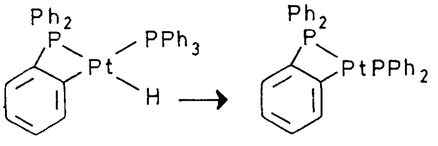
Platinum–Phosphine Cluster Compounds

By FRANK GLOCKLING,* THOMAS MCBRIDE, and R. J. IVAN POLLOCK
(*Chemistry Department, The Queen's University, Belfast* BT9 5AG)

Summary Previously prepared platinum cluster compounds derived from $Pt(PPh_3)_2$ are characterised as associated platinum(II) complexes $[Pt(PPh_2)(C_6H_4\text{-}PPh_2)]_{2,3,\text{or}4}$ formed through *o*-metallation reactions.

IT was reported[1] that brown or red platinum cluster compounds were formed by removal of triphenylphosphine from $Pt(PPh_3)_4$. These were formulated as $[Pt(PPh_3)_2]_3$ and $[Pt(PPh_3)]_4$ based on triangular or tetrahedral metal clusters and subsequent workers[2,3] have accepted these structures.



(III) (I)

We have investigated[4] the mass spectral behaviour of PtR_2L_2 complexes [R = alkyl or aryl; L = t-phosphine or $L_2 = (Ph_2P)_2(CH_2)_n$, $n = 1,2$] and find that they produce Pt containing ions except for L = PPh_3 and R = Ph, *m*- or *p*-FC_6H_4, when only phosphine and hydrocarbon ions are produced. Pyrolysis of these three compounds *in vacuo* gave brown, orange, or red solids analysing as $(PtP_2Ph_4C_6H_4)_n$ (osmometer molecular weights correspond to $n = 2$ and 3 for Ar = *m*-FC_6H_4, the more extreme conditions giving the dimer, and $n = 4$ for Ar = Ph or *p*-FC_6H_4) together with benzene and biaryl as the only detectable volatile products. Thermogravimetric analyses were within 2% of the values required by equation (1).

$$Pt(PPh_3)_2Ar_2 \xrightarrow[240\text{—}260\ ^\circ C,\ Ar\ =\ m\text{-}FC_6H_4]{\substack{150\text{—}190\ ^\circ C,\ Ar\ =\ Ph \\ 180\text{—}210\ ^\circ C,\ Ar\ =\ p\text{-}FC_6H_4}} \underset{(I)}{(PtP_2Ph_4C_6H_4)} + C_6H_6 + Ar_2 \qquad (1)$$

The similarity of these pyrolyses to the decomposition of $Pt(C_2H_4)(PPh_3)_2$ (II) previously reported[2] as yielding $[Pt(PPh_3)_2]_3$ led us to reinvestigate this reaction. We found that passing N_2 through a solution of (II) in *o*-xylene at 25 °C over 24 h resulted in loss of ethylene and benzene with 50% conversion into the dimer derived from (I).

I.r. spectra of these oligomers contain bands in the regions characteristic of *o*-metallated phenyl complexes.[5] Mass spectrometry of the trimer at 250 °C produced fragment ions with more than one Pt atom. The pyrolysis reactions clearly proceed by concerted reductive elimination of Ar_2 forming $Pt(PPh_3)_2$ which, on *o*-metallation, would produce the hydride (III).[5] Elimination of benzene from (III) produces the associated (16-electron) complexes derived from (I). The dimer is presumably planar with bridging PPh_2 groups; the trimer could be based on a triangle of Pt atoms with PPh_2 bridging each edge, each Pt atom being 6-co-ordinate. A tetramer could be based on an 8-membered –Pt–PPh_2– ring with 4-co-ordinate Pt, or a tetrahedron of Pt atoms with PPh_2 bridging each face.

(*Received, 2nd July* 1973; *Com.* 948.)

---

[1] R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Comm.*, **1966**, 869.
[2] R. Ugo, G. LaMonica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta*, 1970, **4**, 390.
[3] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.
[4] F. Glockling, T. McBride, and R. J. I. Pollock, *Inorg. Chim. Acta*, in the press.
[5] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.