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# π-COMPLEXES OF *cis,cis*-1,4-CYCLONONADIENE

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## SUMMARY

The syntheses and spectral properties of the *cis,cis*-1,4-cyclononadiene π-complexes of copper(I), palladium(II) and platinum(II) are described. The diene does not give an isolable silver(I) complex. The attempted rhodium(I) complex formation of the diene gives the rhodium(I) complex of *cis,cis*-1,5-cyclononadiene.

## INTRODUCTION

Our studies of the chemistry of the medium-ring diene, *cis,cis*-1,5-cyclononadiene[1–4] prompted us to examine the chemistry of the isomeric diene, *cis,cis*-1,4-cyclononadiene, in order to establish the similarities and differences in their chemical behaviour. No study has previously been reported on the π-complexes of a medium-ring 1,4-diene with various transition metals in their low oxidation state but it is known that a 1/2 adduct is formed between *cis,cis*-1,4-cyclooctadiene and silver(I) nitrate[5]. The present work deals with the syntheses and spectral properties of copper(I), palladium(II) and platinum(II) complexes of *cis,cis*-1,4-cyclononadiene, and the ready isomerization of *cis,cis*-1,4-cyclononadiene to *cis,cis*-1,5-cyclononadiene during rhodium(I) complex formation.

## RESULTS AND DISCUSSION

The 1/2 diene–copper(I) chloride was prepared by modification of the procedure desribed by Haight *et al.*[6]. The complex dissociates under vacuum, and slowly at room temperature when exposed to air; this dissociation increases with rise in temperature. The IR spectrum shows a weak band at 1615 $cm^{-1}$ which has been assigned to the complexed diene double bond stretching. In view of this and the insolubility of the complex, we feel that a polymeric structure is more likely for this complex.

Our attempts to prepare the diene–silver(I) nitrate complex by treatment of the diene with aqueous silver nitrate of different concentrations under various conditions were not successful.

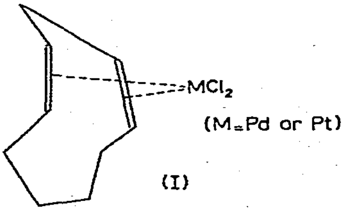
The orange-yellow diene–palladium complex was prepared by stirring a benzene solution of bis(benzonitrile)palladium(II) chloride with a slight excess of diene at room temperature[7]; it decomposes above 150° without melting.

The orange diene–platinum complex was prepared by modification of one of the methods recommended by Chatt[8]; it was precipitated when a 2 *N* acetic acid solution of potassium tetrachloroplatinate(II) was stirred with a slight excess of the diene; this complex also decomposes above 150° without melting.

Analyses showed that in each case one molecule of the diene is complexed with one molecule of $MCl_2$ (M = Pd or Pt).

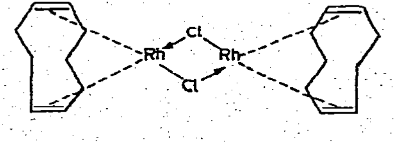
Both the palladium and platinum complexes were found to be quite stable, and could be vacuum-dried over Drierite without appreciable change in the elemental analysis. They are insoluble in most of the common organic solvents, but dissolve in dimethyl sulfoxide with immediate decomposition. The NMR spectra of both the complexes recorded in dimethyl sulfoxide-$d_6$ were identical to that of the original diene, which shows that the diene does not undergo any isomerization during complexation. The infrared spectra of the $Pd^{II}$– and $Pt^{II}$–diene complexes are very similar. The carbon–carbon double bond frequencies between 1580–1650 $cm^{-1}$ are absent, the new strong bands appear at 1495 and 1510 $cm^{-1}$ and can be assigned to coordinated double bonds.

No exact structures can be assigned to the complexes because neither other spectra, such as NMR, nor molecular weights could be studied because of the insolubility of the compounds, but it is likely that they have structures similar to that proposed for the *cis,cis*-1,5-cyclononadiene–platinum(II) or palladium(II) complex[2]. Molecular models of *cis,cis*-1,4-cyclononadiene show that the two double bonds are capable of coming closer to each other in the conformation shown in (I).



(I)

Following Chatt's procedure[9], an orange coloured rhodium(I)–diene complex of 1/1 stoichiometry was prepared. The complex could be dried under vacuum, and was found to be easily soluble in common organic solvents like chloroform, carbon tetrachloride, benzene, and hexane. The IR spectrum of the complex does not show carbon–carbon double bond absorption band(s) between 1600–1675 $cm^{-1}$, indicating a strong interaction of the rhodium(I) with the olefin double bonds. The NMR spectrum of the rhodium(I)–diene complex was identical in all respects with the rhodium(I)–*cis,cis*-1,5-cyclononadiene complex[1]. Hence the complex was decomposed with aqueous potassium cyanide, and the displaced diene was identified as *cis,cis*-1,5-cyclononadiene by IR spectroscopy and vapour phase chromatography in conjunction with an authentic sample. Molecular weight determination and elemental analysis indicated that the rhodium(I) complex was a dimer, (II), with 1/1 stoichiometry.



(II)

The reactions of *cis,cis*-1,4-cyclononadiene with bis(benzonitrile)palladium(II) chloride and potassium tetrachloroplatinate(II) correspond with those observed in the investigations involving *cis,cis*-1,5-cyclooctadiene[10,11], *cis,cis*-1,5-cyclononadiene[2] and *cis,cis*-1,6-cyclodecadiene[12]. However, it has been shown very recently that 1,3-cyclooctadiene reacts with bis(benzonitrile)palladium(II) chloride to give a mixture of 1,5-cyclooctadiene–palladium(II) chloride complex and 1,4-cyclooctadiene–palladium(II) chloride complex, whereas with platinum(II) only the 1,5-cyclooctadiene complex is formed. On the basis of these facts, it has been concluded that 1,4-cyclooctadiene is involved in the rearrangement of 1,3- to the 1,5-diene[14]. Our findings show that $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$ complexes of *cis,cis*-1,4-cyclononadiene are much more stable than the corresponding $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$ complexes of 1,4-cyclooctadiene. This difference in behaviour may be attributed to the difference in size.

The observed rhodium catalysed isomerization of *cis,cis*-1,4-cyclononadiene to *cis,cis*-1,5-cyclononadiene is not unexpected, since isomerizations are well documented in eight-membered dienes[15–17]. However, the mechanism of such reactions is extremely complex, and several reaction paths can coexist under a given set of conditions. More recently it has been shown that π-allylic complexes are intermediates in at least some cases[17]. Since the NMR spectra of the rhodium(I) complex formed from *cis,cis*-1,4-cyclononadiene and rhodium(I)–*cis,cis*-1,5-cyclononadiene complex are identical, we conclude that no isomerization is occurring during the displacement reaction. Our results reveal the differences in behaviour between isomeric 1,4- and 1,5-dienes in nine-membered rings with transition metal ions such as silver(I), copper(I), palladium(II), platinum(II) and rhodium(I).

A study on the metal–1,3-cyclononadiene complexes is in progress, and will be described later.

## EXPERIMENTAL

### *General*

The *cis,cis*-1,4-cyclononadiene was synthesized by a three-step sequence starting from *cis,cis*-1,3-cyclooctadiene[18,19]. Its reaction with bromoform and potassium tert-butoxide afforded 9,9-dibromobicyclo[6.1.0]non-2-ene, which was reduced with sodium–ammonia to give bicyclo[6.1.0]non-2-ene. Its thermal isomerization afforded *cis,cis*-1,4-cyclononadiene, the properties of which were in agreement with those reported in the literature[19]. The *cis,cis*-1,3-cyclooctadiene was obtained from the Columbia Carbon Co., Lake Charles Chemical Research Center, Lake Charles, Louisiana, U.S.A. The salts used were B.D.H. reagent grade copper(II) chloride dihydrate, Fischer Scientific Co. rhodium(III) chloride trihydrate, palladium(II) chloride and potassium tetrachloroplatinate(II). Bis(benzonitrile)palladium(II) chloride was prepared by Kharasch's method[20].

Elemental analyses were performed by A. H. Siddiqui, microanalyst, of this department.

Melting points are uncorrected. The IR absorption spectra were obtained on a Perkin–Elmer Model 521 spectrophotometer equipped with a linear wavelength scale and chloride optics. Vapour phase chromatographic analyses were made with an Aerograph Model 90P instrument using a 15 ft. by $\frac{1}{4}$ in. Carbowax 20M column.

*Preparation of copper(I) complex*

To a stirred solution of 270 mg (1.6 mmol) of copper(II) chloride dihydrate in 5 ml of absolute ethanol was added 270 mg (1.5 mmol) of *cis,cis*-1,4-cyclononadiene. Sulphur dioxide gas was passed in carefully until the green colour disappeared. On standing for about 2 h the complex precipitated slowly as a white solid. This was allowed to stand overnight. The complex was filtered off, and washed with absolute ethanol and then with a minimum quantity of cold pentane to remove unreacted diene (yield of 1/2 complex 220 mg). (Found: C, 32.94; H, 4.10. $C_9H_{14}Cl_2Cu_2$ calcd.: C, 33.75; H, 4.35%.) The crystals of the complex collapse at 140°. It decomposes even at room temperature, and releases the diene as the temperature is raised. It is insoluble in most of the common organic solvents.

*Preparation of palladium(II) complex*

Bis(benzonitrile)palladium(II) chloride (740 mg, 2 mmol) was dissolved in benzene and *cis,cis*-1,4-cyclononadiene (244 mg, 2 mmol) was added. The diene–palladium(II) chloride complex precipitated out. After standing overnight, the complex was filtered off, washed with benzene and dried over Drierite (yield of 1/1 complex 500 mg). (Found: C, 35.80; H, 4.70. $C_9H_{14}Cl_2Pd$ calcd.: C, 36.08; H, 4.67%.) The complex blackens at about 150°, and decomposes without melting. It is insoluble in common organic solvents.

*Preparation of platinum(II) complex*

The diene (183 mg, 1.5 mmol) was added to a solution of potassium tetrachloroplatinate (360 mg, 0.75 mmol) in dilute acetic acid (2 *N*). The solution was stirred at room temperature when a light-orange complex precipitated out. This was filtered off and washed with absolute ethanol followed by a minimum quantity of dry pentane (yield of the complex 280 mg). (Found: C, 28.46; H, 3.80. $C_9H_{14}Cl_2Pt$ calcd.: C, 27.83; H, 3.60%.) It decomposes above 150° without melting. It is insoluble in most common solvents.

*Preparation of rhodium(I) complex*

*cis,cis*-1,4-Cyclononadiene (366 mg, 3 mmol) was added to a solution of rhodium(III) chloride trihydrate (250 mg, 1 mmol) in 10 ml of 95% ethanol, and the solution was refluxed for 1 h. The complex precipitated as an orange solid which was filtered, washed with 5 ml of cold absolute ethanol and dried over Drierite (yield of 1/1 complex 200 mg). (Found: C, 42.00; H, 5.38. $C_9H_{14}ClRh$ calcd.: C, 41.60; H, 5.41%.) The complex darkens at 220° and decomposes without melting at 241°.

*Olefin-displacement reaction*

A 0.2 g sample of each complex was stirred in a solution of 0.5 g of potassium cyanide in 5 ml of water in presence of 5 ml A.R. carbon tetrachloride until the complex disappeared. After stirring for 1 h more, the carbon tetrachloride layer was separated, washed with water and dried over anhydrous magnesium sulphate. No isomerization was observed in the case of copper(I) or palladium(II) or platinum(II) complex. However, in the case of the rhodium(I) complex *cis,cis*-1,5-cyclononadiene was identified in the residue by comparison of the IR spectra and GLC retention times on a carbowax–silver initrate column with those of an authentic sample.

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## REFERENCES

1 G. Nagendrappa and D. Devaprabhakara, *J. Organometal. Chem.*, 15 (1968) 225.
2 G. Nagendrappa and D. Devaprabhakara, *J. Organometal. Chem.*, 17 (1969) 182.
3 G. Nagendrappa and D. Devaprabhakara, *Tetrahdron Lett.*, (1970) 4687.
4 I. Mehrotra and D. Devaprabhakara, *Tetrahedron Lett.*, (1970) 4493.
5 W. O. Jones, *J. Chem. Soc.*, (1954) 312.
6 *i*. L. Haight, J. R. Doyle, N. C. Baenziger and G. F. Richards, *Inorg. Chem.*, 2 (1963) 1301.
7 M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Amer. Chem. Soc.*, 60 (1938) 882.
8 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, (1955) 2787.
9 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, (1957) 4735.
10 J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, (1957) 2596.
11 J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, (1957) 3413.
12 J. C. Trebellas, J. R. Olechowski and H. B. Jonassen, *J. Organometal. Chem.*, 6 (1966) 412.
13 H. Frye, E. Kulijian and I. Viebrock, *Inorg. Chem.*, 4 (1965) 1495.
14 H. A. Tayim and A. Vassilian, *J. Chem. Soc. D*, (1970) 630.
15 R. E. Rinehart and J. S. Lasky, *J. Amer. Chem. Soc.*, 86 (1964) 2516.
16 S. D. Robinson and B. L. Shaw, *Tetrahedron Lett.*, (1965) 3533.
17 K. Moseley, J. W. Kang and P. M. Maitlis, *J. Chem. Soc. D*, (1969) 1155.
18 C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, M. V. Cortez and P. D. Gardner, *J. Amer. Chem. Soc.*, 87 (1965) 3158.
19 D. S. Glass, R. S. Boikess and S. Winstein, *Tetrahedron Lett.*, (1966) 999.
20 M. S. Kharash, R. C. Seyler and F. R. Mayo, *J. Amer. Chem. Soc.*, 60 (1938) 882.