920. *Transition-metal–Carbon Bonds. Part V.* Hydrido-cyclo-octa-*1,5-*diene Complexes of Iridium*(III)

By S. D. Robinson and B. L. Shaw

Chloroiridous acid reacts with cyclo-octa-1,5-diene in ethanol to give a bridged chloro-hydrido-cyclo-octa-1,5-dieneiridium(III) complex $[IrHCl_2(C_8H_{12})]_2$. Analogous bromo- and iodo-complexes were also made. The chloro-complex $[IrHCl_2(C_8H_{12})]_2$ when treated with sodium carbonate in methanol gave a bridged methoxyiridium(I) complex $[Ir(OMe)(C_8H_{12})]_2$ and was also converted into mononuclear complexes of the type $[IrL(C_8H_{12})]$ (L = cyclopentadienyl and acetylacetonato). The bridged methoxy-complex $[Ir(OMe)(C_8H_{12})]$ with hydrochloric acid gave back the bridged chloro-hydrido-iridium(III) complex $[IrHCl_2(C_8H_{12})]_2$. Infrared and nuclear magnetic resonance data are given.

cis,cis-CYCLO-OCTA-1,5-DIENE is known to be one of the best diolefins for chelating to transition metals. Examples of such complexes are known for chromium(0), molybdenum(0), and tungsten(0);[1-3] iron(0);[4,5] ruthenium(II);[2] rhodium(I);[6] nickel(0);[7] palladium(II);[8] platinum(II);[9] copper(I);[10] and silver(I)[11] and gold.[12]

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However, the halides of iridium were reported not to give an olefin complex with cyclo-octa-1,5-diene, even though rhodium trichloride when treated with this diolefin readily gives the bridged chloro-rhodium(I) complex $[Rh_2Cl_2(C_8H_{12})_2]$,[6] the structure (I) of which has been confirmed by *X*-ray investigation.[13]

We have reinvestigated the action of cyclo-octa-1,5-diene on chloroiridous acid (prepared *in situ* by reduction of chloroiridic acid) and find that, in boiling ethanol, a hydrido-cyclo-octa-1,5-dieneiridium(III) complex $[IrHCl_2(C_8H_{12})]_x$ is formed in 70% yield as cream microcrystals. This compound was too insoluble for molecular-weight and nuclear magnetic resonance (n.m.r.) studies, but from the evidence presented below, and by analogy with the known rhodium(I) complex $[RhCl(C_8H_{12})]_2$, we assign to it the binuclear structure (II). A bromo-complex $[IrHBr_2(C_8H_{12})]_2$ was prepared from sodium bromoiridate and hydrobromic acid and an iodo-complex also prepared but less well characterised. These hydrido-complexes showed a strong band at *ca.* 2200 cm.$^{-1}$ due to an iridium–hydrogen stretching mode. This assignment was confirmed for the chloro-complex by making the corresponding deuteride, *i.e.*, by using deuteroethanol C_2H_5OD as solvent in the preparation; the frequencies ν(Ir–H), ν (Ir–D) had the expected ratio of approximately $\sqrt{2}$ (Table 1).

TABLE 1

Iridium–hydrogen stretching frequencies (in cm^{-1}) for some hydrido-cyclo-octa-1,5-dieneiridium(III) complexes of type $[IrHX_2(C_8H_{12})]_2$

X	ν(Ir–H)	ν(Ir–D)	
Cl	2261	1613	Ratio 1·40
Br	2239		
I	2188		

As can be seen from Table 1, ν (Ir–H) decreases in the order of increasing *trans*-effect of the halide ligands; ν (Pt–H) decreases in the same order in the series of platinum hydrides of type *trans*-$[PtHX(PEt_3)_2]$.[14]

These compounds of type $[IrHX_2(C_8H_{12})]_2$ are the first examples of metal complexes with both hydrogen and an olefin bonded to the same metal atom; such complexes have been postulated as intermediates in hydroformylation reactions.

The infrared (i.r.) spectrum of $[IrHCl_2(C_8H_{12})]_2$ (KCl disc) showed a strong band at 1470 cm.$^{-1}$, which we assign to a carbon–carbon double-bond stretching frequency lowered by co-ordination. In agreement with this, the i.r. spectrum of cyclopentadienylcyclopentadieneiridium(I) showed a band at 1451 cm.$^{-1}$ which was assigned to a carbon–carbon double-bond stretching frequency in the cyclopentadiene ligand.[15] Our compound $[IrHCl_2(C_8H_{12})]_2$ showed two very intense i.r. absorption bands at 303 and 278 cm.$^{-1}$ due to iridium–chlorine stretching frequencies; these bands were absent from the spectrum of the corresponding bromo-complex $[IrHBr_2(C_8H_{12})]_2$ (otherwise very similar down to 230 cm.$^{-1}$).

When the hydrido-cyclo-octa-1,5-diene complex $[IrHCl_2(C_8H_{12})]_2$ was treated with diethylphenylphosphine the known dichlorohydridotris(diethylphenylphosphine)-iridium(III), white isomer, configuration (III),[16] was obtained. When treated with cyclopentadienylsodium, $[IrHCl_2(C_8H_{12})]_2$ gave a mononuclear iridium(I) complex $[IrC_5H_5(C_8H_{12})]$ as stable white crystals, readily soluble in organic solvents and subliming at 100°/10^{-4} mm. The i.r. spectrum of this complex showed the characteristic bands of a π-cyclopentadienyl group at 3077, 1400, 1096, 993, and 814 cm.$^{-1}$, corresponding well with bands at 3058, 1404, 1097, 995, and 810 cm.$^{-1}$ reported for the analogous complex $[IrC_5H_5(C_5H_6)]$.[15] This, and n.m.r. evidence (see below), favour the structure (IV; Y = cyclopentadienyl), for the complex $[IrC_5H_5(C_8H_{12})]$. A volatile and mononuclear acetylacetonato-complex

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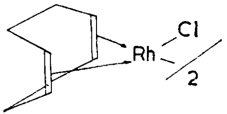
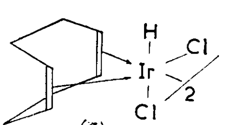
[Ir acac (C_8H_{12})] was prepared by treating [$IrHCl_2(C_8H_{12})$] with thallous acetylacetonate, or with acetylacetone in the presence of an excess of sodium carbonate; it presumably has the structure (IV; Y = acac), analogous to the known[6] rhodium complex [Rh acac (C_8H_{12})].

When the bridged chloro-hydrido-cyclo-octa-1,5-dieneiridium(III) complex [$IrHCl_2(C_8H_{12})]_2$ was treated with sodium carbonate in methanol, the elements of hydrogen chloride were lost, and the bridging chlorine atoms replaced by methoxy-groups, giving an iridium(I) complex, [$Ir(OMe)(C_8H_{12})]_2$, for which we suggest structure (V).



(I)



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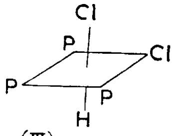
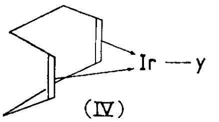
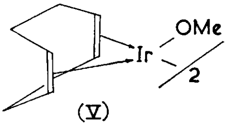


(III)



(IV)



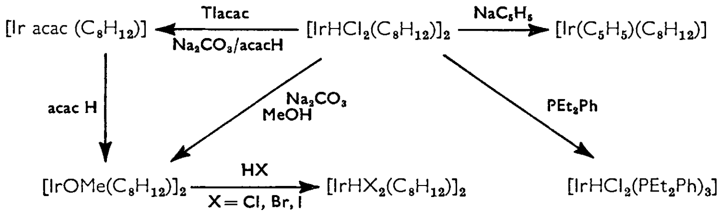
(V)

Chatt and Venanzi[6] found that, on boiling the rhodium(I) complex [$RhCl(C_8H_{12})]_2$ with sodium carbonate in methanol, a yellow dimeric complex was obtained, which analysed for [$Rh(OMe)(C_8H_{12})]_2$ but showed an i.r. absorption band at 3280 cm.$^{-1}$ assigned to a hydroxyl group. We prepared this complex and found the band at 3280 cm.$^{-1}$ to be weak, but that at ~1050 cm.$^{-1}$ due to the carbon–oxygen stretching mode of the methoxyl group to be very strong. Moreover the n.m.r. spectrum showed no signal due to a hydroxyl proton, only resonances due to methoxyl and cyclo-octadiene protons (Table 2). We therefore give this rhodium complex a structure analogous to (V); the band at 3280 cm.$^{-1}$ could be due to a small amount of hydroxyl-bridged compound formed in a side-reaction, or not to a hydroxyl group at all, but, *e.g.*, to a combination band.

When treated with hydrogen halides the bridged methoxy-iridium(I) complex [$Ir(OMe)(C_8H_{12})]_2$ readily gives the iridium(III) hydrido-bridged halo-complexes [$IrHX_2(C_8H_{12})]_2$, and with acetylacetone the acetylacetonato-complex [Ir acac C_8H_{12})].

For convenience, the reactions of these cyclo-octa-1,5-dieneiridium complexes are summarised in Scheme 1.

Scheme 1. Reactions of cyclo-octa-1,5-dieneiridium complexes



N.m.r. data for some cyclo-octa-1,5-dienerhodium compounds, together with data for the two mononuclear cyclo-octa-1,5-dieneiridium(I) compounds, are given in Table 2. In general, the spectra of the cyclo-octa-1,5-diene ligands were complex, but the total number of olefinic protons and protons on saturated carbon atoms could readily be estimated by integration, and were always present in the ratio of 4 : 8. Resonances due to other protons were sharp singlets.

The very large difference in τ-values (1·6) for the olefinic protons of the analogous complexes of type [M acac (C_8H_{12})] (M = Rh and Ir) is surprising, and we cannot account for it.

TABLE 2

N.m.r. data (τ-values) for cyclo-octa-1,5-diene-rhodium and -iridium complexes. Measured in deuterochloroform at 60 Mc./sec. using $SiMe_4$ tetramethyl silane as internal standard. Band-widths for complex bands given in parentheses (in c/sec.)

	C_8H_{12}				
Complex	" Olefinic " protons	" Saturated " protons	Other protons	Rel. intensity	Assignment
$[RhCl(C_8H_{12})]_2$	5·73 (38)	7·45 (90)			
		8·23 (36)			
$[Rh(OAc)(C_8H_{12})]_2$	5·86 (18)	7·26 (26)	8·25	3	–OAc
		8·12 (20)			
$[Rh(OMe)(C_8H_{12})]_2$	6·4 (54)	7·5 (48)	7·3	3	–OMe
		8·3 (28)			
$[Rh (acac) (C_8H_{12})]$	5·86 (26)	7·8 (95)	4·65	1	acac C–H
			8·08	6	acac–Me
$[Ir (acac) (C_8H_{12})]$	4·26 (24)	7·4 (78)	4·36	1	acac C–H
			7·86	6	acac–Me
$[Ir(C_5H_5)(C_8H_{12})]$	6·17 (25)	8·1 (60)	4·80	5	$-C_5H_5$

A preliminary account of this work has been published[17] and the hydrido-cyclo-octa-1,5-dieneiridium complex $[IrHCl_2(C_8H_{12})]$ has since been reported, without details, by Rinehart and Lasky.[18] Schrauzer[19] has described an impure hydrido-duroquinone complex of iridium(III) of composition $[IrHCl_2(\text{duroquinone})]$.

We have so far been unable to prepare complexes of iridium with other chelating di-olefins, *e.g.*, dicyclopentadiene or norbornadiene. Dicyclopentadiene with chloroiridic acid in ethanol gives a buff-coloured product which appears to be a polymer, but which we have not investigated further.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus, and are corrected. Operations involving free cyclo-octa-1,5-diene or tertiary phosphines were carried out in an atmosphere of nitrogen. Infrared spectra were measured as Nujol mulls.

*Di-μ-chloro-dichlorodihydridobis(cyclo-octa-*1,5-*diene)di-iridium*(III).—A solution of chloroiridic acid (50% Ir) (0·65 g.) in ethanol (15 c.c.) was heated on a steam-bath until the purple colour disappeared (*ca.* 10 min.). Cyclo-octa-1,5-diene (1 c.c.) was added, and the mixture heated for a further 2 hr. The precipitate was filtered off at 0° and washed with ethanol, then diethyl ether, to give the *product* as cream microcrystals (0·38 g.), decomposing above 200°; ν (Ir–H) 2261 cm.$^{-1}$ (Found: C, 25·7; H, 3·3; Cl, 18·95. $C_{16}H_{26}Cl_4Ir_2$ requires C, 25·8; H, 3·5; Cl, 19·05%).

*Di-μ-bromo-dibromodihydridobis(cyclo-octa-*1,5-*diene)di-iridium*(III).—Sodium bromoiridate (19% Ir) (1·9 g.) was suspended in ethanol (15 c.c.), hydrobromic acid (1 c.c. conc. aqueous solution) was added, and the mixture heated on a steam-bath until the purple colour was discharged. Cyclo-octa-1,5-diene (2 c.c.) was added, and the solution was heated for a further 2 hr. The precipitate was filtered off at 0° and washed with water, ethanol, and finally diethyl ether to give the *product* as cream microcrystals (0·40 g.) decomposing above 200°; ν (Ir–H) 2234 cm.$^{-1}$ (Found: C, 21·35; H, 2·75; Br, 34·45. $C_{16}H_{26}Br_4Ir_2$ requires C, 20·85; H, 2·85; Br, 34·65%).

*Di-μ-chloro-dichlorodideuterobis(cyclo-octa-*1,5-*diene)di-iridium*(III) was prepared in the same manner as the hydrido-complex (88% deuteroethanol, EtOD, replacing ethanol as solvent). The i.r. spectrum of the product showed ν (Ir–H) 2261 cm.$^{-1}$ (weak) and ν (Ir–D) 1613 cm.$^{-1}$ (strong).

*Dimethoxybis(cyclo-octa-*1,5-*diene)di-iridium*(I).—Di-μ-chloro-dichlorodihydridobis-(cyclo-octa-1,5-diene)di-iridium (0·254 g.) suspended in methanol (10 c.c.) was treated with sodium carbonate (0·10 g.). The mixture was heated on a steam-bath for 10 min., cooled to 0°, and the

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[17] S. D. Robinson and B. L. Shaw, *Tetrahedron Letters*, 1964, 1301.
[18] R. E. Rinehart and J. S. Lasky, *J. Amer. Chem. Soc.*, 1964, **86**, 2516.
[19] G. N. Schrauzer and K. C. Dewhirst, *J. Amer. Chem. Soc.*, 1964, **86**, 3265.

yellow precipitate washed with water and cold methanol; recrystallisation from methylene chloride–methanol gave the *product* as yellow microcrystals (0·07 g.) decomposing above 180° (Found: C, 32·55; H, 4·5. $C_{18}H_{30}Ir_2O_2$ requires C, 32·6; H, 4·55%).

*Acetylacetonato(cyclo-octa-*1,5-*diene)iridium*(I).—*Method* 1. A suspension of di-μ-chloro-dichlorodihydridobis(cyclo-octa-1,5-diene)di-iridium (0·25 g.) in acetone (10 c.c.) was treated with anhydrous sodium carbonate (0·15 g.) and acetylacetone (0·08 c.c.). The mixture was boiled for 1 min., then shaken at room temperature for 2 hr. Evaporation to dryness followed by recrystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave the *product* as yellow prisms (0·20 g.) subliming above 120°, m. p. 145—150° (slight decomp.) (Found: C, 39·2; H, 4·75%; *M* (osmometrically in 1·04% $CHCl_3$ solution), 405. $C_{13}H_{19}IrO_2$ requires C, 39·1; H, 4·8%; *M*, 399).

Method 2. A suspension of di-μ-chloro-dichlorodihydrobis(cyclo-octa-1,5-diene)di-iridium(III) (0·20 g.) in methylene chloride (10 c.c.) was treated with a solution of thallous acetylacetonate (0·185 g.) in hot methylene chloride (10 c.c.). The white precipitate of thallous chloride was filtered off and the yellow filtrate evaporated to dryness. Recrystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave yellow prisms (0·10 g.) subliming above 120°, m. p. 148—154° (slight decomp.) (Found: C, 39·5; H, 5·0%). The i.r. spectrum was identical with that of the product prepared by Method 1.

*Cyclopentadienyl(cyclo-octa-*1,5-*diene)iridium*(I).—A suspension of di-μ-chloro-dichlorodihydridobis(cyclo-octa-1,5-diene)di-iridium(III) (0·45 g.) in tetrahydrofuran (20 c.c.) was treated with a tetrahydrofuran solution of cyclopentadienylsodium (2·2 mol.). The mixture was allowed to react for 30 min. and then evaporated to dryness. The residue was extracted with light petroleum (b. p. 60—80°), the extract was evaporated, and the residue purified by repeated vacuum sublimation ($100°/10^{-4}$ mm.), followed by recrystallisation from ethanol to give the *product* as white prisms (0·213 g.), m. p. 122—127° (Found: C, 43·05; H, 4·75. $C_{13}H_{17}Ir$ requires C, 42·7; H, 4·7%).

*Conversion of Di-μ-methoxybis(cyclo-octa-*1,5-*diene)di-iridium*(I) *into Di-μ-chloro-dichlorodihydridobis(cyclo-octa-*1,5-*diene)di-iridium*(III).—The di-μ-methoxy-complex (0·10 g.) in methanol (3 c.c.) was heated under reflux with concentrated hydrochloric acid (0·1 c.c.) for 30 min. The resultant cream precipitate was washed with ethanol, then with diethyl ether. The i.r. spectrum was identical to that of an authentic sample of di-μ-chloro-dichlorodihydridobis(cyclo-octa-1,5-diene)di-iridium(III).

*Conversion of Di-μ-methoxybis(cyclo-octa-*1,5-*diene)di-iridium*(I) *into Acetylacetonato(cyclo-octa-*1,5-*diene)iridium*(I).—The di-μ-methoxy-complex (0·17 g.), suspended in acetone (10 c.c.), was treated with acetylacetone (0·1 c.c.), and the mixture shaken for 3 hr. The orange yellow solution was evaporated to dryness and the residue recrystallised from benzene–light petroleum (b. p. 80—100°) to give yellow prisms (0·047 g.), m. p. 148—154°, subliming slowly at 120°. The i.r. spectrum was identical with that of an authentic sample of acetylacetonato(cyclo-octa-1,5-diene)iridium(I).

*Conversion of Di-μ-chloro-dichlorodihyridobis(cyclo-octa-*1,5-*diene)di-iridium into Dichlorohydridotris(diethylphenylphosphine)iridium*(III) (*White Isomer*).—Di-μ-chloro-dichlorodihydridobis(cyclo-octa-1,5-diene)di-iridium) (0·10 g.), suspended in benzene (10 c.c.), was treated with diethylphenylphosphine (0·15 g.); the yellow solution was heated under reflux for 30 min., then evaporated to dryness. The residue was recrystallised from benzene–light petroleum (b. p. 60—80°) to give white microcrystals (0·12 g.). The i.r. spectrum was identical with that of an authentic sample.

*Di-μ-iododi-iododihydridobis(cyclo-octa-*1,5-*diene)di-iridium*(III).—Di-μ-methoxy-bis(cyclo-octa-1,5-diene)di-iridium(I) (0·40 g.) in methanol (10 c.c.) was heated under reflux with concentrated hydriodic acid (0·2 c.c.) for 10 min. The resultant brown preicpitate was washed with ethanol to give the product as light brown microcrystals (0·50 g.); ν (Ir–H) 2188 cm.$^{-1}$.

We thank the D.S.I.R. for a maintenance award (to S. D. R.).

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[*Received, March* 23*rd*, 1965.]