

A Dehydrodiimide Complex of Platinum(II): the Reduction of *cis*-Bistriphenylphosphineplatinum Dichloride by Hydrazine

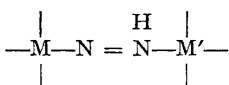
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INCREASING interest is being shown in nitrogen complexes of transition-metal ions and in model systems for nitrogen fixation. A simple analogue of nitrogen reductase has been described by Parshall¹ who suggests that the adduct, formed



from the reaction of the metal hydride and nitrogen

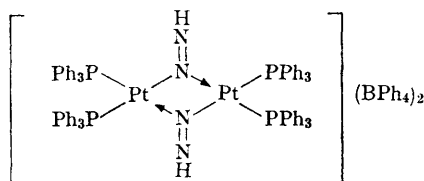
complex may subsequently be reduced to ammonia. We now report unequivocal evidence for a dehydrodi-imide-bridged binuclear platinum(II) cation.

The reduction of hydrazine by platinum(II) complexes with tertiary phosphines has been studied earlier by Malatesta and Cariello,² and Chatt and Shaw.³ When aqueous 85% hydrazine is added slowly to an alcoholic suspension of *cis*-[PtCl₂(PPh₃)₂] a yellow solution is obtained,

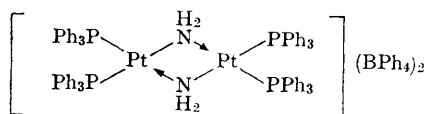
nitrogen gas being evolved; cooling to -78° leads to the separation of excess of hydrazine hydrochloride. Evaporation of the solution under reduced pressure (0.5 mm.) gives pale yellow crystals which are very soluble in alcohol and difficult to purify completely. The analytical data are consistent with the stoichiometry $\text{PtN}_2\text{H}_x(\text{PPh}_3)_2\text{Cl}$; there is no indication of Pt-H and Pt-Cl stretching vibrations in the infrared spectrum. The complex decomposes rapidly in benzene with the evolution of pure nitrogen (determined by vapour phase chromatography) and a thermogravimetric analysis again shows the evolution of nitrogen, the residue being pure *trans*-PtHCl(PPh₃)₂. The data support the stoichiometry $\text{PtN}_2\text{H}(\text{PPh}_3)_2\text{Cl}$. Addition of sodium tetraphenylborate to an alcoholic solution of $\text{PtN}_2\text{H}(\text{PPh}_3)_2\text{Cl}$ precipitates a pale cream tetraphenylborate complex and single crystals of suitable quality for an X-ray examination have been grown from acetone-benzene.

The crystals are monoclinic with $a = 14.09$, $b = 26.45$, $c = 15.01$ Å, $\beta = 103.0^\circ$; the space group is $P2_1/n$, $Z = 2$ so that short of molecular disorder (*vide infra*), the complex ion has exact C_2 symmetry. The essential geometry of the complex is shown in the Figure and results from a block-diagonal least-squares analysis of 1257 independent reflexions observed on a 'Paired' diffractometer (the present discrepancy index, R , is 0.079).

The X-ray analysis shows that the crystals are a mixture of the dehydrodi-imide species,

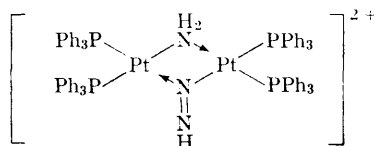


and the amino-complex



The evidence that the crystals contain a mixture of the dehydrodi-imide and amino-species is that the two nitrogen atoms of the N₂H bridging groups have considerably different peak heights in a Difference Fourier Synthesis. The nitrogen-nitrogen bond length of 1.18 Å ($\sigma = 0.09$ Å) is not

statistically significantly different from the equivalent value of 1.24 Å in azoimide.⁴ If molecular disordering is present around crystallographic centres of symmetry, the asymmetric bridged species



may be also imagined to be present in the crystal as well as the symmetrical dehydrodi-imide and amino-species. The platinum, phosphorus, and nitrogen (2) atoms are co-planar to within 0.005 Å while N(1) is displaced 0.1 Å from this plane. The terminal difference electron density synthesis reveals the presence of a disordered benzene molecule in the lattice which is consistent with the observed and calculated crystal densities; contributions to the structure factor amplitudes of the benzene carbon atoms have not, as yet, been included in the structure refinement.

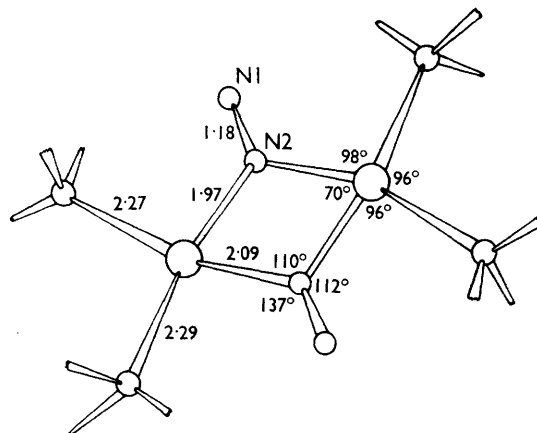


FIGURE. The estimated standard deviations are: Pt-P, 0.02 Å; Pt-N, 0.05 Å; N-N, 0.09 Å; \angle P-Pt-P, 0.8° ; \angle N-Pt-P, 1.4° ; \angle Pt-N-N, 5.1° ; and \angle NP-t-N, 1.8° .

The n.m.r. spectrum of the complex (in CDCl_3) shows a complex pattern centred at τ 2.8 due to the phenyl protons and a singlet at τ 8.75; the complex is a uni-uni-bivalent electrolyte in nitrobenzene.

cis-PtHCl(PPh₃)₂ separates from an alcoholic solution of $[\text{PtN}_2\text{H}(\text{P}(\text{Ph}_3))_2\text{Cl}]_2$ after several hours at room temperature but a mixture of the *cis*- and

trans-monohydrido-complexes is obtained on warming the solution. Only the *cis*-complex is formed if HCl is added to an alcoholic solution.

In contrast to the reaction at room temperature, the addition, at 40–50°, of excess hydrazine to an alcoholic solution of *cis*-PtCl₂(PPh₃)₂ gives a mixture of the bis- and tris-triphenylphosphine platinum(0) complexes which are also formed by the treatment of the *cis*- and *trans*-PtHCl(PPh₃) complexes with excess hydrazine.

Analogous palladium–dehydrodi-imide complexes can be prepared but are less stable than the platinum complexes while other complexes than those described here are formed with rhodium and iridium and will be discussed later.

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¹ G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822.

² L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

³ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

⁴ "Tables of Interatomic Distances", *Chem. Soc. Spec. Publ.*, No. 11, p. M49.