CHEMICAL AND STRUCTURAL CHARACTERIZATION OF SOME π-ALLYLIC DERIVATIVES OF RHODIUM(III)

GASTONE PAIARO, ALFREDO MUSCO AND GIUSEPPINA DIANA
Laboratorio di Chimica Generale e Inorganica dell'Istituto Chimico dell'Università di Napoli – Sez. VII del Centro Nazionale di Chimica Macromolecolare del C.N.R., Naples (Italy).

(Received May 11th, 1965)

It has been reported that rhodium(I) may form olefinic complexes which are isoelectronic with the corresponding complexes of palladium(II)[1–3].

Before the present work, no π-allylic or olefinic complexes of rhodium(III) had been isolated, although several cyclopentadienyl compounds were known[1–6]. In the course of a systematic study of the reaction between cyclododecatriene and transition-metal compounds we have isolated a π-allylic complex of rhodium(III)*. This is obtained in high yield by boiling an ethanolic solution of rhodium trichloride trihydrate and *trans,trans,trans*-1,5,9-cyclododecatriene (*t,t,t*,CDT) according to the reaction:

$$RhCl_3 + C_{12}H_{18} + CH_3CH_2OH \longrightarrow \underset{(I)}{C_{12}H_{19}RhCl_2} + HCl + CH_3CHO \qquad (1)$$

In this paper we describe the chemical and structural characterization of this compound, through the study of some of its derivatives.

CHEMICAL CHARACTERIZATION OF DICHLOROCYCLODODECA-1,5-DIENYLRHODIUM(III)

Compound (I) is intensely red in colour, insoluble in water, concentrated mineral acids, and all conventional organic solvents. It is easily soluble in aqueous ammonia and reacts with many Lewis bases (2,2'-bipyridine, amines, carbon monoxide, mono-olefins and diolefins such as 1,3-butadiene and 1,5-hexadiene) to give the compounds reported in Fig. 1. In all these compounds the cyclic C_{12} hydrocarbon is retained and does not break up on treatment with aqueous solutions of KCN or KSCN. This behaviour is typical of a π-allylic but not of an olefinic complex. By treating compound (I) and its derivatives with $NaBH_4$, cyclododecane is quantitatively obtained.

When L is a mono-dentate amine (*e.g.*, *p*-toluidine) the reaction may be described as:

$$(C_{12}H_{19}RhCl_2)_n + nL \longrightarrow \frac{n}{2}\,(C_{12}H_{19}RhCl_2L)_2 \qquad (2)$$

and

$$(C_{12}H_{19}RhCl_2L)_2 + 2\,L \rightleftharpoons 2\,C_{12}H_{19}RhCl_2\,L_2 \qquad (3)$$

---

* In a preliminary note[7] the compound was reported as π-cyclododeca-1,5,9-trienylrhodium(III) dichloride, $C_{12}H_{17}RhCl_2$.

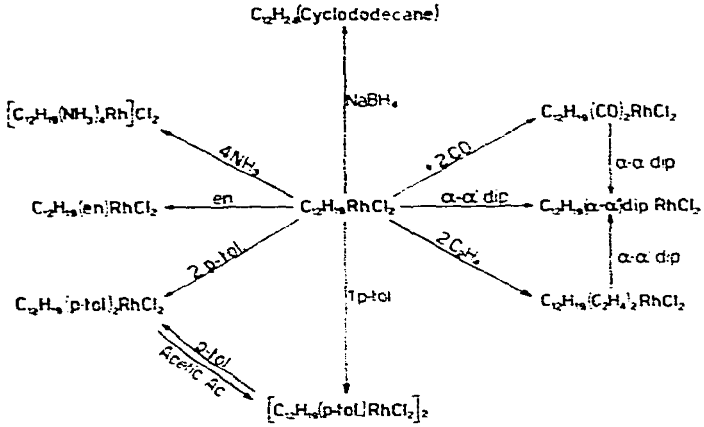

Fig. 1. Reactions of dichlorocyclododeca-1,5-dienylrhodium(III).

Reaction (3), is displaced to the left in diluted solutions or by the action of acids. This enables the dimer to be isolated as a crystalline sparingly soluble compound.

When B is a bidentate base (*e.g.*, ethylenediamine, 2,2'-bipyridine, 1-3-butadiene, etc.) the reaction is:

$$(C_{12}H_{19}RhCl_2)_n + n\,B \longrightarrow n\,C_{12}H_{19}RhCl_2B \qquad (4)$$

The resultant compounds are very stable. Reactions (2), (3) and (4) suggest that the insoluble compound (I), has a polymeric structure with chlorine bridges which are split by the bases. It may be supposed that in (I), each rhodium atom is bonded to four halogen atoms; thus an octahedral configuration arises, with an edge occupied by the olefin, as shown in Fig. 2.

Compound (I) and all its derivatives are in fact diamagnetic. By consideration of the valence bond structure along elementary lines, it is easy to envisage the attain-

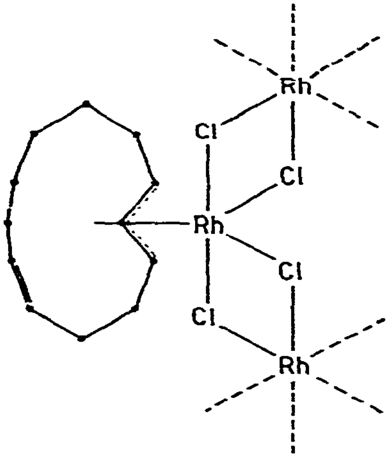

Fig. 2. Configuration of dichlorocyclododeca-1,5-dienylrhodium(III)

ment of the configuration of the inert gas xenon, by the rhodium atom in the structure postulated for (I) and its derivatives.

Complete proof of the π-allylic nature of the complex has been achieved by an X-ray determination of the structure of the derivative, *trans*-dichloro(ethylenediamine)(cyclododeca-1,5-dienyl)rhodium(III), $(C_{12}H_{19})(C_2H_8N_2)RhCl_2$, which will be described later.

STRUCTURAL CHARACTERIZATION BY PHYSICAL METHODS

The presence of the allylic bond between rhodium and the olefin has been definitely proved by X-ray analysis.

IR and NMR data are also consistent with a π-allylic formulation of the bond between CDT and Rh; furthermore, they give some indication of the presence in the derivatives of (I), of a non-coordinated double bond in the C_{12} ring.

(1) *X-ray studies*

Weissenberg photographs have been taken with CuKα radiation on single crystals of *trans*-dichloro(ethylenediamine)(cyclododeca-1,5-dienyl)rhodium(III) previously shaped to optimum sizes.

The unit cell parameters are:

$a = 12.63 \pm 0.03$ Å; $b = 15.69 \pm 0.04$ Å; $c = 8.96 \pm 0.02$ Å.

In accordance with the fact that $Z = 4$ (X-ray density, 1.49 g/cm^3; experimental, 1.48 g/cm^3) the space group is $P\,b\,c\,2_1$.

By means of Patterson syntheses on (001) and (100) the coordinates of Rh and Cl atoms have been found:

	x/a	y/b	z/c
Rh	0.085	0.116	0.250
1-Cl	0.085	0.116	0.010
2-Cl	0.085	0.116	0.490

From these figures most of the phases were assigned to the *hk*0 reflections. The corresponding electron density projection on (001) is shown in Fig. 3. Rh and Cl atoms, having approximately the same x and y coordinates, give rise to a single maximum. This proves that the chlorine atoms are *trans*-coordinated with respect to the rhodium atom.

Almost all the light atoms appear well-resolved in the projection; in particular, the atoms of the cyclic olefin lie approximately in a plane perpendicular to c. Three atoms of the cyclic olefin are at about the same distance from the rhodium atom, thus providing good evidence of the existence of a π-allylic bond, the system of the three allylic carbons being slightly inclined as found also by OBERHANSLI AND DAHL[8] in $[(C_3H_5)PdCl]_2$.

The (100) electron density projection has also been made with phases determined by Rh and Cl atoms only. Although this introduces a plane of symmetry arbitrarily

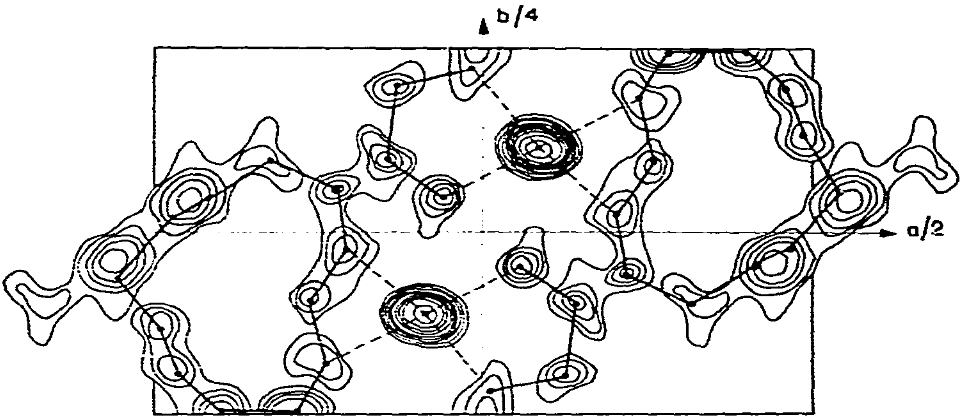

Fig. 3. Electron density projection of *trans*-dichloro(ethylenediamine)(cyclododeca-1,5-dienyl)-rhodium(III).

in the projection, it nevertheless provides confirmation of the structure resulting from the (001) projection.

(2) *IR spectra*

The more important IR absorption frequencies of each compound are reported in the experimental section of this paper. Besides the absorption of the particular basic coordinated ligands, the spectra show many typical bands which can be assigned to the coordinated cycloolefins. According to FRITZ[10], the absorption, varying with the basic ligand present in the compound, in the range 1560–1635 and the bands at 1030, 565 and 533 cm^{-1} may be assigned to the π-allylic bond.

With reference to the question (which could not be solved by X-ray diffraction) regarding the presence of residual double bonds around the ring, there exists some evidence of the presence of: (*i*) a $(CH_2)_n$ sequence (absorption at 720 cm^{-1} due to rocking vibrations when $n \geqslant 4$ and absorption at 1460 cm^{-1} due to bending vibration of the paraffinic CH_2); (*ii*) a *trans* –CH=CH– bond (strong absorption at 972 cm^{-1}, which appears in all the complexes, due to out-of-place CH deformation of HC=CH *trans* group)[11].

(3) *NMR studies*

The derivatives of (I) with ethylenediamine and *p*-toluidine are too insoluble for NMR measurements. The spectra are very complex and accompanied by much noise.

The NMR spectrum of the carbonyl derivative, $C_{12}H_{19}$ $RhCl_2(CO)_2$, dissolved in $CDCl_3$ plus dimethyl sulfoxide-d_6 (20 %), in which it is sufficiently soluble, shows three different regions of resonance due to protons.

Chemical shifts (δ) are in ppm at the low field side of $SiMe_4$ as the internal standard. The spectrum was measured at 100 Mc/sec and integrated.

The nineteen protons obtained from the intensity measurement of the peaks give a multiplet at δ 5.5 (three protons), a triplet at δ 4.3 (two protons) and a set of multiplet from δ 0.7–3.0 (fourteen protons). This spectrum agrees with the molecular structure for the cyclic olefin, containing a π-allylic and an olefinic double bond, which we propose for this compound (Fig. 2).

DISCUSSION OF A POSSIBLE MECHANISM OF FORMATION OF (I)

Compound (I) is prepared in ethanol according to reaction (1) and the alcohol clearly behaves as a reducing agent since it is transformed to acetaldehyde, one mole of aldehyde being formed for each mole of (I) (see experimental section). We suppose that, in this reaction, rhodium hydride is formed as an intermediate which leads to the formation of the π-allylic bond. Rhodium hydride, the formation[12] of which in ethanol may be schematically represented as

$$CH_3CH_2OH + RhCl_3 \longrightarrow HRhCl_2 + HCl + CH_3CHO \qquad (5)$$

has been isolated from the reaction between $RhCl_3$ and ethanol in the presence of phosphines and hypophosphorous acid[13-14].

It is possible that compound (I) is formed through isomerization of *t,t,t*CDT by means of a reversible nucleophilic attack on the olefinic bond by the hydride according to the mechanisms proposed recently by several authors[15-18].

The allylic bond forms when the hydride adds to a conjugated double bond formed in the preceding isomerization, as in the reaction between $HCo(CO)_4$ and 1,3-butadiene[19].

EXPERIMENTAL

Melting points were carried out on a Kofler hot plate. Infrared spectra were recorded by a Beckman I.R. 9 Spectrophotometer. Some of the elemental analyses were performed on samples carefully dried at 0.1 mm in this laboratory and the others in the Mikroanalytisches Laboratorium of the Max-Planck Institut, Mülheim. Solvents were of analytical grade.

$RhCl_3 \cdot 3H_2O$ was purchased from Fluka and *t,t,t*,CDT, was kindly supplied by the Montecatini Co. of Milan.

Dichloro(cyclododeca-1,5-dienyl)rhodium(III) $C_{12}H_{19}RhCl_2$, *(I)*

In a typical preparation, a solution of rhodium trichloride trihydrate (2 g) and *t,t,t*,CDT (1.27 g) in ethanol (40 ml) was refluxed in a nitrogen atmosphere for 4 h. The resultant red precipitate was filtered off, washed with ethanol, and finally with benzene and dried (2.2 g, yield 84 %), m.p. 219–222° (decomp.). The mother liquor was strongly acidic. (Found: C, 42.53, 42.67; H, 5.58, 5.79; Cl, 20.87, 21.05; Rh, 30.53, 30.44. $C_{12}H_{19}Cl_2Rh$ calcd.: C, 42.75; H, 5.68; Cl, 21.03; Rh, 30.52 %.)

The infrared spectrum (mull in nujol and hexachlorobutadiene) shows absorptions at 3018 (w), 2939 (s), 2913 (w), 2863 (w), 2853 (m), 1534 (m), 1461 (m), 1441 (m), 1345 (m), 1255 (w), 1176 (w), 1035 (m), 974 (s), 718 (w), 565 (w), 523 (w).

This product may also be prepared in isopropyl alcohol or *tert*-butyl alcohol; in methanol or cyclohexanol we observed the formation of a rhodium mirror. The acetaldehyde formed in the reaction was determined by reacting 0.20 g of $RhCl_3 \cdot 3H_2O$ with 0.126 g of di-*t,t,t*,CDT in 10 ml of ethanol at 80° in a closed vessel. At the end of the reaction the mixture was distilled into a solution of 2,4-dinitrophenylhydrazine (0.84 g) in 2 N HCl, prepared according to Iddless and Jackson[20]. The residue of the distillation after recovering, washing and drying was 0.210 g. Acetaldehyde 2,4-dinitrophenylhydrazone, 0.125 g, yield 88 % calcd. on (I), was isolated and recrystallized from ethanol. It was identified by an IR spectrum[21] and an X-ray diffraction pattern[22].

Bis[chloro(p-toluidine)(cyclododeca-1,5-dienyl)dichlororhodium(III)], $[(C_{12}H_{19})(C_7H_9N)RhCl_2]_2$

p-Toluidine (109 mg) dissolved in methylene chloride (10 ml), was added dropwise to a suspension of $C_{12}H_{19}RhCl_2$ (344 mg) in the same solvent (10 ml). The mixture was filtered and evaporated in *vacuo*. After the removal of solvent, the residual red oil was dissolved again in acetic acid and a pale-yellow solid precipitated, m.p. 158–160° (decomp.). (Found: C, 50.18; H, 6.12; N, 3.18; Cl, 16.23. $C_{19}H_{28}Cl_2NRh$ calcd.: C, 51.37; H, 6.35; N, 3.15; Cl, 15.96 %.)

The same product is obtained by crystallization from acetic acid or carbon tetrachloride solution of dichloro(bis-*p*-toluidine)(cyclododeca-1,5-dienyl)rhodium (III).

The infrared spectrum (KBr disc) shows absorptions at: 3300 (m), 3082 (m), 2946 (s), 2850 (m), 1581 (m), 1514 (s), 1460 (s), 1440 (m), 1385 (w), 1345 (w), 1250 (w), 1190 (m), 1176 (w), 1135 (m), 1040 (m), 975 (s), 821 (s), 715 (w), 563 (w), 552 (w).

Dichloro(bis-p-toluidine)(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(C_7H_9N)_2RhCl_2$

A suspension of $C_{12}H_{19}RhCl_2$ (344 mg) in dry benzene (30 ml) was treated with *p*-toluidine (224 mg) at room temperature. The red solution was evaporated *in vacuo*. The oily residue, after washing with light petroleum, gave an orange-red amorphous compound. (Found: C, 55.27; H, 6.52; Cl, 13.45; N, 5.26. $C_{26}H_{37}Cl_2N_2Rh$ calcd.: C, 56.63; H, 6.70; Cl, 12.85; N, 5.08 %.)

The infrared spectrum (KBr disc) shows absorptions at: 3260 (w), 3130 (w), 3030 (w). 2940 (s), 2868 (m), 1590 (m), 1517 (s), 1461 (m), 1443 (m), 1381 (w), 1260 (w), 1244 (w), 1190 (w), 1107 (w), 1031 (m), 975 (s), 817 (s), 742 (w), 712 (w), 555 (w), 530 (m)

trans-Dichloro(ethylenediamine)(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(C_2H_8N_2)RhCl_2$

A suspension of $C_{12}H_{19}RhCl_2$ (200 mg) in benzene (10 ml), under nitrogen, was treated with ethylenediamine (0.2 ml). The mixture was stirred at room temperature for 10 min and then evaporated to dryness. The resulting yellow residue was crystallized from toluene, m.p. 193-195° (decomp.). (Found: C, 42.49; H, 6.74; Cl, 17.75; N, 7.21. $C_{14}H_{27}Cl_2N_2Rh$ calcd.: C, 42.33; H, 6.85; Cl, 17.85; N, 7.05 %.)

Infrared spectrum (KBr disc) shows absorptions at: 3300 (m), 3252 (s), 3158 (m), 3020 (w), 2936 (s), 2854 (m), 1584 (s), 1460 (m), 1451 (s), 1395 (w), 1368 (w), 1345 (w), 1317 (w), 1255 (w), 1190 (w), 1178 (w), 1133 (m), 1034 (s), 971 (s), 859 (m), 720 (m), 524 (w), 464 (w), 436 (w).

trans-Dichloro(2,2′-bipyridine)(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(C_{10}H_8N_2)RhCl_2$

A solution of 2,2′-bipyridine (156 mg) in methylene chloride (10 ml) was added dropwise to a suspension of $C_{12}H_{19}RhCl_2$ (336 mg) in CH_2Cl_2 (50 ml). The mixture was stirred at room temperature for 30 min, evaporated to dryness and the resulting yellow residue crystallized from xylene, m.p. 210° (decomp.). $C_{12}H_{19}(C_{10}H_8N_2)RhCl_2$ can also be obtained by displacing ethylene, butadiene or carbon monoxide from the related compounds in benzene (see later). The sparingly soluble compound was recognized by X-ray powder spectrum. (Found: C, 54.26; H, 5.83; Cl, 13.87; N, 5.72. $C_{22}H_{27}Cl_2N_2Rh$ calcd.: C, 53.56; H, 5.51; Cl, 14.37; N, 5.68%.)

The infrared spectrum (KBr disc) shows absorptions at: 3110 (w), 3081 (w), 3030 (w), 2980 (w), 2929 (s), 2860 (m), 1602 (s), 1576 (w), 1566 (w), 1490 (m), 1470 (m), 1460 (w), 1446 (s), 1350 (w), 1310 (m), 1250 (m), 1195 (w), 1172 (w), 1157 (w), 1107 (w), 1074 (w), 1059 (w), 1044 (w), 1030 (m), 974 (m), 766 (s), 732 (m), 660 (w), 645 (w), 560 (w), 530 (w).

The unit cell parameters determined on a single crystal (not dried *in vacuo*) with usual Weissenberg methods using CuKα radiation are $a = 11.61 \pm 0.03$, $b = 16.18 \pm 0.05$, $c = 16.81 \pm 0.05$ Å, $\beta = 127° \pm 30'$; the space group is $P\ 2_1/c$. The experimental density of 1.55 g/ml is consistent with an X-ray density of 1.56 g/ml calculated for a 1:1 clathrate with xylene. From the Fourier syntheses on (010) and (100), the chlorine atoms appear to be *trans*-coordinated to the rhodium atom.

Dichlorodicarbonyl(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(CO)_2RhCl_2$

A suspension of $C_{12}H_{19}RhCl_2$ (450 mg) in dry benzene (20 ml) was stirred in a carbon monoxide atmosphere for 2 h. The orange-coloured mixture was filtered and evaporated to dryness *in vacuo* at 20°. The orange-coloured residue was crystallized from toluene (133 mg of yellow product), m.p. 139–141° (decomp.). (Found: C, 43.01; H, 5.05; Cl, 18.67; Rh, 27.30. $C_{14}H_{19}Cl_2O_2Rh$ calcd.: C, 42.77; H, 4.87; Cl, 18.03; Rh, 26.17%.)

The infrared spectrum (KBr disc) shows absorptions at: 3020 (w), 2938 (s), 2860 (m), 2060 (vs), 2010 (m), 1535 (m), 1460 (m), 1450 (m), 1400 (m), 1348 (w), 1250 (w), 1190 (w), 1173 (m), 1080 (w), 1050 (w), 978 (s), 920 (w), 860 (m), 840 (w), 825 (w), 800 (w), 732 (w), 720 (m), 698 (w), 600 (w), 562 (w), 528 (m), 510 (m), 498 (m).

Dichloro(bisethylene)(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(C_2H_4)_2RhCl_2$

A suspension of $C_{12}H_{19}RhCl_2$ (290 mg) in dry benzene (20 ml) was stirred overnight in an atmosphere of ethylene at room temperature. The mixture was filtered and evaporated to dryness. The solid residue was washed with light-petroleum and yielded an amorphous solid. (Found: Cl, 20.35; Rh, 29.30. $C_{14}H_{23}Cl_2Rh$ calcd.: Cl, 19.42; Rh, 28.18%.)

The infrared spectrum (KBr disc) shows absorptions at: 3030 (w), 2930 (s), 2850 (s), 2076 (w), 2010 (w), 1548 (w), 1537 (w), 1447 (m), 1435 (w), 1360 (w), 1175 (m), 1124 (w), 1082 (w), 1046 (m), 973 (s), 951 (w), 912 (w), 870 (w), 824 (w), 762 (w), 719 (m), 564 (w), 525 (w).

trans-Dichloro(1,3-butadiene)(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(C_4H_6)RhCl_2$

1,3-Butadiene was added to a suspension of $C_{12}H_{19}RhCl_2$ (500 mg) in dry benzene (30 ml) at room temperature. The solid dissolved in a few minutes. The resulting solution was filtered and evaporated to yield an amorphous solid, which was washed with light petroleum. (Found: Cl, 19.32; Rh, 27.10. $C_{16}H_{25}RhCl_2$ calcd.: Cl, 18.12; Rh, 26.30%.)

The infrared spectrum (KBr disc) shows absorptions at: 3030 (w), 2940 (s), 2864 (s), 2070 (w), 2000 (w), 1533 (m), 1463 (m), 1433 (m), 1346 (w), 1255 (w), 1190 (w), 1177 (w), 1034 (m), 974 (s), 870 (w), 719 (m).

Dichlorotetraammine(cyclododeca-1,5-dienyl)rhodium(III), $C_{12}H_{19}(NH_3)_4RhCl_2$

A few drops of aqueous ammonia were added to a suspension of $C_{12}H_{19}RhCl_2$ in water. The mixture was shaken until all the solid had dissolved and the resulting solution was evaporated to dryness. The residue was dissolved in ethanol and precipitated with diethyl ether. (Found: Cl, 18.32; Rh, 24.67. $C_{12}H_{31}Cl_2N_4Rh$ calcd.: Cl, 17.55; Rh, 25.42 %.)

Conductivity measurements. The molar conduction was 259 $\Omega^{-1}\cdot cm^2$ at 25° and a concentration of 10^{-3} *M*.

Reduction with sodium borohydride

A suspension of $C_{12}H_{19}RhCl_2$ (150 mg) was solubilized in THF with the stoichiometric amount of *p*-toluidine (96 mg), and $NaBH_4$ (0.5 g) was added with stirring. Metallic rhodium precipitated. The mixture was acidified with dilute sulfuric acid and extracted with ether. The ether extracts were washed with $NaHCO_3$, dried over anhydrous $CuSO_4$, filtered and evaporated *in vacuo*. The resulting residue was crystallized from ethyl acetate, m.p. 61°. The IR spectrum was identical to that of an authentic sample of cyclododecane.

ACKNOWLEDGEMENTS

We thank Prof. RENATO CINI of Florence University for magnetic measurement and Dr. A. MELLERA of Varian A.G. of Zürich for NMR spectra. We are indebted to Prof. PAOLO CORRADINI for many helpful discussions and for critical reading of the manuscript.

SUMMARY

The reaction of rhodium trichloride trihydrate and *trans,trans,trans*-1,5,9-cyclododecatriene in boiling ethanol yields the red, diamagnetic dichloro(cyclododeca-1,5-dienyl)rhodium(III), insoluble in all common organic solvents.

This compound is polymeric through chlorine bridges and reacts with many Lewis bases (*e.g.*, carbon monoxide, amines, olefins) to give octahedral derivatives such as $C_{12}H_{19}RhCl_2B_2$ (B is a monodentate basic ligand).

The chemical and structural characterization of this compound is reported through a study of its derivatives by X-rays, IR and NMR spectra and a possible mechanism is proposed.

REFERENCES

1 R. G. GUY AND B. L. SHAW, in H. J. EMELÉUS AND A. G. SHARPE, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 4, Academic Press, New York, 1962, pp. 77–131.
2 M. A. BENNETT, *Chem. Rev.*, 62 (1962) 611.
3 R. CRAMER, *Inorg. Chem.*, 1 (1962) 722.
4 M. L. H. GREEN, L. PRATT AND G. WILKINSON, *J. Chem. Soc.*, (1959) 3753.
5 R. J. ANGELICI AND E. O. FISCHER, *J. Am. Chem. Soc.*, 85 (1963) 3733.
6 M. L. H. GREEN AND P. L. I. NAGY, in F. G. A. STONE AND R. WEST, *Advances in Organometallic Chemistry*, Vol. 2, Academic Press, New York, 1964, pp. 325–363.
7 G. PAIARO AND R. PALUMBO, *Angew. Chem. Intern. Ed.*, 2 (1963) 620.
8 W. E. OBERHANSLI AND L. F. DAHL, *J. Organometal. Chem.*, 3 (1965) 43.
9 F. AMBROSINO, N. NETO AND S. CALIFANO, *Spectrochim. Acta*, 21 (1965) 409.

10 H. P. Fritz, *Chem. Ber.*, 94 (1961) 1217.
11 L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen, London, 1962, chap. 3.
12 J. Chatt, B. L. Shaw and A. E. Field, *J Chem. Soc.*, (1964) 3466.
13 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1962) 5075.
14 A. Sacco and R. Ugo, *Chim. Ind.* (*Milan*), 45 (1963) 1096.
15 R. F. Heck and D. Breslow, *J. Am. Chem. Soc.*, 83 (1961) 4023.
16 M. Orchin and G. L. Karapinka, *J. Org. Chem.*, 26 (1961) 4187.
17 I. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, 86 (1964) 1776.
18 I. F. Harrod and A. J. Chalk, *Nature*, 205 (1965) 280.
19 H. B. Jonassen, R. I. Steans, J. Kenttämaa, D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, 80 (1958) 2586.
20 H. A. Iddlis and C. E. Jackson, *Anal. Chem.*, 6 (1934) 454.
21 J. H. Ross, *Anal. Chem.*, 25 (1953) 1288.
22 G. L. Clark, W. I. Kaye and T. D. Park, *Anal. Chem.*, 18 (1946) 310.