Studies of the Bonding in Iron(II) Cyclopentadienyl and Arene Sandwich Compounds. Part 3.[1] Carbon-13 Nuclear Magnetic Resonance and Iron-57 Mössbauer Spectroscopic Studies on [(η-Cyclohexadienyl)(η-cyclopentadienyl)]iron(II) Complexes

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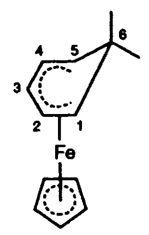
A series of [Fe(η-C_5H_4X)(η-$C_6H_{7-n}X_n$)] (X = H or Me, n = 0–6) complexes has been prepared. A detailed analysis of their ^{13}C NMR spectra is presented, the assignments being confirmed using distortionless enhancement by polarisation transfer (DEPT) techniques. The co-ordination shift of the cyclohexadienyl ligand shifts are not uniform and these anomalies are discussed in terms of possible bonding schemes. The effect of substitution by chlorine and methyl groups is also included. For the case where X = Me, evidence is presented for the occurrence of conformational isomers due to restricted rotation of the ligands. The ^{57}Fe Mössbauer parameters are reported as well as a temperature-dependence study. The results are discussed in terms of the somewhat distorted nature of the cyclohexadienyl ligand in these complexes.

We have recently reported on correlations of ^{13}C NMR shifts with ^{57}Fe Mössbauer quadrupole splittings (q.s.s)[1] and have shown how such an approach can shed light on the bonding of iron sandwich complexes. In a prior publication a qualitative approach to the understanding of substituent effects on such bonding was presented[2] again using ^{57}Fe Mössbauer parameters as a probe of the iron environment. We have now extended our studies to include (η-cyclohexadienyl)(η-cyclopentadienyl)iron(II) complexes [Fe(η-C_5H_5)(η-$C_6H_{7-n}X_n$)] (X = Me, n = 0–6; X = Cl, n = 1 or 2) and report our findings in this paper.

Results and Discussion

Product-distribution Studies.—The cyclohexadienyl complexes discussed here are those derived from hydride addition to [Fe(η-C_5H_5)(η-$C_6H_{6-n}X_n$)] salts. These can be prepared by using $NaBH_4$ for the more activated salts (X = Cl) or $LiAlH_4$ for the heavily methylated species. The complexes have been known for some time and their syntheses and chemistry has been reviewed.[3] Product-distribution studies[4,5] for hydride additions were non-regiospecific for alkyl substituents whereas eelectron-withdrawing substituents such as chlorine directed hydride attack mainly to the *ortho* position (*ipso* substitution is rarely observed in these systems). For most of the salts used attack by hydride is regiospecific due to the substitution patterns of the arene ligand. Exceptions are where the arene is (*a*) methylbenzene, (*b*) 1,2-dimethylbenzene and (*c*) 1,3-dichlorobenzene. For (*b*) there is a slight preference for attack at the 3 position (60%) over that of the 4 position. For (*c*) attack is favoured at the 2 position (93%) over the 4(6) position after taking into account statistical factors. This is to be expected since the 2 position is doubly activated by the adjacent chlorine substituents which do not appear therefore to impede attack by $NaBH_4$.

*Carbon-*13 *NMR Spectra of Cyclohexadienyl Complexes.*—The data appear in Table 1. The following numbering scheme is adopted. The most striking feature of the data is the absence of any appreciable co-ordination shift for carbon 3, and the very large upfield shifts of ≈53 ppm for carbons 1(5) and 2(4) relative to the corresponding cyclohexadienyl anions.[6] These co-ordination shifts are much larger than those observed for ferrocene (−34.0 ppm), [Cr(η-arene)$(CO)_3$] complexes (−32.3 ppm),[7] [Fe(η-C_5H_5)(η-arene)]$^+$ complexes [−41.2 (arene), −26.5 ppm (C_5H_5)[8] and [Fe(η-arene)$_2$]$^{2+}$ complexes (−33.6 ppm).[9]



Similar upfield shifts have also been reported in the ^1H NMR spectra of the cyclohexadienyl complexes.[5] The cause of upfield shifts on complexation to transition metals has been the subject of much speculation and several explanations have been offered (see ref. 7 for an overview). More recently it has been suggested that the phenomenon is due to a specific increase in the radial shielding tensor[10] though the origins of this dramatic change are unknown. For the cyclohexadienyl complexes it is clear that, whatever the causes of the complexation shifts, the effect does not operate uniformly on the η^5 moiety. The available crystal structures of cyclohexadienyl complexes[11–14] indicate that all five carbons are approximately equidistant from the metal atom. This therefore appears to rule out the oft-quoted explanation of changes in hybridisation as a cause of co-ordination shifts. Another attractive suggestion is that of back bonding from metal e_2 orbitals into ligand π^*,[15] thus increasing the electron density on the ligand carbon atoms. If this is true then back bonding must exclude carbon 3. Shielding by metal-based electrons has also been advanced but again such an effect seems to be specific for $C^1(C^5)$ and $C^2(C^4)$ and the shielding zone would have to have a horseshoe geometry open ended at C^3. It is pertinent here to consider the molecular orbital (MO)

Table 1 Carbon-13 NMR data[a] for cyclohexadienyl complexes obtained by hydride addition to $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_{6-n}X_n)]PF_6$ salts

Arene	C^1	C^2	C^3	C^4	C^5	C^6	C_5H_5	Methyl
Benzene	21.78	79.44	79.24	79.44	21.78	25.65	72.40	—
Benzene[b]	21.55	79.40	79.14	79.40	21.55	25.03	72.40	—
Methylbenzene[c]	35.14	79.53[d]	79.73[d]	79.43[d]	26.78	31.69	73.50	21.62
1,2-Dimethylbenzene[e,f]	33.01	91.14	76.86	78.71	21.44	33.21	73.61	18.71(C^2), 24.16(C^1)
1,2-Dimethylbenzene[f,g]	20.54[d]	91.43[d]	91.31[d]	79.66	22.23[d]	26.73	73.52	18.89,[d] 19.90[d](C^2,C^3)
1,4-Dimethylbenzene	30.87	77.00	78.40	91.14	22.14	32.41	73.68	24.87,[d] 23.30[d](C^1,C^4)
1,3,5-Trimethylbenzene	34.48	80.11	89.34	80.11	34.48	38.47	74.88	21.36(C^1), 25.55(C^1,C^5)
1,2,3,4-Tetramethylbenzene	34.30	89.16	89.97	89.16	21.50	33.97	75.33	15.75[d](C^1,C^3), 15.93,[d] 23.77(C^2,C^4)
1,2,4,5-Tetramethylbenzene	32.99	88.72	78.81	88.72	32.99	41.08	75.06	18.33(C^1,C^5), 22.01(C^2,C^4)
Pentamethylbenzene	30.93	87.83	87.28	87.83	30.93	40.79	76.01	15.9(C^1,C^5), 16.03(C^3) 23.52(C^2,C^4)
Hexamethylbenzene	33.06	88.68	88.48	88.68	33.06	35.96	75.96	16.26,[d] 16.46(C^3), 16.69[d](C^1,C^2,C^4,C^5), 17.27(C^6)
Chlorobenzene[c]	56.23	79.41[d]	78.75[d]	78.10[d]	28.07	37.58	76.34	—
1,2-Dichlorobenzene[e]	55.56	102.11	77.21[d]	76.69[d]	27.72	38.43	77.92	—
1,3-Dichlorobenzene[c]	60.36	77.00	74.42	77.00	60.36	47.50	78.50	—
1,3-Dichlorobenzene[g]	53.98	79.50[d]	—[h]	79.83[d]	24.32	36.59	77.71	—
1,4-Dichlorobenzene	55.87	77.24[d]	75.65[d]	103.04	29.38	39.13	78.23	—

[a] Shifts in ppm from $SiMe_4$, solvent $CDCl_3$ unless stated otherwise. [b] Reduction by $NaBD_4$, for C_6 J_{CD} = 19.8 Hz. [c] Hydride attack at C^2. [d] Absolute assignment uncertain. [e] Hydride attack at C^3. [f] Solvent C_6D_6. [g] Hydride attack at C^4. [h] Not observed.

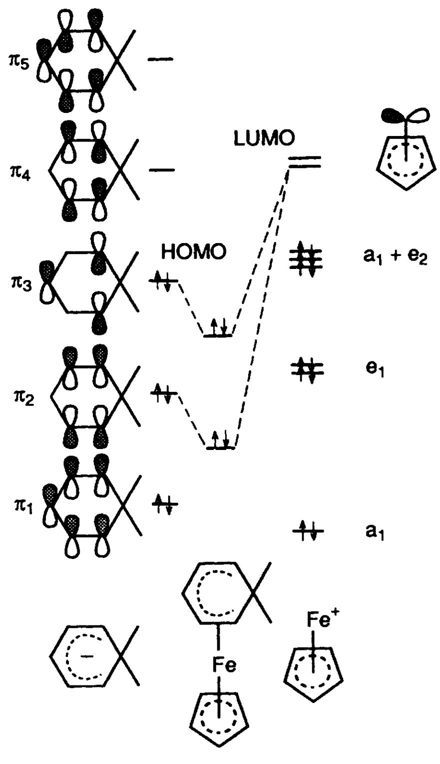


Fig. 1 Schematic MO diagram for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_7)]$ showing the major bonding interactions between the cyclohexadienyl ligand and the $Fe(\eta\text{-}C_5H_5)^+$ moiety

scheme for bonding of the $Fe(C_5H_5)^+$ moiety to the cyclohexadienyl ligand. Hoffmann and Hofmann[16] have shown that secondary interactions between the appropriate iron orbitals and the CH_2 are antibonding in nature and thus can be ignored. The major bonding interactions for the cyclohexadienyl ligand are π_2 to e_1* and π_3 to e_1* as shown in Fig. 1 (after Green *et al.*[17]).

Both π_2 and π_3 of the ligand have the correct symmetry for overlap with the degenerate e_1* (d_{xz}, d_{yz}) orbitals. However, π_2 has a better geometry for overlap with a centrally located iron atom than does π_3. If indeed the major bonding component were the π_3–e_1* combination this should result in some 'slippage' of the iron from a central position. In most of the crystal structures of cyclohexadienyl and pentadienyl complexes such a phenomenon has not been found. The exception is bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) where a small displacement of the iron towards the central carbon atoms (C^2–C^4) of the cyclohexadienyl ligands is observed.[11] However, if the π_2–e_1* combination is the major bonding component, then this would explain the co-ordination shifts observed since π_3 would remain virtually unchanged with, in particular, the same π-electron density on C^3.† Compelling evidence for a change in bonding from that found in symmetrical iron sandwiches comes from ^{57}Fe NMR data. The chemical shift (relative to ferrocene) for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ (**1**) was +32.9 ppm[18] (positive values are downfield) whereas those for the cyclohexadienyl complexes $[Fe(\eta\text{-}C_6H_7)(CO)_3]^+$ (**2**) and $[Fe(\eta\text{-}C_6H_5)(\eta\text{-}C_6H_7)]$ (**3**) (−431.6 and +735.1 ppm)[18] differ widely. The charge on the iron atom does not appear to be the primary cause of these extraordinary differences in shifts which must therefore be attributed to changes in bonding. The ^{13}C NMR co-ordination shifts[19] of **2** also differ markedly from those of **3** (values in parentheses), *viz.* C^1 −10.8 (−54.0), C^2 −29.0 (−52.4) and C^3 + 11.4 (+1.2) ppm, suggesting a significant difference in the bonding of the cyclohexadienyl ligand.‡ A complete description of such bonding must, however, await full MO calculations for these complexes. Similar trends in co-ordination shifts are observed for the closely related $Fe(\eta\text{-}C_5H_7)_2$ complexes[20] [C^1(C^5) − 16.4, C^2(C^4) − 55.0 and C^3 + 4.0 ppm].

It must be pointed out, however, that these shifts are calculated using the W conformation of the pentadienyl anion[21] since no data are available for the less thermodynamically stable U conformer. In addition, Olah *et al.*[6] used potassium cyclohexadienide in liquid ammonia as opposed to Sebastian *et al.*[21] who studied the lithium salts in tetrahydrofuran–hexane mixtures for the pentadienyl anions. The latter system would clearly involve considerable ion pairing of the salts which in turn would cause changes in the chemical shifts.

The ^{13}C NMR assignments were facilitated by using distortionless enhancement by polarisation transfer (DEPT) experiments to identify the CH_2 carbon signals. This proved of great value in the analysis of the methylcyclopentadienyl derivatives.

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† It is worth noting that overlap is possible between the e_2 [d_{xy}, $d_{x^2-y^2}$ highest occupied molecular orbital (HOMO) of the $Fe(C_5H_5)+$ fragment] and ligand π_4 [lowest unoccupied molecular orbital (LUMO)] both of which have the correct symmetry. However, the e_1* orbitals have better directional geometry for overlap.

‡ The observed ^{13}C chemical shifts of both complexed (**2**) and uncomplexed cyclohexadienyl ligands correlate reasonably well with the total charge[16] on each carbon atom (slopes 161 and 174 ppm e^{-1} respectively).

Table 2 Iron-57 Mössbauer parameters for $[Fe(\eta-C_5H_5)(\eta-C_6H_{7-n}X_n)]$ complexes at 80 K

Cyclohexadienyl substituents								
C^1	C^2	C^3	C^4	C^5	C^6	i.s.[a]	q.s.[a]	$\Gamma_{\frac{1}{2}}$[a]
H	H	H	H	H	H	0.51(1)	1.93(1)	0.15(1)
Me[b]	H	H	H	H	H	0.49(1)	1.87(1)	0.15(1)
Me	H	Me	H	H	H	0.50(1)	1.79(1)	0.14(1)
Me[c]	H	H	Me	H	H	0.49(1)	1.95(1)	0.14(1)
Me[c]	H	Me	H	Me	H	0.48(1)	1.89(1)	0.14(1)
Me	Me	Me	Me	H	H	0.50(1)	1.95(1)	0.13(1)
Me	Me	H	Me	Me	H	0.47(1)	1.89(1)	0.15(1)
Me	Me	Me	Me	Me	H	0.47(1)	1.95(1)	0.12(1)
Me[c]	Me	Me	Me	Me	Me	0.49(1)	1.94(1)	0.13(1)
Cl	H	H	H	H	H	0.49(1)	1.90(1)	0.15(1)
Cl[d]	H	H	H	H	H	0.41(1)	1.87(1)	0.11(1)
Cl[c]	Cl	H	H	H	H	0.46(1)	1.95(1)	0.12(1)
Cl[e]	H	H	H	Cl	H	0.51(1)	1.71(1)	0.16(1)
Cl	H	H	Cl	H	H	0.48(1)	1.92(1)	0.15(1)

[a] Values in mm s^{-1}; $\Gamma_{\frac{1}{2}}$ = linewidth at half-height. [b] Mixture of 1-, 2- and 3-methylated complexes. [c] Frozen benzene solution. [d] At 298 K. [e] Contains 14% of the 1,3-dichloro complex.

Table 3 Iron-57 Mössbauer parameters for $[Fe(\eta-C_5H_4Me)(\eta-C_6H_{7-n}X_n)]$ complexes at 80 K

Cyclohexadienyl substituents								
C^1	C^2	C^3	C^4	C^5	C^6	i.s.	q.s.	$\Gamma_{\frac{1}{2}}$
H[a]	H	H	H	H	H	0.50(1)	1.90(1)	0.17(1)
Me[b]	H	H	H	H	H	0.48(1)	1.85(1)	0.15(1)
Me	H	Me	H	H	H	0.47(1)	1.80(1)	0.15(1)
Me	H	Me	H	Me	H	0.48(1)	1.82(1)	0.15(1)
Me	Me	H	Me	Me	H	0.47(1)	1.90(1)	0.15(1)
Me	Me	Me	Me	Me	H	0.52(1)	1.96(1)	0.15(1)
Me	Me	Me	Me	Me	Me	0.51(1)	1.97(1)	0.17(1)

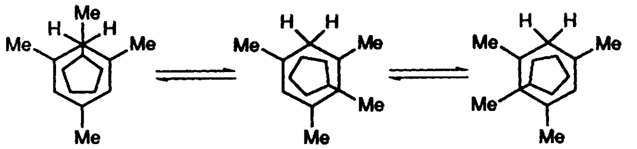
[a] Frozen benzene solution. [b] Mixture of 1-, 2- and 3-methylated complexes.

Table 4 Effect of variation of temperature on the ^{57}Fe Mössbauer parameters of $[Fe(\eta-C_5H_5)(\eta-C_6H_7)]$

T/K	i.s.	q.s.	$\Gamma_{\frac{1}{2}}$
298	0.43(1)	1.52(1)	0.14(1)
216	0.48(1)	1.67(1)	0.18(1)
212	0.48(1)	1.70(1)	0.19(1)
176	0.48(1)	1.89(1)	0.17(1)
150	0.49(1)	1.92(1)	0.17(1)
126	0.50(1)	1.92(1)	0.18(1)
80	0.51(1)	1.93(1)	0.15(1)

The product of hydride attack on $[Fe(\eta-C_5H_4Me)(\eta-C_6H_3Me_3-1,3,5)]PF_6$ showed *two* inverted signals in the DEPT spectrum at δ 33.47 and 26.89. In addition, two signals were observed for the cyclopentadienyl methyl group at δ 13.77 and 13.60. Five other signals were found in the δ 18–26 region. These results indicated the presence of two products closely related in structure. The most plausible explanation is the occurrence of three rotamers, a *meso* conformer with the cyclopentadienyl methyl group eclipsing the CH_2 group (**I**) and an enantiomeric pair (**II** and **III**) with the methyl group eclipsing $C^2(C^4)$ of the cyclohexadienyl ligand.

Statistically, one would expect a 2:1 ratio of the enantiomeric to the *meso* form. The observed intensities of the pair of signals for CH_2 and the corresponding cyclopentadienyl methyl signals indicate a preponderance (57%) of one isomer (chemical shifts of δ 26.89 and 13.60) and it is tempting to assign these signals to conformers **II** and **III**. Conformer **I**, unlike **II**(**III**), is symmetrical and should show two signals for the cyclohexadienyl methyl groups in a 2:1 ratio. These are indeed found at δ 22.30 and 23.74 respectively among the five remaining alkyl signals, the remaining three signals being assigned to the corresponding methyl substituents in conformers **II** and **III** (δ 25.36, 20.05 and 18.88). Such conformational equilibria result in a complex set of signals for the cyclopentadienyl and cyclohexadienyl carbon atoms in the δ 70–80 range which are difficult to analyse. The existence of conformational equilibria implies, of course, a significant rotational barrier in these complexes. Such barriers have already been identified for the 'open' ferrocenes with methyl substituents.[22]

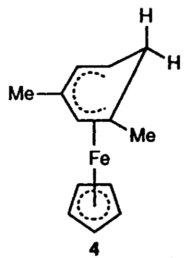


I II III

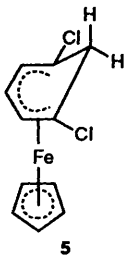
Iron-57 Mössbauer Spectroscopy.—The ^{57}Fe Mössbauer parameters for the cyclohexadienyl complexes are listed in Tables 2–4. For the $[Fe(\eta-C_5H_5)(\eta-C_6H_{7-n}X_n)]$ series (Table 2) there are no discernible trends in the isomer shifts (i.s.), the values being somewhat lower than those of ferrocene derivatives but much higher than those of the $[Fe(\eta-C_6H_7)(CO)_3]^+$ salts.[24] This reflects the much greater electron-withdrawing power of the $Fe(CO)_3$ moiety, increasing the s-electron density at the iron. This is also manifest in the very large upfield shift of the ^{57}Fe NMR signal which itself is again probably due to contraction of s-electron density around the more positive iron atom. The isomer shifts of the 'open' ferrocenes show very similar values[25] to those of the $[Fe(\eta-C_5H_5)(\eta-C_6H_{7-n}X_n)]$ series (0.46–0.50 mm s^{-1}). The quadrupole splittings (q.s.) of the cyclohexadienyl complexes, however, do show some interesting variations. That of the parent complex $[Fe(\eta-C_5H_5)(\eta-C_6H_7)]$ (1.93 mm s^{-1}) lies half-way between the values for ferrocene (2.38 mm s^{-1}) and $[Fe(\eta-C_5H_7)_2]$ (1.40 mm s^{-1}).[25] Quadruple shift values of iron sandwich complexes depend on the relative populations (p_i) of the e_2 (d_{xy}, $d_{x^2-y^2}$) and e_1 (d_{xz}, d_{yz}) orbitals according to relationship[1,2] (1).

$$\text{q.s.} \propto 2p_2 - p_1 \qquad (1)$$

Molecular orbital studies for ferrocene show that relatively little metal-ligand orbital mixing occurs[25] leaving the e_2 levels heavily populated and resulting in the large observed q.s. Such calculations[23] for the open ferrocenes predict a redistribution of the electron occupancy bringing p_2 and p_1 more into balance and resulting in the observed smaller q.s.[25] The cyclohexadienyl complexes presumably undergo a similar redistribution. The cyclohexadienyl ligand is bound less strongly than the cyclopentadienyl ligand in these systems. This is evident in the ease with which the former is removed[26] and also in the markedly lower thermal stability of these complexes compared with ferrocene illustrated by the ease of pyrolysis.[27] The C_5H_5 ligand thus is the major supplier of electron density to the iron. Evidence for this comes from the downfield ^{13}C NMR shift of the C_5H_5 resonance (δ 72.4) compared with ferrocene (δ 67.9). To compensate, back-bonding from the e_2 iron-based orbitals must occur thus lowering p_2 and hence the q.s. Substituent effects on q.s. for the $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_{7-n}X_n)]$ series are quite small as might be anticipated for a rather weakly bound ligand. There are, however, two interesting exceptions which show significant variation from the parent value of 1.93 mm s^{-1} and are depicted below. A methyl substituent at C^3 seems to cause a lowering of q.s. (see also the lower value of 1.89 mm s^{-1} for the 1,3,5-trimethyl-substituted complex). Previous work on the open ferrocenes also shows that the position of the methyl substituent has an important effect on q.s.[25] (see below). The sequence shown suggests a lowering of q.s. by 3-methyl substituents and a raising by methyl groups at 2,4. However, the existence of conformational isomers for the less heavily methylated complexes is an additional complication in such analyses. In this context it is to be noted that the structure of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II)[11] shows that substituents on carbons 1, 2, 4 and 5 are approximately 0.25 Å below the five-carbon plane whereas the substituent on C^3 lies in the plane. This will modify the substituent effects at C^1, C^2, C^4 and C^5 compared to the optimum effect at C^3. These distortions are probably the cause of the restricted rotation inferred from the ^{13}C NMR data above.



4
q.s. 1.79 mm s^{-1}



5
q.s. 1.71 mm s^{-1}

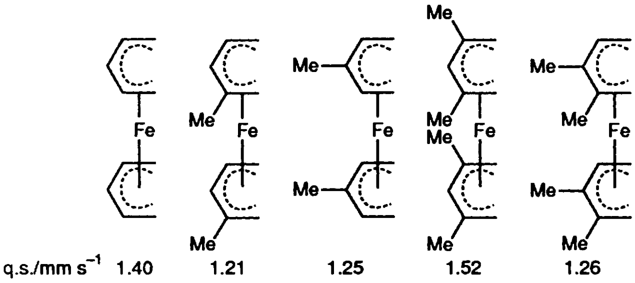


Table 5 Yields and analytical data for $[Fe(\eta\text{-}C_5H_4Me)(\eta\text{-}C_6H_{6-n}X_n)]PF_6$ complexes

Arene, $C_6H_{6-n}X_n$	Yield (%)	Analysis* (%) C	Analysis* (%) H
Benzene	11		
Methylbenzene	16	38.8 (39.2)	4.7 (4.7)
1,3-Dimethylbenzene	29		
1,3,5-Trimethylbenzene	21		
1,2,4,5-Tetramethylbenzene	28		
Pentamethylbenzene	24	42.6 (43.2)	5.9 (5.8)
Hexamethylbenzene	14		

* Calculated values in parentheses.

For ferrocene itself, chlorine substituents significantly increase q.s.,[28] an effect which has been interpreted as being due to an increase in the electric field gradient.[29] The cyclohexadienyl complexes, however, do not show this behaviour. The reason must lie in a subtle reorganisation of e_2 and e_1 orbital components which we are at present unable to describe.

For the $[Fe(\eta\text{-}C_5H_4Me)(\eta\text{-}C_6H_{7-n}X_n)]$ series (Table 3), one or two methyl substituents cause a decrease in q.s. but further methylation results in a significant increase. There is however some controversy as to the exact electronic role of methyl groups in the cyclohexadienyl anions.[21,30] From the work described here and elsewhere,[25] it is the position of the methyl group which appears critical to its electron-donor ability as is manifest in the q.s. values.

Temperature dependence. Temperature-dependent Mössbauer data for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_7)]$ is presented in Table 4. The variation of i.s. can be ascribed to the second-order Döppler effect. The variation in q.s. for low-spin Fe^{II} is not so readily accounted for. Molecular motion in iron sandwich complexes in the solid state has been shown to affect q.s. values in surprising ways.[31–34] When tumbling within the lattice is involved, the spectra can be computer-simulated from theory. The temperature dependence we observe is not in accord with such tumbling motion and a different explanation must be sought. Two possible explanations are: (*i*) the asymmetry parameter is changing from 1 to 0 over the temperature range 80–298 K; (*ii*) the cyclohexadienyl ring is spinning increasingly faster as the temperature is raised. The observed effects may be a combination of both of these.

Experimental

NMR Spectra.—Proton NMR spectra were run on JEOL PMX60 and EX90 spectrometers, ^{13}C and ^{13}C DEPT spectra on a JEOL EX 270 instrument.

Iron-57 Mössbauer Spectra.—Mössbauer spectra were recorded using solids or frozen solutions in aluminium holders. The samples were placed in the cryostat under dinitrogen, quenched to 78 K and transferred to a cryostat. The spectrometer (previously described)[35] was calibrated with a natural iron absorber 25 μm thick, which was used as zero for the isomer shift measurements. The spectra were computer fitted.

Syntheses of the Complexes.—$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_{6-n}Me_n)]PF_6$. Standard ligand-exchange reactions were used to make these complexes.[8]

$[Fe(\eta\text{-}C_5H_4Me)(\eta\text{-}C_6H_{6-n}Me_n)]PF_6$.1,1′-Dimethylferrocene (Aldrich Chemical Co.) was used in standard ligand-exchange procedures to produce the desired complexes (Table 5).

$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_{7-n}Me_n)]$ (n = 0–3). The procedure detailed is typical of the synthetic methods used. The complex

$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$ (3.7 g, 0.01 mol) was added to dry ethylene glycol dimethyl ether (20 cm^3) and $NaBH_4$ (2.04 g, 0.054 mol) was added with stirring. The mixture turned dark red within 5 min (n = 1, 10 min; 2, 25 min; 3, overnight). It was then quenched with water (2 cm^3) and extracted with diethyl ether (100 cm^3). Filtration and evaporation gave the product as a red solid (2.07 g, 96%). Other yields: n = 1 (72%, red oil), 2 (86%, red oil).

$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_{7-n}Me_n)]$ (n = 4–6). The complex $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6HMe_5)]PF_6$ (1 g, 2.42 mmol) was dissolved, as before, in ethylene glycol dimethyl ether (20 cm^3); $LiAlH_4$ (0.10 g, 2.42 mmol) was carefully added and in all cases a dark red coloration appeared within 1 h. Work-up as before gave 0.47 g (73%) of a red oil. Other yields: n = 4 (70%, red oil), 6 (41%, red oil).

Although the cyclohexadienyl complexes could be stored at −20 °C for long periods without decomposition, at room temperature they began decomposing after 24 h. Only the more stable complexes were therefore analysed and characterisation was by ^1H and ^{13}C NMR spectroscopy.

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