ortho-Metallation and Related Reactions. Part VI.[1] Triaryl Phosphite Derivatives of Dodecacarbonyltriruthenium

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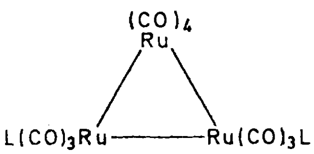
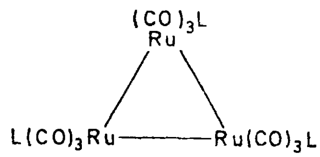
Reactions between Ru$_3$(CO)$_{12}$ and P(OR)$_3$ afford the complexes Ru$_3$(CO)$_{12-n}$[P(OR)$_3$]$_n$ (R = Ph, n = 2 or 3; R = *p*-tolyl, n = 3). The trisubstituted complexes undergo intramolecular metallation and degradation reactions in refluxing decalin, to give Ru(CO)$_2$[P(OC$_6$H$_3$R)(OC$_6$H$_4$R)$_2$]$_2$ [R = H (2 isomers) or Me], Ru$_2$H(CO)$_3$[P(OC$_6$H$_3$R)(OC$_6$H$_4$R)$_2$]$_2$[OP(OC$_6$H$_4$R)$_2$] (R = H or Me), and H$_4$Ru$_4$(CO)$_9$[P(OPh)$_3$]$_3$. Possible mechanisms of formation of these complexes are discussed.

RECENTLY we described[2] an investigation into the nature of the complexes formed in reactions between substituted phosphines or arsines, and the trinuclear carbonyl, Ru$_3$(CO)$_{12}$. Some of these complexes were also obtained as by-products during the preparation of mixed ruthenium–platinum cluster complexes.[3] In this paper we report the synthesis and properties of triaryl phosphite derivatives of Ru$_3$(CO)$_{12}$. Many intramolecular metallation reactions of triaryl phosphite complexes of the later transition metals have been described;[4] we also report some reactions of this type, studied as part of our work on *ortho*-metallation and related reactions.[5]

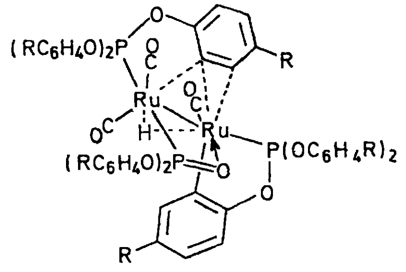
The simple di- and tri-substituted complexes Ru$_3$(CO)$_{10}$L$_2$ [I; L = P(OPh)$_3$] and Ru$_3$(CO)$_9$L$_3$ [II; L = P(OPh)$_3$ or P(O-*p*-tol)$_3$] were readily obtained pure by chromatography of the products from reactions between the phosphite and Ru$_3$(CO)$_{12}$. A similar preparation of a complex of formula Ru$_3$(CO)$_9$[P(OPh)$_3$]$_3$ has been described previously,[6] but the physical properties [colour, m.p., ν(CO) spectrum] of this complex differ from ours; it may be an isomer. I.r. and ^{1}H n.m.r. data (see Table 1) for these complexes indicate structures containing only terminal carbonyl groups, with the phosphite ligands attached to different ruthenium atoms; these complexes are thus similar to those formed



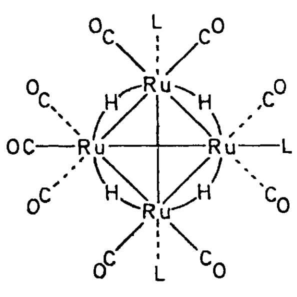
(I) L = P(OPh)$_3$



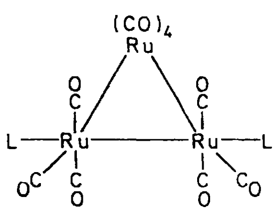
(II) L = P(OPh)$_3$ or P(O-*p*-tol)$_3$



(IV) R = H or Me



(V) L = P(OPh)$_3$



(VI) L = AsPh$_3$

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[1] Part V, M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **40**, 393.

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

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

[4] E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc.* (*A*), 1971, 3413; E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, 1972, **11**, 964, and references cited therein.

[5] R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 1787, and previous papers.

[6] F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1389.

by tertiary phosphines. We have found no evidence for the formation of a tetra-substituted complex, as in the case of $PPh(OMe)_2$.[2]

Interest in *ortho*-metallated aryl phosphite complexes arises from the catalytic activity exhibited by compounds of this type, particularly in respect of H–D exchange reactions.[7] Earlier, we described controlled pyrolytic reactions of the complexes $Ru_3(CO)_9L_3$ (L = tertiary phosphine), from which metallated bi- and tri-nuclear complexes were obtained.[2] Others[8] have reported related reactions of the analogous osmium compounds, and a natural extension has been the present work on the triaryl phosphite–ruthenium complexes.

TABLE 1

^1H N.m.r.[a] and i.r. data for some ruthenium–carbonyl–phosphite complexes

Compound	τ (Phenyl)	τ (Methyl)	$\nu(CO)/cm^{-1}$ [b]	δ(CH)
$Ru_3(CO)_{10}[P(OPh)_3]_2$	2·81m		2089w, 2038s, 2018sh, 2010s, 1993sh	
$Ru_3(CO)_9[P(OPh)_3]_3$	3·10m		2070w, 2012s, 1999s, 1977sh	
$Ru_3(CO)_9[P(OC_6H_4Me)_3]_3$	3·02m	7·73	2065w, 2009s, 1995s, 1977sh [c]	
$Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$	2·40m, 3·07m, 3·38m, 3·58m		2068s, 2022s	1108, 795
$Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ [d]	2·76m(17), 3·16m(11)		2064s, 2020s	1100, 820
$Ru_2H(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$ [e]	2·37m, 2·72m, 3·05m, 3·22m		2066s, 2020s, 1986s	1110, 803
$Ru(CO)_2[P(OC_6H_3Me)(OC_6H_4Me)_2]_2$	2·98m(19), 3·77m(3)	7·65(3), 7·71(9), 7·82(3), 8·07(3)	2064s, 2016s	1130, 760
$Ru_2H(CO)_3[P(OC_6H_3Me)(OC_6H_4Me)_2]_2[OP(OC_6H_4Me)_2]$ [f]	2·53—3·86	7·66, 7·72, 7·78, 7·81, 7·86	2065s, 2017s, 1985s	1130, 755
$H_4Ru_4(CO)_9[P(OPh)_3]_3$	2·80m	Ru–*H* 27·31br	2075s, 2049s	

[a] Recorded in $CDCl_3$ solution at 100 MHz using TMS as internal standard. Relative intensities given in parentheses. [b] In cyclohexane. [c] In chloroform. [d] Second isomer (see text). [e] Ru–H at τ 20·82; *J*(PH) 4, 6·5, and 12 Hz. [f] Ru–H at τ 20·77; *J*(PH) 4, 6·5, and 12 Hz.

Heating the trisubstituted complexes (II) in refluxing decalin for short times afforded mono-, bi-, and tetranuclear complexes, separated by extensive chromatography, and whose formulae were established as $Ru(CO)_2[P(OC_6H_3R)(OC_6H_4R)_2]_2$ (III), $Ru_2H(CO)_3[P(OC_6H_3R)(OC_6H_4R)_2]_2[OP(OC_6H_4R)_2]$ (IV), and $H_4Ru_4(CO)_9[P(OPh)_3]_3$ (V), respectively (R = H or Me).

Complexes of type (III) showed monomeric parent-ion clusters in their mass spectra, together with other ions formed by the stepwise loss of two CO groups. In the carbonyl region, their i.r. spectra showed two strong ν(CO) bands at *ca.* 2065 and 2020 cm^{-1}, consistent with the presence of two mutually *cis* CO groups. In the fingerprint region, absorptions at *ca.* 1100—1130 and 800—760 cm^{-1} are present, and these bands have been assigned[9] to C–H out-of-plane vibrations for 1,2-di-(R = H) and 1,2,4-tri-substituted (R = Me) aryl phosphite ligands in which the aryl group is *ortho*-(2-) metallated. The ^1H n.m.r. spectrum of (III; R = H) contained four complex multiplets in the region τ 2·0—4·0, while the spectrum of (III; R = Me) contained similar multiplets in the region τ 2·5—4·0, together with four singlets in the methyl region.

These data are all consistent with an octahedral complex containing two *ortho*-metallated phosphite ligands as well as the two *cis* CO groups. It is not possible to assign a definite configuration to complex (III), since, excluding optical isomers, a total of seven isomeric molecules of this type is possible (Figure 1). Indeed, a second isomer of (III) was isolated from a reaction carried out for a longer period (see Experimental section). This complex showed only a slight shift in ν(CO) frequency, but the ^1H n.m.r. spectrum was markedly different. Other complexes of this formula can be formed by thermal dehydrochlorination of $RuCl_2(CO)_2[P(OPh)_3]_2$ isomers; this reaction affords an inseparable mixture of isomers, and it has not been possible to determine whether any of the complexes formed were the same as those obtained from $Ru_3(CO)_9[P(OPh)_3]_3$. Pyrolysis of complex $Ru_3(CO)_{10}[P(OPh)_3]_2$ (I) gave complex (III), together with other, unidentified, carbonyl-containing compounds.

The tetranuclear phosphite hydride $H_4Ru_4(CO)_9[P(OPh)_3]_3$ (V) was isolated in low yield from some of these reactions, being characterised by analysis. The ^1H n.m.r. spectrum contains a multiplet at τ 2·80 from the phenyl protons, and a broad multiplet resonance at τ 27·31, which can be assigned to the Ru–H protons. Although not fully resolved, the complexity of this resonance relative to that found in the analogous trimethyl phosphite complex,[10] suggests that rearrangement processes are more difficult with complex (V).

Relatively few binuclear ruthenium carbonyl complexes have been described, and thus the formation of complexes (IV) was of unusual interest. As details of the structure were deduced, and later confirmed by a

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[7] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

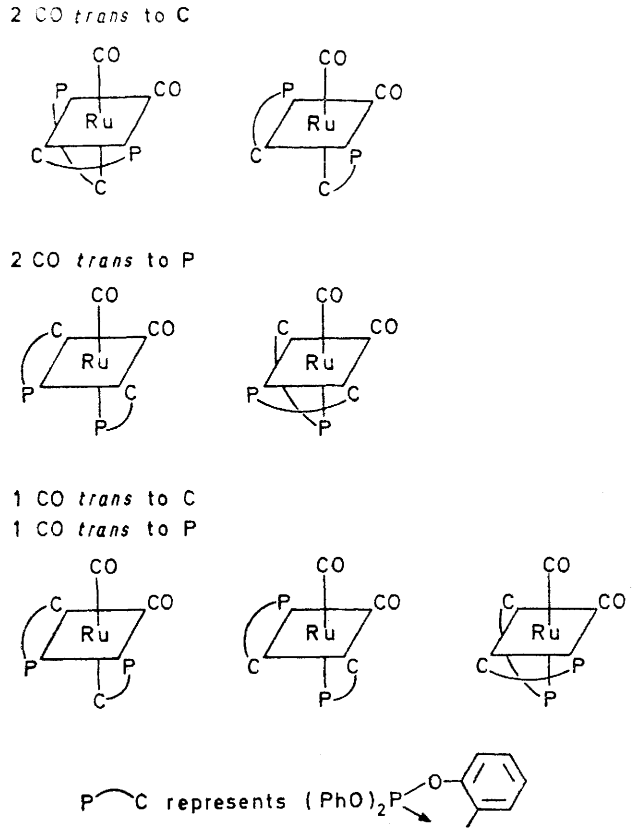
[8] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J.C.S. Chem. Comm.*, 1972, 87; G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organometallic Chem.*, 1972, **40**, C70.

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

[10] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.

single crystal *X*-ray determination,[11] it became evident that these complexes were of more importance than at first thought.

The carbonyl i.r. spectra of complexes (IV; R = H or Me) show three equally intense ν(CO) bands in the terminal region, while the lower frequency region of the spectra contained absorptions consistent with the presence of an *ortho*-metallated ligand. This feature was confirmed by the ^{1}H n.m.r. spectra of both complexes, which contained several multiplets in the aromatic region. Reproducible complete elemental analyses were consistent with there being only eight aryl groups, instead of the nine expected with three phosphite ligands. This feature was supported by the number of methyl resonances observed in the ^{1}H n.m.r. spectrum of the *p*-tolyl derivative; five signals, of relative intensities 2 : 2 : 2 : 1 : 1 suggest several different environments for these groups. The mass spectrum of complex (IV; R = H) contained a parent ion cluster centred on *m/e* 1137, together with ions formed by stepwise loss of three carbonyl groups. The i.r. spectrum contained a strong absorption at *ca.* 1080 cm^{-1}, not present in the initial Ru$_3$(CO)$_9$L$_3$ complexes, nor in complexes of type (III), and which is assigned to ν(PO). This is lower by some 100 cm^{-1} than similar absorptions found in diarylphosphonate complexes of molybdenum [12] and iron,[13] and suggests co-ordination of this group to the second metal atom.



Possible structures for Ru(CO)$_2$[P(OC$_6$H$_4$)(OPh)$_2$]$_2$ (III; R = H) (excluding optical isomers)

All these features were confirmed by the results of the *X*-ray determination on (IV; R = H), which revealed the structure shown.[11] In addition, two novel features were the interaction of one of the metallated aryl groups with both metal atoms, and a vacant asymmetric bridging site between the two ruthenium atoms, which an electron count suggested might be occupied by a hydrogen atom. This was not located during the *X*-ray study. In the high field ^{1}H n.m.r. spectrum, an eight-line multiplet at τ 20·8 confirmed the presence of this proton, which was coupled to all three phosphorus atoms. The chemical shift lies between those found for face-bonded [τ 27·3 in complex (V)] and terminal hydride ligands [τ 17·62 in H$_2$Ru(CO)$_4$ (ref. 14)], and is consistent with the site suggested, which is near the intersection of two octahedral axes.

The formation of complex (IV) probably involves several types of reaction, although it is not possible to determine the order in which they occur. Although we do not have any *X*-ray structural evidence, it is likely that the precursor Ru$_3$(CO)$_9$[P(OR)$_3$]$_3$ (R = Ph or *p*-tol) is the symmetrically trisubstituted complex shown (II). In the *p*-tolyl case, the single methyl resonance supports this proposal. Consequently, migration of one of the phosphite ligands to a ruthenium already bearing a phosphite must occur prior to formation of (IV). This is not unprecedented: the formation of RuCl$_2$(CO)$_2$(AsPh$_3$)$_2$ from Ru$_3$(CO)$_{10}$(AsPh$_3$)$_2$ [now believed to have structure (VI)] on treatment with chlorinated solvents involves this type of ligand migration.[15] During the formation of mixed ruthenium–platinum cluster complexes, similar exchange of CO and tertiary phosphine ligands occurs.[3] Indeed, the formation of mononuclear complexes of type (III), containing two *ortho*-metallated phosphite ligands, must also proceed *via* ligand migration reactions. Finally, the isolation of the tetranuclear hydride (V), whose formation probably involves a disproportionation reaction between Ru$_3$(CO)$_9$[P(OPh)$_3$]$_3$ and a phosphite-free ruthenium carbonyl species, lends support to the transient existence of the latter species, and thus also to the migration of phosphite from one metal atom to another.

Complex (IV) contains two metallated phosphite ligands, formed by cleavage of the *ortho* C–H bond of one of the aryl groups by the metal. We have already shown that this reaction is facilitated, at least with nitrogen-donor ligands, by the presence of a good leaving

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[11] M. I. Bruce, J. Howard, I. W. Nowell, G. Shaw, and P. W. Woodward, *J.C.S. Chem. Comm.*, 1972, 1041.

[12] R. J. Haines and C. R. Nolte, *J. Organometallic Chem.*, 1970, **24**, 725.

[13] R. J. Haines, A. L. du Preez, and I. L. Marais, *J. Organometallic Chem.*, 1971, **28**, 405.

[14] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

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

group, such as methyl.[16] Others have reported that hydride complexes may be isolated in the case of iridium, and that molecular hydrogen may also be eliminated in these reactions.[4] We propose that metallation of one of the phosphite ligands is either concomitant with, or at least closely related to, the formation of the diarylphosphonate ligand which is also present.

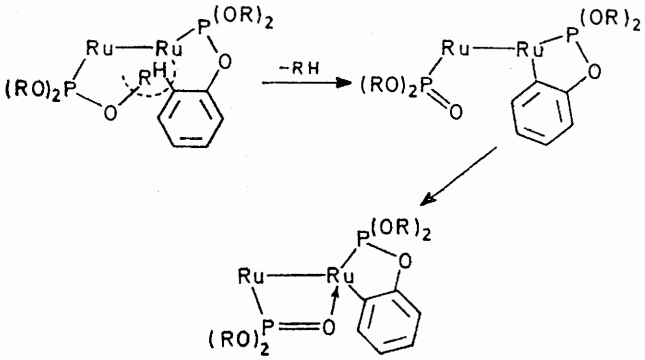
Rearrangements of tertiary phosphites to arylphosphonates have been studied in depth in the cases of π-cyclopentadienyl-molybdenum [12] and -iron [13] carbonyl complexes, and a mechanism involving ionic intermediates has been suggested, *e.g.*

$$(\pi\text{-}C_5H_5)Fe(CO)_2Cl + P(OR)_3 \longrightarrow [(\pi\text{-}C_5H_5)Fe(CO)_2P(OR)_3]Cl \longrightarrow (\pi\text{-}C_5H_5)Fe(CO)_2[OP(OR)_2] + RCl$$

which these authors proposed is analogous to the Michaelis–Arbuzov reaction: [17]

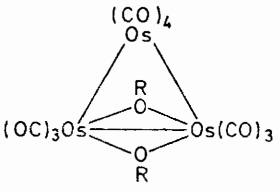
$$R'X + P(OR)_3 \longrightarrow [R'P(OR)_3]X \longrightarrow R'PO(OR)_2 + RX$$

In the present case, however, this explanation is unlikely, since the Michaelis–Arbuzov reaction generally does not occur with aryl phosphites. An alternative process for this unusual reaction could involve a metal-assisted loss of the aryl group as hydrocarbon (benzene or toluene), followed by co-ordination of the P=O group to the metal:



The third reaction which may occur during the formation of (IV) is addition of one of the aryl rings across the metal–metal bond. This is still a relatively new variant of the metallation reaction, several examples having been reported recently[8] as a result of structural studies on triphenylphosphine derivatives of $Os_3(CO)_{12}$. Addition reactions across metal–metal bonds are now common features of the chemistry of the trinuclear carbonyls $M_3(CO)_{12}$ (M = Ru or Os), and to a lesser extent, of other compounds containing metal–metal bonds. Three recent examples are the reactions of alcohols or thiols to $M_3(CO)_{12}$ to give complexes such as (VII) [18] or (VIII),[19] and of $(CF_3)_2PS(CF_3)$ to $Mn_2(CO)_{10}$ to give (IX).[20]

In the present case, cleavage of the *ortho*-C–H bond of one of the aryl groups by the metal–metal bond occurs to give the system found in (IV); in the course of the reaction, further interaction of the metallated ring with one of the metal atoms results in the four-centre three-electron multicentre type of bonding found.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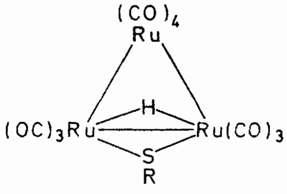
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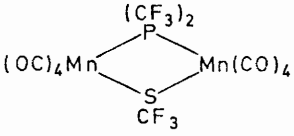
(IX)

Interaction of the *ortho*-carbon atom of a ligand with two transition metal atoms has also been described [21] in the tetrameric complex $[Cu(2\text{-}Me_2NC_6H_3Me\text{-}5)]_4$ [derived from a ligand known to be *ortho*-metallated by more conventional substrates, *e.g.* $PdCl_2$,[22] $MeMn(CO)_5$ [23]]. Phenyl groups have also been found to bridge two non-transition metal atoms, *e.g.* in Al_2Ph_6 and $Al_2Me_4Ph_2$.[24]

Our observations concerning possible reactions involved in the formation of complex (IV) have application to other systems, the most notable being the recently reported detailed study of the reaction between $Os_3(CO)_{12}$ and PPh_3.[8] Some nine complexes isolated from this reaction have been fully characterised, all of which retain the Os_3 framework. This feature is not surprising since the greater strength of the metal–metal bonds in the osmium cluster compared with those in the ruthenium cluster is now well known. However, the further reactions of the triphenylphosphine ligand parallel some of the processes described above. Thus cleavage of an *ortho* C–H bond is found in $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$, the resulting ligand bridging two metal atoms. Elimination of an aryl group from PPh_3 as benzene gives $Os_3(CO)_7(PPh_2)_2(C_6H_4)$, while addition across the three atom cluster occurs in $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$. Aryl groups symmetrically bridging

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[17] R. G. Harvey and E. R. de Somber, *Topics Phosphorus Chem.*, 1964, **1**, 57.

[18] G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 797.

[19] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[20] J. Grobe, *Z. anorg. Chem.*, 1964, **331**, 63.

[21] J. M. Guss, R. Mason, G. van Koten, and J. G. Noltes, *J.C.S. Chem. Comm.*, 1972, 446.

[22] A. C. Cope and E. D. Friedrich, *J. Amer. Chem. Soc.*, 1968, **90**, 909.

[23] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, unpublished work.

[24] J. F. Malone and W. S. McDonald, *Chem. Comm.*, 1967, **444**; 1970, 280.

two metal atoms are found both in the latter complex, and in $HOs_3(CO)_3(PPh_3)(PPh_2C_6H_4)$. Finally, the so-called ' benzyne ' ligand should perhaps be regarded as an *ortho*-dimetallated ligand which further interacts with a third metal atom in a similar fashion to the bridging metallated aryl group found in complex (IV). It is evident that much further work remains to be done with these and related cluster systems, which will undoubtedly reveal other characteristic reactions of metal-atom frameworks.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. ^1H N.m.r. spectra were obtained with a Varian HA 100 spectrometer. Mass spectra were obtained with an AEI MS 902 double focussing mass spectrometer.

All reactions were carried out under nitrogen. Light petroleum had b.p. 40—60°. Chromatography was performed on Florisil columns initially made up in light petroleum. Analytical data, m.p.s, *etc.*, are collected in Table 2.

TABLE 2

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

Compound		% Yield	M.p. (t/°C)	C	H	O	P	Ru	*M* [b]
$Ru_3(CO)_{10}[P(OPh)_3]_2$	Red	38	116—118	46·0 (45·9)	3·0 (2·5)	21·25 (21·25)	5·1 (5·15)	24·05 (25·2)	1276 (1204)
$Ru_3(CO)_9[P(OPh)_3]_3$	Red	95	125—126	50·6 (50·9)	3·0 (3·05)	19·7 (19·4)	6·5 (6·25)	19·7 (20·4)	
$Ru_3(CO)_9[P(OC_6H_4Me)_3]_3$	Red	33	151—152	54·2 (53·65)	4·1 (3·95)	17·55 (17·85)	5·6 (5·75)	18·2 (18·8)	1668 (1612)
$Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$	White	26	120—122	58·85 (58·85)	3·6 (3·65)	16·4 (16·5)	7·7 (8·0)		
$Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ [c]	White	2	154—155	58·9 (58·85)	3·75 (3·65)				
$Ru_2H(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$	Pale yellow	16	180—181	53·8 (53·75)	3·45 (3·55)	17·2 (16·85)	8·2 (8·15)	17·8 (17·75)	1042 (1139)
$Ru(CO)_2[P(OC_6H_3Me)(OC_6H_4Me)_2]_2$	White	16	162—163	61·55 (61·45)	4·7 (4·7)	15·0 (14·9)	7·1 (7·2)	11·9 (11·75)	
$Ru_2H(CO)_3[P(OC_6H_3Me)(OC_6H_4Me)_2]$-$[OP(OC_6H_4Me)_2]$	Pale yellow	9	175—176	56·7 (56·6)	4·25 (4·5)	14·4 (15·35)	7·4 (7·4)	16·65 (16·15)	1179 (1252)
$H_4Ru_4(CO)_9[P(OPh)_3]_3$	Yellow	25	169—171	47·55 (47·6)	3·2 (3·1)	17·8 (18·1)	5·6 (5·85)	24·4 (25·5)	

[a] Calculated values in parentheses. [b] Determined in chloroform solution. [c] Second isomer (see text).

$Ru_3(CO)_{10}[P(OPh)_3]_2$ (I).—A suspension of dodecacarbonyltriruthenium (0·3 g) in benzene (7 ml) containing triphenyl phosphite [0·32 g, 2·2 mol per mol of $Ru_3(CO)_{12}$] was refluxed for 2 h and then chromatographed. Elution with 1 : 49 diethyl ether–light petroleum gave the product as *prisms*. Further elution with 1 : 19 diethyl ether–light petroleum gave $Ru_3(CO)_9[P(OPh)_3]_3$ (15%).

$Ru_3(CO)_9[P(OPh)_3]_3$ [II; L = $P(OPh)_3$].—A suspension of dodecacarbonyltriruthenium (0·2 g) in n-hexane (20 ml) containing triphenyl phosphite [0·386 g; 4 mol per mol of $Ru_3(CO)_{12}$] was refluxed for 2 h. The product separated as prisms on cooling.

$Ru_3(CO)_9[P(OC_6H_4Me\text{-}p)_3]_3$ [II; L = $P(OC_6H_4Me\text{-}p)_3$].—This was similarly prepared from dodecacarbonyltriruthenium (0·6 g) and *p*-tolyl phosphite (1·65 g) in n-hexane (40 ml) and the product recrystallised from diethyl ether–light petroleum as *prisms*.

Action of Refluxing Decalin on $Ru_3(CO)_9[P(OPh)_3]_3$.—(a) A suspension of $Ru_3(CO)_9[P(OPh)_3]_3$ (0·59 g) in decalin (15 ml) was refluxed for 10 min and the resulting deep yellow solution chromatographed. Decalin was washed through with light petroleum. Elution with 1 : 49 diethyl ether–light petroleum gave $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ (III) which recrystallised from warm methanol as *prisms*. Further elution with 1 : 4 diethyl ether–light petroleum gave $Ru_2H(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$ (IV; R = H) which recrystallised from diethyl ether–methanol as *prisms*.

(b) A suspension of $Ru_3(CO)_9[P(OPh)_3]_3$ (1·175 g) in decalin (15 ml) was refluxed for 15 min and then chromatographed. Decalin was removed by washing with light petroleum. Elution with 1 : 49 diethyl ether–light petroleum gave separately $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ (IIIa, 41% yield) and a second isomer of $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ (III) which recrystallised from diethyl ether–methanol to give the product as prisms. Further elution gave $H_4Ru_4(CO)_9[P(OPh)_3]_3$ (V) which recrystallised from methanol to give the product as yellow prisms.

Action of Refluxing Decalin on $Ru_3(CO)_9[P(OC_6H_4Me\text{-}p)_3]_3$.—A suspension of $Ru_3(CO)_9[P(OC_6H_4Me\text{-}p)_3]_3$ (0·75 g) in decalin (10 ml) was refluxed for 10 min and then chromatographed. Elution with 1 : 99 diethyl ether–light petroleum gave separately, $Ru(CO)_2[P(OC_6H_3Me)(OC_6H_4Me)_2]_2$ which recrystallised from diethyl ether–methanol as *prisms* and $Ru_2H(CO)_3[P(OC_6H_3Me)(OC_6H_4Me)_2]_2[OP(OC_6H_4Me)_2]$ (IV; R = Me) which recrystallised from dichloromethane–methanol as *prisms*.

Action of Refluxing Mesitylene on $Ru_3(CO)_9[P(OPh)_3]_3$.—A suspension of $Ru_3(CO)_9[P(OPh)_3]_3$ (0·8 g) in mesitylene (6 ml) was refluxed for 20 min and then chromatographed. Elution with 1 : 99 diethyl ether–light petroleum gave $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ (III) (13% yield), and further elution with 1 : 19 diethyl ether–light petroleum gave $Ru_2H(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$ (IV; R = H) (21% yield). Both compounds were identified by comparison of their i.r. spectra with those of authentic samples.

Action of Refluxing Decalin on $Ru_3(CO)_{10}[P(OPh)_3]_2$.—A suspension of $Ru_3(CO)_{10}[P(OPh)_3]_2$ (0·64 g) in decalin (10 ml) was refluxed for 10 min and then chromatographed.

Elution with 1 : 40 diethyl ether–light petroleum gave $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ (III) (10% yield) whose i.r. spectrum was identical with that of an authentic sample. Further elution with mixtures of diethyl ether–light petroleum gave trace quantities of unidentified carbonyl containing compounds.

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