

## New Precursors for Platinum(0) and Palladium(0) Complexes: Photochemical Decomposition of Oxalatobis(triphenylphosphine)platinum(II) and Related Complexes

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**Summary** Oxalatobis(triphenylphosphine)platinum(II) reacts photochemically to give a novel diphenylphosphido-bridged dimeric complex.

COMPLEXES of platinum(0) and palladium(0) are notable for their activity in oxidative-addition reactions<sup>1</sup> and their reactivity toward olefins and acetylenes.<sup>2</sup> Among the more novel and interesting zero-valent species reported<sup>3</sup> is [Pt(PPh<sub>3</sub>)<sub>2</sub>] which could be an intermediate in reactions of tris(triphenylphosphine)platinum(0).<sup>1</sup>

We report the synthesis of the compounds in Table 1 by

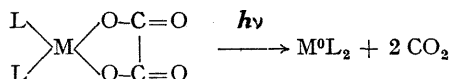
TABLE

Complex	M.p. (decomp.)	$\nu_{C=O}$ (in Nujol)
Pt(PPh <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .. ..	290—295°	1675 cm. <sup>-1</sup>
Pt(AsPh <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .. ..	270—275	1675
Pd(PPh <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .. ..	176—181	1650
Pt(diphos)C <sub>2</sub> O <sub>4</sub> .. ..	265—269	1700

Diphos = 1,2-bis(diphenylphosphino)ethane.

reaction of oxalic acid with the corresponding carbonate complexes. All are colourless, crystalline solids, stable indefinitely in the absence of light.

Their instability towards light prompted us to investigate them as precursors for zerovalent, co-ordinatively unsaturated platinum or palladium species. Irradiation of these complexes with u.v. light produces orange to brown mixtures and two moles of carbon dioxide are evolved per mole of complex. Under similar conditions in the absence of light no decomposition occurs. Only in the case of the palladium complex is any free metal formed during the irradiation. We suggest that the reaction



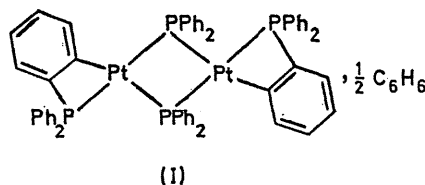
<sup>1</sup> J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, 1968, **7**, 2672.

<sup>2</sup> S. Cenini, R. Ugo, F. Bonati, and G. La Monica, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 191.

<sup>3</sup> R. Ugo, F. Cariati, and G. La Monica, *Chem. Comm.*, 1966, 868.

<sup>4</sup> M. A. Bennett and D. L. Milner, *Chem. Comm.*, 1967, 581.

may occur, producing a system free of competing ligands. However, under the conditions of the reaction the initial products may undergo secondary photochemical or thermal reactions.



Thus, in the case of [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>], the reaction gives a colourless solid (30%), m.p. 244—248°, which can be recrystallized from benzene but has very low solubility in common organic solvents. We suggest that the compound is (I). Molecular weight determinations in benzene gave values of 1379, 1345, and 1324 (calc.: 1322) and elemental analyses are consistent with (I). Decomposition of (I) with aqueous potassium cyanide produces triphenylphosphine, diphenylphosphine, and benzene in a ratio of 1.00:1.06:0.20 (calc.: 1.00:1.00:0.25). The i.r. spectrum shows a strong sharp band at 725 cm.<sup>-1</sup> which may be attributed to the C-H out-of-plane deformation mode of the *ortho*-disubstituted phenyl groups.<sup>4</sup> A sufficient amount of benzene is found in the original reaction mixture to account for the displaced phenyl groups. There is no evidence of a metal-hydrogen stretching frequency in the i.r. spectrum. No n.m.r. measurements were possible because of the low solubility of the complex.

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