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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

VII *. STRUCTURE AND REACTIONS OF [1]FERROCENOPHANES

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Summary

The effect of ring tilt on quadrupole splitting (QS) for ferrocenophanes is discussed. For the [1]ferrocenophanes, the reduced QS values are explained in terms of overlap of ligand-based orbitals with *d* orbitals on the heteroatom [P,Si]. (1,1′-Ferrocenediyl)phenylphospine reacts with MeI or with mercuric chloride to form 1/1 adducts whose QS values are almost identical but significantly smaller than the starting material. The reduction in QS is discussed. On dissolution of the phosphine in even weakly acidic media (CH_3CO_2H), the iron is abstracted as high spin iron(II). The corresponding silane behaves differently in acid, the principal reaction being one of Si–C bond fission to give normal ferrocene Mössbauer parameters. Reaction of the phosphine with $AgNO_3$, $FeCl_3$ and I_2 results in oxidation to the corresponding ferrocinium derivative which shows an unusually high QS value. The NMR spectra of the derivatives are also discussed, particularly in respect of assignment of the cyclopentadienyl hydrogen resonances.

Introduction

Our work on ferrocene compounds has demonstrated the usefulness of Mössbauer spectroscopy in probing changes in the electronic environment at the iron nucleus [1–6]. In this work we have already demonstrated a large range of quadrupole splittings (QS) from 3.09 mms^{-1} for the $FeCp_2 \cdot HgCl_2$ adduct [2] to 1.78 mm s^{-1} for protonated ferrocenyl diketones [5].

During this work our attention was drawn to the work of Osborne et al. [7] who have reported the synthesis, structures, and properties of a range of [1]ferrocenophanes. The Mössbauer data for these compounds by comparison with ferro-

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* For part VI see ref. 1.

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cene and non-bridged ferrocene derivatives show a fall in QS from values of 2.4 mm s^{-1} to 1.95–2.0 mm s^{-1}. These results are in contrast to those of Hillman and Nagy [8] for other bridged ferrocene derivatives (some containing several bridges) in that the latter authors found a linear relationship between the changes in QS and IS and the mean iron–ring distance. Hillman and Nagy suggest that this distance is the significant factor rather than the angle of tilt on the rings. In Osborne's data [7] changes in iron–ring distances are relatively small, yet the change in QS is much larger than would be expected from the linear relationship observed by Hillman and Nagy. Similar large changes in QS (relative to ferrocene) were reported by us for the $FeCp_2/HgCl_2$ [2] and $FeCp_2/HAlCl_4$ [3] complexes, which we have interpreted as being due to electron withdrawal via metal based e_{2g} orbitals. Here where ring tilt is likely to be large these also do not fit the arguments of Hillman and Nagy. So it appears that at both extremes of QS values, the mean iron–ring distance arguments break down.

We have recently reported a detailed examination of a series of acylferrocenes [4] which show low QS values (1.8–2.2 mm s^{-1}) which we have interpreted as being due to removal of charge via ring-based orbitals (e_1). For [1]ferrocenophanes, d_π–d_π overlaps between the iron atom e_1 orbitals and P and Si, should result in similar QS values. Withdrawal of charge from the e_2 orbitals alone would have increased the QS value [2,3]. However, in this case the e_2 orbitals are probably involved in the formation of the lone pair located diametrically opposite the heteroatom and thus unavailable for d_π–d_π overlaps with the heteroatom. It therefore seemed expedient to investigate further the chemistry of some of the compounds reported by Osborne et al. We report here NMR and Mössbauer studies on the previously described [1]ferrocenophanes, data for some new complexes derived from them, and reactivities in acidic media. We also include a reassessment of current views on the Mössbauer data from these derivatives.

Results and discussion

The Mössbauer data are presented in Table 1. The MeI derivative of $Fe(C_5H_4)_2PPh$ shows an even smaller QS than the parent compound, whereas the isomer shift shows little change. The addition of the methyl group to the phosphorus atom will have the effect of changing the phosphorus coordination from a "very distorted tetrahedral environment" [11] to a less distorted environment, since the phosphonium salt is isoelectronic with the silicon analogue [10], resulting in an increase in θ to a value approaching 99°. P, Si and Ge derivatives have very similar QS values [7] but have significantly different values of both θ and α [9,10] which indicates that factors other than ring-tilt are involved in determining the QS. Increasing θ in the phosphonium salt brings the phosphorus atom closer to the iron by about 0.1 Å. This would increase the overlap of the phosphorus d orbitals with those of the iron and increase the redistribution of d_{xz},d_{yz} components, giving rise to the observed decrease in QS (1.87 mm s^{-1}).

Osborne [9,10] et al. maintain that the Fe–Si distance of 2.60 Å and the Fe–P distance of 2.77 Å in the [1]ferrocenophanes are too long to indicate bonding, based on calculations using metallic covalent radii. However, known crystal structures of compounds containing iron–phosphorus bonds show a wide range of bond lengths, from 2.22 Å in $[Fe(SMe)(CO)_2(PMe_3)]_2$ [11] to 2.44 Å in $Fe(CO)_4PPh_3$ [12]. Even

TABLE 1

MÖSSBAUER PARAMETERS FOR [1]FERROCENOPHANES AT 80 K

	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Half width at half height (mm s^{-1})
$FeCp_2SiPh$	0.51(1)	1.97(1)	0.13(1)
	0.51[a]	1.97[a]	
$FeCp_2SiPh_2$ in CF_3CO_2H	0.57(3)	2.30(6)	0.37(7)
$FeCp_2PPh$	0.53(1)	1.98(1)	0.16(1)
	0.52[a]	1.97[a]	
$FeCp_2PPhMeI$	0.52(1)	1.87(1)	0.16(1)
$FeCp_2PPhHgCl_2$	0.51(1)	1.89(1)	0.13(1)
$[FeCp_2PPh]^+$	0.45(1)	0.83(1)	0.25(1)
$FeCp_2PPh/CF_3COOH$	1.47(2)	2.69(3)	0.21(3)
$FeCp_3PPh/CH_3COOH$	1.38(2)	2.60(3)	0.25(2)
Fe dissolved in a HCl/CF_3COOH mixture	1.29(1)	2.66(1)	0.16(1)
	1.34(1)	3.12(1)	0.15(1)

[a] Data from ref. 7.

longer bond distances have recently been found (2.58–2.71 Å) in other iron(II) phosphine complexes [13]. Thus a distance of 2.77 Å does not preclude some bonding interaction. Available structural data on iron–silicon bonds are limited. The two reported structures have Fe–Si bond distances of 2.25 Å [14,15] which are only 0.43 Å shorter than that in 1,1′-(ferrocenediyl)diphenylsilane [10]. We are of the opinion that both P and Si atoms would be close enough to the central iron atom to perturb the electronic environment which should be reflected in the magnitude of QS. Both phosphorus and silicon possess empty 3*d* orbitals capable of overlap with both e_1 (d_{xz} and d_{yz} iron orbitals) and e_2 ($d_{xy}, d_{x^2-y^2}$) orbitals). Table 2 summarises

TABLE 2

CORRELATION OF RING TILT ANGLE (α) WITH QS VALUES FOR SOME FERROCENOPHANES

Compound	α	QS (mm s^{-1})	ΔQS[a]	Ref.
$(C_5H_5)Fe(C_5H_5)$	0	2.40	0.00	19
$(C_5H_4)Fe(C_5H_4)$ $(CH_2)_4$	4.4	2.35	0.05	8,20
$(C_5H_4)Fe(C_5H_4)$ $(CH_2)_3$	10	2.30	0.10	19
$(C_5H_4)Fe(C_5H_4)$ CH_2COCH_2	10	2.27	0.13	19
$(C_5H_4)Fe(C_5H_4)$ $GePh_2$	16.6	2.02	0.38	7
$(C_5H_4)Fe(C_5H_4)$ $SiPh_2$	19.2	1.97	0.43	7
$(C_5H_4)Fe(C_5H_4)$ PPh	26.7	1.97	0.43	7

[a] $\Delta QS = QS_{\text{ferrocene}} - QS_{\text{bridged ferrocene}}$.

the Mössbauer data available for ring-tilted ferrocenes. A plot of these data gives an apparent correlation between change in QS ($\Delta QS = QS_{\text{ferrocene}} - QS_{\text{bridged ferrocene}}$) and $\alpha (r = 0.940, \chi = 0.40)$. However, if the data are separated into those pertaining to homogeneous bridges (all carbon) and to those containing heteroatoms, the correlation for the latter disappears. It appears that, for the former series, the lowering of QS (2.30 mm s^{-1}) is due simply to the presence of a carbon chain $(CH_2)_n$, which is close enough ($n \leq 4$) to the iron atom to cause distortion to the electronic environment, altering the lattice contribution which is greatly enhanced in ferrocene derivatives [16]. Far smaller QS values occur where the bridge contains a heteroatom with available '*d*' orbitals. Unfortunately [1]ferrocenophanes with a carbon atom in the bridge have not yet been synthesised, thus preventing a direct comparison with bridging atoms lacking available *d* orbitals.

Osborne presents an alternative explanation that the distortion at the C(1) carbon atoms in $(Fe(C_5H_4))Si(C_6H_5)_2$ leads to changes in the metal–ring bonding and that such changes may cause the withdrawal of electrons from the iron d_{xy} orbital and a reduction in the QS. This explanation has in the past been used to account for the collapse of the QS when ferrocene is oxidised to the ferrocinium ion [17], but in this case an electron is completely removed from the iron. Withdrawal of electrons from the d_{xy} orbitals is puzzling since it is not clear where withdrawn electrons are located. Also redistribution of e_{2g} orbitals (which comprise d_{xy} components) in complexes with $HgCl_2$ and $HAlCl_4$ lead to enhanced QS values.

(1,1′-ferrocenediyl)phenylphosphine reacts with $HgCl_2$ to give a red adduct with a QS of 1.89 mm s^{-1} which indicates that the mercury is bonded to the phosphorus (cf. QS 3.09 mm s^{-1} for Fe–Hg bonding) [2]. This value is almost identical to that obtained for the phosphonium derivative. Again the phosphorus will make a closer approach to the iron atom than in the parent.

Also we note that the Group IV and Group V ferrocenophanes, the ferrocene mercuric halide adducts and the H-bonded ferrocene complexes are all red in colour due to electronic excitations of similar energies, as would be expected from similar electronic orbital arrangements at the Fe atom and indeed ferrocene complexes, where the rings are parallel, are orange or yellow.

The known structures of the P, Si and Ge [1]ferrocenophanes show that the cyclopentadienyl rings are tilted open so that the Fe may be expected to generate a lone pair of electrons on the side opposite to the bridging atom. This directional lone pair would be expected to modify the QS and this is seen to decrease in both our and Osborne's data for the ferrocenophanes. This decrease in QS must be interpreted as a change in the symmetry of the electronic environment at the iron nucleus as a result of ring tilting causing '*d*' electron redistribution. Also the '*d*' electron configuration will be modified by the proximity of the heteroatom in the bridge [9,10] (Fe–Si, 2.64 Å; Fe–P, 2.77 Å). There will also be a contribution from direct fields of the electrons in the bridging group itself.

We note that in the crystal structures of Si and Ge ferrocenophanes, the lone pairs are projected into cavities in the crystal structure and so no other atoms are close enough to interact with these lone pairs. To investigate the availability of the lone pair for bonding the parent complex was dissolved in CF_3COOH. When this was done and the resulting solution frozen, only high spin iron(II) was found in the Mössbauer spectrum. Even in a weak acid (CH_3COOH) the same result was obtained.

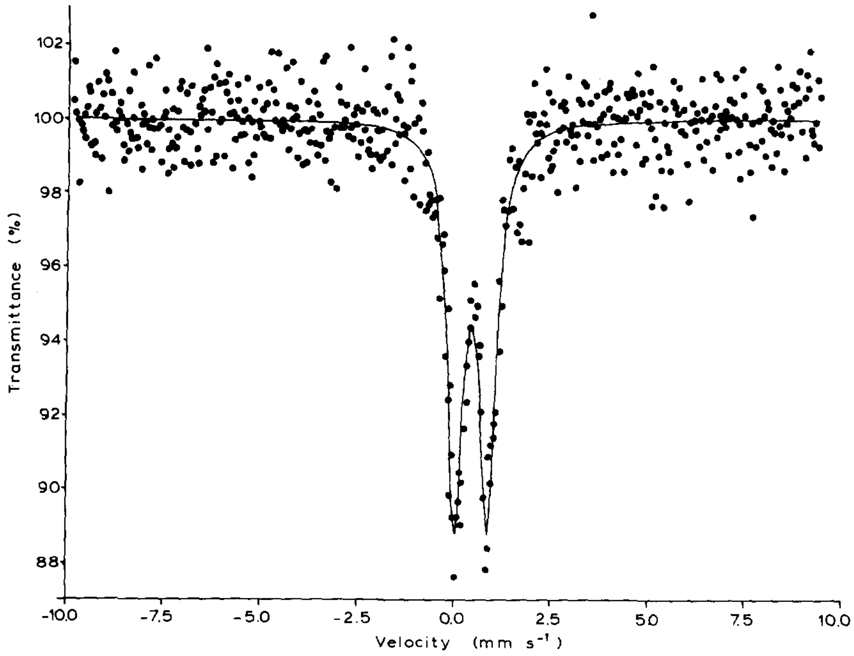

Fig. 1. Mössbauer spectrum of $[Fe(C_5H_4)_2PPh]^+ NO_3^-$.

Indeed, when iron metal was dissolved in a HCl/CF_3COOH mixture a solid separated which gave two high spin iron(II) Mössbauer sites, one of which was similar to the above materials. It seems that the iron is removed from the $FeCp_2PPh$ in even weakly acid media such as acetic acid. No such removal from a ferrocene complex has previously been reported. The lone pair on the Fe in ferrocene is the most likely agent to act as a catalyst for this removal, aided by the initial formation of a hydrogen bond which possibly changes the crystal field at the iron nucleus to high spin causing the iron to be ejected from the complex as high spin iron(II).

Indirect support for this mechanism comes from the fact that the phosphonium salt is itself relatively stable and this decomposition in acid media via phosphorus protonation seems unlikely, although there is evidence for protonation during the reaction (vide infra). A corollary of the above postulate is that the lone pair on the iron must be very considerably more basic than that of ferrocene itself. This could be the result of its much greater directional properties and enhanced accessibility resulting from ring tilt.

Reaction of $FeCp_2PPh$ with $FeCl_3$ or with iodine yields materials which give rise to Mössbauer spectra similar to that of Fig. 1 obtained from oxidation with $AgNO_3$. In all cases, oxidation has taken place and an oxidised iron(III) environment results. The QS recorded here is the largest yet recorded for a ferrocinium type environment. Here, the QS is caused by the bridging ligand distorting the environment. The phosphonium salt, on exposure to light, also yields a material which gives a spectrum similar to that shown in Fig. 1.

It is of obvious interest that oxidation does not remove the iron from Cp_2FePPh.

NMR spectra

The spectra of the parent phosphorus and silicon compounds were essentially the same as those reported by Osborne [7], who assigned the resonances of the phosphorus compound at 4.18 ppm (4H) to the H(3,4) protons. The two proton signals at 4.53 and 4.29 ppm were assigned to H(2) and H(5) protons, where H(2) is the proton in the *syn* position relative to the phenyl substituent. The analysis was made by assuming that H was deshielded by the neighbouring phenyl group. However, it is clear from the X-ray structure of the phosphine that the phenyl group is almost orthogonal to the Cp rings, with the result that H(2) lies in the shielding cone of the π electron cloud. Using the coordinates of H(2) relative to the centre of the benzene ring calculated from X-ray data, it can be shown the H(2) should be shielded by about 0.3 ppm relative to H(5) [18]. This difference in chemical shift is close to that observed (0.244 ppm). The original assignment should, therefore, in our opinion, be reversed. A similar shielding effect occurs in the silane. Here the two triplets observed for H(2,5) and H(3,4) (4.16 and 4.53 ppm) are 0.37 ppm apart.

On methylation, the phosphine shows an aromatic multiplet at 7.6–8 ppm, two 2H signals at 4.58 and 5.13 ppm due to H(2) and H(5) and a four proton signal (H(3,4)) at 4.95 ppm. The methyl resonance appears as a doublet (J(H–^{31}P) 15 Hz) at 2.62 ppm. The phosphine $HgCl_2$ adduct gave a qualitatively similar spectrum in DMSO-d_6 with H(2), H(5) and H(3,4) appearing at 4.08, 5.03 and 4.38 ppm respectively.

On dissolving the phosphine in CF_3CO_2H, the reddish-brown solution became green after about ten minutes. The PMR spectrum comprised broad signals for the aromatic (2–4 ppm) and the proton on phosphorus at -1.0 ppm. Ferrocenyl protons were absent due to extreme line broadening resulting from proximity to the paramagnetic centre.

For the silane, clear evidence of Si–C bond fission was obtained in even weakly acidic media. Thus, in CH_3CO_2H, the Cp ring protons appeared as one sharp singlet (5H) at 3.8 ppm and two triplets (each 2H) at 4.05 and 4.17 ppm respectively, typical of mono-substituted ferrocenes.

Experimental

The Mössbauer spectra were recorded and fitted using methods previously reported [2]. NMR spectra were recorded on a Varian EM 360 spectrometer using DMSO-d_6, benzene-d_6 or $CDCl_3$ as solvents. Microanalyses were performed by the Manchester University Microanalytical Department.

All reagents were used as provided except ferrocene which was recrystallized from n-hexane. $FeCp_2$, $(C_6H_5)_2SiCl_2$, $C_6H_5PCl_2$ and CF_3CO_2H were all purchased from the Aldrich Chemical Co. Hexane was freshly distilled from molecular sieve under N_2, CH_2Cl_2 dried over $CaCl_2$ and CH_3CN and C_6H_6 used as supplied.

$Fe(C_5H_4)_2$ $Si(C_6H_5)_2$ and $Fe(C_5H_4)_2PC_6H_5$ were prepared by the methods previously reported [7]

Preparation of $Fe(C_5H_4)_2PC_6H_5HgCl_2$

$Fe(C_5H_4)_2PC_6H_5$ (0.25 g, 0.85 mmol) was dissolved in 50 ml nitrogen-flushed dichloromethane and placed in a 3-necked round bottom flask fitted with a dropping funnel. To this was added, with stirring, a solution of $HgCl_2$ (0.23 g, 0.85 mmol) in 50 ml acetonitrile over a period of 5 min. A pink precipitate rapidly appeared. The mixture was left to stir for a further 15 min then filtered, washed with dichloromethane and acetonitrile and dried in air. The yield was 0.36 g (74.2%) of a powdery pink air stable material which decomposes at approximately 100°C. Found: C, 33.7; H, 2.3; P, 5.3; Hg, 34.9; Fe, 9.7. $C_{16}H_{13}Cl_2HeHgP$ calcd.: C, 34.1; H, 2.3; P, 5.5; Hg, 35.6; Fe, 9.9%.

Preparation of $Fe(C_5H_5)_2P^+ (C_6H_5)(CH_3)I^-$

$Fe(C_5H_4)_2PC_6H_5$ (0.5 g, 1.7 mmol) was dissolved in 100 ml nitrogen-flushed benzene and placed in a 3-necked flask. Methyl iodide (0.55 ml, 8.8 mmol) was rapidly added and the solution left to stir for 12 h, after which time a precipitate appeared. This was then filtered off, washed with benzene and air dried. The yield was 0.17 g (22.8%) of a brick red material which decomposes on heating. The compound was also light sensitive but could be stored in the dark for 4-5 days without significant decomposition. Found: C, 46.2; H, 3.7; P, 6.7; Fe, 12.3. $C_{17}H_{16}FeIP$ calcd.: C, 47.0; H, 3.7; P, 7.1; Fe, 12.8%.

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