

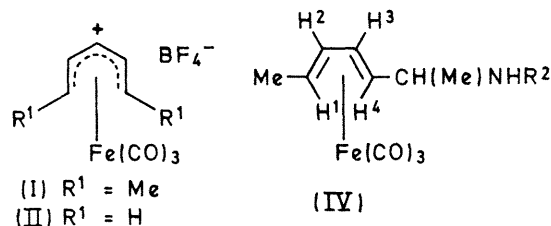
Stereochemistry of Additions of Amines to the *syn,syn*- π -1,5-Dimethylpentadienyliron Tricarbonyl Cation

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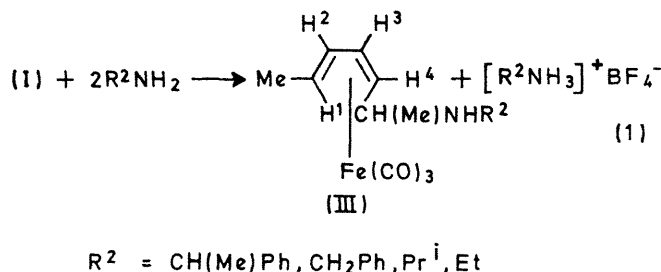
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Summary The reaction of amines with the title cation gives π -dienylamine- $\text{Fe}(\text{CO})_3$ complexes: n.m.r., c.d., and X-ray studies on the reaction products indicate a *trans,trans*- or *cis,trans*-co-ordination of the diene according to the basic strength of the amine.

THE stereochemistry of the reaction of the 1,5-dimethylpentadienyliron tricarbonyl cation (I) with a nucleophile such as water has been firmly established by Pettit and Mahler.¹ The reaction proceeds with geometrical inversion affording 2-hydroxy-*trans,trans*-hepta-3,5-dienyliron tricarbonyl. Moreover, the nucleophilic attack is stereospecific, the *ψ-exo*-alcohol² being quantitatively formed. The reaction of (I) and (II) with nucleophiles does not seem to be necessarily accompanied by geometrical inversion. The heterogeneous reaction of (II) with sodium borohydride gives a mixture of 80% *cis*-penta-1,3-dienyl- and 20% *trans*-penta-1,3-dienyl-iron tricarbonyl complexes.¹



Here we present preliminary results on the reaction of (I) with amines. All the reactions have been carried out in a homogeneous phase by adding methylene chloride solutions of (I) to the amine dissolved in the same solvent. The oily residue obtained upon filtration and successive evaporation of the solvent was shown by t.l.c. to be mainly one compound except in the case of *S*- α -methylbenzylamine where the two expected diastereoisomers (*vide infra*) could be isolated by column chromatography. From n.m.r., c.d., and X-ray studies on the isolated products, it appears that reaction (1) takes place.



The stereochemistry of the products in reaction (1) may be inferred by correlating the n.m.r. data with those reported

for other diene-iron tricarbonyl complexes.³ In almost all the compounds (III) the *anti*-1-H and the *syn*-4-H protons† have similar values for chemical shifts, τ ca. 7.5, while in the *trans,trans*-diene- $\text{Fe}(\text{CO})_3$ complexes their chemical shifts are in the region τ 8.9–9.4. Thus, if compounds (III) are thermodynamically less stable than the related compounds (IV) with the bulky $-\text{CH}(\text{Me})\text{NHR}^2$ group in a *syn*-position, it appears that the reaction of strong nucleophiles with (I) affords kinetically-controlled products through an *exo*-attack of the base on the co-ordinated pentadienyl group. However, thermodynamically-controlled products of type

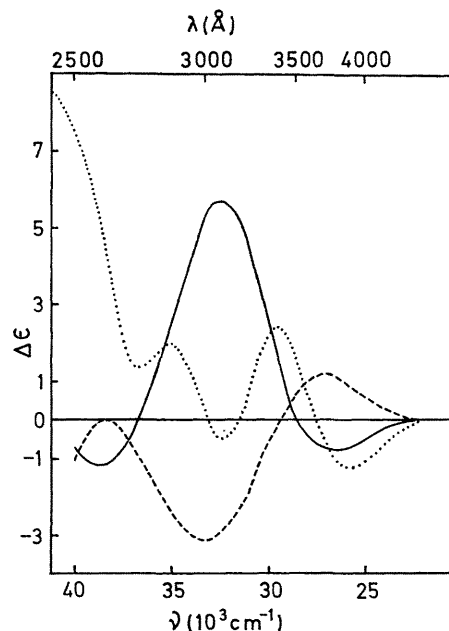


FIGURE 1. C.d. spectra of (+)-1-carboxy-*trans,trans*-hexa-2,4-dienyliron tricarbonyl (.....) and (+)- and (–)-2-(*S*- α -methylbenzylamino)-*cis,trans*-hepta-3,5-dienyliron tricarbonyl, (—) and (---), respectively, in methanol.

(IV) can be obtained if weakly basic amines such as aniline, *p*-bromoaniline, and *p*-nitroaniline are used as the nucleophiles. The 1-H and 4-H chemical shifts of the last compounds occur at τ 8.5–9.2, consistent with a *trans,trans*-diene co-ordination. The reaction mechanism which leads to (IV) might be analogous to that suggested by Pettit for the stereospecific reaction of (I) with water.

When *S*- α -methylbenzylamine is used as the amine two diastereoisomeric compounds of type (III) were isolated from the reaction mixture since in this case the nucleophilic attack may occur on both the terminal carbon atoms of (I) which have opposite configurations. The c.d. spectra of the two diastereoisomers (Figure 1) substantially differ from

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† *Syn*- and *anti*-positions are referred to the inner protons 2-H and 3-H.

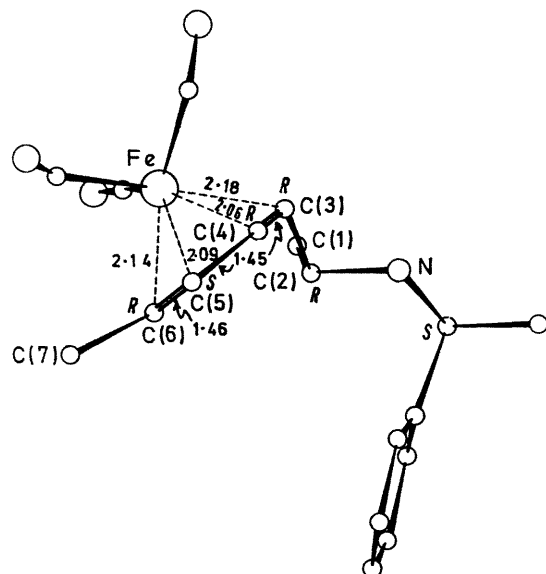


FIGURE 2. Molecular model of the (-)-2-(S- α -methylbenzylammonium)-cis,trans-hepta-3,5-dienyliron tricarbonyl ion.

(Received, October 2nd, 1970; Com. 1698.)

§ P. Pino, R. Lazzaroni, and P. Salvadori (Proceedings of 3rd *Inorg. Chim. Acta Symposium*, Venice, 1970) have shown that the sign of the $d \rightarrow d$ transitions of olefin-platinum complexes reflects the configuration of the carbon atoms bound to the metal, the contribution of an eventual asymmetric carbon atom α to the co-ordinated double bond being negligible. We believe that the same argument may be used for the diene-iron complexes.

¹ J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955.

² N. A. Clinton and G. P. Lillya, *J. Amer. Chem. Soc.*, 1970, **92**, 3058.

³ G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, 1964, **29**, 3620.

⁴ A. Musco, G. Paiaro, and R. Palumbo, *Chimica e Industria*, 1968, **50**, 669.

⁵ P. Corradini, S. F. Mason, G. Paiaro, A. Panunzi, and G. H. Searle, *J. Amer. Chem. Soc.*, 1966, **88**, 2863; A. D. Wrixon, E. Premuzic, and A. I. Scott, *Chem. Comm.*, 1968, 639.

that of (+)-1-carboxy-*trans,trans*-hexa-2,4-dienyliron tricarbonyl⁴ in the long wavelength region (320–450 nm) which should reflect the absolute configuration of the co-ordinated ligand.⁵ The terminal carbon atoms of the diene group co-ordinated to the metal have opposite configuration in the acid complex, while they have the same configuration in the amine one. The *exo*-attack of S- α -methylbenzylamine, which leads to the same configuration for the two independent chiral centres C-2, C-3 (Figure 2), has been unambiguously proved by an X-ray structure determination of the (-)-diastereoisomer hydrochloride. The molecular and crystal structures were determined by single-crystal X-ray methods. The orthorhombic, $P2_12_12_1$ unit cell of dimensions $a = 22.69(5)$, $b = 11.43(3)$, $c = 7.35\text{\AA}(2)$ contains four molecular units of formula $(C_{18}H_{22}NO_3Fe)^+Cl^-$. The intensity data were collected by the Weissenberg photographic method using Fe- K_α ($\lambda = 1.937\text{\AA}$) radiation. The structure was solved by the Patterson method and refined by full-matrix least-squares method over 768 independent reflections. Isotropic temperature factors were used for all but the chlorine and iron atoms. The R factor at the present stage is 0.137.