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INTERNAL vs. EXTERNAL DIASTEREOTOPISM IN HOMOCHIRAL CIS vs. TRANS OLEFIN METAL π COMPLEXES *

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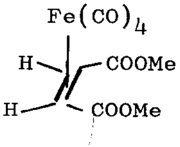
Metal-π-complexation on the homotopic faces of achiral *cis* olefins possessing pairwise homotopic groups (C_{2v}), e.g. dimethylmaleate (1), leads to a configuration (C_s) with pairwise internally enantiotopic [1] groups. As has been shown [2] for dimethylmaleate tetracarbonyliron (3), the vinyl and methyl protons become *internally* diastereotopic [1] in a chiral environment permitting $^3J_{cis}$ of the vinyl protons (AB system) to be determined by ^{1}H-NMR.

Metal-π-complexation on the enantiotopic faces of prochiral *trans* olefins possessing pairwise homotopic groups (C_{2h}), e.g. dimethylfumarate (2), leads to enantiomers (C_2) [3] with pairwise internally homotopic but externally enantiotopic groups. As has been shown [2] for dimethylfumarate tetracarbonyliron (4), the vinyl and methyl protons become *externally* diastereotopic in a chiral environment permitting enantiomeric compositions to be determined by ^{1}H-NMR.

No auxiliary chiral probe is required to observe internal and external diastereotopism if the olefin metal π complex possesses elements of inherent chirality. Thus, proton chemical shift nonequivalence has been detected [4] in π complexes of (1) and (2), respectively, in which the metal atom constitutes an asymmetric center.

We now report on an alternative case where *cis* and *trans* olefins, carrying two chiral groups of equivalent constitution and configuration, e.g. homochiral [5] di-l-menthylmaleate (5) [7] and di-l-menthylfumarate (6) [7], are coordinated to an achiral metal atom. This situation is realized for di-l-menthylmaleate tetracarbonyliron (7) and di-l-menthylfumarate tetracarbonyliron (8).



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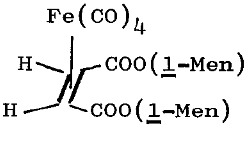

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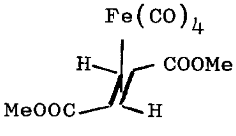

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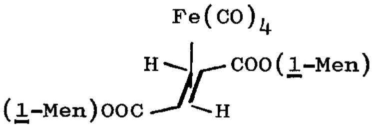

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In homochiral (5) (C_2 axis in the molecular plane) the vinyl protons and the olefinic faces are homotopic. After metal π complexation one single diastereoisomer (C_1) (7) is formed in which the vinyl protons are internally diastereotopic. In homochiral (6) (C_2 axis perpendicular to the molecular plane) the vinyl protons are homotopic but the olefinic faces are diastereotopic. After metal π complexation two diastereoisomers (C_2) (8) are formed in each of which the vinyl protons are internally homotopic but externally diastereotopic [8,9].

We provide chemical and NMR spectroscopic evidence for the stereochemical relationships discussed hitherto.

Homochiral (7) has been obtained [11] as a single diastereoisomer. The occurrence of internal diastereotopism is evident from the ^{1}H-NMR spectrum of (7) (FIG.1) exhibiting an AB quartet for the vinyl protons from which the coupling constant $^3J_{cis}$ can be calculated (see TABLE).

TABLE. $^3J_{cis}$ coupling constants of olefin tetracarbonyliron π complexes

π complex	Methylacrylate·$Fe(CO)_4$	Dimethylmaleate·$Fe(CO)_4$ (3)	Di-l-menthylmaleate·$Fe(CO)_4$ (7)
$^3J_{cis}$ (Hz)	10.2 [12]	9.4 [2]	9.67

Internally diastereotopic groups in homochiral configurations have been observed only in a few instances [10,13]. It should be noted that inherent to symmetry properties, in tetrahedral assemblies $A\,b^*b^*cc$, the geminal groups c are internally diastereotopic in heterochiral ($b^R b^S$) configurations and homotopic in homochiral ($b^R b^R$, $b^S b^S$) isomers [14].

Homochiral (8) occurs in two diastereoisomeric forms. Pure (+)-(8a) has been obtained [11] by fractional crystallization from n-hexane (22°C) and pure (-)-(8b) has been isolated from the concentrated mother liquor. Complete resolution of (8) and occurrence of external diastereotopism is evident from the ^{1}H-NMR spectra of (8a) and (8b) (FIG. 2) showing different resonance absorptions for the vinyl and part of the methyl protons, whereby the protons of (8a) are less shielded. Determination of the diastereoisomeric composition of crude (8) by ^{1}H-NMR (FIG. 1) reveals asymmetric induction, i.e. preferential metal π complexation on one diastereotopic face of (6), slightly favouring formation of (8a) under the reaction conditions employed [11].

The results establish that homochiral (or heterochiral) configurations and cis/trans isomerism in olefin metal π complexes [15] may be distinguished by NMR chemical shift nonequivalence criteria. Homo- or heterochiral derivatization may be used to create internal diastereotopism and thereby to obtain NMR coupling constants for vicinal nuclei.

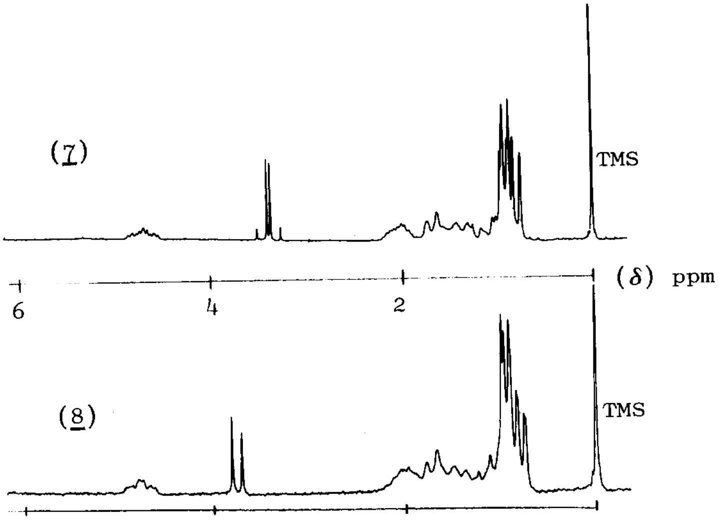

FIG. 1: 90 MHz ^{1}H-NMR spectra (CDCl$_3$, 25°C) of (7) (internal diastereotopism) ν_H: 3.45 and 3.36 ppm, $^3J_{cis}$: 9.67 Hz; ν_{CH_3}: 0.75, 0.83, 0.87, 0.89, 0.94, 0.97 ppm and of (8) (external diastereotopism) mixture of diastereoisomers, resonances cf. Fig. 2.

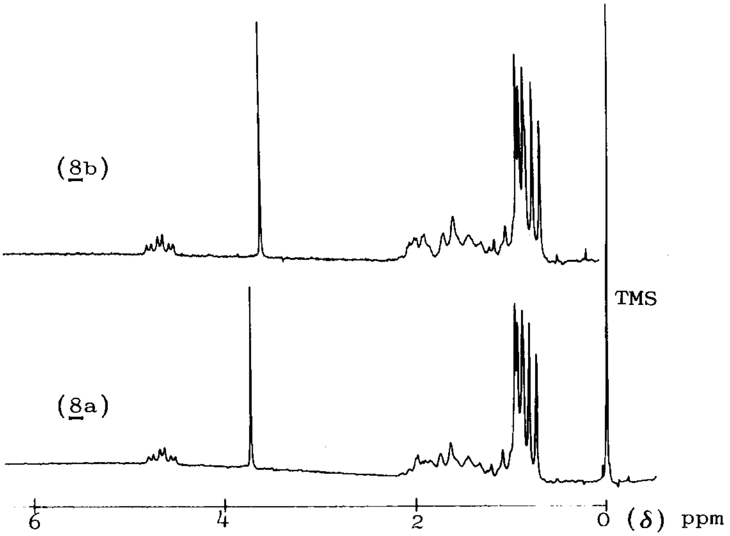

FIG. 2: 90 MHz ^{1}H-NMR spectra (CDCl$_3$, 25°C) of resolved diastereoisomers (8a): ν_H: 3.78 ppm; ν_{CH_3}: 0.74, 0.82, 0.89, 0.94^5, 0.97 ppm and (8b): ν_H: 3.67 ppm; ν_{CH_3}: 0.72, 0.80, 0.89, 0.93^5, 0.97 ppm.

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5 We adopt the terminology[6] 'homochiral' (RR or SS) for racemic (dl) stereoisomers and 'heterochiral' (RS, SR) for meso stereoisomers

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8 In heterochiral assemblies the relation between internal and external diastereotopism to cis/trans isomerism is reversed:
In heterochiral (5) (σ plane perpendicular to the molecular plane (C_s)) the vinyl protons are enantiotopic but the olefinic faces are diastereotopic. After metal π complexation two achiral diastereoisomers (C_s) are formed (containing a pseudoasymmetric plane[10]) in each of which the vinyl protons are internally enantiotopic but externally diastereotopic.
In heterochiral (6) (molecular center of symmetry (C_i)) the vinyl protons and the olefinic faces are enantiotopic. After metal π complexation enantiomers (C_1) are formed in each of which the vinyl protons are internally diastereotopic[9].

9 The stereochemical analysis presupposes rapid internal rotations on the NMR time scale

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11 Acc. to the general proc. of ref. 12. Calcd % C: 60.00 H: 7.19 Fe: 9.96
(7) : Found % C: 60.06 H: 7.22 Fe: 9.98; m.p.: 108°C (yellow needles)
$[\alpha]^{20}$ (c 0.25, $CHCl_3$): -118°(D) -124°(578) -143°(546) -274°(436).
(8a): Found % C: 60.03 H: 7.11 Fe: 9.90; m.p.: 152°C (dec)(yellow cryst.)
$[\alpha]^{20}$ (c 0.25, $CHCl_3$): +306°(D) +324°(578) +380°(546) +650°(436).
(8b): Found % C: 60.00 H: 7.15 Fe: 9.80; m.p.: 162°C (dec)(yellow needles)
$[\alpha]^{20}$ (c 0.25, $CHCl_3$): -350°(D) -367°(578) -426°(546) -710°(436).

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15 This statement should be valid also for epoxides, aziridines and related carbo- or heterocyclic compounds