486. *Olefin Co-ordination Compounds. Part IV.* Diene Complexes of Platinum*(II). *The Structure of Hofmann and von Narbutt's* [Dicyclopentadiene(RO)PtCl].
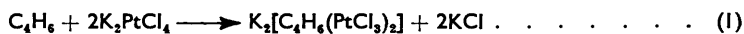
By J. Chatt, (Miss) L. M. Vallarino, and L. M. Venanzi.

A number of chelate complexes of the type [dienePtX$_2$] (X = halogen) (V) have been prepared. Of the dienes used, the stabilities of the complexes are in the order, cycloocta-1 : 5-diene $\simeq$ dicyclopentadiene $>$ dipentene $>$ hexa-1 : 5-diene. The stabilities of the dihalides decrease in the order Cl $>$ Br $>$ I. The dithiocyanate is not of the same type, and perhaps it should be formulated as [dienePt(SCN)$_2$Ptdiene](SCN)$_2$.
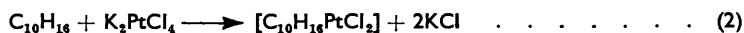
With anhydrous sodium carbonate in alcohol the dihalides give crystalline, stable alkoxy-halides (dieneOR)$_2$Pt$_2$X$_2$ (Table 1) of structure (X) in which one double bond has been opened by Pt(OR)X and the other is co-ordinated to the metal. The dicyclopentadiene methoxy-chloride [(C$_{10}$H$_{12}$OMe)$_2$Pt$_2$Cl$_2$] is especially easy to prepare; its chlorine atoms are readily replaced by I$^-$, SCN$^-$, and SEt$^-$, but the methoxy-group is very firmly bound. p-Toluidine splits the halogen bridge to give monomeric [C$_{10}$H$_{12}$OMe,C$_7$H$_9$NPtCl]. The corresponding iodide does not react with p-toluidine. The methoxy-group can be replaced by boiling concentrated hydrochloric acid to reform [C$_{10}$H$_{12}$PtCl$_2$]. The compounds are thus analogous to the alkoxymercuric compounds formed from olefins and mercuric salts, but are much more stable to hydrochloric acid.

A few peculiar cycloocta-1 : 5-diene derivatives approximating to [C$_8$H$_{12}$Pt(OR)$_2$]$_n$ (R = Me and H) were discovered but not investigated.

When dienes (diolefins) react with platinous salts, *e.g.*, K$_2$PtCl$_4$, in water or aqueous alcohol, three types of reaction may occur. (*a*) Platinum or some other decomposition products may be produced as with hexa-2 : 4-diene.[1] (*b*) The double bonds may react independently with different platinum atoms to give complex salts, as does butadiene :[2]

$$\text{C}_4\text{H}_6 + 2\text{K}_2\text{PtCl}_4 \longrightarrow \text{K}_2[\text{C}_4\text{H}_6(\text{PtCl}_3)_2] + 2\text{KCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(1)}$$

(*c*) The olefin may chelate to one platinum atom, as does dipentene[3] [reaction (2)] and cyclooctatetraene.[4] Only two double bonds of the tetraene are attached to the platinum atom. The three types of reaction are not mutually exclusive and indeed hexa-1 : 5-diene reacts according to either (*b*) or (*c*) depending on the conditions of the reaction.[1,5]

$$\text{C}_{10}\text{H}_{16} + \text{K}_2\text{PtCl}_4 \longrightarrow [\text{C}_{10}\text{H}_{16}\text{PtCl}_2] + 2\text{KCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(2)}$$

Apart from the above dienes, cycloocta-1 : 5-diene (I) and dicyclopentadiene (II) are of special interest at the present time : the former because it forms the most stable olefin complexes yet discovered, and the latter because it is known to yield what are apparently alkoxy-chlorides with potassium chloroplatinite in aqueous methanol or ethanol.[6,7]

Alkoxy-complexes are otherwise unknown in the complex chemistry of platinum, and attempts to prepare them usually cause decomposition. We have therefore examined the non-ionic platinous halide complexes of cycloocta-1 : 5-diene (I), dicyclopentadiene (II), and dipentene (III). In general formulæ, the dienes are being represented by the symbol (IV). We found that under very mild conditions the complexes can be converted into

* Part III, *J.*, 1953, 2939.

[1] Jensen, *Acta Chem. Scand.*, 1953, **7**, 866.
[2] Hel'man, *Compt. rend. Acad. Sci., U.R.S.S.*, 1939, **23**, 532.
[3] Chatt and Wilkins, *J.*, 1952, 2622.
[4] Jensen, *Acta Chem. Scand.*, 1953, **7**, 868.
[5] Hel'man, *Compt. rend. Acad. Sci., U.R.S.S.*, 1941, **32**, 347.
[6] Hofmann and von Narbutt, *Ber.*, 1908, **41**, 1625.
[7] Doyle and Jonassen, *J. Amer. Chem. Soc.*, 1956, **78**, 3965.

alkoxy-halides, with an ease varying from case to case. The di*cyclo*pentadiene complexes yield the alkoxy-compounds most readily.

Diene Complexes of Platinous Halides.—Diene complexes [dienePtCl₂] were prepared by previous workers by treating aqueous-alcoholic solutions of chloroplatinites with the diene. We find that they are more conveniently prepared in organic solvents such as the lower alcohols, particularly propan-1-ol. The chelate complex crystallises from the mixture in 2—3 days at room temperature.

(I)   (II)   (III)   (IV)
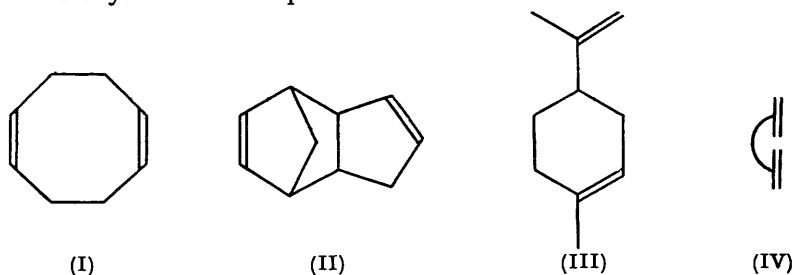
The dibromo- and di-iodo-complexes are readily obtained by treating the dichloro-complexes with lithium bromide and lithium iodide respectively in hot acetone. The bromides may also be obtained directly by adding lithium bromide to the reaction mixture used to prepare the chlorides, but the iodides are less stable and better prepared from the chlorides. Two dipentene complexes [dipentenePtCl₂] are known,[3, 8] and the one obtained by the above method is identical with Chatt and Wilkins's β-isomer. The di*cyclo*pentadiene complex $C_{10}H_{12}PtCl_2$ obtained as above is identical with the compound $C_{10}H_{12}PtCl_2$ to which Hofmann and von Narbutt [6] ascribed structure (VI).

The diene complexes [dienePtX₂] (X = halogen), are monomeric, and non-electrolytes in nitrobenzene; they are best formulated as chelate complexes of type (V).[1, 3, 4, 7] They are very much more stable than the platinous complexes of mono-olefins, and their stabilities decrease in the order Cl > Br > I, in accordance with the increasing *trans*-effect of the halogens Cl < Br < I. In contrast with the complexes of mono-olefins the diene complexes do not darken immediately on contact with slightly alkaline water, and give colourless solutions in dilute aqueous sodium hydroxide; these darken and deposit black decomposition products.[9] *cyclo*Octadiene (I) and di*cyclo*pentadiene (II) in which the double bonds are suitably placed for chelation form exceptionally stable complexes. Dipentene (III), where various conformations of the diene are possible, gives rather less stable complexes. Hexa-1 : 5-diene, where the double bonds can be arranged relatively as in *cyclo*octadiene but are not fixed rigidly, gives still less stable complexes.

(V)   (VI)   (VII)   (VIII)
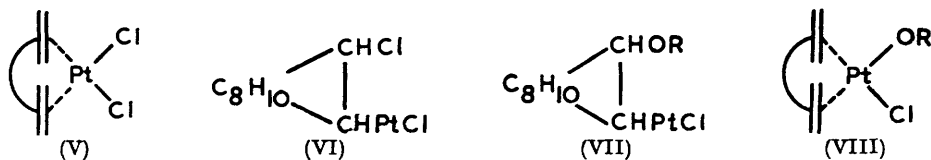
The *cyclo*octadiene complex [C₈H₁₂PtCl₂] can also be prepared, but more slowly, by using sodium chloroplatinate instead of the platinite in the above preparation.

A dithiocyanate [C₁₀H₁₂Pt(SCN₂)]ₓ, very sparingly soluble in all the solvents tried, has been examined in a preliminary way and has a structure different from that of the dihalides. Its infrared spectrum, kindly measured by Dr. L. A. Duncanson, has very strong absorption bands at 2159 and 2055 cm.⁻¹; these can be due only to the thiocyanate groups and indicate that there are two types of such groups in the structure. The SCN⁻ ion in

⁸ Kharasch and Ashford, *J. Amer. Chem. Soc.*, 1936, **58**, 1733.
⁹ K. A. Jensen, Conference on Co-ordination Chemistry, Copenhagen, 1953; his diolefin compounds dissolved in alkali.

4 N

potassium thiocyanate absorbs at 2063 cm.$^{-1}$, terminal thiocyanate groups in platinous complexes in the range 2100—2120 cm.$^{-1}$, and bridging thiocyanate groups in platinous complexes in the range 2150—2182 cm.$^{-1}$.[10] It appears therefore that the dithiocyanate contains bridging and ionic thiocyanate groups. This suggests a formula such as $[C_{10}H_{12}Pt(SCN)_2PtC_{10}H_{12}](SCN)_2$.

Alkoxy-derivatives of the Diene Complexes.—In 1908 Hofmann and von Narbutt [6] described three compounds obtained by the reaction of di*cyclo*pentadiene with potassium chloroplatinite in aqueous alcohol at 35°. The reaction required 10—14 days and yielded, from aqueous methanol and ethanol, compounds of the composition $C_{10}H_{12}Pt(OMe)Cl$ and $C_{10}H_{12}Pt(OEt)Cl$ respectively, but from aqueous propanol they isolated the dichloride. These they formulated as addition products (VII) and (VI) respectively, from analogy with the compounds formed by mercuric salts and olefins in alcoholic solution, where reaction occurs as follows : [11]

$$C_2H_4 + Hg(OAc)_2 + EtOH \longrightarrow EtO\cdot CH_2\cdot CH_2\cdot Hg\cdot OAc + AcOH$$

These structures do not accord with our present knowledge of platinous chemistry, for platinum(II) never has a co-ordination number of less than four. The dihalides definitely have the structure (V), but the analogous structure (VIII) for the alkoxy-halides can be ruled out because they are dimeric. There appear to be three other possible types of structure (IX), (X), and (XI). In (IX), the alkoxy-groups are bridging groups and the chlorine atoms occupy fifth, or if they are also bridging groups, fifth and sixth positions on the platinum atoms. Such structures are theoretically possible. In (X), one double bond has been

(IX)   (X)   (XI)
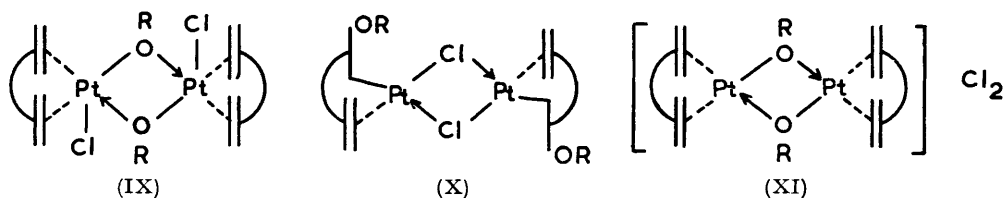
saturated so that effectively Pt(OR)Cl has been added across the double bond. In (XI), the methoxyl groups are bridging groups and the chlorine is ionic. Our experiments lead us to structure (X), and so we have formulated them as, for example, $(C_{10}H_{12}OR)_2Pt_2Cl_2$ rather than $(C_{10}H_{12})_2Pt_2(OR)_2Cl_2$ in the following description of their reactions and properties.

Preparation of the Alkoxy-derivatives, [(dieneOR)$_2$Pt$_2$X$_2$].—Hofmann and von Narbutt's method is slow and of limited applicability. We find, however, that the alkoxy-derivatives can be most readily prepared by the reaction of the dihalogen complexes, [dienePtX$_2$], with the appropriate alcohol used as solvent, in the presence of a weak base such as anhydrous sodium carbonate or acetate :

$$2[\text{dienePtX}_2] + 2ROH + 2Na_2CO_3 \longrightarrow [(\text{dieneOR})_2Pt_2X_2] + 2NaX + 2NaHCO_3$$

Stronger bases such as sodium alkoxide react similarly, but they cause some decomposition if used in excess of the equivalent proportions.

Di*cyclo*pentadiene–alkoxy-complexes are very readily obtained (doubtless because saturation of a double bond releases some strain in the *cyclo*pentene ring system), but those of the other dienes more difficultly, and the conditions are more critical. Methoxy-chloro-complexes, [(dieneOMe)$_2$Pt$_2$Cl$_2$] of all the cyclic dienes were prepared, and various alkoxychloro-complexes of di*cyclo*pentadiene (see Table).

Properties of the Alkoxy-derivatives.—In spite of containing carbon and platinum(II)

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[10] Chatt and Duncanson, *Nature*, 1956, **178**, 997.
[11] See Chatt, *Chem. Rev.*, 1951, **48**, 7.

in direct combination, the alkoxy-chlorides are remarkably stable. They are insoluble in water, but are soluble to varying degress in organic solvents, notably chloroform. They are dimeric and non-electrolytes in nitrobenzene solution, so ruling out structure (XI). The reactions of the compound [(C$_{10}$H$_{12}$OMe)$_2$Pt$_2$Cl$_2$] were studied as a representative member of the series.

Alkoxy-derivatives of the diene complexes of platinum(II).

Compound	Decomp. pt.	
(C$_{10}$H$_{12}$OMe)$_2$Pt$_2$Cl$_2$	205—220°	White plates
(C$_{10}$H$_{12}$OMe)$_2$Pt$_2$I$_2$	190—220	Pale yellow plates
(C$_{10}$H$_{12}$OMe)$_2$Pt$_2$(SCN)$_2$	260—270	White plates
(C$_{10}$H$_{12}$OMe)$_2$Pt$_2$(SEt)$_2$	145—146 *	Pale yellow needles
(C$_{10}$H$_{12}$OMe), *p*-toluidinePtCl	160—170 *	White needles
(C$_{10}$H$_{12}$OEt)$_2$Pt$_2$Cl$_2$	200—220	White plates
(C$_{10}$H$_{12}$OPr^n)$_2$Pt$_2$Cl$_2$	205—215	White plates
(C$_8$H$_{12}$OMe)$_2$Pt$_2$Cl$_2$	150—170	White powder
(C$_8$H$_{12}$OMe)$_2$Pt$_2$I$_2$	150—160	Cream needles
(C$_8$H$_{12}$OMe), *p*-toluidinePtCl	140—142 *	White needles
(C$_{10}$H$_{14}$OMe)$_2$Pt$_2$Cl$_2$	135—145	Cream needles

* Melts to an oil which does not solidify again.

The chlorine atoms are very readily replaced by anions such as iodide, thiocyanate, and EtS$^-$ by treating methanolic or acetone solutions of the alkoxy-chloride with lithium iodide, sodium thiocyanate, or sodium ethyl sulphide respectively, *e.g.*, :

$$[(C_{10}H_{12}OMe)_2Pt_2Cl_2] + 2LiI \longrightarrow [(C_{10}H_{12}OMe)_2Pt_2I_2] + 2LiCl$$
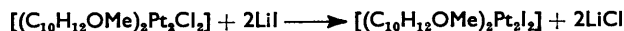
In these reactions the chlorine atom is readily replaced by the anions I$^-$ and SCN$^-$ whose affinity for platinum exceeds that of Cl$^-$.[12] On the other hand, the methoxyl group which normally has a very poor affinity for platinum(II) remains in the molecule. This suggests that the halogen may be attached to the platinum atom and that the methoxyl group is not. Even the SEt$^-$ ion, which is the strongest bridging group known in platinous chemistry,[13] failed to displace the methoxyl group, which suggests that it is not a bridging group, as required by structures (IX) and (XI).

The methoxyl group is very firmly bound in the complex, but Hofmann and von Narbutt showed that it is removed, to yield the dichloride [C$_{10}$H$_{12}$PtCl$_2$], by boiling concentrated hydrochloric acid in 3—4 hours. We confirm this. The resistance to hydrochloric acid is also evidence that the methoxyl group is not attached to the platinum atom. The methoxyplatinous compounds have evidently much greater resistance to hydrochloric acid than the methoxymercurials, which immediately evolve the olefin in cold dilute hydrochloric acid, but the mechanism of the elimination of the methoxyl group is probably similar,[14, 15] except that the resulting olefin complex, [C$_{10}$H$_{12}$PtCl$_2$], is a stable product in hydrochloric acid, whereas the mercuric complexes, [olefinHgCl]$^+$ or such, decompose immediately in dilute hydrochloric acid.

It is well established that chloro-bridged platinous complexes are readily " split " by *p*-toluidine to monomeric complexes according to the following scheme (L = an uncharged ligand) :

$$[L_2Pt_2Cl_4] + 2p\text{-Toluidine} \rightleftharpoons 2[L,p\text{-toluidinePtCl}_2]$$

and that the equilibrium lies well to the right-hand side. In the case of iodo-bridged complexes, however, the equilibrium lies so far to the left-hand side that the mixed product cannot always be isolated.[16]

[12] Leden and Chatt, *J.*, 1955, 2936.
[13] Chatt and Hart, *J.*, 1953, 2363.
[14] See Chatt, *Chem. Rev.*, 1951, **48**, 39.
[15] Brandt and Plum, *Acta Chem. Scand.*, 1953, **7**, 97.
[16] Chatt and Venanzi, *J.*, 1955, 3858.

We found similar behaviour with the di*cyclo*pentadiene complexes $[(C_{10}H_{12}OMe)_2Pt_2X_2]$. The methoxy-chloride reacted readily with *p*-toluidine to give a monomeric product :

$$[(C_{10}H_{12}OMe)_2Pt_2Cl_2] + 2C_7H_9N \longrightarrow 2[C_{10}H_{12}OMe,C_7H_9NPtCl]$$
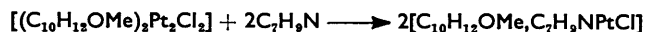
but the methoxy-iodide was recovered unchanged on attempted reaction with *p*-toluidine. Further, on attempting to replace the chlorine (or methoxyl) in the monomeric $[C_{10}H_{12}OMe,C_7H_9NPtCl]$ by reaction with lithium iodide, both the chlorine and *p*-toluidine were eliminated, indicating that the compound $[C_{10}H_{12}OMe,C_7H_9NPtI]$ is unstable and readily reverts to the bridged iodo-complex :

$$2[C_{10}H_{12}OMe,C_7H_9NPtCl] + 2KI \longrightarrow 2[C_{10}H_{12}OMe,C_7H_9NPtI] \longrightarrow [(C_{10}H_{12}OMe)_2Pt_2I_2] + 2C_7H_9N$$

This behaviour accords with our knowledge of the reaction of amines with halogen-bridged platinous (and palladous) complexes. There can be no doubt, therefore, that the dimerisation of the alkoxy-halide takes place through halogen bridges only.

The most probable structure according with these facts is (X). The *trans*-arrangement of co-ordinated double bonds about the $PtCl_2Pt$ ring was confirmed in the case of $[(C_{10}H_{12}OPr^n)_2Pt_2Cl_2]$ and $[(C_{10}H_{16}OMe)_2Pt_2Cl_2]$ by determining $\Delta\varepsilon/f$ in benzene solution, ($\Delta\varepsilon$ = the increment in dielectric constant caused by the solute and f the mole fraction of solute).[17] The low values of 9·1 and 12·3 respectively leave no doubt about the *trans*-arrangement as shown in (X).

This conclusion is supported by the infrared spectra of the methoxy-thiocyanate and of the dipentene complexes, and we are indebted to Dr. L. A. Duncanson for his examination and interpretation. The methoxy-thiocyanate $[(C_{10}H_{12}OMe)_2Pt_2(SCN)_2]$ has a strong absorption band at 2158 cm.$^{-1}$, but none in the region 2100—2120 cm.$^{-1}$, indicating that the thiocyanate groups are bridging (see p. 2498).

Dipentene, $C_{10}H_{16}$, itself has a single strong band at 1674 cm.$^{-1}$ due to the C=C stretching modes. The complex $[C_{10}H_{16}PtCl_2]$ has a strong absorption band at 1512 cm.$^{-1}$ which can be assigned to these modes modified by co-ordination to the platinum atom : the lowering of 135 cm.$^{-1}$ caused by co-ordination is of the same order as the 143 cm.$^{-1}$ difference between the C=C frequency of gaseous propene and its platinous chloride complexes.[18] The only absorption band in the 1500—2000 cm.$^{-1}$ region of the spectrum of $[(C_{10}H_{16}OMe)_2Pt_2Cl_2]$ is a comparatively weak one at 1505 cm.$^{-1}$, and the remainder of the spectrum is altered considerably from that of the dichloride, $[C_{10}H_{16}PtCl_2]$.

It is evident that in dipentene and in $[C_{10}H_{16}PtCl_2]$ the two double bonds give absorption bands which are not resolved. The absorption due to the terminal C=CH$_2$ bond will be much more intense than that due to the more symmetrical double bond in the ring, and together they give the strong bands observed at 1647 and 1512 cm.$^{-1}$ in the spectra of dipentene and of its platinous chloride complex respectively. In the methoxy-complex the strongly absorbing C=CH$_2$ is destroyed by the addition of MeO and PtCl across the double bond, leaving the weakly absorbing endocyclic double bond ; and since the latter absorbs at 1505 cm.$^{-1}$ it must be co-ordinated to the metal.

If in analogy with the methoxymercurials, we can assume that the platinum atom has attached itself to the CH$_2$ group of the double bond, the dipentene complex $[(C_{10}H_{16}OMe)_2Pt_2Cl_2]$ must have the structure (XII).

There can be little doubt that the alkoxy-derivatives of the [dienePtCl$_2$] complexes are truly organometallic platinum compounds in which the metal has a valency of two and its normal co-ordination number of four. It might be argued against this that platinous alkyls are unknown and therefore very probably unstable. However, when the platinum(II) atom is co-ordinatively saturated, the alkyls may be stable. *E.g.*, Chatt and Foss [19] have prepared a platinous methyl, $(PPr^n_3)_2PtMeI$, which melts without decomposition at 48°, and is stable in air and to hydrolysis by dilute acids. During three years

[17] Chatt and Wilkins, *J.*, 1953, 70.
[18] Chatt and Duncanson, *J.*, 1953, 2939.
[19] Chatt and Foss, unpublished work.

in store, it has not decomposed. It seems possible that platinum(II), when it is so co-ordinatively saturated, might have an organic chemistry somewhat similar to that of mercury(II).

Dimethoxy- and Dihydroxy-derivatives of [dienePtCl$_2$].—Attempts to replace both halogen atoms in [(C$_{10}$H$_{12}$OR)$_2$Pt$_2$Cl$_2$] by reaction with sodium methoxide lead to the formation of black decomposition products. This is the usual result when one attempts

(XII)
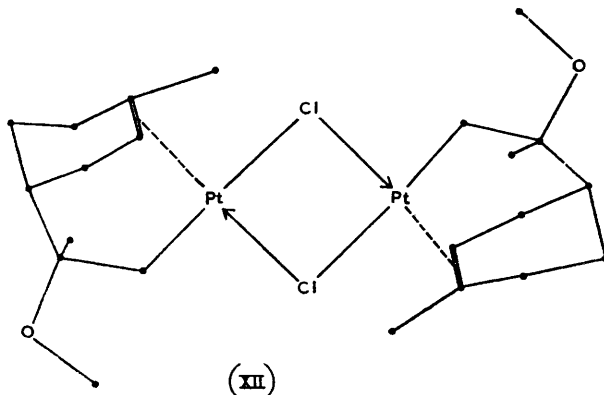
Proposed structure of [(C$_{10}$H$_{16}$OMe)$_2$Pt$_2$Cl$_2$].
(The configurations about asymmetric centres are arbitrarily chosen.)

to attach a methoxyl group to platinum(II). However, a number of compounds which do not contain halogen, and appear to bear some relation to dimethoxy- and dihydroxy-derivatives were obtained in the above research. They were only cursorily investigated but are recorded.

A substance of composition approximating closely to [C$_8$H$_{12}$Pt(OMe)$_2$]$_n$ ($n > 2$, perhaps 3 or 4) separates when [C$_8$H$_{12}$PtCl$_2$] in methanol is treated with anhydrous sodium carbonate. This " α-dimethoxide " is soluble in hot methanol and crystallises in needles. If it is left in the reaction mixture at −70° for 24—48 hours, the dimethoxide is converted into [(C$_8$H$_{12}$OMe)$_2$Pt$_2$Cl$_2$]. The iodide [C$_8$H$_{12}$PtI$_2$] by a similar reaction does not give a dimethoxide but gives [(C$_8$H$_{12}$OMe)$_2$Pt$_2$I$_2$] directly.

A substance giving analyses as for [C$_8$H$_{12}$Pt(OH)$_2$]$_x$ was obtained by direct reaction of the *cyclo*octadiene with sodium chloroplatinite in methanol in the presence of anhydrous sodium carbonate. Its infrared spectrum showed no absorption bands in the OH stretching region, and the substance should perhaps be formulated in some way with oxide or ether bridges. In dilute aqueous sodium hydroxide it gives a clear solution which is much more stable than that given by the dichloride. On treatment with sodium carbonate in boiling methanol the " dihydroxide " is converted into a substance of composition approximating to [C$_8$H$_{12}$Pt(OMe)$_2$]$_x$, " β-dimethoxide," and different from the " α-dimethoxide." This substance is almost insoluble in hot methanol and crystallises in plates. The above three substances are crystalline, but the " dimethoxides " darken on storage for some weeks. They are soluble in chloroform, benzene and such organic solvents, but the " dihydroxide " is less soluble and was recrystallised from glacial acetic acid.

In all these substances it seems improbable that the oxygen is attached to the platinum atom. It is more likely to be bound to carbon only.

<p style="text-align:center">EXPERIMENTAL</p>

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

Dicyclopentadienedichloroplatinum, [C$_{10}$H$_{12}$PtCl$_2$].—Di*cyclo*pentadiene (4 c.c.) was added to a solution of sodium chloroplatinite tetrahydrate (4 g.) in propan-1-ol (80—100 c.c.) and kept at room temperature for 2 days. The crystals which separated were filtered off, washed with

ether and then water, and dried. The compound was purified by dissolving it in hot chloroform, treating the solution with a small amount of charcoal, filtering it, and diluting the filtrate with ether. It was obtained in white needles (3·2 g.), decomp. 200—220° (Found : C, 30·0; H, 3·1. Calc. for $C_{10}H_{12}Cl_2Pt$: C, 30·2; H, 3·0%).

This reaction also occurs in methanol or ethanol but gives rather poorer yields, and in methanol the reaction is appreciably slower.

Dicyclopentadienedibromoplatinum, $[C_{10}H_{12}PtBr_2]$, was prepared and purified analogously to the chloride, but with the addition of lithium bromide (2 g.) to the reaction mixture. The reaction takes 5 days for completion. The product (0·98 g.) was obtained in canary-yellow prisms, decomp. 200—225°. It is also obtained as follows : Dicyclopentadienedichloroplatinum (0·45 g.) and lithium bromide (0·5 g.) in acetone (approx. 20 c.c.) were boiled for a few minutes. The complex dissolved and the dibromide separated on cooling. The yield of pure product was 0·41 g. and it was identical (infrared spectrum) with that obtained above (Found : C, 24·7; H, 2·65. $C_{10}H_{12}Br_2Pt$ requires C, 24·65; H, 2·5%). It is slightly more soluble than its chloro-analogue.

Reaction between Dicyclopentadienedichloroplatinum and Sodium Thiocyanate.—The chloro-complex (0·3 g.) and sodium thiocyanate (0·24 g.) in acetone (20 c.c.) were boiled for a few minutes, to give a pale yellow solution from which sodium chloride soon separated. The solution was cooled, filtered, and taken to dryness at 15 mm. The residue, washed with water and dried, was purified by reprecipitation from a large amount of chloroform by diethyl ether, and so obtained in very small white needles (0·2 g.), decomp. 200—205° (Found : C, 32·75; H, 2·75; N, 6·3. $C_{12}H_{12}N_2S_2Pt$ requires C, 32·5; H, 2·7; N, 6·3%). The *dithiocyanate* is sparingly soluble in boiling acetone, chloroform, and benzene, and is decomposed by boiling methylene chloride.

cyclo*Octa*-1 : 5-*dienedichloroplatinum,* $[C_8H_{12}PtCl_2]$, was prepared in the same way as its dicyclopentadiene analogue from sodium chloroplatinite hydrate (4·0 g.) and cyclooctadiene (4·0 c.c.) and crystallised from acetic acid (charcoal) in white needles, decomp. 220—278° (1·9 g.) (Found : C, 25·55; H, 3·2. $C_8H_{12}Cl_2Pt$ requires C, 25·7; H, 3·2%), insoluble in most organic solvents except boiling chloroform, methylene chloride, and acetic acid. The same product is obtained but more slowly by the reaction between sodium chloroplatinate and cyclooctadiene in ethanol.

cyclo*Octa*-1 : 5-*dienedibromoplatinum,* $[C_8H_{12}PtBr_2]$, was prepared in good yield from hydrated sodium chloroplatinite, diene, and lithium bromide in the same way as its dicyclopentadiene analogue, but in ethanol. It recrystallised from acetic acid in pale yellow needles, decomp. 200—270° (Found : C, 20·6; H, 2·6. $C_8H_{12}Br_2Pt$ requires C, 20·7; H, 2·6%), slightly more soluble than its chloro-analogue in organic solvents.

cyclo*Octa*-1 : 5-*dienedi-iodoplatinum,* $[C_8H_{12}PtI_2]$, was prepared analogously to the corresponding bromide. It crystallised from acetic acid in orange-yellow needles contaminated with some brown crystalline by-product. Precipitation from boiling methylene chloride by light petroleum (b. p. 40—60°) gave an orange-yellow powder, decomp. about 250° (Found : C, 17·4; H, 2·2. $C_8H_{12}I_2Pt$ requires C, 17·25; H, 2·2%).

Dipentenedichloroplatinum, $[C_{10}H_{16}PtCl_2]$, was prepared and purified in the same way as its dicyclopentadiene analogue (chloroplatinite, 4 g., and pure dipentene, 2·2 c.c., in propanol, 80 c.c., gave 1·5 g. of cream-coloured needles). This product has the same infrared spectrum as that product prepared by Chatt and Wilkins's method [3] and described as the β-isomer. In methanol instead of propanol, this reaction requires 5 days.

Hexa-1 : 5-dienedichloroplatinum, $[C_6H_{10}PtCl_2]$, was obtained from the chloroplatinite (2 g.) and diene (2·5 c.c.) in propanol (60 c.c.) but only in poor yield (0·4 g.) The main product was $Na_2[C_6H_{10}(PtCl_3)_2]$.

*Bis(dicyclopentadiene Methoxide)-*μμ'-*dichlorodiplatinum,** $[(C_{10}H_{12}OMe)_2Pt_2Cl_2]$.—Dicyclopentadienedichloroplatinum (0·4 g.), suspended in methanol (25 c.c.), was heated to boiling and sodium acetate (approx. 0·2 g.) added. The solids dissolved and on continued heating a white solid was precipitated. After cooling, the solid was filtered off, washed with methanol, and dried. Recrystallisation was effected by diluting a solution in chloroform with ether (yield 0·3 g.) (Found : C, 33·7; H, 3·9; OMe, 7·9%; M, ebullioscopic in 1·1% chloroform solution, 726. Calc. for $C_{22}H_{30}O_2Cl_2Pt_2$: C, 33·55; H, 3·8; Pt, 49·5; OMe, 7·9%; M, 788). It is a non-electrolyte in nitrobenzene solution. This compound is identical (infrared spectra) with

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* Trivial names of this type have been adopted when it is not known which double bond has been destroyed and when systematic names would be very involved.

a sample obtained by Hofmann and von Narbutt's method [6] (Found : C, 33·2; H, 3·9; Pt, 49·15; OMe, 7·9%). It can also be obtained as follows :

(*a*) The dichloro-derivative (0·3 g.) was suspended in boiling methanol (20 c.c.), and a small amount of anhydrous sodium carbonate added. The chloro-compound dissolved and the solution was filtered. The methoxy-chloride separated from the filtrate as it cooled (yield, pure, 0·24 g.).

(*b*) The dichloro-derivative (0·4 g.) was suspended in cold methanol (8 c.c.), and sodium methoxide from metallic sodium (0·025 g.) and methanol (5 c.c.) was added. After a few minutes the solid had changed in appearance and the solution was neutral. The solid was filtered off, washed with methanol, and dried (yield, 0·13 g.) (Found : C, 33·6; H, 3·8%).

Bis(dicyclopentadiene Methoxide)-μμ'-di-iododiplatinum, $[(C_{10}H_{12}OMe)_2Pt_2I_2]$.—The corresponding chloride (0·35 g.), boiled for a few minutes with lithium iodide (*ca.* 4 mols.) in acetone (15—20 c.c.), gave a pale yellow solution which was filtered and diluted with methanol. On cooling, the *product* (0·32 g.) separated and was purified in the same way as its chloro-analogue (Found : C, 27·0; H, 3·2. $C_{22}H_{30}O_2I_2Pt_2$ requires C, 27·2; H, 3·1%); it is slightly more soluble in organic solvents than its chloro-analogue.

The iodo-compound (0·27 g.) in chloroform (25 c.c.) was treated with *p*-toluidine (0·046 g.); there was no apparent colour change; the solution was boiled for 2 min. and then taken to dryness at 15 mm.; 0·16 g. of the iodo-starting material was recovered (identified by infrared spectrum).

Bis(dicyclopentadiene Methoxide)-μμ'-dithiocyanatodiplatinum, $[(C_{10}H_{12}OMe)_2Pt_2(SCN)_2]$.— A methanol (*ca.* 15 c.c.) suspension of the methoxy-chloride (0·3 g.) and sodium thiocyanate (approx. 0·2 g.) was boiled for a few minutes. The starting material did not dissolve but changed in appearance. After cooling, the mixture was filtered, and the residual *product* washed with water, dried, and purified in similar manner to the methoxy-chloride (yield, 0·12 g.) (Found : C, 34·6; H, 3·6; N, 3·5. $C_{24}H_{30}O_2N_2S_2Pt_2$ requires C, 34·6; H, 3·6; N, 3·4%). It is sparingly soluble in boiling chloroform, acetone, and benzene.

Bis(dicyclopentadiene Methoxide)-μμ'-di(ethylthio)diplatinum, $[(C_{10}H_{12}OMe)_2Pt_2(SEt)_2]$.— A solution of sodium ethyl sulphide (1·5 c.c. of a solution containing 0·5 c.c. of ethanethiol and 0·16 g. of sodium in 10 c.c. of methanol) was added to a suspension of the methoxy-chloride (0·4 g.) in methanol (25 c.c.). The mixture was warmed slightly for a few minutes, and the resulting pale yellow solution taken to dryness at 15 mm. The residual solid was extracted with chloroform and the *product* obtained as an oil by the evaporation of the extract at 15 mm. The oil crystallised on contact with hot methanol, from which it was recrystallised (yield 0·16 g.) (Found : C, 37·5; H, 4·9; S, 7·3. $C_{26}H_{40}O_2S_2Pt_2$ requires C, 37·2; H, 4·8; S, 7·65%). It is a non-electrolyte in nitrobenzene. It is very soluble in chloroform and benzene and moderately so in acetone, ether, boiling methanol, or light petroleum.

(Dicyclopentadiene Methoxide)-p-toluidinechloroplatinum, $[C_{10}H_{12}OMe,p\text{-toluidine}PtCl]$.— *p*-Toluidine (0·107 g.) was added to the methoxy-chloride (0·4 g.) in chloroform, and the solution taken to dryness at 15 mm. The residual *product* recrystallised from methanol (yield 0·4 g.) (Found : C, 43·0; H, 4·8; N, 3·15; Pt, 38·7%; *M*, ebullioscopic in 1·5% benzene solution, 526. $C_{18}H_{24}ONClPt$ requires C, 43·15; H, 4·8; N, 2·8; Pt, 38·9%; *M*, 501). It is a non-electrolyte in acetone; it is very soluble in cold chloroform, moderately so in benzene, methanol, acetone, and ether, and insoluble in nitrobenzene.

From methanol (10 c.c.) solution of $[C_{10}H_{12}OMe,p\text{-toluidine}PtCl]$ (0·1 g.) and lithium iodide (*ca.* 0·05 g.), boiled for 2 min., pale yellow $[(C_{10}H_{12}OMe)_2Pt_2I_2]$, decomp. 192—215° (0·07 g.; identified by its infrared spectrum), was recovered.

Bis(di*cyclo*pentadiene ethoxide)-μμ'-dichlorodiplatinum, $[(C_{10}H_{12}OEt)_2Pt_2Cl_2]$, was prepared and purified analogously to the methoxy-chloride by using ethanol and sodium carbonate (yield 0·23 g. from 0·3 g. of dichloride) (Found : C, 35·5; H, 4·2%; *M*, ebullioscopic in 1·9% benzene solution, 858. Calc. for $C_{24}H_{34}O_2Cl_2Pt_2$: C, 35·3; H, 4·2%; *M*, 816).

It was also prepared by using the stoicheiometric amount of sodium ethoxide (0·07 g. from 0·4 g. of dichloride), but decomposition products were also formed.

We attempted to prepare it as described by Hofmann and von Narbutt,[6] at 40° and at room temperature, but obtained only the dichloro-complex $[C_{10}H_{12}PtCl_2]$.

Bis(dicyclopentadiene n-Propoxide)-μμ'-dichlorodiplatinum $[(C_{10}H_{12}OPr^n)_2Pt_2Cl_2]$.—A small amount of anhydrous sodium carbonate was added to a solution of hydrated sodium chloroplatinite (2 g.) in propan-1-ol (35 c.c.) containing di*cyclo*pentadiene (3 c.c.), and the mixture

kept at room temperature for 5 days. The white crystalline *product* was filtered off, washed with ether and water, and dried (yield, 1·90 g.). It was then practically pure, but can be purified further by dissolving it in boiling chloroform and reprecipitating it with ether (Found : C, 37·1; H, 4·7. $C_{28}H_{38}O_2Cl_2Pt_2$ requires C, 37·0; H, 4·5%). It is soluble in cold chloroform and hot benzene, moderately so in acetone, and insoluble in propanol, ether, and light petroleum. It was also obtained from the dichloride by the sodium carbonate method, but then contained a small amount of impurity which was not eliminated by recrystallisation. The presence of the impurity was confirmed by comparing the infrared spectra of the two samples.

Bis-(8-methoxycyclooct-4-enyl)-μμ'-dichlorodiplatinum, [$(C_8H_{12}OMe)_2Pt_2Cl_2$].—Finely powdered *cyclo*octa-1 : 5-dienedichloroplatinum (1·4 g.) and anhydrous sodium carbonate were boiled in methanol (70 c.c.) for a few minutes and the hot solution filtered. Cooling the filtrate to room temperature gave white needles but keeping it at −70° for 3 days gave a white microcrystalline powder which was filtered off and dried. This, the required *product*, was purified by reprecipitation from chloroform with ether (yield, 0·81 g.) (Found : C, 29·1; H, 4·2. $C_{18}H_{30}O_2Cl_2Pt_2$ requires C, 29·2; H, 4·1%). It is slightly more soluble than its di*cyclo*pentadiene analogue in organic solvents.

Bis-(8-methoxycyclooct-4-enyl)-μμ'-di-iododiplatinum, [$(C_8H_{12}OMe)_2Pt_2I_2$].—*cyclo*Octa-1 : 5-dienedi-iodoplatinum (0·5 g.) and a small amount of anhydrous sodium carbonate were boiled in methanol (25 c.c.) for a few minutes. The di-iodide dissolved and the hot solution was filtered. On evaporation at 15 mm. pressure, the crude *product* was obtained as a brown solid. It was purified by precipitating it thrice from chloroform with ether (yield 0·2 g.) (Found : C, 23·8; H, 3·4. $C_{18}H_{30}O_2I_2Pt_2$ requires C, 23·4; H, 3·3%).

*8-Methoxycyclooct-4-enyl-*p*-toluidinechloroplatinum,* [$C_8H_{12}OMe,p$-toluidine,PtCl].—*p*-Toluidine (0·093 g.) was added to the methoxy-chloride (0·32 g.) in chloroform (10 c.c.), and the resulting solution taken to dryness at 15 mm. The product remained as a solid which was purified by repeated precipitation from benzene by ligroin (yield, 0·34 g.). A better *product* is obtained, but wastefully, by recrystallisation from methanol (Found : C, 40·6; H, 5·0; N, 3·35. $C_{16}H_{24}ONClPt$ requires C, 40·3; H, 5·1; N, 2·9%). It is a non-electrolyte in nitrobenzene.

Bis(dipentene Methoxide)-μμ'-dichlorodiplatinum, [$(C_{10}H_{16}OMe)_2Pt_2Cl_2$].—A methanol (40 c.c.) suspension of dipentenedichloroplatinum (1 g.) and a small amount of anhydrous sodium carbonate was boiled for a few minutes. The dichloride dissolved, giving a light brown solution which was filtered and kept at −70° for 3 days. The solid which had separated was filtered off and purified by precipitation from chloroform with ether (yield 0·1 g.) (Found : C, 33·4; H, 4·9. $C_{22}H_{38}O_2Cl_2Pt_2$ requires C, 33·2; H, 4·8%). It is the least stable and most soluble of the methoxy-chlorides obtained.

Dimethoxy- and Dihydroxy-derivatives of [$C_8H_{12}PtCl_2$].—The " α-dimethoxide " was obtained as a solid by evaporating to dryness the methanol reaction mixture from which the [$(C_8H_{12}OMe)_2Pt_2Cl_2$] had been filtered {see preparation of [$(C_8H_{12}OMe)_2Pt_2Cl_2$]}. (Yield, pure, 0·1 g.) Also it is the primary product which separates in white needles on first cooling the reaction mixture to room temperature. (0·4 g. from 0·7 g. of dichloride). When purified by reprecipitating it from chloroform with methanol, it decomposed at 140—150° (Found : C, 33·1; H, 5·1; Pt, 53·25%; *M*, ebullioscopic in 2·1% benzene solution, *ca.* 1150. $C_{10}H_{18}O_2Pt$ requires C, 32·9; H, 5·0; Pt, 53·4%; *M*, 365). It is probably a polymeric dimethoxide [$C_8H_{12}Pt(OMe)_2$]$_n$ (*n* ∼ 3 or 4). It is very soluble in chloroform, hot methanol and hot benzene, slightly soluble in ether, and insoluble in light petroleum.

The " dihydroxide " was obtained when sodium chloroplatinite tetrahydrate (4 g.) and *cyclo*octa-1 : 5-diene (*ca.* 4 c.c.) in methanol (40 c.c.) with the addition of a little anhydrous sodium carbonate were kept for 3 days. The crystalline *product* (1·7 g.) was filtered off, washed with methanol and then water, and dried. Recrystallised twice from much acetic acid it was obtained in white needles, decomp. 190—210° (0·8 g.) (Found : C, 28·5; H, 4·0; Pt, 57·1. $C_8H_{14}O_2Pt$ requires C, 28·5; H, 4·2; Pt, 57·8%). It is a non-electrolyte in nitrobenzene and only sparingly soluble in most organic solvents. The " β-dimethoxide " was obtained when a methanol (45 c.c.) solution of the dihydroxide (0·54 g.) was boiled for a few minutes with a little anhydrous sodium carbonate and the hot solution was filtered. The *product* separated as the filtrate cooled. A further quantity was obtained by extracting the residue from the filtration with cold chloroform (20 c.c.) and diluting the extract with methanol (30 c.c.). Purified by reprecipitation from chloroform with methanol, it was obtained in white plates,

decomp. 140—160°, slowly becoming cream-coloured (Found : C, 32·2; H, 4·8%). It is less soluble in methanol than the " α-dimethoxide " and has a different infrared spectrum.

The compounds were finely ground and suspended in " Nujol " for examination of their infrared spectra, which were measured with a Grubb-Parsons S3A spectrometer with a rock-salt prism.