CONFIGURATIONAL AND CONFORMATIONAL STUDIES IN THE METALLOCENE FIELD

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ABSTRACT

The special molecular geometry of metallocenes offers many stereochemical problems. From these, in the present review especially the optical activity ('metallocene chirality') is treated with its particular aspects, such as configurational correlations, absolute configurations, optical rotatory dispersion and circular dichroism as well as the relationship between the activity of the 'metallocene chromophores' and preferred conformations. In this context optically active [3] ferrocenophanes and biferrocenyls are discussed in some detail.

HARDLY any other discovery has influenced any field of chemistry as much as the discovery of ferrocene[1] in 1951 the field of organometallic chemistry. Metallocenes, as ring-metal π-complexes are usually called, are of general interest not only because of their aromaticity as manifested in their reactivity towards electrophilic substitution, but also from many theoretical points of view[2]. For the stereochemist, they are fascinating because of their interesting molecular geometry which offers many new stereochemical aspects.

Monosubstituted metallocenes belong to the point group C_s. Homoannular substitution with a group R' different from the first (R) affords disubstituted products belonging to the point group C_1. Such compounds are chiral[3] and may therefore be resolved into enantiomers.

In the metallocene field this was demonstrated for the first time by Thomson[4] in 1959, who resolved the *homo*annular bridged ferrocene ketone (ferrocenocyclohexenone) which is obtained as a racemic mixture on cyclization of γ-ferrocenyl butyric acid (cf. *Chart 1*).
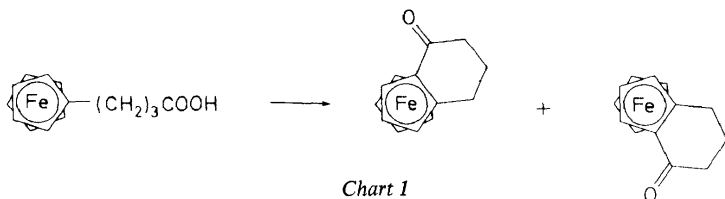

Chart 1

Ketones of similar structure type have proved to be key compounds in stereochemical research; they will be frequently referred to in this review (*Charts 4, 7, 8, 10, 11, 16, 18* and *20*).

We have been interested for several years in the stereochemistry of metal-

locenes, particularly in the field of 'metallocene chirality'[5] (i.e. in optically active metallocenes) and especially in ferrocene derivatives[5].

So far, more than 200 optically active metallocenes have been prepared and their configurations established; in many cases some ideas have been put forward as to the correlation of their configurations, conformations and optical properties[6].

In *Chart 2* the four metallocenes used in our stereochemical studies are shown together with the Newman type projection formulae which have proved very useful for stereochemical discussions.

Ferrocene

Ruthenocene

Cymantrene

Benchrotrene

Chart 2†
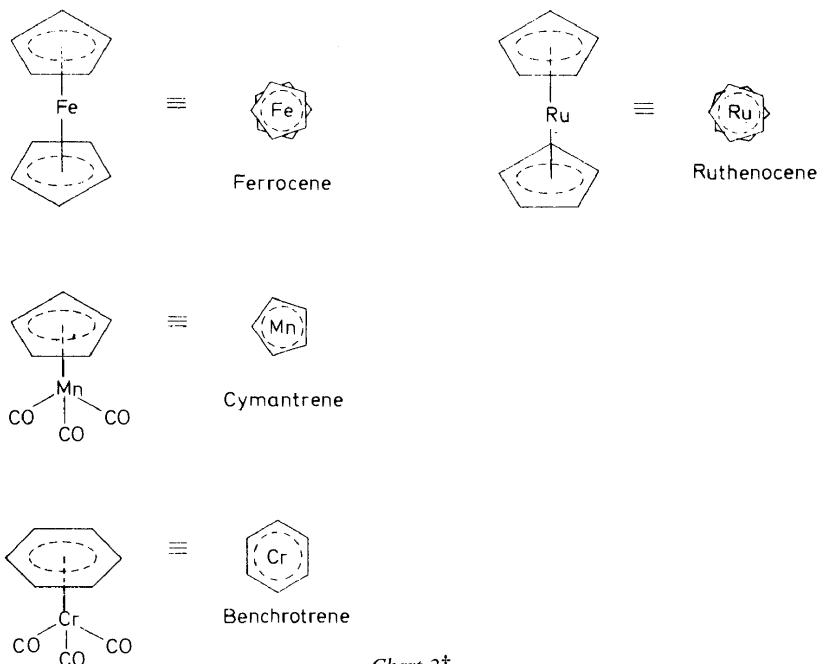
Because of the comprehensive material collected during recent years, this review will be confined to a few aspects of metallocene chirality, especially to some recent results of configurational and conformational analyses.

The sometimes laborious syntheses of isomerically pure metallocenes required as racemic starting materials cannot be discussed in detail. It should be recalled, however, that there are three possible isomers of disubstituted ferrocenes, ruthenocenes or benchrotrenes, from which only two, namely the *homo*annular ferrocenes and ruthenocenes and *o*- and *m*-substituted benchrotrenes, are chiral and hence of interest for our purposes. Only two isomeric disubstituted cymantrenes are possible, both of which are chiral.

One is, therefore, often dealing with isomeric mixtures which have to be separated (mainly by chromatographic methods); subsequently, the correct structures have to be assigned to the pure isomers. This is generally readily

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† Cymantrene is cyclopentadienyl-Mn-tricarbonyl; benchrotrene is benzene-Cr-tricarbonyl.

achieved by n.m.r. spectroscopy[5,7]. There are some preparative methods which yield pure isomers. One of them, an important cyclization reaction (of metallocenyl butyric acids) will be referred to below (*Charts 7, 8*, see also *Chart 1*).
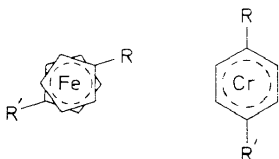
Chiral:
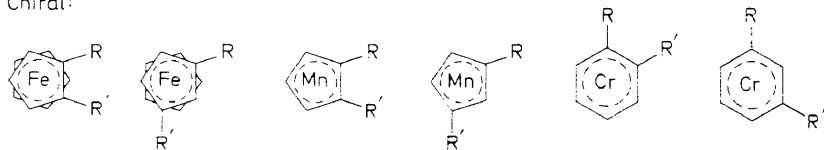
Achiral:

Chart 3

Optical resolutions can usually be achieved by classical methods, i.e. crystallization of diastereomeric derivatives, such as the α-phenethylamine salts (of carboxylic acids), dibenzoyl tartrates (of amines) and menthydrazones (of ketones and aldehydes). Optically active metallocene ketones obtained via their menthydrazones are shown on *Chart 4*.
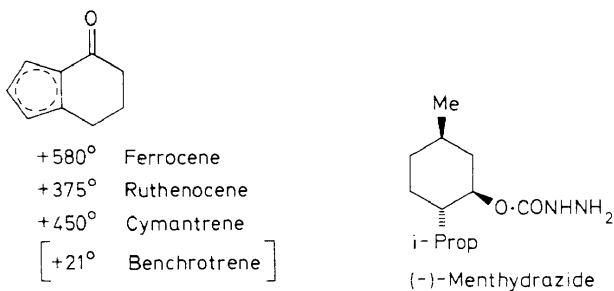

+580°	Ferrocene
+375°	Ruthenocene
+450°	Cymantrene
[+21°	Benchrotrene]

Me

O·CONHNH$_2$

i-Prop

(−)-Menthydrazide

Chart 4†

In some cases, modern methods have been employed. Thus, the benchrotrene ketone (*Chart 4*) or the ferrocene derivative was resolved by chromatography on acetylated cellulose[5]. Recently also, a countercurrent distribution in the system (+)-diethyl tartrate–cyclohexane was employed successfully[8]. Although the optical yields with these methods are not very high, the active material can be further purified by crystallization[8].

With a set of several optically active metallocenes available by direct resolution of racemic material, the next steps (in the stereochemical investigations) include the following:

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† Here and in the following, all rotations refer to specific rotations, $[\alpha]_D$, in alcohol or cyclohexane.

1. Determination of optical purity of at least one key compound.

2. Chemical correlations of this compound with many others, not only in order to establish their optical purities (absolute rotations), but mainly to obtain a series of compounds which are configurationally correlated (i.e. the relative configurations of which are known).

3. Determination of the absolute configuration—again of at least one key compound.

4. Elucidation of the preferred conformation(s) in order to correlate conformations with optical properties.

5. Attempts to interpret all data, including optical rotatory dispersion (*ORD*) and circular dichroism (*CD*).

Chart 5 shows the key compounds of the ferrocene series: two methyl-ferrocene carboxylic acids, the above mentioned ketone (*Chart 1*) and a recently prepared [3]ferrocenophane-α-carboxylic acid, the reference substance for more than 40 optically active ferrocenophanes[9].
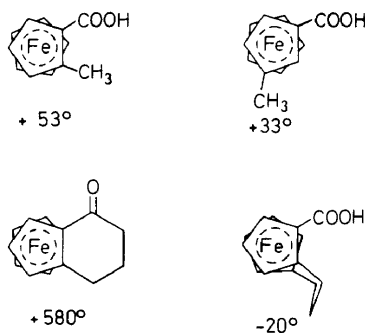

Chart 5

(*1*). The optical purity of methylferrocene-α-carboxylic acid (*Chart 5*) was established by the isotope dilution method introducing deuterium at the ring-methyl group as well as by an n.m.r. method[10].

(*2*). The compounds shown in *Chart 5* have—amongst many others—been correlated as shown in *Charts 6–9*.

−COMe
−COCH$_2$CH$_2$ $\overset{+}{N}$(Me)$_3$ I$^-$
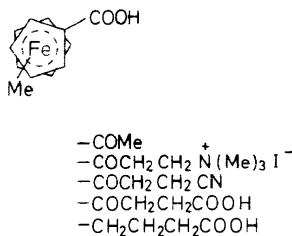−COCH$_2$CH$_2$CN
−COCH$_2$CH$_2$COOH
−CH$_2$CH$_2$CH$_2$COOH

Chart 6

By chain lengthening, as shown in *Chart 6*, the active methylferrocene carboxylic acids were converted into the corresponding butyric acids[11]. These were cyclized by trifluoroacetic anhydride to give the *homo*annular
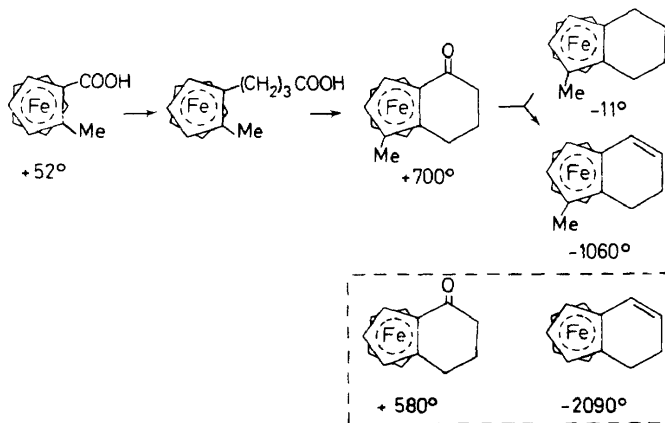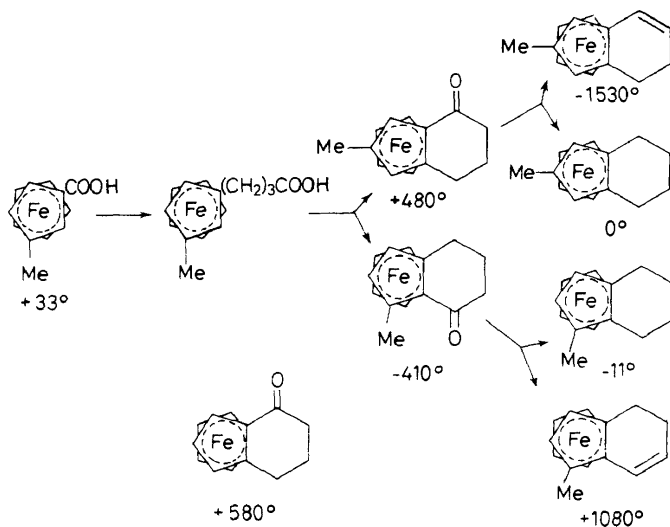
Chart 7

Chart 8

bridged ketones. Whilst from the α-isomer only *one* ketone can be obtained (*Chart 7*), the β-derivative yields *two*, easily separable isomeric ketones (*Chart 8*); their structures were determined both by n.m.r. spectroscopy and by their reduction products. From the dextrorotatory ketone ($[\alpha]_D$ +480°) a symmetrical and hence inactive 'hydrocarbon' was obtained, whilst the second ketone ($[\alpha]_D$ −410°) yielded an active 'hydrocarbon'; this is the key compound for the correlation of both isomeric methylferrocenecarboxylic acids (cf. *Chart 7* and *Chart 8*). Reduction (LiAlH₄) and dehydration of the carbinols obtained furnished cyclic vinyl derivatives. They exhibit optical rotations opposite to those of the parent ketones (*Charts 7* and *8*). This significant shift is very useful in assigning configurations in the metallocene series (see *Chart 11*).

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Figure 1 shows the *ORD*s of (+)-ferrocenocyclohexenone and its methyl derivatives obtained in the correlation reactions. It is apparent that the methyl group has no significant influence on shape or sign of the Cotton effect: hence, the optical comparison of the parent ketone with its methyl derivatives is justified.
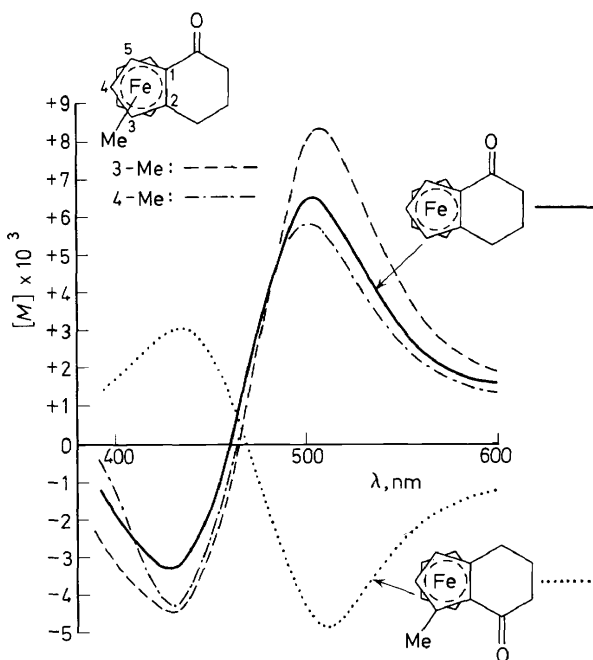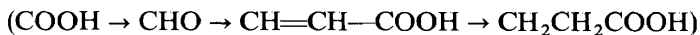

Figure 1. *ORD* of ferrocenocyclohexenone and its methyl derivatives in ethanol[11].

Similar transformations were performed in the cymantrene series and gave analogous results[12].

The correlation of the [3]ferrocenophane with the methylferrocene–α–carboxylic acid is shown in *Chart 9*. By chain lengthening

$$(COOH \rightarrow CHO \rightarrow CH{=}CH{-}COOH \rightarrow CH_2CH_2COOH)$$

from the latter a methylferrocenylpropionic acid was accessible, which after cyclization to α-methylferrocenophanone and reduction of the latter ($LiAlH_4/AlCl_3$) gave a dextrorotatory α-methyl-[3]ferrocenophane. The same 'hydrocarbon' was obtained from (+)-ferrocenophane–α–carboxylic acid after reduction[9] of COOH to CH_3. The same sequence of reactions was also conducted in the β-series[9].

Besides the few examples presented, various other optically active metallocenes have been correlated with the methylmetallocenecarboxylic acids and with the *homo*annularly bridged ketones (*Chart 4*)[5].

(3). The determination of the absolute configuration of any of these compounds should, of course, immediately reveal the configurations of all compounds correlated with them.

Chart 9
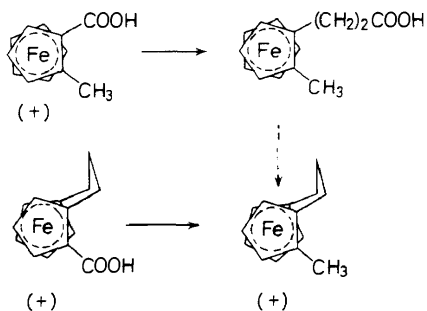
This problem was solved for the first time in 1964 starting with the dextro-rotatory ferrocenocyclohexenone[5, 13]. The principle, afterwards successfully applied to other metallocene ketones of analogous structures[14], is outlined in *Chart 10*.

Reduction of the ketone with $LiAlH_4$ (or $NaBH_4$) furnishes two epimeric, easily separable carbinols. The *exo*-isomer (in which the position of the OH group has been established unambiguously[5]) is shown in *Chart 10*. The configuration of the chiral centre was then elucidated employing Horeau's elegant method[15] by reaction with rac. α-phenylbutyric anhydride. Since laevorotatory butyric acid was liberated, the configuration of the asymmetric carbon atom is (S), and consequently the (+)-ketone has the configuration shown in *Chart 10*.
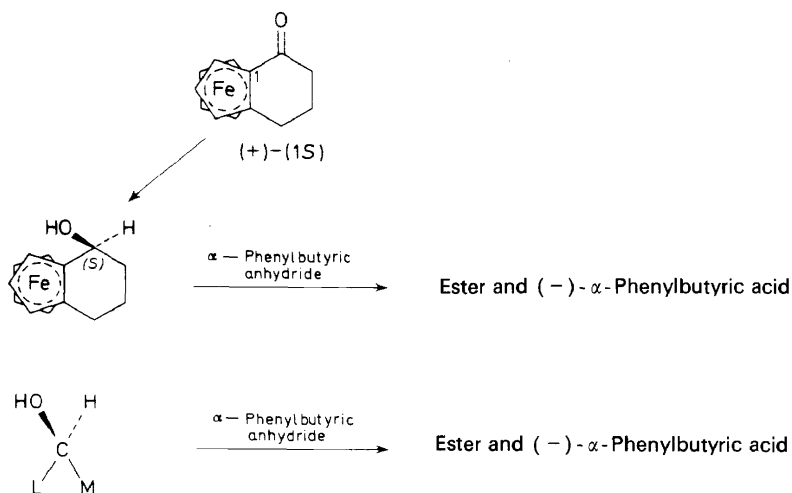
Chart 10†

In all cases the dextrorotatory ketones have the same configurations[11, 14] (cf. also *Charts 7* and *8*) and give—as already mentioned—on reduction and dehydration strongly laevorotatory cyclohexadienes (*Chart 11*).

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† Cf. refs. 3, 5 for the configurational (R) (S) nomenclature of metallocenes.

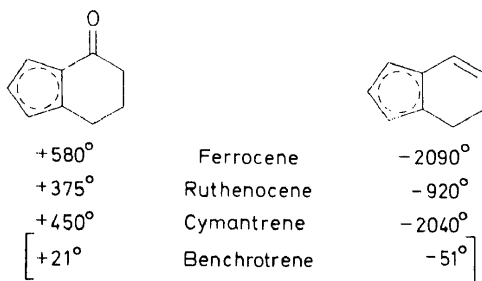|		
+580°	Ferrocene	−2090°
+375°	Ruthenocene	−920°
+450°	Cymantrene	−2040°
+21°	Benchrotrene	−51°

Chart 11

Three years later, in 1967, our results on the configurations of ferrocenes were confirmed by an absolute, unambiguous method, namely by an x-ray structure analysis of the 1,1′-dimethylferrocene–β-carboxylic acid[16] (*Chart 12*) which we had previously correlated with methylferrocene–α-carboxylic acid and hence with the cyclic ketone (*Charts 6, 7*)[17].

Carter, McPhail, Sim (1967)   Schlögl, Falk, Haller (1967)
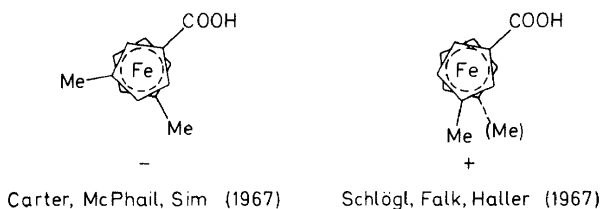
Chart 12

Subsequently, Professor G. A. Sim[18] also elucidated the configuration of the methylcymantrene–α- and of both methylbenchrotrene-carboxylic acids (*Chart 13*). Again his results were in agreement with ours[19].

+83°   +103°   −88°
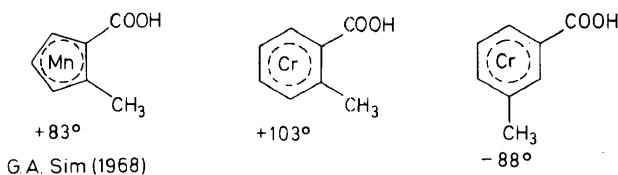
G. A. Sim (1968)

Chart 13

As mentioned above, the kinetic resolution as employed in Horeau's method proved to be of great value. Kinetic resolutions could then be successfully applied to the configurational correlation of methylmetallocene–α-carboxylic acids as well as to the above-mentioned [3]ferrocenophane–α-carboxylic acid (*Chart 9*) and a biferrocenyl–α-carboxylic acid[20]. (*Chart 14*). The stereochemistry of biferrocenyls will be discussed at the end of this review.

Reactions of the anhydrides of the racemic acids with (−)-α-phenethyla-mine yield (mostly dextrotatory) acids with identical configurations. The optical yields are shown on *Chart 14*.
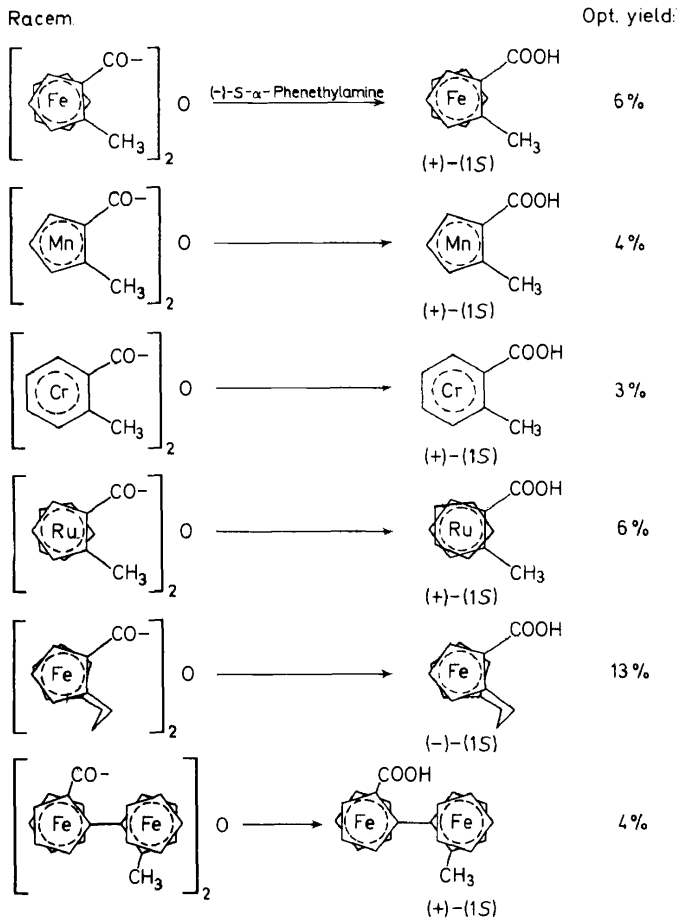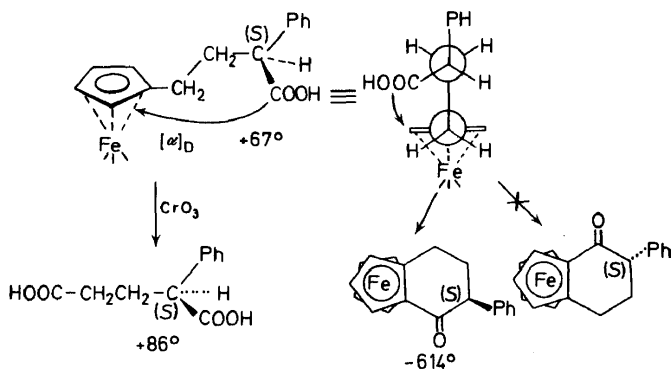
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Chart 14

Chart 15

Another approach to the problem of establishing the absolute configuration of a metallocene derivative is presented in *Chart 15* (cf. ref. 21).

Cyclization of (+)-γ-ferrocenyl-α-phenyl–butyric acid—with the configuration (S) at the chiral centre, as shown by oxidative degradation to (+)-α-phenylglutaric acid—proceeds with high stereoselectivity (>95 per cent): only *one* (strongly laevorotatory) ketone of the two possible stereoisomers is formed. The configuration of this product (as shown in *Chart 15*) may be deduced from an inspection of the transition state with its preferred conformation. Since this reaction is fast and hence kinetically controlled, the cyclization will predominantly proceed in one direction. This assumption as to the configuration could then be confirmed by chemical correlations[21].

Subsequently, this principle was applied to cymantrene ketones[12] and to ferroceno methylcyclohexenone[22].

It has already been pointed out that all cyclic metallocene ketones of the same absolute configuration (*1S*) are dextrorotatory, whilst the corresponding vinyl derivatives are strongly laevorotatory (*Chart 11*).

From methylmetallocenecarboxylic acids (of known absolute configurations (cf. *Charts 13, 14*) acetyl- and vinyl-methylmetallocenes were accessible, which—although having the same configurations as the corresponding cyclic compounds—exhibit opposite signs of rotation (*Chart 16*). The same relationship holds also in the ferrocenophane series, where methyl is replaced by trimethylene (cf. *Chart 17*)[9].

+580°   −540°   76% ($\Delta G = -0.6$ kcal)

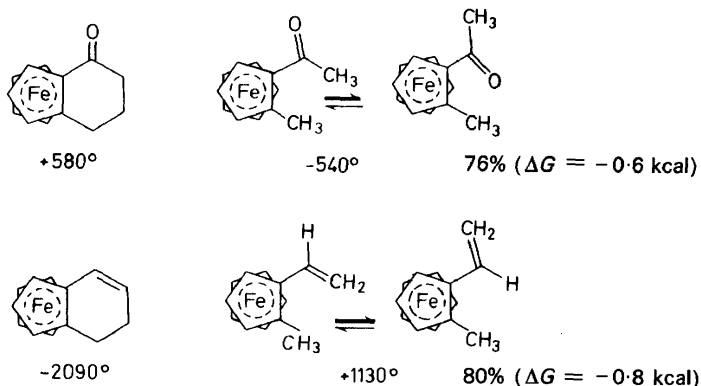−2090°   +1130°   80% ($\Delta G = -0.8$ kcal)

Chart 16

Making use of this phenomenon, it is possible to establish with a high degree of certainty the configurations of metallocenes by optical comparison[5,9,20].

(4). Moreover, these optical properties also offered access to a conformational analysis of metallocenes. Whilst the chromophoric groups ($C=O$ or $C=C$) in the cyclic compounds are more or less conformationally fixed by the ring (*Chart 16*), in the analogous open chain compounds two coplanar conformers are possible with the acetyl- or vinyl-groups either in *s-cis* or *s-trans* conformations. Their opposite rotations—as compared with the cyclic derivatives (*Chart 16*)—might therefore be interpreted as

being due to 'opposite' conformations. Hence, the preferred conformations, as shown in *Chart 16*, will be determined by the neighbouring groups in the α-position (methyl or trimethylene, ferrocenyl in the biferrocenyls) in order to avoid steric interactions, e.g. *Me---Me* in acetylmethylferrocene.

So far (with one exception, *Figure 1*) only rotations at the sodium D line, i.e. at 589 nm, have been discussed. This value is, of course, a rather arbitrary point out of the whole dispersion curve.

For a more exact treatment of optically active metallocenes, their *ORD* and *CD* have also to be considered.

According to the long wavelength electronic transition in their absorption spectra (presumably more or less pure d-d-transitions at the metals[23]) at 440, 350, 330 and 390 nm for ferrocene, ruthenocene, cymantrene and benchrotrene, respectively, the active metallocenes exhibit corresponding Cotton effects in their *ORD* and *CD* curves. These effects are sometimes more or less shifted from the absorption maximum, usually towards longer wavelengths; this problem will be discussed briefly below. *Figure 2* shows a typical example.
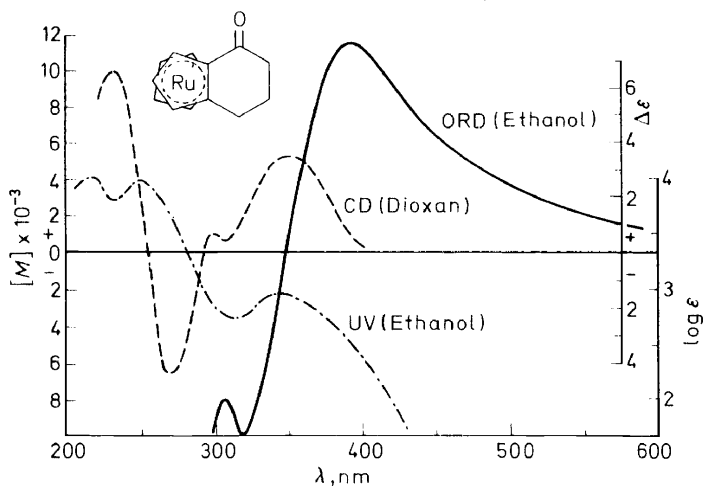

Figure 2. ORD, CD and u.v. spectrum of (+)-ruthenocenocyclohexenone[14c].

If one compares the *CD* curves of analogous cyclic and open chain metallocenes of identical configurations, it is apparent that the curves are of similar shape but of opposite sign, as if the compounds were enantiomeric (*Figure 3*).

This observation, too, is in favour of the concept of preferred conformations. This assumption could then be confirmed by measurements of the temperature dependence of *ORD* (and *CD*). The conformational equilibrium (as shown in *Chart 16*) is, of course, temperature dependent. Hence, on heating, the amplitudes of the Cotton effects under investigation decrease— in contrast to the amplitudes of the cyclic compounds which are more or less temperature independent (*Figure 4*).

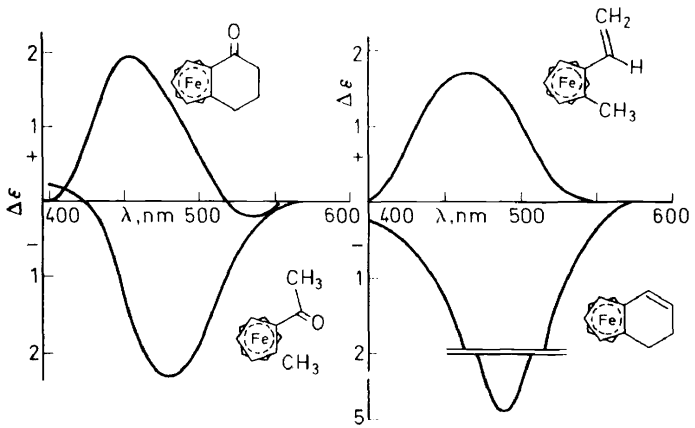From the parameters, the ΔG-values (at 10°C) could be calculated (with

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Figure 3. CD of ferrocenocyclohexenone and ferrocenocyclohexadiene, acetyl and vinyl ferrocene (in ethanol and cyclohexane respectively).
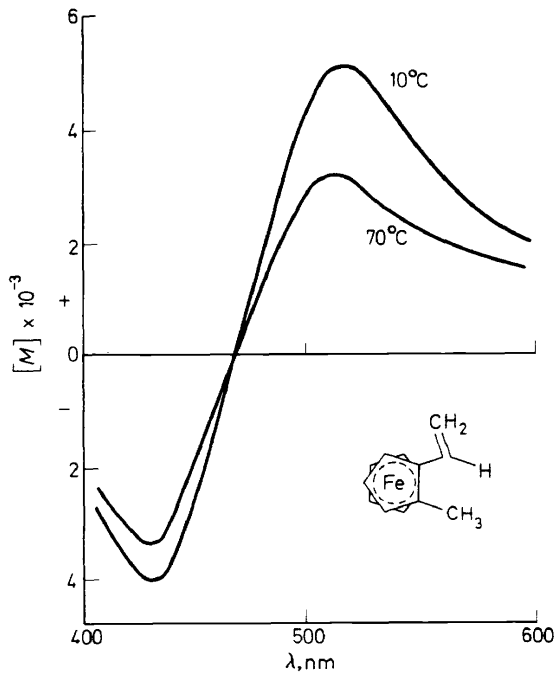

Figure 4. Temperature dependence of the *ORD* of vinylmethylferrocene[6b].

$\Delta S = 0)^{6b, 24, 31}$. The values found are shown in *Chart 16*. Accordingly, approximately 80 per cent of the preferred conformations are present at equilibrium.

These results were then confirmed by dipole moment measurements[25]. These studies also revealed[26] that in the case of acetylmethylcymantrenes and methylbenchrotrenes—because of dipole–dipole interactions—the preferred conformations are not coplanar and that a higher torsional barrier exists than with acetylmethylferrocenes.

Before discussing the theoretical aspects, some recent results of configurational and conformational studies on [3]ferrocenophanes[9] and biferrocenyls[20] are first presented.

STEREOCHEMISTRY OF [3]FERROCENOPHANES

When [3]ferrocenophane (1,1'-trimethylene ferrocene) is acylated with N,N-diphenylcarbamyl chloride, a mixture of two isomeric (α- and β-) diphenylamides is formed, in which the β-product predominates. Chromatographic separation and subsequent hydrolysis afford the desired carboxylic acids, which were resolved via their salts with (−)-α-phenethylamine (*Chart 17*).
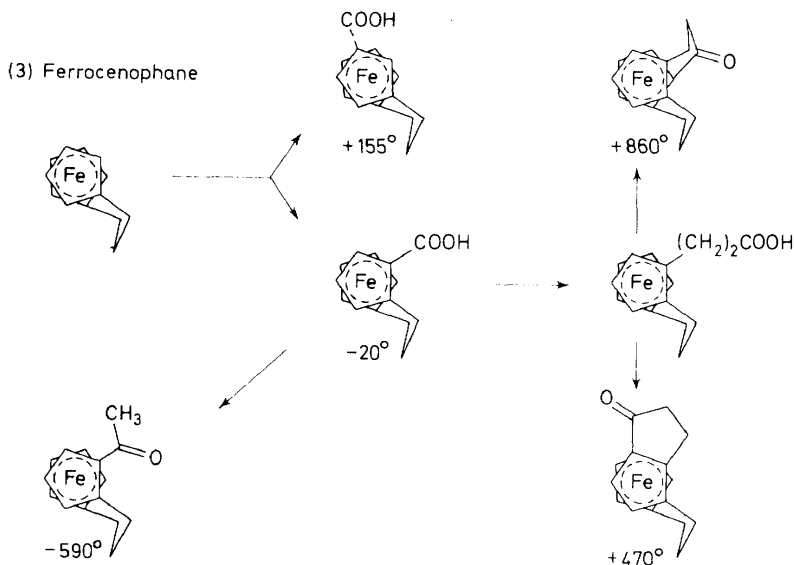

Chart 17

The configurational correlation of the α-carboxylic acids with the methylferrocene–α-carboxylic acid has been presented in *Chart 9*.

From these ferrocenophanecarboxylic acids a series of derivatives was accessible, amongst which the acetyl and vinyl derivatives were of interest because of the optical comparison with corresponding methylferrocene derivatives. The propionic acid (*Chart 17*), obtained by chain lengthening, was cyclized to the *hetero*annularly bridged ketone. This, as well as the

isomeric products with the CO group in the 'other' ring and methyl ferro-cenophanones, obtained from methylferrocenocarboxylic acids by chain lengthening (COOH → CH_2CH_2COOH) and cyclization (*Chart 18*) are of interest in comparison with the *homo*annularly bridged ketone (ferroceno cyclohexenone).

Whilst in the latter the C═O group has to adopt an almost coplanar conformation, in the *hetero*annularly bridged products—because of the conformation of the bridge—the C═O group is twisted from coplanarity to a large extent (cf. *Figure 5*). Moreover, in these compounds the cyclo-pentadienyl rings are no longer parallel as in ferrocene, but tilted to about 12° (cf. x-ray analysis)[27].
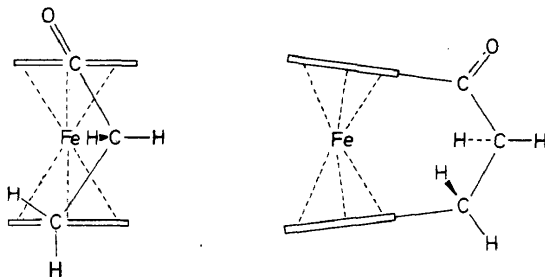

Figure 5. Molecular geometry of [3] ferrocenophan-6-one (for the nomenclature of ferroceno-phanones, see ref. 9).

The preferred conformations of the oxotrimethylene bridges (with regard to the adjacent substituents, cf. *Chart 18*) could be deduced from the optical rotations of the ketones.

The results obtained on the basis of this more or less qualitative approach (regarding only the $[\alpha]_D$ values) are quite reasonable and were afterwards also confirmed by CD measurements (*Chart 18*).

A more detailed analysis of the CD curves revealed[28], however, that in contrast to the methylferrocene derivatives, the ferrocenophane skeleton with its own chirality owing to the conformations of the bridges and the distorted ferrocene geometry itself exerts a pronounced effect on the optical rotation. This may in some cases outweigh (or at least compensate) the chirality caused by the preferred conformations of the ⟩C═O or ⟩C═C⟨ chromophore.

In order to gain insight into this conformational problem, a computer curve fit analysis of the CD was carried out[28].

STEREOCHEMISTRY OF BIFERROCENYLS

Some stereochemical investigations on the biferrocenyl system originated from a collaboration with Dr B. Rockett and his group from Wolverhampton; these will now be discussed briefly.

These authors found that on coupling of α-(dimethylaminomethyl)-ferrocene boronic acid (*Chart 19*) two separable stereoisomeric bisamines
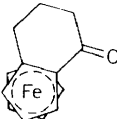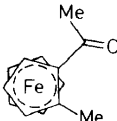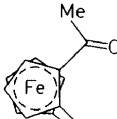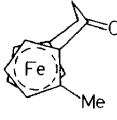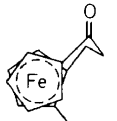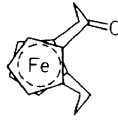
	$[\alpha]_D$	Cotton effect	
		nm	$\Delta\varepsilon$
	$-580°$	465	$-2\cdot9$
	$-540°$	485	$-2\cdot5$
	$-587°$	435	$-7\cdot6$
	$-400°$		
	$+246°$	490	$+0\cdot95$
	$-860°$	454	$-13\cdot0$

Chart 18

are formed (**A**, m.pt 203° and **B**, m.pt 103°)[29]. From **A** a monomethyl derivative is accessible which in turn can be converted into many α-substituted α'-methyl biferrocenyls, such as the carboxaldehyde, the carboxylic acid or the acetyl derivative[20].

Whilst attempts to resolve **A** failed, from both **B** and the just-mentioned methyl derivative via their dibenzoyl tartrates highly dextrorotatory amines were obtained (*Chart 19*).

These results, together with the fact that the active monomethyl derivative on conversion into α,α'-dimethyl biferrocenyl became optically inactive at all wavelengths, proved unambiguously that **A** was the meso form and **B** the racemate.

As shown by x-ray analysis[30] biferrocenyls exist in the *s-trans* conformation with both *Fc*-residues in the favoured *transoid* arrangement.
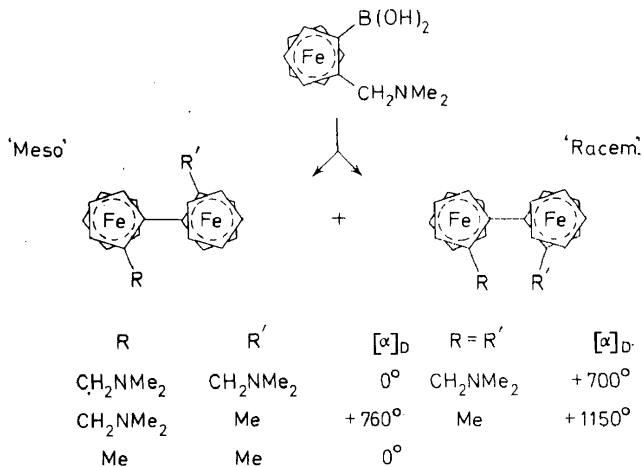
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Chart 19

This means that in the meso form (and its derivatives) the two groups (R and R') are on different sides; hence the molecule can adopt a coplanar conformation (*Chart 19*). In the racemate, however, (and its optically active derivatives) because of the steric interactions of the two groups (R and R') being on the same side some twisting of the biferrocenyl moiety is to be expected (*Figure 6*).

$R = R' = CH_3$, 85 % (a)

(a) $\Delta G = 0.9$ kcal (20°C)   (b)
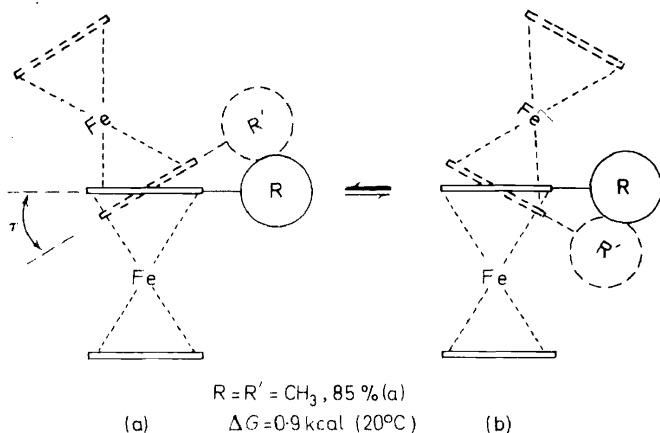
Figure 6. Conformational equilibrium of one stereoisomer of α,α'-disubstituted biferrocenyls (racemate and derivatives thereof)[20].

These *a priori* assumptions could be confirmed by u.v. and n.m.r. spectroscopy[20] as well as by dipole moment measurements. The latter not only supported the configurational assignments to **A** and **B** (meso- and racem.-form, respectively), but also made a torsional angle τ of about 30° probable for the racemate (**B**) (*Figure 6*). The meso form, as expected, is coplanar.

This result has interesting consequences with regard to the optical activity of the biferrocenyl system. Between the two possible (twisted) conformers as shown in *Figure 6* a conformational equilibrium should exist, which ought to be in favour of (a), since in (b) an interaction between R and the second ferrocenyl residue occurs.

Consequently, some sort of atropisomerism should come into play with a twisted biferrocenyl chromophore; this should manifest itself in the temperature dependence of the *CD*. Indeed, the dimethyl derivative (R==R' = CH₃) with an $[\alpha]_D$ of 1150° and a $\Delta\varepsilon$-value of +4·9 at 465 nm (cf. *Figure 7* for the *CD* curve) exhibits a significant temperature dependence of its *CD*. From the data, a ΔG-value of 0·9 kcal/mole (at 20°C) was calculated, corresponding to 85 per cent of the stable conformer (a) at equilibrium.

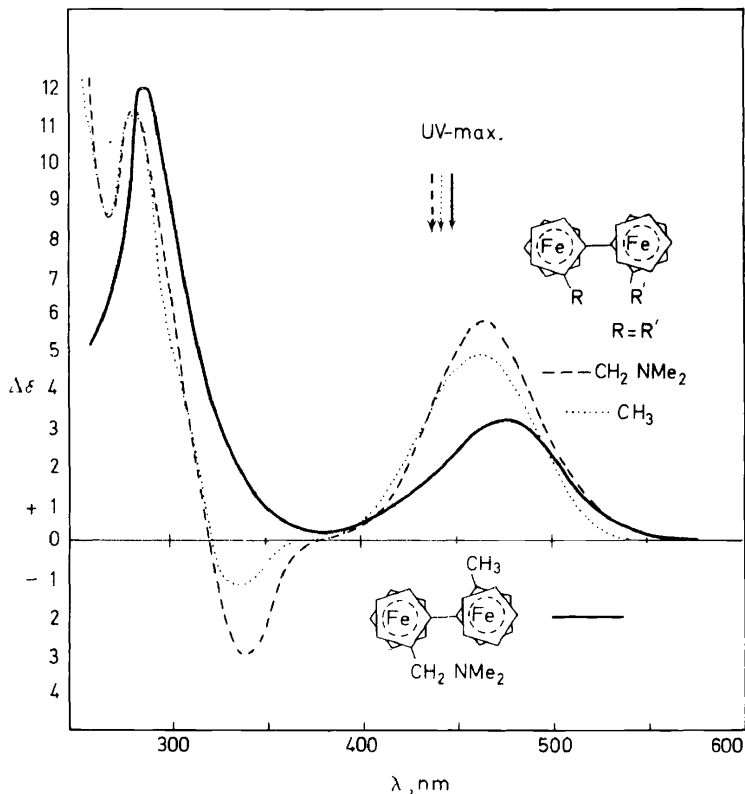*Figure 7.* CD of optically active biferrocenyls (in ethanol)[20]. The u.v. maxima are indicated by arrows.

As was briefly mentioned earlier, the configurations of the biferrocenyls, shown in *Chart 19*, were established by optical comparison with analogous methylferrocene derivatives and by kinetic resolution of the carboxylic acid (*Chart 14*).

A discussion of the optical properties (*ORD* and *CD*) of the biferrocenyls

is complicated by the fact that we deal with ferrocene chiral compounds (asymmetrically substituted ferrocenes) on to which chirality the 'atropisomerism' of the biferrocenyl skeleton may be superimposed—at least in the derivatives of one stereoisomer (*Figure 6*). Usually a rather large difference between the positions of the u.v. maxima and the corresponding Cotton effects is observed (cf. *Figure 7*). (Sometimes also an additional effect is present around 500 nm which may be attributed to a singlet–triplet transition.)

A computer curve fit analysis revealed[31] that here and with the ferrocenophanes the observed Cotton effects (between 440 and 480 nm) are composed of two effects of opposite signs with a $\Delta\lambda$ of 20–30 nm. This effect causes the above-mentioned shift of the positions of the Cotton effects with regard to the u.v. maxima. This splitting is due to electronic effects (change of the symmetry of the system) and not to solvation or conformational equilibria, as was shown by temperature dependence studies[31].

(5). This phenomenon (observed also with other ferrocene derivatives) is one reason why we hesitate at the moment to discuss in detail any relationship between configurations, conformations and signs of the Cotton effect (after all which one of the two 'partial effects' should be considered?).

However, an empirical rule on the relationship between configuration, (the preferred) conformation and the sign of $[\alpha]_D$ holds—rather surprisingly —for almost all metallocenes investigated so far (cf. ref. 6a for a first attempt to formulate a rule for these correlations).
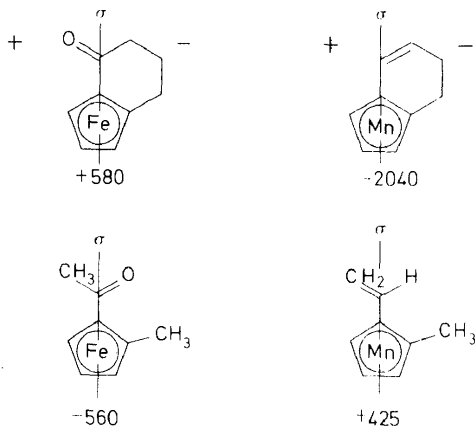

Chart 20

The compound is viewed along the molecular axis (from the outside) with the substituent of lower symmetry pointing upwards. A plane (σ) bisects the molecule as indicated in *Chart 20*. If the disturbing chromophoric group (C=O or C=C) is on the left side (as seen from the observer) the compound is dextrorotatory, and vice versa. This rule is illustrated in *Chart 20* by four typical examples.

With regard to the origin of the optical activity some preliminary ideas have been put forward[32].

In simple cases, the inherently achiral metallocene chromophore (corresponding to a more or less pure d–d-transition) might be perturbed by the chiral surrounding (which is generally caused by the preferred conformations of the chromophoric groups) and hence becomes active. In cases where no conformational chirality is possible, such as with halogen methylcymantrenes[33], the rotations (and amplitudes of the Cotton effects) are rather low (*Chart 21*).

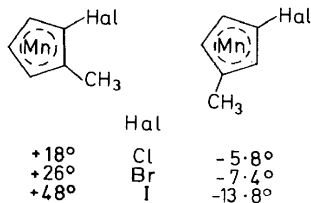|	Hal	
+18°	Cl	−5·8°
+26°	Br	−7·4°
+48°	I	−13·8°

Chart 21

With ferrocenophanes and biferrocenyls, however, the chromophore itself might be inherently chiral; in these cases, therefore, a rather high activity (large amplitudes of Cotton effects, high $\Delta\varepsilon$-values) may be observed.

Although, as mentioned at the outset, at present more than 200 optically active metallocenes are known and their configurations have been established, many problems—especially theoretical ones—remain to be solved in the field of metallocene chirality.

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