955. *Olefin Co-ordination Compounds. Part VI.* Diene Complexes of Rhodium*(I).

By J. Chatt and L. M. Venanzi.

Chloro-bridged rhodium(I) complexes of the type [diene$_2$Rh$_2$Cl$_2$] containing *cyclo*octa-1 : 5-diene, di*cyclo*pentadiene, and *cyclo*octatetraene functioning as a diene are described. Those of *cyclo*octa-1 : 5-diene (C_8H_{12}) are the most stable and their reactions have been extensively studied. The stabilities of the halogeno-complexes fall in the sequence Cl > Br > I. Amines react with the halogeno-bridged complexes to give mononuclear complexes of the type [C_8H_{12},amRhX]. There are cationic and anionic complexes of the types [C_8H_{12},diamineRh]$^+$ and [$C_8H_{12}RhCl_2$]$^-$, but they are not easily obtained as pure salts. The *cyclo*pentadienyl complex [$C_8H_{12}RhC_5H_5$] and an α-acetylacetonyl-compound [C_8H_{12}Rh acac] are described, also a dinuclear diacetate [$(C_8H_{12})_2Rh_2(OAc)_2$] in which the acetate groups are symmetrically bound, and a dinuclear methanol derivative approximating to [$(C_8H_{12})_2Rh_2(MeOH)_2$], of unknown structure.

Easily isolable olefin complexes are formed more readily by *cyclo*octa-1 : 5-diene than by any other olefin. Its silver(I), copper(I), and palladium(II) complexes are precipitated immediately when the diene is shaken with aqueous silver nitrate,[1] chlorocuprous acid, and ammonium chloropalladite [2] respectively. Its platinum(II) complexes, *e.g.*, [$C_8H_{12}PtCl_2$], in keeping with the more inert character of platinous salts, are produced more slowly but are undoubtedly the most stable olefin co-ordination complexes known, in spite of there being two double bonds attached to one platinum atom.[3] This diene is therefore eminently suitable for finding the limits in the Periodic Table of the region containing metals which form olefin complexes. At present the triangle of elements Cu(I), Pd(II), Ag(I), Pt(II), and Hg(II) is known to form reasonably stable complexes. There are also iron complexes of the type [butadieneFe(CO)$_3$] but their structures are unknown.[4]

In an attempt to extend this rather limited region of stable olefin complexes we have treated ethanolic solutions and suspensions of the commoner halides of rhodium, iridium, ruthenium, and osmium with the *cyclo*octadiene but only rhodium has given stable olefin complexes by this method.

When an ethanolic solution of rhodium trichloride trihydrate is boiled under reflux with an excess of the diene an orange solid of composition $C_8H_{12}RhCl$ slowly separates; [5] this reaction is hastened, but the quality of the product is reduced, by the addition of anhydrous sodium carbonate. The complex can also be obtained by reaction of the diene with rhodium carbonyl chloride $(CO)_4Rh_2Cl_2$ (I), and, in poorer yield, by the careful reduction of the trichloride in ethanolic solution with sodium borohydride in presence of the diene at room temperature.

The complex, $C_8H_{12}RhCl$, is dimeric, diamagnetic, and a non-electrolyte in nitrobenzene. Its chemical properties accord with the structure (II; X = Cl) in which the rhodium atom would have a planar 4-co-ordination and be in the *dsp*^{2} hybridised state. In this complex the rhodium is isoelectronic with palladium(II) in its 4-co-ordinated complexes, and co-ordinated exactly as in the carbonyl halide (I). Again, the close parallelism between olefin complexes and carbonyl halides is observed.

The complex (II; X = Cl) is most soluble in chlorinated solvents and moderately soluble in other organic solvents, but insoluble in water. It is converted into the corresponding bromide (X = Br) and iodide (X = I) by shaking its acetone solution with

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* Part V, *J.*, 1957, 3413.

[1] W. O. Jones, *J.*, 1954, 312.

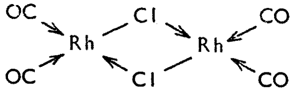
[2] Chatt, Vallarino, and Venanzi, *J.*, 1957, 3413.

[3] *Idem*, *J.*, 1957, 2496.

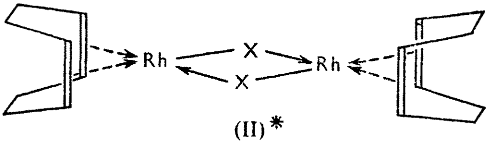
[4] Reihlen, Gruhl, Hessling, and Pfrengle, *Annalen*, 1930, **482**, 161.

[5] Chatt and Venanzi, *Nature*, 1956, **177**, 852.

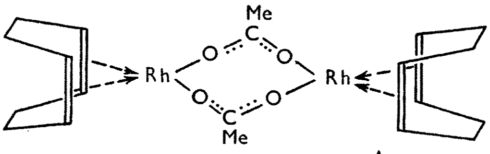
finely powdered lithium bromide and sodium iodide, respectively. The iodide is rather unstable, especially in solution. This is paralleled in the palladium(II) and platinum(II) series of olefin complexes, where the chlorides are most stable, the iodides often too unstable to be isolated, and the bromides of intermediate stability. This instability is usually attributed to increasing loosening of the olefin in the complex by increasing *trans*-effects of the halogens in the order Cl < Br < I. If this attribution is correct. its observation here indicates that the *trans*-effect operates also in complexes of rhodium(I). An attempt to obtain the diethylthio-derivative (II; X = EtS) led to decomposition, presumably owing to the high *trans*-effect of the EtS^- ion.



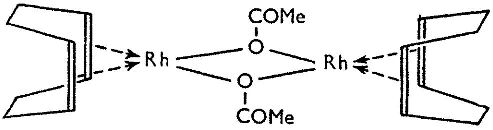
(I)



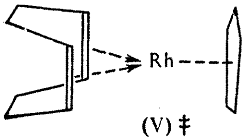
(II)*



(III)†



(IV)†



(V)‡

* The dotted lines representing the olefin-to-metal bonds imply a scheme of bonding such as that suggested in the ion $[C_2H_4PtCl_3]^-$ (see ref. 9).

† Arrows are omitted from the bonds in the bridge to emphasise the true symmetry of the bridging groups.

‡ The bond between the rhodium atom and the *cyclo*pentadienyl anion will be of the "sandwich" type.

The acetate (II; X = OAc) was prepared by boiling an acetone solution of the corresponding chloride and potassium acetate. It is quite stable. Its infrared spectrum, kindly examined for us by Dr. L. A. Duncanson, has two very strong bands at 1530 and 1419 $cm.^{-1}$, *i.e.*, in the characteristic frequency range for the carboxyl ion; otherwise the spectrum closely resembles that of the dichloro-complex (II; X = Cl). It does not give a conducting solution in nitrobenzene. These facts indicate that the acetate ion bridges symmetrically through both oxygen atoms, *e.g.*, as in (III), rather than through only one as in (IV), whose spectrum would have a band characteristic of the CO group in esters. In (III) the ring must be puckered, with intervalency angles of about 120° at the oxygen atoms to accommodate the normal intervalency angles of the acetato-groups and the rhodium atoms.

The existence of the halogen bridge in compounds (II) was confirmed by bridge-splitting reactions with amines to give mononuclear complexes:

$$[(C_8H_{12})_2Rh_2X_2] + 2\text{ amine} \longrightarrow 2[C_8H_{12},\text{amine}RhX] \quad . \; . \; . \; . \; . \; . \quad (1)$$

(where X = Cl, Br and I, amine = piperidine; X = Cl, amine = *p*-toluidine).

$[C_8H_{12}$,piperidineRhI] is the least stable of these derivatives and readily loses piperidine with reversion to the parent bridged iodide. This is analogous to the behaviour of amines with all classes of bridged iodide in the palladous and platinous series of complexes.[6,3] It serves to emphasise the much greater resistance to fission by nucleophilic reagents of the iodo- as compared with the chloro- and bromo-bridges between these metals, and that the

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[6] Chatt and Venanzi, *J.*, 1957, 2445; 1955, 3858.

instability of the bridged iodide (II; X = I) relative to the corresponding chloride and bromide is not due to weakness at the bridge, but more probably at the olefin-to-metal bonds as required by *trans*-effect theory.

Other uncharged ligands react with the chloro-bridged complex (II; X = Cl), but of those tried (PPh_3, $AsPh_3$, Ph_2S) only the phosphine gave a product $[C_8H_{12},PPh_3RhCl_2]$ sufficiently stable to be isolated.

Similar bridge-splitting reactions with ionic halides and chelating diamines (diam) afforded evidence of the existence of unstable anionic and cationic olefin complexes:

$$[(C_8H_{12})_2Rh_2Cl_2] + 2HCl \rightleftharpoons 2H[C_8H_{12}RhCl_2] \quad . . . . . . (2)$$

$$[(C_8H_{12})_2Rh_2Cl_2] + 2\ \mathrm{diam} \rightleftharpoons 2[C_8H_{12},\mathrm{diam}Rh]Cl \quad . . . . . . (3)$$

The chloro- and bromo-complexes (II; X = Cl and Br) dissolve in warm concentrated hydrochloric acid, but crystallise again when their solutions cool. They are insoluble in alkali halide solutions. In this respect the chloro-complex is exactly analogous to the bridged platinous complex $[(Et_2S)_2Pt_2Cl_4]$ and differs from $[(C_2H_4)_2Pt_2Cl_4]$ which gives the stable anion $[C_2H_4PtCl_3]^-$ with chloride solutions. This behaviour can be explained by supposing that equilibria of type (2) are established in the warm hydrochloric acid, and the halogeno-bridged complex separates before the acid on cooling.

Attempts to obtain a stable salt of $[(C_8H_{12})RhCl_2]^-$ with bulky cations, *e.g.*, $[AsPh]_4^+$, failed, but a red insoluble salt of this type with approximately the correct analysis was obtained by reaction (4).

$$[(C_8H_{12})_2Rh_2Cl_2] + \mathrm{dpy} \longrightarrow [C_8H_{12},\mathrm{dpy}Rh][C_8H_{12}RhCl_2] \quad . . . . . (4)$$

The reaction of chelating diamines with the chloro-complex (II; X = Cl) gave salts approximating to the products of reaction (3), and by employing a bulky anion a salt of this type was obtained pure, *viz.*, $[C_8H_{12},C_2H_4(NHEt)_2Rh][BPh_4]$. 1 : 1′-Dipyridyl and *o*-phenanthroline gave beautifully crystalline red salts, presumably containing cations of this type, but repeated recrystallisation failed to give products with exactly the correct analysis. In general these compounds tended to contain too much nitrogen. Some typical examples are described in the Experimental section.

Mononuclear products were also obtained by the reaction of (II; X = Cl) with acetylacetone (acac) in alkali and with *cyclo*pentadienylsodium. The α-acetylacetonyl-compound $[C_8H_{12}Rh\ acac]$ decomposes when kept for several weeks, but the pure *cyclo*pentadienyl (V) is stable. It is exactly analogous to the carbonyl complex $(CO)_2CoC_5H_5$.[7]

Attempts to obtain rhodium complexes with other olefins and diolefins had little success. The reaction of hexa-1 : 5-diene, *cyclo*octatetraene, di*cyclo*pentadiene (tetrahydro-4 : 7-methanoindene), and styrene with $(CO)_4Rh_2Cl_2$ was not accompanied by appreciable evolution of gas, and led only to orange gummy residues. By boiling an alcoholic solution of rhodium trichloride trihydrate containing the olefin, only *cyclo*octatetraene and di*cyclo*pentadiene gave solid orange products; hexa-1 : 5-diene and dipentene both caused reduction to the metal. The *cyclo*octatetraene complex was too unstable to be purified but that of di*cyclo*pentadiene was stable and had the formula $(C_{10}H_{12})_2Rh_2Cl_2$ exactly analogous to (II; X = Cl).

Methoxides, in which one double bond of the diene has been saturated, are formed by the reaction of the diene complexes of platinous and palladous halides with anhydrous sodium carbonate in hot methanol.[2,3] By a similar reaction, $(C_8H_{12})_2Rh_2Cl_2$ (II; X = Cl) yielded a stable crystalline substance, which appeared from its analysis and molecular weight to be $(C_8H_{12})_2Rh_2(OMe)_2$, but its infrared spectrum indicates that it contains an OH group: its nature is uncertain. Its infrared spectrum is closely similar to that of the parent dichloride (II; X = Cl), suggesting that the diene has not changed during the reaction, but that methanol has added on as such. The formula $[(C_8H_{12})_2Rh_2(MeOH)_2]$ satisfactorily accounts for the spectrum, but there is no obvious structure.

It is interesting that the only olefin complexes of rhodium should contain rhodium(I),

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[7] Fischer and Hafner, *Z. Naturforsch.*, 1955, **10*b***, 140.

isoelectronic with palladium(II), and that attempts to oxidise some of the rhodium(I) complexes to rhodium(II) or rhodium(III) with the theoretical quantity of chlorine led to indefinite half-oxidised products. There was no clean oxidation to the commoner tervalent state. 4-Co-ordinated rhodium(I), but not 6-co-ordinated rhodium(III), has a vacant p_z orbital which, by combination with the d_{xz} and d_{yz} orbitals, can form hybrid orbitals suitable for forming strong dative π-bonds with the anti-bonding orbitals of the diene.[8, 9]

The metals known to form stable olefin complexes, all do so in a valency state which admits the possibility of *dp*-hybridisation in the dative π-bond. It may be that the *d*-orbitals alone do not give a sufficiently good overlap with the anti-bonding orbitals of the olefin to make a stable metal-to-olefin bond, and that some *p*-character is always necessary. This harmonises with the fact that olefin complexes corresponding to $Ni(CO)_4$ and such carbonyls, where there is no vacant *p*-orbital, do not appear to be obtainable. We have tried to obtain the substitution

$$C_8H_{12} + Ni(CO)_4 = C_8H_{12}Ni(CO)_2 + 2CO$$

but there was no displacement of carbon monoxide.

If a vacant *p*-orbital as well as filled *d*-orbitals is necessary for the formation of stable olefin complexes, we would expect the diene to form complexes with the iron group of metals when they are in their hitherto unknown planar 4-co-ordinated zero-valent states. Nevertheless, with decreasing valency and nuclear charge of the metal atom a point to the left of Group VIII may eventually be reached when the d_{xz}-type of orbital will reach out sufficiently to stabilise olefin complexes without the addition of *p*-character.

EXPERIMENTAL

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

Bis(cyclo*octa*-1 : 5-*diene*)-$\mu\mu'$-*dichlorodirhodium* (II; X = Cl).—*Preparation* 1. Rhodium trichloride trihydrate (1 g.) in ethanol (30 c.c.) was boiled under reflux with the diene (2 c.c.) for 3 hr. The solution was cooled, and the orange *solid* filtered off, washed with ethanol, dried, and recrystallised from acetic acid (yield 60%). It darkens from about 220°, m. p. 256° (decomp. with effervescence at 258°) (Found: C, 39·05; H, 5·0; Cl, 14·4%; *M*, ebullioscopically in 0·9% chloroform solution, 513. $C_{16}H_{24}Cl_2Rh_2$ requires C, 39·0; H, 4·9; Cl, 14·4%; *M*, 493). It is soluble in dichloromethane, moderately so in chloroform, acetic acid, and acetone, slightly soluble in ether, methanol, ethanol, and benzene, and insoluble in water. Its magnetic susceptibility, χ, is $-0{\cdot}52 \times 10^{-6} \pm 4\%$ per g.

Preparation 2. Sodium borohydride (0·5 g.) in ethanol (100 c.c.) was added during 3 hr. to a well-stirred solution of rhodium trichloride trihydrate (5 g.) and *cyclo*octa-1 : 5-diene (3 c.c.) in ethanol (125 c.c.) at 20°. The reaction is exothermic and some rhodium is deposited. After 2 days the mixture was filtered and the residue extracted with methylene chloride. The extract was taken to dryness at 15 mm., and the orange residue recrystallised from acetic acid (yield 0·67 g.). The reaction mixture still contained a considerable quantity of rhodium trichloride.

Bis(cyclo*octa*-1 : 5-*diene*)-$\mu\mu'$-*dibromodirhodium* (II; X = Br).—A suspension of the dichloro-complex (II; X = Cl) (3 g.) and finely powdered lithium bromide (3 g.) in acetone (200 c.c.) was shaken until an orange opalescent solution was obtained. This was filtered and taken to dryness at 15 mm. The residue was extracted with chloroform, and the extract on evaporation at 15 mm. gave 3 g. of crude *bromo-compound*. This was purified by the action of charcoal on its cold chloroform solution and reprecipitation with light petroleum (b. p. 60—80°), then decomposing at 207—212° (Found: C, 32·8; H, 4·2. $C_{16}H_{24}Br_2Rh_2$ requires C, 33·0; H, 4·2%). Its solubility is similar to that of the chloride except that it is very soluble in chloroform and only moderately soluble in dichloromethane. It slowly decomposes in boiling solvents.

Bis(cyclo*octa*-1 : 5-*diene*)-$\mu\mu$-*di-iododirhodium* (II; X = I).—A solution of the dichloro-complex (II; X = Cl) (1·3 g.) in acetone (100 c.c.) was shaken with powdered sodium iodide

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[8] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[9] Chatt and Duncanson, *J.*, 1953, 2939.

(0·8 g.). The brick-red *iodo-compound* (1·6 g.) formed was filtered off, washed with acetone, and dried. Recrystallised from benzene and washed with methanol it decomposed at 180—200° (Found: C, 29·2; H, 3·7. $C_{16}H_{24}I_2Rh_2$ requires C, 28·4; H, 3·6%). It decomposes in hot solvents.

Bis(cyclo*octa*-1 : 5-*diene*)-$\mu\mu'$-*diacetatodirhodium* (II; X = OAc).—An acetone solution of the dichloro-complex (1 g.) and potassium acetate (1 g.) was boiled under reflux for 2 hr. The solution was then filtered and the filtrate taken to dryness at 15 mm. The residue, recrystallised from ethyl acetate, gave orange crystals of the pure *product*, m. p. 197—198° (0·54 g.) (Found: C, 44·4; H, 5·7%; *M*, ebullioscopically in 1·4% benzene solution, 597; in 1·5% solution, 587; in 0·9% solution, 554. $C_{10}H_{15}O_2Rh$ requires C, 44·5; H, 5·6%; *M*, 540). Its 10^{-3}M-solution in nitrobenzene is non-conducting.

cyclo*Octa*-1 : 5-*dienepiperidinechlororhodium*, [C_8H_{12},$C_5H_{11}N$,RhCl].—Piperidine (0·4 c.c.) was added to the dichloro-complex (II; X = Cl) (1 g.) in dichloromethane (50 c.c.), and the yellow solution taken to dryness at 15 mm. The residue, recrystallised from light petroleum (b. p. 60—80°), gave the *product* as yellow needles, decomp. 150—170° (74%) (Found: C, 47·0; H, 7·0; N, 4·4; Cl, 11·2. $C_{13}H_{23}NClRh$ requires C, 47·0; H, 7·0; N, 4·2; Cl, 10·7%). It is a non-electrolyte in nitrobenzene. Similarly prepared were cyclo*octa*-1 : 5-*dienepiperidinebromorhodium* (71%) (from methanol), m. p. 185°, darkens 145°, sinters 165° (Found: C, 41·5; H, 6·1; N, 3·9%; *M*, ebullioscopically in 1% benzene solution, 347. $C_{13}H_{23}NBrRh$ requires C, 41·5; H, 6·2; N, 3·7%; *M*, 376), and cyclo*octa*-1 : 5-*dienepiperidineiodorhodium* (10%) [from light petroleum (b. p. 60—80°)], decomp. 150—155° (Found: C, 37·0; H, 5·4; N, 3·5. $C_{13}H_{23}NIRh$ requires C, 36·9; H, 5·5; N, 3·3%). The iodide is decomposed by boiling solvents except light petroleum, and in boiling methanol it reverts to the bridged di-iodo-complex (II; X = I).

cyclo*Octa*-1 : 5-*diene*-p-*toluidinechlororhodium*, [C_8H_{12},p-$MeC_6H_4{\cdot}NH_2$,RhCl].—This *complex* separates immediately on the addition of *p*-toluidine (0·43 g.) in dichloromethane (10 c.c.) to the dichloro-complex (II; X = Cl) (1 g.) in the same solvent (50 c.c.). Recrystallised from benzene and then methanol, it forms yellow felted needles which sinter at 206°, decomp. 213—214°. It is a non-electrolyte in nitrobenzene (Found: C, 50·7; H, 6·35; N, 4·3. $C_{15}H_{21}NClRh$ requires C, 50·9; H, 6·0; N, 4·0%).

cyclo*Octa*-1 : 5-*dienetriphenylphosphinechlororhodium*, [C_8H_{12},PPh_3RhCl].—Triphenylphosphine (1·07 g.) was added to a solution of the dichloro-complex (II; X = Cl) (1 g.) in dichloromethane, and the resultant solution taken to dryness at 15 mm. The residual *phosphine complex*, washed with methanol, filtered, and recrystallised from ethanol, had m. p. 146° (decomp.) (Found: C, 61·6; H, 5·6. $C_{26}H_{27}ClPRh$ requires C, 61·4; H, 5·35%).

cyclo*Octa*-1 : 5-*dienedipyridylrhodium* cyclo*octa*-1 : 5-*dienedichlororhodate* [C_8H_{12},dpyRh][$C_8H_{12}RhCl_2$].—2 : 2′-Dipyridyl (0·4 g.) was added to the dichloro-complex (II; X = Cl) (1 g.) in dichloromethane, and the deep red solution evaporated to a small volume at 15 mm. in the cold. The red crystals were filtered off and dried. After several recrystallisations from dichloromethane–light petroleum (b. p. 40—60°) they decomposed at 215° with previous darkening at 180—190° (Found: C, 47·9; H, 5·2; N, 4·9. $C_{26}H_{32}N_2Cl_2Rh_2$ requires C, 48·1; H, 5·0; N, 4·3%). Its molecular conductivity in 1·5 × 10^{-2}M-nitrobenzene solution at 20° is 18 ohm^{-1} cm.^{2}.

cyclo*Octa*-1 : 5-*diene*-NN′-*diethylethylenediaminerhodium tetraphenylboron*, [C_8H_{12},$C_2H_4(NHEt)_2Rh$][BPh_4].—The dichloro-complex (II; X = Cl) (0·6 g.) in dichloromethane was shaken with the diamine (0·6 c.c.), and sodium tetraphenylboron (1 g.) added. Sodium chloride separated and was removed. The filtrate was taken to dryness at 15 mm., and the residue taken up in a minimum of hot dichloromethane. The *product* was precipitated from this by addition of methanol (yield 0·6 g.) (Found: C, 70·5; H, 7·45; N, 4·4. $C_{38}H_{48}N_2BRh$ requires C, 70·6; H, 7·5; N, 4·3%). This salt has a molecular conductivity of 18·5 ohm^{-1} cm.^{2} at 20° in 5·0 × 10^{-3}M-nitrobenzene solution.

Attempted Preparation of Dipyridyl and o-*Phenanthroline Salts containing Cations of Type* [C_8H_{12},diamRh]$^+$.—2 : 2′-Dipyridyl (0·7 g.) was added to the dichloro-complex (II; X = Cl) (1 g.) in dichloromethane (30 c.c.), and the solution evaporated at 14 mm. The residual red solid was treated with 20% perchloric acid. It changed in appearance and was filtered off, washed with water, dried, and recrystallised from methanol, the *product* forming red needles, decomp. 265—267° (effervescence) (darkens at 210—240°) (Found: C, 40·55; H, 4·3; N, 6·75. $C_{18}H_{20}O_4N_2ClRh$ requires C, 46·32; H, 4·3; N, 6·0%).

The above reaction, when conducted in ethanol, gave an orange red precipitate on addition of one equivalent of sodium tetraphenylboron (decomp. 180—188°), which was recrystallised by precipitation from dichloromethane with ethanol (Found: C, 70·4; H, 5·8; N, 4·3. $C_{42}H_{40}N_2BRh$ requires C, 73·5; H, 5·9; N, 4·1%). Further recrystallisation lowered the carbon content of the *complex*.

o-Phenanthroline (0·76 g.) in dichloromethane (20 c.c.) was added to the dichloro-complex (II; X = Cl) (1 g.) in dichloromethane (40 c.c.). The red precipitate formed at once was filtered off and recrystallised from methanol (1 g.); it decomposed at 285—290°, with darkening from 250° (Found: C, 55·7; H, 5·2; N, 7·2. $C_{20}H_{20}N_2ClRh$ requires C, 56·3; H, 4·7; N, 6·6%). Further recrystallisation of this *complex* from dilute hydrochloric acid gave a product with the following analysis: C, 56·1; H, 4·8; N, 7·7%.

When this reaction was conducted in water, and dilute nitric acid added to the solution, a red crystalline *nitrate* was obtained which recrystallised from ethanol (Found: C, 53·0; H, 4·45; N, 9·3. $C_{20}H_{20}O_3N_3Rh$ requires C, 52·5; H, 4·5; N, 9·6%).

cyclo*Octa*-1 : 5-*diene*cyclo*pentadienylrhodium*, $[C_8H_{12}RhC_5H_5]$.—The preparation was performed under nitrogen. *cyclo*Pentadienylsodium was prepared by the dissolution of sodium (0·2 g.) in *cyclo*pentadiene (10 c.c.) diluted with tetrahydrofuran (40 c.c.). This solution (10 c.c.) was then added to the dichloro-complex (II; X = Cl) (0·5 g.) in the same solvent (30 c.c.). After 12 hours' storage the solution was evaporated spontaneously in the air, leaving an orange-yellow crystalline product and a brown gum. The product was dissolved in a minimum of dichloromethane and treated with charcoal at room temperature, and the filtrate cooled to −70°. The yellow *complex* separated (m. p. 108—108·5°) (Found: C, 56·0; H, 6·1%; *M*, ebullioscopically in 0·9% acetone solution, 251. $C_{13}H_{17}Rh$ requires C, 56·5; H, 6·2%; *M*, 276). It is a non-electrolyte in nitrobenzene solution. It is very soluble in chloroform, dichloromethane, and benzene, and moderately soluble in alcohols, light petroleum, and ether. The latter solvents decompose the product with the formation of brown flocculent precipitates. The solid product is stable on long storage (>18 months).

*Bisdi*cyclo*pentadiene-μμ'-dichlorodirhodium*, $(C_{10}H_{12})_2Rh_2Cl_2$.—An ethanolic (120 c.c.) solution of rhodium trichloride trihydrate (5 g.) and di*cyclo*pentadiene (5 c.c.) was boiled under reflux for several hours, then cooled. A brown solid separated and was removed and dried. This was extracted with benzene, and the extract taken to dryness at 15 mm. to leave an orange residue (4 g.). Recrystallisation from acetic acid gave orange crystals of the *complex* which darkened at 198° and decomposed at 205—210° (Found: C, 44·4; H, 4·5. $C_{20}H_{24}Cl_2Rh_2$ requires C, 44·4; H, 4·5%).

Attempted Preparation of Methoxides.—A methanolic solution (40 c.c.) of the dichloro-bridged complex (II; X = Cl) (1 g.) was boiled under reflux for 1 hr. with anhydrous sodium carbonate (0·6 g.). The hot reaction mixture was filtered, and the yellow plates which separated as the filtrate cooled were filtered off, washed, and dried; they decomposed slowly on heating, becoming black at 180° (Found: C, 44·7; H, 6·3%; *M*, ebullioscopically in 1·1% benzene solution, 537. Calc. for $C_{18}H_{30}O_2Rh_2$: C, 44·6; H, 6·2%; *M*, 484. Calc. for $C_{18}H_{32}O_2Rh_2$: C, 44·5; H, 6·6%; *M*, 486).

Infrared Spectra.—Those of the dichloro- (II; X = Cl), diacetato- (II; X = AcO), and methoxy-complexes were kindly examined for us by Dr. L. A. Duncanson. The three spectra are very similar, indicating that the diene remains in the same form throughout. The absorption bands (cm.$^{-1}$) are listed in the table.

Infrared spectra of $[(C_8H_{12})_2Rh_2Cl_2]$, $[(C_8H_{12})_2Rh_2(OAc)_2]$, *and the " methoxide."*

$(C_8H_{12})_2Rh_2Cl_2$		$(C_8H_{12})_2Rh_2(OAc)_2$		" Methoxide "	
	993	1530 vs *	997 s	3280 s †	994
		1419 vs *			976 vw
1325 s	961 s	1327 s	960 s	1325 s	958 sh
1301 s		1299 s	953 s	1299 s	949 s
1227 m	878 w	1227 m	892 w	1225 m	889 w
1210 m		1209 m	875 s	1209 s	
1172 s	866 s	1174 m	866 s	1172 s	873 s
1153 s	831 w	1154 m	835 m	1152 s	829 w
1076 w	817 s	1075 w	817 s	1076 vs §	813 s
	795 m	1042 w	797 m		793 m
	771 s	1020 m	776 s	1004 sh	772 s

* Characteristic of $R\cdot CO_2^-$. † OH group. § OMe group (1030 in $CH_3\cdot OH$).

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