METAL–OLEFIN COMPLEXES
III. THE RHODIUM(I) π-COMPLEX OF cis,cis-1,6-CYCLODECADIENE BY THE METAL-CATALYZED ISOMERIZATION OF cis,trans-1,5-CYCLODECADIENE

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INTRODUCTION

In recent years numerous complexes have been reported in which diolefins are chelated to transition metals[1]. The most widely studied cyclic diolefin complexes are those prepared from cis,cis-1,5-cyclooctadiene and transition metals in their low oxidation states. Recently we reported the preparation of a series of metal–diolefin complexes prepared from cis,trans-1,5-cyclodecadiene and cis,cis-1,6-cyclodecadiene[2,3]. Hüttel et al.[4] have reported the gold(I) chloride complex of 1,5-cyclodecadiene. We have now investigated the complex formation and isomerization of cyclodecadiene with rhodium trichloride. Chatt and co-workers[5] have prepared the rhodium(I) complex of 1,5-cyclooctadiene.

Several papers have appeared describing the metal-catalyzed isomerization of 1,5- to 1,3-cyclooctadiene as well as the isomerization of 1,3- to 1,5-cyclooctadiene[6-9]. We have found that the cis,trans-1,5-isomer of cyclodecadiene is isomerized in ethanol containing rhodium trichloride to cis,cis-1,6-cyclodecadiene with subsequent formation of a dimeric 1,6-cyclodecadiene rhodium(I) chloride complex.

$$2 \, C_{10}H_{16} + 2 \, RhCl_3 + 2 \, C_2H_5OH \rightarrow [C_{10}H_{16}RhCl]_2 + 4 \, HCl + 2 \, CH_3CHO$$
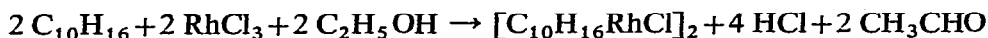
A chemical and physical investigation of the product was undertaken in order to determine its structure. Several currently accepted mechanisms involving olefin isomerization are discussed.

RESULTS AND DISCUSSION

Structure

An orange, crystalline rhodium(I) π-complex of the type [diene·RhCl]₂ was prepared from cis,cis-1,6-cyclodecadiene by the extension of Chatt's method for

preparing the 1,5-cyclooctadiene analog[5]. Surprisingly, with *cis,trans*-1,5-cyclodeca-diene the 1,6-cyclodecadiene rhodium(I) chloride complex again was obtained rather than the expected 1,5-cyclodecadiene complex. This was substantiated when cyanide displacement of complexed olefin gave only 1,6-cyclodecadiene, identified by infrared and NMR spectra and by ozonolysis to glutaric acid. Molecular weight determination and elemental microanalysis indicated that the rhodium complex was a dimer with 1:1 stoichiometry.

The infrared spectrum of the complex does not show the double-bond frequencies between 1675 and 1650 cm^{-1} characteristic of 1,5- or 1,6-cyclodecadiene, indicating a strong interaction of the rhodium(I) ion with the olefinic double bonds. The olefin complex of rhodium(I) is isoelectronic with palladium(II).

TABLE 1

NMR SPECTRUM PARAMETERS[a]

Compound	Chemical shifts δ (rel. TMS)				Spin-coupling constants (cps)	
	H_A	H_B	CH_2	CH_2'	J_A	J_B
cis,trans-1,5-Cyclodecadiene	5.24	5.42	2.08	1.58	5	11
cis,cis-1,6-Cyclodecadiene	5.29		2.00	1.45	6	
cis,cis-1,6-Cyclodecadiene-rhodium(I) chloride	4.82		1.95	0.80	6	

[a] Rhodium complex run in $CDCl_3$, olefins neat.

The NMR spectra of *cis,cis*-1,6-cyclodecadiene (Table 1) and of the olefin–rhodium(I) complex again illustrate the strong π-bonding character of rhodium. The olefinic proton multiplet at δ 5.29 ppm in the spectrum of the free diolefin is shifted to 4.82 ppm in that of the complex. Shifts to higher fields of a few tenths to over three ppm are the rule in metal olefin π complexes[10].

The experimental evidence suggests structure (I) with rhodium(I) ion in the square planar configuration as established for the dimeric 1,5-cyclooctadiene rhodium(I) complex[11].

(I)   (II)   (III)
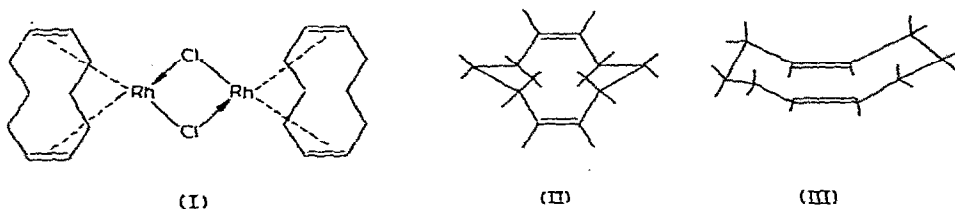
Isomerization and conformation

The rhodium-catalyzed isomerization of *cis,trans*-1,5-cyclodecadiene to *cis,cis*-1,6-cyclodecadiene is not unexpected[12–14]. Rinehart and Lasky[15] proposed the hydrido-π-allylic mechanism for the isomerization of 1,3- to 1,5-cyclooctadiene with

rhodium trichloride. Nicholson and Shaw[7] postulated the same mechanism for the isomerization with iridium–cyclooctadiene complexes. Harrod and Chalk[13,16,17] proposed a reversible hyc idoalkyl mechanism. Their objection to the π-allyl mechanism is based on the inactivity of palladium π-allyl complexes in promoting isomerization under conditions where olefin complexes are effective. A third mechanism (carbene) which does not involve the formation of a metal hydride intermediate has been suggested by Davies[18]. More recently Harrod and Chalk[17] have attributed this supposed isotope effect to presence of peroxide in the deuterio-olefin. Recent work by Cramer[19] has, however, shown strong evidence that the rhodium-catalyzed isomerization occurs by addition and elimination of metal hydride. He proposes a modified hydrido–alkyl mechanism which includes exchange of the metal hydride with solvent deuterium.

The formation of metal hydride by reduction of Rh(III) to Rh(I) has been shown to occur readily in the presence of ethylene[20] and ethanol[21,22]. We found that rhodium(III) chloride is capable of oxidizing ethyl alcohol to acetyldehyde. The reaction was conducted in an autoclave and the resulting mixture treated with a solution of 2,4-dinitrophenylhydrazine in HCl. Acetaldehyde 2,4-dinitrophenylhydrazone was isolated in about 90% yield; mixed m.p. showed no depression with an authentic sample.

The formation of the 1,6-cyclodecadiene rhodium chloride complex may therefore be through the hydride mechanism.

$$C_2H_5OH + RhCl_3 \rightarrow HRhCl_2 + HCl + CH_3CHO$$

The reversible nucleophilic attack of $HRhCl_2$ on the olefin leads then to a hydrido alkyl bond, followed for 1,5-cyclodecadiene by isomerization to the 1,6-isomer.

$$2\ C_{10}H_{16} + 2\ HRhCl_2 \rightleftharpoons 2\ C_{10}H_{17}RhCl_2 \rightarrow (1,6-C_{10}H_{16}RhCl)_2 + 2\ HCl$$

Several points appear to be of critical importance. First, the reaction must take place in a proton-donor solvent. Second, it does not occur to any measurable extent at room temperature. Finally, cis,trans-1,5-cyclodecadiene is known[23,24] to begin rearranging thermally to cis-1,2-divinylcyclohexane at above 80°. Since only a trace of cis-1,2-divinylcyclohexane was found, the complexed olefinic intermediate seems to exist at a lower temperature.

Structural considerations explain the appearance of cis,cis-1,6-cyclodecadiene as the principle isomer. The cis,cis-isomer is more symmetrical and this symmetry relieves the strain due to hydrogen–hydrogen interaction across the ring. The symmetrical structure of the cis,cis-1,6-isomer is apparent when its NMR spectrum is compared with that of cis,trans-1,5-cyclodecadiene (Table 1). The appearance of only a single olefin resonance pattern at δ 5.29 ppm (four protons) suggests that the double bonds of the 1,6-isomer are identical and symmetrically located.

Dale and Moussebois[25] have demonstrated that the chair conformation (II) is the thermodynamically favored structure for cis,cis-1,6-cyclodecadiene. Dreiding models show this conformation affords the least strained system.

The copper(I) and palladium(II) complexes of 1,6-cyclodecadiene were found to form only polymeric complexes, and the chair conformation of the diene permits an extended chain structure[2,3].

However, the molecular weight of the rhodium(I) complex suggests a chloride-

bridged dimer structure (I). Only the boat conformation (III) would have the π-orbitals properly oriented to complex with the metal in the square planar configuration. We suggest that at the reaction temperature (80°) a significant amount of the diene exists in the boat conformation. This is trapped by complexation with the metal atom.

The NMR spectrum of the 1,6-diene shows the protons of the CH_2 groups at carbons 3, 5, 8 and 10 as a broad peak at δ 2.00 ppm (eight protons). The spectrum of the rhodium complex (Table 1) shows a better resolved pattern for the CH_2 group centered at δ 1.95 ppm (eight protons). The broadened methylene signals in the free olefin suggest a slow interconversion between chair and boat conformations with consequent time-averaging of chemical shifts of nonequivalent sites. Also evident is a shift of the CH_2' pattern of carbons 4 and 9 from δ 1.45 ppm (four protons) in the 1,6-diene to δ 0.80 ppm (four protons) in the complex. This up-field shift could be due to the CH_2' group of the 1,6-diene in the boat conformation interacting with the centrally located rhodium atom.

The differences in the NMR spectra of the two decadienes and the rhodium complex are readily interpreted. The uncomplexed cyclodecadiene molecule is free to move through a wide range of conformations whereas in the rhodium complex it is constrained to a single geometry. The relatively small chemical-shift changes which arise from π-complex formation reflect a small net transfer of electron density. The effects of magnetic anisotropy however, reveal marked differences in molecular environment arising from the local field of the π-electron system.

In the NMR spectrum of the 1,6-cyclodecadiene and 1,5-cyclodecadiene (Table 1) the protons are clearly differentiated into olefinic and methylene types. The latter are resolved into two groups by virtue of the chemical shift differences between positions one and two carbon atoms removed from the double bond.

The effect of complex formation with the 1,6-cyclodecadiene in the boat conformation is to split the eight α-methylene protons into two groups (Table 1) whose NMR peaks are separated about 1 ppm, while increasing their average shift the same amount upfield. These effects arise from increased shielding by the metal atom as well as fixation of the protons of the α-methylene group in positions of differing local field.

Further evidence for the nonequivalence of the protons in each α-methylene group appears in the fine structure of the olefinic proton multiplets. The uncomplexed 1,6-cyclodecadiene shows a triplet with the six cps splitting characteristic of spin-coupling between a proton on an sp^2 hybridized carbon and two equivalent protons on an sp^3 carbon. In the complex the corresponding fine structure suggests spin-coupling between an olefinic proton and several nonequivalent protons. (Possibly both α-methylene groups are involved in spin-coupling with each olefinic proton, in which case four different spin-coupling interactions would be possible.)

The fine structure for the methylene protons is not as readily interpreted, since the number of possible spin-coupling interactions is much greater. In the case of the 1,6-cyclodecadiene, however, rapid time averaging of all possible spin-coupling geometries should simplify the spectrum. The two multiplet groups indicate the extent of this averaging. Although there is some fine structure suggesting the five-line multiplet expected for the β-methylene protons, the peak representing the eight α-methylene protons is severely broadened by the many unresolved splittings.

A similar isomerization of *cis,trans*-1,5-cyclodecadiene to *cis,cis*-1,6-cyclo-

decadiene has recently been observed by Heimbach[26]; the 1,5-diene was irradiated by UV light with $Fe[CO]_5$ at 60°, isomerization was 92% complete after 48 hours.

A study of the isomerization mechanism with variable temperature NMR is in progress.

EXPERIMENTAL

General comments

The *cis,trans*-1,5-cyclodecadiene and *cis,cis*-1,6-cyclodecadiene were obtained from the Columbian Carbon Company, Lake Charles Chemical Research Center.- The olefins were purified by vacuum distillation to yield (VPC) 93% *cis,trans*-1,5-cyclodecadiene, b.p. 63.0° at 12 mm, n_D^{25} 1.4955 and 96% *cis,cis*-1,6-cyclodecadiene, b.p. 69–69.5° at 12 mm, m.p. 28.5–29°, n_D^{25} 1.4990.

Elemental microanalyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Mulheim, Germany.

The infrared absorption spectra were obtained on a Beckman IR-8 Spectrophotometer equipped with a linear wave length scale and sodium chloride optics. The spectra of the complex were obtained by using potassium bromide pellets. Nuclear magnetic resonance spectra were obtained on deuterated chloroform solutions using the Varian A-60. Gas chromatographic analysis was performed on a Perkin Elmer 154-L. Column packing consisted of a 35% solution of silver nitrate (39%) in tetraethylene glycol (61%) on a support of 50–100 mesh C-22 firebrick. Column temperature was 90°.

Molecular weights were obtained on a Mechrolab Vapor Pressure Osmometer, Model 301A. Measurements were made on solutions containing the solute dissolved in chloroform. The concentration used in the determination ranged from 0.05 to 0.65 weight %. The solvent was calibrated within the concentration range of 0.02 to 0.40 molal by using benzil as a standard.

Preparation of 1,6-cyclodecadienerhodium(I) *chloride,* $[C_{10}H_{16}RhCl]_2$

A. To a solution of 1.0 g (0.004 mole) of rhodium trichloride trihydrate in 40 ml of 95% ethanol was added 2 ml (0.01 mole) of *cis,trans*-1,5-cyclodecadiene. The solution was heated at 78–80° for 4–6 h with stirring. An orange precipitate was obtained which was washed with 10 ml of cold absolute ethanol and dried under vacuum (13 mm) over calcium chloride. The complex was recrystallized from chloroform/n-hexane (yield 415 mg). The complex decomposes without melting at 215–220°. (Found: C, 43.99; H, 5.80; Cl, 12.87; Rh, 37.63; mol. wt., 544. $C_{20}H_{32}Cl_2Rh_2$ calcd.: C, 43.73; H, 5.87; Cl, 12.90; Rh, 37.50%; mol. wt., 548.)

B. The previously described complex was also prepared by the same method with the addition of *cis,cis*-1,6-cyclodecadiene in place of the 1,5-diene to 0.5 g of rhodium trichloride trihydrate. The product was washed and recrystallized as above (yield 240 mg). (Found: C, 43.76; H, 5.91; Cl, 12.76; Rh, 37.49%; mol. wt., 543.)

Infrared absorption spectra: 2975 (vs), 2900 (vs), 2840 (vs), 1446 (m), 1421 (vs), 1370 (m), 1320 (s), 1307 (m), 1249 (s), 1188 (m), 1130 (m), 1030 (m), 987 (vs), 964 (m), 903 (m), 844 (s), 808 (s), 796 (s), 748 (m).

The method of olefin displacement was described in a preceding paper[2]. The displaced olefin was examined by infrared and NMR. Only *cis,cis*-1,6-cyclodecadiene

was found. The structure of the olefin was also proven by ozonolysis of the displaced olefin to the diacid followed by esterification with methanol. The ester obtained was identical in m.p. and in retention time on the VPC to that of pure dimethyl glutarate.

SUMMARY

The dimeric rhodium(I) metal π-olefin complex, cis,cis-1,6-cyclodecadiene rhodium(I) chloride $[C_{10}H_{16}RhCl]_2$, was prepared. The rhodium-catalyzed isomerization of cis,trans-1,5-cyclodecadiene was investigated and a mechanism involving a hydrido–alkyl intermediate was proposed. Certain general observations concerning possible conformational isomerizations were briefly discussed.

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