Novel Cluster Compounds of Platinum(0)

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A NUMBER of complex compounds of transition metals are known which contain clusters of metal atoms[1] (three, four, or six) directly bonded together, with ligands at the periphery of the cluster. We report two new complexes of this type, which contain platinum(0).

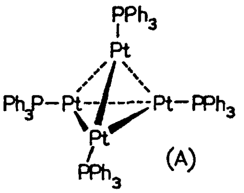
The first cluster compound, mono-triphenylphosphineplatinum(0), (A), was obtained by allowing tetrakis(triphenylphosphine)platinum(0)[2] to react (in air) with either cyclo-octa-1,5-diene, or its 1,3-isomer. A number of products with co-ordinated olefin occur in each case, but a brown compound (A) may be isolated (*ca.* 50% yield) by virtue of its low solubility in ether. Entirely different (monomeric) products are obtained by performing the reactions in the absence of oxygen. In no case does isomerisation of the olefin occur, though phosphine ligands are always displaced from tetrakis(triphenylphosphine)platinum(0).

Analytical data confirm the stoicheiometry $[Pt(PPh_3)]_n$. The infrared spectrum and n.m.r. spectrum (in deuterobenzene) show the absence of aliphatic or alicyclic protons, and confirm the presence of the triphenylphosphine ligand. The molecular weight (osmometric in benzene) shows that (A) is tetrameric in solution (calc. for tetramer 1828; found 1860, 1963). It is diamagnetic in the solid state and in solution.

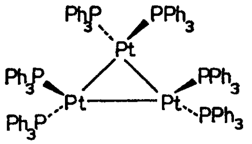
When yellow bistriphenylphosphineplatinum(0) (B), is allowed to melt under nitrogen, and the resulting red melt is cooled rapidly, a red compound, possibly trimeric bistriphenylphosphineplatinum(0)

(C) is obtained. Analytical data are satisfactory and the infrared spectrum of (C) differs only slightly from that of the yellow compound (B). The patterns of absorption between 500 and 550 cm.$^{-1}$ are quite distinct. Further, (B) shows a very strong absorption at 420 cm.$^{-1}$, whereas (C) has only a very weak band at 450 cm.$^{-1}$. Bands occur for (C) at 720 and 670 cm.$^{-1}$, where (B) shows no absorption. In the region 1180—1190 cm.$^{-1}$, (B) shows a singlet absorption, (C) a doublet, and in the region 1090—1130 cm.$^{-1}$, although both have a doublet, that for (B) is made up of a strong and a weak band, whereas both components for (C) are strong. (C) reverts very slowly in the solid and rapidly in solution to (B), which can be recovered by recrystallisation from benzene–hexane. The observed molecular weight (1100) of a fresh sample dissolved in benzene (calc. for trimer, 2169) fell to 652, 617, 585 (calc. for monomer, 723) in 5 min. at 37°.

The structures of the new polymeric compounds are most likely as shown:



(A)



(C)

The trimeric cluster dissociates very readily {unless additional stabilisation is present, as in the carbonyl bridges[3] of [$Pt_3(PPh_3)_4(CO)_3$].} However, the tetrameric cluster is very stable, (A) being a rather unreactive compound.

Work is in progress on the reactivity of these cluster compounds, and on the nature of the new olefinic paltinum(0) compounds.

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