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FORMATION OF NITROXIDE RADICALS IN THE α-FERROCENYLCARBONIUM ION—NITROSOBENZENE SYSTEM

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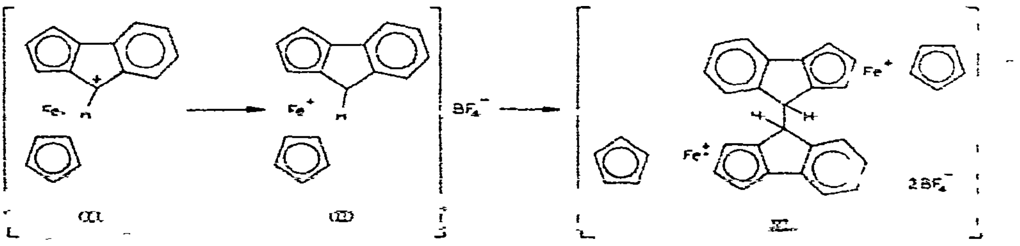
Summary

The nitroxide radicals produced by treatment of α-ferrocenylcarbonium ions with nitrosobenzene have been studied and characterized by ESR spectroscopy and by chemical transformation to ferrocenyl-containing substituted anilines Possible mechanisms for the formation of these nitroxides are discussed, and their relevance to structural problems of the α-ferrocenylcarbonium ions considered.

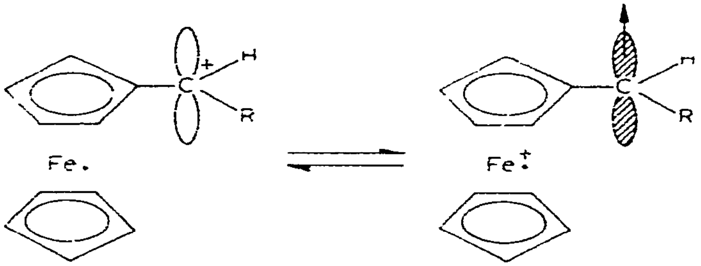
Introduction

In synthesizing transition-metal complexes of otherwise relatively labile compounds, we successfully utilized the unusual stability of α-ferrocenylcarbonium ions for the synthesis of iron complexes of sesquifulvalene (pentaheptafulvalene) and diphenylcalicene (diphenyltriapentafulvalene) [1] However, a similar approach [2] aimed at preparing an iron π-complex of the unknown benzopentalene failed because the hoped-for [3] diamagnetic α-ferrocenylcarbonium ion I, behaved as a diradical cation, II, and underwent spontaneous dimerization to form a paramagnetic diferricenium derivative III

The possibility that α-ferrocenylcarbonium ions IV may generate the diradical



cation structure V by internal electron transfer had already been suggested by Rinehart and co-workers [4] to explain the formation of 1,2-diferrocenylethane upon treatment of ferrocenylmethylcarbinol with sulfuric acid.



(IV) (V)

Similar diradical cation species were postulated in the mechanism of the reaction of 2-ferrocenylpropene with sulfuric acid to yield diferrocenylalkanes [5]. The unusual elimination of the elements of HOCl upon treating either ferrocenyl(trichloromethyl)methanol or ferrocenyl(dichloromethyl)methanol with conc. sulfuric acid was believed [6] to occur via a radical mechanism involving the diradical cation V. In view of other reactions [3] in which α-ferrocenylcarbonium ions behave as closed-shell, diamagnetic species, the question arose whether this apparent dualism in chemical behaviour might have a bearing on the unusual stability of the α-ferrocenylcarbonium ions.

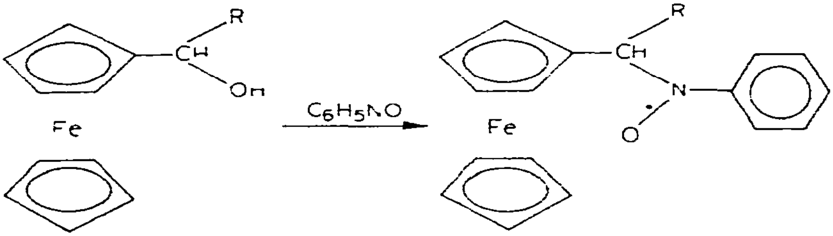
At the height of the debate on structural features of these carbonium ions we proposed [3] that the exocyclic carbinyl atom might be bent towards the iron atom through a distortion of the substituted cyclopentadienyl ring. An extended Hückel calculation of ferrocenylmethyl cation by Gleiter and Seeger [7] generated a structure with about equal overlap population between all Fe—C bonds in which the methylene group was bent towards the iron ($\alpha = 40°$) and the two rings were tilted. This structure was thought to be due to the interaction of the filled non-bonding $3d_{z^2}$ orbital of iron with the empty π^* orbital of the fulvene moiety leading to a weakening of the exocyclic bond and thus facilitating the bending of the carbinyl atom towards the iron. Interestingly, these calculations also indicated that the bent structure should have a singlet ground state, whereas retention of full planarity in the fulvene moiety should have a triplet ground state. The latter form was suggested [7] as possibly responsible for the observed spontaneous dimerization II → III mentioned above [2].

A subsequent [8] X-ray analysis of diferrocenylcarbonium fluoroborate confirmed that indeed the bond C_5H_4—C is bent towards the Fe atom relative to the plane of the cyclopentadienyl ring by a dihedral angle of ~20°. More recently an X-ray analysis [9] of the carbonium ion of the diphenylcalicene π-iron complex [1] showed a bending angle for the same bond of ~15° and the neutral diphenylfulvenechromium tricarbonyl complex [10] was found [11] by X-rays to exhibit a bending angle of 31°.

On the assumption that the proposed diradical cation V may have a finite even though brief, half-life, and since the X-ray data could not throw any light on this aspect, we became interested in the possibility of trapping such a radical by chemical means In two brief communications [12,13] we reported preliminary results on the reaction between organometallic cations and nitroso compounds A more detailed description of this work and additional data are presented in this paper

Results and discussion

Previously we reported [12,13] that dichloromethane solutions of ferrocenylphenylcarbonium fluoroborate (or other similar cations) and nitrosobenzene exhibited an ESR spectrum which was ascribed to the nitroxide radical VII such as might have been expected to form in a spin-trapping experiment * However, only a limited analysis of the spectra was possible because of rather poor resolution of the hyperfine structure anticipated for such a nitroxide We have since found that much better resolved ESR spectra can be obtained by mixing a well degassed dichloromethane solution of the carbonium ion precursor ferrocenylcarbinol VI, rather than the ferrocenylcarbonium fluoroborate itself, with nitrosobenzene



(VI) (VII)

Usually a sufficient concentration of nitroxide radicals was present within 20—30 min to allow recording of well-resolved spectra at temperatures around —20°C The ESR spectrum obtained with diferrocenylcarbinol (VI, R = C_5H_5-FeC_5H_4) as the carbonium ion precursor is shown in Fig 1 A computer-simulated ESR spectrum gave a good fit with the hyperfine splitting constants shown in Table 1. The same experiment carried out with diferrocenyldeuterocarbinol and computer-simulation of the ESR spectrum (Fig 2) provided the value for the hyperfine splitting constant ($a(H^\beta)$ = 2 95 G) due to H^β, the carbinyl hydrogen substituent The same value for H^β was obtained for the nitroxide radical generated from (ferrocenyl)(*p*-tolyl)carbinol, (VI, R = p-C_6H_4) To obtain some information on the effect of the gegenion, nitrosobenzene was treated with ferrocenylphenylcarbinol (VI, R = C_6H_5) and, separately, with the acetate derivative of VI (R = C_6H_5). Identical ESR spectra were obtained from both experiments, the only difference being in the much quicker appearance of the nitroxide signal (vide supra) with the acetate derivative. The acetate function being a much better leaving group than a hydroxyl, it is reasonable to expect quicker formation of the nitroxide radical, if the carbonium ion species is involved

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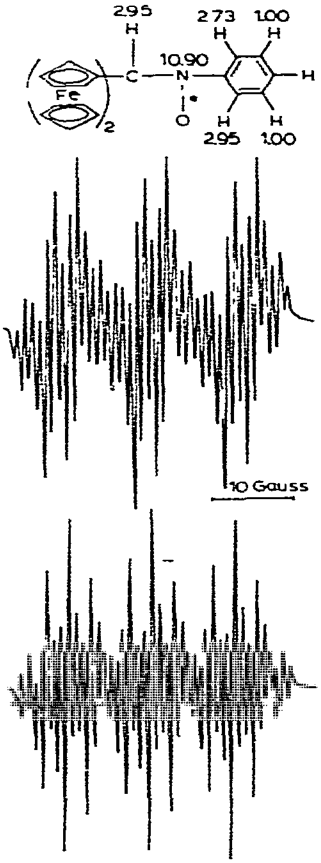
* For a review of the spin-trapping technique see ref 14



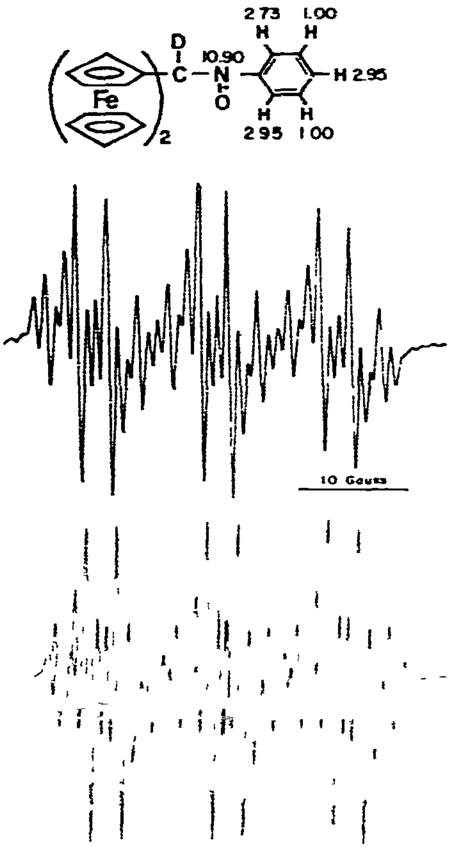


Fig. 1 ESR spectrum of (top) nitroxide radical obtained from reaction of diferrocenylcarbinol and nitrosobenzene and (bottom) the computer simulation obtained with hyperfine splitting constants (Gauss) shown in formula.

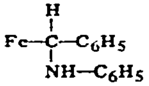
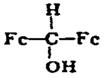
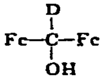
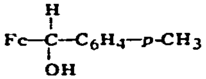
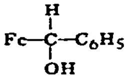
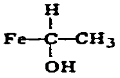
Fig 2 ESR spectrum of (top) nitroxide radical obtained from reaction of diferrocenyldeuterocarbinol and nitrosobenzene and (bottom) the computer simulation obtained with hyperfine splitting constants (Gauss) shown in formula.

The magnitude of the hyperfine splitting due to the carbinyl proton was also determined directly. Nitrosodeuterobenzene was reacted with ferrocenylphenylcarbinol (VI, R = C_6H_5) and with ferrocenylmethylcarbinol (VI, R = CH_3). A simplified six-line ESR spectrum (Fig. 3) was obtained with both compounds and the values for a(N) and $a(H^{\beta})$ as measured form the experimental spectra are given in Table 1.

The above results provided strong support for the assigned structure VII to the nitroxides responsible for the observed ESR signals. However, in order to dispel any suspicion that the observed nitroxide ESR signals might originate from some non-organometallic artifact of the system, two additional sets of experiments were carried out.

TABLE 1

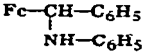
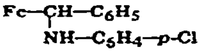
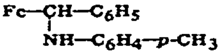
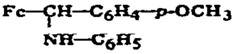
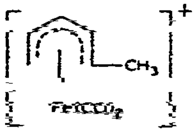
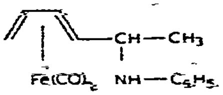
HYPERFINE SPLITTING CONSTANTS OF THE NITROXIDES FORMED IN REACTION BETWEEN FERROCENYL COMPOUNDS AND NITROSOBENZENE (Fc=$C_5H_5FeC_5H_4$)

Compounds Ferrocenyl precursor	Hyperfine splitting (Gauss)					g factor
	a(N)	a(Ho p)	a(Ho)	a(Hm)	a(H$^{\beta}$)	
 $Fc{-}\overset{H}{\underset{NH{-}C_6H_5}{C}}{-}C_6H_5$ [a]	11 60	2 80	2 73	1 00	2 95	2 0067
 $Fc{-}\overset{H}{\underset{OH}{C}}{-}Fc$	10 90	2 95	2 73	1 00	2 95	2 0067
 $Fc{-}\overset{D}{\underset{OH}{C}}{-}Fc$	10 90	2 95	2 73	1 00		2 0067
 $Fc{-}\overset{H}{\underset{OH}{C}}{-}C_6H_4{-}p{-}CH_3$	11 60	2 80	2 73	1 00	2 95	2 0067
 $Fc{-}\overset{H}{\underset{OH}{C}}{-}C_6H_5$ [b]	11 0				3 5	
 $Fe{-}\overset{H}{\underset{OH}{C}}{-}CH_3$ [b]	11 0				2 0	

[a] Nitroxide formed by in situ oxidation of the amine [b] Nitroso deuterobenzene used as reactant

TABLE 2

SECONDARY AMINES PREPARED BY $LiAlH_4$ REDUCTION OF PRODUCT FORMED IN THE ORGANOMETALLIC CATION—NITROSOBENZENE REACTION (Fc=$C_5H_5FeC_5H_4$)

Carbonium ion	Nitroso compound	Amino derivative
$[Fc{-}CH{-}C_6H_5]^+$	C_6H_5NO	 $Fc{-}\underset{NH{-}C_6H_5}{CH}{-}C_6H_5$
$[Fc{-}CH{-}C_6H_5]^+$	$p{-}ClC_6H_4NO$	 $Fc{-}\underset{NH{-}C_5H_4{-}p{-}Cl}{CH}{-}C_6H_5$
$[Fc{-}CH{-}C_6H_5]^+$	$p{-}CH_3C_6H_4NO$	 $Fc{-}\underset{NH{-}C_6H_4{-}p{-}CH_3}{CH}{-}C_6H_5$
$[Fc{-}CH_2]^+$	C_6H_5NO	$Fc{-}CH_2NH{-}C_6H_5$
$[Fc{-}CH{-}C_6H_4{-}p{-}OCH_3]^+$	C_6H_5NO	 $Fc{-}\underset{NH{-}C_6H_5}{CH}{-}C_6H_4{-}p{-}OCH_3$
	C_6H_5NO	
$[Fc_2CH]^+$	C_6H_5NO	$Fc_2{-}CH{-}NH{-}C_6H_5$

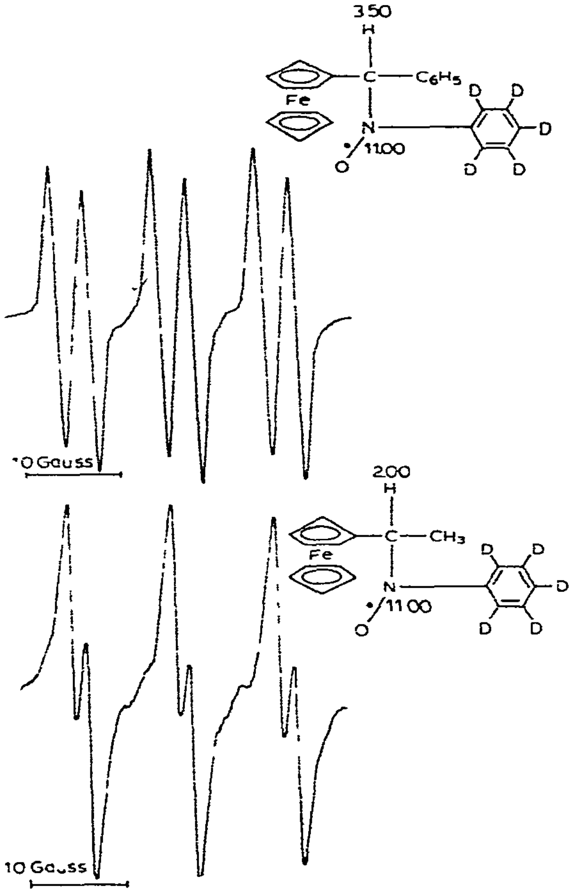


Fig 3 ESR spectrum of nitroxide radicals obtained in the reaction of nitrosodeuterobenzene with ferrocenylphenylcarbinol (top) and ferrocenylmethylcarbinol (bottom) Hyperfine splitting constants (Gauss) shown in formulae

Several α-ferrocenylcarbonium ions were treated with a variety of nitroso derivatives on a preparative scale followed by reduction of the reaction mixture with $LiAlH_4$ The ferrocenyl-containing substituted anilines, VIII expected from the reduction of the nitroxides VII were isolated and identified by comparison with authentic samples synthesized by independent routes. The data are summarized in Table 2.

In addition, availability of the amines VIII, enabled us to carry out in situ oxidations with *m*-chloroperbenzoic acid, a reagent known to oxidize amines to nitroxides [15].

The ESR spectrum of the generated nitroxide VII is shown in Fig. 4. The hyperfine splitting constants calculated from the simulated spectrum are given in Table 1.

The results leave no doubt that a ferrocenyl-containing nitroxide is formed.

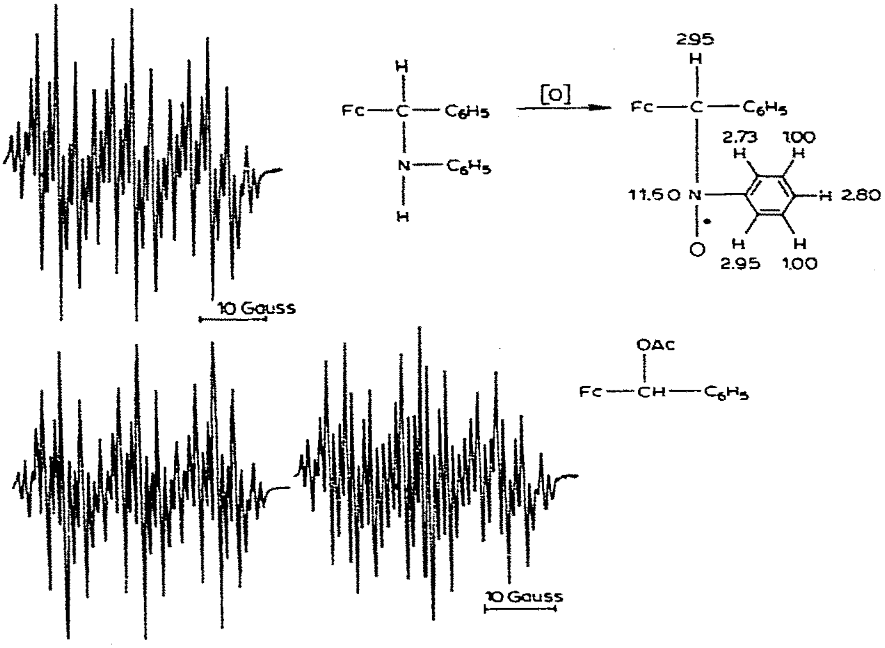
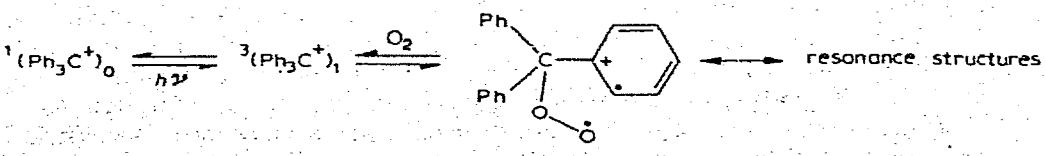


Fig. 4. ESR spectrum of nitroxide radical obtained from oxidation in situ of *N*-(ferrocenylphenylmethyl)-aniline (top) and the computer simulation (bottom left) obtained with hyperfine splitting constants (Gauss) shown in formula. The ESR spectrum of the radical produced in the reaction of ferrocenylphenylcarbinol acetate with nitrosobenzene is shown for comparison (bottom right).

from the interaction of a ferrocenylcarbonium ion and a nitroso compound. It also seems certain that the nitroxide has the structure indicated in VII. What cannot be indicated with certainty is the mechanism of formation of VII and in Fig. 5 we present a choice of three different mechanistic pathways. We favour the hypothesis involving spin-trapping of the diradical cation V by nitrosobenzene to form a charged nitroxide species which is then reduced to the neutral nitroxide radical VII. The examples presented in the introductory paragraphs [3—6] provide support for this preference. Mention must also be made of a recent proposal by Barton and co-workers [16] in which the triplet cation was



envisaged to react with triplet oxygen to form the diradical cation, which then reacts by 1,4-addition with a conjugated diene to form a peroxide (e.g. ergosterol acetate peroxide).

In our case, formation of the diradical cation V does not require light excitation and could be chemically induced (e.g. approach of reagent). We have suggested [12,13] the term "electron tautomerism" for the pictorial formalism of

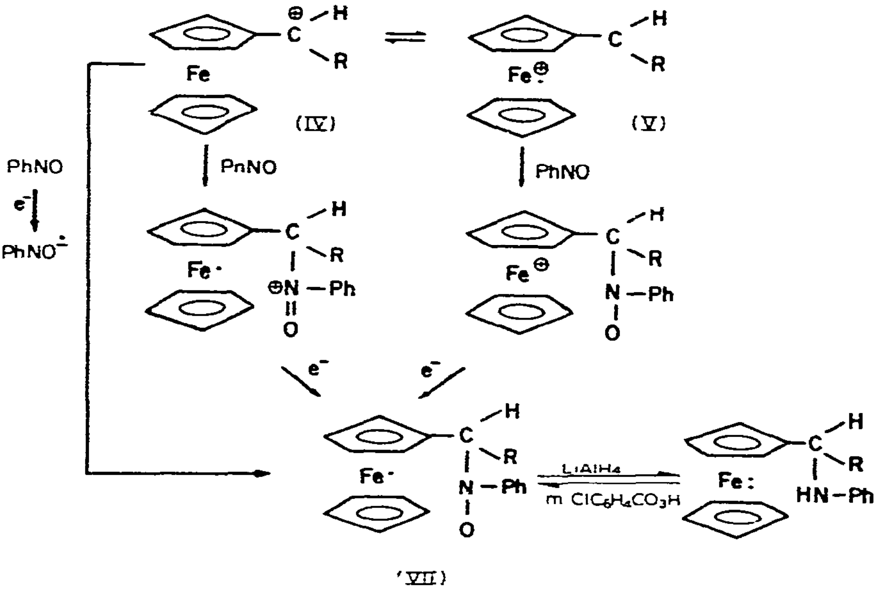


Fig 5 Mechanistic pathways for formation of nitroxide radicals in the reaction of ferrocenylcarbonium ions with nitrosobenzene

this type of intramolecular electron transfer However, at present, it is reasonable to include the possibility of initial nucleophilic attack by the nitroso compound on the closed-shell structure IV, yielding the immonium intermediate, which is subsequently reduced to the nitroxide VII Similarly, in view of the ability of nitroso derivatives to act as electron acceptors we must consider the likelihood of direct attack by nitroso-anion radicals on the ferrocenylcarbonium ion, whether IV or V, to form the observed nitroxide radical VII

Experimental

ESR spectra were recorded on a Varian E-4 spectrometer, using a three-pronged Pyrex semi-capillary vessel which allowed for degassing (ten cycles) and sealing under vacuum prior to mixing the reactants NMR spectra were measured using a Varian T-60 spectrometer. IR spectra were obtained with a Perkin—Elmer Model 237 grating spectrometer and mass spectra were recorded with an Atlas CH-4 spectrometer. All solvents and reagents used were of analytical grade. Nitrosobenzene and perdeuteronitrosobenzene were resublimed prior to use The ferrocenylcarbinols were prepared by published procedures [3]

General procedure for $LiAlH_4$ reduction of nitroxide radicals formed in the α-ferrocenylcarbonium ion—nitrosobenzene system

A solution of the carbonium ion fluoroborate salt (1—2 mmol) and an excess of nitrosobenzene in methylene chloride was stirred, under nitrogen, for 2 h at room temperature The solvent was then removed under vacuum and replaced by anhydrous diethyl ether $LiAlH_4$ was added and the reaction mixture stirred at room temperature for 12 h Solid ammonium chloride, followed by wet diethyl ether and then water were added to destroy residual $LiAlH_4$ The reaction mixture was extracted with diethyl ether (3 × 25 ml) and the organic layer was washed with water (3 × 25 ml), dried ($MgSO_4$) and evaporated to dryness The residue was chromatographed first on a dry basic alumina column and then on preparative TLC. The secondary amines isolated in this reaction are listed in Table 2 In all the above reactions, the respective azobenzenes and azoxybenzenes, resulting from reaction of $LiAlH_4$ with nitrosobenzenes, were also isolated

Preparation of $C_5H_5FeC_5H_4C(C_6H_5)=NC_6H_5$

A solution of $TiCl_4$ (3 5 g) in benzene (10 ml) was added to a cold solution of benzoylferrocene (0 493 g, 1 7 mmol) and aniline (10 ml) in benzene (20 ml) After stirring for 4 h at room temperature, water (50 ml) was added and the mixture extracted with benzene (3 × 30 ml) The organic layer was washed with water (3 × 25 ml), dried ($MgSO_4$) and evaporated to dryness Chromatography on basic alumina yielded orange crystals, which after recrystallization from methylene chloride/hexane had m p 145—146°C Yield 55% Analysis Found C, 75 20, H, 5 98, N, 3 67, Fe, 15 21, mol wt 365 (mass spectrum) $C_{23}H_{19}NFe$ calcd . C, 75 63, H, 5 24, N, 3 83, Fe, 15 29%, mol wt 364 6 NMR spectrum ($CDCl_3$) δ (ppm) 4 1 (s, 5H), 4 4 (t, 2H), 4 7 (t, 2H) 6.7—7 4 (m, 5H)

Preparation of $C_5H_5FeC_5H_4CH(C_6H_5)NHC_6H_5$

$NaBH_4$ was added to a metanolic solution of the imine prepared above and the mixture was stirred at room temperature for 4 h, then diluted with water to destroy excess $NaBH_4$ The solution was concentrated in vacuum to remove most of the methanol The remaining aqueous solution was extracted three times with methylene chloride The organic extract was washed with water, dried ($MgSO_4$) and evaporated to dryness Chromatography over basic alumina gave upon elution with petroleum ether brownish crystals, m p 83—84°C Analysis· Found 75 16, H, 6.16, N, 3 82, Fe, 15 25, mol wt 367 (mass spectrum) $C_{23}H_{21}NFe$ calcd . C, 75 22, H, 5 76, N, 3 81, Fe, 15 20%, mol wt 366 6 NMR spectrum ($CDCl_3$) δ (ppm) 4 18 (m, 9H), 4 7 (br, NH), 5.05 (s, 1H), 6.5—7.6 (m, 5H)

By following the same procedures as described in the two experiments above, the following imines and amines were synthesized

(i) $C_5H_5FeC_5H_4CH=NC_6H_5$, orange-red oil, [17]

(ii) $C_5H_5FeC_5H_4CH_2NHC_6H_5$ brown crystals, m p. 75—76°C (lit. [18] m p. 85—86°C).

(iii) $C_5H_4FeC_5H_4$-1,1'-$[C(C_6H_5)=NC_6H_5]_2$, reddish oil, NMR spectrum ($CDCl_3$) δ (ppm) 4 55 (t, 4H); 4.75 (t, 4H), 6 5—7 5 (m, 20H) Molecular ion (mass spectrum) 544

(iv) $C_5H_4FeC_5H_4$-1,1'-$[CH(C_6H_5)NHC_6H_5]_2$, orange oil NMR spectrum ($CDCl_3$) δ (ppm) 4 3 (m, 8H from C_5H_4 rings and 2H from NH groups), 5 3 and 5.7 (m, $-\underline{CH}-NH$ protons), 6 6—7.9 (m, 20H). Molecular ion (mass spectrum) 546.

(v) $(C_5H_5FeC_5H_4)_2C=NC_6H_5$, orange brown crystals, m p 157°C, NMR ($CDCl_3$) δ (ppm) 4.26 and 5.26 (m, 18H); 6.65—7.60 (m, 5H); Molecular ion (mass spectrum) 473.

(vi) $(C_5H_5FeC_5H_4)_2CHNHC_6H_5$, yellow-orange crystals, NMR ($CDCl_3$) δ (ppm) 4.00 (18H from C_5H_4 rings, and 1H from NH), 5.05 (s, 1H), 6.60—7.40 (m, 5H), Molecular ion (mass spectrum 475)

General procedure for the reaction of ferrocenylcarbonium ions with primary amines

A simple method used for the preparation of α-aminoferrocenes was as follows

A five-fold excess of a primary amine was added to a solution of the ferrocenylcarbonium ion salt in methylene chloride, under nitrogen After stirring at room temperature for 4 h, the mixture was evaporated to dryness under vacuum. The residue was triturated several times with CCl_4 and the combined organic extracts were evaporated The crude product was chromatographed on basic alumina The following amines were prepared by this procedure

(i) $C_5H_5FeC_5H_4CH(C_6H_5)NHC_6H_4$-*p*-Cl, brown oil, NMR spectrum ($CDCl_3$) δ (ppm) 3.7 (br, NH), 4.2 (C_5H_5, C_5H_4, 9H), 5.05 (s, 1H), 6.4—7.6 (m, C_6H_4, C_6H_5, 9H), Molecular ion (mass spectrum) 401

(ii) $C_5H_5FeC_5H_4CH(C_6H_5)NHC_6H_4$-*p*-$CH_3$, brown oil, NMR spectrum ($CDCl_3$) δ (ppm) 2.2 (CH_3, xx), 4.2 (C_5H_4, C_5H_5, NH, 10H), 5.1 (s, 1H), 6.5—7.6 (m, C_6H_4, C_6H_5, 9H), Molecular ion (mass spectrum) 381

(iii) $C_5H_5FeC_5H_4CH(C_6H_5)NHC(CH_3)_3$, yellow crystals, m.p. 82—83°C, NMR spectrum ($CDCl_3$) δ (ppm) 1.05 (s, 9H), 1.7 (br, NH), 4.1 (m, C_5H_5, C_5H_4, 9H) 4.7 (s, 1H), 7.2—7.7 (m, 5H), Molecular ion (mass spectrum) 347

(iv) $C_5H_5FeC_5H_4CH(CH_3)NHC(CH_3)_3$, brown oil, NMR spectrum ($CDCl_3$) δ (ppm) 1.1 (s, $C(CH_3)_3$, 9H), 1.45 and 1.55 (—CH_3 and 1NH—, 4H), 3.8 (—CH—, 1H), 4.25 (C_5H_5, C_5H_4, 9H); Molecular ion (mass spectrum) 428.

(v) $(C_5H_5FeC_5H_4)_2CHNHC(CH_3)_3$, yellow crystals m.p. 115—120°C, NMR spectrum ($CDCl_3$). δ (ppm) 0.98 (s, $C(CH_3)_3$, 9H), 3.80 (C_5H_5, C_5H_4, 18H), 4.00 and 4.60 (CH, NH, 2H).

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