

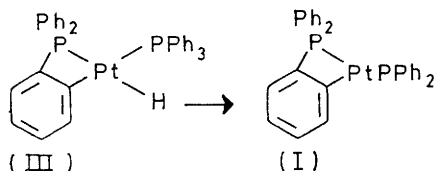
## Platinum-Phosphine Cluster Compounds

By FRANK GLOCKLING,\* THOMAS MCBRIDE, and R. J. IVAN POLLOCK

(Chemistry Department, The Queen's University, Belfast BT9 5AG)

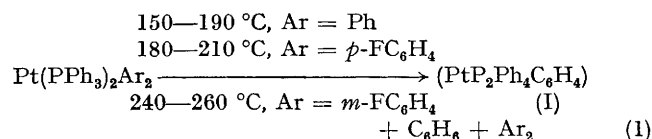
**Summary** Previously prepared platinum cluster compounds derived from  $\text{Pt}(\text{PPh}_3)_2$  are characterised as associated platinum(II) complexes  $[\text{Pt}(\text{PPh}_2)(\text{C}_6\text{H}_4\text{-PPh}_2)]_{2,3,\text{or } 4}$  formed through *o*-metallation reactions.

It was reported<sup>1</sup> that brown or red platinum cluster compounds were formed by removal of triphenylphosphine from  $\text{Pt}(\text{PPh}_3)_4$ . These were formulated as  $[\text{Pt}(\text{PPh}_3)_2]_3$  and  $[\text{Pt}(\text{PPh}_3)]_4$  based on triangular or tetrahedral metal clusters and subsequent workers<sup>2,3</sup> have accepted these structures.



We have investigated<sup>4</sup> the mass spectral behaviour of  $\text{PtR}_2\text{L}_2$  complexes [ $\text{R}$  = alkyl or aryl;  $\text{L}$  = *t*-phosphine or  $\text{L}_2 = (\text{Ph}_2\text{P})_2(\text{CH}_2)_n$ ,  $n = 1, 2$ ] and find that they produce Pt containing ions except for  $\text{L} = \text{PPh}_3$  and  $\text{R} = \text{Ph}$ , *m*- or *p*- $\text{FC}_6\text{H}_4$ , when only phosphine and hydrocarbon ions are produced. Pyrolysis of these three compounds *in vacuo* gave brown, orange, or red solids analysing as  $(\text{PtP}_2\text{Ph}_4\text{C}_6\text{H}_4)_n$  (osmometer molecular weights correspond to  $n = 2$  and 3 for  $\text{Ar} = m\text{-FC}_6\text{H}_4$ , the more extreme conditions giving the dimer, and  $n = 4$  for  $\text{Ar} = \text{Ph}$  or *p*- $\text{FC}_6\text{H}_4$ ) together with benzene and biaryl as the only detectable volatile products.

Thermogravimetric analyses were within 2% of the values required by equation (1).



The similarity of these pyrolyses to the decomposition of  $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  (II) previously reported<sup>2</sup> as yielding  $[\text{Pt}(\text{PPh}_3)_2]_3$  led us to reinvestigate this reaction. We found that passing  $\text{N}_2$  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.<sup>5</sup> 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  $\text{Ar}_2$  forming  $\text{Pt}(\text{PPh}_3)_2$  which, on *o*-metallation, would produce the hydride (III).<sup>5</sup> Elimination of benzene from (III) produces the associated (16-electron) complexes derived from (I). The dimer is presumably planar with bridging  $\text{PPh}_2$  groups; the trimer could be based on a triangle of Pt atoms with  $\text{PPh}_2$  bridging each edge, each Pt atom being 6-co-ordinate. A tetramer could be based on an 8-membered  $-\text{Pt}-\text{PPh}_2-$  ring with 4-co-ordinate Pt, or a tetrahedron of Pt atoms with  $\text{PPh}_2$  bridging each face.

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

<sup>1</sup> R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and F. Bonati, *Chem. Comm.*, 1966, 869.

<sup>2</sup> R. Ugo, G. LaMonica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta*, 1970, **4**, 390.

<sup>3</sup> C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.

<sup>4</sup> F. Glockling, T. McBride, and R. J. I. Pollock, *Inorg. Chim. Acta*, in the press.

<sup>5</sup> M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.