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ASYMMETRIC CYCLOPALLADATION OF DIMETHYLAMINOMETHYLFERROCENE

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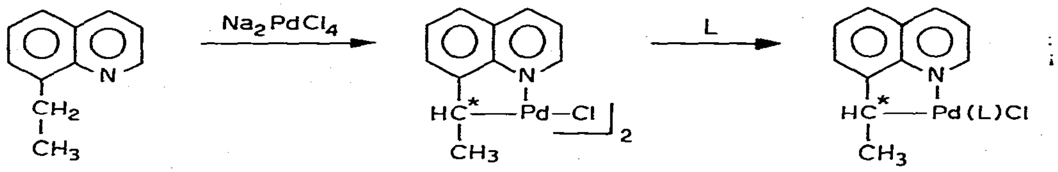
Summary

Palladation of dimethylaminomethylferrocene (I) catalyzed by salts of optically active acids affords optically active planar chiral 2-dimethylaminomethylferrocenylpalladium chloride dimer (II) in high yield. Absolute rotation and optical purity of II were determined by conversion to 2-methylferrocenecarboxylic acid and 2-methylferrocenealdehyde. Factors affecting enantiomeric excess are examined and conditions for maximal asymmetric induction are found.

Introduction

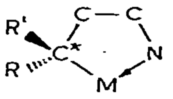
Cyclopalladation of tertiary benzylic amines with replacement of hydrogen in the aromatic ring by metal was first observed by Cope and Friedrich [1] after discovering a similar reaction for azobenzene [2]. The reaction was considered as electrophilic substitution on the basis of substituent effects. The presence of a "directing" atom, such as nitrogen, phosphorus or sulphur, is a necessary condition for cyclometalation to proceed with formation of a chelate metallocycle. Variation of structural fragments was discussed previously [3], here we shall take into account only metallocycles containing nitrogen, and of the metals we shall consider only palladium and platinum since the reaction mechanisms seem to be quite different for different metals [4]. A comprehensive review of cyclometalation literature was recently given [5—7].

It should be noted that cyclometalation into the alkyl group has been rarely observed and practically exclusively for phosphines [8,9]. As for nitrogen as a directing atom, reactions involving 8-methylquinoline [10] and 8-ethylquinoline [11] have been reported. In the latter case, a chiral center is formed on the carbon atom bonded to the metal and partial resolution of enantiomers of the palladium derivative was observed.



Chirality in chelated metallocycles

It is known that 5-membered chelate metallocycles are most easily formed, although 4-membered rings containing nitrogen and platinum have also been reported [12,13]. The following possibilities for introducing chirality into the chelated metallocycle system have been proposed [14]



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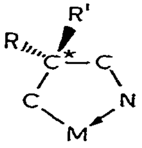

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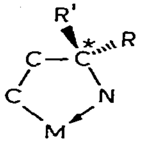

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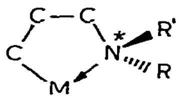

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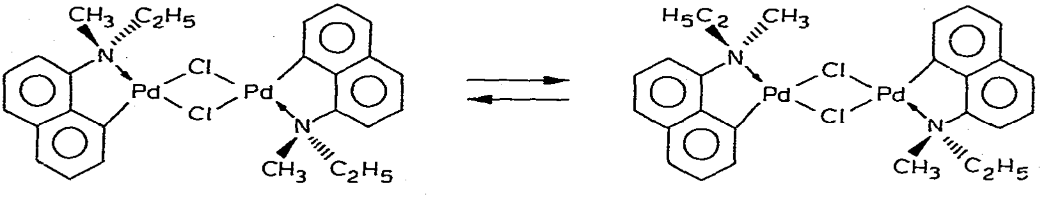
Case 1 has been described for the 8-ethylquinoline system in our work [11], case 4 for *N*,*N*-methylethyl-α-naphthylamine [15] where two diastereomers were obtained differing in configurations of both nitrogen chiral centers:

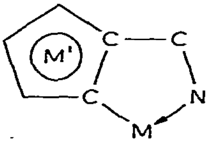


dl

meso

Case 3 is easily realized when C_1 and C_2 are incorporated in the aromatic system and C_3 is the chiral center as exemplified by α-phenylethylamine. Otsuka et al. [16] used the cyclopalladated derivative of this compound as a chiral reagent for optical resolution of tertiary phosphine. Hence, of these simple models only case 2, with C_2 as the chiral center, has not been realized experimentally.

There exists, however, another method for introducing chirality illustrated by cases 5, 6 and 7. Those models imply the structural pattern of a planar



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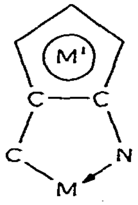

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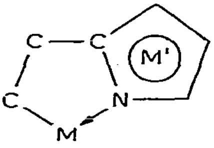

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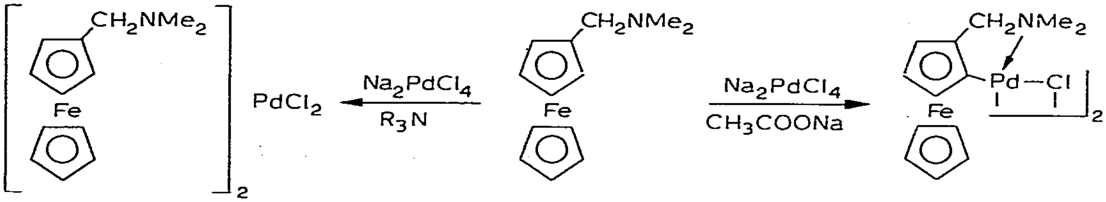
chiral moiety fused with the chelated metallocycle. On account of the poorly studied chemistry of azaarene π-complexes case 7 does not seen very practicable as yet. Case 6 appears to present considerable experimental difficulties since it requires metalation into the alkyl group or indirect synthetic routes. Case 5, on the other hand, represents the well-known structural type constructed on the basis of metallocene, precisely like the benzylamine derivative. The aryl fragment, which is achiral in itself, should be replaced by any π-complex organometallic moiety possessing planar chirality. Due to the structural asymmetry of the chelated metallocycle, any condensed π-complex moiety will make the molecule planar chiral. In this study we chose dimethylaminomethylferrocene (I) as the starting compound.

Results and discussion

The role of carboxylate ions in cyclometalation and asymmetric catalysis

Ideas about cyclopalladation and cycloplatination as electrophilic substitution reactions were formulated in the first work of Cope et al. [1]. The presence of tertiary nitrogen was considered a necessary structural condition and the role of tertiary amine as the reaction catalyst was reduced to binding of liberated HCl equivalent. These ideas have undergone some changes since then, but the postulated mechanism remains essentially unchallenged [4—7]. However, cyclopalladation of several secondary and primary amines has been reported [17,18]. On the other hand, amine I, which satisfies Cope's requirements, yield under usual conditions L_2MCl_2 complexes as the sole reaction product [19], although the ferrocene nucleus more readily undergoes electrophilic substitution than the benzene ring. In 1975, Shaw and Gaunt [20] established that cyclopalladation of I in the presence of sodium acetate results in formation of dimeric organopalladium chloride (II). This suggests that the acetate ion participates in an important early step of this reaction and its presence in an intermediate or transition state leading to the cyclopalladated product is necessary. It is unlikely that the role of acetate ion is restricted only to binding of liberated HCl.



(III) (I) (II)

We assumed that if carboxylate ions participate in formation of the transition state, the anion of an optically active carboxylic acid and prochiral dimethylaminomethylferrocene I will create conditions for realization of asymmetric induction in the course of cyclopalladation. As a result, the planar chiral product II may be formed in optically active form, one of the enaniomers being in excess. Previously, we examined intramolecular asymmetric induction during cyclopalladation of enantiomeric 1-dimethylaminoethylferrocene [21,22] and 1-deuterodimethylaminomethylferrocene [23] and determined the degree of diastereomeric excess during formation of planar chirality by a chiral center of a given configuration.

Optically active dimer II was indeed obtained by carrying out cyclopalladation of I in the presence of sodium salts of optically active carboxylic acids; preliminary results in which only a small degree of asymmetric induction was observed were reported in a short communication [24]. *N*-Acyl-α-amino acids were found to give higher induction than α-hydroxy acids (lactic and mandelic), whereas replacement of Na^+ by Cs^+, Bu_4N^+ or Li^+ does not significantly affect the enantiomer yield. pH was found to be a determining factor. The pH-dependence of chemical and enantiomeric yields of II when carrying out the reaction in aqueous methanol in the presence of Na salt of *N*-acetyl-L-valine is shown in Fig. 1, data are listed in Table 1. In acidic media ferrocene is oxidized into ferrocenium, reducing the chemical yield of II. In alkaline solutions both curves in Fig. 1 vary simbatically reaching maxima and then falling off. The maxima of chemical and enantiomeric yields do not coincide, the latter being reached at about pH 8 in the absence of amine, i.e. at nearly pH 9 after the amine is added.

The procedure for preparing II in maximum chemical and enantiomeric yields is as follows. An aqueous solution of an equimolar mixture of *N*-acetyl-L-valine and NaOH is added to Na_2PdCl_4 in methanol, pH is set at 6.7—7.5 using 50% aqueous NaOH, and a solution of I in methanol is then added. Optically active dimer II, having $[\alpha]_D$ 470—500°, rapidly precipitates, and it may then be converted into the monomeric acetylacetonate.

These findings unambiguously point to the direct involvement of the carboxylate anion in the reaction transition state. Possibly, it is incorporated into

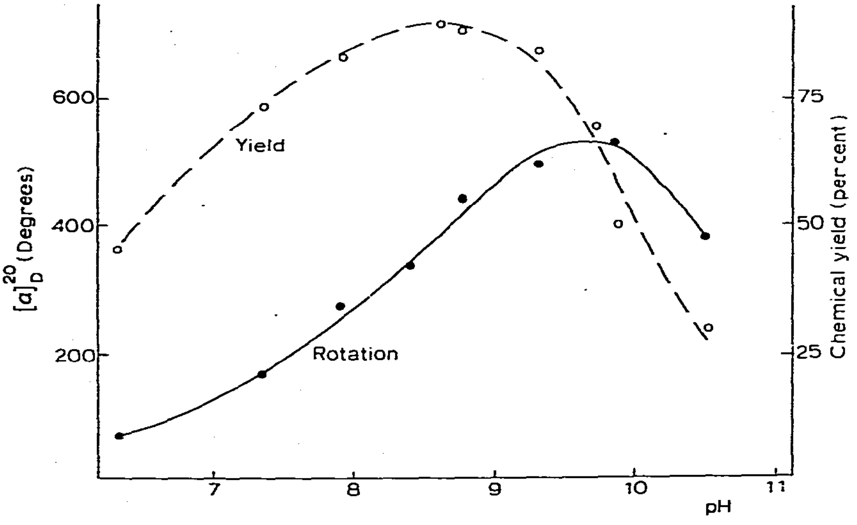


Fig. 1. pH dependence of the chemical and enantiomeric yields of II. Na salt of *N*-acetyl-*S*(+)-valine as catalyst, in 4/1 $MeOH/H_2O$.

TABLE 1

EFFECT OF pH ON ENANTIOMETRIC EXCESS OF PRODUCT II DURING CYCLOMETALATION OF DIMETHYLAMINOMETHYLFERROCENE (I) [a]

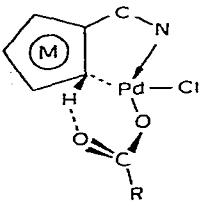
pH^1	pH^2	Chemical yield	$[\alpha]_D^{20}$ of product II (°C)	Enantiomeric excess (%)
5.48 [b]	6.28	46	+54	8.0
6.0	7.35	73	+167	24.5
6.45	7.90	83	+276	40.5
6.70	8.75	89	+442 [c]	65.0
7.60	9.30	85	+496 [c]	73.0
7.95	9.82	50	+535	78.8
8.50	10.30	37	+380	56.0

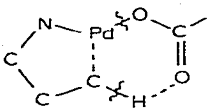
[a] The reaction was carried out in the presence of 1 eq. of the Na salt of *S*(+)-*N*-acetylvaline, solvent methanol/water 4/1, $[\alpha]_D^{20}$ (CH_2Cl_2 1.8—4.4). pH^1 measured in the reaction mixture before addition of amine I in methanol, pH^2, after addition (which is less accurate if product II immediately starts to precipitate). Enantiomeric excess was calculated based on $[A]_D^{20}$ +679° for II in CH_2Cl_2 (see Discussion), absolute configuration of the chiral plane in the predominant enantiomer is R_p. [b] pH value of the solution of aminoacid salt and Na_2PdCl_4 without addition of NaOH. [c] Specific optical rotations of these samples in benzene are +560 and 600°, respectively.

the metalation agent, for instance according to the equilibria

$$PdCl_4^{2-} \underset{Cl}{\overset{solv}{\rightleftharpoons}} PdCl_3(solv)^- \overset{^-OCOR}{\rightleftharpoons} Pd(OCOR)Cl_3^{2-} \underset{Cl^-}{\rightleftharpoons} Pd(OCOR)Cl_2^-$$

Cyclopalladation in alkaline medium without any carboxylic acid salt did lead to a mixture of the cyclopalladated compound II and the L_2PdCl_2 complex. Therefore nucleophilicity of the anion is in itself not a determining factor in the cyclopalladation of amine I. One can imagine the general topology of the bicyclic transition state during cyclometalation of I as follows:





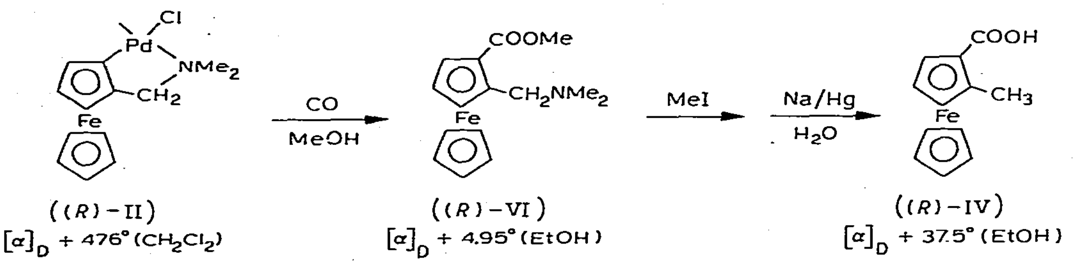
Transition states of similar topology were first considered by Newman [25].

Determination of the degree of asymmetric induction of planar chirality during cyclopalladation of dimethylaminomethylferrocene

In order to determine the dgree of asymmetric induction the absolute rotation of optically pure II should be known. This is determined by correlation with any enantiomeric 1,2-disubstituted ferrocene whose enantiomeric purity is known. Absolute rotation and enantiomeric purity for many ferrocenes were determined in the classical works of Schlogl et al. (for review see [26,27]. Therein 2-methylferrocenecarboxylic acid (IV) was used as a reference, its absolute rotation was determined by isotopic dilution and NMR spectroscopy [28]. Our task was made easier by the high reactivity of σ-organopalladium compounds although multi-step conversions were necessary.

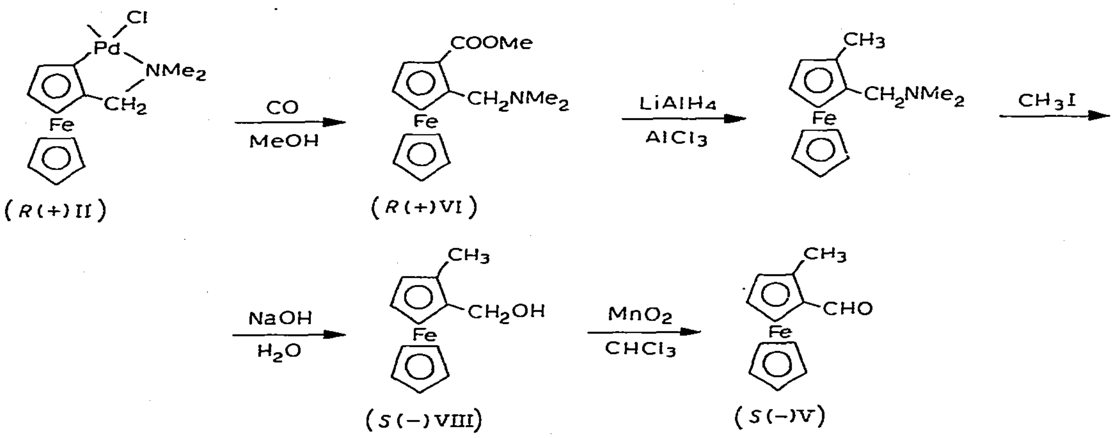
We employed two different reaction sequencies which lead from dimer II to 2-methylferrocenecarboxylic acid (IV) (Scheme 1) and 2-methylferrocenealdehyde (V) (Scheme 2).

SCHEME 1



Carbonylation of II in methanol readily yields aminoester VI, which in the form of the iodomethylate, was directly reduced into the ester of acid IV, the latter being hydrolized without isolation. As shown in Scheme 2, the ester group in VI was reduced to a methyl group to give amine VII, which was converted via iodomethylate into alcohol VIII and then oxidized to aldehyde V. Since the group CH_2NMe_2 was converted into methyl according to Scheme 1 and into CHO in Scheme 2, this means that from the same enantiomer *R*(+) II both *R*(+) IV and *S*(—) V with opposite configurations were obtained *.

SCHEME 2



The products were isolated by using chromatography (silica gel) so as not to distort the enantiomeric composition. The optical purity of *R*(+) IV obtained from *R*(+) II ($[\alpha]_D$ +476°) was calculated as 71.5%, taking absolute rotation $[A]_D$ +53° [28] and of *S*(—) V prepared from *R*(+) II ($[\alpha]_D$ +511°) was calculated as 73.8%, taking $[A]_D$ +225° for V [28]. Assuming that racemization

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* Here, as in our other works on ferrocene stereochemistry, we follow the nomenclature of planar chiral disubstituted ferrocenes proposed by Schlögl [26] and consistently applied by Ugi [35]. According to this system, a planar chiral moiety is characterized by a single configuration index.

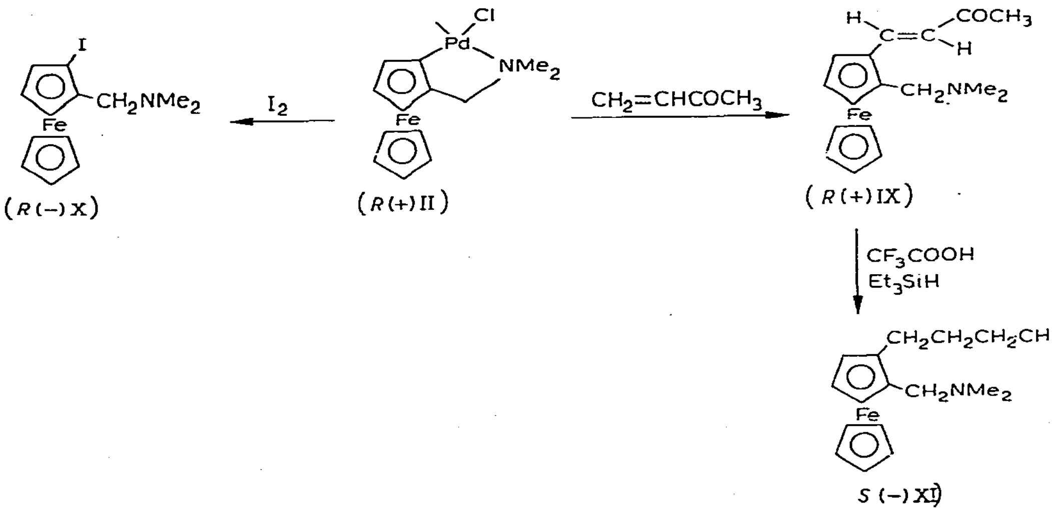
of the planar chiral fragment does not occur during these reactions we found the absolute rotation of dimeric 2-dimethylaminomethylferrocenyl palladium chloride (II) to be 666° and 692° according to Scheme 1 and 2 respectively. Such agreement should be considered as quite satisfactory, therefore the absolute rotation of pure enantiomers of II is $[A]_D^{20}$ 679 ± 13° in CH_2Cl_2. Accordingly, the maximum enantiomeric excess of II during cyclopalladation of I in the presence of a sodium salt of *N*-acetyl-L-valine is 78.8% and in conditions of maximal chemical yield 73%. Absolute rotation of the monomeric acetylacetonate was calculated to be $[A]_D^{20}$ 523° in CH_2Cl_2.

The above-mentioned correlations unambiguously prove the R_p absolute configuration for the (+) enantiomer of II, that is in agreement with the conclusion drawn from comparison with RS_p and RR_p diastereomers of *1*-(*1*'-dimethylaminoethyl)-2-palladio(acetylacetonate)-ferrocene) [21,27] the optical rotation sign of which is determined by the absolute configuration of the chiral plane and not of the center.

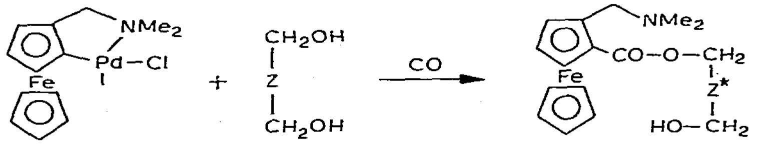
Prospects for synthesis of enantiomeric compounds

Due to the high reactivity of the Pd—C bond and the readiness of nucleophilic substitution of the quaternary ammonium group, II is a convenient starting compound for the synthesis of many 1,2-disubstituted enantiomeric ferrocenes. Carbonylation in methanol and water has already been described here (Scheme 1 and 2). We have also briefly reported on another useful reaction involving α,β-unsaturated ketones [29]. The reaction with vinylketones for chelate palladium rings has been described in the literature [30,31]. Izumi et al. [32] applied it to racemic II, but obtained product IX only in fair yield. In our experiments, we achieved a 80% yield and reduced IX with silane in CF_3COOH to amine XI. II can be also reacted with iodine to give iodoamine X (Scheme 3).

SCHEME 3



Along with the synthetic value for the stereochemistry of various organometallic π-complexes, of considerable interest is the use of chelated metallocycles of type II for enantioselective organic synthesis. The general idea can be depicted by the following scheme:



(II)

where Z is a prochiral moiety. In the course of carbonylation, which affords the ester product, a new chiral center is formed. Depending on which hydroxyl group reacts, Z acquires one of two possible enantiomeric configurations. In the case of the bulky enantiomeric II with rather rigorous steric requirements, effective asymmetric induction becomes possible.

Experimental

^{1}H NMR spectra were recorded on a Perkin-Elmer R-20 spectrometer, working frequency 60 MHz. Optical rotation was measured with a Perkin-Elmer 241 polarimeter. The melting points of optically impure substances are not distinct and therefore are omitted.

(+)-Di-μ-chloro-bis(dimethylaminomethylferrocenyl-C,N-)dipalladium (II). As mentioned in the Discussion, chemical and optical yields of II are pH dependent. Here we shall describe the standard procedure for preparing optically active (+) or (—) II of high enantiomeric purity. All samples were prepared according to this procedure, the only difference being in the amount of alkali added to reach the pH^2 value given in Table 1.

A solution of 1.3 g (8 mmol) of *N*-acetyl-L-valine and 0.35 g NaOH in 40 cm^3 of water (8.75 mmol) were added to a solution of 2.4 g (8 mmol) of Na_2PdCl_4 in 120 cm^3 of MeOH. The solution was brought to pH 7 using 50% NaOH and 2.0 g (8 mmol) of I in 40 cm^3 of MeOH was added. A precipitate formed after 5—10 min. The reaction mixture was stored overnight, then evaporated in vacuo without heating to remove most of the methanol and diluted with water. The dried precipitate was dissolved in benzene, the solution filtered and evaporated to give 2.7 g (90%) of II, $[\alpha]^{20}_{D}$ +461° (CH_2Cl_2, c 1.28). Fractional crystallization from benzene-heptane mixture by gradual evaporation of solution II on a rotary evaporator at room temperature gave a fraction of II with higher specific rotation. This technique was used to prepare a sample of analytically pure II used for chemical correlation: $[\alpha]^{20}_{D}$ +511° (CH_2Cl_2, c 0.35), ^{1}H NMR ($CHCl_3$) δ (ppm) 2.85 and 3.00 (NMe_2); 3.27 and 3.68 (part of NCH_2 quadruplet): 3.93 (C_5H_3); 4.27 (C_5H_5).

Found: C, 43.63; H, 4.78; Cl, 8.53; Fe, 13.82; Pd, 26.07. $C_{13}H_{16}NClFePd \cdot 0.5\ C_6H_6$, calcd.: C, 43.17; H, 4.37; Cl, 8.79; Fe, 13.84; Pd, 26.37%.

Acetylacetonate ((+) III). To a solution of the above prepared sample of (+) II in benzene a double quantity of sodium acetylacetonate in methanol was added whereupon the color changed from red to yellow. The solution was evaporated to dryness and the product was extracted with pentane to give acetylacetonate (+) III, $[\alpha]_D^{20}$ +370° (CH_2Cl_2, c 0.5).

2-Dimethylaminoethyl-1-carbomethoxyferrocene (VI). A flow of CO was passed for 2 hours through a solution of 1.0 g (2.5 mmol) of II, $[\alpha]_D^{20}$ +511°, in MeOH, metallic palladium was removed, methanol evaporated, the residue treated with 5% NaOH and extracted with pentane. Chromatography of the pentane solution (SiO_2; eluent, benzene/triethylamine 5/1) gave 0.63 g (84%) of VI, $[\alpha]_D^{20}$ +4.8° (ethanol, c 6.27) —10.0° (CH_2Cl_2, c 6.24). ^1H NMR ($CHCl_3$) δ (ppm): 2.23 (NMe_2); 3.13 and 3.32 (part of NCH_2 quadruplet); 3.78 (COOMe); 4.12 (C_5H_5).

1-Dimethylaminomethyl-2-methylferrocene (VII). 2.66 g (20 mmol) of powdered $AlCl_3$ was added with cooling to a suspension of 0.8 g (20 mmol) of $LiAlH_4$ in 50 cm^3 of abs. ether and then 0.62 g (2 mmol) of (+) VI in 50 cm^3 of ether was added dropwise. After 30 min the mixture was quenched with water and $NaHCO_3$ was added. Extraction with ether gave 0.53 g (100%) of VII, $[\alpha]_D^{20}$ —33.8° (ethanol, c 10.6). ^1H NMR ($CHCl_3$); δ (ppm) 1.97 (CH_3); 2.17 (6H, NMe_2); 3.35 (2H, CH_2N); 4.05 (8H, C_5H_5 and C_5H_3). The iodomethylate was obtained in acetone and precipitated with ether.

1-Hydroxymethyl-2-methylferrocene (VIII). 0.77 g (1.73 mmol) of (—) VII iodomethylate was treated at 70°C with 10% NaOH, boiled for 2 hours and extracted with pentane. Chromatography (silica gel, eluent benzene/ether 5/1) gave 0.36 g (90%) of VIII, $[\alpha]_D^{20}$ —1.24° (ethanol, c 4.5) * ^1H NMR ($CHCl_3$) δ (ppm): 1.95 (4H, CH_3 and OH); 4.12 (multiplet, 10H, C_5H_5, C_5H_3 and CH_2).

2-Methylferrocenealdehyde (V). 0.36 g (1.56 mmol) of (—) V was oxidized with 1.0 g of MnO_2 [33] in 20 cm^3 of $CHCl_3$. After an hour the reaction was terminated and the usual work-up gave 0.34 g (95%) of V, $[\alpha]_D^{20}$ —166.5° (ethanol, c 0.76). ^1H NMR ($CHCl_3$) δ (ppm): 2.24 (3H, CH_3); 4.19 (5H, C_5H_5); 4.49 and 4.69 (3H, C_5H_3); 10.29 (CHO). Found: C, 63.28; H, 5.60; Fe, 23.09. $C_{12}H_{12}FeO$, calcd.: C, 63.19; H, 5.30; Fe, 24.48%.

2-Methylferrocenecarboxylic acid (IV). Carbonylation of (+) II, $[\alpha]_D^{20}$ +476° (CH_2Cl_2, c 0.56) **, in methanol as described above gave (+) III, $[\alpha]_D^{20}$ +4.95° (ethanol, c 4.4). A solution of 0.63 g of III aminoester iodomethylate in 50 cm^3 of water was added under argon to an amalgam prepared from 2.5 cm^3 of mercury and 2 g of sodium (about 5.5%). The reaction mixture was boiled for 8 hours, after usual work-up with diluted H_3PO_4 (1/1), extraction with ether gave 0.243 g (70.5%) of (+) IV which was chromatographed on SiO_2, $[\alpha]_D^{20}$ +37.5° (ethanol, c 1). ^1H NMR ($CHCl_3$) δ (ppm): 2.30 (3H, CH_3); 4.25 (5H, C_5H_5); 4.42 and 4.87 (3H, C_5H_3); 7.95 (1H, COOH). Found: C, 59.23; H, 5.13; Fe, 22.48. $C_{12}H_{12}FeO_2$, calcd.: C, 59.05; H, 4.95; Fe, 22.88%.

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* Schlögl [34] gave the value of $[\alpha]_D^{20}$ —9° (ethanol) for this compound. The higher specific rotation was possibly due to presence of the related ether, since the substance was distilled at 75—85°C. We have observed earlier [23] the unusually easy formation of bis(ferrocenyl) methyl ether or ethoxymethylferrocene in a two-phase water/benzene systems or in aqueous ethanol.

** Acetylacetonate, $[\alpha]_D^{20}$ +366° (CH_2Cl_2, c 0.95).

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