678. *Olefin Co-ordination Compounds. Part V.*[1] *Some Diene Complexes of Palladium*(II) *and their Alkoxy-derivatives.*

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Compounds of the types [diene PdX_2], [(diene·OR)$_2Pd_2X_2$], and [(diene·OR), *p*-toluidine PdCl] have been prepared. Their properties indicate that they have similar structures to those of their platinous analogues. Generally, the compounds are more deeply coloured, more easily formed, more reactive, and less stable than the corresponding platinous compounds. The alkoxy-derivatives are the first strictly organometallic derivatives of palladium to be reported.

In Part IV [1] we recorded the preparation of a number of chelated platinous complexes of the type [diene $PtCl_2$] and their conversion into alkoxy-derivatives of the type [(diene·OR)$_2Pt_2Cl_2$]. It was interesting to see whether palladium(II) would give similar derivatives and how they compared with their platinum analogues.

Stable diene derivatives were obtained from the cyclic diolefins *cyclo*octa-1 : 5-diene, C_8H_{12}, and di*cyclo*pentadiene, $C_{10}H_{12}$, but not from dipentene, $C_{10}H_{16}$, which reduced palladous salts to the metal. The compounds prepared are listed in the Table.

Diene complexes of palladium(II) *and their alkoxy-derivatives.*

Compound	Decomp. pt.	Description
*cyclo*Octa-1 : 5-diene :		
$C_8H_{12}PdCl_2$	205—210°	Pale orange needles
$C_8H_{12}PdBr_2$	213	Orange-red needles
$(C_8H_{12}\cdot OMe)_2Pd_2Cl_2$	130—135	Very pale yellow
$(C_8H_{12}\cdot OMe)_2Pd_2Br_2$	125—135	Very pale yellow
Di*cyclo*pentadiene :		
$C_{10}H_{12}PdCl_2$	165—170°	Orange needles or plates
$(C_{10}H_{12}\cdot OMe)_2Pd_2Cl_2$	166—170	Yellow plates
$(C_{10}H_{12}\cdot OEt)_2Pd_2Cl_2$	150—160	Yellow plates
$(C_{10}H_{12}\cdot OPr^n)_2Pd_2Cl_2$	150—156	Yellow plates
$(C_{10}H_{12}\cdot OPr^i)_2Pd_2Cl_2$	150—160	Yellow plates
$C_{10}H_{12}\cdot OMe$,*p*-toluidine, PdCl	145—160	White

The *cyclo*octadiene complex with palladous chloride is exceptionally stable. It is rapidly formed by shaking an aqueous solution of ammonium chloropalladite with the diene; this is in contrast to the mono-olefin complexes of palladium(II) which are formed in anhydrous media,[2] and are decomposed in contact with water.

Preparation and Properties of the Complexes, [diene $PdCl_2$].—These complexes are readily prepared by the reaction of the diene with sodium chloropalladite in acetone :

$$\text{diene} + Na_2PdCl_4 \longrightarrow [\text{diene } PdCl_2] + 2NaCl \quad . \; . \; . \; . \; . \; . \quad (1)$$

The *cyclo*octadiene complex can also be prepared in alcoholic solutions, but di*cyclo*pentadiene gives the alkoxy-derivative :

$$2C_{10}H_{12} + 2Na_2PdCl_4 + 2ROH \longrightarrow [(C_{10}H_{12}\cdot OR)_2Pd_2Cl_2] + 4NaCl + 2HCl \quad . \; . \; . \quad (2)$$

This parallels our observation in the platinous series that di*cyclo*pentadiene gave alkoxy-derivatives more readily than the other dienes. The dichlorides can also be prepared by Karasch, Seyler, and Mayo's method for mono-olefin complexes : [2]

$$[(PhCN)_2PdCl_2] + \text{diene} \longrightarrow [\text{diene } PdCl_2] + 2PhCN$$

As in the platinous series the bromides and iodides are less stable than the chlorides, and of these only $C_8H_{12}PdBr_2$ was obtained pure.

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[1] Part IV, *J.*, 1957, 2496.

[2] Kharasch, Seyler, and Mayo, *J. Amer. Chem. Soc.*, 1938, **60**, 882.

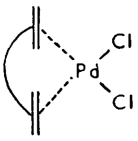
The palladous complexes [diene PdX_2] (X = Cl or Br) are more deeply coloured than their platinous analogues. They are also less stable and more reactive. There is no reason to doubt that they are chelated complexes of type (I), in which the double bonds are perpendicular to the $PdCl_2$ plane, or almost so.

Preparation and Properties of the Alkoxy-derivatives, [(diene $OR)_2Pd_2X_2$].—These derivatives are prepared in the same way as their platinous analogues, by the reaction of the dihalide with the appropriate alcohol in presence of anhydrous sodium carbonate :

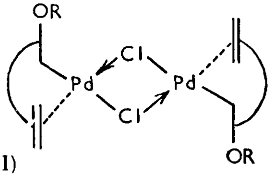
$$2[\text{diene } PdX_2] + 2ROH + 2Na_2CO_3 \longrightarrow [(\text{diene } OR)_2Pd_2X_2] + 2NaX + 2NaHCO_3 \quad . \quad . \quad (3)$$

or in the case of di*cyclo*pentadiene complexes also by reaction (2). The alkoxy-chlorides are nicely crystalline and moderately stable. Those of di*cyclo*pentadiene are more thermally stable than those of *cyclo*octadiene. The alkoxy-bromides and -iodides are too unstable to be purified easily although $(C_8H_{12}\cdot OMe)_2Pd_2Br_2$ was obtained pure. The compounds prepared are listed in the Table.

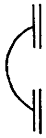
These alkoxy-derivatives are formed more easily than their platinum analogues and, in contrast to their platinum analogues, are readily reconverted into the dichloro-complex, [diene $PdCl_2$], by reaction with hydrochloric acid. $[(C_8H_{12}\cdot OMe)_2Pd_2Cl_2]$ and the corresponding bromide are photosensitive.



(I)

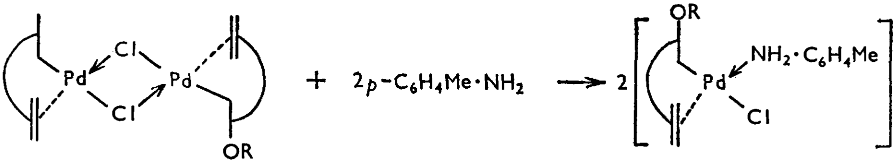


(II)



represents a molecule of the diene

The palladous complexes are too unstable for so full a structural investigation as was made in the platinous series, but they appear to be exactly analogous. In this case the alkoxy-chlorides will have structures of the type (II) in which PdX·OR has added across one double bond of the diolefin whilst the other remains co-ordinated to the metal atom and approximately perpendicular to the plane of the Pd_2Cl_2 ring. As evidence for the halogen-bridged structure we split the bridge in $[(C_{10}H_{12}\cdot OMe)_2Pd_2Cl_2]$ with *p*-toluidine and isolated a simple *p*-toluidine derivative as in the platinous series (reaction 4).



....(4)

The salts of mercury(II), palladium(II), and platinum(II) are now known to add to olefins in alcoholic solutions to give alkoxy-derivatives, which are true organometallic derivatives of those metals. These show a gradual transition in properties in that order. The mercury compounds are very readily formed, even from mono-olefins, and are very sensitive to hydrochloric acid.[3] Those of platinum are the most difficult to obtain and surprisingly stable to concentrated hydrochloric acid, whereas the palladium compounds show intermediate ease of formation and sensitivity to hydrochloric acid. Thermally the palladium compounds are the least stable.

EXPERIMENTAL

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

cyclo*Octa*-1 : 5-*dienedichloropalladium,* $[C_8H_{12}PdCl_2]$.—The diene (2 c.c.) was added to a solution of sodium chloropalladite tetrahydrate (2 g.) in methanol (75 c.c.). A yellow precipitate

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[3] See Chatt, *Chem. Rev.*, 1951, **48**, 7.

formed almost at once, and after 1 hr. it was filtered off, washed with methanol, and dried. The *complex* recrystallised from glacial acetic acid (yield 1·06 g.) (Found: C, 33·8; H, 4·3. $C_8H_{12}Cl_2Pd$ requires C, 33·6; H, 4·2%). It is sparingly soluble in cold alcohol and benzene, and slightly soluble in hot benzene, chloroform, acetone, ethyl methyl ketone, and diethyl carbonate.

cyclo*Octa-1 : 5-dienedibromopalladium*, $[C_8H_{12}PdBr_2]$.—Pure *cyclo*octa-1 : 5-dienedichloropalladium (0·45 g.) and lithium bromide (0·1 g.) in acetone (20 c.c.) were boiled under reflux for 2 hr. The solution was filtered, then taken to dryness at 15 mm., and the solid *complex* washed with water, dried (0·22 g.), and recrystallised from glacial acetic acid (Found: C, 25·8; H, 3·3. $C_8H_{12}Br_2Pd$ requires C, 25·7; H, 3·2%).

*Di-(8-methoxy*cyclo*oct-4-enyl)-μμ′-dichlorodipalladium*, $[(C_8H_{12}\cdot OMe)_2Pd_2Cl_2]$.—Finely powdered *cyclo*octa-1 : 5-dienedichloropalladium (0·35 g.) was suspended in methanol and heated to the b. p. A small amount of anhydrous sodium carbonate was added and the complex dissolved, giving a very pale yellow solution which was filtered hot. The residue was extracted with a few c.c. of boiling methanol, and the extract added to the bulk of the solution. The *product* separated from this solution on cooling and recrystallised from methanol (this operation must be carried out as rapidly as possible to minimise decomposition) (yield 0·12 g.) (Found: C, 38·6; H, 5·4. $C_{18}H_{30}O_2Cl_2Pd_2$ requires C, 38·4; H, 5·4%).

*Di-(8-methoxy*cyclo*oct-4-enyl)-μμ′-dibromodipalladium*, $[(C_8H_{12}\cdot OMe)_2Pd_2Br_2]$, was prepared and purified analogously to the methoxychloro-complex from *cyclo*octa-1 : 5-dienedibromopalladium (0·3 g.), anhydrous sodium carbonate, and methanol (yield 0·13 g.) (Found: C, 33·4; H, 4·65. $C_{18}H_{30}O_2Br_2Pd_2$ requires C, 33·2; H, 4·6%).

*Di*cyclo*pentadienedichloropalladium*, $[C_{10}H_{12}PdCl_2]$.—Dibenzonitriledichloropalladium (1 g.), prepared by the method of Kharasch *et al.*,[2] was dissolved in benzene (50 c.c.), and di*cyclo*pentadiene (2 c.c.) added. Orange plates separated during 48 hr. These were filtered off, washed with a small amount of benzene, and dried. The crude *product* was purified by dissolving it in chloroform and reprecipitating it by ether (yield 0·54 g.) (Found: C, 39·2; H, 3·8; Pd, 34·4. $C_{10}H_{12}Cl_2Pd$ requires C, 38·8; H, 3·9; Pd, 34·4%). The same product is also obtained on adding di*cyclo*pentadiene (2 c.c.) to a solution of sodium chloropalladite tetrahydrate (1·3 g.) in acetone (30 c.c.) and keeping the mixture for 24 hr.; the orange solid which formed was filtered off, washed with acetone and water, and dried. It was purified as above (yield 0·72 g.).

*Bis(di*cyclo*pentadienemethoxide)-μμ′-dichlorodipalladium*,* $[(C_{10}H_{12}\cdot OMe)_2Pd_2Cl_2]$.—Di*cyclo*pentadiene (3 c.c.) was added to a solution of sodium chloropalladite tetrahydrate (2 g.) in methanol (10 c.c.), and the mixture left overnight. The solid *complex* which had separated was filtered off, washed with methanol, water, dried, and purified by dissolving it in boiling chloroform and diluting the solution with ether (yield 0·92 g.) (Found: C, 43·3; H, 5·0. $C_{22}H_{30}O_2Cl_2Pd_2$ requires C, 43·3; H, 5·0%). It is slightly soluble in cold chloroform and benzene. It is also obtained by shaking di*cyclo*pentadienedichloroplatinum (0·27 g.) with methanol (25 c.c.) for 2 hr. (yield 0·2 g.).

The following complexes were prepared and purified analogously to the methoxy-complex from sodium chloropalladite tetrahydrate, di*cyclo*pentadiene, and the corresponding alcohol:

Bis(dicyclo*pentadiene-ethoxide)-μμ′-dichlorodipalladium*, $[(C_{10}H_{12}\cdot OEt)]_2Pd_2Cl_2]$ (0·81 g. from 1 g. of palladite) (Found: C, 44·9; H, 5·4. $C_{24}H_{34}O_2Cl_2Pd_2$ requires C, 45·2; H, 5·4%), slightly more soluble than its methyl analogue.

*Bis(di*cyclo*pentadiene-*n*-propoxide)-μμ′-dichlorodipalladium*, $[(C_{10}H_{12}\cdot OPr^n)_2Pd_2Cl_2]$ (0·7 g. from 1 g. of palladite) (Found: C, 46·5; H, 5·8. $C_{26}H_{38}O_2Cl_2Pd_2$ requires C, 46·9; H, 5·75%), appreciably more soluble than its methoxy-analogue.

*Bis(di*cyclo*pentadiene*iso*propoxide)-μμ′-dichlorodipalladium*, $[(C_{10}H_{12}\cdot OPr^i)_2Pd_2Cl_2)$ (0·86 from 1·5 g. of palladite) (Found: C, 46·6; H, 5·8. $C_{26}H_{38}O_2Cl_2Pd_2$ requires C, 46·9; H, 5·75%), less soluble than its *n*-propoxy-analogue.

*Di*cyclo*pentadienemethoxide-*p*-toluidinechloropalladium*, $[C_{10}H_{12}\cdot OMe,$*p*-toluidine PdCl].—*p*-Toluidine (1 g.) was added to a suspension of the methoxychloro-complex (1 g.) in chloroform (15 c.c.). The resulting solution was cooled to −70° and diluted with light petroleum (b. p. 40—60°) which had been cooled to −70°. Scratching the walls of the vessel and keeping the mixture at −70° afforded a white microcrystalline powder. This *complex* was filtered off,

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* Trivial names of this type have been adopted because it is not known which double bond in the diene has been destroyed.

washed with light petroleum which had been cooled to −70°, and dried (yield 0·44 g.) (Found: C, 52·5; H, 6·1; N, 3·7. $C_{18}H_{24}ONClPd$ requires C, 52·5; H, 5·9; N, 3·4%).

*Reaction of Bis(di*cyclo*pentadienemethoxide)-μμ′-dichlorodipalladium with Concentrated Hydrochloric Acid.*—The complex (0·44 g.) was shaken in concentrated hydrochloric acid (20 c.c.) for 15 min. The orange solid was filtered off, washed with acetone and ether, and dried. The crude product was purified by dissolving it in hot chloroform and diluting the solution with ether (yield 0·2 g.). Its infrared spectrum was identical with that of di*cyclo*pentadienedichloropalladium.

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