Fraction 5 was dried overnight under vacuum and reanalyzed.

Anal. Calcd. for $ClMgBH_4 \cdot 1.7THF$: Cl, 18.0 Mg, 12.3; B, 5.5; H, 2.0; THF, 62.2. Found: Cl, 18.5; Mg, 12.2; B, 5.2; H, 1.9; THF, 62.3.

The cryoscopic molecular weight of this sample in benzene was 445 and the dipole moment was 6.0 D. The product was identical with that prepared from Grignard and diborane.

(3) **From $MgCl_2$ and Alkali Metal Borohydrides.**—A mixture of 0.50 mole of $MgCl_2$ and 0.50 mole of $NaBH_4$ in about 700 ml. of tetrahydrofuran was refluxed for 1 week. Periodically the mixture was cooled and allowed to settle in order to allow sampling the supernatant liquid. This was analyzed so that the progress of the reaction could be followed. After 1 week the reaction had only gone to about 60% completion.

The reaction proceeds faster when KBH_4 is substituted for $NaBH_4$ but this is still not a satisfactory preparation for $ClMgBH_4$. This reaction reached 80% completion after 1 week compared to 60% for $NaBH_4$ and about 50% for the reaction of $LiBH_4$ with $MgCl_2$ in ether.

When $MgCl_2$ was allowed to react with 2 moles of KBH_4 in refluxing tetrahydrofuran, the product was a mixture of $ClMgBH_4$ and $Mg(BH_4)_2$, showing that $ClMgBH_4$ reacts further with KBH_4 to form $Mg(BH_4)_2$. Even after 10 days the amount of $Mg(BH_4)_2$ formed was only 25% of theory. It should be possible to "titrate" the product with $MgCl_2$ to form $ClMgBH_4$; however, the Grignard–diborane route to $ClMgBH_4$ is easier.

Desolvation of $ClMgBH_4 \cdot 2THF$ to $ClMgBH_4 \cdot THF$.—A 29-g. sample of $ClMgBH_4 \cdot 2THF$ was placed in a weighed round-bottom flask equipped with a stopcock. This was attached to a vacuum line and the flask was heated to 100° with an oil bath. Periodically the flask was removed from the vacuum line and weighed in order to follow the desolvation. After 5 hr. the weight loss reached 13.00 g. No more tetrahydrofuran could be removed even after an additional 15 hr.

The product was off-white in color and slightly wet or gummy in appearance.

Anal. Calcd. for $ClMgBH_4 \cdot THF$: Cl, 24.2; Mg, 16.6; B, 7.4; H, 2.7; THF, 49.2. Found: Cl, 24.0; Mg, 16.7; B, 7.1; H, 2.4; THF, 49.8.

Reaction of LiC_2H_5 with $ClMgBH_4$.—Ethyllithium (0.089 mole of 1.01 *N* benzene solution) was added to 0.089 mole of $ClMgBH_4 \cdot 2THF$ in 200 ml. of benzene. Lithium chloride precipitated immediately in quantitative yield.

The solution, then, must contain $C_2H_5MgBH_4$ or a mixture of $Mg(C_2H_5)_2$ and $Mg(BH_4)_2$. Ebullioscopic molecular weight determination showed that $C_2H_5MgBH_4$ is a monomer. This, of course, does not allow distinguishing monomeric $C_2H_5MgBH_4$ from a physical mixture of $Mg(C_2H_5)_2$ and $Mg(BH_4)_2$, both of which are monomeric also. Removal of solvent under vacuum from the solution resulted in a viscous oil which could not be crystallized.

Physical Measurements.—The cryoscopic molecular weights in benzene and the ebullioscopic molecular weights were done according to standard techniques. The solutions used contained approximately 2 wt. % of $ClMgBH_4 \cdot 2THF$. Dipole moments were determined by the dilute solution method in benzene. The dielectric constant measurements required were made with a Sargent Model V chemical oscillometer at 5 Mc.

Acknowledgment.—We wish to thank Dr. Martin B. Smith for performing the physical measurements and Messrs. R. A. Ashby and J. B. Chidester for analytical data.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Metal–Olefin Complexes. I. The Cyclodecadiene Complexes of Silver(I) and Copper(I)

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The reactions of olefinic and acetylenic hydrocarbons with silver(I) nitrate, copper(I) chloride, and copper(I) bromide have received a considerable amount of attention.[3] Recently the use of cyclic olefins as complexing agents has created much excitement. A variety of cyclic olefin complexes of the eight through twelve carbon atom series have been reported.[4–6] Cope, McLean, and Nelson[7] have prepared the silver(I) complexes of both *cis*- and *trans*-cyclodecene; however, no complexes with the unconjugated dienes of the cyclic C_{10} series have been reported. We have now synthesized some silver(I) and copper(I) diolefin compounds of *cis,trans*-cyclodeca-1,5-diene and *cis,cis*-cyclodeca-1,6-diene.[8,9]

Experimental

Reagents.—Cyclodeca-1,5-diene and cyclodeca-1,6-diene were obtained from the Columbian Carbon Co., Lake Charles Chemical Research Center, Lake Charles, La. The olefins were purified by vacuum distillation to yield (v.p.c.) 93% 1,5- and 96% 1,6-diene.

The salts used were Matheson Coleman and Bell reagent grade silver nitrate and anhydrous copper(II) bromide and Baker analyzed reagent grade copper(II) chloride dihydrate. Infrared spectra were taken on a Beckman Model IR-8 spectrophotometer.

Preparation of the Silver(I) Olefin Complexes.—To a solution of 1.7 g. (0.01 mole) of silver nitrate in 10 ml. of water was added a solution of 3 ml. of carbon tetrachloride or methanol and 3 ml. (0.04 mole) of cyclic olefin. The mixture was stirred for a few minutes. The white precipitate formed was filtered, washed with two 5-ml. portions of carbon tetrachloride, and dried under vacuum over calcium chloride (analysis in Table I).

Preparation of Copper(I) Olefin Complexes.—To a solution of 3.4 g. (0.02 mole) of copper(II) chloride dihydrate in 35 ml. of 95% ethanol was added 3 ml. (0.04 mole) of cyclic diolefin. Sulfur dioxide was bubbled into the solution while maintaining the temperature at 20–25°. Addition of sulfur dioxide was stopped after precipitation of product was noted. The mixture was kept at 20° for several hours and filtered, and the crystalline product was washed with 2 ml. of olefin followed by several 10-ml.

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TABLE I
PROPERTIES AND ANALYSIS OF METAL–OLEFIN COMPLEXES

Olefin	Complex formula	Max. yield, %		Analysis,[a] %				Physical properties
				M[b]	X[c]	C	H	
cis,trans-Cyclodeca-1,5-diene	$C_{10}H_{16}AgNO_3$	78	Calcd.	35.24	...	39.24	5.27	White solid, m.p. 138–139°
			Found	35.35	...	39.40	5.38	
	$C_{10}H_{16}CuCl$	85	Calcd.	27.01	15.07	51.06	6.86	White crystalline solid, dec. >50°
			Found	27.12	15.30	50.87	6.70	
	$C_{10}H_{16}(CuBr)_2$	70	Calcd.	30.03	37.78	28.38	3.81	Tan crystalline solid, dec. >50°
			Found	29.93	36.86	28.65	3.57	
cis,cis-Cyclodeca-1,6-diene	$C_{10}H_{16}AgNO_3$	75	Calcd.	35.24	...	39.24	5.27	White solid, darkens at 165°, turns red-brown and melts at 213°
			Found	35.53	...	39.61	5.36	
	$C_{10}H_{16}(CuCl)_2$	82	Calcd.	38.02	21.21	35.94	4.83	White crystalline solid, dec. >60°
			Found	37.86	21.27	36.09	4.84	
	$C_{10}H_{16}(CuBr)_2$	83	Calcd.	30.03	37.78	28.38	3.81	Tan crystalline solid, dec. >60°
			Found	30.53	38.64	27.03	3.21	

[a] Analysis by Alfred Bernhardt, Microanalytisches Laboratorium, Mulheim, Ruhr, Germany. [b] M is % metal (Cu or Ag). [c] X is % halogen (Cl or Br).

portions of cold absolute ethanol. The product was dried in a desiccator over calcium chloride.

The copper(I) bromide complex of cyclodeca-1,6-diene was prepared in the same manner with substitution of copper(II) bromide for copper(II) chloride dihydrate. The copper(I) bromide complex of cyclodeca-1,5-diene was prepared by the same method except that precipitation occurred after addition of the olefin to the copper(II) bromide solution without addition of sulfur dioxide (analysis in Table I).

Results and Discussion

The silver(I) nitrate complexes were prepared by allowing a 50% olefin–carbon tetrachloride or olefin–methanol solution to react with 1 *M* aqueous silver nitrate; 1:1 complexes were obtained from each of the cyclic diolefins.

The copper(I) chloride complexes were prepared by a method, recently introduced by Haight, Doyle, Baenziger, and Richards,[10] in which an ethanol solution of copper(II) chloride dihydrate and olefin is treated with sulfur dioxide. The copper(I) complexes could also be prepared by the addition of the olefin to a hydrochloric acid solution of copper(I) chloride or by the direct addition of anhydrous copper(I) chloride to the olefin.[11] All methods gave products in good yield and high purity. The sulfur dioxide reduction method gave a crystalline product. The experimental conditions and analyses (Table I) for only the latter method are reported. The complex obtained from *cis,trans*-cyclodeca-1,5-diene has 1:1 stoichiometry, whereas that obtained from *cis,cis*-cyclodeca-1,6-diene was a 1:2 cyclodecadiene–copper(I) chloride complex.

The complex of copper(I) bromide with *cis,cis*-cyclodeca-1,6-diene was prepared by the sulfur dioxide reduction method using anhydrous copper(II) bromide. The product obtained was the 1:2 cyclodecadiene–copper(I) bromide complex. *cis,trans*-Cyclodeca-1,5-diene reacted directly with an ethanol solution of copper(II) bromide without addition of sulfur dioxide to form a 1:2 cyclodecadiene–copper(I) bromide complex. Presumably the copper(II) ion was reduced with a corresponding oxidation of some of the olefin. Abel, Bennett, and Wilkinson[12] have reported a similar reaction of norbornadiene with the formation of a 1:2 norbornadiene complex of copper(I) bromide from the copper(II) salt.

In the preparation of the copper(I) complexes by sulfur dioxide reduction the yield and purity of the product were strongly influenced by the concentration of reactants in solution and by the amount of sulfur dioxide added. The highest yields were obtained by using the minimum amount of ethanol necessary to obtain a homogeneous solvent, olefin, and copper(II) salt mixture. Variations in concentration resulted in low yields and impure products. These results are similar to those reported by Haight, *et al.*[10]

Because of their low solubility the complexes could not be recrystallized. The silver(I) complexes were insoluble but stable in hydrocarbon solvents and could be washed without decomposition. The copper(I) complexes could only be washed in a minimum amount of cold hydrocarbon solvent; extensive washing or attempts to recrystallize resulted in dissociation and/or decomposition of the complexes.

The silver(I) complexes could be vacuum dried over calcium chloride, whereas the copper(I) complexes decomposed under vacuum or when exposed to conditions of high humidity. The silver(I) complexes could be heated to 100° without significant decomposition, whereas the copper(I) complexes began decomposing at about 50–60°.

Each of the silver(I) and copper(I) complexes was decomposed with aqueous potassium cyanide, and the olefin was recovered from the carbon tetrachloride phase. The solvent was removed on a rotating evaporator at 0° and the diene was identified by infrared and n.m.r. In all cases the cyclodecadiene recovered was the same isomer used in preparing the respective complex.

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(11) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962).

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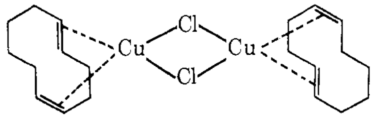
Although no definite structures can be assigned without X-ray data, some general correlation can be drawn from the infrared spectra of these complexes and those of similar complexes whose crystal structures have been determined.

The generally accepted Dewar[13] concept of π bonding appears applicable to the silver(I) and copper(I) cyclodecadiene complexes. The double bond frequencies of the silver(I)–1,5-diene complex have been lowered from two peaks of equal intensity at 1667 and 1639 cm.$^{-1}$ to a weak band from 1660 to 1600 cm.$^{-1}$. A similar change is noted in the 1,6-diene complex, in line with the Dewar concept's prediction that the double bonds of the olefin should not be changed significantly in π complexing with the silver(I) ion.

For both isomers of the 1:1 cyclodecadiene–silver nitrate complexes two possible structures may be proposed. One would be a polymeric structure where the silver ions are associated with two double bonds each from a different olefin molecule. In the other the silver ion is located approximately in the center of the olefin molecule, the cyclic olefin being in a boat configuration with the metal π-bonded to both pairs of double bonds, similar to the arrangement found in the 1:1 cyclooctatetraene–silver nitrate complex.[14]

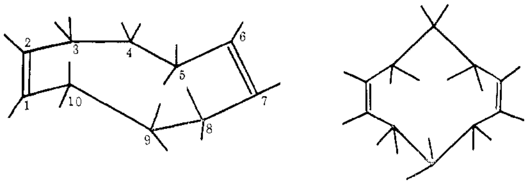
The spectra of all the copper(I) complexes are similar and indicate a π-bonded complex analogous to the silver(I) complexes. The double bond absorption bands characteristic of *cis,trans*-cyclodeca-1,5-diene at 1667, 1669 cm.$^{-1}$ and of *cis,cis*-cyclodeca-1,6-diene at 1675, 1655 cm.$^{-1}$ are absent. A new band at 1613 cm.$^{-1}$ appears which has been assigned to the complexed olefin. The bands in the 1300–650 cm.$^{-1}$ region of the copper(I) complexes are identical with those of the uncomplexed olefins. This seems to indicate no changes in the skeletal vibrations of the C_{10} ring or in the structural conformation of the olefin.

Recent studies by van den Hende and Baird[15] on the structure of cycloocta-1,5-diene–copper(I) chloride indicate this complex to be a chloride-bridged dimer with the copper ion quasi-tetrahedrally bonded to two chloride ions and the two double bonds of the olefin molecule. A similar structure could be postulated for the 1:1 cyclodeca-1,5-diene–copper(I) chloride complex (I). The 1:2 cyclodecadiene–copper(I) bromide complex, on the other hand, is apparently polymeric with bromide bridging groups.



I

Both chair and boat structural conformation of the cyclodeca-1,6-diene molecule are possible (II). Structural models of the chair conformation indicate a high degree of transannular strain from intraannular interactions of the hydrogen atoms on carbons 3, 4, 9, and 10. The boat conformation has interactions of the hydrogen atoms of carbons 3, 5, 8, and 10, but these can be relieved somewhat by a staggered arrangement of the atoms. If the boat form is the preferred conformation, a 1:1 complex should exist. Such a complex would be similar in structure to the 1,5-diene–copper(I) chloride complex. At this time, we have been able to prepare only the 1:2 cyclodeca-1,6-diene–copper(I) halide complex. Therefore, it is not as yet possible to make any statement as to which conformation is preferred. Work with other metal ions is in progress and will be reported shortly.



Chair conformation Boat conformation

II

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The Kinetics of Exchange of Thiocyanate between Iron(III)–Thiocyanate Complexes and Free Ligand in Concentrated Aqueous Solution[1]

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The work reported here is a continuation of studies on thiocyanate complexes. Results were reported earlier for the Ni(II) system[3] while here we are concerned with Fe(III) complexes.

Experimental

The general procedures and equipment have been described.[3] Solutions were prepared using redistilled water and analytical grade reagents (KNCS, HNO_3, and $Fe(NO_3)_3\cdot 9H_2O$). The Fe(III)–thiocyanate solutions decomposed slowly and extrapolations of the line width data to "zero time" were made when necessary.

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