Cyclopropane Adducts of Platinum(IV): The Stabilisation of an Ylide

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THE reaction of cyclopropane with chloroplatinic acid dissolved in acetic anhydride gives a brown complex, (A), formulated[1,2] as the polymer $(C_3H_6PtCl_2)_n$. We have not succeeded in obtaining single crystals of this complex, but the radial distribution function (Figure 1), based on powder-diffractometer *X*-ray data, suggests that the description[2] of the structure as a chloro-bridged species is correct. It is to be noted that values of the radial density function are relative and that such an analysis of powder data will not, of necessity, give peaks of area proportional to the product of the atomic numbers of the atoms forming the vector.

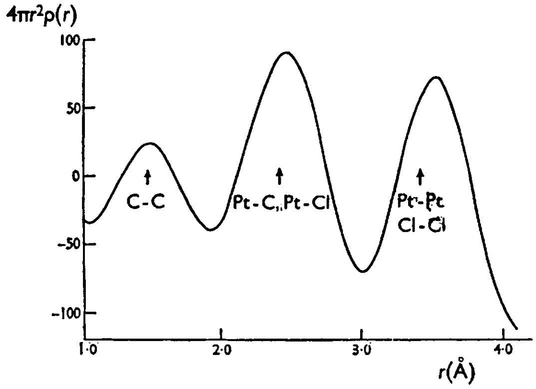


FIGURE 1

The polymer may be converted,[1] using pyridine, into the monomeric white complex $[(C_3H_6)Pt(py)_2Cl_2]$, (B), whose structure, shown in Figure 2, has been determined by single-crystal *X*-ray methods ($R = 0{\cdot}097$ for 1150 independent reflexions; average e.s.d. for Pt–Cl 0·015, Pt–C and Pt–N 0·04, C–C and C–N 0·06Å). The mode of attachment of the cyclopropane to the platinum is essentially that suggested[2] earlier.

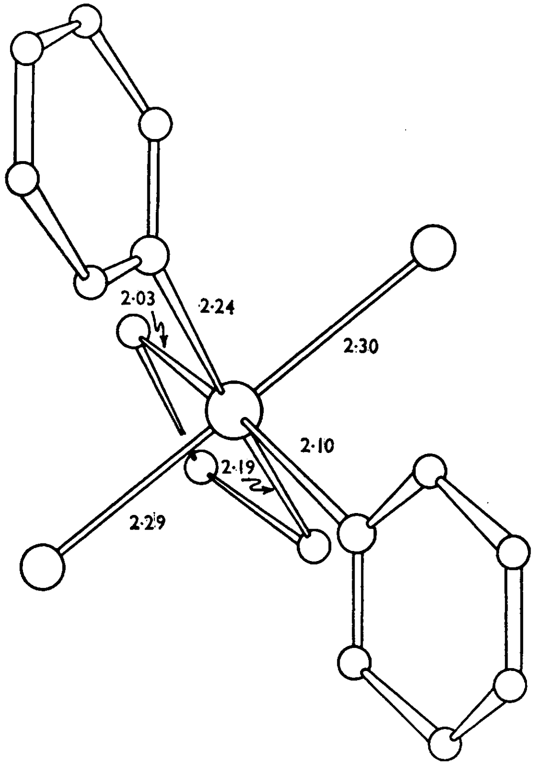
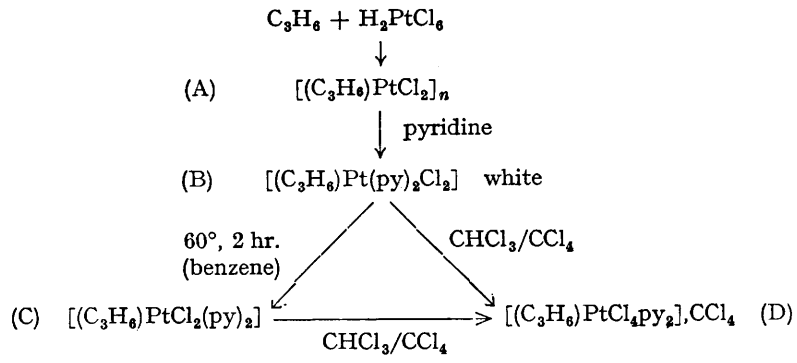


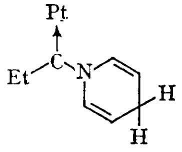
FIGURE 2

A solution of (B) in warm benzene slowly becomes yellow[2] and we have isolated a pure compound, (C), which is isomeric with (B); preliminary unit-cell data suggest that (C) is dimeric. When (C) is "recrystallised" from chloroform–carbon tetrachloride, or when the white complex, (B), is allowed to reflux in the same solvent, beautiful yellow prisms of a new compound, (D), are obtained. The conversions are summarized below:

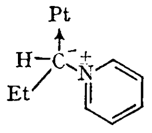


The structure of (D) has also been determined by *X*-ray methods ($R = 0{\cdot}082$ for 1950 independent reflexions; average e.s.d. for Pt–Cl 0·01, Pt–C and Pt–N 0·03, C–C and C–N 0·04Å) and is shown in Figure 3. The platinum, nitrogen, and carbon atomic positions, observed in the *X*-ray analysis, suggest the possible partial structures (I) or (II) for the ligand *trans* to the pyridine.

Structure (I) is a platinum–carbene complex, (II) being that of the isomeric ylide. We favour an ylide structure for (D) for several reasons. The infrared spectra of (C) and (D) are extremely similar so that the C_3-unit in both is similarly constituted. In (C), the proton resonance spectrum shows signals due to CH_3, CH_2, and CH groups. The last is split



(I)



(II)

by the ^{195}Pt nucleus (spin $\frac{1}{2}$, abundance 33%) by 120 c./sec.; the partial structure (II) therefore appears to be established for (C) and, by comparison, for (D) also [(D) is insufficiently soluble for direct proton resonance experiments]. The stoicheiometry of the complex (D) is $[Pt(py)_2Cl_4(C_3H_6)]$-CCl_4; on thermal decomposition of the crystals the solvating carbon tetrachloride is first lost, followed quantitatively by propene and, finally, by pyridinium chloride. The production of propene completely supports the ylide formulation of (D), as does the observation that the stereochemistry of

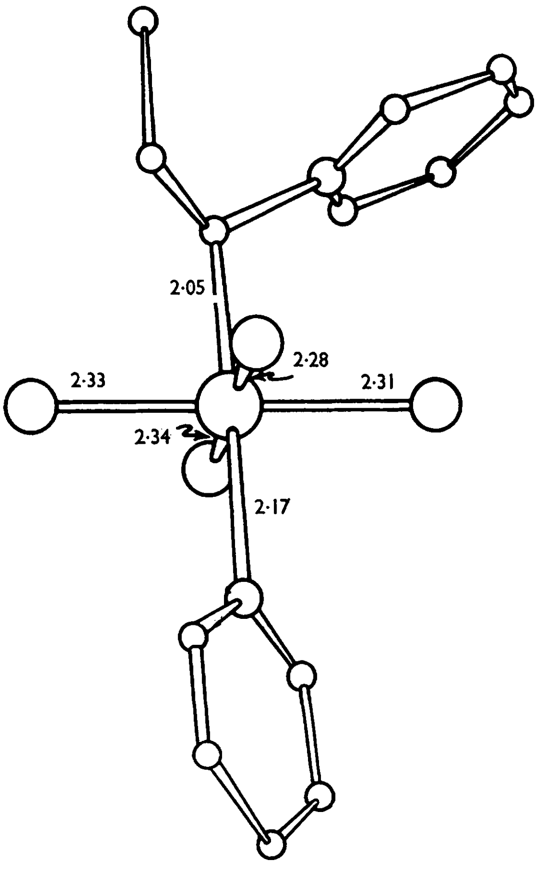


FIGURE 3

the σ-bonded carbon atom is not trigonal planar [the perpendicular distance of the platinum ion from the plane containing the carbon and nitrogen atoms, $C(H_2)–C(H)–N$, is 1·8Å].

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[1] C. F. Tipper, *J. Chem. Soc.*, 1955, 2045.

[2] D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *J. Chem. Soc.*, 1961, 738.