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SOLVENT-DEPENDENT DYNAMIC STEREOCHEMISTRY ABOUT Fe IN FERROCENYLCYCLOHEXENONES AND ACCESS TO OPTICALLY ACTIVE Cp^*Fe^+ ARENE SALTS *

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Summary

Intramolecular inversion of the chiral plane in ferrocenylcyclohexenones in the presence of $AlCl_3$ occurs in CH_3NO_2 but not in benzene. In this latter solvent ligand exchange occurs with retention of configuration, and gives optically active $Cp^*Fe^+C_6H_6$ salts with an optical purity close to 100%. This solvent dependence is best accounted for in terms of $AlCl_3$ cleavage of Cp—Fe bonds in benzene and by $AlCl_3$ cleavage of acylcyclopentadiene—iron bonds or rearrangement in CH_3NO_2. The intramolecularity of the inversion process observed in CH_3NO_2 is confirmed by tritium labelling experiments, and can be explained by rotation of the ions $CpFe^+$ and $(AlCl_3 \cdot \text{acylcyclopentadiene})^-$ in a caged ion pair; an alternative mechanism involves a σ-π rearrangement which can proceed by $\eta^1 \leftrightarrow \eta^5$ interconversion of the $AlCl_3 \cdot$ acylcyclopentadiene ligand or by direct insertion of Fe into a fulvene C—H bond. Epimerization of substituted ferrocenylcyclohexenones also proceeds by inversion of the quaternary asymmetric carbon.

The dynamic stereochemistry of ligand exchange in organometallic compounds has been a subject of interest for several decades, one of the main aims being the preparation of optically active catalysts in which the chirality is centered on the metal atom [1]. Unfortunately, those complexes which appeared most promising with respect to asymmetric catalysis are so "labile" that loss of chirality is also a feature of their reactivity. Attention has now turned towards other asymmetric frameworks, namely chiral clusters [2], although cluster breakdown in the course of catalytic reactions [3] presents a problem in this case.

Most stereochemical studies have dealt with two-electron ligands in 18-elec-

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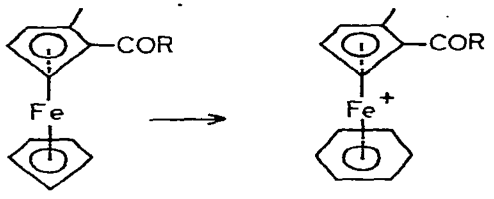
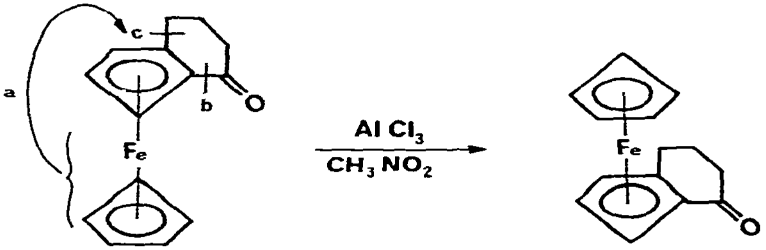
* This paper overlaps with the thesis of E.R. [30]. See also the following paper in this issue [29].

tron complexes which are not themselves catalysts but are possible catalyst precursors. However, preparation of optically active 18-electron complexes (A → B) is an interesting challenge when these complexes show interesting redox properties. In such complexes, the chirality should be as close as possible to the metal so that the chiral redox catalysts can promote asymmetric synthesis. This goal appears reasonable since electron-transfers often proceed via charge transfer complexes [4].



A B

CpFe$^+$ arene cations are extremely stable sandwiches which act as redox catalysts for the electroreduction of nitrate to ammonia, especially when the arene ring is hexasubstituted by alkyls [5]. It was therefore of interest to prepare optically active sandwiches in this series having a plane of chirality. We therefore undertook a study of the dynamic stereochemistry of ligand exchange with ferrocenylcyclohexenones. The ferrocenylcyclohexenone was first synthesized by Thomson [6] in 1959 and resolved into enantiomers by Schlögl [7] in 1963. Slocum [8] showed in 1970 that racemization in CH_3NO_2 occurs under the influence of $AlCl_3$ (eq. 1) and suggested that cleavage of the iron—acylcyclopentadiene ring bond occurred.



(1)

In 1971, Falk [9] published a kinetic study in conflict with this hypothesis, and showed the racemization to be intramolecular, and this was confirmed by des Abbayes in 1973 using tritium-labelled samples [10]. This substrate should provide an ideal starting material for CpFe$^+$ arene salts with a chiral substituted Cp plane, since we have shown [11,12] that exchange using acylferrocenes provides the only method for synthesis of an acylcyclopentadieneFe$^+$ arene (eq. 2). (The ligand exchange reaction between diacyl-1,1′-ferrocenes and arenes in the presence of $AlCl_3$ gives only bis(arene)Fe^{2+} in our hands, although Nesmeyanov reported the preparation of acylcyclopentadieneFe$^+$ arene by this procedure [13]).

$$\eta^5\text{-RCOC}_5\text{H}_4\text{Fe}\eta^5\text{-Cp} \xrightarrow[\text{arene}]{\text{AlCl}_3} \eta^5\text{-RCOC}_5\text{H}_4\text{Fe}^+ \text{ arene} \qquad (2)$$

The reaction observed by Slocum [8] seemed to provide a serious obstacle to obtaining optically active acylcyclopentadieneFe$^+$ arene complexes. Indeed it was also known from the work of Bublitz [14,15] that unsymmetrical dialkyl 1,1'-ferrocenes yield symmetrical ferrocenes by intermolecular ring exchange (eq. 3);

$$\eta^5\text{-R}^1C_5H_4Fe\eta^5\text{-R}^2C_5H_4 \xrightarrow[\text{neat}]{AlCl_3} (\eta^5\text{-R}^1C_5H_4)_2Fe + (\eta^5\text{-R}^2C_5H_4)_2Cp \tag{3}$$

We report here details of the epimerizations of ferrocenylcyclohexenones by inversion of the chiral plane and of the quaternary chiral carbon in nitromethane [10] and of the retention observed during the ligand exchange in benzene [16].

Results

I. Studies in nitromethane

The four ketones (I—IV) (the configurations are as in Scheme 1) were synthesized by a published procedure and labelled with tritium on each Cp ring [27]. They contain both a metallocenic chirality and an ancillary chiral center which we assumed to remain unchanged. Thus, the racemization process becomes an epimerization, the rate of which allows an evaluation of the struc-

SCHEME 1

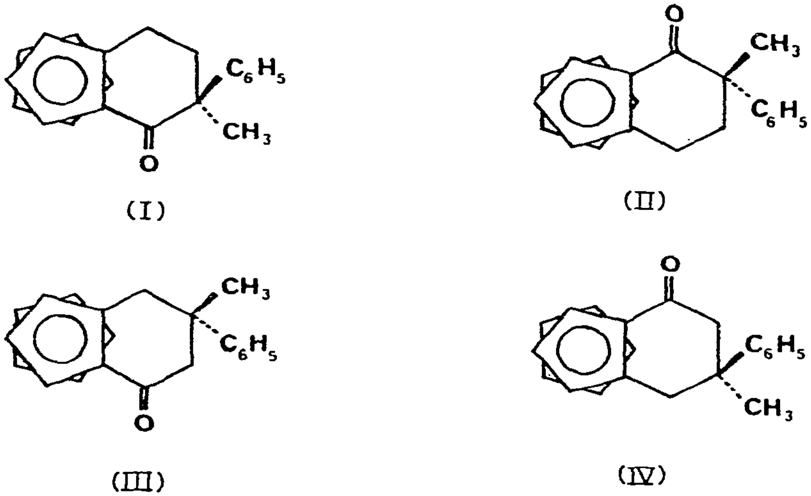


TABLE 1

EPIMERIZATION OF THE RACEMIC KETONES I—IV

Starting ketone	% of ketone obtained				Rate (%) of ketones obtained/starting
	I	II	III	IV	
I (Ph *exo*)	73	27			50
II (Ph *endo*)	73	27			50
III (Ph *endo*)			43	57	35
IV (Ph *exo*)			41	59	34

TABLE 2

EPIMERIZATION OF THE OPTICALLY ACTIVE KETONES I—IV

Starting ketones (optically pure)				Obtained ketones Number and $[\alpha]_D^{20}$ [b] (°)
configuration [a]			$[\alpha]_D^{20}$ [b] (°)	
I	2 *Rp*	6 *S*C	−347	I (−347) and II (+336)
II	2 *Sp*	6 *S*C	+380	I (−347) and II (+343)
III	2 *Rp*	5 *R*C	−40	III (−27.3) and IV (+251)
IV	2 *Sp*	5 *R*C	+262	III (−20) and IV (+262)

[a] R_P or S_P give the metallocenic chirality; R_C or S_C give the carbon-centered chirality. [b] *c* ~0.5; toluene.

tural effects of the chiral center on the inversion of the metallocenic chiral plane. All the reactions were carried out under the same conditions: reflux 4 h; ketone/$AlCl_3$ = 0.77. The results for the racemic series are summarized in Table 1 and those for the optically active series in Table 2. In the tritium-labelled series, the specific radioactivities of all the ketones are completely preserved during the epimerization.

When the reaction is carried out with a mixture of the unlabelled ketone I and tritium-labelled ketone IV* and the reaction mixture chromatographed on silica gel, the set of ketones I and II is obtained unlabelled while the set of ketones III* and IV* is obtained labelled, and retaining the specific radioactivity of the precursor IV*. This indicates that no intermolecular exchange of the acylcyclopentadiene ring occurs during the epimerization.

The results shown in Table 1 indicate that the same proportions of epimers are obtained regardless of the starting isomer, and that the main ketone obtained is the sterically favored one (*exo*-phenyl). Thus this epimerization process is probably under thermodynamic control.

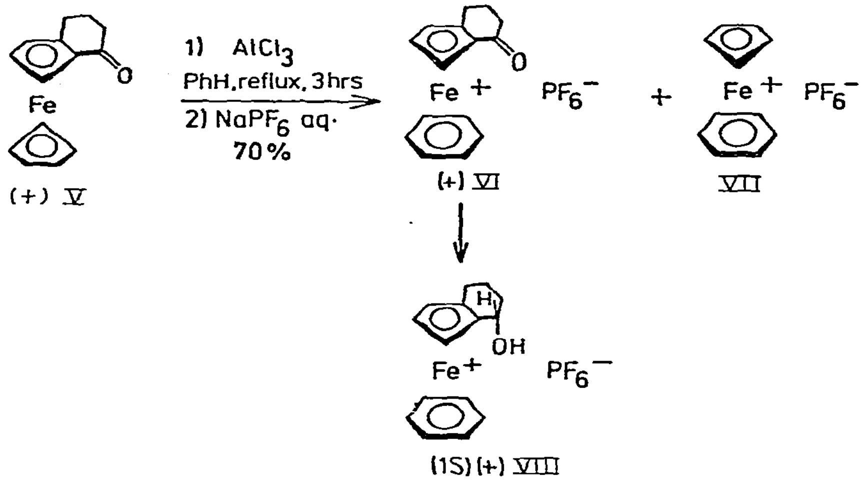
The signs and values of the rotations obtained for the ketones I and IV (Table 2) show that the ketones II and III (C_6H_5 in *endo* position) are essentially epimerized by inversion of the metallocenic chiral plane. On the other hand, the obtained ketones II and III show a marked degree of racemization whatever be the starting ketones. Thus the chiral carbon unexpectedly loses its configuration during the epimerization process.

II. Studies of the ligand exchange in benzene

The ligand exchange reactions were performed in benzene using (+)-1,2-(α-ketotetramethylene)ferrocene V (Slocum's ketone, eq. 1). The synthesis [6], separation [7] and racemization [8] in $AlCl_3$ + CH_3NO_2 have been reported previously. The following reaction conditions were used (Scheme 2): reflux 3 h, ketone/$AlCl_3$/benzene = 1/4/excess (solvent). Under these conditions, the ketone recovered after the reaction (15%) was not racemized, as indicated by the optical purities (100%) before and after reaction.

The mixture of VI and VII, obtained in a ratio VI/VII = 3, was found to be optically active. Since the maximum rotation calculated by isotopic dilution for the salt VI was found to be +249°, we conclude from the rotary power of

SCHEME 2



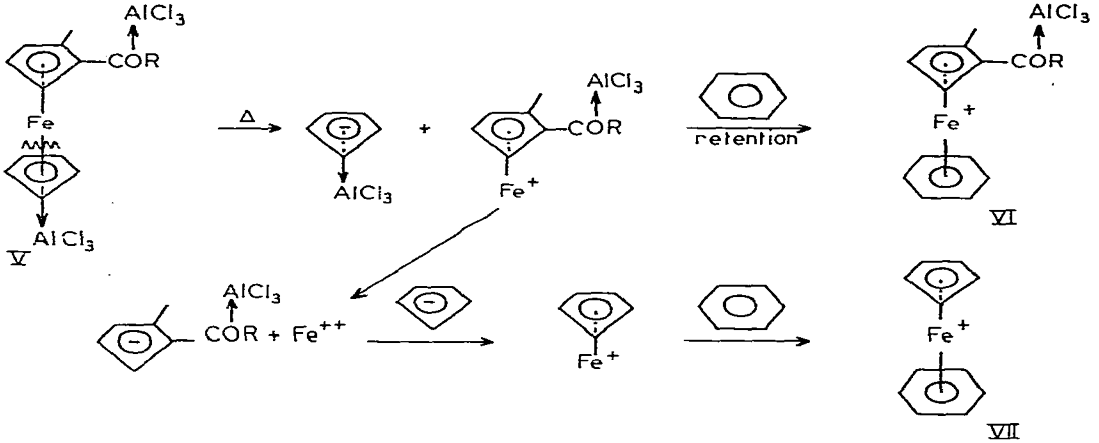
the mixture VI + VII (+181°) and its composition, that the optical purity of the salt VI was close to 100%. Its abolute configuration was demonstrated by Horeau's technique [19] applied to the *endo* alcohol VIII synthesized by a stereospecific electroreduction of the salt VI [29]. The laevorotation of the α-phenylbutyric acid obtained after hydrolysis of the esterification reaction indicates an *S* configuration for the functional carbon. This confirms that the ligand exchange between the unsubstituted Cp ring in V and benzene occurs with retention of configuration of the chiral acylcyclopentadiene ring on the iron atom, in sharp contrast to the racemization obtained with the V and its analogous I—IV in nitromethane.

Mechanisms and discussions

A. Ligand exchange with benzene

We have previously proposed that the ligand exchange of an acylferrocene with benzene giving an acylcyclopentadienyliron-arene cation (eq. 2) proceeds by selective cleavage of the unsubstituted Cp—iron bond due its larger π density compared with that of the acyl-substituted ring [12]. The retention now observed indicates that, in contrast to an unsubstituted Cp ring, an acyl-substituted Cp cannot be reversibly cleaved (Scheme 3). We have previously made such a proposal to explain the formation of unsubstituted CpFe$^+$ benzene in the reaction [12,16], which we suggested did not proceed by replacement of the acyl-substituted Cp ring by benzene but by cleavage of the unsubstituted Cp ring followed by complete breakdown of the moiety to give Fe^{2+}, which would then recombine with one Cp and one benzene ring (alternatively Cp$_2$Fe can be formed and further cleaved). This hypothesis is now confirmed. Thus the mechanism of cleavage of acylferrocenes is very different from that of alkylferrocenes, for which the rings are reversibly cleaved [22]. The mechanism of ligand replacement in acylferrocenes which involves only cleavage of the Fe—C$_5$H$_5$ bond, leading to both CpFe$^+$C$_6$H$_6$ and acylcyclopentadieneFe$^+$-

SCHEME 3



C_6H_6, is consistent with the inertness of 1,1'-diacylferrocenes which do not contain Cp rings of sufficient π density to be complexed with $AlCl_3$ and then be cleaved off.

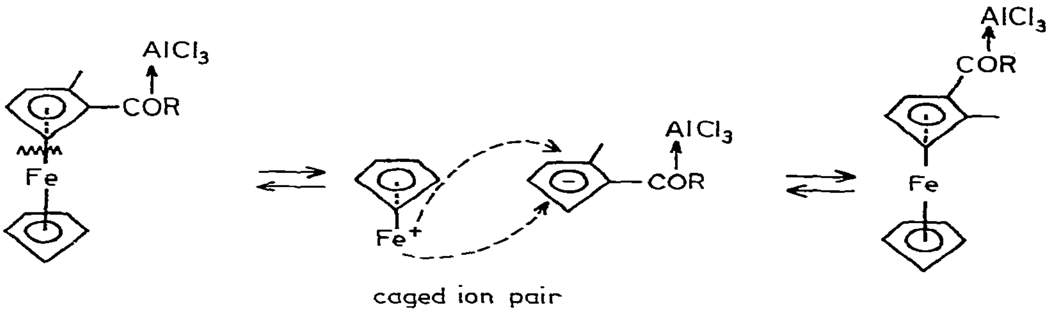
B. Inversion of the metallocenic chiral plane

The results confirm Falk's conclusions [9]. An intermolecular ring exchange is excluded by our study on a mixture of unlabelled and tritium labelled ketones. A cleavage at a ring carbon in b followed by recyclization by a retro-Friedel-Crafts mechanism is not compatible with the stereochemistry observed. The cyclizations of the γ-ferrocenyl butyric acids, which are under kinetic control, lead preferentially to the *endo*-phenyl ketone, whereas the epimerization mostly gives the *exo*-phenyl isomer. The same conclusion is reached from the study of the reactions of the tritium-labelled ketones I*, II*, III* and IV*, which also allows us to eliminate a C—C cleavage (c, eq. 1) followed by cyclization. These mechanisms involving a C—C cleavage (b or c, eq. 1) would imply a lowering of the specific radioactivity by about 10% for the four ketones, due to the probability of recyclization on a tritium-labelled Cp carbon, whereas the recovered ketones show no loss of radioactivity (precision 2%).

The inversion at the "quaternary" chiral center is completely unexpected, and so far cannot be explained on the basis of our experimental data. Such a racemization of a "quaternary" carbon has been observed in a steroid in position 13 [21]. The selectivity of the present racemization is noteworthy, since it is marked for only ketones II and III, which contain an *endo*-phenyl group.

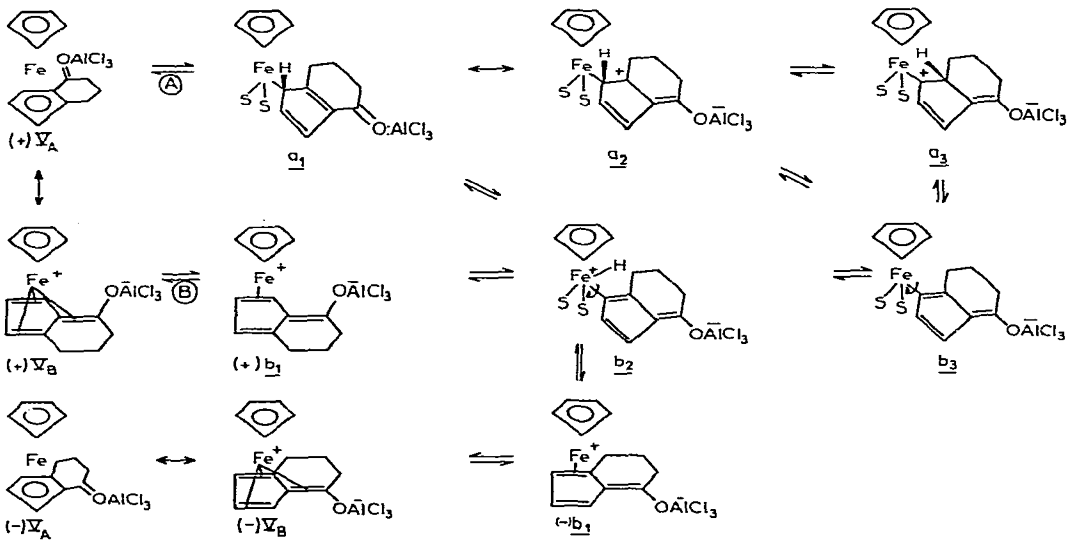
Since the inversion of the chiral plane is now shown to be an intramolecular process, it can be accounted for by the formation of a caged ion pair (Scheme 4) resulting from the thermal cleavage of the Fe—ring bond due to electron withdrawal by $AlCl_3$ complexes to the carbonyl group [22]. Fast rotation and recombination of the two ions, leading to loss of the metallocenic chirality could occur even though CH_3NO_2 is a good ionizing solvent (dielectric constant $\epsilon = 34$). An alternative mechanism would involve a σ—π rearrangement, as we have recently proposed [16]. $\eta^5 \leftrightarrow \eta^1$ interconversion is a well known process [23]. Recently Casey showed by X-ray analysis of the product that η^1-CpRe$(PMe_3)_2(CH_3)(NO)(CO)$ is produced by treatment of η^5-CpRe$(CH_3)(NO)(CO)$ with excess PMe_3 [24]. The reverse of this process, formation of ferrocene by a $\sigma \rightarrow \pi$ rearrangement of Cp is also known [25]. In a recent communication, Slocum indicated that both the deuteration of certain substituted ferrocenes in pyridine and the racemization of V in the presence of $AlCl_3$ can be accounted for in terms of the classical σ—π rearrangement of Cp [26]. However, we have spectroscopic evidence available indicating that the purple complex V · $AlCl_3$ has a fulvene-like structure rather than the regular Cp involved in Slocum's mechanism; moreover no base is present in the medium to deprotonate the ipso carbon and induce the loss of its chirality in the σ intermediate. Scheme 5 depicts the hypothesis A based on a simple σ—π arrangement although we

SCHEME 4



favor the hypothesis B involving insertion of Fe into a C—H bond of the fulvene ligand. Note that the key σ intermediate, in which the rotation about the Fe—η^1-ring bond induces the inversion of the chiral plane, must involve an olefinic carbon, and could be either the cation b_2 or the neutral complex b_3 (Scheme 5).

SCHEME 5



Experimental

Epimerization of the ketones I—IV

A solution (A) of 100 mg $AlCl_3$ (0.74 mmol) in 5 ml CH_3NO_2 (predried over $CaCl_2$ and distilled over N_2) is prepared (A). The ketone (100 mg, 0.3 mmol) is placed in a 20 ml flask and after purging with N_2, 7.5 ml of CH_3NO_2 and, then 2.5 ml of A are added. The solution is refluxed under N_2 for 4 hours, hydrolyzed with water, and extracted with CH_2Cl_2. The organic layer is washed with water, filtered, dried, concentrated in vacuo and chromatographed on silica gel (eluant: 10% ether in petroleum ether). The four ketones are easily separated. The R_f are as follows: I, 0.28; II, 0.19; III, 0.117; IV, 0.07. As soon as the solution A is added to the ketone, a purple color appears due to complexation of the carbonyl group by $AlCl_3$, as confirmed by the IR spectrum in which the ν(CO) band (1680 cm^{-1}, CH_2Cl_2) has disappeared.

Epimerization with the tritium-labelled ketones I—IV [27]

The ketones I—IV were labelled in each Cp ring (random labelling, 1 carbon per ring was labelled). The average activity was 40000 disintegrations per min and per mg. For each tritium-labelled ketone I—IV (specific activity, 100% as a reference) the two ketones obtained always had a specific activity of 100% (I^* and II^* both give the I^*, II^* mixture, III^* and IV^* both give the III^*, IV^* mixture).

Crossover reactions with mixtures of tritium-labelled and unlabelled ketones

Starting from the mixture of II^* (specific activity 100%) and III (specific activity 0%), ketones obtained as described above were I^* and II^*, with specific activities of 100% and III and IV with specific activities of 0%. These results indicate that the epimerizations are intramolecular. The same conclusion was reached from an experiment starting with the mixture of the unlabelled ketone I and of a labelled ketone IV^*, with the experimental conditions as indicated above.

Ligand exchange between (+)-1,2-(α-ketotetramethylene)ferrocene and benzene

1,2-(α-ketotetramethylene)ferrocene was synthesized by a published procedure [6] and resolved into enantiomers as described by Schlögl [7]. The α_D^{21} = +656° was larger than previously reported (α_D^{21} = 580° [7]).

254 mg of (+)-ketone (1 mmol, α_D^{21} = +656°, optical purity 100%) and 540 mg of $AlCl_3$ (4 mmol) are introduced under N_2 into 30 ml of degassed benzene. After 3 h of reflux, the mixture is cooled to 0°C and hydrolyzed with 50 g of ice water. The organic layer is washed with 2 × 10 ml water and dried over $MgSO_4$, and the solvent removed in vacuo. The solid residue is chromatographed twice on plates of 1 mm silica gel with a mixture of hexane/ether (1/1) as eluent. This leads to isolation of 25 mg (10%) of crystalline ketone. Its melting point (84°C), IR spectrum (ν(CO) = 1682 cm^{-1}, Nujol) and α_D^{21} = +656° are identical with those of the starting material.

The aqueous layer is washed with 2 × 10 ml ether, filtered and an aqueous solution of 0.5 g $NaPF_6$ (3 mmol) is added. The precipitate is collected and dried (250 mg, α_D^{21} = +181°). The ^1H NMR spectrum in CD_3COCD_3 indicates that 3/4 of the mixture is the ketone VI and 1/4 the parent salt VII (±5%). After two recrystallizations, VI is obtained pure, since α_D (+249°) is not changed by a third crystallization.

The same ligand exchange reaction with the racemate on a 3 mmol scale gave a 60% yield of the ketone VI (racemate) after two recrystallizations from water.

Determination of the optical purity of VI by the isotopic dilution method

a. Synthesis of $[\eta^5\text{-}C_5H_3CO(CH_2)_3Fe\eta^6\text{-}C_6D_6]^+PF_6^-$. The same procedure is used with 0.3 g of C_6D_6 in 30 ml of heptane and 0.128 g of B (0.5 mmol). After two recrystallizations in water 0.14 g of VI-d^6 is obtained (70%).

b. Isotopic dilution. 6.8 mg (n) of VI* and 6.8 mg (m) of VI-d^6 are dissolved in 15 ml of acetone. The solution is filtered and, after slow evaporation and cooling to 0°C, 3.7 mg of salt is obtained with $\alpha_D^{21} = +173°$ (αi): the mass spectrum indicates the presence of 44% (S_i) of C_6D_6 in the benzene obtained by decomplexation of the mixture. With $S_0 = 100\%$ and $\alpha = 249°$, we can calculate the rotation:

$$A = \frac{S_i n^2(\alpha)^2 - S_0 mn(\alpha)(\alpha i)}{S_i(m+n) - S_0 m(m+n)} = 256.5°$$

This gives an optical purity $\frac{(\alpha)}{A}$ of 97%.

*Synthesis of the alcohol VIII**

100 ml of H_2SO_4N is de-aerated in an electrochemical cell for reduction at a controlled potential, and the solution is submitted to a pre-electrolysis at —1 V/SCE until the residual intensity is reduced to 0.75 mA. 25 mg of VI* (0.073 mmol) is then introduced and electrolysis at —1 V/SCE is carried out until the residual intensity is reduced to 0.75 mA. VIII* is extracted with CH_2Cl_2 after addition of 0.17 g (1 mmol) of $NaPF_6$. The CH_2Cl_2 solution is washed with 20 ml H_2O, dried over $KHCO_3$, concentrated under reduced pressure and added to 50 ml ether to precipitate VIII*. The solid is dissolved in CH_2Cl_2, the solution is filtered, and solid reprecipitated by addition of ether to give 15 mg (60%) of VII* with $\alpha_D^{21} = +56°$. Spectroscopic characterization of the racemate has been described elsewhere [29—31].

Absolute configuration of the alcohol VIII by Horeau's method*

To a solution of 10 mg of VIII* (2.4×10^{-5} mol) in 0.5 ml of pyridine is added 34.2 mg of α-phenylbutyric anhydride (10^{-4} mol). The solution is left for 3 days in the dark, then extracted with 3 ml of benzene. The α-phenylbutyric acid coming from the excess anhydride is titrated with 2 *N* NaOH (9.6 ml), which gives the yield of the esterification reaction (33%). The aqueous phase is extracted with 2 × 10 ml benzene, and acidified with 1 ml *N* HCl. After extraction with benzene (2 × 10 ml) and drying over $MgSO_4$ (1 g), this phase is concentrated to 5 ml. The rotation is —0.010 for the *D* absorption (Perkin-Elmer Polarimeter 241 MC, 1 dm quarz cell). Thus the anhydride obtained by hydrolysis of the dextrorotatory acid has reacted to give the alcohol of *S* configuration according to Horeau's rule [19]. The optical yield is given by $P = \frac{\alpha}{\alpha'\rho}$ in which α' is the rotation corresponding to complete splitting ($\alpha' = 0.077°$), $\alpha = 0.010$, $\rho = 33\%$, $P = 39\%$. The S configuration corresponds to the *endo* alcohol, according to the extension to the metallocenes by Schlögl [31] of the nomenclature for absolute configuration proposed by Cahn, Ingold and Prelog [32].

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References

1 H. Brunner, Advan. Organometal. Chem., 18 (1980) 151.
2 E. Band and E.L. Muetterties, Chem. Rev., 78 (1978) 639.
3 (a) F. Richter and H. Vahrenkamp, Angew. Chem. Intern. Ed. Engl., 17 (1977) 864; (b) R.T. Edinin, L.A. Zyzyck and J.P. Norton, J. Chem. Soc. Chem. Commun., (1979) 580; (c) H. Beurich and H. Vahrenkamp, Angew. Chem. Intern. Ed. Engl., 20 (1981) 98.
4 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, pp. 445—465.
5 (a) D. Astruc, J.-R. Hamon, G. Althoff, E. Roman, P. Batail, P. Michaud, J.-P. Mariot, F. Varret and D. Cozak, J. Amer. Chem. Soc., 101 (1979) 5445. (b) D. Astruc, A. Darchen and C. Moinet, DGRST Report, Dec. 1979. (c) A. Buet, A. Darchen and C. Moinet, J. Chem. Soc. Chem. Commun., (1979) 447. (d) E. Roman, R. Dabard, C. Moinet and D. Astruc, Tetrahedron Lett., (1979) 1439.
6 J.B. Thomson, Tetrahedron Lett., (1959) 26.
7 K. Schlögl, M. Fried and H. Falk, Montasch. Chem., 95 (1964) 576.
8 D.W. Slocum, S.P. Tucker and T.G. Engelmann, Tetrahedron Lett., 621 (1970).
9 H. Falk, M. Lehner, J. Paul and U. Wagner, J. Organometal. Chem., 28 (1971) 115.
10 H. des Abbayes and R. Dabard, J. Organometal. Chem., 61 (1973) C51.
11 D. Astruc, Tetrahedron Lett., 3437 (1973).
12 D. Astruc and R. Dabard, Tetrahedron, 32 (1976) 245.
13 A.N. Nesmeyanov, N.A. Vol'kenau and L.S. Shilovtseva, Dokl. Akad. Nauk SSSR, 160 (1965) 1327.
14 D.E. Bublitz, Can. J. Chem., 42 (1964) 2381.
15 D.E. Bublitz, Can. J. Chem., 16 (1969) 149.
16 E. Román and D. Astruc, Nouv. J. Chim., 1 (1977) 183.
17 H. des Abbayes, C.R. Acad. Sci., Paris, 273 (1971) 1009.
18 H. des Abbayes, C.R. Acad. Sci., Paris, 276 (1973) 1763.
19 (a) A. Horeau, Tetrahedron Lett. (1961) 506 and (1962) 965. (b) A. Horeau and H.B. Kagan, Tetrahedron, (1964) 2431.
20 E. Román, D. Astruc and A. Darchen, J. Chem. Soc. Chem. Commun., (1976) 512.
21 I. Khattak, D.N. Kirk, C.M. Peach and M.A. Wilson, J. Chem. Soc. Chem. Commun., (1973) 341.
22 D. Astruc and R. Dabard, J. Organometal. Chem., 111 (1976) 339.
23 D.W. Slocum, S. Duraj, J. Bencini, K. Webber, R. Noble, K. Kuchel and M. Hodgman, in Y.Z. Huang, Y. Ishii and M. Tsutsui (Eds.), Fundamental Research in Organometallic Chemistry, Reinhold, Van Nostrand, in press.
24 C.P. Casey and W.D. Jones, J. Amer. Chem. Soc., 102 (1980) 6154.
25 M. Tsutsui, M. Hancock, J. Ariyoshi and M.N. Levy, J. Amer. Chem. Soc., 91 (1969) 5233.
26 D.W. Slocum, D.L. Beach, C.R. Ernst, R. Fellows, M. Moronski, B. Conway, J. Bencini and A. Siegel, J. Chem. Soc. Chem. Commun., (1980) 1043.
27 H. des Abbayes and R. Dabard, Tetrahedron, 31 (1975) 2111.
28 C. Moinet and D. Peltier, Bull. Soc. Chim. (1969) 690. The assistance of Dr. A. Darchen is acknowledged for this reaction.
29 E. Román, D. Astruc and A. Darchen, J. Organometal. Chem., 219 (1981) 221.
30 E. Román, Thêse d'Etat, Rennes, 1979.
31 K. Schlögl, Fortschr. Chem. Forschg., 6 (1966) 479.
32 (a) R.S. Cahn, C.K. Ingold and V. Prelog, Experimentia, 12 (1956) 81 and Angew. Chem., 78 (1966) 413. b) R.S. Cahn, J. Chem. Ed., 41 (1964) 116.