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PREPARATION AND CIRCULAR DICHROISM OF RHODIUM(I) COMPLEXES CONTAINING OPTICALLY ACTIVE *trans*-CYCLOOCTENE

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Summary

Three new rhodium(I) compounds containing optically active *trans*-cyclooctene (*trans*-C_8H_{14}) were prepared: $[RhL\{(+)_D\text{-}trans\text{-}C_8H_{14}\}_2]$ (L = acetylacetonate and 1,3-diphenyl-1,3-propanedionate) and $[Rh_2Cl_2\{(+)_D\text{-}trans\text{-}C_8H_{14}\}_4]$. The absorption and circular dichroism spectra were measured and compared with those of $[Pt_2Cl_4\{(-)_D\text{-}trans\text{-}C_8H_{14}\}_2]$. The absolute configuration of coordinated alkenes is correlated with the CD spectra in the wave number regions, (20—30) × 10^3 cm^{-1} and 40 × 10^3 cm^{-1}. In the former range the CD sign is the reverse of that of platinum(II)—alkene complexes, but in the latter region the CD signs are equal.

Introduction

The relationship between the CD spectrum and the absolute configuration of asymmetrically coordinated η^2-alkenes in square planar complexes has been discussed mainly on the basis of experimental data for platinum(II) complexes [1—3]. Scott et al. [2] reported that the positive and the negative CD peaks at 27 × 10^3 cm^{-1} corresponded to the *S,S* and *R,R* configurations, respectively. This wavelength region was believed to be due to the *d—d* transition region of the platinum(II) ions.

Much less is known concerning the CD spectra of η^2-alkenes coordinated to other metal ions. Scott and Wrixon [4] tried to extend such studies to η^3-allyl complexes of palladium(II), but found that the stereochemical relationship was ambiguous. Musco et al. [5] also found that η^2-fumaric acid tetracarbonyliron(0) gives a positive CD peak in the (27.8—28.1) × 10^3 cm^{-1} region, but the absolute

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configuration of η^2-fumaric acid was established as *R,R* by an X-ray crystallographic study [6].

With the aim of elucidating the relationship between the CD spectrum and the absolute configuration of η^2-alkenes, we have synthesized rhodium(I) complexes containing optically active *trans*-cyclooctene and examined the absorption and CD spectra in the visible and ultraviolet region.

Experimental

(1) Resolution of trans-cyclooctene

trans-Cyclooctene was prepared according to an established method [7] and resolved by a modification of Cope's method [8]. *trans*-Cyclooctene (3 g) was added dropwise with stirring to 50 cm^3 of acetonitrile containing 10 g of *trans*-(*N*-alkene)—[PtCl(L-prol)(C_2H_4)] * (L-prol = L-prolinate) [3]. The solution was evaporated to dryness and the yellow residue was dissolved in 500 cm^3 of acetonitrile and kept at 5°C in a refrigerator for several days. Very fine crystals and comparably larger block crystals were formed. The crystals were filtered, washed with diethyl ether, and the block crystals (yield 2.0 g) were sieved from finer crystals (yield 1.5 g). The block crystals gave a satisfactory elemental analysis for [PtCl(L-prol)(*trans*-C_8H_{14})] (Found: C, 34.21; H, 4.95; N, 3.15. $C_{13}H_{22}ClNO_2Pt$ calcd.: C, 34.32; H, 4.88; N, 3.08%. The $\Delta\epsilon_{368}$ of the block crystals is —0.87 in acetonitrile. The [PtCl(L-prol)(*trans*-C_8H_{14})] complex (1 g) could be suspended in 15 cm^3 of a nonpolar organic solvent (e.g. n-pentane, toluene, and benzene) and treated with potassium cyanide (1.2 g in 20 cm^3 of water) with stirring to give free *trans*-cyclooctene and tetracyanoplatinum(II) complex. The *trans*-cyclooctene in the n-pentane layer showed $[\alpha]_D$ (+)430 ** (the reported $[\alpha]_D$ value of optically active *trans*-cyclooctene is (+)450 [8]) and was used for preparing [Rh(acac)(*trans*-$C_8H_{14})_2$] (acac = acetylacetonate).

Less optically pure *trans*-cyclooctene ($[\alpha]_D$ (+)350) was used for preparing [Rh(dbm)(*trans*-$C_8H_{14})_2$] (dbm = 1,3-diphenyl-1,3-propanedionate) and [Rh_2Cl_2-(*trans*-$C_8H_{14})_4$] because only a small amount of optically pure alkene was obtained.

(2) Preparation of rhodium(I) complexes

All procedures should be carried out in a nitrogen atmosphere. The solutions of the rhodium(I) compounds are air sensitive, but the solids apparently are stable in air. All the solvents were degassed with a current of nitrogen or in vacuo.

(a) Acetylacetonato-bis{η^2-(+)$_D$-trans-cyclooctene}rhodium(I). [Rh(acac)-($C_2H_4)_2$] was prepared according to Cramer's method [9] with some modifications as follows. Methyl alcohol (200 cm^3) was added to a mixture of [Rh_2Cl_2-($C_2H_4)_4$] (1 g, 2.6 mmol) and bis(acac)barium (3 g, 9.0 mmol). The red-brown suspension was stirred at room temperature for 2 h. The resulting yellow-brown solution was evaporated to dryness under reduced pressure to give a yellow-brown residue which was sublimed at 60—80°C under 3 mmHg. The orange

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* *trans*-(*N*-Alkene) indicates the structure in which the nitrogen atom of the chelated L-prolinate anion is coordinated to the platinum atom in the *trans* position to the alkene.

** The concentration was determined from the weight of the platinum(II) complex by assuming that the extraction of *trans*-cyclooctene to the organic layer is quantitative.

yellow crystals were found to be [Rh(acac)(C_2H_4)$_2$] on the basis of the infrared (IR) spectrum and the melting point (144—145°C, dec.). Yield 1.2 g.

An n-heptane solution (15 cm^3) of $(+)_D$-*trans*-cyclooctene which was obtained from 1.2 g of [PtCl(L-prol)($(+)_D$-*trans*-C_8H_{14})] ($\Delta\epsilon$ —0.87) was degassed in vacuo and added to solid [Rh(acac)(C_2H_4)$_2$] (0.22 g, 0.86 mmol) at room temperature. [Rh(acac)(C_2H_4)$_2$] dissolved instantly with foaming. Nitrogen was bubbled into the solution to remove the solvent completely. The orange residue was recrystallized from 5 cm^3 of diethyl ether and 20 cm^3 of acetonitrile. Needle-like crystals (290 mg, 80%) were obtained. Found: C, 59.24; H, 4.92. $C_{21}H_{35}O_2Rh$ calcd.: C, 59.71; H, 5.01%. The IR absorptions are summarized in Table 1.

(b) (1,3-Diphenyl-1,3-propanedionato)bis(η^2-$(+)_D$-trans-cyclooctene)rhodium-(I). To a mixture of [Rh(acac)(C_2H_4)$_2$] (300 mg) and Hdbm(Hdbm = 1,3-diphenyl-1,3-propanedione) (1 g) was added petroleum ether (20 cm^3). The solution was stirred for 10 h. The crystals were filtered off and recrystallized from 5 cm^3 of toluene by adding methyl alcohol. Red needle-like crystals (150 mg, 34%) were obtained. Found: C, 59.24; H, 5.19. $C_{19}H_{19}O_2Rh$ calcd.: C, 59.71; H, 5.01%.

A benzene solution (15 cm^3) of *trans*-cyclooctene which was obtained from 400 mg of [PtCl(L-prol)($(+)_D$-*trans*-C_8H_{14})] ($\Delta\epsilon_{368}$ —0.71) was degassed in vacuo and added to 130 mg of solid [Rh(dbm)(C_2H_4)$_2$] at room temperature. Nitrogen was bubbled into this solution for 2 h and methyl alcohol was added. The resulting orange crystals were filtered and recrystallized from a small amount of benzene by adding methyl alcohol, 100 mg (53%). Found: C, 68.11; H, 7.27. $C_{31}H_{39}O_2Rh$ calcd.: C, 68.12; H, 7.19%. The IR absorptions are summarized in Table 1.

TABLE 1

IR SPECTRA OF [RhL(*trans*-C_8H_{14})$_2$]

[Rh(acac)(*trans*-C_8H_{14})$_2$]	[Rh(dbm)(*trans*-C_8H_{14})$_2$]	[Rh_2Cl_2(*trans*-C_8H_{14})$_4$]	[Rh(acac)(C_2H_4)$_2$] [18]
			3415 m
	3060 w		3060 w
2980 m	2980 w		2985 w
2915 s	2915s	2924s	
2845s	2845m	2850s	
1580s	1588m	1603m	1575s
	1534s	1558s	
1518s	1518s		1524s
	1487s	1462m	
1448s	1449s	1445s	1425m
1385s	1383s	1342m	1372m
1340m	1305m		1361m
1270s		1265m	1267m
1240w		1230w	1233m
1210m	1221w	1205m	1221w
1195m	1176w	1140w	1199w
1071m	1068m	1068m	1029m
1021m	1023m		1015w
945m	940m	968w	987w
910s	906m	938m	936m
778s	760m	815m	788m

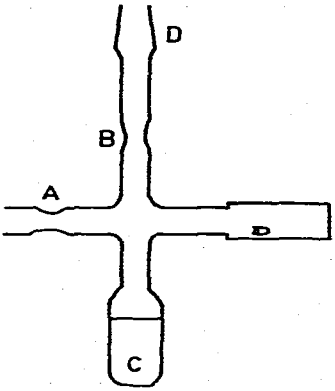


Fig. 1. The quartz cell for optical measurements used in this study.

(c) μ-Dichlorotetrakis(η^2-(+)$_D$-trans-cyclooctene)dirhodium(I). To $[Rh_2Cl_2(C_2H_4)_4]$ (0.2 g, 0.51 mmol) was added a toluene solution (15 cm^3) of (+)$_D$-*trans*-cyclooctene obtained from 1.0 g of [PtCl(L-prol)((+)$_D$-*trans*-C_8H_{14})] ($\Delta\epsilon_{368}$ —0.71). The solution was degassed in vacuo and nitrogen was bubbled into this solution for 2 h. The red-orange solution was filtered, and the filtrate was treated with methyl alcohol to give orange crystals. These were recrystallized from a small amount of toluene by adding methyl alcohol, 200 mg (53%). Found: C, 53.40; H, 8.09. $C_{32}H_{56}Cl_2Rh_2$: C, 53.56; H, 7.87%. The IR absorptions are summarized in Table 1.

Measurements

All measurements were carried out using the cell shown in Fig. 1. A given amount of sample in a capillary was introduced into the quartz cell through A, and then A was sealed. The solvent in C was degassed in vacuo. This procedure was repeated several times to complete degassing (10^{-3} Torr) and B was sealed. The solvent was transfered to the quartz cell containing the sample. The vessel was shaken well and used for the measurements.

Acetonitrile was refluxed over phosphorus pentoxide and distilled three times. Diethyl ether was refluxed over sodium and distilled. n-Hexane was of spectroscopic grade and used without further purification.

Visible and ultraviolet spectra were recorded with a Hitachi 323 spectrophotometer. CD spectra were recorded on a JASCO J-20 spectropolarimeter. IR spectra were measured with a JASCO IRA-2S Diffraction Grating spectrophotometer.

Results and discussion

Cramer [9] studied the stabilities of a number of η^2-alkene complexes of rhodium(I) and indicated that alkyl substituents on alkene carbons destabilize rhodium(I) complexes. However, C_2F_4 coordinates very strongly while propene and the 2-butenes do so weakly. Such a difference was attributed to a stronger π- or back-bond between rhodium(I) and C_2F_4. In this study, however, it was found that *trans*-cyclooctene coordinates quite easily to rhodium(I) and its complexes are stable in the solid state in air. The high stability of the complexes might be due to the relief of the tortional strain of a twisted *trans*-cyclooctene on complexation with rhodium(I) through σ-donation. The π-orbital ionization potential (*IP*) of *trans*-cyclooctene is much lower than those of other cycloalkenes [10b,11], so that the σ-donation ability to a metal ion should be strong. *cis*-Cyclooctene also gives stable complexes with rhodium(I) [12], and its *IP* is lower than those of other smaller cycloalkenes [11]. Thus the stability of alkene complexes of rhodium(I) is determined not only by π-back-bonding but also by its σ-bonding to metals.

Reactions of [Rh(trifluoroacetyl-*d*-camphorato)$(C_2H_4)_2$] [13] with a variety of η^2-alkenes such as fumaronitrile, acrylonitrile and methacrylonitrile were tried in order to obtain optically active compounds. Pure compounds were not obtained, although the CD and absorption spectra indicated the formation of such compounds.

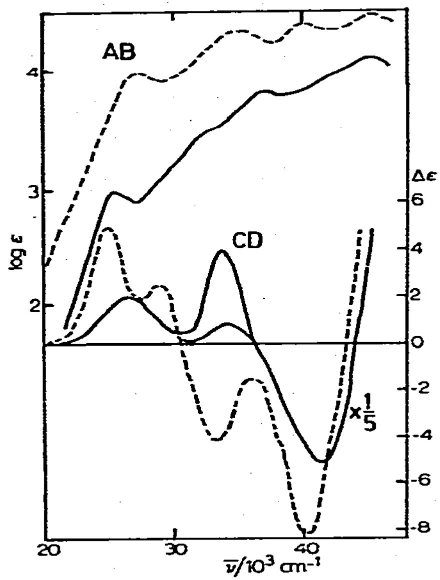
Circular dichroism and absolute configuration of alkene

The $(+)_D$-*trans*-cyclooctene used in this study has the *S* absolute configuration, which was determined by a chemical method [14]. Steric requirements due to the methylene chain of the ring of *trans*-cyclooctene results in exclusive coordination to one side of the double bond. The resulting π-complex has the (*R*,*R*) configuration on complexation with rhodium(I) and platinum(II) ion, as a result of the priority rule [15].

The CD spectrum of [$PtCl_2$(α-methylbenzylamine)($(+)_D$-*trans*-C_8H_{14})] is similar to that of [$PtCl_2$(α-methylbenzylamine)(*trans*-2-butene)] [2] of which the absolute configuration was determined by X-ray crystallography as the (*R*,*R*) configuration for the olefinic carbons [16].

The ultraviolet and visible absorption (AB) and CD spectra of [Rh(acac)(*R*,*R*-*trans*-C_8H_{14})$_2$] and [Rh(dbm)(*R*,*R*-*trans*-C_8H_{14})$_2$] in hexane are given in Fig. 2. [Rh(dbm)(*R*,*R*-*trans*-C_8H_{14})$_2$] is unstable to light so that the AB and CD spectra were measured with freshly prepared solutions. Both complexes exhibit one or two positive CD peaks in (20—30) × 10^3 cm^{-1} region and a negative peak at about 40 × 10^3 cm^{-1} (Fig. 2).

The AB and CD spectra for [Rh_2Cl_2(*R*,*R*-*trans*-C_8H_{14})$_4$] and [Pt_2Cl_4(*S*,*S*-*trans*-C_8H_{14})$_2$] in hexane and in CH_2Cl_2 respectively are given in Fig. 3. The CD spectrum of the former exhibits a positive peak at (20—25) × 10^3 cm^{-1} and a negative peak at about 40 × 10^3 cm^{-1}. On the other hand, the CD spectrum of the latter exhibits a positive peak at (20—25) × 10^3 cm^{-1} and a positive peak at about 40 × 10^3 cm^{-1}. The spectral pattern in the long wavelength region of the rhodium(I) complexes is not considered to be due to pure *d*—*d* transitions because of the large log ϵ value (~3). It has been suggested from the theoretical point of view that the mixing of a variety of absorptions such as *d*—*d* transitions and charge transfer absorptions occurs in the long wavelength region of transition metal alkene complexes [17]. This may be one of the reasons for the difference between the rhodium(I) and platinum(II) complexes. The absorption data are summarized in Table 2.



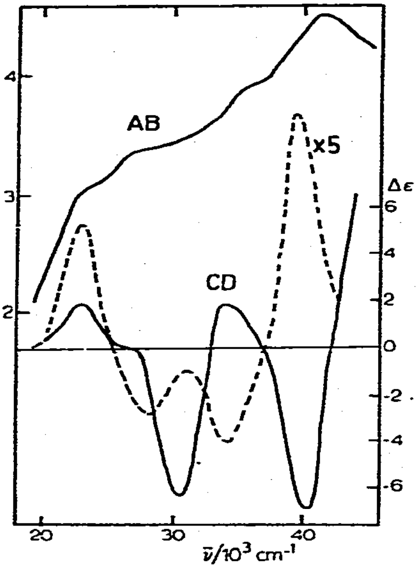


Fig. 2. Absorption and CD spectra of ——— [Rh(acac)(*R,R-trans*-$C_8H_{14})_2$] and - - - - - - [Rh(dbm)(*R,R-trans*-$C_8H_{14})_2$].

Fig. 3. Absorption and CD spectra of ——— [Rh_2Cl_2(*R,R-trans*-$C_8H_{14})_4$] and - - - - - - [Pt_2Cl_4(*S,S-trans*-$C_8H_{14})_2$] [2].

Complexes without alkenes do not give strong absorptions at about 40 X 10^3 cm^{-1}. The CD of the *trans*-cyclooctene complexes of rhodium(I) and platinum(II) in this region exhibit negative peaks for the coordinated (*R,R*)-alkenes regardless of the kind of central metal ions and the other ligands. Hence, the origin of the CD seems to arise mainly from the alkene itself (e.g. $\pi^* \leftarrow \pi$ transitions).

In conclusion, we can suggest the two points in this paper: (1) The sign of the CD at ca. (20—30) X 10^3 cm^{-1} is useless for assigning absolute configurations of a variety of transition metal alkene complexes, and (2) the sign at 40 X 10^3 cm^{-1} may be useful for such purposes.

TABLE 2. ABSORPTION SPECTRAL DATA

Complexes	$\tilde{\nu}(10^3\ cm^{-1})$	(log ε)	$\tilde{\nu}(10^3\ cm^{-1})$	(log ε)
[Rh(acac)$(CO)_2$] [a]	25.00	1.91 [e]	41.00	3.68 [e]
[Rh(acac)$(C_2H_4)_2$] [b]	25.00	3.31	41.32	4.00
[Rh(dbm)$(C_2H_4)_2$] [b]	27.40	3.98	40.00	4.08
[Rh(acac)(*trans*-$C_8H_{14})_2$] [b]	25.32	2.95	40.98(sh)	3.94
[Rh(dbm)(*trans*-$C_8H_{14})_2$] [b]	27.40	3.96	40.00	4.38
[Rh_2Cl_2(*trans*-$C_8H_{14})_4$] [b]	22.73(sh)	2.97	40.98	4.48
[PtCl(L-prol)(C_2H_4)] [c]	24.8(sh)	1.54	40.00	3.20
[PtCl(L-prol)(*trans*-C_8H_{14})] [d]	27.03(sh)	1.73	40.00(sh)	3.32
K[$PtCl_2$(L-prol)] [c]	23.8(sh)	1.37	40.00	2.62 [e]

[a] In diethyl ether. [b] In hexane. [c] Ref. 3. [d] In acetonitrile. [e] These values are given for comparison.

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