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Molecular Asymmetry of Organometallic Complexes: Iron Carbonyl Complexes of Prochiral Mono and Diolefins

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The preparation of optically active iron carbonyl complexes of prochiral mono and diolefins is described. The circular dichroism spectra of the complexes are reported and related to the absolute configuration of the coordinated olefin.

Introduction

The molecular asymmetry which occurs on coordination of a prochiral olefin to a transition metal atom and the relevant implications with the polymerization mechanism of α-olefins by Ziegler-Natta catalysts have been put forward[2] since 1964.

Since then several papers have been published on the asymmetry of olefin-platinum[3] and π-allyl-palladium complexes.[4] In this paper we report on the molecular asymmetry of olefin-iron carbonyl complexes. Some preliminary data have already been published.[5,6] The CD spectra of the compounds will be presented and interpreted, as far as possible, with regard to the absolute configuration of the coordinated olefin.

Experimental Section

The electronic spectra were recorded on a Beckman DK2 Spectrophotometer, circular dichroism spectra on a Jouan-Roussel CD 185 dichrograph, infrared spectra on a Beckman IR9. Melting points are uncorrected. All the optical activity measurements have been performed, as the solvent, in acetone by an automatic Perkin Elmer 141 polarimeter. Elemental analyses were performed by A. Bernhardt, Mikroanalitische Laboratorium of the Max Plank Institut, Mülheim. S–α–phenylethylamine used had $[\alpha]_{589}-39$ (neat).

(–) *Fumaric acid-irontetracarbonyl* ($[\alpha]_{578}-607$) and (+) *Acrylic acid-irontetracarbonyl* ($[\alpha]_{578}+391$) were prepared according to the procedure previously described by us.[5] Brucine was used as the resolving agent.

(±) *Trans-trans-2,4-hexadienoic acid-irontricarbonyl.* The racemic complex was prepared according to the method described by Cais and Maoz.[7] The crude reaction product was repetitively crystallized from an acetone-water solution (5:1) containing a few drops of hydrochloric acid, m.p. 193° (lit. 182).

I.R.: $\nu_{C=O}$ 1670 cm^{-1} (Nujol); $\nu_{C\equiv O}$ 1985, 2000, 2060 cm^{-1} (CS_2).

Anal. Calcd. for $C_9H_8O_5Fe$: C, 42.89; H, 3.19; Fe, 22.16. Found: C, 43.08; H, 3.29; Fe, 22.03.

(+) *and (–)-trans-trans-2,4-hexadienoic acid-irontricarbonyl.* 4.5 ml of S–α–phenylethylamine were added dropwise to a stirred acetone solution (150 ml) of 9.0 g of racemic complex. Three crops of crystals were obtained by fractional crystallization: 1°, 3.3 g, $[\alpha]_{578}+92$; 2°, 3.9 g, $[\alpha]_{578}-54$; 3°, 6.1 g, $[\alpha]_{578}-79$. The first fraction was crystallized twice from acetone to yield 2.1 g of product, $[\alpha]_{578}+112$. The optical activity did not change after successive crystallizations. The third fraction after four crystallizations from diethylether afforded 2.5 g of product, $[\alpha]_{578}-172$. The enantiomeric complexes were obtained by treating acetone-water solutions of the diastereoisomeric salts with hydrochloric acid. By slow evaporation of the solvent, red-orange crystals of the enantiomeric acid complexes separated out. In a typical run, 0.56 g of the (+) diastereoisometer ($[\alpha]_{578}+112$) were dissolved in 15 ml of acetone. The solution was acidified with hydrochloric acid, 5 ml of water were added. The red-orange crystals of (+) 2,4-hexadienoic acid-Fe$(CO)_3$ (0.32 g) had $[\alpha]_{578}+213$. (–) 2,4-hexadienoic acid-Fe$(CO)_3$, $[\alpha]_{578}-204$, was obtained with the same procedure starting from the (–) diastereoisomer.

(±) *trans-1,3-pentadienoic acid-irontricarbonyl.* 9 g (92) mmoles) of 1,3-pentadienoic acid were added to a suspension of 32 g (88 mmoles) of $Fe_2(CO)_9$ in 450 ml of anhydrous and oxygen free hexane. The mixture was stirred under nitrogen atmosphere for 24 h at 70°. A brown solid was filtered at room temperature. The solution was discarded, the solid was extracted several times with $CHCl_3$. The crude product obtained on evaporation of the solvent was crystallized from an acetone water solution containing a few drops of hydrochloric acid to yield 4.75 g of yellow orange needles, m.p. 158-160°.

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[1] Istituto Chimico dell'Università di Napoli.

[2] G. Paiaro, P. Corradini, R Palumbo, and A. Panunzi, *Makromol. Chem.*, *71*, 184 (1964).

[3] A. Panunzi and G. Paiaro, *J. Am. Chem. Soc.*, *88*, 4843 (1966) and references quoted therein.

[4] F. De Candia, G. Maglio, A. Musco, and G. Paiaro, *Inorg. Chim. Acta*, *2*, 233 (1968).

[5] G Paiaro, R. Palumbo, A. Musco, and A. Panunzi, *Tetrahedron Letters*, 1067 (1965); G. Paiaro and R. Palumbo, *Gazzetta*, *97*, 265 (1967).

[6] A. Musco, G. Paiaro, and R. Palumbo, *Chim. & Ind.* (Milan) *50*, 669 (1968).

[7] M. Cais and N. Maoz, *J. Organometal. Chem.*, *5*, 370 (1966).

Anal. Calcd. for $C_8H_6FeO_5$: C, 40.34; H, 2.54; Fe, 23.46. Found: C, 40.62; H, 2.30; Fe, 22.15.

I.R. $\nu_{C=O}$ 1670 cm^{-1} (Nujol); $\nu_{C\equiv O}$ 2069, 2008, 1993 cm^{-1} (CS_2).

(+) *and* (–) *trans-1,3-pentadienoic acid-irontricarbonyl.* 1.1 ml of *S*-α-phenylethylamine were added to a chloroform solution (70 ml) of 2 g of racemic complex. By crystallization from the same solvent at 0° a first fraction (1A, 0.35 g, $[\alpha]_{578}+58$) and a second fraction (2A, 0.40 g, $[\alpha]_{578}+50$) were obtained. Following fractions having optical activity between +17 and –45 were discarded. The mother liquor was evaporated yielding 0.40 g of product (1B) having $[\alpha]_{578}-113$. Fractions 1A and 2A were collected and after several crystallizations from chloroform afforded 0.35 g of product having $[\alpha]_{578}+95$. The value of the optical activity did not change on further crystallizations. Fraction 1B after several crystallizations from chloroform reached the value $[\alpha]_{578}-126$. The optically active acid complexes were obtained from the diastereoisomeric salts with the same procedure as for *trans, trans*-2-4-hexadienoic acid-Fe(CO)$_3$. (+) *trans*-1,3-pentadienoic acid-Fe(CO)$_3$ had $[\alpha]_{578}+221$, (–) *trans*-1,3-pentadienoic acid-Fe(CO)$_3$ had $[\alpha]_{578}-148$.

Trans-trans-2,4-hexadienylidenepyrrolidinium-irontricarbonyl-perchlorate. 0.6 g (4 mmoles) of pyrrolidine perchlorate were added to 1.7 g (7.2 mmoles) of 2,4-hexadienal-Fe(CO)$_3$[8] dissolved in anhydrous benzene (50 ml). A clear solution was obtained. After 30 min at 40-50° a yellow microcrystalline solid separated out (1.0 g). The solid was isolated by filtration and washed with benzene and ethylether.

Anal. Calcd. for $C_{13}H_{16}O_7NClFe$: C, 40.08; H, 4.13. Found: C, 40.07; H, 4.30.

(+) *and* (–)*-trans,trans-2,4-hexadienal-Fe(CO)$_3$.* 1.95 g of potassium *d*-camphor-10-sulphonate were added to 2.65 g of 2,4-hexadienylidene-pyrrolidinium-Fe(CO)$_3$ perchlorate suspended in 30 ml of absolute methanol. The mixture was stirred for 13 h at room temperature; the solvent was evaporated at reduced pressure and then the residue was extracted with anhydrous acetone. The acetone was evaporated off and the red-orange solid residue was partially dissolved in 30 ml of toluene. Methylene chloride (~ 1 ml) was added dropwise to the suspension until a clear solution was obtained. On crystallization at 0° a first fraction (1A, 0.37 g, $[\alpha]_{578}+350$) was obtained. A second fraction (0.54 g, $[\alpha]_{578}+30$), and a third fraction (0.41 g, $[\alpha]_{578}+50$) were discarded. By adding n-hexane to the mother liquor 0.41 g of product (1B) having $[\alpha]_{578}-228$) were obtained.

Anal. (Fraction 1A) calcd. for $C_{23}H_{21}O_7NSFe$: C, 52.98; H, 5.99; Fe, 10.71. Found: C, 52.03; H, 5.83; Fe, 11.32.

(+) and (–) *trans, trans*-2,4-hexadienal-Fe(CO)$_3$ were obtained from the camphor sulfonate salt by alkaline hydrolysis. In a typical run 15 ml of a diluted solution of NaOH (5%) were added tropwise to 1.0 g of fraction 1A suspended in 30 ml of pentane. The yellow organic layer was separated and the aqueous solution extracted with pentane. The combined pentane extracts were dried on $MgSO_4$. On evaporation of the solvent a red oil was obtained which was trap by trap distilled to yeld 0.32 g of (–) *trans-trans*-2,4-hexadienal-Fe(CO)$_3$, $[\alpha]_{578}-60$. The I.R. spectrum was identical with that of the racemic compound. From fraction 1B with a similar procedure (+) *trans, trans*-2,4-hexadienal-Fe(CO)$_3$, $[\alpha]_{578}+40$, was obtained.

(+) *trans, trans-2,4-heptadien-6-one-irontricarbonyl.* 8.5 ml of PCl_3 and a few drops of pyridine were added to 2.52 g of (+) 2,4-hexadienoic acid-Fe(CO)$_3$ ($[\alpha]_{578}$ +204) suspended in 40 ml of anhydrous benzene. The mixture was refluxed under stirring for 1 h, then the solvent was evaporated off. The residue was extracted with 25 ml of dry benzene. The benzene solution was added dropwise to an ethereal solution of $Cd(CH_3)_2$ (prepared from 12 mmoles of CH_3MgI and 1.1 g of anhydrous $CdCl_2$). The mixture was kept for 30 min at 40°, then was cooled at 0° and hydrolized with diluted sulfuric acid. The ether layer was separated and the aqueous solution extracted with ether. The combined ether extracts were washed with sodium carbonate solution, water and then dried over sodium sulphate. Removal of the solvent left a thick red-orange oil which was distilled trap by trap. The distilled product (0.9 g) was then crystallized from pentane at –10°. The crystals melted before reaching room temperature, $[\alpha]_{578}+352$.

Anal. Calcd. for $C_{10}H_{10}FeO_4$: C, 47.28; H, 3.96; Fe, 21.98. Found: C, 47.81; H, 4.05; Fe, 23.08.

I.R. $\nu_{C=O}$ 1683 cm^{-1} (neat); $\nu_{C\equiv O}$ 1983, 1995, 2058 cm^{-1} (CS_2).

((+) *trans-1-3-hexadien-5-one-irontricarbonyl,* $[\alpha]_{578}$ +237, was prepared from (+)-*trans*-1,3-pentadienoic acid-irontricarbnyl, $[\alpha]_{578}+221$, with the same procedure as (+) 2,4-heptadien-6-one Fe(CO)$_3$.

Anal. Calcd. for $C_9H_8O_4Fe$: C, 45.80; H, 3.41; Fe, 23.66. Found: C, 46.18; H, 3.87; Fe, 25.02.

I.R. $\nu_{C=O}$ 1685 cm^{-1} (neat); $\nu_{C\equiv O}$ 2064, 2002, 1110 cm^{-1} (CS_2).

Results and Discussion

The specific rotations of the optically active iron carbonyl complexes which have been studied in this work are reported in Table I. Racemic monoolefin and diolefin carboxylic acid-iron-carbonyl complexes have been resolved by formation of salts with brucine and *S*-α-phenylethylamine respectively. (+) Acrylic acid-Fe(CO)$_4$, (–) fumaric acid-Fe(CO)$_4$, (+) *trans, trans*-2,4-hexadienoic acid-Fe(CO)$_3$, and (+) *trans*-1,3-pentadienoic acid-Fe(CO)$_3$ may be assumed opctically pure since the specific rotation of a given enantiomer did not change after several crystallizations of the corresponding diastereoisomer.

The resolution of *trans,trans*-2,4-hexadienal-Fe(CO)$_3$ through its menthydrazone was found to be unsuccessful, thus we attempted the resolution *via* fractional crystallization of the corresponding pyrrolidinium salt, having as the optically active anion *d*-camphor-10-sulfonate.[9,10] The optically active aldehyde complex

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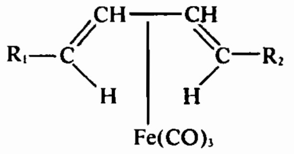
[8] J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, *85*, 3955 (1963).

can be easily obtained by alkaline hydrolisis of the pyrrolidinium salt in very mild conditions. The optical purity has not been estimated owing to the difficulty of crystallizing repetitively the diastereoisomeric salt.

Table I. Optical activity data of diene-Fe(CO)$_3$ complexes [a]



R$_1$	R$_2$	$[\alpha]_{578}$
CH$_3$	COOH	+213
H	COOH	—204
H	COCH$_3$	+352
H	CHO	+ 40
CH$_3$	CHO	— 60
CH$_3$	COOH	+221
CH$_3$	COOH	—148
CH$_3$	COCH$_3$	+237

[a] The rotations are referred to acetone as the solvent. The monoolefinic complexes have the following specific rotations: fumaric acid-Fe(CO)$_4$,$[\alpha]_{578}$—607; acrylic acid-Fe(CO)$_4$,$[\alpha]_{578}$+391.

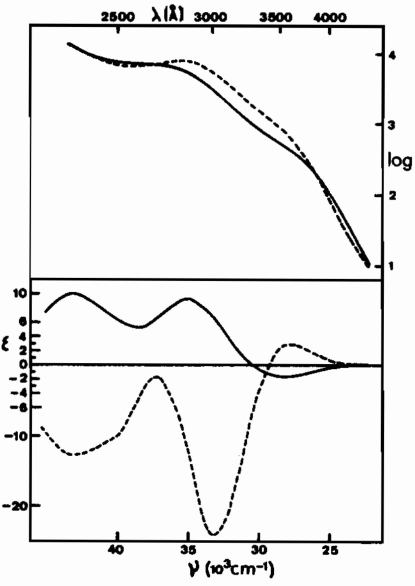


Figure 1. The electronic and circular dichroism spectra of (—) Fumaric acid-Fe(CO)$_4$ (-----) and (+) Acrylic acid-Fe(CO)$_4$ (———) in methanol solution.

Optically active *trans,trans*-2,4-heptadien-6-one and *trans*-1,3-hexadien-5-one-irontricarbonyl can be prepared in high yields from the chloride of the corresponding optically active acid by reaction with dimethyl cadmium.[11]

The absolute configuration of several platinum-olefin complexes has been determined by combining circular dichroism and X-rays anomalous diffraction studies. It has been proposed that the absolute configuration of the coordinated olefin is reflected in the sign of the lowest energy *d-d* transition of the metal atom.[12,13] The main scope of the present work has been to seek a similar relationship between circular dichroism and absolute stereochemistry of optically active iron carbonyl complexes of prochiral olefins.

The electronic and circular dichroism spectra of (—) fumaric acid-Fe(CO)$_4$ ($[\alpha]_{578}$—607) and (+) acrylic acid-Fe(CO)$_4$ ($[\alpha]_{578}$+391) are reported in Figure 1. The CD spectra have the same pattern but are opposite in sign; moreover, in the region 350-360 mμ the magnitude of the dichroism $(\varepsilon_l - \varepsilon_r)_{max}$ for acrylic acid-Fe(CO)$_4$ is half the value of fumaric acid-Fe(CO)$_4$. If the maxima at 350-360 mμ are assignable to *d—d* transitions of iron the following conclusions may be reached: a) the sign of the *d—d* transition may be related to the absolute stereochemistry of the complexes, therefore the two olefins coordinated to the Fe(CO)$_4$ moiety have opposite configuration; b) each asymmetric carbon atom contributes by the same amount to the optical activity.

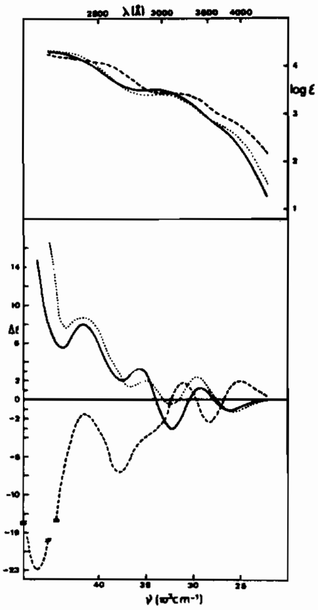


Figure 2. The electronic and circular dichroism spectra of (+) *trans,trans*-2,4-hexadienoic acid-irontricarbonyl (.....), (+) *trans*,1,3-pentadienoic acid-irontricarbonyl (———), and (—) *trans,trans*-2,4-hexadienal-irontricarbonyl (-----) in methanol solution.

The absolute configurations of the asymmetric centers of (—) fumaric acid-Fe(CO)$_4$, according to the X-rays work by Pedone and Sirigu[14] may be described as R, R, thus (+) acrylic acid-Fe(CO)$_4$ requires S configuration for the unique asymmetric carbon atom.

The uv and cd spectra of (+) *trans,trans*-2,4-hexadienoic acid- (+) *trans*-1,3-pentadienoic acid- and (—)

(9) W. R. Adams, O. L. Chapman, J. B. Sieja, and W. J. Welstead. Jr., *J. Am. Chem. Soc.*, *88*, 162 (1966).

(10) N. J Leonard and J. V. Paukstelis, *J. Org. Chem.*, *28*, 3021, (1963).

(11) H. Falk and K. Schlögl, *Tetrahedron*, *22*, 3047 (1966).

(12) P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *J. Am. Chem. Soc.*, *88*, 2863 (1966).

(13) A. D. Wrixon, E. Premuzic, and A. I. Scott, *Chem. Comm.*, 639 (1968).

(14) C. Pedone and A. Sirigu, *Inorg. Chem.*, *7*, 2614 (1968).

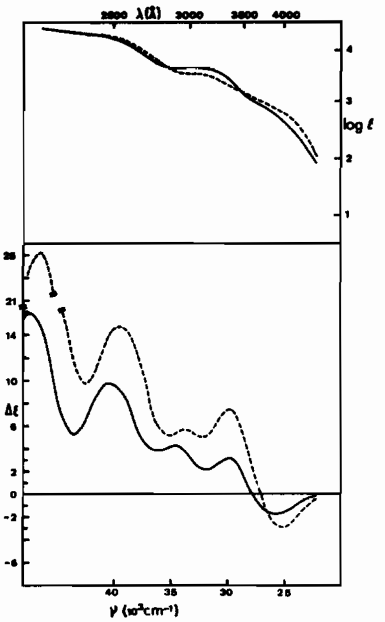


Figure 3. The electronic and circular dichroism spectra of (+) *trans*-1,3-hexadien-5-one-irontricarbonyl (———), (+) *trans-trans*-2,4-heptadien-6-one-irontricarbonyl (- - - - -) in methanol solution.

trans, trans-2,4-hexadienal-Fe(CO)$_3$ are reported in Figure 2. At first glance it appears evident that the two acids have the same absolute configuration, but opposite to that of the aldehyde complex. The two lowest energy transitions at ~390 and ~340 mμ may be assignable to dissymmetrically perturbed *d–d* transitions, the absolute configuration of the coordinated olefin being most probably reflected in the lowest (390 mμ) energy transition. The circular dichroism maximum at ~390 mμ is observed also for *trans,trans*-2,4-heptadien-6-one and *trans*-1,3-hexadien-5-one-Fe(CO)$_3$ (Figure 3).

The determination by X-rays of the absolute configuration of some optically active diene-Fe(CO)$_3$ complexes is being pursued in our laboratory. By knowing the absolute configuration of one diene complex it will probably be possible to infer the absolute configuration of any diene-Fe(CO)$_3$ complex by comparing the sign of the lowest energy *d–d* transition.

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