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Preliminary communication

DIASTEREOSPECIFICITY IN THE FORMATION OF CHELATED ORGANOMETALLIC COMPLEXES

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Summary

Three types of intramolecular cyclization reactions in organoiron complexes having one or more chiral centers are shown to proceed with high diastereospecificity.

Diastereospecificity [1] in chelate ring formation is a phenomenon commonly encountered in coordination complexes derived from chiral ligands [2] Its occurrence in similar reactions of organometallic complexes is less well recognized We wish to report several examples of this important phenomenon in closely related organoiron complexes in which the factors responsible for asymmetric induction may be identified

We recently reported the first example of such diastereospecificity in the conversion of the η^2-allyl alchohol complex Ia to the lactone IIa [3]. A closely related ring closure occurs when complex Ib is treated with two equivalents of tri-n-butylamine. In each of these transformations a new chiral center, in addition to the one at the olefin, is created at the metal atom by chelation. In each of these reactions only a single diastereomer is formed as indicated by PMR spectral evidence* [3].

The stereochemical factors which control these reactions are readily perceived Models** show that closure of Z to one of the two diastereotopic carbonyl groups constrains the olefin ligand to a plane either roughly parallel

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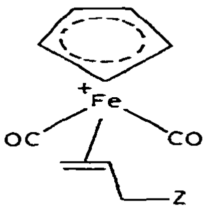
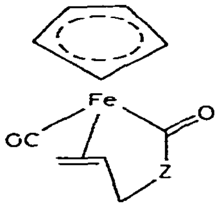
*The PMR spectrum of IIb closely resembles that of IIa All proton resonances corresponding to a single diastereomer are readily assignable Complexes IIa and IIb are obtained in 70 and 80% yields respectively

**For Dreiding models based on molecular parameters for a $CpFe(CO)_2R$ complex see ref 4 and for a $CpFe(CO)_2(ol)^+$ complex ref. 5.

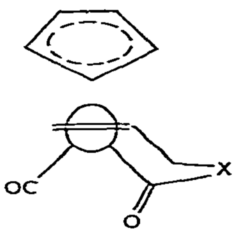


(Ia, Z = OH,
Ib, Z = NH_3^+)

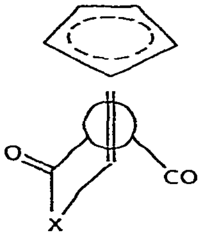


(IIa, Z = O,
IIb, Z = NH)

with or perpendicular to that of the cyclopentadienyl ring and hence to a structure with minimal or maximal interaction between these groups (IIIa or IIIb).

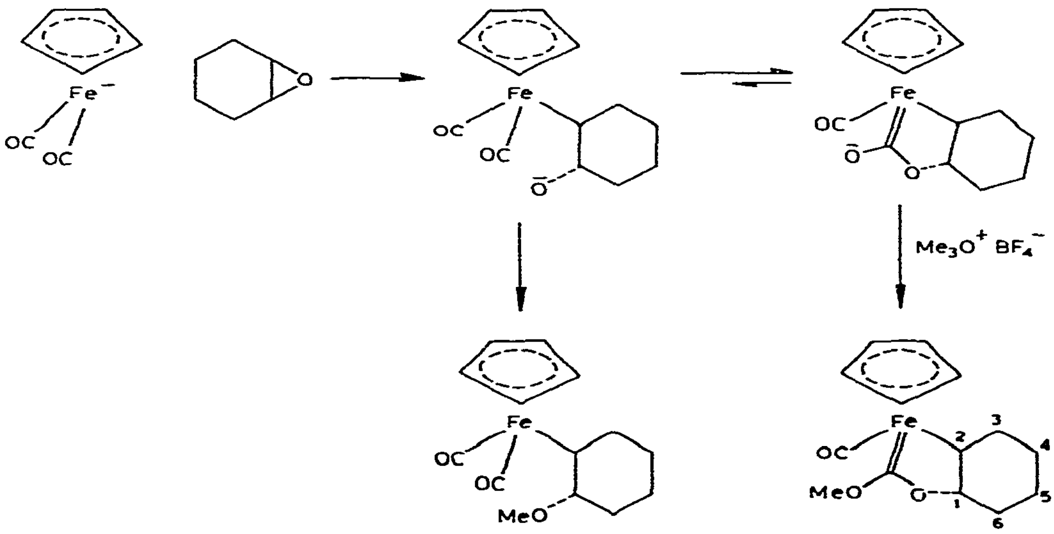


(IIIa)



(IIIb)

Closely related to these transformations is the intramolecular process leading to the carbene complex IV (Scheme 1) [6].



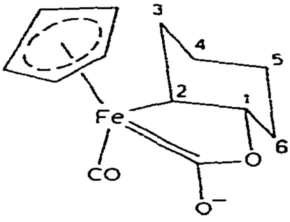
SCHEME 1

(V)

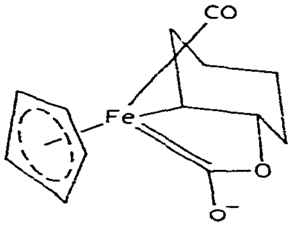
(IV)

Epoxide opening by the complex anion creates chirality on the ligand, and cyclization of the resulting alkoxide introduces a second chiral center at the metal. A PMR spectrum of the methylated complex (IV) provides little information about the number of diastereomers formed*. However, a ^{13}C NMR spectrum of this product shows it to be a single diastereomer; (CD_3NO_2) δ (ppm) 26.14, 29 32, 33 88, 39.73 (C(3,4,5,6)), 39.47 (C(2)), 57.09 (CH_3), 84.79 (Cp), 97.47 (C(1)), 224.99 (CO), 265.70 (carbene C).

Those steric factors controlling the cyclization step in the sequence leading to IV may readily be identified. Models show appreciable steric interactions between the axial proton at C(3) on the cyclohexane ring and cyclopentadienyl protons in structure VIa. Such interactions are absent in VIb**.

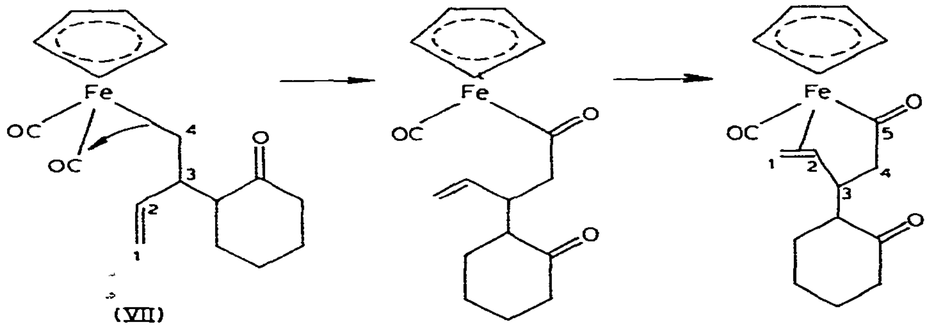


(VIa)



(VIb)

The transformation of VII to the chelate IX provides perhaps the most striking example of a diastereospecific reaction (Scheme 2).



SCHEME 2

(VIII)

(IX)

Complex VII is obtained by condensation of cyclohexanone pyrrolidine enamine with the (η^5-C_5H_5)Fe(CO)$_2$ (η^2-butadiene) cation, followed by hydrolysis [7]. A PMR spectrum of VII shows two cyclopentadienyl proton

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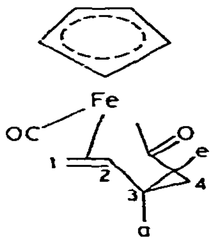
*Complexes IV and V are each obtained in 40% yield from cyclohexene epoxide

**The interchange of Cp and CO ligands in VIa and VIb does not exchange their bond vectors since the configuration about the iron atom is not tetrahedral Provided the configuration about the iron atom is not too different from that found in CpFe(CO)$_2$R [4], the exchange of ligands sends the CO vector into one at 180° to it and the Cp vector into a new one roughly perpendicular to it.

resonances ($\delta(CS_2)$ 4.76, 4.78 ppm), indicative of the presence of the two anticipated diastereomers, in approximately equal proportion. On brief warming of this product in acetonitrile it is smoothly converted to the chelate IX. A PMR spectrum of this product is uninformative as to the number of diastereomeric forms present. However, examination of the ^{13}C NMR spectrum revealed the presence of three signals at δ 88 26, 88 10 and 87.29 ppm (intensity ratio 52/35/13)*, which were readily identified as cyclopentadienyl ring carbons by a single frequency proton decoupling experiment**. Thus, although two additional centers of chirality are created in the conversion of VII to IX, only three of a possible eight diastereomeric pairs are formed, and one of these is a relatively minor component.

The steric factors controlling asymmetric induction at the iron atom in the chelation step VIII → IX may be identified with the configuration at C(3) in IX. Models show that for the chelate in which the olefin center has the preferred configuration (see IIIa), the ring may adopt a chairlike conformation in which the cyclohexanone substituent at C(3) is fixed as either equatorial or axial (X). The latter configuration would clearly be disfavored on steric grounds since appreciable nonbonded interactions exist between a large axial group at C(3) and *cis*-protons of C(1) and C(4). Coordination of the prochiral iron atom in the conversion of VIII to IX simultaneously establishes the configuration at iron and the stereochemistry at the C(3) center Thus, provided this step is essentially irreversible under the reaction conditions, asymmetry at the iron atom is induced in a kinetically controlled chelation process, in which the configuration at C(3) determines the configuration at iron. It seems unlikely that such asymmetry is induced in the conversion of VII to VIII since there is no apparent mechanism by which the distant chiral center at C(3) may control such a process. It follows, then that the activation energy for the chelation step must be greater than that for interconversion of nonplanar, enantiomeric iron centers in intermediate VIII. These conclusions do not, of course, provide any information regarding the preferred geometry at the coordinatively unsaturated iron atom, that is, whether the equilibrium configuration at iron in VIII is planar or nonplanar [8].



(X)

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*The high field portion of the spectrum exhibits fifteen of the eighteen signals anticipated for CH and CH_2 centers in the two principal diastereomers.

**Irradiation of the cyclopentadienyl proton signal at δ 4 66 ppm led to the collapse of ^{13}C doublet signals for these resonances to three singlets.

These examples serve to illustrate the diverse forms which steric interactions may take in controlling the stereochemical course of chelation reactions at prochiral centers in organometallic complexes. Diastereospecificity in these reactions should prove to be an important and general phenomenon.

Acknowledgement

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