

New Substituted Heteronuclear Cluster Carbonyls Containing Platinum and a Metal from the Fe, Ru, Os Triad

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Summary Low-valent phosphine-platinum complexes react with $\text{Fe}_3(\text{CO})_9$, $\text{Ru}_3(\text{CO})_{12}$, or $\text{H}_2\text{Os}(\text{CO})_4$ to give heteronuclear cluster compounds of the types $\text{Fe}_2\text{Pt}(\text{CO})_{10-n}\text{L}_n$ ($n = 1$ or 2), $\text{MPt}_2(\text{CO})_5\text{L}_3$, and $\text{M}_2\text{Pt}(\text{CO})_7\text{L}_3$ ($M = \text{Ru, Os}$); the ligand L may be any one of a variety of substituted phosphines or phosphites, or triphenylarsine.

ALTHOUGH the chemistry of cluster carbonyls of the Fe, Ru, Os triad has been extensively described, and that of the polynuclear platinum-phosphine complexes is now beginning

to be unravelled, we are only aware of one complex, namely *trans*-(Ph_3P) $_2\text{PtCl}[\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)]$,[†] containing platinum bonded to a metal of this sub-group.

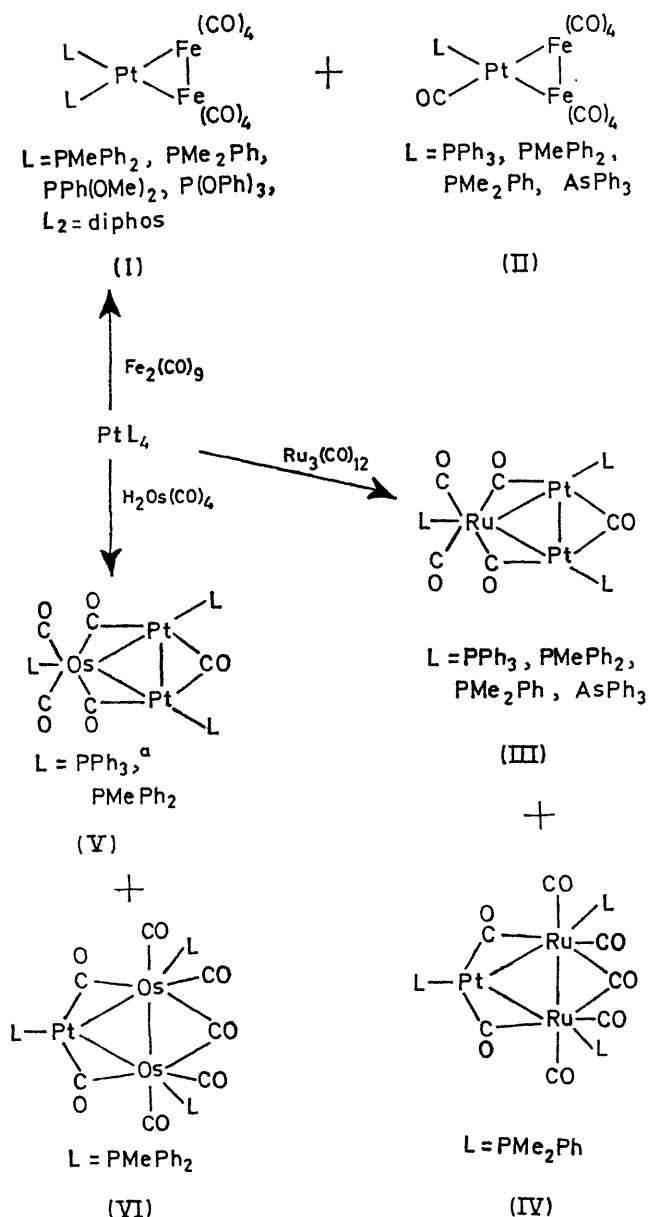
We have found that reactions between the low-valent platinum complexes $\text{Pt}(\text{PR}_3)_4$ or $(\text{Ph}_3\text{P})_2\text{Pt}(\text{olefin})$, and $\text{Fe}_2(\text{CO})_9$, $\text{Ru}_3(\text{CO})_{12}$ or $\text{H}_2\text{Os}(\text{CO})_4$, are prolific sources of new types of substituted cluster carbonyls containing these elements (see Scheme). Thus, with $\text{Fe}_2(\text{CO})_9$, complexes of stoichiometry $\text{PtFe}_2(\text{CO})_8\text{L}_2$ (I) and $\text{PtFe}_2(\text{CO})_9\text{L}$ (II) were obtained.[‡] These compounds show only terminal $\nu(\text{CO})$ bands (Table), and when $\text{L} = \text{PPhMe}_2$ or PPh_2Me ,

[†] Ref. 1 does not consistently formulate this complex as shown, although the text suggests that this is the structure assumed by the authors.

[‡] All complexes mentioned had satisfactory analyses (C, H, O, P, Pt, and Fe, Ru or Os) and solution molecular weights.

Representative i.r. spectra (in cyclohexane)

Complex	L	$\nu(\text{CO}), \text{cm}^{-1}$
(I)	Me_2PPh	2051s, 1998s, 1971m, 1948m, 1892w, br
(II)	Me_2PPh	2074m, 2049w, 2028s, 2012s, 1996sh, 1985s, 1968m, 1936w
(III)	Me_2PPh	2024s, 1964sh, 1952s, 1848w, 1784s
(IV)	Me_2PPh	2022s, 1956sh, 1944s, 1853w, 1816s, 1768s
(V)	MePPh_2	2019s, 1947s, 1843w, 1793s, 1771s
(VI)	MePPh_2	2018s, 1944m, 1848w, 1820m, 1756m

SCHEME. ^a $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ was used in this experiment.

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the ^1H n.m.r. spectra show that the phosphine ligand remains attached to platinum. Thus, for (I; $\text{L} = \text{PPh}_2\text{Me}$), the methyl group appears at τ 7.98 m (J_{PtH} , 32.0 Hz). Complexes of type (II) are formed *via* an interesting carbonylation reaction; $\text{Fe}(\text{CO})_4\text{L}$ can also be isolated from the reaction products. As expected, this reaction is more prevalent with the less basic phosphines.

Complexes of different types are obtained from reactions involving $\text{Ru}_3(\text{CO})_{12}$, namely $\text{RuPt}_2(\text{CO})_5\text{L}_3$ (III) and $\text{Ru}_2\text{Pt}(\text{CO})_7\text{L}_3$ (IV). Both bridging and terminal $\nu(\text{CO})$ bands are found in their i.r. spectra. The ^1H n.m.r. spectra of the appropriate phosphine (*e.g.* $\text{L} = \text{PPhMe}_2$) complexes indicate that in (III), two phosphines are attached to platinum, [CH_3 at τ 7.94 m (J_{PtH} , 43.75 Hz)] and the third to ruthenium [CH_3 at τ 8.92 d (J_{PtH} , 9.0 Hz)], whereas in (IV), only one phosphine exhibits the characteristic platinum coupling [CH_3 at τ 8.07 m (J_{PtH} , 43.0 Hz), and 8.90 (app. triplet, separation 6.5 Hz)]. The illustrated structures are consistent with these data, containing triangular clusters of metal atoms, each metal being bonded to one phosphine ligand, and joined to the other metal atoms *via* both a metal-metal bond and a bridging carbonyl group. These are notable as unusual examples of carbonyl groups bridging two metals of different sub-groups *and* different periods. Complexes of the type $\text{Ru}_3(\text{CO})_{12-n}\text{L}_n$ ($n = 1-3$) were also isolated from these reactions.

With $\text{Os}_3(\text{CO})_{12}$, only the known² complexes $\text{Os}_2(\text{CO})_{12-n}\text{L}_n$ ($n = 1-3$) could be isolated from similar reactions with the platinum complexes. However, complexes (V) and (VI) were obtained from $\text{H}_2\text{Os}(\text{CO})_4$, the structures being assigned on the basis of similar spectral properties to the ruthenium analogues.

Complexes (I) to (VI) join the growing number of such cluster compounds which do not obey the 18-electron rule. This is a common feature of platinum chemistry, and several recent communications³ have pointed out that classical valence-bond type structures often cannot be written for cluster complexes.

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