

THE *cis,cis*-1,5-CYCLONONADIENE COMPLEXES OF SILVER(I), COPPER(I) AND RHODIUM(I) SALTS

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SUMMARY

The syntheses and spectral properties of *cis,cis*-1,5-cyclononadiene complexes of silver(I), copper(I) and rhodium(I) are described.

INTRODUCTION

The use of unconjugated medium size cyclic dienes as complexing agents is well-known, and several studies¹⁻¹⁵ have been reported on the complexes of *cis,cis*-1,5-cyclooctadiene, *cis,trans*-1,5-cyclodecadiene and *cis,cis*-1,6-cyclodecadiene with silver(I), copper(I), rhodium(I), gold(I), palladium(II) and platinum(II). This prompted us to study the complexes of *cis,cis*-1,5-cyclononadiene with transition metals in their low oxidation state. Such complexes are of especial interest because the molecule is asymmetric, unlike the eight or the ten-membered cyclic diene. The present work deals with the syntheses and the spectral properties of silver(I), copper(I), and rhodium(I) complexes of *cis,cis*-1,5-cyclononadiene.

RESULTS AND DISCUSSION

The 1/1 silver(I) nitrate-1,5-cyclononadiene complex was prepared by stirring the diene with 10 ml of 1 *M* aqueous silver nitrate solution. It turns black when heated to about 180° and when exposed to atmosphere for some time. The IR double bond absorption bands of *cis,cis*-1,5-cyclononadiene which appear at 1646 and 1653 cm⁻¹ are shifted to 1592 and 1602 cm⁻¹ in the silver(I) complex, which is in keeping with Dewar's concept of π -bonding in metal-olefin complexes¹⁶. These results are not sufficient for us to make any statement regarding the correct structure of the complex, which could have either a polymeric structure in which the silver ions are associated with two double bonds one from each diene molecule, or a structure wherein the silver ion is located in the centre of the diene molecule. In the latter case the diene would have to be in the boat conformation (I) for the silver ion to be bonded to both the double bonds, while in the former the diene could have either a chair or a boat conformation.

The 1/2 diene-copper(I) chloride was prepared by mixing anhydrous copper(I) chloride and the diene. The complex dissociates under vacuum, and slowly at room temperature when exposed to air; this dissociation increased 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 of the insolubility of the complex, we feel that the polymeric structure would be more likely for the diene-copper(I) chloride complex.

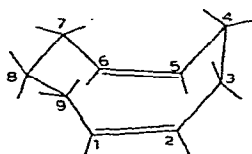
Following Chatt's procedure⁴, an orange coloured rhodium(I)-diene complex of 1/1 stoichiometry was prepared. The complex could be dried under vacuum and was found to be easily soluble in common organic solvents like chloroform, carbon tetrachloride, benzene and hexane. The IR spectrum of the complex does not show carbon-carbon double bond absorption band(s) between $1600\text{--}1675\text{ cm}^{-1}$ indicating a strong interaction of the rhodium(I) with the olefin double bonds.

TABLE 1
NMR DATA

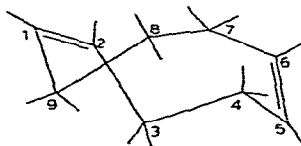
Compound	Chemical shifts (δ) (rel. TMS)		
	Olefinic ($C_{1,2,5,6}$)	Methylene ($C_{3,4,7,9}$)	Methylene (C_8)
1,5-Cyclononadiene	5.46	1.90	1.45
1,5-Cyclononadiene- -rhodium(I) complex	4.65 ($C_{1,6}$) 4.22 ($C_{2,5}$)	2.00	0.87

The NMR data of *cis,cis*-1,5-cyclononadiene and of the 1,5-diene-rhodium(I) complex are recorded in Table 1. In each spectrum the protons are clearly differentiated into olefinic and methylene types. The latter are resolved into two groups by virtue of the chemical shift difference between positions of one and two carbon atoms removed from the double bond. In the NMR spectrum of the complex the olefinic region is shifted to the higher field indicating the strong π -bonding between the diene and the rhodium. The signal due to olefinic protons in the 1,5-diene is very broad and extends from δ 5.07 to 5.88.

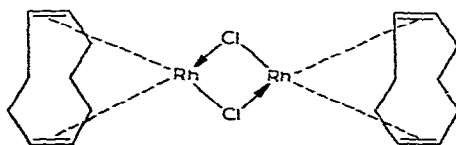
In the spectrum of the rhodium complex the olefinic proton signal has split into two peaks. One is an ill-resolved multiplet centred at δ 4.65 (two protons). The



(I)



(II)



(III)

other is an eight-line band centred at δ 4.22 (two protons). These two values strikingly compare, respectively, with the chemical shifts of the olefinic protons of the rhodium complexes of *cis,cis*-1,6-cyclodecadiene (δ 4.82)¹ and *cis,cis*-1,5-cyclooctadiene (δ 4.25)⁷. A reasonable explanation for this splitting would be that the conformation of the diolefin in the complex is fixed and the change in the chemical shifts of the protons 2,5 and 1,6 is to different extent.

Because of the asymmetry in the molecule, the equivalent protons on methylenes 3 and 4 are different from the equivalent protons on the methylenes 7 and 9. In the complex, the protons of each one of these two sets can have different spatial arrangements. Thus the olefinic proton on carbon atom 2 has spin-coupling with the proton on carbon atom 1 and two non-equivalent protons on carbon atom 3, and can give an eight-line pattern. The olefinic proton on carbon atom 5 is in identical environment. But in the case of the olefinic protons 1 and 6, the spin coupling is in greater number due to the methylene protons on carbon 8, and thus we observe an ill-resolved multiplet.

Because of the non-equivalence of the α -methylene protons, we see a much broader signal for these protons in the complex. The upfield shift of the signal due to methylene protons of carbon atom 8 from δ 1.45 to 0.87 could be due to the interaction of these protons with the rhodium atom.

Both boat (I) and chair (II) conformations of the *cis,cis*-1,5-cyclononadiene are possible. Dreiding models of these conformations indicate that the chair conformation has less steric interaction and is more flexible than boat conformation. We favour the bridge dimeric structure (III) for the 1,5-diene-rhodium complex with the 1,5-diene existing in the boat conformation on the basis of the following facts:

- (i) the complex is readily soluble in common organic solvents;
- (ii) it is known that *cis,cis*-1,5-cyclooctadiene and *cis,cis*-1,6-cyclodecadiene form similar type of rhodium(I) complexes of comparable properties.

Each of the silver(I), copper(I) and rhodium(I) complexes was decomposed with aqueous potassium cyanide. The recovered substance was identified as *cis,cis*-1,5-cyclononadiene in each case by infrared spectroscopy and vapour phase chromatography.

EXPERIMENTAL

General

The *cis,cis*-1,5-cyclononadiene was prepared in two-step synthesis starting from *cis,cis*-1,5-cyclooctadiene as described in the literature¹⁷. Its properties corresponded well with those reported. The *cis,cis*-1,5-cyclooctadiene was obtained from the Columbia Carbon Co., Lake Charles Chemical Research Center, Lake Charles, Louisiana, U.S.A. The salts used were Sarabhai Merck Company A.R. grade silver nitrate, B.D.H. reagent grade copper(II) chloride dihydrate and Fischer Scientific Co., rhodium(III) chloride trihydrate.

Elemental microanalyses were performed by A.H. Siddiqui, Microanalyst, Department of Chemistry, Indian Institute of Technology, Kanpur, India.

Melting points are uncorrected. The IR absorption spectra were obtained on a Perkin-Elmer Model 521 spectrophotometer equipped with a linear wave-length scale and sodium chloride optics. Nuclear magnetic resonance spectra were obtained

with a Varian Associates A-60 NMR spectrometer. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane. Vapour-phase chromatographic analyses were made with Aerograph Model 90P instrument using 6 ft. by $\frac{1}{4}$ inch carbowax-silver nitrate column.

Preparation of silver(I) complex

To a stirred solution of 1.70 g (10 mmole) of silver nitrate in 10 ml of water, was added 1.22 g (10 mmole) of *cis,cis*-1,5-cyclononadiene. The complex precipitated immediately as white solid. The stirring was continued for 10 min more. Then the complex was filtered, washed with water till the washings were free from silver(I) nitrate, then washed with cold absolute ethanol and dried over drierite (yield of 1/1 complex 2.2 g). (Found: C, 36.67; H, 4.89. $C_9H_{14}AgNO_3$ calcd.: C, 37.00; H, 4.82 %.) The solid blackens at 180° and melts with decomposition at 184–185°. It is insoluble in most of the common organic solvents.

Preparation of copper(I) complex

Copper(I) chloride was precipitated by passing sulphur dioxide into a solution of copper(II) chloride dihydrate. It was filtered, washed with water and then with absolute ethanol and dried in dark on drierite. 0.96 g (5 mmoles) of copper(I) chloride was thoroughly mixed with 2.44 g (20 mmoles) of *cis,cis*-1,5-cyclononadiene and allowed to stand overnight. The excess diene was removed by washing with minimum of pentane (yield of 1/2 complex 1.5 g). (Found: C, 32.94; H, 4.10. $C_9H_{14}Cl_2Cu$ calcd.: C, 33.75; H, 4.35 %.) The crystals of the complex collapse at 140°. It decomposes even at room temperature, and gives back the olefin as the temperature is raised. It was insoluble in most of the common organic solvents.

Preparation of rhodium(I) complex

A 1.22 g (10 mmole) sample of *cis,cis*-1,5-cyclononadiene was added to a solution of 0.50 g (2 mmole) rhodium(III) chloride trihydrate in 20 ml of 95 % ethanol and the solution was refluxed for 1 h. The complex precipitated as an orange solid which was filtered, washed with 10 ml cold absolute ethanol, and dried over drierite (yield of 1/1 complex 0.40 g). (Found: C, 41.74; H, 5.38. $C_9H_{14}ClRh$ calcd.: C, 41.49; H, 5.41 %.) The complex darkens at 220° and melts at 242° with decomposition.

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 water in the presence of 5 ml of 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. After as much solvent as possible had been removed, *cis,cis*-1,5-cyclononadiene was identified in the residue in each case by comparison of IR spectra and GLC retention times on a carbowax-silver nitrate column using an authentic sample.

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