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Diastereotopy in Transition Metal Complexes

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Cases of diastereotopy—the stereochemical non-equivalence of atoms or groups within a single molecule—in transition metal complexes are examined. The application of the concept of diastereotopy, introduced into stereochemistry several years ago, makes it possible to interpret correctly complex nuclear magnetic resonance spectra and to reach on their basis conclusions about the fine structure of the molecule. Instances of the diastereotopy of the atoms of coordinated ligands and other groups in π-complexes are classified.
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I. INTRODUCTION

In the middle of the 1960's enormous factual NMR data required a detailed analysis of the stereochemistry of molecules containing seemingly equivalent atoms or groups of atoms, which, however, are manifested in the spectra by different signals. Such generalisations were made by Mislow and Raban[1]

It was found that sometimes atoms or groups, which are at first sight identical, are in fact in different steric environments. Structurally identical atoms or groups have been divided into three categories in accordance with the stereochemical characteristics of the environment. Atoms or groups capable of being interchanged by simple rotation of the molecule about an n-fold axis are called equivalent. As an example, one may quote the hydrogen atoms in methyl chloride (rotation about the threefold axis passing through the carbon and chlorine atoms), the geminal hydrogen atoms in ethylene, the methyl groups in acetone (in both cases the atoms or groups are interchangeable on rotation about the twofold axis passing along the double bond). It the atoms or groups are not interchangeable on rotation but each occupies the site of the other on reflection in a mirror plane (in the more general case when they are linked by a rotation-reflection axis S_n), then such atoms are referred to as enantiotopic (by analogy with the relations between molecules linked by mirror symmetry, which are known as enantiomers). An example of enantiotopic atoms is provided by the two protons in bromochloromethane.

Equivalent and enantiotopic atoms and groups are subject to identical magnetic shielding and hence are manifested in NMR spectra by signals having equal, equivalent chemical shifts. One should note that in the majority of molecules two stereochemically equivalent or enantiotopic nuclei respond differently to other nuclei in the molecule as regards spin–spin interaction. Thus the equivalent hydrogen atoms in the molecule of 1,1-difluoroethylene should have spin–spin coupling constants with two fluorine atoms (for each hydrogen nucleus, one of the fluorine nuclei is in the *cis*-position and the other is in the *trans*-position). Such hydrogen nuclei are referred to as magnetically non-equivalent (as regards the spin–spin coupling). Two nuclei with identical chemical shifts are magnetically equivalent as regards spin–spin coupling only when they are disposed symmetrically relative to any "trial" nucleus within the limits of the given group of magnetically interacting nuclei. Magnetically equivalent nuclei should be interchangeable on reflection in a plane perpendicular to the line connecting these nuclei and passing through the "trial" nucleus[2]. In *p*-chloronitrobenzene the stereochemically equivalent *ortho*-protons have the same chemical shift. However, two such protons interact differently with one of the *meta*-protons and are therefore non-equivalent as regards spin–spin coupling. The four protons of *p*-chloronitrobenzene form the AA'XX' system.

Cases are possible in which structurally identical atoms or groups within the limits of a single molecule are in diastereoisomeric environments and cannot change places whatever the symmetry operation. Such atoms or groups have been called diastereotopic (by analogy with diastereoisomeric relations between molecules). The hydrogen atoms of the methylene groups of chlorocyclobutane (two pairs of diastereotopic atoms) and of bromodichloroethane $ClCH_2$–$CHClBr$ are diastereotopic; in the second molecule the methylene group is linked to an asymmetric tetrahedral carbon atom. However, it must be emphasised that the presence of a chiral centre in the molecule is not an obligatory condition for the occurrence of diastereotopy. Thus the chlorocyclobutane molecule is achiral†. Another important example is the diastereotopy of the geminal protons in achiral monosubstituted ethylene. Since the diastereotopic atoms are in somewhat different steric environments, their magnetic shielding should differ (for example, the hydrogen atoms in the chlorocyclobutane molecule in the *trans*-position with respect to chlorine are influenced by the halogen atom less than the *cis*-atoms) and in the general case diastereotopic atoms should be manifested in the NMR spectra in the form of signals with different chemical shifts (it is said that such atoms are anisochronous). Naturally the resolving power of a specific NMR apparatus can be insufficient to detect different signals for diastereotopic nuclei: diastereotopic nuclei remain isochronous.

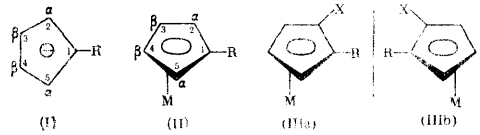
The groups $-CH_2R(R \neq H)$ and $-C(CH_3)_2R(R \neq CH_3)$ proved to be convenient and fairly sensitive indicators reflecting the stereochemistry of the molecule. In most cases these groups are enantiotopic and hence isochronous. When a

† The molecule is called chiral, if it cannot be made to coincide with its image in a planar mirror[3].

chiral centre is introduced into the molecule the H atoms or CH_3 group become diastereotopic, which is reflected in the splitting of the corresponding signals in the NMR spectra. We may note that the carbon atoms linked to H or CH_3 in these groups are prochiral centres, since the replacement of one of the hydrogen atoms or one of the methyl groups by some other atom or group makes the carbon atoms chiral.

Potentially diastereotopic organometallic groups have been recently attracting increasing attention. In the monosubstituted cyclopentadienyl anion (I) the α-atoms (as well as β-atoms) of carbon and hydrogen are stereochemically equivalent, since they are linked by a twofold axis of rotation passing through the substituent and the nodal $C_{(1)}$ atom. The coordination of the cyclopentadienyl anion to a metal atom as in formula (II) makes the two sides ("above" and "below") of the plane of the cyclic ligand non-equivalent and the atoms in the α-position with respect to the substituent become enantiotopic, because they can be interchanged only on reflection in the mirror plane passing through the substituent, the $C_{(1)}$ atoms linked to it, and the metal atom; the same applies also to the β-atoms. At the same time the protons in the 2- and 5- (or 3- and 4-) positions in a monosubstituted cyclopentadienyl anion (stereochemically equivalent) and ferrocene (enantiotopic) are magnetically non-equivalent as regards spin–spin coupling. Indeed the 2- and 5-nuclei are disposed asymmetrically relative to the 3-nucleus and interact with the latter in different ways. The system of four magnetically interacting protons in a monosubstituted metallocene can be described as AA'BB'.

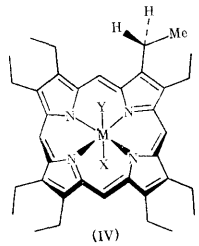
We may note that the replacement of one of the hydrogen atoms of the substituted cyclopentadienyl (CPD) by a group X gives rise to chirality in the molecule, the so called planar chirality. Two enantiomers (IIIa) and (IIIb) are therefore possible:



(I) (II) (IIIa) (IIIb)

Thus the monosubstituted CPD ligand coordinated to a metal atom is a group with enantiotopic carbon and hydrogen atoms within the 2/5 and 3/4 pairs; under certain conditions, these atoms can be converted into diastereotopic atoms. The present review is devoted to the discussion of various cases of the diastereotopy of atoms in this and similar indicator groups.

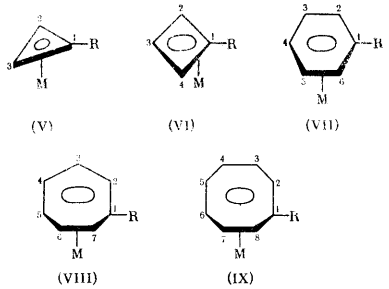
The study of the diastereotopy of atoms and groups is important for several reasons. Such analysis permits an exact interpretation of the NMR spectra of the compounds synthesised and is therefore essential for the determination of their structures. Enantiotopic and diastereotopic relations between atoms within a single molecule are linked directly to the stereochemical (enantiomeric and diastereoisomeric) relations between molecules. For example, the diastereotopy of indicator groups makes it possible to establish in many instances the presence of chirality in the molecule (either its appearance or disappearance). Thus the appearance of diastereotopy in the $-Sn(CH_3)_2R$ indicator group when the migration of this fragment in the cyclopentadiene ring is retarded, has been used to determine the energetics of the metallotropic process[4]. The observation of diastereotopy makes it possible to establish the fine features of the molecular structure. Thus the diastereotopy of the protons of the methylene groups in derivatives of metal octaethylporphyrinates (IV)[5] indicates either the coordination of two different ligands X and Y to the metal atom or the displacement of the metal atom from the plane of the porphyrin ring.



(IV)

In both cases the diastereotopy is due to the non-equivalence of the two sides of the porphyrin ring arising under these conditions (consequently the difference between the chemical shifts is not related to the hindered rotation of the ethyl groups). Finally, diastereotopic atoms have somewhat different reactivities, which must be taken into account, in particular, in the study of reaction mechanisms. Analysis of the stereochemical relations of the atoms and groups within the limits of a single molecule makes it possible to predict the direction of the reaction. It is not therefore surprising that such analysis is beginning to be formulated as a special branch of stereochemistry. We may note several reviews devoted to the theory of diastereotopy[1,2,8] (see also Sokolov[6] and Shul'pin[7]). The diastereotopy of the nuclei in transition metal complexes has not been considered in special reviews.

A coordinated monosubstituted CPD ligand is one of the most convenient organometallic indicator groups which have been investigated in comparative detail. However, the coordination of other cyclic ligands to transition metal atoms should also lead to the appearance of the enantiotopy of the atoms in these ligands and under certain conditions should also lead to diastereotopy. In a coordinated cyclopropenylium cation (V) this refers to the 2/3 pair of atoms. In the cyclobutadiene ligand (VI) and 2/4 nuclei are enantiotopic (and can become diastereotopic). In the coordinated substituted benzene (VII) there are two pairs of enantiotopic atoms (2/6 and 3.5), as in CPD. In the cycloheptatrienyl ligand (VIII) there are three such pairs: 2/7, 3/6, and 4.5. In the cyclooctatetraenyl groups (IX) there are also three such pairs: 2/8, 3/7, and 4/6. The observation of the diastereotopy of the nuclei in some of these systems is a task for the future.



(V) (VI) (VII) (VIII) (IX)

As already pointed out, the diastereotopy of atoms is not always manifested in NMR spectra, i.e. such atoms are not necessarily anisochronous. Whether or not diastereotopy is detected in the spectra depends on many factors. The account below will make it clear that the diastereotopy of a coordinated substituted CPD ligand has been observed much more frequently in ^{13}C NMR spectra than in proton resonance spectra. It is therefore understandable why the phenomenon of the diastereotopy in metallocenes has attracted the attention of investigators only recently when ^{13}C NMR has begun to be used widely. The manifestation of diastereotopy in the spectra is influenced greatly by the solvent. The overall signal of the diastereotopic atoms is sometimes split on

passing to a more polar solvent. We may note that in the general case enantiotopic atoms can become anisochronous in an enantiomeric solvent[1].

Certain cases of the diastereotopy of the atoms in a substituted coordinated cyclopentadienyl group and other cyclic ligands, caused by the stereochemical features of the metallocene molecules, are examined below. The diastereotopy of other indicator groups, indiced by the chirality of the metallocenyl fragment linked to them and the chemical non-equivalence of the diastereotopic nuclei in ferrocene derivatives, are discussed in the last sections of the review.

II. DIASTEREOTOPY IN CYCLIC LIGANDS LINKED TO AN ASYMMETRIC ATOM

1. The Classical Asymmetric Carbon Atom

The ^{1}H NMR spectrum of a coordinated monosubstituted CPD ligand depends greatly on the electron-donating or electron-accepting capacity of the substituent. In the spectra of monosubstituted ferrocenes and other metallocenes with electron-accepting substituents (for example, with the acetyl group) the protons of the substituted ring are manifested by two pseudotriplets in the range $\delta = 4-5$ p.p.m. relative to tetramethylsilane (TMS). The unsubstituted ring gives rise to a singlet with a chemical shift of ~4 p.p.m. In the spectra of alkyl derivatives of metallocenes the protons of the substituted ring usually give rise to a narrow multiplet and are frequently manifested actually in the form of a singlet signal. Thus the ^{1}H NMR spectrum of 1,1'-di-(2-cyanoethyl)ferrocene has a single fairly narrow unresolved multiplet centred at 4.09 p.p.m. In the calculated spectrum the chemical shift of the α-protons is assumed equal to -1.1 Hz and that of the β-protons is assumed to be +1.1 Hz from the centre of the multiplet (in $CHCl_3$ at a frequency of 90 MHz).[9] It is not therefore surprising that for a long time it was impossible to observe the effect of the stereochemistry of the substituent in the ^{1}H NMR spectra of metallocenes.

Table 1. The chemical shifts of the protons of the substituted CPD ring in the ^{1}H NMR spectra of cymantrenes containing an asymmetric carbon atom in the substituent [in $CHCl_3$, δ(p.p.m.) relative to TMS].[11,12]

Substituent	$H_{(2,5)}$	$H_{(3,4)}$	References
—CH (OH) CH_3	4.78	4.61	11
—CH (OH) CF_3	4.87; 5.03	4.68	11
—CH (OH) C_6H_5	4.63; 4.86	4.58	11
—C (CH_3) (OH) P (O) $(OC_2H_5)_2$	4.90; 5.20	4.51; 4.70	11
—C (CH_3) (OH) P (O) $(OC_4H_9)_2$ CH_3	4.91; 5.23	4.53; 4.72	11
—C (OH) (CH_3) C_6H_5	4.76; 4.94	4.61	12
—C (OH) (CH_3) C_6H_5	4.82; 4.89	4.51	12
—C (OH) (C_6H_5) $C_6H_4OCH_3$-*p*	4.84	4.64	12

The stereochemical non-equivalence of the α-protons of the CPD ring was first observed in 1971 in the ^{1}H NMR spectra of 1,1,1-trifluoro-2-hydroxyethylcymantrene[10]. The α-protons were manifested in the spectrum in the form of two signals (Table 1). The splitting of the signals of both α- and β-protons was observed in the spectra of cymantrenes containing some cumbersome asymmetric substituents with a phosphorus atom[11]. On the other hand, the influence of the asymmetry of a substituent such as the α-hydroxyethyl group was insufficient to split the signals even in the case of α-protons.

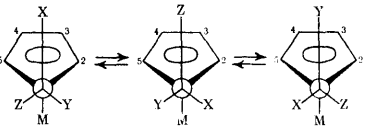


Figure 1. Certain conformations of a metallocene containing a substituent with an asymmetric carbon atom: $M = Mn(CO)_3$, FeC_5H_5, etc.

Fig.1 shows that, in the presence of the classical asymmetric carbon atom, linked directly to the CPD ligand of the metallocene, the 2- and 5-atoms (or 3- and 4-atoms) are subjected to different shielding in any possible conformation. The presence of the asymmetric centre leads to the appearance of two enantiomers. However, the spectra of the two enantiomers are identical. The 2-nucleus in the molecule of one of the enantiomers has the same shielding as the nucleus designated by the same number in the molecule in the second enantiomer (Fig.2). This also applies to the remaining nuclei in these molecules.

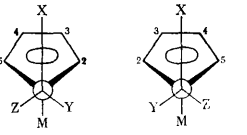


Figure 2. Enantiomers of a metallocene with an assymetric carbon atom.

Whereas the diastereotopy of the 2/5 and 3/4 nuclei of the CPD ring has been observed in the ^{1}H NMR spectra only for certain cymantrenes containing an asymmetric carbon atom in the substituent, following the introduction of ^{13}C NMR it was possible to distinguish the diastereotopic nuclei in the ferrocene analogue, ruthenocene, and other metallocene derivatives as well as derivatives of benzenechromium tricarbonyl and cyclobutadieneiron tricarbonyl. The splitting of the 2/5 and 3/4 signals was first observed in the spectra of α-hydroxyethyl- and α-hydroxybenzylferrocenes[13], although it was not explained #. Fairly numerous examples of the diastereotopy of the nuclei of a monosubstituted CPD ligand, with an asymmetric carbon, in different transition metal complexes have been found in recent years, (Table 2).

Bridged metallocenes constitute a special case[25], because the substitution of one hydrogen atom in the bridge of such compounds can lead to the appearance of an asymmetric carbon atom, which induces in its turn the diastereotopy of the

See also the study of Sokolov et al.[53], which is discussed in Section V.

nuclei of two ligands at once. It a ferrocenophane drivative[3] (X) one of the CPD rings (*A*) adjoins directly an asymmetric carbon atom, while the *B* ring is separated from it by a chain of two carbon atoms. The signals of the 2/5 and 3/4 atoms of both rings were found to be split in the ^{13}C NMR spectrum of this compound[19] (seven peaks: 67.2, 71.1, 71.8, 68.6,69.5, 68.0, and 72.2 p.p.m.). In the molecule of the isomeric ferrocenophane (XI) the asymmetric carbon atom is separated by equal distances from the ligands. In the carbon resonance spectrum of compound (XI) the 2-, 3-, 4-, and 5-atoms of the CPD rings give rise to eight signals (*A* ring: 69.6, 70.1, 68.0, and 72.0 p.p.m.; *B* ring: 73.2, 72.0, 72.4, and 66.4 p.p.m.). It is of interest that in compounds (X) and (XI) the protons in the two rings are also spectroscopically distinguishable. In the ^{1}H NMR spectrum of compound (X) the protons of the *A* ring give signals at $\delta = 4.64$, 4.05, 3.94, 4.46 p.p.m. The *B* ring also gives rise to four signals: 4.87, 4.33, 4.29, and 4.70 p.p.m. The spectrum of compound (XI) consists of eight signals (*A* ring: 4.68, 4.07, 3.90, and 4.39 p.p. m.; *B* ring: 5.02, 4.36, 4.28, and 4.61 p.p.m.). In the ^{13}C NMR spectrum of the bridged cyclopentadienyl derivative of titanium (XII) the 2-, 3-, 4-, and 5-carbon atoms in the two rings give seven signals: 115.4, 116.8, 121.3, 121.6, 123.5, 123.7, and 123.9 p.p.m. [19]

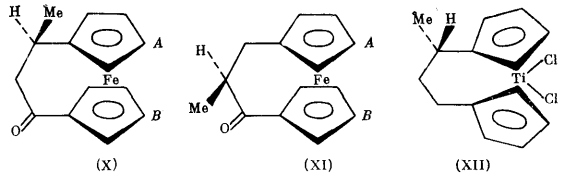


Table 2. Chemical shifts of the signals due to the carbon nuclei of the substituted CPD ring in the ^{13}C NMR spectra of certain derivatives of π-complexes [δ(p.p.m.) relative to TMS].

Substituent	$C_{(1)}$	$C_{(2,5)}$	$C_{(3,4)}$	Refs.
	Ferrocene			
—CH (OH) CH_3	94.1	65.4; 66.0	67.4; 67.5	14
—CH (OH) C_6H_5	93.9	65.3; 67.0	67.7; 67.8	14
—CH (OH) CH_2CN	90.0	65.5; 66.2	68.1; 68.2	14
—CH (CH_3) C_6H_5	94.2	65.9; 66.7	67.3; 67.7	15
—C (OH) (CH_3) C_6H_5	100.3	65.6; 67.1	67.6; 68.0	15
—CH (OH) CH $(CH_3)_2$	92.6	68.5; 64.5	67.4; 67.1	16
—CH (OH) C $(CH_3)_3$	91.4	69.4; 65.2	67.3; 67.2	16
—C (OH) (CH_3) CH $(CH_3)_2$	99.3	65.3; 68.4	67.4; 67.7	17,18
—C (OH) (CH_3) C $(CH_3)_3$	98.4	66.8; 69.3	66.7; 67.3	17,18
—CH (CH_3) CH_2COOH	93.7	65.8; 66.3	67.1	19
—CH_2CH (CH_3) COOH	85.2	67.3	69.2	19
	Ruthenocene			
—CH (OH) CH $(CH_3)_2$	98.9	73.9; 69.9	72.3; 68.8	20
	Cymantrene			
—CH (OH) CH_3	110.4	82.1; 81.6	81.4; 80.8	21
—CH (OH) CF_3	97.1	84.1; 83.2	82.0; 81.6	21
—C (OH) (CH_3) P (O) (OCH_2CH_3)$_2$	106.7	85.8; 83.8	82.0; 78.0	21
—CH (OH) C_6H_5	108.2	82.1; 82.5	80.0; 81.2	22
—C (OH) (CH_3) C_6H_5	114.1	83.3; 82.5	80.7; 78.7	22
—C (OH) (CH_3) C_6H_5	114.0	84.4; 83.7	81.2; 79.4	22
—C (OH) (C_6H_5) $C_6H_4OCH_3$-*p*	112.1	89.7	80.1; 79.9	22
—CH (OH) $C_5H_4Mn(CO)_2P(C_6H_5)_3$*	107.8	80.2; 81.6; 85.5	80.9; 83.3; 87.9	23
—CH (OH) $C_5H_4FeC_5H_5$	108.7	81.0; 82.7	81.6	23
	Cyclopentadienyltriphenylphosphinemanganese dicarbonyl			
—CH (OH) C_6H_5	107.0	84.9; 83.1	84.2; 80.0	24
—C (OH) (CH_3) C_6H_5	112.6	85.2; 82.8	81.5	24
	Dicyclopentadienyltitanium dichloride			
—CH (CH_3) C_6H_5	115.4	117.9; 122.0	119.2	19

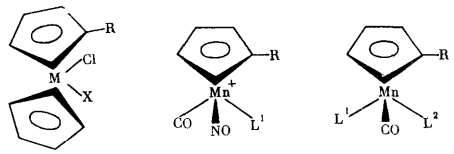
*The $C_{(2,3,4,5)}$ signals of both CPD ligands.

The diastereotopy of the 2/6 and 3/5 nuclei was observed in the ^{13}C NMR spectra of benzenechromium tricarbonyl derivatives [VII, M = $Cr(CO)_3$] containing an asymmetric carbon atom in the substituent. Thus, for R = $CH(OH)C_6H_5$, the unsubstituted carbon atoms of the benzene ring give rise to four signals: 90.1, 91.7, 91.9, and 92.1 p.p.m. The diastereotopy of both pairs is reflected in the spectrum of the analogous derivative with R = $C(OH)(CH_3)C_6H_5$: $\delta = 90.0$, 90.6, 92.8, 93.1, and 94.1 p.p.m.[26] The splitting of the signal due to the 2/4 nuclei was also discovered in the ^{13}C NMR spectra of carbinols of the cyclobutadieneiron tricarbonyl series [VI, M = $Fe(CO)_3$]: $\delta = 62.6$ and 62.7 p.p.m. for R = $CH(OH)CH_3$ and $\delta = 63.4$ and 63.6 p.p.m. for R = CH. .$(OH)C_6H_5$.[27]

The splitting of the signal of the 2/5 and 3/4 carbon atoms in the cyclopentadienyl complexes containing a substituent with an asymmetric carbon atom in the ring was used to determine the nature of the bond in the cyclopentadienyl complexes of thallium[15].

2. The Asymmetric Transiton Metal Atom

The diastereotopy of the atoms in a substituted cyclic π-ligand arises also when the chiral centre of the molecule consists of the transition metal atom itself. In compound [XIII, M = Ti, R = CH_3, X = $OC_6H_3(CH_3)_2$-*o*,*o*] the titanium atom is linked to four different substituents. Four signals due to the 2-, 3-, 4-, and 5-atoms of the substituted CPD ring were found in the ^{13}C NMR spectrum of this complex with the chemical shifts $\delta = 109.6$, 115.6, 121.1, and 121.8 p.p.m.[19]



Cymantrene gives rise to extensive possibilities in this sense. The diastereotopy of the 2/5 and 3/4 nuclei was observed for two types of complexes. The first type (XIV) is formed when one of the CO ligands in the monosubstituted cymantrene is replaced by NO and the other arises when it is substituted by an *n*-donor (phosphine, arsine). In this case the complex has a positive charge. The second type of compound with a chiral manganese atom (XV) has been obtained on replacement of two carbonyl ligands by different *n*-donors (phosphine and phosphite). The NMR data for complexes of both types are listed in Table 3. It is of interest that the slight difference between triethyl phosphite and trimethyl phosphite is not reflected in the spectrum—diastereotopy is not manifested for these ligands.

3. The Asymmetric Carbon Atoms

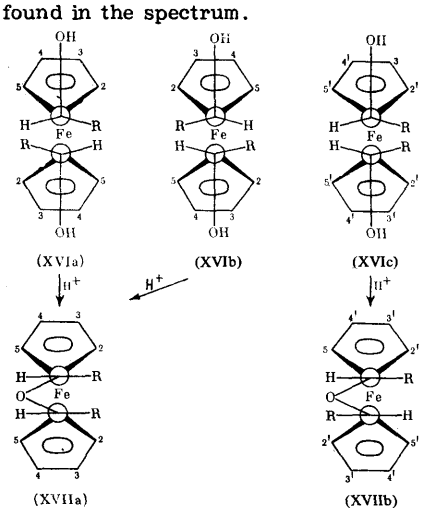
Numerous ferrocene derivatives containing two identical asymmetric carbon atoms in two different rings are known. Such compounds are usually obtained on reduction of heteroannular diacylferrocenes. The presence of two asymmetric centres leads to the appearance of two diasteroisomers. For identical centres, these consist of a pair of enantiomers [for example, (XVI, a and b)] and the *meso*-form (XVIc). Naturally the diasteroisomers should give rise to different NMR spectra and in the spectrum of each diastereoisomer one should be able to observe the diastereotopy of the 2/5 and 3/4 nuclei of each CPD ring.

In the ^{13}C NMR spectrum of a mixture of diastereoisomers of 1,1'-di-(1-hydroxyethyl)ferrocene (XVI, *a,b*, and *c*, R = CH_3) (in CH_2Cl_2) nine signals were found in the range δ = 60–70 p.p.m.[30]: 65.2, 65.5, 65.7, 66.1, 66.3, 66.7, 67.5, and 67.7 (with a double intensity), and 68.0 p.p.m. Two of these peaks correspond to the carbon atoms linked to the hydroxy-group and the remaining seven signals indicate the non-equivalence of the 2/5, 3/4, 2'/5', and 3'/4' atoms (two signals are accidentally superimposed). The signals with δ = 25.3 and 26.0 p.p.m. correspond to the methyl groups of different diastereoisomers. In the spectrum of the mixture of the diastereoisomers of 1,1'-di-(1-hydroxybenzyl)ferrocene (XVI, a, b, and c; R = C_6H_5) (in CH_2Cl_2) ten signals were found[30] for the 2/5, 3/4, and 2'/5', 3'/4', and C–OH atoms: 66.3, 66.7, 66.9, 67.3, 68.0, 68.2, 68.4, 68.5, 71.9, and 72.8 p.p.m. The signals with δ = 94.0 and 94.5 p.p.m. refer to the 1- and 1'-atoms of the two diastereoisomers [in the spectrum of (XVI, a, b, and c; R = CH_3) the key 1- and 1'-atoms give rise to a single peak at 95.3 p.p.m.].

Table 3. Chemical shifts in the ^1H and ^{13}C NMR spectra of cymantrene derivatives [δ(p.p.m.) relative to TMS].

Compound	R	L^1	L^2	H(2,5)	H(3,4)	C(2,5)	C(3,4)	Refs.
(XIV)	CH_2CH_3	$P(C_6H_5)_3$		5.10; 5.23	5.63	91.6; 94.0	93.5; 97.5	28
(XIV)	CH_2CH_3	$As(C_6H_5)_3$		5.65; 5.75	5.38	90.8; 92.8	92.4 95.9	28
(XIV)	CH_2CH_3	$P(CH_2C_6H_5)_3$		4.80; 5.35	5.10	90.7; 93.4	91.4 95.7	28
(XV)	$CO(CH_2)CO_2{\cdot}CH_3$	$P(OCH_3)_3$	$P(C_6H_5)_3$	4.76; 4.96	3.76; 4.01	—	—	29
		$P(OCH_3)_3$	$P(OC_6H_5)_3$	4.93	4.41	—	—	29

On treatment with acid, the isomers are converted stereoselectively into oxygen-containing ferrocenophanes[31]: the racemate of the enantiomers (XVI, a and b) gives rise to the *cis*-isomer (XVIIa) and the *meso*-form (XVIc) is converted into the *trans*-isomer (XVIIc). Eight signals, two of which are due to the C–OH atoms and the remainder are associated with the 2-, 3-, 4-, 5-, 2'-, 3'-, 4'-, and 5'-carbon atoms in the ring, were observed in the spectrum of ferrocenophane (XVII) obtained from (XVI, R = CH): δ(in CH_2Cl_2) = 62.6, 65.3, 67.5, 68.3, 69.4, 70.2, 71.4, and 72.1 p.p.m.[30] Presumably only the signals of the 2/5 and 2'/5' pairs are split. In addition, two signals for each of the 1- and 1'-atoms (89.2 and 90.9 p.p.m.) and for the methyl groups (19.3 and 22.3 p.p.m.) were found in the spectrum.



Only two signals due to the peak $C_{(1)}$ atoms, corresponding to two different types of ferrocene fragments (mono- and di-substituted ferrocene rings), were found in the ^{13}C NMR spectrum of 1,1'-di-[2-ferrocenyl-4-methoxycarbonyl)butyl]-ferrocene containing two identical asymmetric centres §. In the region of the signals due to the 2-, 3-, 4-, and 5-nuclei six peaks were observed, which indicates the diastereotopic anisochronicity of only the 2/5 atoms in each type of ferrocene fragment[32].

Two asymmetric carbons can be linked to the same π-ligand. In this case three isomers are possible for compounds with two identical asymmetric centres: the racemate of the two enantiomers (XVIII, a and b) and the two *meso*-forms (XVIIIc) and (XVIIId).

In the benzenechromium tricarbonyl compounds (XVIIIc) and (XVIIId) there is a plane of symmetry, by virtue of which the atoms within the 3'/6' and 4'/5' pairs in the first compound and the 3''/6'' and 4''/5'' pairs in the second are enantiotopic. Indeed, two overall signals were observed in the ^{13}C NMR spectrum of each compound for these atoms: 90.2 and 93.3 p.p.m. in the spectrum of (XVIIIc) and 91.5 and 93.5 p.p.m. in the spectrum of (XVIIId). The carbon atoms linked to the substituents in the two compounds are isochronous [118.2 p.p.m. for (XVIIIc) and 114.4 p.p.m. for (XVIIId)].

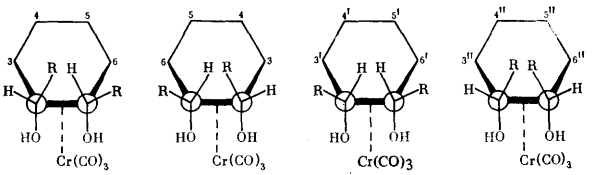


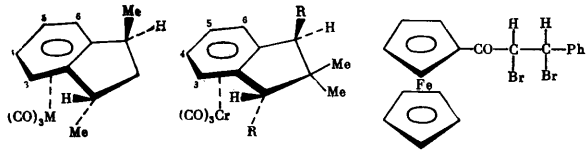
Table 4. ^1H NMR spectra of arenechromium tricarbonyl and arenemolybdenum tricarbonyl derivatives [δ(p.p.m.) relative to TMS].[33]

Compound	H(3)	H(4)	H(5)	H(6)
(XIX), M=Cr	5.12	5.36	5.00	5.43
(XIX), M=Mo	5.52	5.66	5.35	5.73
(XX), R=$OCOCH_3$	5.36	5.36	5.20	5.50

In either of the two enantiomers (XVIIIa) and (XVIIIb) the 3/6 and 4/5 atoms are diastereotopic, which is manifested in the carbon resonance spectra (89.7, 92.6, 92.5, and 94.5 p.p.m.) and in ^1H NMR (5.78, 5.56, 5.51, and 5.76 p.p.m.). The atoms of the benzene ring carrying substituents are also anisochronous (113.1 and 120.1 p.p.m.).[26] The non-equivalence of the 3/6 and 4/5 atoms was observed as early as 1969 in the ^1H NMR spectra of compounds (XIX) and (XX), which exist in the form of two enantiomers[33]. The chemical shifts are listed in Table 4.

§ The stereochemistry of ferrocene derivatives containing two identical or different asymmetric centres has been discussed[63].

Two signals of the 2/5 protons were observed in the ^1H NMR spectrum of the substituted ferrocene (XXI) ($\delta = 4.90$ and 4.66 p.p.m.).[34] However, one should note that the splitting of the signal of the α-protons can be induced both by the diastereotopy of the 2/5 atoms and by the non-equivalence of the α-protons in the two diastereoisomers of compound (XXI) containing two asymmetric carbon atoms in the side chain.

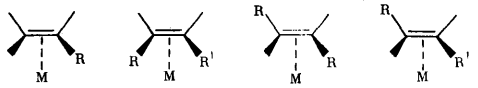


(XIX) (XX) (XXI)

III. DIASTEREOTOPY INDUCED BY PLANAR CHIRALITY

The coordination of a planar cyclic (cyclopentadienyl, benzene) or non-cyclic (monoolefin, diene) π-ligand to a transition metal atom makes the hitherto equivalent sides of the ligand non-equivalent. If two different substituents are linked to a cyclic ligand, then, after coordination, there is a possibility of two different dispositions of these substituents [see structures (IIIa) and (IIIb)] and two enantiomers appear. Such planar chirality (induced by the non-equivalence of the sides of planar ligands) is most typical for organometallic complexes of transition metals, although one can imagine cyclophane, triquinacene, and corannulene molecules containing two different substituents in the ring and exhibiting planar chirality. Chiral cyclophanes have been obtained in an optically active form.

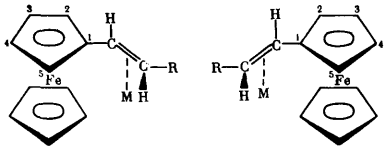
One of the important instances of the manifestation of planar chirality is the existence of the enantiomers of mono-olefins coordinated to organometallic groups. The enantiomers can be obtained for a monosubstituted olefin (XXII), a disubstituted olefin with different substituents in the *cis*-positions (XXIII) and also with identical [compound (XXIV)] or different [compound XXV] substituents in the *trans*-positions.



(XXII) (XXIII) (XXIV) (XXV)

1. Planar Chirality of the Substituent

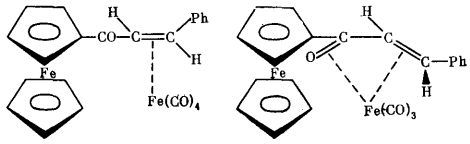
When rotation about the C^1–CH= bonds is possible in the vinylferrocene molecule, the 2/5 and 3/4 atoms of the CPD ligand are enantiotopic. The coordination of the double bond to the organometallic group leads to diastereotopy of these nuclei. In the resulting enantiomers (XXVIa) and (XXVIb) the nuclei having identical environments are designated by identical numbers ¶.



(XXVIa) (XXVIb)

¶ The molecules of the enantiomers (XXVIa) and (XXVIb) have a planar chiral fragment (a double bond coordinated to the metal atom) and a planar prochiral fragment FeC_5H_4X.

The diastereotopy of the 2/5 and 3/4 nuclei of the CPD ligand, induced by the presence of a chiral fragment in the substituent—a coordinated double bond—was observed for the complexes of certain vinylferrocenes with iron tetracarbonyl and iron tricarbonyl groups and also with the cyclopentadienylmanganese dicarbonyl group (Table 5).[35-37] Two features may be noted. Diastereotopy was not manifested in the ^{13}C NMR spectrum of the complex of cinnamoylferrocene with the iron tetracarbonyl group (XXVII) using CH_2Cl_2 as the solvent. In the more polar solvents acetone and nitromethane it was possible to observe the splitting of the signals due to the 2/5 and 3/4 nuclei. In the ^1H NMR spectra the anisochronicity of the nuclei of the CPD ring of ferrocene was not observed with the exception of the complex of cinnamoylferrocene with iron tricarbonyl (XXVIII). In this case the presence of a very cumbersome chiral group led to the splitting of the H 2/5 signal (4.64 and 4.99 p.p.m. in $CHCl_3$).

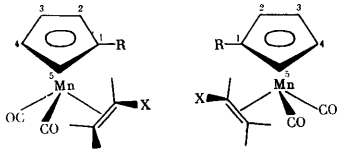


(XXVII) (XXVIII)

Table 5. Chemical shifts in the ^{13}C NMR spectra of certain derivatives of vinylferrocenes [δ (p.p.m.) relative to TMS].

Compound	M	R	Solvent	$C_{(2,5)}$	$C_{(3,4)}$	Refs.
(XXVI)	$Fe(CO)_4$	COC_6H_5	CH_2Cl_2	62.4; 68.0	70.0; 70.4	35,36
(XXVII)	$Fe(CO)_4$	—	CH_2Cl_2	68.7	72.5	35,36
(XXVII)	$Fe(CO)_4$	—	$(CH_3)_2CO$	69.1; 71.2	72.6; 72.9	35,36
(XXVII)	$Fe(CO)_4$	—	CH_3NO_2	69.8; 71.8	73.2; 73.6	35,36
(XXVIII)	—	—	CH_2Cl_2	67.8; 71.2	71.5; 72.8	35,36
(XXVI)	$Mn(CO)_2C_5H_5$	H	CH_2Cl_2	67.4; 68.1	68.6	37
(XXVI)	$Mn(CO)_2C_5H_5$	COC_6H_5	CH_2Cl_2	62.4; 68.1	68.6	37

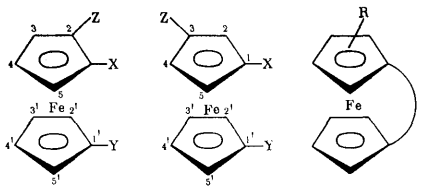
The diastereotopy of the 2/5 and 3/4 nuclei of the monosubstituted CPD ring can be expected in the NMR spectra of the complex of cyclopentadienylmanganese dicarbonyl with a monosubstituted olefin. In this case there is a possibility of two enantiomers (XXIXa) and (XXIXb).



(XXIXa) (XXIXb)

2. The Planar Chirality of the Metallocene Molecule

In chiral trisubstituted ferrocenes (XXX, a and b; $X \neq Y \neq Z \neq H$ or $X = Y \neq Z \neq H$) the 2'/5' and 3'/4' atoms of the monosubstituted ring are diastereotopic. The possibility of the anisochronicity of these nuclei is most evident in the case of monosubstituted ferrocenophanes (XXXI, R = acetyl, for example).



(XXXa) (XXXb) (XXXI)

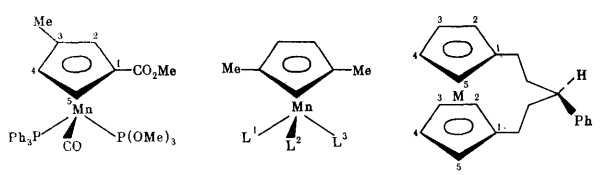
Indeed it is seen from literature data[38-40] that the α-protons (as well as the β-protons) of the monosubstituted ring in the spectra of compounds (XXXI) in general give rise to different signals. It is more difficult to observe the anisochronicity of the protons of the monosubstituted ring in the spectra of non-bridged derivatives (XXX). However, on comparing the results of a whole series of investigations[41-45], one may conclude that the appearance of a multiplet structure in the signal of the monosubstituted ring protons (a CPD ring linked to a single alkyl substituent usually gives rise to a narrow singlet) is associated precisely with the diastereotopy of the 2′/5′ and 3′/4′ protons. It is of interest that the anisochronicity of the monosubstituted ring protons is more distinct when two different substituents in the second ring occupy the 1- and 3-positions. Thus, whereas in the spectra of compounds (XXXa, $X = Y = C_2H_5$, $Z = CH_2^+$ [43] or $X = Y = CH_2C_6H_5$, $Z = COCH_3$ or COC_6H_5) [45] the signal due to the protons in the ring with the substituent Y consists of a narrow singlet, in the spectra of the corresponding derivatives (XXXb) the monosubstituted ring is manifested by a fairly broad multiplet.

The splitting of the signal due to the 2′/5′ and 3′/4′ nuclei in the ^{13}C NMR spectra has been observed for compounds [XXXb, $X = Y = CH_3$, $Z = C(OH)(CH_3)_2$ [18] and $X = Y = CH_2C_6H_5$, $Z = COC_6H_5$ [45]]. As in the case of proton resonance, the signals of the 2′/5′ and 3′/4′ atoms in the ^{13}C NMR spectrum of the 1,2-isomer of (XXXa, $X = Y = CH_2C_6H_5$, $Z = COC_6H_5$) are not split[45].

3. Combination of an Asymmetric Atom and Planar Chirality

The presence in one ring of a metallocene molecule of two different substituents, one of which contains a chiral centre, leads to the appearance of two diastereoisomers [a more complex case, involving two chiral substituents in a single ring, was analysed above in relation to compound (XVIII)]. Such diastereoisomers of the 1,2-isomers of [XXXa, $X = Y = CH_3$, $Z = CH(OH)CH_3$ [46-48] or $X = Y = CH_2C_6H_5$, $Z = CH(OH)CH_3$ [45]] can be separated chromatographically. They give rise to readily distinguishable ^1H NMR spectra. It is of interest that in the case of compounds [XXXa, $X = Y = CH_2C_6H_5$, $Z = CH(OH)CH_3$] the diastereotopy of the protons in the methylene group is observed for only one isomer[45].

An example of the combination in one molecule of planar chirality and a chiral transition metal atom is known. Since the manganese derivative (XXXII) exists in the form of two diastereoisomers, the ^1H NMR spectrum of their mixture was found to contain four signals associated with the 2/5 atoms and two signals associated with the 4-atom[29].



(XXXII) (XXXIII) (XXXIV)

The two methyl groups in the CPD ring of the complex with a chiral manganese atom are diastereotopic. They give rise to two signals in the proton resonance spectra ($\delta = 1.86$ and 1.93 p.p.m.) for compound [XXXIII, $L^1 = P(OMe)_3$, $L^2 = PPh_3$, $L^3 = CO$]. [29] If the methyl groups are in the 1- and 3-positions, then the hydrogen and carbon atoms in the 4/5 positions are also diastereotopic. When the methyl groups are in vicinal positions, the 3/5 atoms of the CPD ring are diastereotopic.

IV. DIASTEREOTOPY IN ACHIRAL MOLECULES

An achiral molecule can also contain diastereotopic atoms and groups. In the series of metallocenes such a compound is, for example, the phenyl derivative of [5] ferrocenophane (XXXIV, M = Fe). In contrast to the unsubstituted [5] ferrocenophane, whose molecule is divided by a plane of symmetry passing through the iron atom and through all the carbon atoms of the bridge and $C_{(1)}$ and in which the 2/5 and 3/4 atoms of both rings are enantiotopic, in the phenyl derivative there is no plane of symmetry. As a result, the 2/5 and 3/4 atoms in the molecule of compound (XXXIV) become diastereotopic in each ring. It is of interest that the atoms in different rings, designated by identical numbers, form enantiotopic pairs, since they are linked by a mirror plane. In order to account for the non-equivalence of the 2/5 and 3/4 nuclei in compounds resembling (XXXIV), one can also employ a different, more traditional approach. The point is that the above nuclei are involved in *syn/anti (cis/trans)* relations with the phenyl substituent.

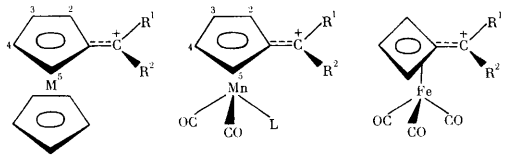
As was to be expected, two common signals for the 2/5 and 3/4 atoms of both rings are observed in the ^{13}C NMR spectrum of [5] ferrocenophane[49] ($\delta = 68.4$ and 66.9 p.p.m. in CH_2Cl_2 at 15 °C). In the spectrum of the γ-phenyl derivative of (XXXIV, M = Fe), the 2-, 3-, 4-, and 5-carbon atoms of the CPD rings give rise to four signals ($\delta = 66.0$, 66.9, 67.8, and 68.9 p.p.m. in CH_2ClCH_2Cl at 30 °C). [50] Analogous splitting has been observed in the spectrum of the γ-phenyl derivative of [5] ruthenocenophane (XXXIV, M = Ru): 68.0, 68.8, 71.1, 72.6 p.p.m. [51] We may note that in both cases the 2/5 and 3/4 carbon atoms of the CPD rings are sensitive to the introduction of a substituent in the γ-position in the bridge, separated from the ring by 2–3 atoms. For comparison, we may point out that the diastereotopy of the 2/5 and 3/4 atoms could not be observed when the asymmetric carbon atom was separated from the ring by one methylene group [the compound $C_5H_5FeC_5H_4CH_2CH(CH_3)COOH$; see Table 2]. Naturally, the fact that in the above compound the γ-methylene group with the methyl substituent is in spatial proximity to the ferrocene ring has an effect in the case of ferrocenophane.

In contrast to compounds (XXXIV), the molecules of the bridged metallocenes (X), (XI), and (XII) are no longer achiral, because the carbon atom in the bridge, linked to the substituent, is also linked to four different groups and in this case one can assume that the diastereotopy of the 2/5 and 3/4 nuclei is induced by the presence of an asymmetric carbon atom in the bridge.

V. DIASTEREOTOPY IN α-METALLOCENYL-SUBSTITUTED CARBONIUM IONS

When carbinols, containing metallocenyl (ferrocenyl, ruthenocenyl, osmocenyl, cymantrenyl, and cyclobutadiene-iron tricarbonyl) fragments in the α-position are dissolved in acids, unusually stable carbonium ions are formed[52]. The

signals of the 2/5 and 3/4 atoms of the CPD ligand are found to be split in both ^1H and ^{13}C NMR spectra of such ions containing two different substituents at the carbonium centre in addition to the metallocenyl fragment. This served as a basis for the hypothesis that the rotation about the $\overset{+}{C}-C_{(1)}$ bond is hindered, because such a bond has partial double bond character. The ^1H and ^{13}C NMR data for certain metallocenes having a single carbonium centre as a substituent are compiled in Tables 6 and 7. More complex carbonium ions, particularly those of the ferrocenophane series, have been discussed in the literature[41-44,47,48,57].

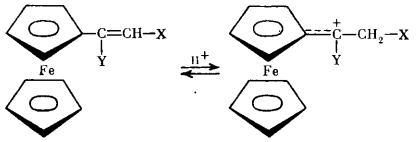


(XXXV) (XXXVI) (XXXVII)

Table 6. Chemical shifts in the ^1H NMR spectra of α-metallocenylcarbonium ions [δ(p.p.m.) relative to TMS].

Compound	R^1	R^2	H(2,5)H(3,4)	Refs.
(XXXV), M=Fe	H	$CH(CH_3)_2$	6.45 5.18 4.58	20
(XXXV), M=Fe	H	CH_3	5.03 6.36 4.49 6.21	54
(XXXV), M=Fe	H	C_6H_5	5.52 6.45 4.77 6.24	54
(XXXV), M=Ru	H	$CH(CH_3)_2$	6.19 6.07 5.11	20
(XXXV), M=Os	H	$CH(CH_3)_2$	6.26 5.23	20
(XXXVI), L=CO	CH_3	C_2H_5	5.70 6.25 7.78	12
(XXXVI), L=CO	H	C_6H_5	5.91 6.12 5.45	12
(XXXVI), L=CO	CH_3	C_6H_5	5.73 5.91 6.16	12
(XXXVI), L=CO	C_6H_5	p-$C_6H_4OCH_3$	5.72 6.34 5.88	12
(XXXVI), L=$P(C_6H_5)_3$	H	C_6H_5	5.00 5.45 5.82	24

The splitting of the signals due to the 2/5 and 3/4 carbon atoms in the spectra of α-ferrocenylcarbonium ions was first noted by Sokolov et al.[53]. Subsequently the ^{13}C NMR spectra of metallocenylcarbonium ions were discussed frequently[16-18, 20,22-24,27,55,56]. The exact assignment of the signals to the 2/5 and 3/4 atoms was made by Koridze et al.[16] Nesmeyanov et al.[55] observed for the first time the splitting of the signals of the 2/5 and 3/4 carbon atoms in the spectra of the carbonium ion (XXXIX) formed on protonation of the double bond in the vinylferrocenes [XXXVIII, X = C_6H_5, Y = H(a); X = $CO_2C_2H_5$, Y = CH_3(b)]. However, it was given an incorrect explanation. The cation (XXXIXb) was investigated in greater detail in another study by Nesmeyanov et al.[56]



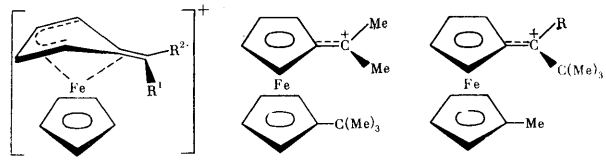
(XXXVIIIa and b) (XXXIXa and b)

The spectra of the derivative (XXXVII) show that the 2- and 4-carbon atoms are also anisochronous [δ(2/4) = 78.8 and 80.4 p.p.m. for R^1 = H and R^2 = CH_3], but, for R^1 = H and R^2 = C_6H_5, the chemical shifts of the 2- and 4-atoms fortuitously coincide and a common signal with δ = 80.0 p.p.m. is observed[27].

Table 7. Chemical shifts in the ^{13}C NMR spectra of certain α-metallocenylcarbonium ions [δ(p.p.m.) relative to TMS].

Compound	R^1	R^2	C(2,5)	C(3,4)	Refs.
(XXXV), M=Fe	H	CH_3	80.9; 80.0	93.3; 93.0	16
(XXXV), M=Fe	H	$CH(CH_3)_2$	79.7; 78.9	93.2; 92.6	16
(XXXV), M=Fe	H	$C(CH_3)_3$	81.4; 80.2	93.8; 93.6	16
(XXXV), M=Fe	CH_3	$CH(CH_3)_2$	76.9; 77.9	94.5; 94.9	18
(XXXV), M=Fe	CH_3	$C(CH_3)_3$	79.2; 80.3	95.1; 95.3	18
(XXXV), M=Fe	H	$CH_2COC_6H_5$	80.9; 82.8	96.2; 96.5	55
(XXXV), M=Fe	CH_3	$CH_2CO_2CH_3$	78.0; 78.6	94.4; 94.8	56
(XXXVI), L=CO	H	C_6H_5	92.8; 100.2	97.6; 98.3	22
(XXXVI), L=CO	CH_3	C_6H_5	93.3; 94.4	94.6; 98.3	22
(XXXVI), L=$P(C_6H_5)_3$	H	C_6H_5	103.9; 103.6	96.3; 92.3	24
(XXXVI), L=$P(C_6H_5)$	CH_3	C_6H_5	104.2; 103.4	92.1; 91.6	24

The diastereotopy of the 2/5 nuclei in metallocenylcarbonium cations shows some similarity with the diastereotopy of the geminal protons in monosubstituted olefins. Even if the carbonium ion has the non-planar structure (XL), as was assumed, the diastereotopy of the 2/5 and 3/4 nuclei should persist for $R^1 \neq R^2$.



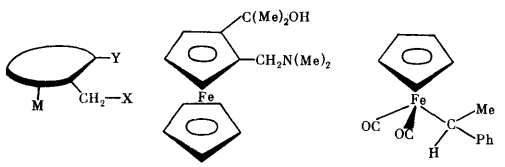
(XL) (XLI) (XLII)

An attempt has been made[44,48] to demonstrate the deviation of the carbonium fragment from the planar configuration. A comparison was made of the ^1H NMR spectra of the two isomeric carbonium ions (XLI) and (XLII, R = CH_3) or (XLIIa). The spectrum of compound (XLI), due to the protons of the ring to which the t-butyl group is attached, is manifested by a slightly broadened singlet. Hence it follows that the differences in the shielding of the 2'-, 3'-, 4'-, and 5'-protons are small. In the spectrum of the cation (XLIIa) the protons of the ring linked to the methyl group give rise to two well resolved multiplets. The authors[44,48] concluded that the mutual rotation of the rings in this compound is hindered, which leads to a time-averaged non-equivalence of the α- and β-protons of the methyl-substituted ring. Since the rotation is not hindered in the first isomer, it is concluded that in compound (XLIIa) rotation is hindered by the mutual repulsion of the $C(CH_3)_3$ and CH_3 groups, arising in connection with the deformation illustrated in structure (XL). However, an alternative explanation is also possible[45]. The hydrogen atoms in the ring without a cationic centre (2'/5' and 3'/4') are enantiotopic in compound (XLIa), while in compound (XLIIa) they are diastereotopic (this is a special case of diastereotopy associated with the planar chirality of the molecule discussed above) and can be anisochronous. However, one cannot rule out the possibility that the anisochronicity of the diastereotopic 2'/5' and 3'/4' nuclei is manifested solely by virtue of the deformation postulated by the authors[44,48]. An unambiguous choice in favour of one of the explanations could be made by measuring the spectrum of

compound [XLII, R = $C(CH_3)_3$]. In this molecule the 2'/5' and 3'/4' atoms again become enantiotopic, but the postulated hindered rotation persists.

VI. CERTAIN OTHER CASES OF DIASTEREOTOPY

The diastereotopy of different groups in the molecules of π-complexes of transiton metals may not be associated with the specific features of the geometry of the metallocene (it can be caused, for example, by the presence of an asymmetric carbon atom in the side chain), but it is possible to quote examples where the structure of the metallocene sandwich does in fact induce diastereotopy. Thus, if one of the substituents in the homoannular disubstituted metallocene contains a methylene group, then its protons will be diastereotopic [see compound (XLIII)]. This phenomenon was observed for the first time in the spectra of the substituted ferrocene (XLIV) (the methyl groups in the neighbouring substituent are also diastereotopic).[58] Similarly the diastereotopy of the protons of the CH_2 groups was noted in a derivative of benzenechromium tricarbonyl[59]. It is of interest that in the ^1H NMR spectra of acetyl-1,1'-dibenzylferrocenes the diastereotopic anisochronicity could be observed only for the protons of the benzyl group in the disubstituted ring and only when the acetyl group was located in the α-position relative to this group[45].

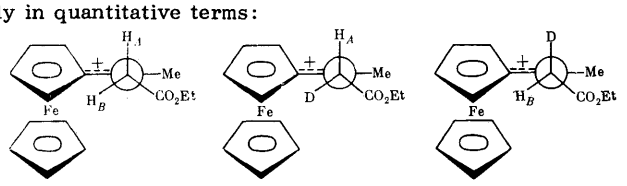


(XLIII) (XLIV) (XLV)

The diastereotopic anisochronicity of the carbonyl groups (δ = 217.1 and 217.5 p.p.m.), due to the presence of the asymmetric carbon atom, has been observed in the ^{13}C NMR spectrum of compound (XLV).[60] The magnetic non-equivalence of phosphorus atoms has been noted in cationic phosphine complexes of a cymantrene derivative[61]. The non-equivalence of the methyl groups has been observed in derivatives of dicyclopentadienyl compounds of zirconium and hafnium containing asymmetric metal atoms[62].

VII. CHEMICAL NON-EQUIVALENCE OF DIASTEREOTOPIC ATOMS

The observation of the chemical non-equivalence of diastereotopic atoms is an important and interesting task. Naturally, diastereotopic atoms have different chemical properties only in quantitative terms:



(XXXIXb) (XLVIa) (XLVIb)

In the carbonium ion (XXXIXb) the hydrogen atoms of the methylene group are diastereotopic. They are manifested in the ^1H NMR spectrum by an *AB* quartet [δ = 3.53 and 3.87 p.p.m.; $J(AB)$ = 16 Hz].[56] It was found that these protons undergo deuterium exchange at different rates. The more rapid exchange was observed for the H_A proton whose signal is at a higher field. Evidently the H_A proton, sterically less shielded than the H_B proton, should in fact be more reactive. The diastereoisomer (XLVIb) is formed more rapidly as a result of the exchange[56].

REFERENCES

1. K.Mislow and M.Raban, in "Topics in Stereochemistry", (Edited by N.Allinger and E.L.Eliel), Interscience, New York, 1967, Vol.1, p.1.
2. R.M.Silverstein, G.C.Bassler, and T.C.Morrill, "Spectrometric Identification of Organic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1977, p.322.
3. W.Prelog, Uspekhi Khim., 38, 952 (1969)[Russ.Chem. Rev., No.5 (1969)].
4. A.Davison and P.E.Rakita, J.Organometal.Chem., 23, 407 (1970).
5. C.A.Busby and D.Dolphin, J.Magn.Res., 23, 211 (1976).
6. V.I.Sokolov, "Novoe v Stereokhimii" (Advances in Stereochemistry), Izd.Znanie, Moscow, 1975.
7. G.B.Shul'pin, Khimiya i Zhizn', No.10, 20 (1978).
8. V.I.Sokolov, "Vvedenie v Teoreticheskuyu Stereokhimiya" (Introduction to Theoretical Stereochemistry), Izd.Nauka, Moscow, 1979.
9. G.B.Shul'pin, A.A.Koridze, A.A.Pogrebnyak, M.I.Rybinskaya, and A.N.Nesmeyanov, Synth.Inorg. Metal Org.Chem., 3, 83 (1973).
10. D.N.Kursanov, Z.N.Parnes, and N.M.Loim, "Tezisy Dokladov V Mezhdunarodnogo Kongressa po Metalloorganicheskoi Khimii" (Abstracts of Reports at the Vth International Congress on Organometallic Chemistry), Moscow, 1971, Vol.2, p.262.
11. D.N.Kursanov, Z.N.Parnes, N.M.Loim, N.E.Kolobova, I.B.Zlotina, P.V.Petrovskii, and E.I.Fedin, J.Organometal.Chem., 44, C15 (1972).
12. N.M.Loim, L.A.Malutschenko, Z.N.Parnes, and D.N.Kursanov, J.Organometal Chem., 108, 363 (1976).
13. A.N.Nesmeyanov, P.V.Petrovskii, L.A.Fedorov, V.I.Robas, and E.I.Fedin, Zhur.Strukt.Khim., 14, 49 (1973).
14. A.A.Koridze, P.V.Petrovskii, A.A.Mokhov, and A.I.Lutsenko, J.Organometal.Chem.. 136, 57 (1977).
15. A.A.Koridze, N.A.Ogorodnikova, and P.V.Petrovskii, J.Organometal.Chem., 157, 145 (1978).
16. A.A.Koridze, P.V.Petrovskii, S.P.Gubin, V.I.Sokolov, and A.A.Mokhov, J.Organometal.Chem., 136, 65 (1977).
17. S.Braun and W.E.Watts, J.Organometal.Chem., 84, C33 (1975).
18. S.Braun, T.S.Abram, and W.E.Watts, J.Organometal. Chem., 97, 429 (1975).
19. M.L.Martin, J.Tirouflet, and B.Gautheron, J.Organometal.Chem., 97, 261 (1975).
20. V.I.Sokolov, P.V.Petrovskii, A.A.Koridze, and O.A.Reutov, J.Organometal.Chem., 76, C15 (1974).
21. N.M.Loim, D.N.Kursanov, Z.N.Parnes, N.N.Sul'dina, and E.I.Fedin, J.Organometal.Chem., 52, C33 (1973).
22. N.M.Loim, P.V.Petrovskii, V.I.Robas, Z.N.Parnes, and D.N.Kursanov, J.Organometal Chem., 117, 265 (1976).
23. A.G.Ginzburg, V.N.Setkina, Sh.G.Kasumov, G.A.Panosyan, P.V.Petrovskii, and D.N.Kurzanov, Dokl.Akad.Nauk SSSR, 228, 1368 (1976).

24. A.G.Ginzburg, V.N.Setkina, P.V.Petrovskii, Sh.G.Kasumov, G.A.Panosyan, and D.N.Kursanov, J.Organometal.Chem., 121, 381 (1976).
25. G.B.Shul'pin and M.I.Rybinskaya, Uspekhi Khim., 43, 1524 (1974)[Russ.Chem.Rev., No.8 (1974)].
26. J.Tirouflet, J.Besancon, and F.Mabon, Org.Magn. Resonance, 8, 444 (1976).
27. C.S.Eschbach, D.Seyferth, and P.C.Reeves, J. Organometal.Chem., 104, 363 (1976).
28. A.G.Ginzburg, V.N.Setkina, P.V.Petrovskii, V.I.Robas, and D.N.Kurzanov, Koord.Khim., 1, 1542 (1975).
29. M.Le Plouzennec, F.Le Moigne, and R.Dabard, J. Organometal.Chem., 132, 409 (1977).
30. G.B.Shul'pin, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1975.
31. K.Yamakawa and M.Hisatome, J.Organometal.Chem., 52, 407 (1973).
32. A.T.Nielsen and W.P.Norris, J.Org.Chem., 41, 655 (1976).
33. D.E.F.Gracey, W.R.Jackson, W.B.Jennings, S.C.Rennison, and R.Spratt, J.Chem.Soc., (B), 1210 (1969),
34. S.Toma, M.Sališová, and E.Solčániová, J.Organometal.Chem., 90, 335 (1975).
35. A.N.Nesmeyanov, G.B.Shul'pin, L.A.Fedorov, P.V.Petrovskii, and M.I.Rybinskaya, J.Organometal. Chem., 69, 429 (1974).
36. A.N.Nesmeyanov, G.B.Shul'pin, L.V.Rybin, N.T.Gubenko, M.I.Rybinskaya, P.V.Petrovskii, and V.I.Robas, Zhur.Obshch.Khim., 44, 2032 (1974).
37. A.N.Nesmeyanov, G.B.Shul'pin, L.M.Korneva, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 217, 1091 (1974).
38. K.L.Rinehart, D.E.Bublitz, and D.H.Gustafson, J.Amer.Chem.Soc., 85, 970 (1963).
39. M.I.Levenberg and J.H.Richards, J.Amer.Chem.Soc., 86, 2634 (1964).
40. T.H.Barr, E.S.Bolton, H.L.Lentzner, and W.E.Watts, Tetrahedron, 25, 5245 (1969).
41. J.Feinberg and M.Rosenblum, J.Amer.Chem.Soc., 91, 4324 (1969).
42. M.Hisatome and K.Yamakawa, Tetrahedron Letters, 3533 (1971).
43. R.G.Sutherland, J.R.Sutton, and W.M.Horspool, Tetrahedron Letters, 328 (1973).
44. T.D.Turbitt and W.E.Watts, J.Organometal.Chem., 49, C30 (1973).
45. G.B.Shul'pin and A.N.Kitaigorodskii, Izv.Akad. Nauk SSSR, Ser.Khim., No.1, 168 (1980).
46. E.A.Hill and J.H.Richards, J.Amer.Chem.Soc., 83, 4216 (1961).
47. N.M.D.Brown, T.D.Turbitt, and W.E.Watts, J. Organometal.Chem., 46, C19 (1972).
48. T.D.Turbitt and W.E.Watts, J.Chem.Soc., Perkin Trans.II, 177 (1974).
49. A.N.Nesmeyanov, G.B.Shul'pin, P.V.Petrovskii, V.I.Robas, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 215, 865 (1974).
50. A.N.Nesmeyanov, G.B.Shul'pin, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 218, 1107 (1974).
51. A.N.Nesmeyanov, G.B.Shul'pin, D.V.Zagorevskii, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 229, 881 (1976).
52. M.Cais, Organometal.Chem.Rev., 1, 435 (1966).
53. V.I.Sokolov, P.V.Petrovskii, and O.A.Reutov, J. Organometal.Chem., 59, C27 (1973).
54. M.Hisatome and K.Yamakawa, Tetrahedron, 27, 2101 (1971).
55. A.N.Nesmeyanov, G.B.Shul'pin, M.I.Rybinskaya, and P.V.Petrovskii, Dokl.Akad.Nauk SSSR, 215, 599 (1974).
56. A.N.Nesmeyanov, B.A.Surkov, I.F.Leshcheva, and V.A.Sazonova, Dokl.Akad.Nauk SSSR, 222, 848 (1975).
57. A.Ratajczak, B.Czech, B.Misterkiewicz, A.Piorko, and H.Zyzik, Bull.Acad.Polon.Sci., Ser.Sci.Chim., 24, 775 (1976).
58. P.Smith, J.J.McLeskey, and D.W.Slocum, J.Org. Chem., 30, 4356 (1965).
59. W.R.Jackson and W.B.Jennings, J.Chem.Soc., B, 1221 (1969).
60. T.Yu.Orlova, P.V.Petrovskii, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., 67, C23 (1974).
61. A.G.Ginzburg, V.N.Setkina, and D.N.Kursanov, J.Organometal.Chem., 77, C27 (1974).
62. P.Renaut, G.Tainturier, and B.Gautheron, J. Organometal.Chem., 148, 43 (1978).
63. S.I.Goldberg, W.D.Bailey, and M.L.McGregor, J.Org.Chem., 36, 761 (1971).

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