496. Olefin Co-ordination Compounds. Part II.* Compounds with Two Double Bonds attached to One Platinum Atom.

By J. Chatt and R. G. Wilkins.

Dichlorodiethyleneplatinum, $(C_2H_4)_2PtCl_2$ (I), has been prepared in yellow crystals by passing ethylene through an almost saturated solution of dichlorodiethylene-μμ'-dichlorodiplatinum (II), in acetone at −70°. It dissociates at −6° in an ethylene atmosphere and most probably has a *trans*-configuration. The existence of this compound renders Hel'man's structure for olefin–platinous complexes invalid. The possible existence of the *cis*-isomer is reported.

Dipentene was examined as a possible chelating olefinic ligand. It forms two comparatively stable complexes of empirical formula, $C_{10}H_{16},PtCl_2$. One of these is monomeric and must be either a chelate complex or an addition compound, but not an analogue of dichlorodiethylene-μμ'-dichlorodiplatinum. Both regenerate dipentene with potassium cyanide. They are probably structural isomers.

In all except the olefin series of platinous complexes, at least one geometric isomer of the simple non-ionic compound, L_2PtCl_2 (L = ligand) is known and is usually more stable than the related ionic complexes, $[LPtCl_3]^-$, $[L_3PtCl]^+$, and $[L_4Pt]^{2+}$. The olefin complexes are notable exceptions; $K[C_2H_4PtCl_3]$ was first recognised in 1830 (Zeise, *Mag. Pharm.*, **35**, 105) but $(C_2H_4)_2PtCl_2$ (I), in spite of repeated attempts to prepare it (Hel'man, "Complex Compounds of Platinum with Unsaturated Molecules," Soviet Acad. Sci., 1945; Anderson, *J.*, 1936, 1042), was unknown until 1950 (Chatt and Wilkins, *Nature*, **165**, 859). Hel'man has based a vaguely described structure for olefin–platinous complexes on the apparent fact that not more than one double bond could be co-ordinated to one platinum atom (Hel'man, *Compt. rend. Acad. Sci., U.R.S.S.*, 1939, **24**, 549) and summarily rejected Anderson's evidence (*loc. cit.*) for an unstable distyrene complex. Our isolation of $(C_2H_4)_2PtCl_2$ shows that Hel'man's structure, in the manner in which she conceived it, is untenable and no structure described before 1949 (Chatt, *J.*, 1949, 3340) can be regarded as satisfactory.

Dichlorodiethyleneplatinum (I) was rapidly precipitated in canary-yellow crystals by passing ethylene into a concentrated solution of dichlorodiethylene-μμ'-dichlorodi-

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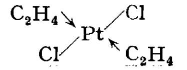
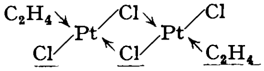
* Part I, *J.*, 1949, 3340.

platinum (II) in acetone or in ethyl methyl ketone at about −70°. It is only slightly soluble in the ketone at this temperature but dissolves to a yellow solution at about −50° and reverts, with evolution of ethylene, to the orange solution of (II) at room temperature. The yellow solid is thermally very unstable. It was obtained, damped with acetone or ether, by sucking off the acetone–ethylene mother-liquor through a sintered-glass filter and washing the solid with acetone or ether at −70° in a closed system which excluded moisture. In this state, the yellow solid reverts to orange (II) at about −6° in an atmosphere of ethylene but is converted again on the surface into yellow (I) by cooling. Even at −70° (I) is sufficiently dissociated in acetone for one molecule of ethylene to be lost, with dissolution of the solid to an orange solution, by passage of carbon dioxide through its acetone suspension.

(I)



$$\begin{array}{ccc} \mathrm{C_2H_4}\searrow & & \diagup\mathrm{Cl} \\ & \mathrm{Pt} & \\ \mathrm{Cl}\diagup & & \nwarrow\mathrm{C_2H_4} \end{array}$$



$$\begin{array}{ccccc} \mathrm{C_2H_4}\searrow & & \diagup\mathrm{Cl}\searrow & & \diagup\mathrm{Cl} \\ & \mathrm{Pt} & & \mathrm{Pt} & \\ \mathrm{Cl}\diagup & & \nwarrow\mathrm{Cl}\diagup & & \nwarrow\mathrm{C_2H_4} \end{array}$$

(II)

The presence of the ketone appears to help the formation of (I) and probably facilitates entry of the ethylene into (II) by opening the bridge, which is known to be split in boiling acetone (Chatt and Williams, *J.*, 1951, 3061):

$$(\mathrm{C_2H_4PtCl_2})_2 + \mathrm{Me_2CO} \rightleftharpoons 2\mathrm{C_2H_4,Me_2CO,PtCl_2}$$

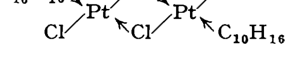
$$\mathrm{C_2H_4,Me_2CO,PtCl_2} + \mathrm{C_2H_4} \rightleftharpoons (\mathrm{C_2H_4})_2\mathrm{PtCl_2} + \mathrm{Me_2CO}$$

Neither gaseous ethylene at −70° nor liquid ethylene at its boiling point has any action on (II).

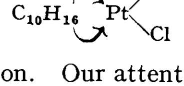
The instability of (I) is best explained by supposing that it has a *trans*-configuration. This instability is the combined effect of the rather weak co-ordinating affinity of ethylene together with the strong *trans*-influence or labilising effect of an ethylene molecule on the group in the *trans*-position to itself. Hel'man has shown that the halogen in the *trans*-position to ethylene in the $[\mathrm{C_2H_4PtCl_3}]^-$ ion can be replaced with the same order of rapidity as ionic halogen, and the rapid formation of the diethylene complex (I) at the very low temperature employed is readily understood if (I) has a *trans*-configuration. The yellow colour is also evidence, although weak evidence, for a *trans*-configuration. The corresponding carbon monoxide and phosphorus trifluoride complexes have a *cis*-configuration and are colourless. The *cis*-isomer of (I) should be formed more slowly and have greater stability than (I) [cf. the analogous carbonyl complex (Chatt and Williams, *loc. cit.*) and triethylphosphine complexes (Chatt and Wilkins, *J.*, 1952, 273)]; in fact, if a dilute solution of the diolefin complex in acetone, which at room temperature is an equilibrium mixture of (II) and $\mathrm{C_2H_4}$, is set aside with precautions to exclude moisture, a greyish solid usually contaminated with platinum separates slowly. It is apparently identical with the insoluble compound obtained by addition of one equivalent of tri-*n*-propylphosphine to (II) in acetone (see Chatt, *J.*, 1951, 652), is insoluble in all solvents, can be obtained only in small quantities, and is possibly *cis*-$(\mathrm{C_2H_4})_2\mathrm{PtCl_2}$.

Since $(\mathrm{C_2H_4})_2\mathrm{PtCl_2}$ has been prepared and the *cis*-isomer once it has been formed should be the more stable, diolefins under the right conditions should give reasonably stable chelate complexes. Hel'man has shown that both butadiene (*Compt. rend. Acad. Sci., U.R.S.S.*, 1939, **23**, 532) and hexa-1 : 5-diene (*loc. cit.*, 1945) do not chelate but that the double bonds react independently with different platinum atoms. We have confirmed Hel'man's findings in the case of butadiene which reacts with potassium chloroplatinite in 3% hydrochloric acid to produce $\mathrm{K_2[C_4H_6(PtCl_3)_2]}$. Kharasch and Ashford (*J. Amer. Chem. Soc.*, 1936, **58**, 1733) describe a dipentene complex of empirical formula $\mathrm{C_{10}H_{16}PtCl_2}$ which, if it is a co-ordination compound, could be either (III) or (IV) according to whether one or both double bonds are involved in complex formation. Our attention was directed to this compound because it is exceptionally stable and has a faint yellow colour in contrast to the orange bridged mono-olefin complexes of type (II). It was prepared by reaction of

(III)



$$\begin{array}{ccccc} \mathrm{C_{10}H_{16}}\searrow & & \diagup\mathrm{Cl}\searrow & & \diagup\mathrm{Cl} \\ & \mathrm{Pt} & & \mathrm{Pt} & \\ \mathrm{Cl}\diagup & & \nwarrow\mathrm{Cl}\diagup & & \nwarrow\mathrm{C_{10}H_{16}} \end{array}$$



$$\mathrm{C_{10}H_{16}} \rightrightarrows \mathrm{Pt}\begin{array}{l}\diagup\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{array}$$

(IV)

dipentene with platinic chloride in glacial acetic acid. We repeated this preparation and obtained the known compound, but also attempted to prepare it by reaction of dipentene with (II) in alcohol. The latter preparation yielded an even more stable substance, $C_{10}H_{16},PtCl_2$, with properties quite distinct from those of Kharasch and Ashford's compound. The compounds, which we shall designate α and β respectively, are described in the Table.

Each of these compounds is formed without contamination by the other, and the dipentene is liberated from each by aqueous potassium cyanide. The α-isomer is too insoluble in cold solvents and too unstable in hot solvents for a molecular-weight determination. The β-isomer is monomeric in boiling benzene and would thus appear to have structure (IV), but such a conclusion must be accepted with reserve because the mono-olefin, pinene, also forms a faintly yellow complex (Kharasch and Ashford, *loc. cit.*). Hofmann and von Narbutt (*Ber.*, 1908, **41**, 1625) have also described faintly yellow compounds, $C_{10}H_{12}PtCl{\cdot}OMe$ and $C_{10}H_{12}PtCl{\cdot}OEt$ obtained by reaction of potassium chloroplatinite with *cyclo*pentadiene in aqueous methanol and ethanol respectively. They claimed that PtCl and the alkoxyl group had added across a double bond in a manner analogous to alkoxymercuric salts in alcoholic solutions. In propyl alcohol they obtained $C_{10}H_{12},PtCl_2$, the colour of which is not stated, but they considered the PtCl–Cl to have added across the double bond. They stress the exceptional stability of these compounds. It is thus possible that the faintly yellow and comparatively very stable α- and β-$C_{10}H_{16}PtCl_2$ and the pinene complex, the stability of which was not stated, are addition products of a type similar to Hofmann and von Narbutt's compounds, and that structural isomerism is involved. The recovery of dipentene with potassium cyanide is no more decisive as evidence of co-ordination complex formation than is the liberation of ethylene from the ethoxymercuric chloride addition compound, $C_2H_4HgCl{\cdot}OEt$ (see Chatt, *Chem. Reviews*, 1950, **48**, 7). The true nature of α- and β-dipenteneplatinous chlorides and the other pale yellow, exceptionally stable olefin–platinous complexes is thus an open question.

	α-$C_{10}H_{16}PtCl_2$	β-$C_{10}H_{16}PtCl_2$
Preparation	$C_{10}H_{16} + PtCl_4$	$C_{10}H_{16} + (C_2H_4)_2Pt_2Cl_4$
Decomposition pt.	148—149°	171—172°
Colour	Very pale yellow	Very pale cream
Crystal form	Rhomb-shaped, *ca.* 77—78° angle (from $CHCl_3$–EtOH)	Needles (from C_6H_6)
Extinction	Symmetrical	Straight
NaI in acetone	Rapid decomp.	Orange-red $C_{10}H_{16}PtI_2$ (isolated as solid by evaporation of acetone)
$AgNO_3$ in aq. acetone	Ppt. within 10 secs.	Ppt. within 10 secs.
Solubility	Generally the less	Generally the greater
in acetone	Used for recrystn.	*Ca.* 0·1 g. in 8 c.c.
in ethanol	Insol. in cold, decomp. in hot	Used for recrystn.
in benzene	Sl. sol. cold, sol. hot	Sl. sol. cold or hot
in ether	Insol. cold or hot	Insol. cold or hot

EXPERIMENTAL

Dichlorodiethyleneplatinum (trans ?) (I).—This complex was prepared, filtered, and washed at a low temperature in an apparatus (Fig. 1) designed by Mr. Curtis of these laboratories. Dichlorodiethylene-μμ′-dichlorodiplatinum (II) (0·5 g.) in acetone (8 c.c.) was filtered and placed in angle *A*. The apparatus was then cooled in solid carbon dioxide–acetone with passage of dry ethylene. The yellow crystalline product separated and was filtered by tilting the apparatus and applying suction at *B*. Pure solvent (acetone followed by ether) was next cooled in angle *A* and used to wash the product, which decomposed at temperatures above —6°, leaving a residue of (II), decomp. 142—166° (Found: C, 8·5; H, 1·6; Pt, 66·4. Calc. for $C_2H_4Cl_2Pt$: C, 8·2; H, 1·4; Pt, 66·4%).

The yellow compound was analysed by measuring: (*a*) the ratio of ethylene evolved on warming to 30°, to that evolved when the residual (II) was decomposed by hot potassium cyanide solution; (*b*) the ratio of ethylene evolved on warming to 30°, to the platinum and chlorine in the residual (II).

(*a*) The compound was prepared in ethyl methyl ketone, to minimise errors arising from the high vapour pressure of acetone. (II) (0·1—0·15 g.) in the ketone (10—20 c.c.) was filtered and placed in *A* (Fig. 2), and all air was displaced from the apparatus by carbon dioxide. The tube *A* was then cooled to −70° and ethylene passed in until no more product separated. The mother-liquor was sucked off at *B*, and carbon dioxide was passed over the wet solid until all gaseous ethylene was displaced. The apparatus was then warmed to 30° and the ethylene collected. Its volume was corrected for the vapour of the surplus ketone which was carried over by the carbon dioxide and was present as liquid in the nitrometer, and also for the volume of ethylene which had remained dissolved in surplus ketone at −70°. The latter, involving an error of about 4%, was estimated from a blank experiment in which the yellow compound was simulated by an equal volume of powdered sodium chloride. When all the ethylene had been evolved at 30°, hot potassium cyanide solution was added through *C* and the extra quantity of evolved ethylene measured [Found: $C_2H_4(1) : C_2H_4(2)$ = (i) 1·02 : 1·00; (ii) 1·03 : 1·00. $C_4H_8Cl_2Pt$ requires 1 : 1].

(*b*) The initial evolution of ethylene was determined as before, the residue in *A* was taken up in dilute sulphuric acid in presence of AnalaR potassium chloride (0·06—0·07 g.), and platinum and chlorine were determined gravimetrically in the solution [Found: $C_2H_4(1)$: Pt : Cl = (i) 1·04 : 1 : 2·05; (ii) 1·09 : 1 : 2·01. $C_4H_8Cl_2Pt$ requires 1 : 1 : 2].

FIG. 1.

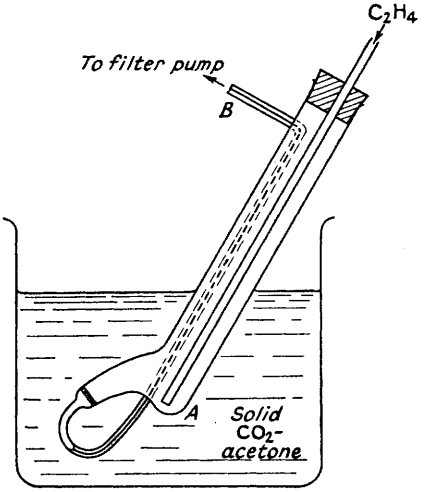
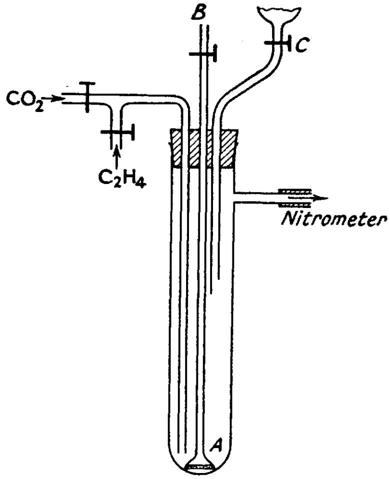


FIG. 2.



In one experiment, after ethylene (29 c.c.) had been evolved on warming to 30°, the moist residual orange (II) was again treated with ethylene at −70° until it became yellow. On warming again, only 5·6 c.c. of ethylene were evolved, indicating surface action only.

Dichlorodiethyleneplatinum (cis ?).—The above yellow *isomer* was washed thrice with cold AnalaR acetone, then dissolved in cold acetone, and the solution allowed to warm to room temperature. A little ethylene was evolved and the solution reddened slightly. After 48 hours, the solution had become cherry-red and deposited a small quantity of almost white crystalline *complex* (Found: C, 15·0; H, 2·4. $C_4H_8Cl_2Pt$ requires C, 14·9; H, 2·5%). This product is very difficult to obtain free from metallic platinum, and dry conditions, without excess of ethylene, are essential. It may be the *cis*-isomer or a polymeric substance. It effervesces with potassium cyanide solution.

Potassium Butadienebistrichloroplatinite, $K_2[C_4H_6(PtCl_3)_2]$.—Potassium chloroplatinite (5 g.) in water (25 c.c.) and concentrated hydrochloric acid (2·5 c.c.) were shaken for 2 days in an atmosphere of butadiene. The final suspension was warmed just sufficiently to dissolve the crystalline product, the whole filtered from a slight brown impurity, and the filtrate cooled to 0°. The *bistrichloroplatinite* (3·2 g.) separated in bright orange crystals (Found: C, 6·7; H, 0·9. $C_4H_6Cl_6K_2Pt_2$ requires C, 6·5; H, 0·8%). This product is stable in dilute hydrochloric acid but decomposes rapidly in neutral solution.

Dipentene Complexes.—The dipentene used was purified through its tetrabromide, m. p. 124·5—125·5°, and regenerated by reaction of the tetrabromide with magnesium in ether (Braun and Lemke, *Ber.*, 1923, **56**, 1652).

α-*Dipenteneplatinous chloride.* Prepared as described by Kharasch and Ashford (*loc. cit.*), this decomposed at 148—149° (they give 150—151°) (Found: C, 29·9; H, 4·3. Calc. for $C_{10}H_{16}Cl_2Pt$: C, 29·9; H, 4·0%).

β-*Dipenteneplatinous chloride.* The compound (II) (6·0 g.) in alcohol (100 c.c.) was filtered, dipentene (2·65 g.) added, and the mixture evaporated at 15—20 mm. The residue (7·66 g.) was extracted with hot alcohol (400 c.c.), filtered, and cooled to −70°. The *product* which separated recrystallised from 2 : 1 alcohol–acetone (yield, 3·0 g.) and then decomposed at 171—172° [Found: C, 30·0, 30·1; H, 4·2, 4·0; Pt, 48·4, 48·4%; *M* (ebullioscopically in 0·90% benzene solution) 406, (in 0·84% solution) 453, (in 1·12% solution) 453. $C_{10}H_{16}Cl_2Pt$ requires C, 29·9; H, 4·0; Pt, 48·5%; *M*, 402].

Reaction with potassium cyanide. Each isomer (0·3 g.) was dissolved separately in chloroform (20 c.c.) and shaken with cold aqueous potassium cyanide (0·3 g. in 20 c.c.) until the chloroform layer became colourless. The chloroform was separated and the aqueous layer extracted twice with chloroform. The combined extracts were dried (Na_2SO_4) and brominated at −10° (*ca.* 0·4 g. of bromine, slight excess). The chloroform was removed at 15—20 mm. and the residue washed out with ethyl acetate (yields: from α-isomer 0·25 g., from β-isomer 0·3 g.). Recrystallised once from ethyl acetate the products had m. p. (α) 122—123° and (β) 120—122°, not depressed on admixture with dipentene tetrabromide.

β-*Dipenteneplatinous iodide.* The β-chloride (0·3 g.) reacted in the cold with sodium iodide (0·25 g.) in acetone (35 c.c.). The precipitated sodium chloride was filtered off from the orange-brown solution, which by evaporation at 15—20 mm. gave a red crystalline *iodide.* This was purified by precipitation twice from chloroform solution with ether, and had decomp. pt. 122—124° (Found: C, 20·4; H, 3·0. $C_{10}H_{16}I_2Pt$ requires C, 20·5; H, 2·75%). It decomposed rapidly in boiling benzene. The α-chloride, under similar treatment, yielded a red oil, which decomposed rapidly at room temperature.

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