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π-COMPLEXES OF SOME CYCLIC ALLENES WITH SILVER(I) AND COPPER(I)

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SUMMARY

The cyclic allenes, 1,2,6-cyclononatriene, 1,2,6-cyclodecatriene and 1,2,6,7-cyclodecatetraene form well-defined crystalline π-complexes with silver(I) nitrate and copper(I) chloride. The IR spectra of these complexes show two new bands between 1650 and 1900 cm^{-1} in place of the single allenic band around 1950 cm^{-1} present in the non-coordinated allenes.

INTRODUCTION

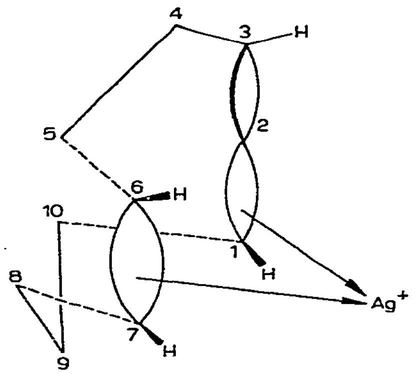
The chemistry of allene–transition metal complexes has only fairly recently attracted the attention of organometallic chemists. Most of the published work deals with structural investigation of the complexes, especially the nature of the bonding between the metal atom and the allene ligand.

In many of their reactions with transition metal salts allenes undergo insertion into metal–halogen bonds, to give π-allyl metal complexes, or dimerize to give bis-π-allyl complexes[1-3]. Iron carbonyls and low-valent platinum and rhodium complexes form simple π-olefin type of complexes[4-8]. The most interesting aspect of the metal–allene bonding is the observation made by Ben–shoshan and Pettit[9], and Vrieze and coworkers[8], that the π-bond between the allene and the metal is not fixed to one of the two allenic double bonds, but rapidly alternates from one π-molecular orbital to the next orthogonal one. This movement of the metal atom is a unimolecular process, and the complexes display unique temperature dependent NMR spectral characteristics[8,9]. The IR spectra should also give valuable information about the complexes, but have received little attention. Such spectra would be expected to show two frequencies in the carbon–carbon double bond stretching region; one for the complexed double bond and the other for the uncomplexed double bond of the allenic linkage, and our results on the 1,2,6-cyclononatriene–silver(I) nitrate complex are in accord with this[10]. To check the generality of this observation, the ideal complexes would be those involving cyclic allenes which can form complexes under very mild conditions with silver(I) and copper(I) salts, which normally do not cause any change in the basic structure of the allenes. In this paper we present our findings obtained on these lines.

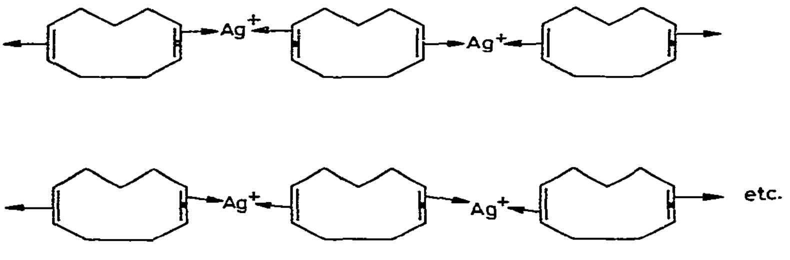
RESULTS AND DISCUSSION

All the allenes used for the present investigation were prepared by the known procedures and their identities were checked by reference to published physical and spectral properties[11,12].

Treatment of 1,2,6-cyclodecatriene with aqueous silver nitrate gave a complex with carbon and hydrogen analyses in agreement with the formula $C_{10}H_{14}\cdot AgNO_3$, showing that it is 1/1 triene–silver nitrate. The IR spectrum (nujol) of the complex consists of bands at 1905, 1745 and 1600 cm^{-1}, just like that of 1,2,6-cyclononatriene–silver nitrate complex[10]. These bands can be assigned respectively to the uncomplexed allenic double bond, the coordinated allenic double bond and the coordinated isolated double bond. These observations indicate that the 1,2,6-cyclononatriene- and 1,2,6-cyclodecatriene–silver nitrate complexes have similar structures. The complex in question may be a polymer or a monomer, and it could have any one of the structures shown in Figure 1.



Monomer



Polymers

Fig. 1.

The copper(I) chloride complex of 1,2,6-cyclodecatriene was prepared by following the procedure of Haight and coworkers[13]. The IR spectrum (nujol) has a band at 1840 cm^{-1} which can be assigned to the uncomplexed allenic double bond, and a weak absorption at 1660 cm^{-1} which can be assigned to coordinated allenic double bond. These results suggest that 1/2 1,2,6-cyclodecatriene–copper(I) chloride complex has a polymeric structure with chlorine bridging groups (Fig. 2).

We had reported earlier[10] that 1,2,6-cyclononatriene does not form copper(I) complex, when it is mixed with copper(I) chloride. However, we have now found that a modified procedure of Haight *et al.*[13] will provide the complex in question (See Experimental section). Its IR spectrum of the complex is very similar to that of 1,2,6-cyclodecatriene–copper(I) chloride complex having bands at 1845 and 1660 cm^{-1}. It may have a structure very much similar to that of the 1,2,6-cyclodecatriene–copper(I) chloride complex (Fig. 2).

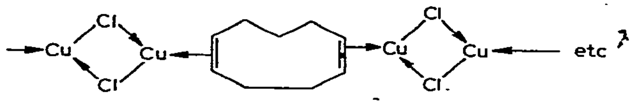


Fig. 2.

Since there is a large shift in the absorption frequencies of the allenic linkage on complexation by comparison with analogous olefin complexes, it is tempting to propose that there is more effective overlapping between the metal–allene π-bonding orbitals, bringing about a greater diminution in the allenic bond character than is usual with metal–olefin complexes. However, the extent of this is not such as to modify the basic structure of the allene molecule (*i.e.*, no isomerization takes place), since the starting allenes can be recovered unchanged on treatment with cyanide ions.

The most interesting complexes we have made in this series are those of 1,2,6,7-cyclodecatetetrane with Ag^1 and Cu^1. This allene is structurally similar to 1,5-cyclooctadiene, and has two allenic linkages, with the correct orientation for complexation, situated symmetrically in the molecule. The tetraene–$AgNO_3$ complex has the formula $C_{10}H_{12} \cdot 2\,AgNO_3$; its IR spectrum in nujol shows two bands at 1890 and 1750 cm^{-1}. The complex is soluble in alcohol, and in view of this we consider three monomeric structures (Fig. 3). In structure (I) all the allenic double bonds are involved in the π-complex formation. The formation of such a π-complex needs a twist of the π-orbitals of the allenic linkage to provide an effective overlap of the filled bonding π-orbital of the allene with the vacant orbital of the metal. One would expect that such a complex would be relatively unstable because of poor overlapping of the parallel π-orbitals from opposite sides of the tetraene with the metal orbitals, and the IR data do not favour such a structure, which would be expected to give only one absorption for the complexed allenic linkage as against the two observed. In structures (II) and (III) (Fig. 3), only one of the double bonds of each allenic linkage forms the π-complex with the silver metal atom. Such formulations are analogous to that for the 1/2 norbornadiene–Ag^I complex[14–17]. The spectral data are compatible with these structures. Since 1,2-cyclononadiene does not form a stable complex with silver[10], the stability of this diallene (1,2,6,7-cyclodecatetraene) complex may be due to the greater relief of strain by coordination. While we favour the

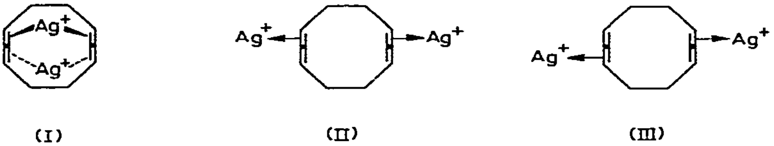
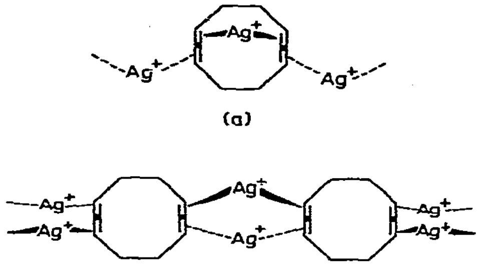
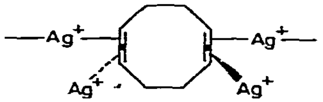


Fig. 3.

monomeric structure, there are no very strong grounds for ruling out polymeric structures, and possible polymers are depicted in Fig. 4.



(b)
Linear polymers



Three dimensional polymer

Fig. 4.

The IR spectrum of the copper(I) chloride complex of 1,2,6,7-cyclodecatetraene has bands at 1840 and 1650 cm^{-1}. By analogy with other copper(I) complexes, this tetraene complex appears to have a polymeric structure, with chlorine bridging groups (Fig. 5).

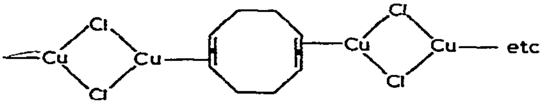


Fig. 5.

If one compares the IR spectra of the silver(I) complexes of the cyclic allenes with those of the copper(I) complexes, one observes that the copper(I) causes a larger shift in the allenic stretching frequency than does silver(I). This is in striking contrast to the observation made with other cyclic diene (*e.g.* 1,5-cyclooctadiene[18]) complexes which exhibit a larger frequency shift in the silver(I) complexes than in the copper(I) complexes. Possibly the X-ray studies would throw some light on the reasons for these differences.

EXPERIMENTAL

General

Melting points were taken in open capillaries and are uncorrected. The infrared (IR) absorption spectra were recorded on a Perkin–Elmer Model 700 spectrophotometer equipped with linear wave-number scale and sodium chloride optics. Elemental analyses were carried out in the Microanalytical Laboratory of our Department.

All the allenes used here were made from *cis,cis*-1,5-cyclooctadiene (obtained from Columbia Carbon Co., Louisiana) by known procedures, and their identities were checked by comparing their physical properties with those in the literature[11,12]. Sarabhai Merck Company A.R. grade silver nitrate and BDH Reagent Grade copper-(II) chloride dihydrate were used.

1,2,6-*Cyclodecatriene–silver(I) complex*

Cyclodecatriene (0.67 g, 5 mmoles) was shaken with solution of 1.02 g (6 mmoles) of silver nitrate in 10 ml water. A white crystalline complex separated immediately, this was filtered off, washed with water to remove silver nitrate, then washed with absolute ethanol, and dried under vacuum. The yield of the product was 1.00 g (66%). (Found: C, 39.68; H, 4.57. $C_{10}H_{14}AgNO_3$ calcd.: C, 39.47; H, 4.60%.)

The product darkens around 95° and melts at 102–103°. It is insoluble in most organic solvents. Its IR spectrum shows bands at 1905, 1745 and 1600 cm^{-1}. When the complex was treated with aqueous potassium cyanide, the recovered liquid was shown to be 1,2,6-cyclodecatriene by comparison of its IR spectrum and GLC retention times with those of an authentic specimen.

1,2,6,7-*Cyclodecatetraene–silver(I) complex*

A solution of 41 mg of 1,2,6,7-cyclodecatetraene in 5 ml of 95% ethanol was mixed with shaking with 2 ml of saturated aqueous silver nitrate solution in water. A white crystalline complex separated out on cooling. It was filtered off, washed successively with water and a small amount of absolute ethanol, and dried over Drierite. The yield was 95 mg (66%). (Found: C, 25.72; H, 2.80. $C_{10}H_{12}\cdot 2\,AgNO_3$ calcd.: C, 25.42; H, 2.54%.)

The product is stable in dark. It decomposes explosively at 150°. It is insoluble in most organic solvents, except alcohol. It was recrystallized from alcohol at room temperature. Its IR (nujol) spectrum has bands at 1880 and 1750 cm^{-1}.

1,2,6-*Cyclononatriene–copper(I) complex*

Sulphur dioxide was passed into a solution of 592 mg (5 mmoles) of 1,2,6-cyclononatriene and 696 mg (4 mmoles) of $CuCl_2\cdot 2H_2O$ in 40 ml 95% ethanol until the green colour was discharged. The solution was set aside overnight at room temperature, and white crystals separated. These were filtered off, washed with absolute ethanol and dried over Drierite. The yield of the complex was 410 mg (64%). (Found: C, 34.05; H, 3.62. $C_9H_{12}Cu_2Cl_2$ calcd.: C, 33.96; H, 3.77%.)

The product melts at 120°. It is insoluble in most of the organic solvents. Its IR spectrum (KBr) has bands at 1845, 1660 and 1550 cm^{-1}. The allene was regenerated by decomposing the complex with aqueous potassium cyanide; its IR spectrum was identical with that of authentic 1,2,6-cyclononatriene spectrum.

1,2,6-*Cyclodecatriene–copper(I) complex*

Sulphur dioxide was passed into a solution of 496 mg (3.5 mmoles) of 1,2,6-cyclodecatriene and 350 mg (2 mmoles) of $CuCl_2\cdot 2H_2O$ in 20 ml 95% ethanol, until complex precipitated out. The mixture was set aside for several hours in the refrigerator and filtered. The complex was washed 3–4 times with absolute ethanol and dried over Drierite in a vacuum desiccator. The yield of the product was 195 mg (45%). (Found:

C, 35.88; H, 4.00. $C_{10}H_{14}Cu_2Cl_2$ calcd.: C, 36.14, H, 4.21%.)

The product decomposes around 150° without melting. It is insoluble in most of the organic solvents. Its IR spectrum (nujol) of the complex has bands at 1840 and 1660 cm^{-1}, which can be respectively assigned to the stretching of the uncoordinated and coordinated allenic double bonds. The IR spectrum of the allene obtained by treating the complex with aqueous potassium cyanide was identical with that of authentic 1,2,6-cyclodecatriene.

1,2,6,7-*Cyclodecatetraene–copper(I) complex*

Sulphur dioxide was passed into a solution of 587 mg (5 mmoles) of the tetraene and 340 mg (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 20 ml 95% ethanol until a white precipitate started to separate. The mixture was then kept in the refrigerator for several hours and the solid filtered off, washed with absolute ethanol and dried over Drierite in a vacuum desiccator. The yield of the complex was 210 mg (50%). (Found: C, 35.85; H, 3.80; $C_{10}H_{12}Cu_2Cl_2$ calcd.: C, 36.36; H, 3.63%.)

The product decomposes around 100° without melting, and is insoluble in most of the organic solvents. Its IR spectrum has a band at 1840 cm^{-1}, assigned to an uncomplexed allenic bond, and a band at 1650 cm^{-1}, assigned to the complexed C=C=C stretch.

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