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Mössbauer studies on ferrocene complexes

XVII *. Ferrocenylamines and ferrocenylphosphines

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Abstract

^{57}Fe Mössbauer data are reported for some ferrocene derivatives in which the ferrocenyl group is bonded to N and P, and are considered in the light of ^{13}C NMR and cyclic voltammetry (CV) data. They highlight the difference in the interaction between the ferrocenyl unit and the exocyclic nitrogen or phosphorus atom.

Introduction

In our continuing study of the effects of substitution on the properties of ferrocenes by ^{57}Fe Mössbauer and NMR spectroscopy we have turned our attention to molecules containing ferrocenyl moieties linked via phosphorus or nitrogen. There have been many previous attempts to rationalise the type of interaction between substituent and ferrocenyl group [2–7]. Little et al. [2,3] reported an excellent correlation between the oxidation potential and Hammett σ_p constants. The less satisfactory correlation with σ_p^+ values led Little to conclude that the resonance contribution of the substituents were mainly with the Cp ring, and were not transmitted directly to the reaction site at the central iron atom. We have previously shown that quadrupole splittings (QS) correlate well with oxidation potentials and Hammett σ constants [4]. Poor correlation was found between QS and σ_I, the inductive substituent constants, or σ_R^0, the mesomeric constants. On the other hand, there was a reasonably good correlation with σ_R^+, suggesting that

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* For part XVI see Ref. 1

resonance involves the partially positively charged iron atom as well as the substituted cyclopentadienyl ring. However, we and others [4–7] have shown that when nitrogen is directly bonded to the Fc unit these correlations are disrupted. We report here the ^{57}Fe Mössbauer data for some ferrocenyl amines ($FcNR_2$) and phosphines ($FcPR_2$) and related compounds and compare them with the electrochemical and ^{13}C NMR data.

Results and discussion

Mössbauer Spectroscopy

The Mössbauer data are shown in Table 1. Only one iron electronic environment was found for compounds involving two or more Fc groups, indicating the equal interaction of the substituent atom/group with the ferrocenyl units. The ferrocenylamine compounds **2–6** (Table 1) all have QS values larger than that of ferrocene itself (compound **1**, Table 1), in keeping with the electron-donating nature of the N atom [4]. This is also consistent with the decrease in oxidation potential relative to ferrocene and the known lack of basicity of ferrocenyl amines [7–9]. QS values range from 2.40 mms^{-1} for $Fc_2N(COMe)$ (**6**) to 2.45 mms^{-1} for Fc_3N (**5**). The difference between the QS of **5** and the other amines gives a measure of the competition for N-electron density between the ferrocenes moieties and the other substituent group/atom. Definitive evidence for the interaction of N with the ferrocenyl unit has been found in the crystal structure of triferrocenylamine (**5**) [10,11]. The structure shows an almost planar trigonal (angle CNC 119.8°) N-atom, only 6 pm out of the plane defined by the nitrogen–carbon atoms bonded to nitrogen. The three ferrocenyl groups are orientated differently with respect to this plane, one of the substituted cyclopentadienyl rings being in the plane. The short C–N bonds (average 141.4 pm) are indicative of some double bond character. These

Table 1

^{57}Fe Mössbauer parameters (data at 78 K) and cyclic voltammetry data for ferrocenylamines and phosphines and related derivatives

Compound		Isomer shift, IS (δ, mm s^{-1})	Quadrupole splitting, QS (Δ, mm s^{-1})	Oxidation potential ($E_{\frac{1}{2}}$, V) [a]
1	Fc	0.54 (1)	2.37 (1)	0
2	$FcNH_2$		2.43 [b]	−0.37
3	Fc_2NH			−0.36
4	Fc_2NPh	0.53 (1)	2.44 (1)	−0.28
5	Fc_3N	0.53(1)	2.45 (1)	−0.31
6	$Fc_2N(COMe)$	0.55 (1)	2.40 (1)	
7	FcNNFc	0.50 (1)	2.32 (1)	
8	$FcPPh_2$	0.52 (1)	2.31 (1)	
9	Fc_2PPh	0.52 (1)	2.32 (1)	
10	$Fe(C_5H_4PPh_2)_2$	0.53 (1)	2.30 (1)	
11	Fc_2PCl [c,d]	0.435	2.296	
12	$[Fc_2P^+][AlCl_4^-]$ [c,e]	0.525(1)	2.328	

[a] Data from ref. 7. Potentials vs. oxidation potential of ferrocene. [b] Data from ref. 4. [c] Data from ref. 8. [d] Room temperature. [e] 60 K.

C–N bonds differ slightly in length (140.2, 141.2, 142.9 pm), the shortest bond being the one to the in-plane cyclopentadienyl ring. However, the presence of only one iron electronic environment in the Mössbauer data shows that electronically they are essentially identical (within line width error Γ 0.32 mm s^{-1} for Fc_3N), and the distortions must arise from packing forces affecting the atomic positions but not the electron distributions. These structural features are consistent with the absence of a stereochemically active lone pair of electrons on the nitrogen, and suggest a marked delocalisation of these electron into the ferrocenyl moieties.

This kind of interaction, while typical of amino-N atoms bonded to ferrocene moieties, is not general for all N-containing groups. For example the diaza –N=N–) group present in **7** reduces the QS to 2.32 mm s^{-1} (below that of ferrocene itself). The diaza group withdraws rather than releases electron density from the ferrocenyl moieties, hence reducing the QS. Further evidence comes from the ^{13}C NMR spectra, which are discussed later [11].

The ferrocenylphosphines all exhibit smaller QS values than ferrocene. Phosphorus has a lower electronegativity than nitrogen and possesses low lying empty *d*-orbitals. It is this latter feature that appears to dominate the chemistry of the P atoms in these compounds. The QS values of compounds **8**, **9** and **10** are lower than that of ferrocene, indicating that electron density is withdrawn from the Fc groups by phosphorus (presumably via the empty 3*d* orbitals), as previously described by McEwan et al. [12,13]. In line with this interpretation is the observation that the stability of the hydrogen bond between ferrocenylphosphines, Fc_nPPh_{3-n} ($n = 0$–3), and phenol increases as the number of ferrocenyl groups at the P atom increases [14]. Similarly, the coordinating ability of the ferrocenylphosphines Fc_nPPh_{3-n} increases with the number of Fc substituents [15]. The ability of the P lone pair to act in dative covalent bonding can be deduced from the existence of many coordination compounds containing ferrocenylphosphines (cf. 16) such as ferrocenylphosphines, $FcPPh_2$ (**8**) [17,20] and diferrocenylphenylphosphine, Fc_2PPh (**9**) [17,20–22].

Further evidence for the lack of involvement of the lone pair on phosphorus in bonding comes from the electrochemistry of diferrocenylphenylphosphine (**9**) [7]. In our initial studies, three oxidation waves were observed: an irreversible process at Ep^{ox} 0.39 V, and two reversible processes at 0.49 and 0.628 V (potentials quoted vs. SCE determined by the ferrocene-ferricinium couple at 0.35 V). The reversibility of the oxidation couples are characterised by the near unity value of the peak current ratio of ip_a/ip_e over the scan range 0.1–5 Vs^{-1}. The peak separations (ΔE_p) were in the range 70–100 mV. These waves were assigned to ferrocene oxidations. The irreversible couple at 0.39 V is tentatively assigned to oxidation of the phosphorus for the following reasons. Controlled potential electrolysis held at 50 mV past the E_p value indicate that a two electron process occurs overall, as would be expected in the oxidation of P^{III} to P^V. The $^{31}P\{^1H\}$ NMR spectrum of the solution after exhaustive electrolysis (ca. 5% of original current) shows that a downfield shift ($\Delta\delta$) of 56 ppm has occurred. This can be compared with $\Delta\delta$ values for the following oxidation at phosphorus: $FcPPh_2 \rightarrow FcP(=O)PPh_2$ (40.0 ppm), and $Ph_3P \rightarrow Ph_3P{=}O$ (33 ppm) (Table 2), and suggests that electrochemical oxidation of the phosphorus atom has also occurred in the case of Fc_2PPh (**9**). The sharp well defined spectrum of the species prepared electrochemically from Fc_2PPh shows it to be diamagnetic, which rules out the possibility of oxidation of the iron centres to formally Fe^{III}

Table 2

^{13}C [a] and ^{31}P [b] NMR data for ferrocenylamines and ferrocenylphosphines and related compounds

Compound		Phenyl resonances				Ferrocenyl resonances				^{31}P
		C1 *ipso*	C2/C6 *ortho*	C3/C5 *meta*	C4 *para*	C1	C2/C5 α	C3/C4 β	Cp	
PhNH [c]		146.9	115.3	129.5	118.7					
Ph_2NH [c]		143.4	118.1	129.6	118.2				–	
Ph_3N		148.5	121.7	129.6	123.1				–	
$FcNH_2$	**(2)**					105.3	58.7 [i]	63.2 [i]	68.7	
FcNHPh		146.0	114.8	129.0	118.7	100.5	61.9	64.5	68.8	
FcNHFc	**(3)**					105.0	58.6	63.5	68.7	
$FcNPh_2$		147.6	124.4	129.0	122.9	107.1	60.3	64.0	69.0	
Fc_2NPh	**(4)**	147.2	128.6	129.2	125.6	108.3	58.9	63.3	68.7	
Fc_3N	**(5)**					107.1	61.5	63.1	69.1	
$Fc_2N(COMe)$	**(6)**					102.8	64.4	66.5	69.5	
FcNNFc	**(7)**					108.1	64.2	69.5	69.8	
$FcPPh_2$ [d]	**(8)**	139.1	133.4	128.2	127.8	78.6	72.8 [i]	70.6 [i]	69.0	−15.1
		(10.0)	(19.2)	(2.5)		(0.0)	(14.7)	(3.4)	–	
Fc_2PPh [d]	**(9)**	139.2	133.8	127.8	128.2	77.9	72.6, 71.9 [i,j]	70.4, 69.8	69.0	−28.9
		(8.9)	(20.8)	(7.4)		(4.9)	(16.6), (12.8)	(2.8), (3.8)		−25.9 [d]
Fc_2PH							70.6	68.7	68.9	
Fc_3P							72.7	70.3	69.3	
$Fe(C_5H_4PPh_2)_2$ [d] **(10)**		140.1	134.2	129.3	128.9	77.6	74.6 [i]	73.1 [i]		−11.2
		(11.2)	(19.8)	(3.3)		(4.0)	(14.9)	(3.5)		
$Fe(C_5H_4P(O)Ph_2)_2$ [e]			131.2	128.2	131.5		73.6	73.7	+28.8	
			(9.9)	(12.1)			(22.4)			
Ph_3P		137.2	133.6	128.4	128.5					−5.6, −8 [f]
		(11.4)	(19.5)	(7.0)						
Ph_3PO [g]		134.3	132.4	128.4	131.5					+25 [h]
		(102.8)	(9.6)	(11.6)	(1.8)					

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[a] Chemical shift in ppm relative to TMS; data taken from Table 3 in ref. 11 except where stated. [b] Chemical shifts in ppm relative to 85% H_3PO_4, +ve downfield convention, coupling constants (J(PC)) in parentheses. [c] Data from ref. 40. [d] This work, ^{31}P spectrum run in DMSO-d_6. For earlier reports on the ^{13}C NMR spectra of **8** see ref. 41, for those of **9** and **10** see ref. 42. [e] This work, ^{13}C and ^{31}P spectra run in $CDCl_3$. [f] Data from refs. 37, 38. [g] Data from ref. 43. [h] Data from ref. 44. [i] Assignment of the ferrocenyl signals to C2/C5 (α) and C3/C4 (β) is tentative (cf. ref. 11). In the case of $FcNH_2$ **(2)** the assignment is supported by comparison with $PhNH_2$ [28]. For the ferrocenylphosphines **8**, **9** and **10**, the assignment is unequivocal on the basis of the coupling constants, J(PC). [j] The increased number of cyclopentadienyl signals observed for C2–C5 in Fc_2PPh **(9)** is due to chemical shift non-equivalence of the prochiral carbon atoms (cf. ref. 45).

paramagnetic species. This ease of phosphorus oxidation contrasts with the irreversible oxidation at much higher potentials of ferrocenyl-amines **2** at 1.0 V, **3** at 1.34 V, and **5** at 1.47 V [7].

The extent to which the phosphorus withdraws electron density from ferrocene will depend on (1) the substituents bonded to P, and (2) the overlap between the ferrocene unit and the phosphorus 3*d* orbitals. This overlap will be conformationally dependent. Distortion of the ferrocene can alter the electron-withdrawing effect of P, as can be seen from the crystal structures of some metal complexes of 1,1′-bis(diphenylphosphino)ferrocene [23–25].

It noteworthy that the compounds **11** and **12** (Table 1) prepared by Baxter et al. [25] also have QS values in keeping with those of the other ferrocenylphosphine complexes and with the arguments presented here.

It is also noteworthy that the quadrupole splittings for the series FcH (**1**), Fc_2PPh (**9**), $FcPPh_2$ (**8**) are 2.37(1), 2.32(1) and 2.31(1) mm s^{-1}. This order suggests that ferrocenyl is less electron withdrawing than phenyl (cf. ref. 27).

^{13}C NMR Spectroscopy

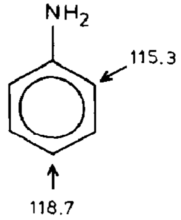
^{13}C NMR spectral data for the ferrocene derivatives are given in Table 2. The substituent effects on the phenyl and cyclopentadienyl rings differ in important respects, and are discussed below. Nesmeyanov et al. [28] have commented on the similarity of substituent effects at the C3/C4 (β) position in the cyclopentadienyl ring to those of the *para* positions in benzene derivatives. The C2/C5 (α) and free Cp ring carbons approximate to the *ortho* and *meta* positions in benzene. Supporting this view are the correlations of the ^{13}C shifts of the β carbons with modified Hammett substituent constants. Thus the following correlation with the resonance parameter σ_{R° is found for β carbon shifts $\Delta\delta\beta$ (relative to ferrocene).

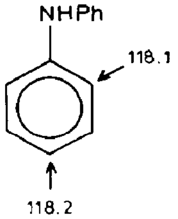
$$\Delta\delta\beta = 14.1\sigma_{R^\circ} + 1.0 \qquad (r = 0.951, 21 \text{ points})$$

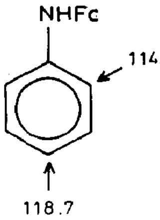
This correlation compares with that obtained for the *para* position of benzene derivatives

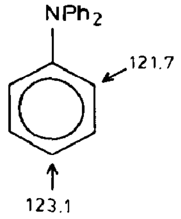
$$\Delta\delta p = 15.5\sigma_{R^\circ} + 1.5 \qquad (r = 0.952, 25 \text{ points, ref. } 29).$$

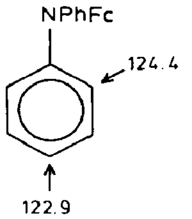
The β-carbon atoms in the cyclopentadienyl ring are rather less sensitive to substituent effects than the C_{para} atoms in the benzene series, and the mechanism of charge transfer may be different for the two cases. Substituent effects at the *para* position in benzene are considered to be largely of the resonance type [$^+$M, $-$M] whereas for the β position π inductive effects may also play a role. ^{13}C chemical shifts correlate well with the total charge density on the relevant carbon atom, both in uncomplexed [30,31] and complexed [32] aromatic ligands. The ^{13}C NMR spectra of the aminoferrocenes show the signals for both α (C2, C5) and β (C3, C4) carbons at somewhat higher field than that of ferrocene itself, indicating a substantial negative charge density at both positions (that at the α positions being somewhat larger). This implies that charge is transferred from the nitrogen atom to the cyclopentadienyl ring, in agreement with the Mössbauer data. Changes in shift at both positions are quite small when bulky substituents (Fc, Ph) are placed on the nitrogen atom. This suggests that changes in the dihedral angle θ between the nitrogen lone pair and the cyclopentadienyl ring π orbitals are relatively small, with

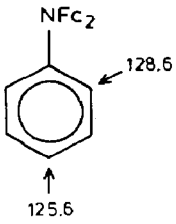












$\theta \sim 0$. The corresponding effects on the *para* carbon of the phenyl substituents are much more marked, as can be seen from the data above.

One bulky substituent has relatively little effect on the chemical shifts of the *ortho* and *para* carbons but two appear to cause substantial reduction in the flow of charge from the nitrogen to the ring substituents. This can be ascribed to an increase in the dihedral angle θ' between the nitrogen lone pair and the benzene ring orbital.

In discussing dihedral angles θ' the following assumptions are made:

(i) $\theta' = 0$ for $PhNH_2$, for which there is likely to be no steric inhibition of resonance.

(ii) For the hypothetical case in which the N lone pair and the cyclopentadienyl orbitals are orthogonal ($\theta' = 90°$), the *para* carbon shift is equal to that for a benzene carbon (δ 128.7 ppm). A crude estimate of θ' can be made for the amines containing phenyl groups (for the general method see refs. 33 and 34). A value of θ' of 42° is calculated for Ph_3N. This compares with values 47 ± 5° in the gas phase as determined by electron diffraction [35], and between 37 and 50° from-X ray crystallography [36], and implies no great change of conformation on going from solution to the gas and solid phases. A similar angle (40°) was deduced for $FcNPh_2$, but that for Fc_2NPh (4) was appreciably larger at 56°. The Fc substituent thus disrupts the N–Ph conjugation much more than does the Ph group. This is reflected in the calculated σ_R° values for the NH_2, NPh_2, and NFc substituents of -0.72, -0.49, and -0.30, respectively.

According to the ^{13}C NMR data, the *N*-acetyl derivative, $Fc_2N(COMe)$ (6), shows reduced electron density in the substituted cyclopentadienyl ring owing to competition by the CH_3CO group for the nitrogen lone pair, an effect supported by the Mössbauer results. A similar but more marked effect is shown by the –N=NFc substituent. Here the ^{13}C shifts indicate electron withdrawal from the ferrocenyl moieties, again in accord with reduced QS values in the Mössbauer spectrum.

In complete contrast to the ferrocenylamines, the phosphorus-substituted derivatives show overall electron withdrawal from the substituted cyclopentadienyl ring, possibly via $p\pi$–$d\pi$ overlap between the ring orbitals and the phosphorus d orbitals. Some evidence for this comes from the ^{31}P shift of Ph_3P (−5.6 ppm [37], −8 ppm [38] and that of Fc_2PPh (**9**) (−28.9 ppm), which implies a greater charge density on the phosphorus when bound to a Fc moiety. However, changes in C–P–C bond angles can also affect ^{31}P shifts. In trivalent phosphorus systems, an increase in the C–P–C bond angle generally causes a deshielding of the P atom [39]. The difference in the resonance effect between the N and P substituents is highlighted [40] if the ^{13}C shifts for the *para* position in $PhNMe_2$ and $PhPMe_2$ (117.2 and 127.7 ppm, respectively) are compared. By use of the method described previously, values of $\sigma_R{}^{\circ}$ of −0.84 and −0.16 can be estimated, and reveal a large difference between the ease of delocalisation of the lone pairs on the two atoms.

The ^{13}C NMR spectrum of Fc_2PPh reveals a multiplicity of signals for the substituted cyclopentadienyl ring, in keeping with the prochiral nature of the α and β protons (and carbons) and the phosphorus–carbon coupling (Table 2). By the same token the *ortho* and the *meta* protons in the phenyl groups of $FcPPh_2$ are also prochiral. However, the ^{13}C NMR spectrum shows both *ortho* and both *meta* carbon atoms to be magnetically equivalent. We are currently investigating this anomaly.

The phosphorus–carbon coupling constants in the ferrocenylphenylphosphines **8**–**10** show some interesting features. The ^2J(PC) and ^3J(PC) data are fairly similar for both phenyl and cyclopentadienyl ring carbons. The coupling constants for the phenyl ring carbons are almost identical to those in triphenylphosphine. The ^1J(PC) constants, however, are generally smaller for the cyclopentadienyl (4–5 Hz) than for the phenyl *ipso* carbons (9–11 Hz). The sign of the coupling constant ^1J(PC) for the cyclopentadienyl ring is not known; the corresponding ^1J(PC) constant for the phenyl *ipso* carbon is assumed to be negative, since phosphines generally have negative ^1J(PC) coupling constants (e.g., PPh_3 (−12.5 Hz) and PMe_3 (−13.6 Hz) [46], $PMeCl_2$ (−45 Hz) [47] or P^nBuPh_2 (−13.7 (^{n}Bu) and −14.8 (Ph) Hz) [48]. [The rather obscure nature of the ^1J(PC) coupling constant is discussed in ref. 49.]

Conclusions

The presence of only one iron site in the Mössbauer spectra of each of the compounds studied here is not unexpected, and is consistent with the ^{1}H and ^{13}C NMR data [11] in that the substituted atom/group interacts equally with each ferrocenyl group in the molecule, but it is noteworthy that the NMR studies were for solutions, whereas the Mössbauer data were for solids. The surprising finding of the planar N in Fc_3N (**5**) (from the structural study [10]) and the similarity of the Mössbauer and ^{13}C NMR parameters of **5** to those for the other ferrocenylamines **2**–**4** raises an interesting question, namely, is a nearly planar nitrogen atom a common feature for such derivatives? The fact that the ferrocenylphosphine derivatives do not show large QS values, and exhibit different ^{13}C NMR parameters, together with the comparative ease of P oxidation in Fc_2PPh (**9**), may indicate a that there is less interaction of the lone pair with the ferrocenyl groups than for N. It would therefore be expected that such derivatives would have a more typical tetrahedral structure around the P, owing to the greater localisation of the lone pair. We are currently undertaking a structural study of Fc_2PPh (**9**) to see if this is correct.

Experimental

All the derivatives used were either synthesised by standard literature methods (ref. 11 and references therein) or purchased from Aldrich Chemical Co. Ltd. [$Fe(C_5H_4PPh_2)_2$, Fc_2PPh]. ^{13}C and $^{31}P\{H\}$ NMR spectra were recorded on a Bruker WP80 spectrometer, and Mössbauer data were recorded and fitted as described previously [50]. Mössbauer chemical shifts are referred to a natural iron foil (25 μm thick) at 298 K as zero shift.

Cyclic voltammetry was carried out using 0.2 *M* solutions of $[NBu_4]^+[BF_4]^-$ in dimethylsulphoxide. The working electrode was a platinum wire, the counter electrode a tungsten wire, and a silver wire pseudo-reference electrode arranged such that the luggin capillary was in close proximity to the working electrode. Controlled potential electrolyses were performed in a four-compartment, three-electrode H-type cell. The working electrode was platinum gauze (nominal area 1.5 cm^2).

Measurements were made with an EG ad G PAR model 362 scanning potentiostat. The current and potential responses were stored on a magnetic disc via an EG and G twin channel 12-bit analogue-to-digital converter (650 μs conversion time) and data was manipulated on an Opus micro computer using EG and G CONDECON 30 (TM) Software version 1.2.

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