149. *The Structure of "Cyclopropane Platinous Chloride."* [1]

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The substance of composition $(C_3H_6Cl_2Pt)_n$ (I), formed from hexachloroplatinic acid and cyclopropane, is shown to be a chloride-bridged polymer built from dichloro(trimethylene)platinum(IV) (III). Pyridine reacts with complex (I) to form the hexaco-ordinated compound dichloro(trimethylene)-dipyridineplatinum(IV) (II). Tertiary phosphines (PR_3) displace cyclopropane from the complexes (I) and (II), reducing the platinum atom to the bivalent state, and forming a mixture of *cis*- and *trans*-$[PtCl_2(PR_3)_2]$. Cl^-, I^-, and CN^- behave similarly.

The infrared and nuclear magnetic resonance spectra of the complexes are consistent with the proposed structures.

OLEFINS and acetylenes readily form complexes with salts of silver(I), copper(I), mercury(II), and platinum(II).[2] In these complexes the hydrocarbon is bonded to the metal atom by interaction of the delocalised π-electrons of the C:C or C⋮C bond with a suitable orbital of the metal atom.[3] Following the suggestion by Walsh [4] that there is considerable delocalisation of the electrons of the cyclopropane ring, Tipper [5] examined the ability of cyclopropane to form similar complexes. He reported that cyclopropane reacts with hexachloroplatinic acid (H_2PtCl_6) in acetic anhydride to form a brown solid of the composition $C_3H_6Cl_2Pt$ (I), which gives a white compound $[PtCl_2(C_3H_6)(py)_2]$ (II) on treatment with pyridine (py). Cyclopropane is liberated quantitatively from both these compounds by aqueous potassium cyanide. This, and the fact that the infrared spectrum of compound (I) showed only two C–H stretching frequencies, led Tipper to suggest that the cyclopropane ring is intact in these complexes. He considered cyclopropane to behave as an unsaturated ligand, like ethylene, and compound (I) to be a dimer analogous to ethyleneplatinous chloride, $[Pt_2Cl_4(C_2H_4)_2]$, with its platinum atoms in the bivalent state.

However, unlike ethyleneplatinous chloride, compound (I) is insoluble in all the usual organic solvents except ethanol, in which its limited solubility varies from sample to sample and depends on the previous history of the sample. This property suggests that compound (I) is a polymer, $[PtCl_2(C_3H_6)]_n$. Furthermore, compound (I) is formed by salts of platinum(IV), *e.g.*, platinic chloride and hydrogen hexachloroplatinate, but not by salts of platinum(II), *e.g.*, sodium and potassium tetrachloroplatinate, and the stoicheiometry of the complex (II) does not accord with the chemistry of olefin–platinum(II) complexes, which give complexes of the type *trans*-$[PtCl_2(olefin)(amine)]$ on treatment with amines. We have, therefore, re-investigated the structures of compounds (I) and (II) and conclude on the basis of their chemistry and infrared and nuclear magnetic resonance spectra that compound (I) is a polymer built from units of dichloro(trimethylene)platinum(IV) (III), in which the cyclopropane ring has opened and chelated to the platinum atom. The polymerisation of the unit (III) must occur through chloride bridges whereby the platinum(IV) atom achieves its normal co-ordination number of six.

The white compound (II) is dichloro(trimethylene)dipyridineplatinum(IV), formed by the normal bridge-splitting reaction of pyridine with the chloride-bridged polymer (I). It is stable, readily soluble in organic solvents, monomeric, a non-electrolyte in nitrobenzene, and diamagnetic, and has a dipole moment of 6·05 D. Three geometric isomers are possible, *i.e.*, (IV), (V), and (VI) and tentatively, on the basis of the infrared spectrum, this white

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[1] For a preliminary communication, see Adams, Chatt, Guy, and Sheppard, *Proc. Chem. Soc.*, 1960, 179.

[2] See Keller, *Chem. Rev.*, 1941, **28**, 229; Helmkamp, Carter, and Lucas, *J. Amer. Chem. Soc.*, 1957, **79**, 1306; Chatt, Duncanson, and Guy, *Chem. and Ind.*, 1959, 430.

[3] See Chatt and Duncanson, *J.*, 1953, 2939.

[4] Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179; cf. Coulson and Moffitt, *Phil. Mag.*, 1949. **40**. 1.

[5] Tipper, *J.*, 1955, 2045.

compound has been assigned the *trans*-configuration (IV). The dipole moment is consistent with this but does not distinguish between structures (IV) and (V). It isomerises in boiling benzene to a bright yellow solid (VII) which was examined only cursorily owing to the difficulty in obtaining reproducible samples. This solid is monomeric, diamagnetic, and a non-electrolyte in nitrobenzene. It may be one of the other two possible stereoisomers of complex (II), or a mixture of both, although its spectra and chemical reactions differ so much from those of compound (II) that a more extensive re-arrangement may have occurred.

Unsuccessful attempts were made to prepare compound (II) by treatment of cyclopropane with *cis*- and *trans*-$[PtCl_2(py)_2]$ and *cis*- and *trans*-$[PtCl_4(py)_2]$ (py = pyridine).

The 2,2′-bipyridyl analogue of compound (II), *i.e.*, $[PtCl_2(C_3H_6)$ (bipy)], was prepared by the reaction of bipyridyl (bipy) with the polymer (I). It is cream-coloured, and insoluble in all common solvents. Tertiary phosphines (PR_3) do not give analogues of compound (II), but form *trans*- and/or *cis*-$[PtCl_2(PR_3)_2]$ with liberation of cyclopropane (identified by its infrared spectrum).

The liberation of cyclopropane with simultaneous reduction to platinum(II) is a general reaction of anionic ligands of high *trans*-effect, and it appears that the three-carbon chain is freed in such a manner by these ligands that it cyclises during the liberation reaction.

$$\text{(II)} + 2\text{NaI} \xrightarrow{\text{Acetone}} [\text{PtI}_2(\text{py})_2] + \text{C}_3\text{H}_6 + 2\text{NaCl}$$

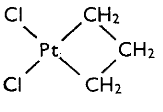
$$\text{(I)} + 4\text{KCN} \xrightarrow{\text{H}_2\text{O}} \text{K}_2[\text{Pt(CN)}_4] + \text{C}_3\text{H}_6 + 2\text{KCl}$$

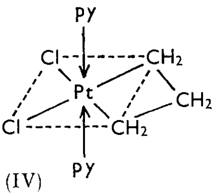
The pyridine derivative (VII) differs from compound (II) in giving no gaseous product even with boiling potassium cyanide solution.

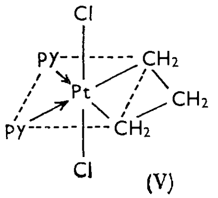
Chlorides reacted only slowly with compounds (I) and (II), sometimes with elimination of the C_3H_6 residue, although the form in which it was liberated was not determined. Thus compound (I) dissolved slowly in aqueous hydrochloric acid and in aqueous sodium chloride; and on addition of $[Pt(NH_3)_4][ClO_4]_2$, Magnus's salt, $[Pt(NH_3)_4][PtCl_4]$, was isolated. Compound (II) behaved similarly in aqueous solution, but in ethereal solution the complex $[pyH]^+[PtCl_3(C_3H_6)(py)]^-$ was formed.

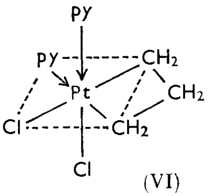
On thermal decomposition the compound (I) gave mainly an unidentified mixture of chlorinated hydrocarbons together with traces of hydrogen chloride and cyclopropane, but no propene that could be detected by infrared analysis. On the other hand, the pyridine derivatives (II) and (VII) gave high yields of propene, containing in the case of compound (II) traces of cyclopropane and pyridine.

Infrared spectra of compounds (I) and (II) and of cyclopropane are recorded in the Table. The spectrum of the complex (I) is more complicated than, and bears no relation to, that of cyclopropane.


(III)


(IV)


(V)


(VI)

When a hydrocarbon is attached as an uncharged ligand to a metal atom, as in Zeise's salt, $K[PtCl_3(C_2H_4)],H_2O$,[6] or dibenzenechromium,[7] the infrared spectrum of the ligand in the complex is similar to that of the free ligand. If, therefore, cyclopropane were bonded to the platinum atom as a ring, its local symmetry would be largely preserved ($D_{3h} \longrightarrow C_{3v}$) and its spectrum should exhibit bands similar in number and position to

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[6] Powell and Sheppard, *Spectrochim. Acta*, 1958, **13**, 69.

[7] Snyder, *Spectrochim. Acta*, 1959, 807.

those of the gas. That this is not so must mean that the cyclopropane ring has opened and that one or two platinum–carbon σ-bonds have been formed. If only one σ-bond were formed, the C_3 chain would probably end with a CH_3, CH_2Cl, or $=CH_2$ group. All three possibilities are clearly ruled out by the spectrum. A sensitive indication of environment is provided by the C–H stretching frequencies. For compound (I) these lie at 3025, 2954, and 2948sh cm.$^{-1}$, which are values intermediate between those of cyclopropane (3103, 3028 cm.$^{-1}$) and open-chain hydrocarbons. Thus, the infrared spectrum is clearly in favour of structure (III) for compound (I). A reasonable assignment of the observed bands can be made on this basis and is included in the Table together with the band positions.

Assignment of bands due to C_3H_6 unit	$[PtCl_2(C_3H_6)]$	$[PtCl_2(C_3H_6)(py)_2]$ (white isomer)	Cyclopropane [8]
		3100vw *	
		3070w *	
		3040vw *	
		3007w *	3102·9
C–H	3025m	2992w	3028·1
	2954m	2938m	
	2948sh	2917m	
		1600s *	
		1565vw *	
		1481m *	
		1444vs *	1441·8
CH_2 deformation	1414m	1437sh	
		1406vw *	
		1380vw *	
		1350w *	
		1250w *	
CH_2 wag	1255s	1238w	
	1237sh		
CH_2 twist	1165w	1217m	
		1195s *	
		1153w *	
Ring deformation	1149s	1134w	
	1125w	1087w	
		1064s *	
CH_2 rock	1087vs	1038s	
	1022vw		1028·7
		1011s *	
Ring deformation	981m	980vw	
CH_2 rock	948m	976w	
		941w *	
	890w	892w	
		873w *	868·5
		756vs *	
		691vs *	
	663w,b		
		632s *	
Ring deformation .... (Mainly Pt–C)	563m		

* Bands due to co-ordinated pyridine.

In the case of the white isomer (II), the spectrum is complicated by the presence of pyridine. By comparison with the spectra of several pyridine complexes of platinum(IV) the pattern of absorption due to pyridine was traced in complex (II), and the remaining bands assigned to the C_3H_6 unit. It is clear that the cyclopropane ring is not intact and the absorption due to C_3H_6 compares reasonably with that found in compound (I) although there are some shifts of frequency and intensity.

The *trans*-configuration of the pyridine ligands in complex (II) was inferred from the absence of splitting of the strong pyridine bands at 756 and 691 cm.$^{-1}$. The complexes *trans*-$[PtCl_4(py)_2]$ and *trans*-$[PtCl_2(py)_2]$ also have very strong single bands, near 760 and

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[8] Baker and Lord, *J. Chem. Phys.*, 1955, **23**, 1636.

680 cm.$^{-1}$. In *cis*-[$PtCl_4(py)_2$] the band near 680 cm.$^{-1}$ splits into two, whilst in *cis*-[$PtCl_2(py)_2$] both bands split into two.

The spectrum of the yellow solid (VII) is more complex than that of compound (II). In particular, extra bands were found near 1600 cm.$^{-1}$ and in the 780—680 cm.$^{-1}$ region, in which absorption characteristic of the pyridine molecule occurs. This is consistent with a *cis*-arrangement of pyridine ligands as in (V) or (VI).

Nuclear Magnetic Resonance Spectra.—The spectrum of the white isomer of compound (II) has been discussed previously[1] and was shown to support the structural formula (IV). The yellow isomer (or mixture of isomers) (VII) gave a rather weak spectrum owing to limited solubility in chloroform. In addition to hydrogen resonances attributable to the pyridine ligands, two main bands were observed. These consisted of a clearly defined triplet at $\tau = 9{\cdot}07$ [tetramethylsilane ($\tau = 10{\cdot}00$) was used as internal standard[9]] ($J_{HH'}$ ~7 c./sec.), and a broader and weaker band with poorly resolved structure at $\tau \sim 7{\cdot}9$. The former band is of the strength and has the fine structure expected from the CH_2–[Pt] group,[1] and the latter might well represent the central [CH_2]·CH_2·[CH_2] group in a [CH_2]$_3$Pt ring. In the spectrum of the white isomer, both types of methylene group had a chemical shift of $\tau = 7{\cdot}5$; the notable change in position of the resonance of the terminal methylene in (VII) seems most likely to be connected with their different relative locations with respect to the highly magnetically anisotropic pyridine ligands. If this is so, the persisting chemical equivalence of the CH_2·[Pt] groups implies that they are possibly symmetrically located with respect to the pair of pyridine rings and that if compound (VII) is a geometric isomer of (II) the more likely configuration is (V).

Unsuccessful attempts were made to prepare complexes from cyclopropane and sodium hexabromoplatinate, sodium tetra- and hexa-chloropalladate, or rhodium trichloride. Solutions of hydrogen hexachloroplatinate and cyclopropyl methyl ketone or dicyclopropyl ketone in acetic anhydride rapidly decomposed, yielding amorphous black solids. Cyclopentane and cyclohexane reacted with hydrogen hexachloroplatinate in acetic anhydride to give amorphous black solids which contained carbon and hydrogen in the approximate ratio of 1 : 2. Attempts to prepare the cyclobutyl and cyclopentyl analogues of compounds (I) and (II) by reaction of Li·[CH_2]$_n$·Li ($n = 4$ or 5) with *cis*- or *trans*-[$PtCl_4(py)_2$] and with platinic chloride gave no identifiable products.

EXPERIMENTAL

Microanalyses were carried out in these laboratories. Cyclopropane was obtained from the British Oxygen Company.

Catenadi-μ-chloro(trimethylene)platinum(IV) (I).—This was prepared from hydrogen hexachloroplatinate in 50—70% yield as described;[5] it decomposed at ~148° without melting (Found: C, 11·75; H, 1·95. Calc. for $C_3H_6Cl_2Pt$: C, 11·7; H, 1·95%). It can be prepared in similar yield from platinum tetrachloride. The colour of samples from apparently identical preparations varied from light yellow to dark brown.

Reactions of Catenadi-μ-chloro(trimethylene)platinum(IV) (I).—(a) *With pyridine.* The complex (I) was dissolved, with cooling, in pyridine, and dichloro(trimethylene)dipyridineplatinum(IV) was isolated in 70—80% yield by dilution with water. Recrystallisation of the complex from cold chloroform gave colourless prisms, m. p. 140—145° (decomp.) [Found: C, 33·2; H, 3·65; N, 6·1%; *M* (cryoscopic in 0·504% benzene solution), 493. Calc. for $C_{13}H_{16}Cl_2N_2Pt$: C, 33·5; H, 3·45; N, 6·0%; *M*, 466].

(b) *With 2,2′-bipyridyl.* A suspension of dichloro(trimethylene)platinum(IV) (0·803 g., 1 mol.) in ethanol (25 ml.) was treated with a solution of 2,2′-bipyridyl (0·406 g., 1 mol.) in ethanol (20 ml.). *Dichloro(trimethylene)-2,2′-bipyridylplatinum*(IV) separated immediately as a cream-coloured solid (1·135 g., 95%), m. p. 340—355° (decomp.) (Found: C, 33·2; H, 3·25; N, 5·85. $C_{13}H_{14}Cl_2N_2Pt$ requires C, 33·65; H, 3·05; N, 6·05%). This compound is insoluble in water and all the common organic solvents.

(c) *With triethylphosphine.* A suspension of dichloro(trimethylene)platinum(IV) (1·685 g.,

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[9] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

1 mol.) in ethanol (20 ml.) was treated under nitrogen with triethylphosphine (1·290 g., 2 mol.). The resulting clear yellow solution was taken to dryness, and the buff-coloured, crystalline residue (2·74 g.) treated with light petroleum (b. p. 60—80°). After removal of the solvent, the soluble fraction (0·74 g., 27%) crystallised from methanol as light yellow prisms, m. p. 142—143° undepressed on admixture with *trans*-bis(triethylphosphine)dichloroplatinum(II) (Found: C, 28·85; H, 6·0. Calc. for $C_{12}H_{30}Cl_2P_2Pt$: C, 28·7; H, 6·0%). The fraction (2·00 g., 73%), insoluble in light petroleum, crystallised from methanol as colourless prisms, m. p. 190—192° undepressed on admixture with *cis*-bis(triethylphosphine)dichloroplatinum(II) (Found: C, 28·8; H, 6·0%).

(d) *With triphenylphosphine.* On similar treatment with triphenylphosphine the complex (I) gave *cis*-bis(triphenylphosphine)dichloroplatinum(II), m. p. 300—310° (decomp.), in quantitative yield (Found: C, 54·55; H, 3·9. Calc. for $C_{36}H_{30}Cl_2P_2Pt$: C, 54·7; H, 3·8%).

(e) *With aqueous hydrochloric acid.* The complex (I) (0·308 g., 1 mol.) was dissolved in 12N-hydrochloric acid (10 ml.), giving a clear yellow solution which was diluted with water (20 ml.) and treated with tetrammineplatinum(II) perchlorate $[Pt(NH_3)_4][ClO_4]_2$ (0·462 g., 1 mol.) in water (20 ml.). Dark green prisms of Magnus's salt (0·483 g.) were formed over a period of 2 weeks (Found: C, 0·0; H, 2·2; N, 9·15. Calc. for $H_{12}Cl_4N_4Pt_2$: C, 0·0; H, 2·0; N, 9·35%).

Reactions of Dichloro(trimethylene)dipyridineplatinum(IV) (II).—(a) *With triphenylphosphine.* The complex (II) (0·466 g., 1 mol.) in benzene (30 ml.) was treated with a solution of triphenylphosphine (0·500 g., 1·9 mol.) in benzene (10 ml.). A yellow colour developed immediately and *cis*-bis(triphenylphosphine)dichloroplatinum(II) (0·733 g.), m. p. 305—315° (decomp.), separated in cream-coloured prisms (Found: C, 54·75; H, 3·9%).

(b) *With sodium iodide.* The complex (II) (0·466 g., 1 mol.) and sodium iodide (0·900 g., 6 mol.) in acetone (20 ml.) were heated under reflux for 30 min. The solid obtained on evaporation of the solvent was dissolved in a large volume of hot chloroform, and addition of light petroleum (b. p. 60—80°) gave di-iododipyridineplatinum(II) as yellow prisms, m. p. 287—288° (decomp.) (Found: C, 19·75; H, 1·85; N, 4·25. Calc. for $C_{10}H_{10}I_2N_2Pt$: C, 19·8; H, 1·65; N, 4·6%).

(c) *With aqueous hydrochloric acid.* The complex (II) (0·295 g.) dissolved slowly in 12N-hydrochloric acid (10 ml.), giving a yellow solution. On addition of tetrammineplatinum(II) perchlorate (0·285 g.) the pink form of Magnus's salt (0·240 g.) immediately separated (Found: C, 0·0; H, 2·2; N, 9·2%).

(d) *With ethereal hydrochloric acid.* Ethereal hydrochloric acid (2 mol.) was added with swirling to a solution of the complex (II) (0·970 g., 1 mol.) in chloroform (30 ml.). The pale yellow *product* separated immediately (Found: C, 30·65; H, 3·5; N, 5·45. $C_{13}H_{17}Cl_3N_2Pt$ requires C, 31·05; H, 3·4; N, 5·55%). It has a molecular conductivity of 5·7 ohm^{-1} $cm.^2$ at 20° in $3·3 \times 10^{-2}$M-nitrobenzene solution.

(e) *Isomerisation in benzene.* A solution of the complex (II) in benzene was heated under reflux for 5—10 min. and the solvent removed under reduced pressure. This yielded compound (VII) as a bright yellow solid, m. p. 160—165° (decomp.) (Found: C, 33·05; H, 3·55; N, 5·95%). The preparation was repeated several times, but, although the elemental analyses were satisfactory, the m. p. and infrared spectrum of the product were not reproducible, even after repeated recrystallisation from chloroform–light petroleum (b. p. 60—80°) and chromatographic treatment on alumina.

To identify the gases evolved in the reactions of compounds (I) and (II) with the tertiary phosphines, sodium iodide, and potassium cyanide, these reactions were repeated *in vacuo* in a small reaction vessel connected to a 5 cm. infrared gas cell. The gases evolved on thermal decomposition of complexes (I), (II), and (VII) were collected similarly and analysed by examination of their infrared spectra.

Infrared spectra were recorded on a Grubb–Parsons GS2A spectrometer. Solids were examined as mulls in " Nujol " and hexachlorobutadiene.

The magnetic resonances of the hydrogen nuclei were obtained at 40 Mc. with a Varian Associates 4300 B spectrometer, with flux stabilisation and sample spinning. The spectra were obtained for solution in chloroform; the positions of the peaks were measured by using sidebands generated by a Muirhead Decade oscillator.

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[*Received, September 5th,* 1960.]