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Mössbauer studies on ferrocene complexes

XVIII *. A comparative study of azaferrocenes and phosphaferrocenes and their derivatives by ^{57}Fe Mössbauer and ^{13}C NMR spectroscopy

A. Houlton, R.M.G. Roberts and J. Silver

Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ (UK)

J. Zakrzewski

Department of Organic Chemistry, University of Łódź, Narutowicza 68, PL-90-136 Łódź (Poland)

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Abstract

The ^{13}C NMR chemical shifts (δ) for azaferrocenes, phosphaferrocenes and their precursor ligands have been used to determine coordination shifts, $\Delta\delta$ ($= \delta_{complex} - \delta_{ligand}$) for the complexes. For azaferrocenes, $\Delta\delta$ values were similar to that of ferrocene, but the phosphaferrocenes showed much larger coordination shifts. These observations are discussed in terms of the difference in bonding in these complexes. The ^{57}Fe Mössbauer data are reported for a number of azaferrocene derivatives and compared with those for the phosphaferrocene analogues in terms of orbital contributions to the electric field gradient that governs the quadrupole splitting (QS). An excellent correlation is found between QS and the orbital population parameter ($2p_2 - p_1$), where p_2 and p_1 are electronic populations of the e_2 and e_1 iron-based orbitals, respectively. Protonation and quaternisation of azaferrocene causes a lowering of QS, in contrast to the slight increase observed for monophosphaferrocene in CF_3CO_2H solution. The results confirm that protonation at the N atom takes place for azaferrocene. The $W(CO)_5$ adduct of azaferrocene shows little change in QS from that for azaferrocene, which is interpreted as evidence for back bonding by the tungsten.

1. Introduction

Heterocyclic analogues of ferrocene have become the focus of a great deal of research in recent years largely owing to the pioneering work of Mathey [2] on phosphaferrocenes. Less attention has been paid to the corresponding azaferrocenes, in spite of the fact that $(C_5H_5)(C_4H_4N)Fe$ was first prepared [3] well before the phosphaferrocenes. For many years 1,1′-diazaferrocene proved elusive. However, examples of these ferrocene analogues have now been synthesised and isolated as their adducts with pyrroles bearing bulky 2 and 5 substituents [4,6]. Over the last twelve years we have been interested in the structure of ferrocenes and related compounds and have carried out extensive Mössbauer spectroscopic studies in this area (see ref. 1, and preceding papers in this series). We have recently put forward ideas on the bonding in iron sandwich compounds that have rationalised $[Fe(cp)_2]$ (cp = cyclopentadienyl) with $[(\eta\text{-arene})(\eta\text{-cp})Fe]^+$ and $[(\eta\text{-arene})_2Fe]^{2+}$ complexes within the same bonding theory [7,8]. In ferrocene chemistry we have confirmed that substituents on the cp rings increase the Mössbauer quadrupole splitting if they are electron donors and decrease it if they are electron acceptors. These effects have been interpreted in terms of back bonding of iron-based e_2 orbitals with antibonding ligand orbitals.

We have also reported the differences between the effect of an exocyclic nitrogen and a phosphorus atom in ferrocenylamines and ferrocenylphosphines [9]. We concluded that, in ferrocenyl-phosphine derivatives (which show significantly smaller quadrupole splittings than their amino counterparts), lone pair delocalisation

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Correspondence to: Dr. R.M.G. Roberts or Dr. J. Silver.

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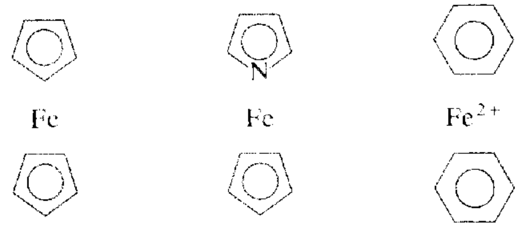
around the ferrocenyl group is much lower. We therefore turned our attention to complexes in which the heteroatom is part of the cyclopentadienyl ligand. Conflicting Mössbauer data for azaferrocene have appeared in the literature [10,11], and this prompted us to reexamine these complexes and compare our findings with the data on phosphaferrocenes [12].

2. Results and discussion

2.1. ^{13}C NMR spectroscopy

Table 1 lists the available ^{13}C data for both complexes and ligands. The pyrrolyl and phospholyl anions both show similar non-uniform chemical shifts. However, for the former a downfield shift of 9.4 ppm is found for C2 relative to pyrrole itself. This cannot be explained in terms of charge distribution, which would lead to substantial shielding. Lippmaa [14] has suggested that these paramagnetic shifts are due to a lowering in the average excitation energy on going from pyrrole to the pyrrolyl anion. This is supported by the accompanying large bathochromic shift of the UV absorption maxima for such systems. By contrast, both ring carbons of the phospholyl anion are shielded relative to those in the parent phosphole. The bonding in the two ligands is therefore rather different, certainly compared with the cyclopentadienyl anion, whose carbon resonances appear well upfield from their N and P counterparts.

Marked changes in shift are observed on going to the iron(II) complexes of these ligands. The coordination shift ($\Delta\delta$) is defined as the shift of a particular carbon atom in the complex relative to that of the same carbon in the ligand. One remarkable finding is that $\Delta\delta$ is almost constant over a wide range of charge type and structure.



$\Delta\delta$ −34.9 ppm −36.7, −33.4, −34.1 ppm (C2) (C3) (Cp) −33.6 ppm

This implies similar bonding in these complexes, and this could be regarded as involving a change from sp^2 character in the ligand to sp^3 character in the complex resulting in the substantial upfield shifts observed. The phosphaferrocenes, however, show exceptionally large values of $\Delta\delta$ for the phospholyl ligand, which suggests a stronger interaction of the C_4H_4P compared with that of C_5H_5, which appears normal.

There is also some evidence for redistribution of charge between rings in the phosphaferrocenes. The ^{13}C shift of the Cp ligand appears downfield from those in azaferrocene or ferrocene itself. The effect is particularly noticeable in the case of the novel $(C_5Me_5)(P_5)Fe$ complex [20]. Similar charge transfer is also found in the (η-arene)(η-Cp)Fe complexes, and has been rationalised in terms of backbonding of the iron to the arene ligand [7]. Such non-uniformity of coordination shifts has been observed in (η-cyclohexadienyl)(η-Cp)Fe. Here the C1(C5) and C2(C4) show large $\Delta\delta$ values of ~ −50 ppm, whereas C3 has

TABLE 1. ^{13}C NMR shifts [a] for cyclopentadienyl and heterocyclopentadienyl iron sandwich complexes and their anionic precursors

Complex	C2	C3	$C_5H_5(C_6H_6)$	Coordination shifts [b] ($\Delta\delta$) C2	C3	$C_5H_5(C_6H_6)$	Ref.
C_5H_5Li	–	–	102.8	–	–	–	13
C_4H_4NLi	126.7	106.0	–	–	–	–	14
C_4H_4PLi	129.7	119.7	–				15
$[3,4\text{-}C_4H_2(CH_3)_2P]Li$	128.7	127.9	–	–	–	–	15
$(C_5H_5)_2Fe$	–	–	67.9	–	–	34.9	16
$(C_5H_5)(C_4H_4N)Fe$	90.0	72.6	68.7	−36.7	−33.4	−34.1	17
$(C_4H_4N)_2Fe$	89.8	72.8		−36.9	−33.2	–	5
$(C_5H_5)(C_4H_4P)Fe$	77.2	79.8	70.2	−52.5	−39.9	−32.6	18
$[3,4\text{-}C_4H_2(CH_3)_2P]_2Fe$	78.2	94.8	71.4	−50.5	−46.6	−31.4	19
$[(C_5H_5)(3,4\text{-}C_4H_2(CH_3)_2P)]Fe$	82.1	97.1	–	−46.6	−30.4	–	19
$[C_5(CH_3)_5]_2Fe$	–	–	78.5	–	–	– [c]	20
$[C_5(CH_3)_5](P_5)Fe$			90.6				20
$[C_6H_6)_2Fe][PF_6]_2$	–	–	94.9	–		−33.6	21
$[(C_5H_5)(C_6H_6)Fe][PF_6]$	–	–	77.4 (88.8)	–	–	−25.4 (−39.7)	This work
$[(C_5H_5)(C_6H_7)]Fe$	– [d]	– [d]	72.4	– [d]	– [d]	30.4	This work

[a] in ppm from TMS; [b] $\Delta\delta = \delta$ complex − δ ligand; [c] values for the $C_5(CH_3)_5^-$ ion are not available; [d] values of $\Delta\delta$ are as follows: C1, −54.0; C2, −52.4; C3, +1.2 ppm.

a value of +1.2 ppm. These results have been interpreted in terms of preferential overlap of the cyclohexadienyl ligand π_2 orbital with metal d_{xz}, d_{yz} orbitals [22].

2.2. ^{57}Fe Mössbauer spectroscopy

The quadrupole splitting parameter for iron complexes is thought to depend on the relative populations of the e_2 ($d_{x^2-y^2}$, d_{xy}) and e_1 (d_{xz}, d_{yz}) orbitals. In all iron sandwich complexes the d_{z^2} orbital appears to be fully occupied and is therefore usually discounted when comparing QS values. The e_2 orbitals contribute twice as strongly to the electric field gradient (efg) as the e_1 orbitals, leading to the relationship

$$\mathrm{QS} \propto 2p_2 - p_1 \qquad (1)$$

where p_2 and p_1 are the electronic populations of e_2 and e_1 MO sets, respectively. This relationship can be verified from comparison of experimental values of QS with values of p_2 and p_1 calculated from INDO SCF MO methodology. These calculations have been carried out by Clack and Warren [23] for uncharged complexes. Assuming that charge on the central metal atom affects p_2 and p_1 equally, values of population distribution can be obtained for $(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Fe^+$ and $(\eta\text{-}C_6H_6)_2Fe^{2+}$. Together with the values calculated for ferrocene, an excellent correlation of QS with $(2p_2 - p_1)$ is found, albeit for only three points ($r = 0.999$), leading to the relationship

$$\mathrm{QS} = 0.192\,(2p_2 - p_1) + 1.07 \qquad (2)$$

Similar MO calculations have been made for monophosphaferrocene [24]. Substituting these population distributions in the above equations leads to a QS of 2.15 mm s^{-1}. This is close to the experimentally observed value of 2.07 mm s^{-1}, and seems to confirm the general applicability of eqn. (2).

From the Mössbauer data listed in Table 2 it is clear that our values for azaferrocene at 298 K (spectrum 3A) are markedly different from those reported by the earliest workers [10] (spectrum 3B). We suspect that this discrepancy is due to the known instability of early Mössbauer spectrometers. Our values are close to those reported more recently [11]. The value of QS of 2.51 mm s^{-1} is higher than that for ferrocene (2.37 mm s^{-1}). The high QS for ferrocene itself is considered to derive from filled and largely unperturbed e_2 levels giving a large imbalance of e_2 and e_1 populations. This must therefore also be true for azaferrocene, with little mixing of iron d orbitals even though the symmetry is reduced from D_{5h} to C_{2h}. This is in keeping with the ^{13}C coordination shifts, which are very similar to those of ferrocene. By contrast, monophosphaferrocene has a much lower QS owing to significant orbital mixing of $d_{x^2-y^2}$ and d_{z^2} [26]. This greater interaction with the ligands is the probable reason for the much larger coordination shifts observed for monophosphaferrocene. These are reminiscent of those observed for the cyclohexadienyl complex described above in which the CH_2 group lies well out of the ligand plane and is essentially non-bonded to the iron. The crystal structure of 3,4-dimethylphosphaferrocene [27] shows the P atom to be bent out of the ligand plane by 0.041 Å away from the iron, and suggests a rather similar bonding scheme.

TABLE 2. ^{57}Fe Mössbauer spectroscopic parameters [a] for azaferrocenes and related phosphaferrocenes

Spectrum no.	Compound	T	IS	QS	$\Gamma_{1/2}$
1	Ferrocene [b]	78	0.52	2.37	–
2	Ferrocene/CF_3CO_2H [c]	80	0.44(1)	2.59(2)	0.18(1)
3	Azaferrocene	78	0.54(1)	2.51(1)	0.14(1)
			0.30(1)	–	0.40(5)
3A	Azaferrocene	298	0.48(1)	2.46(1)	0.11(1)
3B	Azaferrocene [d]	298	0.57	2.14	–
4	Azaferrocene/CF_3CO_2H	78	0.54(1)	2.36(1)	0.18(1)
5	N-Methylazaferrocenyliodide	78	0.54(1)	2.36(1)	0.14(1)
6	2,5-Dimethylazaferrocene [c]	78	0.55(1)	2.48(1)	0.13(1)
7	Azaferrocene-$W(CO)_5$ adduct [f,g]	78	0.58(1)	2.47(3)	0.16(2)
			0.38(2)	0.34(2)	0.13(2)
8	Monophosphaferrocene [h]	78	0.51(1)	2.07(1)	0.19(1)
9	Monophosphaferrocene/CF_3SO_3H [h]	80	0.47(1)	2.10(1)	0.13(1)
10	2,3,4,5-Tetraphenylmonophosphaferrocene [h]	78	0.51(1)	2.07(1)	0.21(1)
11	2,3,4,5-Tetraphenylmonophosphaferrocene/CF_3SO_3H	80	0.52(2)	2.12(3)	0.18(3)
12	2,3,4,5-Tetramethylmonophosphaferrocene	78	0.50(1)	2.05(1)	0.16(1)

[a] IS, isomer shift, QS quadrupole splitting, $\Gamma_{1/2}$ width at half height all in mm s^{-1}, T, K. All data pertain to this work unless otherwise stated. [b] Data from Ref. 8; [c] data from Ref. 29; [d] data from Ref. 9; [c] in frozen CH_2Cl_2 solution; [f] 55% (absorption area) of component with higher IS; [g] this material contains an iron(III) impurity; [h] data from Ref. 24.

The temperature dependence of QS for azaferrocene is outside experimental error and may be due to a slight change in solid state structure. The second minor signal in the 78 K spectrum of azaferrocene is due to an iron(II) impurity which is not apparent at 298 K. It is noteworthy in this context that ^1H NMR studies on solid azaferrocene have revealed a phase change at 281 K [28]. At 77 K there is evidence of a dipole-glass-like state caused by the freezing out of ligand ring motions. Protonation of azaferrocene (spectrum 4) led to a lowering of QS by 0.10 mm s^{-1}. If protonation had occurred on the iron (as with ferrocene itself) an increase in QS would have resulted. Thus protonation must occur at the N atom. It is known that, in contrast to the phosphaferrocenes, azaferrocene displays distinct, though weak, basic properties (pK_a 7.5, close to that of quinoline), and is readily quaternised by methyl iodide [29]. This indicates that the lone pair level is much higher in energy in azaferrocenes than phosphaferrocenes.

The QS of the quaternised azaferrocene (spectrum 5) shows a similar decrease. Protonation removes electron density from the five-membered ring, which therefore requires more backbonding from the e_2 iron based orbitals thus depleting their population and reducing the QS in accordance with relationship 1. However, the isomer shift (IS) is higher than that for ferrocene, suggesting less shielding of the nucleus by iron 3d and 4p electrons, which will be polarised towards the positive pole on the nitrogen. This should cause an overall increase in the radial distributions of their orbitals. The reduced QS for the quaternised azaferrocene is explained in similar terms.

2,5-Dimethylazaferrocene (spectrum 6) has a very similar QS to that of azaferrocene itself. Since the imbalance between e_2 and e_1 populations is almost maximal for ferrocene and azaferrocene, electron-releasing substituents are unlikely to have much effect. The azaferrocene–$W(CO)_5$ adduct (spectrum 7) has a QS identical to that of azaferrocene itself. This suggests that the nitrogen does not overall possess a significant positive charge, and this could be the result of backbonding from the tungsten to antibonding orbitals of the azaferrocene moiety.

3. Experimental section

Azaferrocene [31] and 2,5-dimethylazaferrocene [29] were prepared by standard methods. The former was methylated by use of an excess of methyl iodide [32].

3.1. Preparation of $(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4N \cdot W(CO)_5)Fe$

A solution of $W(CO)_6$ (0.352 g, 1.0 mmol) in dry THF (15 ml) was photolysed in a Pyrex vessel for 1.5 h under argon at room temperature with light from a 600 W mercury lamp. Azaferrocene (0.187 g, 1 mmol) was then added and the solvent evaporated. The residue was chromatographed on silica with dry benzene as eluent to afford the crude complex contaminated with ~ 10% of unreacted $W(CO)_6$. The complex was purified by extraction with dry $CHCl_3$, evaporation of the extract, and repetition of the chromatography. It was finally recrystallised from CH_2Cl_2-heptane to give 0.210 g of pure product (41%).

Analysis: Calc. for $C_{14}H_9NO_5FeW$: C, 32.91; H, 1.78; N, 2.74. Found: C, 32.84; H, 1.66; N, 2.71%. IR ($CHCl_3$): ν(CO) 2069, 1972, 1925 and 1890 cm^{-1}. ^1H NMR ($CDCl_3$, δ in ppm from TMS): 5.63 s (2H, α-pyrrolyl H); 4.70 s (2H, β-pyrrolyl H); 4.47 s (5H, Cp); ^{13}C NMR ($CDCl_3$): 201.71 ($J(^{183}W-^{13}C)$ 153.5 Hz, CO *trans* to azaferrocene), 198.74 ($J(^{183}W-^{13}C)$ 131.2 Hz, CO *cis* to azaferrocene), 94.33 (α-pyrrolyl C), 72.43 (β-pyrrolyl C), 70.98 (Cp).

IR spectra were recorded on a Nicolet FT instrument and ^1H, ^{13}C spectra on a Varian Gemini 200 BB spectrometer. ^{57}Fe Mössbauer spectra were obtained from frozen solutions and solids and fitted as previously described [33–35].

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