Chemistry of the Metal Carbonyls. Part LXV.[1] Reactions Between Dodecacarbonyltriruthenium and Tertiary Phosphines or Arsines

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The preparation of trinuclear ruthenium complexes of the type $Ru_3(CO)_{12-n}L_n$ (L = tertiary phosphine or arsine; n = 1—4) is described. Their i.r. and ^1H n.m.r. spectra are discussed and possible structures suggested.

The complexes $Ru_3(CO)_9L_3$ [L = PPh_3, $P(m\text{-}C_6H_4Me)_3$, $P(p\text{-}C_6H_4Me)_3$ or $PMePh_2$] undergo controlled pyrolytic reactions in boiling decalin, affording complexes of the type $Ru_2(CO)_6(PAr_2)_2$ (Ar = Ph or $m\text{-}MeC_6H_4$), $Ru_2(CO)_6[PPhR(C_6H_4)](PPhR)$ (R = Ph or Me), $Ru_2(CO)_6[PPh_2(C_6H_4)]_2$, and $Ru_3(CO)_7(PAr_3)(PAr_2)$ (Ar = Ph, $m\text{-}MeC_6H_4$, or $p\text{-}MeC_6H_4$). Spectroscopic data suggest structures containing bridging phosphido-ligands, and *ortho*-metallated phenyl rings.

SINCE the discovery of a high-yield route to dodecacarbonyltriruthenium,[2,3] a number of reports have appeared describing reactions between this carbonyl with a variety of substituted phosphines or arsines. Some of these accounts are notable for the discrepancies in physical properties claimed; the most common

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[1] Part LXIV, M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 1781.

[2] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 1238.

[3] J. L. Dawes and J. D. Holmes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 847.

explanation being a ready formation of isomers (of unspecified configuration). Up to the present time, most authors have described the reaction

$$Ru_3(CO)_{12} + 3PR_3 \longrightarrow Ru_3(CO)_9(PR_3)_3 + 3CO$$

as proceeding without the isolation of mono- or disubstituted derivatives. Indeed, a kinetic study [4] of this reaction has suggested that formation of $Ru_3(CO)_{11}L$ is the rate-determining step, the subsequent formation of the complexes $Ru_3(CO)_{12-n}L_n$ ($n = 2$ and 3) being fast. Table 1 summarises the compounds which have been reported, together with their ν(CO) bands.

TABLE 1

Reported complexes of the type $Ru_3(CO)_{12-n}L_n$

L	n	Colour	M.p.	ν(CO), cm^{-1}	Solvent	Ref.
PPh_3	3	Deep red	150—165° d.	2060, 2040, 2020, 1980, 1965, 1958		*a*
		Dark violet		1980s, 1969s, 1945sh	CH_2Cl_2	*b*
				1982, 1969s, 1935s	Nujol	*b*
				2046vw, 1978sh, 1970s, 1933s, 1929s, 1920sh	C_6H_{12}	*c*
				1983, 1971	$C_6H_{11}Me–C_6H_6$	*d*
		Dark violet	174—176			*e*
$P(OPh)_3$	3	Orange	77—78	2001s, 1985s, 1970m, 1945sh	Nujol	*b*
PBu^n_3	3	Dark red	62—63	2035vw, 1960s, 1927sh	CH_2Cl_2	*b*
				2035w, 1964s, 1930m	Nujol	*b*
PEt_3	3	Orange red				*d*
PMe_2CH_2Ph	3	Reddish-purple	171—172	2043w, 2017w, 1973s, 1937m	C_6H_{12}	*f*
$AsPh_3$	2	Red-purple	158—160d	2100vw, 2080w, 2048w, 2027s, 2017s, 1998vs, 1979s, 1958m	C_6H_{12}	*g*
$AsMe_2CH_2Ph$	3	Purple	217—218	2043vw, 2016vw, 1982s, 1971s, 1935m, 1921m	C_6H_{12}	*f*
ffos	(2)			2087m, 2027m(sh), 2019s, 2007s, 1989m(sh), 1974w, 1960w, 1950w(sh)	C_6H_{12}	*h*
ffos	(4)	Dark red	200—202	2048m, 1996m(sh), 1978s(sh), 1972s, 1944m(sh), 1898w(sh)	CS_2	*h*
ffars	(2)	Dark red	191—192	2087m, 2024m(sh), 2014s, 2007s(sh), 1980w(sh), 1967w, 1950w(sh), 1938w(sh)	C_6H_{12}	*h*
ffars	(4)	Dark red	173—175	2045m, 1991m(sh), 1978s, 1971s, 1948m(sh), 1844w	C_6H_{12}	*h*

In addition to the above examples, the complexes $Ru_3(CO)_9L_3$ [L = PPh_2Et, $PPhEt_2$, PBu^n_3, $AsPh_3$, $SbPh_3$ (ref. *d*); L = PPh_2Me, $PPhMe_2$ (ref. *i*)], $Ru_3(CO)_8(PH_3)_4$ (ref. *j*), and $Ru_3(CO)_6(L_2)_3$ (L_2 = diphos, diars) (ref. *i*) have been mentioned cursorily, but no details are available.

[a] J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. and Ind.*, 1966, 1960. [b] F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1389. [c] B. F. G. Johnson, R. D. Johnston, P. L. Josty, J. Lewis, and I. G. Williams, *Nature*, 1967, **213**, 901. [d] Ref. 4. [e] F. Piacenti, M. Bianchi, E. Benedetti, and G. Braca, *Inorg. Chem.*, 1968, **7**, 1815. [f] Ref. 6. [g] Ref. 5. [h] W. R. Cullen and D. A. Harbourne, *Inorg. Chem.*, 1970, **9**, 1839. [i] Mentioned in R. D. Johnston, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 471. [j] F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1968, **90**, 3296.

In the course of an investigation [1] into the reactions between $Ru_3(CO)_{12}$ and a variety of substituted-phosphine platinum complexes, during which the derivatives $Ru_3(CO)_{12-n}L_n$ (n = 1—3) were isolated, it became evident that serious discrepancies existed between the published data and our own results. Accordingly we have reinvestigated the reactions of $Ru_3(CO)_{12}$ with a range of substituted phosphines and arsines.

Generally, we have confirmed the ready formation of trisubstituted complexes, $Ru_3(CO)_9L_3$. However, in several cases, chromatographic separation of the reaction products (in contrast with the crystallisations previously used) has enabled us to isolate in addition several complexes $Ru_3(CO)_{12-n}L_n$ (n = 1 or 2), together with a tetrasubstituted complex with L = $PPh(OMe)_2$.

We have also confirmed our original finding [5] that the disubstituted complex, $Ru_3(CO)_{10}(AsPh_3)_2$, is formed with triphenylarsine, with no evidence for the formation of a tris-derivative. In contrast, however, other arsines, such as $AsMe_2Ph$ and $AsMe_2CH_2Ph$,[6] afforded the trisubstituted compounds. A single product, shown to be $Ru_3(CO)_{10}$(diphos), in which the ligand probably chelates one metal atom, was obtained using $Ph_2PCH_2CH_2PPh_2$ (diphos).

The absolute stereochemistries of these products are difficult to determine unless recourse to *X*-ray diffraction methods is made, but some conclusions may be drawn from the i.r. and ^1H n.m.r. data. Thus, in no case were any bands characteristic of bridging carbonyl groups found, although as might be expected with the more basic phosphines, the lowest ν(CO) bands occurred *ca.* 1940 cm^{-1} (Table 2).

Comparison of the i.r. spectra of the disubstituted complexes also does not provide any information concerning the positions of substitution. The configuration of only one complex is known, namely that of (ffars)$Ru_3(CO)_{10}$ (ffars = $Me_2As{\cdot}C{=}C(AsMe_2){\cdot}CF_2CF_2$), in which the ligand bridges two metal atoms. The ν(CO) pattern reported for this complex closely resembles those of $Os_3(CO)_{10}(PPh_3)_2$ (presumably containing the two ligands attached to different metal

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[4] J. P. Candlin and A. C. Shortland, *J. Organometallic Chem.*, 1969, **16**, 289.

[5] M. I. Bruce, C. W. Gibbs, and F. G. A. Stone, *Z. Naturforsch.*, 1968, **23b**, 1543.

[6] M. I. Bruce, R. L. Bennett, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **38**, 325.

atoms), and the complexes $Ru_3(CO)_{10}[PPh(CMe)_2]_2$, $Ru_3(CO)_{10}(AsPh_3)_2$, and $Ru_3(CO)_{10}$(diphos) reported here.

^{1}H N.m.r. parameters are listed in Table 3. Of most interest were the methyl resonances of the appropriate phosphine complexes, which enable some observations concerning relative stereochemistries to be made. Thus, in the spectra of $Ru_3(CO)_{12-n}(PMe_2Ph)_n$, simple doublet resonances are found at τ *ca.* 8·0, suggesting that each phosphine is attached to a different metal atom, with a stepwise replacement of CO groups. Similar spectra are exhibited by the $PMePh_2$ complexes.

TABLE 2

Carbonyl stretching bands for some trinuclear ruthenium carbonyl derivatives

Compound	ν(CO), cm^{-1} (cyclohexane)
$Ru_3(CO)_{11}PPh_3$	2097m, 2046s, 2030sh, 2023sh, 2014s, 1996sh, 1986m, 1972sh, 1960sh
$Ru_3(CO)_9(PPh_3)_3$ [a]	2044vw, 1978sh, 1967s,br
$Ru_3(CO)_9\{P(m\text{-}MeC_6H_4)_3\}_3$ [a]	2044vw, 1979sh, 1967s,br
$Ru_3(CO)_9\{P(p\text{-}MeC_6H_4)_3\}_3$ [a]	2039vw, 2017w, 1977sh, 1965s,br
$Ru_3(CO)_{10}(PMePh_2)_2$	2070m, 2016s, 1993s,br, 1969sh
$Ru_3(CO)_9(PMePh_2)_3$ [b]	2042w, 1966s, 1939sh
$Ru_3(CO)_{11}(PMe_2Ph)$	2092m, 2039s, 2026s, 2010s, 1998sh, 1991sh, 1980m, 1973sh, 1956sh
$Ru_3(CO)_{10}(PMe_2Ph)_2$	2069w, 2013s, 1989s,br, 1969sh
$Ru_3(CO)_9(PMe_2Ph)_3$	2040w, 1972sh, 1966s, 1938m
$Ru_3(CO)_9\{P(NMe_2)_3\}_3$	1987sh, 1975s, 1937w
$Ru_3(CO)_{10}(AsPh_3)_2$	2099w, 2075w, 2047w, 2026s, 2015s, 1995s, 1979sh, 1959sh
$Ru_3(CO)_9(AsMe_2Ph)_3$	2050w, 1988sh, 1976s, 1943s
$Ru_3(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$	2082m, 2021sh, 2016s, 2001s, 1983sh, 1965w, 1935w,br
$Ru_3(CO)_9\{P(OMe)_3\}_3$	2054w, 2001sh, 1988s, 1963sh
$Ru_3(CO)_{10}\{PPh(OMe)_2\}_2$	2080m, 2029s, 2005s, 1984sh, 1972sh
$Ru_3(CO)_8\{PPh(OMe)_2\}_4$ [b]	2031w, 1983s, 1965s, 1913sh

[a] Measured in benzene. [b] Measured in chloroform.

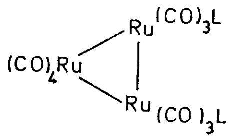
TABLE 3

^{1}H N.m.r. data for some trinuclear ruthenium carbonyl derivatives [a]

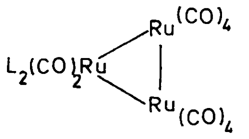
Compound	τ_{phenyl}	τ_{methyl} (J_{PH}, Hz)
$Ru_3(CO)_9\{P(m\text{-}MeC_6H_4)_3\}_3$	2·75m	7·73
$Ru_3(CO)_9\{P(p\text{-}MeC_6H_4)_3\}_3$	2·75m	7·63
$Ru_3(CO)_{10}(PMePh_2)_2$	2·66m	7·93d (8·5)
$Ru_3(CO)_9(PMePh_2)_3$	2·72m	7·98d (8·5)
$Ru_3(CO)_{11}PMe_2Ph$	2·59m	8·08d (9·5)
$Ru_3(CO)_{10}(PMe_2Ph)_2$	2·61m	8·11d (9·25)
$Ru_3(CO)_9(PMe_2Ph)_3$	2·65m	8·20d (9·25)
$Ru_3(CO)_9\{P(NMe_2)_3\}_3$		7·36d (10·25)
$Ru_3(CO)_9(AsMe_2Ph)_3$	2·57m	8·32
$Ru_3(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$	2·54m	7·79m (CH_2)
$Ru_3(CO)_9\{P(OMe)_3\}_3$		6·36d (12·0)
$Ru_3(CO)_{10}\{PPh(OMe)_2\}_2$	2·50m	6·39d (12·5)
$Ru_3(CO)_8\{PPh(OMe)_2\}_4$	2·52m	6·48d (12·0) 6·92d (12·0)

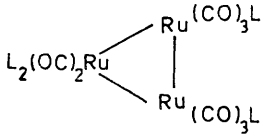
[a] Spectra determined in $CDCl_3$–Me_4Si at 100 MHz.

The phosphonite, $PPh(OMe)_2$, forms di- and tetrasubstituted derivatives. The spectrum of the former exhibits an apparent doublet at τ 6·39, with separation 12·5 Hz, which shows the additional central structure previously found in *cis*-bis-phosphite complexes.[7] The tetrasubstituted complex gives two signals, of equal intensity at τ 6·48 and 6·92. The low-field resonance is a simple doublet (J_{PH} 12·0 Hz), whereas the other signal has a similar pattern to that found in the disubstituted complex. The disubstituted complex may have either of the structures (Ia) or (Ib), neither the ^{1}H n.m.r. or the ν(CO) spectra (above) distinguishing between these. It seems likely, however, that the tetrasubstituted complex has structure (II), with two ligands attached in a relative *cis*-configuration on one metal atom.



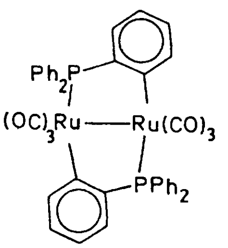
(Ia)



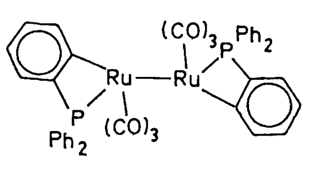


L = $PPh(OMe)_2$

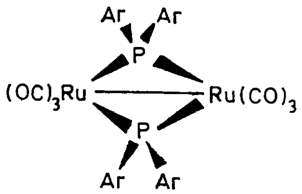
(Ib) (II)



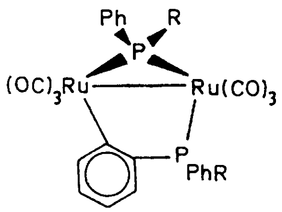
(IIIa)



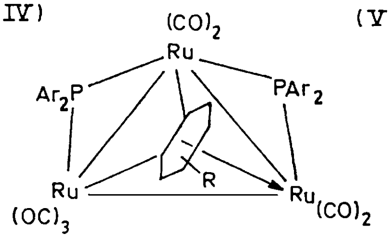
(IIIb)



(IV)



(V)



(VI) Ar = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4
R = H or Me

Controlled Pyrolysis Reactions.—There is currently considerable interest in intramolecular metallation reactions involving co-ordinated tertiary phosphine and

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[7] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

triaryl phosphite ligands.[8-10] Some of the resulting complexes are active catalysts for the hydrogenation of olefins. No tertiary phosphine complexes of ruthenium resulting from *ortho*-metallation of a phenyl phosphine ligand have been isolated, but deuteriation studies have shown that $RuHCl(PPh_3)_3$ and $RuH_2(N_2)(PPh_3)_3$ undergo intramolecular aromatic substitution reactions.[11] The equilibria for these reactions lie well over on the side of the non-metallated complex. A related reaction has been reported for $Ru[Me_2PCH_2CH_2PMe_2]_2$, in which metallation of one of the P–Me groups affords a six-co-ordinate ruthenium(II) hydride complex.[12]

TABLE 4

Analytical data and other physical properties for some polynuclear ruthenium carbonyl complexes [a]

Compound	Colour	% Yield	M.p. (°C)	C	H	O	As or P	Ru	*M* [b]
$Ru_3(CO)_{11}PPh_3$	Yellow	16	131—133	40·2 (39·35)	1·85 (1·75)				
$Ru_3(CO)_9(PPh_3)_3$	Red	86	178—181 [d]	56·15 (56·4)	3·25 (3·35)				
$Ru_3(CO)_9\{P(m\text{-}MeC_6H_4)_3\}_3$	Red	95	172—173	58·6 (58·9)	4·3 (4·3)	11·2 (9·8)	6·5 (6·35)		1211 (1469)
$Ru_3(CO)_9\{P(p\text{-}MeC_6H_4)_3\}_3$	Red	87	182—183	58·5 (58·9)	4·15 (4·3)	9·75 (9·8)	6·15 (6·35)	20·5 (20·65)	
$Ru_3(CO)_{10}(PMePh_2)_2$	Red	17	129—130	44·1 (43·95)	2·8 (2·65)				820 (984)
$Ru_3(CO)_9(PMePh_2)_3$	Red	8	175—177	49·85 (49·8)	3·35 (3·4)				
$Ru_3(CO)_{11}PMe_2Ph$ [c]	Orange-red	3	108—109						
$Ru_3(CO)_{10}(PMe_2Ph)_2$	Red	17	145—147	36·65 (36·3)	3·0 (2·6)				710 (860)
$Ru_3(CO)_9(PMe_2Ph)_3$	Red	19	142—144	40·95 (40·85)	3·4 (3·45)				790 (970)
$Ru_3(CO)_9\{P(NMe_2)_3\}_3$ [e]	Red	66	255—258	31·3 (31·05)	5·5 (5·2)				
$Ru_3(CO)_{10}(AsPh_3)_2$	Red	1·5	170—172 [d]	46·65 (46·2)	2·35 (2·55)	13·6 (13·4)	11·15 (12·55)	25·45 (25·35)	1015 (1196)
$Ru_3(CO)_9(AsMe_2Ph)_3$	Red	47	130—132	35·6 (35·95)	3·0 (3·0)				
$Ru_3(CO)_{10}Ph_2PCH_2CH_2PPh_2$	Red	3	>190 [d]	44·05 (44·05)	2·55 (2·45)				
$Ru_3(CO)_{10}\{PPh(OMe)_2\}_2$	Red	14	120—122	33·3 (33·8)	2·35 (2·4)				
$Ru_3(CO)_8\{PPh(OMe)_2\}_4$	Red	57	165—168	39·5 (39·75)	3·85 (3·65)	20·9 (21·2)	10·7 (10·25)	26·35 (25·1)	
$Ru_3(CO)_9\{P(OMe_3)\}_3$	Red	7	111—114	23·55 (23·3)	2·95 (2·95)				
$Ru_3(CO)_7\{PPh_2\}_2C_6H_4$	Red	23	218—222	46·9 (47·05)	2·55 (2·45)	11·65 (11·85)	6·55 (6·55)	32·1 (32·1)	770 (946)
$Ru_3(CO)_7\{P(m\text{-}MeC_6H_4)_2\}_2MeC_6H_3$	Red	19	122—123	49·9 (49·7)	3·7 (3·45)	11·6 (11·0)	5·85 (6·1)	28·95 (29·8)	678 (1016)
$Ru_3(CO)_7\{P(p\text{-}MeC_6H_4)_2\}_2MeC_6H_3$	Red	8	184—186	49·35 (49·7)	3·35 (3·45)	11·4 (11·0)	5·95 (6·1)	28·85 (29·8)	
$Ru_2(CO)_6\{P(m\text{-}MeC_6H_4)_2\}_2$	White	11	204—206	51·25 (51·25)	3·15 (3·55)	12·1 (12·05)	7·75 (7·75)	25·5 (25·4)	
$Ru_2(CO)_6\{P(C_6H_4)PhMe\}(PPhMe)$	White	6	195—197	44·85 (45·0)	2·9 (3·05)	14·25 (13·85)		29·4 (29·15)	639 (694)
$Ru_2(CO)_6\{P(C_6H_4)(C_6H_5)_2\}_2$	Yellow	10	193—196	56·5 (56·5)	3·15 (3·15)	12·1 (10·75)	7·7 (6·95)		

[a] Calculated figures in parentheses. [b] Determined in chloroform solution using a Mechrolab Osmometer. [c] Not isolated analytically pure. [d] With decomposition. [e] N, 11·55 (12·05)

TABLE 5

^1H N.m.r. data for some ruthenium–carbonyl–phosphine complexes formed by pyrolysis of trinuclear complexes in decalin [a]

Compound	τ_{phenyl}	τ_{methyl}
$Ru_3(CO)_7(PPh_2)_2C_6H_4$	2·38m (2), 2·70m (8), 3·10m (1), 3·62 (1)	
$Ru_3(CO)_7\{P(m\text{-}MeC_6H_4)_2\}_2MeC_6H_3$	2·57m (5), 2·90m (13), 3·30m,br (1), 3·71d (1) $J_{HH} = 8·0$	7·68 (6), 7·77 (6), 8·20 (3)
$Ru_3(CO)_7\{P(p\text{-}MeC_6H_4)_2\}_2MeC_6H_3$	2·50m (4), 3·08m (14), 3·75m (1)	7·69 (6), 7·72 (6), 8·23 (3)
$Ru_2CO)_6\{P(m\text{-}MeC_6H_4)_2\}_2$	3·13m (8)	7·82 (3), 8·02 (3)
$Ru_2(CO)_6\{P(C_6H_4)PhMe\}\{PPhMe\}$	1·82d (1), 2·95m (12) $J_{HH} = 7·0$ 3·56t (1) $J_{HH} = 8·0$	7·86d (3), 8·70d (3) $J_P = 8·75$, $J_P = 8·75$
$Ru_2(CO)_6\{P(C_6H_4)(C_6H_5)_2\}_2$	2·68m (11), 3·04m (1), 3·25m (2)	

[a] Measured in $CDCl_3$ solution at 100 MHz using TMS as internal standard. Relative intensities given in parentheses; m = multiplet, d = doublet, t = triplet, br = broad.

Controlled pyrolytic reactions in an inert solvent, such as decalin, have been found to be useful sources of this type of complex.[12] Heating complexes of the type $Ru_3(CO)_9L_3$ [L = PPh_3, $P(m\text{-}MeC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$, or $PMePh_2$] in refluxing decalin affords a variety of complexes, which have been separated by extensive chromatography on alumina. Complexes with the compositions (Table 4) $Ru_2(CO)_6[PPh_2(C_6H_4)]_2$ (III), $Ru_2(CO)_6(PAr_2)_2$ (Ar = Ph or $m\text{-}MeC_6H_4$) (IV), $Ru_2(CO)_6[PPhR(C_6H_4)](PPhR)$ (R = Me or Ph) (V), and $Ru_3(CO)_7(PAr_3)(PAr_2)$ (Ar = Ph, $m\text{-}MeC_6H_4$, or $p\text{-}MeC_6H_4$) (VI) were isolated. Similar pyrolytic reactions were carried out with complexes containing other phosphines, and also with $Ru_3(CO)_{10}(AsPh_3)_2$, and although other complexes were formed, they could not be isolated in a pure state. These derivatives are presumably analogous to the new compounds described in detail below.

The ^1H n.m.r. spectrum (Table 5) of the yellow air-stable crystalline binuclear compound $Ru_2(CO)_6[PPh_2(C_6H_4)]_2$ exhibits three complex resonances at τ 2·68, 3·04, and 3·25, with relative intensities 11 : 1 : 2. Widely separated chemical shifts for the aromatic protons is now a characteristic feature of co-ordinated phosphorus- or nitrogen-containing ligands where the metal is bonded to an *ortho*-carbon atom of one of the phenyl groups, although overlapping resonances precluded observation of the expected five resonances. The i.r. spectrum (Table 6) showed only terminal ν(CO) bands, and the region 1600—650 cm^{-1} contained new absorptions at 1585, 1200, 1170, and 895 cm^{-1}, which were not present in the spectrum of $Ru_3(CO)_9(PPh_3)_3$. Bands at similar positions have been reported in the spectra of *ortho*-metallated phosphites [9] or phosphines.[10]

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The mass spectrum did not show a parent ion, but ions corresponding to the loss of two phenyl groups, followed by the stepwise loss of six carbonyl groups, were found at the high *m/e* end of the spectrum.

The physical properties of this complex thus suggest the presence of *ortho*-metallated phosphine ligands, and six carbonyl groups attached to two metal atoms. Two structures, (IIIa) or (IIIb), may be considered, and at present no distinction is possible between them.

TABLE 6

Carbonyl stretching frequencies for some ruthenium phosphine complexes formed by pyrolysis of trinuclear complexes in decalin

Complex	ν(CO), cm^{-1} [a]
$Ru_3(CO)_7(PPh_2)_2C_6H_4$	2057s, 2020s, 2009vs, 1998s, 1968s, 1955s
$Ru_3(CO)_7\{P(p\text{-}MeC_6H_4)_2\}_2MeC_6H_3$	2054s, 2016s, 2006vs, 1996s, 1964s, 1950s
$Ru_3(CO)_7\{P(m\text{-}MeC_6H_4)_2\}_2MeC_6H_3$	2054s, 2017s, 2006vs, 1996s, 1965s, 1950s
$Ru_2(CO)_6(PPh_2)_2$	2072s, 2041s, 2011s, 2007sh, 1983s, 1975s
$Ru_2(CO)_6\{P(C_6H_4)Ph_2\}(PPh_2)$	2071s, 2037s, 2010s, 1991w, 1987m, 1969m
$Ru_2(CO)_6\{P(m\text{-}MeC_6H_4)_2\}_2$	2070s, 2067sh, 2039s, 2009s, 2004sh, 1981s, 1972s
$Ru_2(CO)_6\{P(C_6H_4)PhMe\}(PPhMe)$	2068s, 2033s, 2008s, 2003sh, 1987w, 1977m, 1965m
$Ru_2(CO)_6\{P(C_6H_4)(C_6H_5)_2\}_2$	2028s, 1981s, 1968s, 1943s, 1920m

[a] Measured in cyclohexane.

The ν(CO) spectrum of a complex formally related to (IIIb), namely $[Ru(azb)(CO)_3]_2$ (azb = phenylazophenyl-2*C*,*N*′), differs appreciably from that observed for complex (III).[14] The osmium analogue of complex (III), however, exhibits a ν(CO) pattern which is similar to that of the ruthenium complex.[1]

The mass spectrum of the white air-stable complex $Ru_2(CO)_6[P(m\text{-}MeC_6H_4)_2]_2$ (IV; Ar = *m*-MeC_6H_4) exhibited a parent ion corresponding to the indicated composition, together with ions formed by the consecutive loss of the six carbonyl groups. The ^1H n.m.r. spectrum showed two singlets in the methyl region, together with a multiplet for the phenyl protons. The relative intensities, 3 : 3 : 8 respectively, indicate that metallation of the ring has not occurred, and in agreement with this, the 1600—600 cm^{-1} region of the i.r. spectrum is identical with that of the precursor, $Ru_3(CO)_9[P(m\text{-}MeC_6H_4)_3]_3$. Only terminal ν(CO) bands are found, and we suggest that this complex contains two $Ru(CO)_3$ groups bridged by two diarylphosphido-groups. The diamagnetism requires also the presence of a metal–metal bond, and the stereochemistry results in the presence of two chemically inequivalent aryl groups. A similar complex, $Ru_2(CO)_6(PMe_2)_2$, has been reported[15] from the reaction between $Ru_3(CO)_{12}$ and P_2Me_4, and the ^1H n.m.r. spectrum exhibits two apparent triplets at τ 8·08 and 8·40, consistent with the presence of non-equivalent methyl groups.

From the pyrolysis of $Ru_3(CO)_9(PMePh_2)_3$ we have isolated a white crystalline solid, with the composition $Ru_2(CO)_6[PMePh(C_6H_4)](PMePh)$ (V; R = Me). The i.r. spectrum showed only terminal ν(CO) bands, and the ^1H n.m.r. spectrum contained three resonances from aromatic protons (total intensity 14), and two doublets (total intensity 6) at τ 7·86 and 8·70, indicating two non-equivalent methyl groups. The ratio of phenyl to methyl protons is consistent with the above formulation and the wide range of chemical shifts observed for the aromatic protons, suggests the presence of an *ortho*-metallated phenyl ring. Comparison of the i.r. spectra of (V) and of the precursor in the fingerprint region showed new absorptions in the former, at 1548, 1445, 1124, and 871 cm^{-1}. We suggest that this complex also contains two $Ru(CO)_3$ groups, but bridged by a phosphido-group (PMePh), and an *ortho*-metallated phosphine ligand $[PMePh(C_6H_4)]$; again its diamagnetism requires a ruthenium–ruthenium bond. The lower field methyl doublet is probably due to the methyl group attached to the phosphido-group.

The complexes $Ru_2(CO)_6(PPh_2)_2$ and $Ru(CO)_6$-$[PPh_2(C_6H_4)](PPh_2)$ were isolated in trace amounts from the pyrolysis of $Ru_3(CO)_9(PPh_3)_3$, and comparison of their i.r. spectra with those of complexes (IV) and (V) discussed above, suggests that these complexes have similar structures. The mass spectrum of $Ru_2(CO)_6$-$(PPh_2)_2$ exhibits a parent ion and clusters corresponding to stepwise loss of six carbonyl groups.

Also found as products from these reactions are the dark red air-stable crystalline trinuclear complexes of composition $Ru_3(CO)_7(PAr_3)(PAr_2)$ (Ar = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4) (VI), confirmed by analysis and mass spectra, which show parent ions, and ions formed by successive loss of seven carbonyl ligands. The i.r. spectra show terminal ν(CO) bands, and the 1600—650 cm^{-1} region shows little change compared to the spectra of $Ru_3(CO)_9(PAr_3)_3$.

The ^1H n.m.r. spectra of these complexes contain several multiplets in the region τ 2·30—3·80. In the tolyl derivatives, the methyl resonances are found as three singlets, with relative intensities 2 : 2 : 1. Neither in this, nor in any other spectra, were any resonances found in the region τ 10—40, indicating the absence of metal-bonded protons. These results confirm a formulation with five aryl groups, four of which could be involved in bridging diarylphosphido-groups, as discussed above. The nature of the fifth aryl group remains in doubt; an *ortho*-metallated ligand is suggested by the ^1H n.m.r. data, but not confirmed by the i.r. spectra.

When this work had been completed, the results of an investigation of the products obtained from the reaction between $Os_3(CO)_{12}$ and PPh_3 in refluxing xylene were communicated.[16] One of these has a similar com-

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position to the trinuclear complex discussed above, and an *X*-ray determination of the structure revealed that the fifth aryl group is a benzyne group, stabilised by co-ordination to the Os_3 cluster. Other features of the structure confirm the deductions we have made on the basis of spectroscopic evidence.

The present study is complementary to the work on the osmium system, and several interesting differences have been found. In the first place, the preponderance of binuclear complexes for ruthenium, compared with the trinuclear osmium compounds, reflects the greater strength of the metal–metal bonds in the Os_3 cluster. Secondly, we have found no evidence for any ruthenium hydride species, in contrast to the three such complexes observed for the osmium system; the dramatic increase in stability of $H_2Os(CO)_4$ [17] over $H_2Ru(CO)_4$ [18] is now well known. Finally, in the three trinuclear osmium complexes whose structures have been determined, the *ortho*-metallated phosphine ligand bridges two metal atoms, suggesting that for complex (III) the formulation (IIIa) should be preferred.

EXPERIMENTAL

Spectra were obtained with Perkin-Elmer 257 (i.r.), Varian HA 100 (^1H n.m.r.), or AEI MS 902 (mass) instruments. All reactions were carried out under nitrogen. Light petroleum had b.p. 40—60°. Chromatography was on Florisil columns, initially packed in light petroleum. Analytical and m.p. data for all complexes are given in Table 4.

Reactions between $Ru_3(CO)_{12}$ *and Tertiary Phosphines or Arsines.*—Carbonyl stretching frequencies and ^1H n.m.r. data for compounds described in this section are collected in Tables 2 and 3, respectively.

In general, the carbonyl was refluxed with the ligand in equimolar (*i.e.* Ru: P or As = 1 : 1) proportions, in hexane for a short period (1—3 h). Filtration and chromatography enabled the various products to be separated by continued elution from a long (*ca.* 50 cm) column with light petroleum or light petroleum–ether. The complexes were finally purified by recrystallisation from light petroleum–ether or –dichloromethane.

Some complexes were also obtained from reactions between $Ru_3(CO)_{12}$ and platinum–phosphine complexes; [1] details of these experiments can be found in the earlier paper. In other cases (see below), pure products were obtained by crystallisation of the reaction product; chromatography having showed only one complex was present.

(a) *With* $P(NMe_2)_3$. Tris(dimethylamino)phosphine (204 mg; 1·25 mmol) was added to a suspension of $Ru_3(CO)_{12}$ (200 mg; 0·31 mmol) in hexane (25 ml), and the mixture refluxed for 2 h. The solid which precipitated on cooling was washed with *n*-hexane (2 × 10 ml), and recrystallised from light petroleum–dichloromethane to give dark red prisms of *enneacarbonyltris[tris(dimethylamino)phosphine]triruthenium.*

(b) *With* $PPh(OMe)_2$. Dimethyl phenylphosphonite (222 mg; 1·31 mmol) was added to $Ru_3(CO)_{12}$ (200 mg; 0·31 mmol) in hexane (20 ml), and the mixture refluxed for 1 h. Crystallisation (light petroleum–dichloromethane) of the solid which precipitated on cooling afforded pure *octacarbonyltetrakis(dimethyl phenylphosphonite)triruthenium.*

(c) *With* $AsMe_2Ph$. A similar reaction between dimethylphenylarsine (250 mg; 1·37 mmol) and $Ru_3(CO)_{12}$ (250 mg; 0·39 mmol) after 2 h afforded plates of *enneacarbonyltris(dimethylphenylarsine)triruthenium.*

Controlled Pyrolysis Reactions.—I.r. spectra [ν(CO) bands], and ^1H n.m.r. data for complexes described in this Section are given in Tables 5 and 6.

(*a*) $Ru_3(CO)_9(PPh_3)_3$. A suspension of $Ru_3(CO)_9(PPh_3)_3$ (1·12 g) in decalin (15 ml) was refluxed for 20 min, and the resulting solution was chromatographed on alumina. Elution with light petroleum removed the decalin, followed by trace amounts of two white solids, probably $Ru_2(CO)_6(PPh_2)_2$ and $Ru_2(CO)_6[PPh_2(C_6H_4)](PPh_2)$. Further elution afforded $Ru_3(CO)_7(PPh_2)_2(C_6H_4)$, obtained as *prisms* from light petroleum–ether. Elution with light petroleum–ether (9 : 1) gave $Ru_2(CO)_6[PPh_2C_6H_4)]_2$, recrystallised from light petroleum–ether as *prisms.*

The trinuclear product was isolated in 20% (30 min) and 21% yield (60 min) on refluxing for longer periods, and in 31% yield when the reaction was carried out in refluxing mesitylene for 30 min.

(*b*) $Ru_3(CO)_9[P(m\text{-}MeC_6H_4)_3]_3$. A suspension of $Ru_3(CO)_9[P(m\text{-}MeC_6H_4)_3]_3$ (1·14 g) in decalin (15 ml) was refluxed for 20 min as above. Chromatography gave separately $Ru_2(CO)_6[P(m\text{-}MeC_6H_4)_2]_2$, which recrystallised from light petroleum–ether as *prisms*, and $Ru_3(CO)_7[P(m\text{-}MeC_6H_4)_2]_2(MeC_6H_3)$, which afforded *prisms* from light petroleum (b.p. 30—40°).

(*c*) $Ru_3(CO)_9[P(p\text{-}MeC_6H_4)_3]_3$. The complex $Ru_3(CO)_9[P(p\text{-}MeC_6H_4)_3]_3$ (0·92 g) was refluxed in decalin (15 ml) for 15 min. Chromatography afforded $Ru_3(CO)_7[P(p\text{-}MeC_6H_4)_2]_2(MeC_6H_3)$, eluted with light petroleum–ether (9 : 1), and recrystallised from light petroleum (b.p. 30—40°) as *prisms.*

(*d*) $Ru_3(CO)_9(PMePh_2)_3$. A similar reaction using the methyldiphenylphosphine complex (1·2 g) gave $Ru_2(CO)_6[PMePh(C_6H_4)](PMePh)$, which was recrystallised from light petroleum–ether as *prisms.* Further elution with light petroleum gave a red fraction, but no pure complex could be obtained.

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