Chemistry of the Metal Carbonyls. Part LXIV.[1] New Cluster Carbonyl Compounds Containing Platinum and either Ruthenium or Osmium

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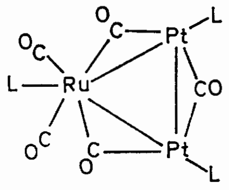
Reactions between dodecacarbonyltriruthenium and low-valent platinum complexes containing tertiary phosphine, phosphite, or arsine ligands afford complexes $RuPt_2(CO)_5L_3$ [L = PPh_3, PPh_2Me, $PPhMe_2$, $PPh(OMe)_2$, or $AsPh_3$], $Ru_2Pt(CO)_7L_3$ (L = $PPhMe_2$), $Ru_2Pt(CO)_8$(diphos), and $RuPt_2(CO)_4L_4$ [L = $PPh(OMe)_2$ or $P(OPh)_3$]. These reactions are also a good source of the complexes $Ru_3(CO)_{12-n}L_n$ (n = 1, 2, or 3). The analogous complexes $Os_3(CO)_{12-n}L_n$ were the only products from reactions between $Os_3(CO)_{12}$ and $Pt(PMePh_2)_4$ or $Pt(PPh_3)_2$(*trans*-stilbene). However, the use of *cis*-$H_2Os(CO)_4$ in place of the osmium carbonyl enabled the cluster compounds $OsPt_2(CO)_5L_3$ (L = PPh_3 or $PMePh_2$) and $Os_2Pt(CO)_7(PMePh_2)_3$ to be isolated. I.r. and ^1H n.m.r. spectra for these compounds are discussed, and likely structures are considered.

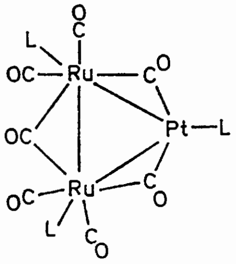
We have described[1] the formation of trinuclear iron–platinum clusters such as $Fe_2Pt(CO)_8(PPh_3)_2$ obtained from reactions between the low-valent platinum phosphine complexes $Pt(PR_3)_4$ or $Pt(PR_3)_2$(olefin) and iron carbonyls, particularly $Fe_2(CO)_9$. It was of interest to study similar reactions with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, where different types of products might be expected. No examples of compounds containing Ru–Pt or Os–Pt bonds have been described previously. A preliminary account of this work has appeared.[2]

Yellow crystalline ruthenium–platinum cluster compounds of stoicheiometry $RuPt_2(CO)_5L_3$ (I) (Table 1) were obtained from reactions between PtL_4 (L = PPh_2Me, PMe_2Ph, or $AsPh_3$) or $Pt(PPh_3)_2$(stilbene), and $Ru_3(CO)_{12}$, carried out in benzene solution at 25°. The pure complexes could be readily isolated by chromatography, and were accompanied by varying amounts of the phosphine-substituted tri-ruthenium carbonyls, $Ru_3(CO)_{12-n}L_n$ (L = PPh_3, $n = 1$; L = PPh_2Me, $n = 2$ and 3; L = $PPhMe_2$, n = 1, 2, and 3; L = $AsPh_3$, $n = 2$).[3]

The i.r. spectra (Table 2) of ruthenium–platinum complexes of type (I) contain two strong bands at *ca.* 2020 and 1950 cm^{-1}, indicating terminal CO groups and strong broad bands at *ca.* 1785 cm^{-1}, suggesting the presence of bridging carbonyl ligands (see Figure 1). The ^1H n.m.r. spectrum (Table 3) of the complex $RuPt_2(CO)_5(PMePh_2)_3$ exhibited two signals for the methyl protons, at τ 7·78 and 8·84, with relative intensities 2 : 1 (Figure 2). The lower-field resonance, which was complex, was accompanied by satellites formed by coupling to ^{195}Pt. The signal at higher field was a simple doublet, due to coupling with phosphorus. These data suggest a structure in which one phosphine ligand is co-ordinated to each metal atom, and the relatively simple ν(CO) spectrum indicates that the molecule has a high degree of symmetry. We consider that complexes of type (I) have the structure illustrated.



(I)



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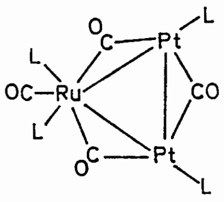

(III)

TABLE 1

Analytical[a] and physical data for some platinum–ruthenium and platinum–osmium cluster compounds

Compound	M.p.	Colour	% Yield	C	H	O	P or As	Ru or Os	Pt	M[b]
$RuPt_2(CO)_5(AsPh_3)_3,C_6H_6$	187—188 [c]	Yellow	31	48·4(47·95)	3·3(3·15)	4·95(4·9)	13·25(13·8)			1418(1628)
$RuPt_2(CO)_5(PPh_3)_3$	220—221 [c]	Yellow	22	50·3(49·95)	3·2(3·2)	5·70(5·65)	5·65(6·55)	9·80(7·15)	28·50(27·5)	1497(1418)
$RuPt_2(CO)_5(PPh_2Me)_3$	155—157	Yellow	23	42·65(42·9)	3·15(3·2)	6·50(6·5)	7·00(7·55)	8·05(8·2)	32·80(31·65)	1010(1232)
$RuPt_2(CO)_5(PPhMe_2)_3$	130—132 [c]	Yellow	10	33·3(33·2)	3·2(3·15)	7·50(7·65)	8·65(8·9)	9·65(9·7)	38·05(37·3)	850(1046)
$RuPt_2(CO)_5\{PPh(OMe)_2\}_3$	112—114	Yellow	1·5	30·4(2·9)	2·85(2·9)		8·75(8·15)			
$RuPt_2(CO)_4\{PPh(OMe)_2\}_4$	116—117	Yellow	27	33·9(33·7)	3·6(3·45)	15·10(14·95)	10·25(9·65)	7·85(7·85)	31·45(30·4)	780(1284)
$Ru_2Pt(CO)_8$(diphos)	184—186 [c]	Red	21	40·0(40·05)	2·4(2·35)	12·00(12·55)	5·95(6·05)	20·20(19·35)	19·55(19·15)	1020(1020)
$OsPt_2(CO)_5(PPh_3)_3$	205—207	Yellow	11	47·0(47·0)	3·2(3·0)	5·30(5·9)	6·1(6·15)	12·55(12·6)	26·05(25·9)	1332(1507)
$Os_2Pt_2H_2(CO)_8(PPh_3)_2$	192—195	Orange-yellow	8	34·8(34·75)	2·2(2·1)	8·60(8·4)	4·1(4·05)	25·80(25·0)	25·70(25·65)	1220(1521)
$Os_2Pt(CO)_7(PPh_2Me)_3$	145—146 [c]	Orange	1·3	40·4(40·25)	3·35(2·9)					

[a] Calculated values in parentheses. [b] Determined in $CHCl_3$ on a Mechrolab Osomometer. [c] With decomposition.

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[1] Part LXIII, M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 1082.

[2] M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Comm.*, 1971, 1288.

[3] M. I. Bruce, G. Shaw, and F. G. A. Stone, unpublished results.

In the reactions involving $Pt(PMe_2Ph)_4$, a second type of ruthenium–platinum complex was isolated, in addition to one of type (I). This complex had the stoicheiometry $Ru_2Pt(CO)_7(PMe_2Ph)_3$ (II; L = PMe_2Ph) and its i.r. spectrum shows two strong terminal and two strong bridging carbonyl stretching frequencies. The ^1H n.m.r. spectrum of this complex again showed two resonances for the methyl protons, at τ 8·07 and 8·90, but with relative intensities 1 : 2. The low-field resonance was a simple triplet of doublets (J_{PH}, 9·5; J_{PtH}, 43 Hz), whereas the signal at higher field was an apparent triplet. The structure of this complex, which again clearly has one phosphine bonded to each metal atom, is believed to be (II; L = PMe_2Ph), from similar considerations to those discussed above in relation to the structure of (I).

TABLE 2

Carbonyl stretching frequencies of some ruthenium–platinum and osmium–platinum cluster compounds

Compound	ν(CO), cm^{-1} (cyclohexane)
$RuPt_2(CO)_5(AsPh_3)_3$ [a]	2019s, 1944m, 1854w, 1792sh, 1787s
$RuPt_2(CO)_5(PPh_3)_3$ [a]	2020s, 1948s, 1845w, 1788s
$RuPt_2(CO)_5(PPh_2Me)_3$ [a]	2023s, 1949s, 1851w, 1787s
$RuPt_2(CO)_5(PPhMe_2)_3$	2024s, 1964sh, 1952s, 1848w, 1784s
$Ru_2Pt(CO)_7(PPhMe_2)_3$ [b]	2022s, 1956sh, 1944s, 1853w, 1816s, 1768s
$RuPt_2(CO)_5\{PPh(OMe)_2\}_3$	2038s, 1971s, 1872w, 1805s, 1773sh
$RuPt_2(CO)_4\{PPh(OMe)_2\}_4$	1955s, 1854w, 1801s, 1780s
$Ru_2Pt(CO)_8$(diphos)	2073s, 2027s, 2001sh, 1989s, 1981sh, 1972sh, 1963sh
$RuPt_2(CO)_4\{P(OPh)_3\}_4$ [b]	1979s, 1875w, 1827s, 1806s
$OsPt_2(CO)_5(PPh_3)_3$	2022s, 1943s, 1847w, 1795s, 1774s
$Os_2Pt_2H_2(CO)_8(PPh_3)_2$	2064s, 2035s, 2024sh, 1988s, 1967w, 1948m
$OsPt_2(CO)_5(PPh_2Me)_3$ [b]	2019s, 1947s, 1843w, 1793s, 1771s
$Os_2Pt(CO)_7(PPh_2Me)_3$	2018s, 1944m, 1848w, 1820m, 1756m

[a] Measured in benzene. [b] Identified only by spectroscopic methods.

TABLE 3

Proton n.m.r. data for some platinum–ruthenium and platinum–osmium complexes [a]

	Chemical shifts (τ) and Coupling constants (Hz)				
Complex	C_6H_5	CH_3(Pt) [b]		CH_3(Ru or Os) [b]	
$RuPt_2(CO)_5(AsPh_3)_3$	2·80m				
$RuPt_2(CO)_5(PPh_2Me)_3$	2·80m	7·78m	J 8·5 J_{Pt} 43·0	8·84d	J_P 8·25
$RuPt_2(CO)_5(PPhMe_2)_3$	2·70m	7·94m	J [c] J_{Pt} 43·75	8·92d	J_P 9·0
$Ru_2Pt(CO)_7(PPhMe_2)_3$ [e]	2·80m	8·07d	J_P 9·5 J_{Pt} 43·0	8·90t	J 6·5
$RuPt_2(CO)_5[PPh(OMe)_2]_3$	2·27m (Pt, *meta*) 2·56m (Pt, *o* and *p*) 3·05m (Ru)	6·33 [e]	J 12·75	6·70d	J_P 12·25
$RuPt_2(CO)_4[PPh(OMe)_2]_4$	2·28m (Pt, *meta*) 2·60m (Pt, *o* and *p*) 3·06m (Ru)	6·44 [e]	J 12·75	6·72 [c]	J 12·0
$Ru_2Pt(CO)_8$(diphos)	2·45m	(7·96m	J 9·25) [d]		
$RuPt_2(CO)_4[P(OPh)_3]_4$ [e]	3·10m				
$OsPt_2(CO)_5(PPh_3)_3$	2·76m				
$OsPt_2(CO)_5(PPh_2Me)_3$ [e]	2·60m	7·68m	J 8·5 J_{Pt} 43·5	8·67d	J_P 9·25
$Os_2Pt(CO)_7(PPh_2Me)_3$	2·74m	7·93d	J_P 9·25 J_{Pt} 41·5	8·48t	J 7·0

[a] In $CDCl_3$; m = multiplet, d = doublet, t = apparent triplet. [b] $J = |J_{AX} + J_{AX'}|$, the separation of the strong doublet; $J_P = J_{P\text{-}CH_3}$; $J_{Pt} = J_{Pt\text{-}CH_3}$. [c] See text. [d] Refers to methylene protons. [e] Identified by spectroscopic methods only.

We have also examined the reactions between $Ru_3(CO)_{12}$ and the phosphite complexes PtL_4 [L = $PPh(OMe)_2$ or $P(OPh)_3$]. In the former case, in addition to $Ru_3(CO)_{10}[PPh(OMe)_2]_2$, two $RuPt_2$ complexes were obtained, containing respectively three and four phosphorus ligands. The ^1H n.m.r. spectra (see below) revealed that in the tris-complex, two ligands are platinum-bonded, while the third is attached to ruthenium. The complex is thus [I; L = $PPh(OMe)_2$]. In the second complex, the fourth ligand is attached to the ruthenium atom, the observed apparent triplet suggesting relative *cis*-substitution of CO groups. This is supported by there being only a single terminal ν(CO) band. It is therefore likely that this complex has structure [III; L = $PPh(OMe)_2$].

With triphenyl phosphite, analysis showed that the heteronuclear $RuPt_2$ complex isolated contained four phosphite ligands, and the similarity in the i.r. carbonyl spectra leads us to suggest that it has structure [III; L = $P(OPh)_3$]. In this case, the trinuclear ruthenium complexes $Ru_3(CO)_{12-n}[P(OPh)_3]_n$ (n = 2 or 3) were also obtained.[3]

The ^1H n.m.r. spectra of most of these complexes are more complex than expected. The spectra of (I; L = $PMePh_2$) and (II; L = PMe_2Ph) have already been discussed in part. One feature of interest in the former is the structure of the ^{195}Pt satellites of the Pt–P*Me*Ph_2 resonance. Although the central signal consists of a strong doublet, with fine structure between these lines, expected for an $A_3XX'A'_3$ system, the platinum satellites appear as simple doublets, separation 8·5 Hz. This is presumably the result of further coupling within the MePPtPtPMe system, which should correctly be considered as an $A_3MXX'M'A'_3$ group. A similar effect is found in the spectrum of the corresponding osmium complex.

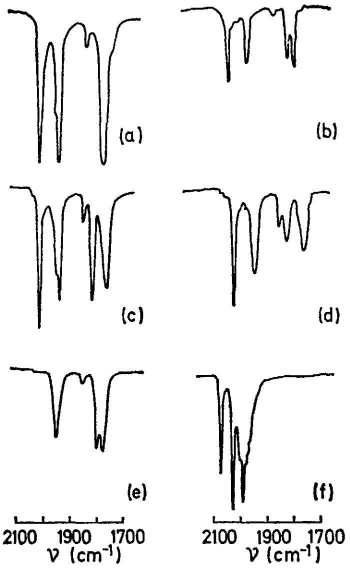


FIGURE 1 Infrared spectra in the ν(CO) region (cyclohexane solutions)

(a) $RuPt_2(CO)_5(PMe_2Ph)_3$; (b) $OsPt_2(CO)_5(PMePh_2)_3$;
(c) $Ru_2Pt(CO)_7(PMe_2Ph)_3$; (d) $Os_2Pt(CO)_7(PMePh_2)_3$;
(e) $RuPt_2(CO)_4[PPh(OMe)_2]_4$; (f) $Ru_2Pt(CO)_8$(diphos)

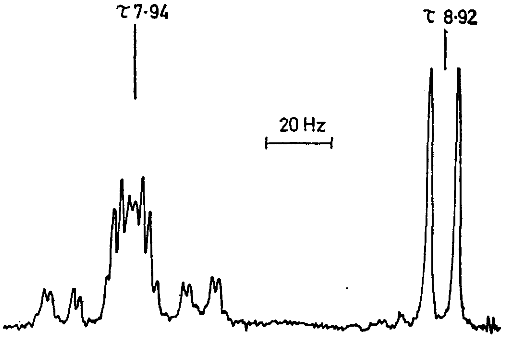
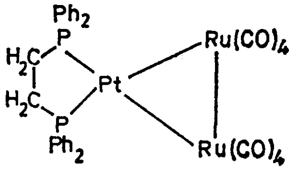


FIGURE 2 Proton n.m.r. spectrum of $RuPt_2(CO)_5(PMe_2Ph)_3$ in the methyl region (see text)

The ^{1}H n.m.r. spectra of the two complexes $RuPt_2(CO)_5[PPh(OMe)_2]_3$ and $RuPt_2(CO)_4[PPh(OMe)_2]_4$ show clearly the location and stereochemistry of the phosphite ligands. In the tris-complex, the signal at lower field of relative intensity 2, can be assigned to the platinum-bonded ligands. This resonance consists of the usual two strong lines (separation 12·75 Hz), in between which is the broad central resonance expected. Under high resolution, the two outer lines are found to be close doublets (*ca.* 1 Hz). The resonance at higher field is a simple doublet (J_{PH} 12·25 Hz). In the tetrakis-complex, this resonance becomes an apparent triplet, the separation between the outer pair being *ca.* 12 Hz. The resonance of the platinum-bonded ligands is almost identical to that in the tris-complex, with the difference that the two outer lines are now close triplets. These two observations suggest that the source of the small coupling is the ruthenium-bonded phosphorus atoms.

It is worth noting that in the ^{1}H n.m.r. spectra of these two types of complex, the methyl resonance of the ruthenium-bonded $PPhMe_2$ ligand occurs at considerably higher field than those recorded for some analogous complexes. Thus, in $Ru_3(CO)_{11}(PMe_2Ph)$,[3] this resonance occurs at *ca.* τ 8·00. This increased shielding is perhaps due to increased electron density in the neighbourhood of the ruthenium atoms caused by the close proximity of the low valent, electron-rich platinum atoms, although the chemical shifts in complexes containing either $RuPt_2$ or Ru_2Pt clusters are identical.[*] Another feature of interest in the n.m.r. spectrum of the Ru_2Pt complex is the observed triplet at τ 8·90 for (II; PMe_2Ph); this arises from coupling of the phosphorus nuclei, similar to that mentioned above, but this time *via* the ruthenium nuclei and Ru–Ru bond, which themselves are magnetically inactive. This type of effect has recently been observed in other homonuclear ruthenium clusters,[4] although not in the phosphine-substituted ruthenium carbonyls.

These reactions provide further examples of the ligand transfer reactions reported previously in the iron–platinum systems, but with the difference that the phosphine lost from the platinum is transferred to the ruthenium atom in the cluster, in addition to forming the $Ru_3(CO)_{12-n}L_n$ complexes. Where the transfer of a molecule of ligand is prevented by chelation, for example, a third type of complex would be expected. This expectation was confirmed in the case of $L_2 = Ph_2P(CH_2)_2PPh_2$(diphos). The reaction between Pt(diphos)$_2$ and $Ru_3(CO)_{12}$ afforded the homonuclear $Ru_3(CO)_{10}$(diphos), together with ruthenium–platinum complex of stoicheiometry $Ru_2Pt(CO)_8$(diphos) (IV). The ν(CO) region of the spectrum bears a marked resemblance to those of the iron–platinum complexes $Fe_2Pt(CO)_8(L)_2$ (*e.g.* L = PPh_2Me),[1] and in contrast to complexes (I) and (II), there are no bridging carbonyl bands. Thus, we are inclined to suggest structure (IV)



(IV)

for this complex, the only example of this formula type we have yet found with ruthenium.

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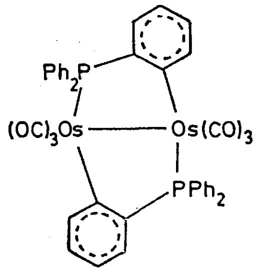
[*] *Note added in proof.* An alternative description of the bonding considers that the structure is a complex of formally positively-charged platinum, and negatively-charged ruthenium moieties [by analogy with $PtFe_2(CO)_9(PPh_3)$: see R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *Chem. Comm.*, 1972, 200]. This would lead to the same prediction of increased shielding of the phosphine methyl groups.

[4] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4596.

The increased stability of the Os_3 cluster over that of the Ru_3 unit in the dodecacarbonyls $M_3(CO)_{12}$ is reflected in the products obtained in reactions involving $Os_3(CO)_{12}$. With $Pt(PPh_3)_2$(stilbene) or $Pt(PPh_2Me)_4$ in benzene at room temperature, the major osmium complexes we isolated were the known species[5] $Os_3(CO)_{12-n}L_n$ ($L = PPh_3$ and PPh_2Me respectively; $n = 1$ or 2). Refluxing a mixture of $Pt(PPh_2Me)_4$ and $Os_3(CO)_{12}$ in toluene for 9 h gave only $Os_3(CO)_9(PPh_2Me)_3$.[6,7]

From the reaction between $Os_3(CO)_{12}$ and $Pt(PPh_3)_2$(stilbene) in refluxing toluene no complexes $Os_3(CO)_{12-n}(PPh_3)_n$ were isolated. However, three minor products were obtained. The first has the stoicheiometry $Os_2(CO)_6[P(C_6H_4)(C_6H_5)_2]_2$, the mass spectrum agreeing with the calculated molecular weight. No metal-bonded protons were detected by n.m.r. methods. The ligand region of the i.r. spectrum was more complex than found for *e.g.* $Os_3(CO)_{10}(PPh_3)_2$, but it was not possible to determine unequivocally whether the various bands in the 1100 and 800 cm^{-1} regions were those characteristic of *ortho*-metallation. However, new bands appear at 658, 911, 1170, 1212, and 1583 cm^{-1}, the latter being close to the 1560 cm^{-1} absorption found for *ortho*-metallated PBu^tPh_2 complexes.[8] Two possible structures can be considered, namely (V) and (VI). In the former, an *ortho*-metallated phosphine ligand bridges two metal atoms, forming the customarily favoured five-membered ring, whereas in (VI), the ligand is chelated to each metal atom.



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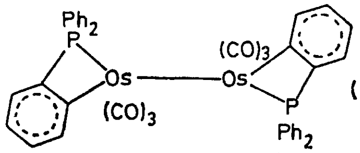
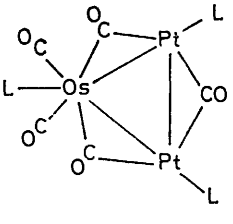


(VI)

The mass spectra of the other two products showed parent ions at *m/e* 995 and 1225, suggesting formulae of the type $Os(PPh_2)(PPh_3)_x(CO)_y$ ($x = 1$ or 2; $y = 6$ or 5), but further characterisation was precluded by the low yields.

In the reaction between *cis*-$H_2Os(CO)_4$ and $Pt(PPh_3)_2(C_2H_4)$ in benzene, three complexes were obtained after chromatography. The first eluted complex was the known[9] $H_2Os(CO)_3(PPh_3)$, and this was followed by two osmium–platinum complexes, of stoicheiometry $OsPt_2(CO)_5(PPh_3)_3$ (VII) and $HOsPt(CO)_4(PPh_3)$ (VIII).

The carbonyl i.r. spectrum of (VII) contained bands due to terminal and bridging carbonyl groups, and closely resembled those of complexes of type (I), and we consider that (VII) and the corresponding PPh_2Me complex (see below), have a similar structure to the $RuPt_2$ complexes (I). The third complex isolated (VIII) has a solution molecular-weight corresponding to the presence of four metal atoms, and the carbonyl i.r. spectrum showed only six terminal ν(CO) bands. The ^1H n.m.r. spectrum showed a complex multiplet at τ 2·70, assigned to the PPh_3 protons, and in the high-field region, an apparent doublet at τ 17·76, of relative intensity 15 : 1. The metal-bonded proton resonance also shows satellites arising from coupling with ^{195}Pt (J_{PtH}, 524 Hz), which, as with the $RuPt_2$ complex mentioned above, do not show the same degree of complexity as the central resonance. The structure of this complex is under investigation, but it is likely that the complex can be related to the $Pt_4(CO)_5(PPh_3)_4$ complexes described by Chatt and Chini[10] recently, and we suggest that the spectral data described can be accommodated by structure (VIII; $L = PPh_3$), in which the two hydrogen atoms either bridge the two platinum atoms, or form terminal Pt–H bonds with them.



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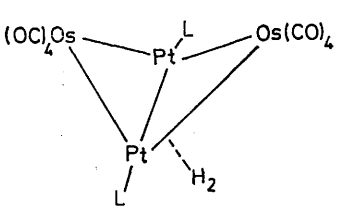

(VIII)

Extension of this reaction of $H_2Os(CO)_4$ to $Pt(PPh_2Me)_4$ afforded two complexes of stoicheiometry $OsPt_2(CO)_5(PPh_2Me)_3$ and $Os_2Pt(CO)_7(PPh_2Me)_3$. The i.r. spectra showed the presence of both bridging and terminal carbonyl groups, and resembled those of complexes (I) and (II), respectively. The ^1H n.m.r. spectra were entirely analogous to those of the corresponding ruthenium complexes. Once again, the methyl groups of the osmium-bonded PPh_2Me groups resonate at considerably higher field than in, *e.g.*, $Os_3(CO)_{11}(PPh_2Me)$. In the Os_2Pt complex, the phosphorus nuclei couple *via* the Os–Os bond to give an apparent triplet, resulting from an $A_6XX'A_6'$ system, whereas for the platinum-

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[5] C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1970, 2889.

[6] M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc.* (*A*), 1969, 987.

[7] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 897.

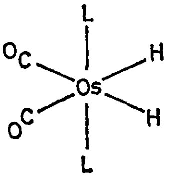
[8] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 3833.

[9] F. L'Epplatenier and F. Calderazzo, *Inorg. Chem.*, 1967, **6**, 2092.

[10] J. Chatt and P. Chini, *J. Chem. Soc.* (*A*), 1970, 1538.

bonded ligand, the methyl signal is a simple triplet of doublets. In the $OsPt_2$ complex, the complexity of the central resonance is not reflected in the platinum satellites.

A third product from this reaction is $H_2Os(CO)_2(PPh_2Me)_2$. The i.r. spectrum shows bands at 2015s, 1982s, and 1868w cm^{-1}, suggesting a *cis*-dicarbonyl, with a weak ν(OsH). The proton n.m.r. spectrum contains a multiplet at τ 2·51 (C_6H_5), an apparent triplet (separation 7·25 Hz) at τ 7·64 (*trans* PPh_2Me groups), and a triplet at τ 18·21 (J_{PH} 11·75 Hz) (OsH_2). Structure (IX; L = PPh_2Me) is consistent with the spectroscopic data reported above.



(IX)

The formation of these complexes, as well as of the iron–platinum clusters described previously, occurs by formal oxidative addition reactions, the platinum inserting into one of the metal–metal bonds. In the case of the ruthenium and osmium derivatives, this reaction is followed by disproportionation and elimination of an $M(CO)_4$ (M = Ru, Os) group. The formation of the Pt_2M clusters can be considered to occur by a second insertion and disproportionation step. It is not clear at present why the trinuclear cluster is favoured over the tetranuclear complex; as discussed above, the latter are formed only in small amounts.

Some analogy may be drawn between the PtM_2 (M = Fe, Ru, Os) compounds and the diphenylvinylidene complex $Ph_2C_2Fe_2(CO)_8$,[11] which may be regarded as containing the complexed carbene $Ph_2C{=}C\colon$. This feature further underlines the similarities between many of the reactions of $Pt(PPh_3)_2$ and those of carbenes.

EXPERIMENTAL

General experimental conditions were similar to those employed in the investigation using $Fe_2(CO)_9$.[1]

Reaction between $Pt(PPh_3)_2$(stilbene) *and* $Ru_3(CO)_{12}$.—A mixture of $Ru_3(CO)_{12}$ (0·7 g, 1·10 mmol) and bis(triphenylphosphine)(*trans*-stilbene)platinum(0) (1·20 g, 1·33 mmol) in benzene (30 ml) was stirred for 7 days. Unchanged dodecacarbonyltriruthenium (0·23 g, 0·358 mmol) was filtered off and the filtrate evaporated (*ca.* 10 ml) and chromatographed on Florisil. *trans*-Stilbene (0·2 g, 1·10 mmol) was obtained on elution with light petroleum. Elution with 1 : 49 diethyl ether–light petroleum gave undecacarbonyl(triphenylphosphine)triruthenium which recrystallised from light petroleum. Elution with 3 : 2 diethyl ether–light petroleum gave $Pt_2Ru(CO)_5(PPh_3)_3$ (Table 1) which recrystallised from acetone as *prisms*.

Reactions of Dodecacarbonyltriruthenium with [PtL_4].—(a) *Tetrakis(diphenylmethylphosphine)platinum*(0). A mixture of dodecacarbonyltriruthenium (0·65 g, 1·01 mmol) and tetrakis(diphenylmethylphosphine)platinum(0) (1·0 g, 1·01 mmol) dissolved in benzene (25 ml) was stirred for 8 days, evaporated (*ca.* 5 ml) and chromatographed. Elution with 1 : 19 diethyl ether–light petroleum gave decacarbonylbis(diphenylmethylphosphine)triruthenium,[3] recrystallised from light petroleum. Elution with 1 : 9 diethyl ether–light petroleum gave enneacarbonyltris(diphenylmethylphosphine)triruthenium which was recrystallised from dichloromethane–light petroleum. The complex $Pt_2Ru(CO)_5(PMePh_2)_3$ was obtained by elution with 1 : 4 diethyl ether–light petroleum and recrystallised from dichloromethane–light petroleum as *prisms*.

(b) *Tetrakis(dimethylphenylphosphine)platinum*(0). Dodecacarbonyltriruthenium (0·695 g, 1·08 mmol) was added to a solution of tetrakis(dimethylphenylphosphine)platinum(0) (0·81 g, 1·08 mmol) in benzene (25 ml) and the mixture was stirred for 7 days. The solution was evaporated and chromatographed. Elution with 1 : 19 diethyl ether–light petroleum gave respectively undecacarbonyl(dimethylphenylphosphine)triruthenium and decacarbonylbis(dimethylphenylphosphine)triruthenium.[3] Further elution with 1 : 4 diethyl ether–light petroleum gave respectively $PtRu_2(CO)_7(PMe_2Ph)_3$ as a pale yellow oil, and $Pt_2Ru(CO)_5(PMe_2Ph)_3$ which was recrystallised from diethyl ether–light petroleum to give the product as *prisms*. The complex $PtRu_2(CO)_7(PMe_2Ph)_3$ was characterised only on the basis of its i.r. and n.m.r. spectra.

In a similar reaction, dodecacarbonyltriruthenium (0·7 g, 1·09 mmol) and tetrakis(dimethylphenylphosphine)platinum(0) (1·26 g, 1·69 mmol) in 2 : 1 benzene–tetrahydrofuran (30 ml) gave after stirring for 7 days enneacarbonyltris(dimethylphenylphosphine)triruthenium as the only product.

(c) *Tetrakis(triphenylarsine)platinum*(0). Dodecacarbonyltriruthenium (0·7 g, 1·09 mmol) was added to a suspension of tetrakis(triphenylarsine)platinum(0) (1·88 g, 1·33 mmol) in benzene (30 ml) and the mixture was stirred for 5 days and then chromatographed. Elution with 1 : 49 diethyl ether–light petroleum gave decacarbonylbis(triphenylarsine)triruthenium (0·02 g), recrystallised from benzene–light petroleum. Further elution with various concentrations of diethyl ether–light petroleum gave mixtures of carbonyl-containing compounds which could not be purified by further chromatography because of decomposition. Elution with acetone gave $Pt_2Ru(CO)_5(AsPh_3)_3$ which was recrystallised from benzene–light petroleum.

(d) *Tetrakis(dimethyl phenylphosphonite)platinum*(0). A suspension of dodecacarbonyltriruthenium (1·0 g, 1·55 mmol) and tetrakis(dimethyl phenyl phosphonite)platinum(0) (1·97 g, 2·25 mmol) in benzene (25 ml) was stirred for 5 days and then chromatographed. Elution with 1 : 19 diethyl ether–light petroleum gave decacarbonylbis(dimethyl phenylphosphonite)triruthenium, from diethyl ether–light petroleum. Elution with 3 : 17 diethyl ether–light petroleum gave $Pt_2Ru(CO)_5\{PPh(OMe)_2\}_3$ as *prisms* from diethyl ether–light petroleum. Further elution with 3 : 7 diethyl ether–light petroleum gave $Pt_2Ru(CO)_4\{PPh(OMe)_2\}_4$ which was recrystallised from diethyl ether–light petroleum as *prisms*.

(e) *Bis{bis(diphenylphosphino)ethane}platinum*(0). A suspension of bis{bis(diphenylphosphino)ethane}platinum(0) (1·98 g, 2·0 mmol) and dodecacarbonyltriruthenium (0·96 g,

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[11] O. S. Mills and A. D. Redhouse, *Chem. Comm.*, 1966, 444; *J. Chem. Soc.* (*A*), 1968, 1282.

1·5 mmol) was stirred for 6 days and then chromatographed. Elution with 1 : 9 diethyl ether–light petroleum gave decacarbonylbis(diphenylphosphino)ethanetriruthenium as prisms from diethyl ether–light petroleum. Further elution with 1 : 4 diethyl ether–light petroleum gave $PtRu_2(CO)_8$(diphos), from diethyl ether–light petroleum.

(f) *Tetrakis*(*triphenyl phosphite*)*platinum*(0). A mixture of tetrakis(triphenylphosphite)platinum(0) (1·78 g, 1·24 mmol) and dodecacarbonyltriruthenium (0·795 g, 1·24 mmol) in dry benzene (20 ml) was stirred for 7 days and then chromatographed. Elution with 1 : 39 diethyl ether–light petroleum mixtures gave respectively decacarbonylbis(triphenyl phosphite)triruthenium and enneacarbonyltris(triphenyl phosphite)triruthenium (19%). The complex $Pt_2Ru\{P(OPh)_3\}_4(CO)_4$ was eluted with 1 : 19 diethyl ether–light petroleum as a pale yellow oil (5%) and was identified by spectroscopic methods only.

Reaction between $Os_3(CO)_{12}$ *and Bis*(*triphenylphosphine*)-(trans-*stilbene*)*platinum*.—A mixture of $Os_3(CO)_{12}$ (0·585 g, 0·645 mmol) and the platinum complex (1·20 g, 1·33 mmol) in toluene (15 ml) was refluxed for 16 h. Evaporation of solvent, extraction of the residue with benzene, and chromatography afforded $Os_2(CO)_6[P(C_6H_4)(C_6H_5)_2]_2$ (V) or (VI) (with 1 : 99 diethyl ether–light petroleum) as yellow prisms (0·03 g), m.p. 228—230° [Found: C, 47·1; H, 3·2; O, 8·8; Os, 35·75; P, 5·95%; *M* (mass spec.), 1073 ± 2; ($CHCl_3$), 962. $C_{42}H_{28}O_6Os_2P_2$ requires C, 47·1; H, 2·65; O, 8·95; Os, 35·5; P, 5·8%; *M*, 1071]; τ [$(CD_3)_2CO$] 2·32—3·36 (ArH); ν(CO) (benzene) 2050s, 2042sh, 1992s, 1981sh, 1948s, and 1928s; ν(CO) (chloroform) 2048s, 1986s, 1948m, and 1925m cm^{-1}.

Further elution with diethyl ether–light petroleum mixtures gave in trace amounts pink prisms, m.p. 213—215°, ν(CO) (benzene), 2078s, 2009s, 1988s, and 1946m cm^{-1}; and a third complex as yellow prisms, m.p. 219—220°, ν(CO) (benzene), 2068s, 2035s, 2001s, 1958m,br, and 1942sh cm^{-1} which were not further investigated.

Reactions of Dihydrido(*tetracarbonyl*)*osmium*.—(a) *Bis*(*triphenylphosphine*)(*ethylene*)*platinum*(0). Dihydridotetracarbonylosmium(II) (0·5 g, 1·65 mmol) was added to a solution of bis(triphenylphosphine)(ethylene)platinum(0) (1·23 g, 1·65 mmol) in benzene (10 ml), and the mixture was stirred for 22 h. The solution was evaporated under reduced pressure to approximately half-volume and then chromatographed. Elution with 1 : 49 diethyl ether–light petroleum gave dihydridotricarbonyltriphenylphosphineosmium(II) (40% yield) which was identified by its i.r. and n.m.r. spectra. Elution with 1 : 4 diethyl ether–light petroleum gave $[OsPtH(CO)_4(PPh_3)]_2$ which recrystallised from diethyl ether–light petroleum as *prisms*. Further elution with 1 : 4 diethyl ether–light petroleum gave $OsPt_2(PPh_3)_3(CO)_5$ as *prisms* from dichloromethane–light petroleum.

(b) *Tetrakis*(*diphenylmethylphosphine*)*platinum*(0).— Dihydridotetracarbonylosmium(II) (0·36 g, 1·18 mmol) was condensed into a solution of tetrakis(diphenylmethylphosphine)platinum(0) (0·7 g, 0·7 mmol) in benzene (10 ml); the mixture was stirred for 3 days and then chromatographed. Elution with 1 : 19 diethyl ether–light petroleum gave dihydridodicarbonylbis(diphenylmethylphosphine)osmium(II) (0·115 g, 15%) as colourless prisms, m.p. 133—134° (Found: C, 51·65; H, 4·85. $C_{28}H_{28}O_2OsP_2$ requires C, 51·85; H, 4·35%). Elution with 1 : 4 diethyl ether–light petroleum gave $Os_2Pt(CO)_7(PMePh_2)_3$ which recrystallised from diethyl ether–light petroleum as *prisms*. Further elution with 3 : 7 diethyl ether–light petroleum gave $OsPt_2(CO)_5(PMePh_2)_3$ (0·02 g, 4·5%) as yellow *prisms*, m.p. 152—153°. The latter compound was identified only on the basis of its i.r. and n.m.r. spectra.

Reaction Between Tetrakis(*diphenylmethyl*)*platinum*(0) *and Dodecacarbonyltriosmium*.—A mixture of tetrakis(diphenylmethylphosphine)platinum(0) (0·7 g, 0·705 mmol) and dodecacarbonyltriosmium (0·64 g, 0·705 mmol) in benzene (20 ml) was stirred for 3 days and then chromatographed. Elution with 1 : 49 diethyl ether–light petroleum gave $Os_3(CO)_{11}(PPh_2Me)$ (11%) as yellow prisms from light petroleum. Further elution with 1 : 24 diethyl ether–light petroleum gave $Os_3(CO)_{10}(PPh_2Me)_2$ (47%) as red prisms from diethyl ether–light petroleum. Both compounds were identified by comparison of their i.r. and n.m.r. spectral data with those reported in the literature.[5]

If a mixture of tetrakis(diphenylmethylphosphine)platinum(0) and dodecacarbonyltriosmium was refluxed in toluene for 9 h, the only product isolated after chromatography was $Os_3(CO)_9(PPh_2Me)_3$ (50%) which was identified by comparison of its i.r. spectrum with that of an authentic sample.[6]

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