenium complexes is suggested by the observed

⁸ A. Misono, Y. Uchida, M. Hidai, and I. Inomata, Chem. Comm., 1968, 704.

⁴ J. J. Levison and S. D. Robinson, Progr. Co-ordination Chem., 1968, 319.

⁵ W. H. Knoth and R. A. Schunn, J. Amer. Chem. Soc., 1969, 91, 2400; G. W. Parshall, W. H. Knoth, and R. A. Schunn, *ibid.*, 1969, 91, 4990.

⁶ T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945; L. Vaska, *Chem. and Ind.*, 1961, 1402. ⁷ L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1957, 1186;

<sup>L. Malatesta and M. Angoletta, J. Chem. Soc., 1987, 1186;
L. Malatesta and C. Cariello,</sup> *ibid.*, 1958, 2323.
⁸ W. Manchot and E. König, Ber., 1924, 57, 2130.
⁹ For collected data see J. A. McCleverty and B. F. G. Johnson, Progr. Inorg. Chem., 1966, 7, 277; J. Chatt and B. L. Shaw, J. Chem. Soc. (D) 1066, 1987. Chem. Soc. (B), 1966, 1811.

evolution of hydrogen and is confirmed by our failure to detect i.r. bands in the region 1600-2500 cm.⁻¹ or highfield n.m.r. signals on spectroscopic examination of the products. The organo-ruthenium complexes derived from triphenyl and tri-p-tolyl phosphites show i.r. bands at 1100 and 800, and 1120 and 750 cm.⁻¹, in addition to the broad strong bands found in the spectra

$$[(\rho - Y \cdot C_{6}H_{4}O)_{3}P]_{3} \xrightarrow{X} P = 0$$

$$(I) a; X = Cl, Y = H$$
b; X = Br, Y = H
c; X = Cl, Y = Me
d; X = Br, Y = Me
d; X = Br, Y = Me
d; X = Cl, Y = H
b; X = Cl, Y = Me
d; X = Cl, Y = H
b; X = Cl, Y = Me
d; X = Cl, Y = H
b; X = Cl, Y = Me
d; X = Cl, Y = Me

of the corresponding simple triaryl phosphite complexes $MX_{2}[P(OR)_{3}]_{4}$. Bands in this region of the i.r. spectrum may be attributed to vibrations of the aryl group and have been used to assign positions of substitution in aryl rings.¹⁰ In order to facilitate a similar assignment we have synthesised the complexes RuCl₂(CO)₂[P(OR)₃]₂ (R = o-tolyl and 2,4-xylyl) containing aryloxy-groups with substitution patterns similar to those suggested for the metal-bonded aryloxy-groups in the organo-ruthenium complexes derived from triphenyl and tri-p-tolyl phosphite respectively. Our observation of very strong bands in the i.r. spectra of these complexes (R = o-tolyl)1100, 800; R = 2,4-xylyl, 1120, 750 cm.⁻¹) corresponding exactly to the extra bands observed in the spectra of the organo-ruthenium derivatives appear to confirm our initial structural assignment. The ¹H n.m.r. spectra (60 MHz) of the simple triphenyl and tri-p-tolyl phosphite complexes MX₂[P(OR)₃]₄ show single, sharp resonances at ca. τ 3.0-3.2 and 7.8-8.0 attributable to aromatic and methyl protons respectively. In marked contrast the related organo-ruthenium derivatives show ¹H n.m.r. spectra of considerable complexity, consistent with chemical modification of an aromatic ring but not readily interpretated in structural terms. Thus the complex $RuCl[P(OC_6H_4)(OPh)_2][P(OPh)_3]_3$ show complicated n.m.r. patterns at τ 2·9-3·2 and 3·5-3·8 while the related complex derived from tri-p-tolyl phosphite shows broad n.m.r. patterns at τ 2.8-3.9 (aromatic protons) and τ 7.6—7.9 (methyl protons). Confirmatory evidence for the suggested structures of the organoruthenium complexes is being sought by X-ray crystallography.

A structural feature similar to that suggested for the organo-ruthenium(II) derivatives has recently been

confirmed in the related iron(II) complex $FeI[\pi-C_5H_4]$. $C_{6}H_{4}OP(OPh)_{2}[P(OPh)_{3}]$. An X-ray structure determination of this compound has revaled the presence of a σ-bond between an ortho-carbon atom of a triphenyl phosphite ligand and a carbon atom of the π -cyclopentadienyl group.11

Interactions between the central metal atom and the C-H bonds of co-ordinated phosphine ligands have been reported for a number of tertiary phosphine complexes of the transition metals.¹² In several examples, involving triphenylphosphine and bis(diphenylphosphino)ethane, evidence has been obtained for σ -bond formation between the central metal atom and an ortho-carbon atom one of the phenyl groups; some complexes containing linkages of this type have been isolated.¹³ However the organo-ruthenium complexes we have discussed are the first examples of triaryl phosphite complexes to show analogous features. The five-membered chelate ring structures [(I) and (II)] suggested for the rutheniumcarbon bonded triaryl phosphite complexes are expected to be less sterically strained than the four-membered rings found in related metal-carbon-bonded triphenylphosphine derivatives. Thus one may predict, on steric grounds at least, that metal-ortho-carbon bond formation will occur more readily in the complex chemistry of triaryl phosphites than in that of triphenylphosphine. This is confirmed by our studies on the triaryl phosphite complexes of rhodium and iridium.

EXPERIMENTAL

Molecular weights were obtained for benzene solutions at 35° with a Perkin-Elmer-Hitachi osmometer. Spectroscopic data were recorded on a Perkin-Elmer 457 grating i.r. spectrometer and a Perkin-Elmer R 10 n.m.r. spectrometer (60 MHz). M.p.s were determined on a Kofler hotstage microscope.

Ruthenium and osmium triphenylphosphine complexes ⁶ and halogenocarbonylruthenium complexes 8 were prepared by standard literature procedures. Triphenyl- (B.D.H.), tri-p-tolyl- (Eastman), and tri-2-chloroethyl phosphites (Fluka) were not further purified; other triaryl phosphites were prepared by literature methods.¹⁴ Reactions were carried out under nitrogen. Analyses and melting points are given in the Table.

Dichlorotetrakis(triphenyl phosphite)ruthenium(II).--Dichlorotris(triphenylphosphine)ruthenium(II) (1.0 g.) in dichloromethane (20 ml.) was gently warmed with triphenyl phosphite (2.0 ml.) for ca. 5 min. and the solution was then filtered, evaporated to small volume, and diluted with n-hexane (50 ml.). Recrystallisation of the resultant grey precipitate from dichloromethane-n-hexane gave the required product as cream prisms (0.9 g., 61%). The reaction may also be performed by gently warming a suspension of finely divided dichlorotris(triphenylphosphine)ruthenium(II) with triphenyl phosphite in n-hexane or ethanol when a precipitate is formed and recrystallised as before. In

¹⁰ L. J. Bellamy, 'The Infrared Spectra of Complex Mole-cules,' 2nd edn., Methuen, London, 1958, p. 54.
¹¹ V. G. Andrianov, Yu. A. Chapovskii, V. A. Semion, and

Yu. T. Struchkov, Chem. Comm., 1968, 282.

¹² N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, Chem. Comm., 1965, 237; S. J. La Placa and J. A. Ibers, Inorg. Chem., 1965, **4**, 778; for additional examples see ref. 5.

¹³ M. A. Bennett and D. L. Milner, Chem. Comm., 1967, 581; W. Keim, J. Organometallic Chem., 1968, 14, 179; G. Hata, H.

Kondo, and A. Miyake, J. Amer. Chem. Soc., 1968, 90, 2278. ¹⁴ G. M. Kosolapoff, 'Organophosphorus Compounds,' Wiley, New York, 1950, 180 New York, 1950, p. 180-210.

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several instances, treatment with activated charcoal, before recrystallisation removed coloured impurity.

The following were similarly prepared: dichlorotetrakis(tri-p-tolyl phosphite)ruthenium(II) as cream prisms (60%); dichlorotetrakis(tri-p-chlorophenyl phosphite)ruthenium(II) as cream prisms (65%); dichlorotetrakis(tri-2-chloroethyl phosphite)ruthenium(II) as white microcrystals (35%).

The following were similarly prepared from dibromotris(triphenylphosphine)ruthenium(II): dibromotetrakis(triphenyl phosphite)ruthenium(II) as cream prisms (60%); dibromotetrakis(tri-p-tolyl phosphite)ruthenium(II) as cream prisms (50%); dibromotetrakis(tri-p-chlorophenyl phosphite)ruthenium(II) as pale yellow prisms (70%). tris(tri-p-tolyl phosphite)ruthenium(II) as yellow crystals (65%); dichlorocarbonyltris(tri-p-chlorophenyl phosphite)ruthenium(II) as cream microcrystals (42%); dibromocarbonyltris(triphenyl phosphite)ruthenium(II) as cream prisms (20%); dibromocarbonyltris(tri-p-chlorophenyl phosphite)ruthenium(II) as yellow prisms (50%); di-iodocarbonyltris(triphenyl phosphite)ruthenium(II) as orange crystals (25%); dibromocarbonyltris(tri-p-tolyl phosphite)ruthenium(II) as pale yellow prisms (65%).

Dichlorodicarbonylbis(triphenyl phosphite)ruthenium(II). A suspension of catena-di- μ -chlorodicarbonylruthenium(II) (0.23 g., 1.0 mmole) and triphenyl phosphite (0.62 g., 2.0 mmoles) in n-heptane (20 ml.) was heated under reflux

Analytical, i.r., and melting-point data for some ruthenium and osmium phosphite complexes

Formula	x	R	M.p. (°c)	ν(CO) *	Found (%)				Required (%)			
					б	н	P	x	б	H	Р	x
RuX ₂ [P(OR) ₃] ₄	Cl Br I Cl Br	Ph Ph Ph <i>p</i> -C ₆ H ₄ Cl <i>p</i> -C ₆ H ₄ Cl	$151 - 152 \\ 163 - 166 \\ 173 - 175 \\ 158 \\ 164 - 165$		$\begin{array}{c} 61 \cdot 05 \\ 57 \cdot 35 \\ 54 \cdot 60 \\ 47 \cdot 85 \\ 45 \cdot 20 \end{array}$	$\begin{array}{c} 4 \cdot 45 \\ 4 \cdot 25 \\ 3 \cdot 80 \\ 2 \cdot 90 \\ 2 \cdot 60 \end{array}$	$9.10 \\ 8.50 \\ 6.60 \\ 6.55$	$5 \cdot 30 \\ 10 \cdot 35 \\ 15 \cdot 90 \\ 26 \cdot 60$	$\begin{array}{c} 61 \cdot 20 \\ 57 \cdot 50 \\ 54 \cdot 20 \\ 47 \cdot 30 \\ 45 \cdot 30 \end{array}$	$\begin{array}{c} 4 \cdot 30 \\ 4 \cdot 00 \\ 3 \cdot 80 \\ 2 \cdot 65 \\ 2 \cdot 55 \end{array}$	$8.75 \\ 8.25 \\ 6.80 \\ 6.45 $	5.00 10.65 15.90 27.15
	Cl Br Cl	<i>p</i> -C ₆ H ₄ Me <i>p</i> -C ₆ H ₄ Me C ₂ H ₄ Cl	$146 - 148 \\ 155 - 157 \\ 173 - 174$		63·80 60·65 23·65	5·20 5·20 3·95	$7.85 \\ 7.60 \\ 10.00$	4·80 9·40 39·60	$63.70 \\ 60.40 \\ 23.00$	5·35 5·05 3·90	7·85 7·40 9·85	4·50 9·55 39·70
RuX ₂ (CO)[P(OR) ₃] ₃	Cl Br Cl Br Cl Br Cl Br	Ph Ph Ph \$\nu\$-C_6H_4Cl\$ \$\nu\$-C_6H_4Cl\$ \$\nu\$-C_6H_4Me\$ \$\nu\$-C_6H_4Me\$	$128 - 129 \\ 141 - 145 \\ 148 - 151 \\ 133 - 134 \\ 140 - 142 \\ 143 - 146 \\ 148 - 150 \\$	2044 2044 2043 2051 2045 2040	57.95 53.90 50.30 45.75 43.25 60.90 57.00	$\begin{array}{c} 4\cdot 10 \\ 3\cdot 75 \\ 3\cdot 65 \\ 2\cdot 80 \\ 2\cdot 35 \\ 4\cdot 80 \\ 4\cdot 85 \end{array}$			$58.40 \\ 54.20 \\ 50.30 \\ 45.85 \\ 43.20 \\ 61.15 \\ 57.20$	$\begin{array}{c} 4\cdot 00\\ 3\cdot 70\\ 3\cdot 45\\ 2\cdot 55\\ 2\cdot 35\\ 5\cdot 05\\ 4\cdot 70\end{array}$		
RuX ₂ (CO) ₂ [P(OR) ₃] ₂	Cl Br Cl Br Cl Cl	Ph Ph p-C ₆ H ₄ Me p-C ₆ H ₄ Me o-C ₆ H ₄ Me 2,4-C ₆ H ₃ (Me) ₂	$\begin{array}{c} 158 - 160 \\ 158 - 160 \\ 164 - 167 \\ 162 - 165 \\ 161 - 163 \\ 158 - 160 \end{array}$	2026, 2082 2027, 2081 2027, 2081 2025, 2080 2026, 2081 2024, 2078	53.50 48.00 56.90 51.70 56.35 59.80	3.50 3.60 4.70 4.30 4.70 5.40	7.95	8.20	53·80 48·70 56·65 51·70 56·65 59·05	3.55 3.25 4.55 4.15 4.55 5.35	7.30	8.75
RuX ₃ (NO)[P(OR) ₃] ₂	Cl Cl	Ph p-C ₆ H ₄ Me	$154 - 161 \\ 152 - 154$	1886 † 1887 †	$50.60 \\ 53.35$	$3.45 \\ 4.55$		12.70	$50.40 \\ 53.50$	$3.55 \\ 4.50$		12.40
$OsX_2[P(OR)_3]_4$	Br Br Br	Ph p-C6H4Cl p-C6H₄Me	$159-161 \\ 212-215 \\ 158-160$		54·30 43·75 56·50	$4 \cdot 10 \\ 2 \cdot 70 \\ 5 \cdot 15$	7·85 6·55 7·10	10∙60 9∙30	$54 \cdot 40 \\ 43 \cdot 20 \\ 57 \cdot 30$	$3.80 \\ 2.40 \\ 4.80$	7·80 6·20 7·05	10.05 9.10
$OsX_2(CO)_2[P(OR)_3]_2$	C1	Ph	178—179	2002, 2069	48 · 4 0	4 ·15			48 .60	3.25		
(Ia) (Ib)	Cl Br	$\begin{array}{l} Y = H \\ Y = H \\ W = M \end{array}$	176-179 182-185 162		$62.55 \\ 60.60 \\ 65.5$	$4.20 \\ 4.30 \\ 5.50 \\ 5.50 \\ 5.50 \\ 1.50 \\ $	9·20	2.70	$62.80 \\ 60.80 \\ 65.8$	4·30 4·20	9·00	2.60
(IC) (Id) (IIa) (IIb)	Br Cl Cl		$ \begin{array}{c} 160 - 169 \\ 162 - 166 \\ 161 - 163 \\ 182 - 195 \\ 011 01 - 163 \\ 011 01 - 105 \\ 011 - 105 \\ 011 $	2026 2024	$62 \cdot 40$ $60 \cdot 00$ $62 \cdot 45$	5.70 5.65 4.45 5.40	7.85	2.55	65.30 63.30 60.40 63.00	$5 \cdot 45 \\ 5 \cdot 30 \\ 4 \cdot 40 \\ 5 \cdot 10$	8.00	2.30

* I.r. data taken for CH_2Cl_2 solutions. † Nitrosyl stretching vibrations $\nu(NO)$.

Di-iodotetrakis(triphenyl phosphite)ruthenium(II).—A mixture of the corresponding dichloro-complex (0.40 g.) and sodium iodide (0.2 g.) in acetone (20 ml.) was heated under reflux for 1 hr. After cooling, the precipitate was filtered off, washed successively with acetone, water, and acetone, dried *in vacuo*, and recrystallised from dichloromethanen-hexane as *pale yellow crystals* (70%).

Dichlorocarbonyltris(triphenyl phosphite)ruthenium(II).— Carbon monoxide was bubbled for 15 min. through a solution of dichlorotetrakis(triphenyl phosphite)ruthenium (0.20 g.) in dichloromethane (10 ml.). The solution was then filtered, diluted with n-hexane (10 ml.), and slowly evaporated. The yellow crystals which formed were washed with n-hexane and dried in vacuo (0.06 g., 38%).

The following were similarly prepared: dichlorocarbonyl-

for 2 hr. The white precipitate which formed on cooling, was washed with n-hexane and recrystallised from dichloromethane-methanol to give the required product as *white* crystals (0.5 g., 60%).

The following were similarly prepared: dichlorodicarbonylbis(tri-p-tolyl phosphite)ruthenium(II) as white crystals (60%); dichlorodicarbonylbis(tri-0-tolyl phosphite)ruthenium(II) as white crystals (63%); dichlorodicarbonylbis(tri-2,4-dimethylphenyl phosphite)ruthenium(II) as white needles

The following were similarly prepared from *catena*-di- μ bromodicarbonylruthenium(II): *dibromodicarbonylbis(triphenyl phosphite)ruthenium*(II) as white microcrystals (33%); *dibromodicarbonylbis(tri-p-tolyl phosphite)ruthenium*(II) as white microcrystals (28%).

Trichloronitrosylbis(triphenyl phosphite)ruthenium(II).---A

stream of nitrosyl chloride was bubbled for 1 min. through a solution of dichlorotetrakis(triphenyl phosphite)ruthenium (0.40 g.) in dichloromethane (15 ml.). The excess of nitrosyl chloride was boiled off, the solution was filtered, diluted with methanol, and evaporated slowly to give the required product as green crystals (0.06 g., 25%).

Trichloronitrosylbis(tri-p-tolyl phosphite)ruthenium(II).— This was similarly obtained as green crystals (25%).

Dibromotetrakis(triphenyl phosphite)osmium(II).—A finely divided suspension of dibromotris(triphenylphosphine)osmium (0.35 g.) in n-hexane (20 ml.) was warmed with triphenyl phosphite (1 ml.) until a grey precipitate formed and the mixture was then set aside overnight. The grey precipitate was filtered off, washed with n-hexane, dissolved in the minimum of dichloromethane and small quantities of coloured impurity removed by treatment with activated charcoal. Dilution of the filtrate with n-hexane and cooling at 0° overnight gave the required *product* as white prisms (0.15 g., 30%).

The following were similarly prepared: dibromotetrakis(tri-p-tolyl phosphite)osmium(II) as white prisms (25%); dibromotetrakis(tri-p-chlorophenyl phosphite)osmium(II) as white prisms (25%).

Dichlorodicarbonylbis(triphenyl phosphite)osmium(II).— Carbon monoxide was bubbled through sodium hexachlorosmate (0.5 g.) in diethylene glycol (25 ml.) heated under reflux for 2 hr. Triphenyl phosphite (1.0 ml.) was added to the cooled solution which was then heated to 100° for 10 min., was diluted with ethanol, and cooled overnight. The resultant precipitate was recrystallised from chloroform-methanol to give the required product as white crystals (0.38 g., 36%).

RuCl[P(OC₆H₄)(OPh)₂][P(OPh)₃]₃ (Ia).—A suspension of chlorohydridotris(triphenylphosphine)ruthenium (1.00 g.) in n-hexane (25 ml.) was warmed with triphenyl phosphite (2 ml.). The precipitate obtained was washed with n-hexane and recrystallised from dichloromethane–n-hexane to give the required product as *white prisms* (1.0 g., 66%; M 1403, for monomer 1376). Recrystallisation from benzene–n-hexane gave a benzene solvated product.

The following complexes were similarly prepared from tri-p-tolyl phosphite: RuCl[P(OC₆H₃Me)(OC₆H₄Me)₂]-[P(OC₆H₄Me)₃]₃ (Ic) as white microcrystals (M 1479, monomer 1545); RuBr[P(OC₆H₄)(OPh)₂][P(OPh)₃]₃ (Ib) from bromohydridotris(triphenylphosphine)ruthenium as white prisms (25%); RuBr[P(OC₆H₃Me)(OC₆H₄Me)₂]-[P(OC₆H₄Me)₃]₃ (complex Id) as white microcrystals (30%).

RuCl[P(OC₆H₄)(OPh)₂](CO)[P(OPh)₃]₂ (IIa).—Carbon monoxide was passed for 30 min. through a solution of RuCl[P(OC₆H₄)(OPh)₂][P(OPh)₃]₃ (0.40 g.) in boiling benzene (15 ml.). The solution was evaporated *in vacuo* and the resultant oil recrystallised from dichloromethane-methanol to give the required product as *white microcrystals* (0.10 g., 32%).

 $\begin{array}{l} RuCl[P(OC_6H_3Me)(OC_6H_4Me)_2](CO)[P(OC_6H_4Me)_3]_2 \ (IIb).\\ --This was similarly prepared from RuCl[P(OC_6H_3Me)-(OC_6H_4Me)_2][P(OC_6H_4Me)_3]_3 as white$ *microcrystals* $(30%). \end{array}$

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