

A Novel Dimeric Platinum(I) Complex

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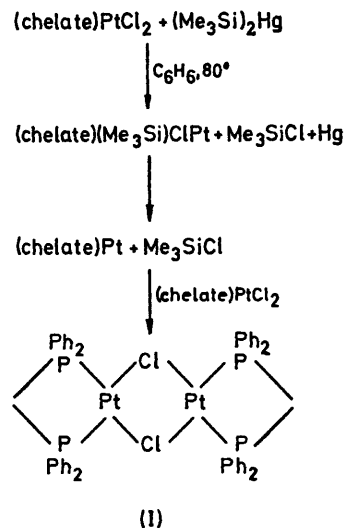
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Summary Reaction of $[(\text{Ph}_2\text{P})_2\text{CH}_2]\text{PtCl}_2$ with $(\text{Me}_3\text{Si})_2\text{Hg}$ yields the diamagnetic complex, $[(\text{Ph}_2\text{P})_2\text{CH}_2]_2\text{Pt}_2\text{Cl}_2$, with chlorine as bridging ligand and the metal in the formal oxidation state of +1.

BISTRIMETHYLSILYLMERCURY has found extensive use in forming Pt-SiMe₃ complexes,¹ and the reaction of $[(\text{Ph}_2\text{P})_2\text{CH}_2]\text{PtCl}_2$ with an excess of $(\text{Me}_3\text{Si})_2\text{Hg}$ yields the expected product, $[(\text{Ph}_2\text{P})_2\text{CH}_2]\text{Pt}(\text{SiMe}_3)_2$. However, if the platinum halide complex is present in excess the reaction takes a different course giving the novel platinum(I) dimer $[(\text{Ph}_2\text{P})_2\text{CH}_2]_2\text{Pt}_2\text{Cl}_2$ (I), probably formed as shown in the Scheme.

The yellow crystalline complex (I) has been characterised by elemental analysis and the presence of a molecular ion centred at 1229 a.m.u. in its mass spectrum, the ion pattern being consistent with that calculated for a framework of Pt_2Cl_2 . Its i.r. spectrum contained a medium band at 249 cm^{-1} assignable to bridging $\nu(\text{Pt}-\text{Cl})$, terminal $\nu(\text{Pt}-\text{Cl})$ being absent. The ^1H n.m.r. spectrum showed only phenyl and methylene protons in the correct ratio, the CH_2 resonance appearing as 9 lines (1:2:1:4:8:4:1:2:1) with $^3J(\text{Pt}-\text{H})$ 56.6 and $^2J(\text{P}-\text{H})$ 3.8 Hz. The compound is diamagnetic and produced no e.s.r. signal.

Complex (I) is remarkably stable, m.p. $291^\circ(\text{decomp.})$ and is unaffected by air over 2 months. The Pt-Cl bridge was incompletely cleaved by excess of the phosphine over 24 h in benzene under reflux.



SCHEME

The structure of (I) involves either two d^9 Pt atoms with sufficient Pt-Pt interaction to make the complex diamagnetic, or two Pt atoms in different oxidation states. During the course of this work a related palladium(I) complex was reported.²

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¹ A. F. Clemmit and F. Glockling, *J. Chem. Soc. (A)*, 1971, 1164.

² S. Otsuka, Y. Tatsuno, and K. Ataka, *J. Amer. Chem. Soc.*, 1971, 93, 6705.