Electronic Conjugation Pathways in Ferrocenyl Schiff Bases†

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Mössbauer spectroscopic data for a large number of ferrocene Schiff-base compounds have been obtained. The ferrocene entities are used as sensitive probes to understand the electron distribution throughout the molecules. The data are discussed in terms of conjugation interactions and the presence or absence of coplanarity in the substituents on the ferrocene molecules. The crystal structures of ferrocenylimines of formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ with R = H, R′ = CH_2Ph and R = R′ = Ph have been determined and the bonding details, and those in other known structures, are used together with the Mössbauer spectroscopic data to obtain a qualitative understanding of the bonding in these compounds.

Metal–metal interactions in molecules have aroused much interest, particularly when they take place between two or more different metals.[1] In extensive studies on ferrocenyl ligands,[2–7] to examine such interactions we[2–10] and others[11–14] have found these molecules to be very versatile in their bonding and response towards other metals.

A wide variety of substitution patterns are available for the ferrocenyl moiety,[15] and in addition this moiety has the inherent ability to act as a redox centre.[16] Such oxidation of the ferrocenyl group permits electronic 'tuning' of a co-ordinated metal.[17,18] Redox-active ligands[12–14] include those based on ferrocenyl Schiff bases. For communications between two metals an aromatic pathway is useful and the understanding of how it functions a necessity. Ferrocenyl derivatives have attracted attention[4–12,19–25] for applications in many areas within the field of molecular electronics. Such molecules have been investigated for many uses including (*a*) as molecular switches in controlling supermolecular assembly,[21] (*b*) as non-linear optical materials where the ferrocenyl moiety acts as the donor of a donor–π acceptor system (D–π–A), (*c*) as molecular sensors, where the ferrocene properties are used to sense the presence of the metals in another part of the molecule,[5–12] and (*d*) as molecular magnetic materials (ferrocenium salts).[25]

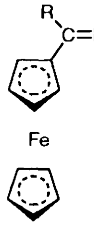
We have previously presented ideas on the bonding in iron sandwich compounds rationalized from a large database of ^{57}Fe Mössbauer spectroscopic data, ^1H and ^{13}C NMR data and crystal structure information.[6,8–10] In this work we present Mössbauer spectroscopic data for a series of closely related ferrocenyl Schiff bases and some metal complexes and discuss aspects of the bonding in these compounds from these data together with crystal structure information and other relevant physical data. We also report the crystal structures of ferrocenyl Schiff bases of the type $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$ with R = H, R′ = CH_2Ph and R = R′ = Ph.

Results and Discussion

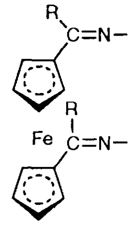
The Mössbauer spectroscopic data for the ferrocenyl Schiff base ligands are presented in Table 1. These data have been listed and will be discussed in terms of the substituents at R and R′ in structures **I**–**III**. We then have four major classes of compounds: (*a*) R = H **6**–**20**; (*b*) R = Me **21**–**26**, **33**, **35**, **36**; (*c*) R = Ph **27**–**32**, **34**; and (*d*) palladium complexes of some of the compounds in classes (*a*)–(*c*) (see Table 2).

It is convenient to discuss their Mössbauer quadrupole splittings relative to more simple ferrocene compounds and to ferrocene itself (**1** in Table 1), $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CN)]$ **2**, $[Fe(\eta^5\text{-}C_5H_4CN)_2]$ **3**, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)]$ **4** and $[Fe(\eta^5\text{-}C_5H_4COMe)_2]$ **5**. We have previously shown that for substituted ferrocenes electron-donating substituents cause an increase in the quadrupole splittings (Δ) relative to ferrocene (Δ ≈2.37 mm s^{-1}), whereas electron-withdrawing substituents cause a decrease in Δ.[8,9]

Inspection of the quadrupole splitting data for the acetylferrocenes **4** and **5** show that relative to ferrocene these are both electron deficient and the acetyl groups are electron withdrawing. Moreover the changes in Δ relative to ferrocene of 0.11 (**4**) and 0.22 mm s^{-1} (**5**) indicate that the effect of two COMe is double that of one COMe group. The cyanoferrocenes **2** and **3**



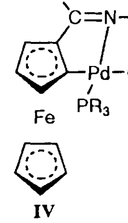
I



II

R–CH_2–CH_2–N=C(H)–R′

III



IV

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Iron-57 Mössbauer spectroscopic parameters (mm s^{-1}) at 78 K for the ferrocenyl Schiff bases studied in this work and relevant literature data

Compound		δ	Δ	Γ^a	Ref.
1 $[Fe(\eta^5\text{-}C_5H_5)_2]$		0.52	2.37(1)		2
2 $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CN)]$		0.50	2.32		26
3 $[Fe(\eta^5\text{-}C_5H_4CN)_2]$		0.55	2.29		26
4 $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)]$		0.54	2.27		26
5 $[Fe(\eta^5\text{-}C_5H_4COMe)_2]$		0.51(1)	2.15(1)	0.13(1)	4, 27
Schiff bases based on structure **I**					
R	R′				
6 H	Ph	0.50(1)	2.28(1)	0.13(1)	This work
7 H	CH_2Ph	0.54(1)	2.29(1)	0.15(1)	This work
8 H	$(CH_2)_2Ph$	0.44	2.34		11[b]
9 H	$N{=}CHC_5H_4Fe(C_5H_5)$	0.52(1)	2.27(1)	0.17(1)	This work
10 H	$(CH_2)_2C_5H_4Fe(C_5H_5)$	0.52(1)	2.35(1)	0.15(1)	This work
11 H	$N{=}CHC_6H_4NO_2\text{-}p$	0.53(1)	2.28(1)		19
12 H	$C_6H_4CN\text{-}p$	0.53(1)	2.31(1)		19
13 H	$C_6H_4NO_2\text{-}p$	0.53(1)	2.25(1)		19
14 H	$C_6H_4F\text{-}p$	0.53(1)	2.31(1)		19
15 H	$C_6H_4Cl\text{-}p$	0.54(1)	2.29(1)		19
16 H	$C_6H_4Br\text{-}p$	0.54(1)	2.31(1)		19
17 H	$C_6H_4NO_2\text{-}m$	0.52(1)	2.27(1)		19
18 H	$NHC_6H_4NO_2\text{-}o$	0.53(1)	2.26(1)		19
19 H	$NHC_6H_4NO_2\text{-}p$	0.53(1)	2.28(1)		19
20 H	NHC_6F_5	0.53(1)	2.33(1)		19
21 Me	Ph	0.52(1)	2.33(1)	0.18(1)	This work
22 Me	$C_6H_4Me\text{-}p$	0.52(1)	2.29(1)	0.15(1)	This work
23 Me	Naphthyl	0.53(1)	2.34(1)	0.13(1)	This work
24 Me	$N{=}CMeC_5H_4Fe(C_5H_5)$	0.51(1)	2.29(1)	0.15(1)	This work
25 Me	$(CH_2)_2C_5H_4Fe(C_5H_5)$	0.51(1)	2.37(1)	0.13(1)	This work
26 Me	OH	0.52(1)	2.30(1)	0.14(1)	This work
27 Ph	Ph	0.51(1)	2.31(1)	0.14(1)	This work
28 Ph	$C_6H_4Me\text{-}o$	0.52(1)	2.27(1)	0.13(1)	This work
29 Ph	$C_6H_4Me\text{-}p$	0.50(1)	2.30(1)	0.15(1)	This work
		0.44(1)	2.26(1)	0.13(1)	This work[b]
30 Ph	$CH_2C_6H_4Me\text{-}o$	0.52(1)	2.29(1)	0.17(1)	This work
31 Ph	$CH_2C_6H_4Cl\text{-}o$	0.54(1)	2.35(1)	0.13(1)	This work
32 Ph	Naphthyl	0.53(1)	2.26(1)	0.15(1)	This work
Bis Schiff bases based on structure **II**					
33 Me	Naphthyl	0.53(1)	2.29(1)	0.14(1)	This work
34 Ph	Ph	0.53(1)	2.24(1)	0.14(1)	This work
35 Me	NHPh	0.53(1)	2.29(1)		4
36 Me	$NHC_5H_4N\text{-}2$	0.53(1)	2.27(1)		4
Schiff bases based on structure **III**					
37 $(C_5H_5)Fe(C_5H_4)$	$C_6H_3Cl_2\text{-}2,6$	0.52(1)	2.41(1)	0.18(1)	This work
38 $(C_5H_5)Fe(C_5H_4)$	$C_6H_2Me_3\text{-}2,4,6$	0.52(1)	2.40(1)	0.20(1)	This work

[a] Half width at half height. [b] Mössbauer data at 297 K.

Table 2 Iron-57 Mössbauer spectroscopic parameters (mm s^{-1}) at 78 K for some cyclopalladated complexes of some of the ferrocenyl Schiff bases studied in this work unless otherwise stated. In all cases the Pd atom is bonded to the ferrocenyl ligands as shown in structure **IV**

Compound			Other ligands				
	R	R′	on Pd	δ	Δ	Γ^a	Ref.
39	H	$(CH_2)_2Ph$	PEt_3, Cl	0.44	2.21		11[b]
40a	H	$(CH_2)_2Ph$	PPh_3, Cl	0.45	2.16		11[b]
40b	H	$(CH_2)_2Ph$	$Ph_2P(CH_2)_2PPh_2$	0.44	2.13		11[b]
41	Me	$C_6H_4Me\text{-}p$	PPh_3, Cl	0.52(1)	2.20(1)	0.13(1)	This work
42	Me	CH_2Ph	PPh_3, Cl	0.54(1)	2.23(1)	0.13(1)	This work
43	Me	$(CH_2)_2Ph$	PPh_3, Cl	0.52(1)	2.27(1)	0.11(1)	This work
44	Ph	Ph	PPh_3, Cl	0.51(1)	2.19(1)	0.13(1)	This work
45	Ph	$C_6H_4Me\text{-}p$	PPh_3, Cl	0.51(1)	2.24(1)	0.13(1)	This work
				0.43(1)	2.24(1)	0.10(1)	This work[b]
46	Ph	$CH_2C_6H_4Me\text{-}o$	PPh_3, Cl	0.52(1)	2.21(1)	0.13(1)	This work
47	Ph	$CH_2C_6H_4Cl\text{-}o$	PPh_3, Cl	0.52(1)	2.22(1)	0.12(1)	This work
48	Ph	Naphthyl	PPh_3, Cl	0.52(1)	2.23(1)	0.13(1)	This work

[a] Half width at half height. [b] Data at 298 K.

are also electron deficient relative to ferrocene, but the CN group is less electron withdrawing than is COMe; again the changes in Δ of 0.05 (**2**) and 0.08 mm s^{-1} (**3**) show that the effects of two CN groups are additive, and roughly double that of one. Most of the Δ values of the Schiff bases in Table 1 (compounds **6**–**38**) are smaller than for ferrocene except for compounds **25**,

37 and **38**, indicating that the C=N core of the Schiff base is electron withdrawing. We have commented on this previously,[19] indeed replacement of a C=O by a C=NR′ group reduces the electron withdrawal at the iron nucleus unless R′ contains a sufficiently strong acceptor group (*i.e.* NO_2 in compounds **13** and **18**).[19]

Compounds **6–20** all contain a proton at position R in structure **I**. Compounds **8** and **10** both show only small changes in Δ relative to ferrocene; both contain CH_2CH_2 units which are electron rich. These units must therefore donate enough electron density to the C=N moiety to offset its need to take so much from the ferrocene moieties, hence the change in Δ is small. For compound **10** the fact that the linewidth is relatively narrow shows that both ferrocene molecules have essentially the same electronic environments, thus the ferrocene in R′ must also donate towards the C=N moiety. This means the CH_2CH_2 unit is both an efficient donor of electron density and due to its polarization a transmitter of electron density (within the confines of these molecules).

Compound **9** is particularly interesting in that the R′ group mirrors the entire other side of the molecules and thus acts as an effective measure for the total electron-withdrawal effect on a ferrocene a C=N can achieve. To cause a greater change in Δ than compound **9** relative to **1**, then the R′ substituent itself must be electron withdrawing. Thus in compounds **11**, **14–16**, **19** and **20** R′ is electron donating and in **13** and **18** it is electron withdrawing. Interestingly in compound **17** R′ is neither electron withdrawing nor donating which clears up our problems in understanding the previous work.[19] In compound **20** R′ is surprisingly electron donating.[19]

The Δ value for compound **6** [2.28(1) mm s^{-1}] is particularly interesting when compared to that of **9**. Clearly the phenyl group donates little or no electron density to the C=N group as there is very little difference in the Δ value between compounds **6** and **9**. Previously we have found that ferrocenyl is only a slightly better donor than is phenyl,[2,3] yet here it would seem to be significantly better. In compound **6**, when both the cyclopentadienyl ring of the ferrocenyl moiety and the phenyl ring are nearly in the same plane [angle between them is 19.0(6)°, Table 3], the latter ring appears to be twisting away to avoid donating more to the C=N group. Thus, although there is significant π-electron density overlapping the entire C_5H_4CN–Ph entity the Δ value means that little is donated from the phenyl group. This implies that the electronic effects of the same two groups in different molecules may differ depending on the other constituent atoms or groups present. (We thank a referee for drawing our attention to this point.)

Compounds **21–26** all have methyl at position R (in **I**). Of these compounds **24** and **25** are directly comparable to **9** and **10** and so when a methyl replaces a hydrogen at R there is a systematic, consistent increase in Δ of ≈0.02 mm s^{-1} (*i.e.* from compound **9** to **24**, and from **10** to **25**). Confirmation of this trend is found in compound **21** for which Δ is 0.05 mm s^{-1} larger than for **6**. Indeed the two ferrocenyl units in compound **25** have Δ values identical to those of ferrocene itself showing that a Me at R and a CH_2CH_2 unit completely satisfy the electron-demanding R′C=N group. Compound **24** can be regarded as the parent for the methyl-substituted compounds and this corresponds to **9** for the hydrogen system. From this we can deduce that R′ in compounds **21** and **23** are all electron donating in this system. Of course these R′ groups are usually thought of as electron withdrawing but here they donate to the CN group allowing the ferrocene to donate less. They may not be exerting their maximum donating effects as they may not be coplanar with the rest of the molecule. Compound **26** has OH at R′ and from the Δ value this is not an electron-donating group compared to R′ in compounds **21** and **23**. Compound **22** is interesting: the R′ group would be expected to donate better here than in **21** and **23**; the fact that it does not suggests a difference in coplanarity of the molecules.

Table 3 Structural data for ferrocenylimines of general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CR{=}NR')]$

	6[a] R = H R′ = Ph	**7** R = H R′ = CH_2Ph	**21**[a] R = Me R′ = Ph	**27** R = Ph R′ = Ph
(*a*) Bond lengths (Å)				
C(10)–C(11)	1.455(8)	1.464(7)	1.494(6)	1.448(10)
C(11)–C(12)	—	—	1.502(6)	1.516(9)
C(11)–N	1.251(8)	1.262(7)	1.269(5)	1.308(9)
N–C(18)	1.347(8)	—	1.413(5)	1.398(9)
Fe–C (average)	2.058(5)	2.035(6)	2.032(5)	2.069(6)
(*b*) Bond angles (°)				
C(10)–C(11)–N	125.4(6)	122.8(5)	119.0(3)	117.5(6)
C(12)–C(11)–N	—	124.8(3)	123.4(6)	123.3(6)[b]
C(18)–N–C(11)	121.0(6)	116.8(5)[c]	122.5(3)	122.4(6)
(*c*) Angles (°) between planes[d]				
A and B	1.7(6)	1.9(3)	1.6(3)	1.7(6)
B and C	19.0(6)	99.6(3)	93.9(3)	73.4(6)
B and D	7.06(6)	18.8(3)	8.3(3)	11.4(6)

Other relevant structural data. (1) For the ferrocenylimines with R = Me and Ph the C(12) atom is out of the plane defined by the substituted C_5H_4 ring. The magnitudes of the deviations are 0.294(5) and 0.1842(6) Å towards the iron atom, respectively. (2) For the compound with R = Ph the orientation of this phenyl group is such that its plane forms an angle of 55.8(6)° with the plane defined by the atoms C(6)–C(10) of the C_5H_4 ring. (3) The conformation of the two rings of the ferrocene moiety is nearly eclipsed. The average values for the twist angle (defined as in ref. 28) are −9.3(6) (R = H), 0.05 (Me) and 2.8(6)° (Ph).

[a] Full details of the crystal structure will be published elsewhere. [b] In this case the C(12) atom represents the *ipso* C atom of the phenyl ring. [c] In this case the C(18) atom represents that in between the iminic nitrogen and the Ph. [d] Planes: A, defined by atoms C(1)–C(5); B, C(6)–C(10); C, C(18)–C(23), phenyl substituent; D, C(10), C(11) and N.

In compounds **27–32** the phenyl group (R) cannot be coplanar with the C_5H_5 ring of the ferrocenyl unit (see **I**). This is apparent in the structure of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}CPh{=}NPh)]$. A comparison of the Δ values for this group of compounds with those of the methyl and hydrogen analogues shows that the phenyl group, when it is not coplanar, is similar or slightly less electron donating than is hydrogen. This can be seen by comparing compounds **27–29** with **21** and **22** and with the hydrogen compounds. We thus suggest that when R = Ph then $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CRC{=}N\text{–})$ has a Δ value of around 2.26–2.27 mm s^{-1}. In this context then R′ is overall electron donating in compounds **30** and **31** and electron withdrawing in **32**. The latter finding is in contrast to the situation in compound **23**, but can be explained if it is coplanar with the $C_5H_4C{=}N$– unit in compound **32** but out of the plane in **23**. Compounds **33–36** all are bis Schiff bases and are like **II** in structure. Compound **33** shows a change in Δ of 0.08 mm s^{-1} relative to ferrocene, which is nearly double that of **27**. Similarly compound **34** has a change in Δ around twice that of **23**. This additivity of electron-withdrawing groups was found in the simpler compounds **2** and **3**, as well as **4** and **5** (see comments earlier in the Discussion). This argument for compounds **32** and **33** assumes the angles of the R′ group to the $C_5H_4C{=}N$ plane are the same as those in **27** and **23**. If this assumption holds, then a value for Δ for a 'parent' of this class of material where R = Me would be 2.19 mm s^{-1}. From this value R′ in compounds **35** and **36** is electron donating.

Compounds **37** and **38** are of the type shown in **III**, as both have Δ values in excess of that of ferrocene. Overall, they are electron-rich relative to ferrocene. This means that the R′ substituents are electron donating and along with the CH_2CH_2 are able to satisfy the needs of the N=CH unit leaving an excess of electron density to enhance the Δ of the ferrocenyl entities.

Thus the results for the compounds in Table 1 demonstrate that both ends of the Schiff-base molecules respond to the nature of the electron distribution in the rest of the molecule.

Evidence in keeping with this and in support of our interpretation of the Mössbauer spectroscopic data can be found in the known crystal structures.

Crystal Structure Data.—The structure of compound **7** is shown in Fig. 1 and the important bond lengths and angles are presented in Table 3. The cyclopentadienyl rings are as expected nearly parallel, and the angle between the C(6)–C(10) ring and the C(11)–N bond is 7.0(6)°.

The structure of compound **27** is shown in Fig. 2, again the important bond lengths and angles are presented in Table 3 and other relevant structural information is given in the footnotes to the Table. The cyclopentadienyl rings are almost parallel, and the angle between the C(6)–C(10) ring and the C(11)–N bond is 11.4(6)°. Thus the C–N bond lies just out of the cyclopentadienyl plane, but the phenyl ring bonding to N is 73.4(6)° out of that plane. This is very different to the angle the phenyl groups in compounds **11**[19] and **6** (Table 3) make to the cyclopentadienyl plane and illustrates how this angle and hence the π-electron overlap alters from molecule to molecule. This latter point is also apparent in the change in N–C(18) bond lengths in Table 3 and in the N–C [1.272(7) Å] bond length in ref. 19. Thus the phenyl ring is more conjugated to the cyclopentadienyl ring in compounds **6** and **11** than in **21**, **27** and in the *p*-nitrophenyl compound **13**, and this observation from the crystal structures is consistent with the interpretation of the Mössbauer spectroscopic data reported herein. Also the N–C(18) bond length in **21**, **27** and in the *p*-nitrophenyl complex[7] range between 1.398(9) and 1.418(5) Å.[7] This indicates that they are much less conjugated than in compound **6** where the corresponding length is 1.347(8) Å.

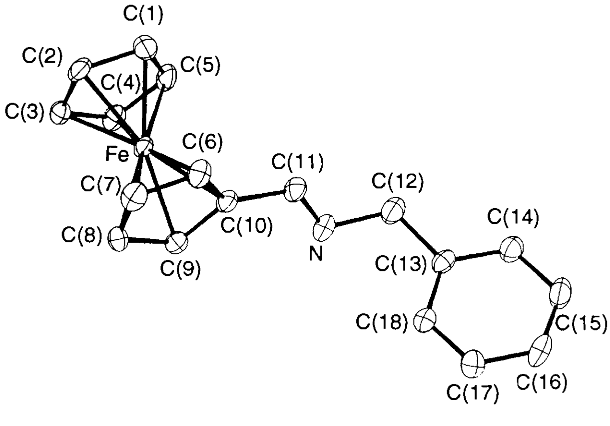

Fig. 1 Molecular structure and atom labelling scheme for [Fe(η^5-C_5H_5)(η^5-$C_5H_4CH{=}NCH_2Ph$)] **7**

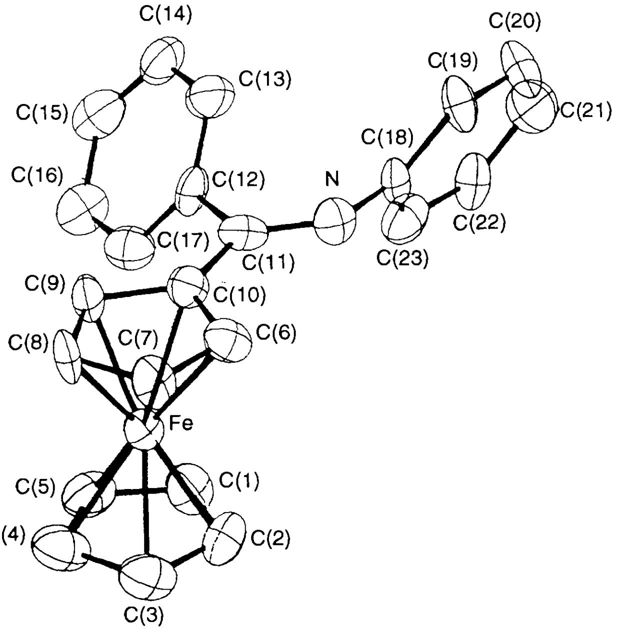

Fig. 2 Molecular structure and atom labelling scheme for [Fe(η^5-C_5H_5)(η^5-$C_5H_4CPh{=}NPh$)] **27**

Structural Information relevant to Interpretation of Mössbauer Spectroscopic Data.—Inspection of the crystal structure data in Tables 3 and 4 and those of compound **11**[19] is illuminating. The C(11)–N bond in Fig. 1 is only 1.251(8) Å in the R = H complex **6** (Table 3), much shorter than the others in the Table and those of refs. 7 and 19. This is the structure that has the $C_5H_4C{=}NPh$ unit closest to the plane (BCD) so the conjugation goes straight across the molecule. In the R = Me structure **21** (Table 3) the C(10)–C(11), C(11)–N and N–C(18) bond lengths total 0.02 Å greater than the same three bonds in the R = Ph structure **27**. This reflects the greater donating power of Me over an out-of-plane phenyl moiety and is consistent with the larger Δ value found for the former molecule. In both these molecules the C ring is far out of the BD plane so the conjugation does not include the C ring.

These facts illustrate that the R′ ring may often be out of the BD plane. Indeed compound **11**[19] is nearly planar and is one of only two compounds in the group that is a true D–π–A type molecule by formulation, though the other complex of this type (**13**) is not at all planar (the $C_6H_4NO_2$ group is ≈66° from the cyclopentadienyl plane[7]) and any conduction is *via* a σ- rather than π-bonding network. The fact that the R′ ring may differ in its orientation from molecule to molecule may explain why we could not easily plot the Δ values in Table 1 against any of the Hammett substituent constants[29] to obtain a linear plot. We could do this for simpler ferrocenyl derivatives.[10]

The cyclopalladated complexes, shown in **IV**, could be easily visualized as arising from the interchange of a σ(C sp^2, ferrocene H) bond by a σ{Pd[(PR$_3$)Cl]-C sp^2, ferrocene}. As a first approach to the elucidation of the influence of such interchange upon the iron environment, the Mössbauer spectra of a few derivatives were recorded. Comparison of data shown in Tables 1 and 2 reveals that the Δ value for the cyclometallated complexes is clearly smaller than those obtained for the corresponding free ligands.

Compounds **39**, **40a** and **40b** all show changes in Δ (δΔ) relative to **7** of Table 1. For these δΔ is -0.13 mm s^{-1} or larger.

Table 4 Structural data for cyclopalladated compounds of general formula [Pd{(η^5-C_5H_5)Fe(η^5-$C_5H_3CR{=}NR'$)}Cl(PX_3)]

	42[a] R = Me R′ = $(CH_2)_2Ph$ PX_3 = PPh_3	**44**[a] R = Ph R′ = Ph PX_3 = PPh_3	**39**[b] R = H R′ = $(CH_2)_2Ph$ PX_3 = PEt_3
(*a*) Bond lengths (Å)			
C(10)–C(11)	1.418(11)	1.441(9)	1.467(9)
C(11)–C(12)	1.510(13)	1.480(8)	—
C(11)–N	1.305(9)	1.296(8)	1.280(8)
N–C(18)	1.458(10)	1.448(9)	1.456(7)
Fe–C (average)	2.044(8)	2.037(7)	2.055(8)
(*b*) Bond angles (°)			
C(10)–C(11)–N	114.7(7)	113.4(7)	117.0(7)
C(12)–C(11)–N	123.9(7)	124.3(7)	—
C(18)–N–C(11)	121.9(7)	119.5(5)	120.0(7)
(*c*) Angles (°) between planes[c]			
A and B	1.2(7)	3.74(7)	1.8(7)
B and C	—	79.7(7)	98.0(7)
C and D	9.2(7)	4.6(7)	7.1(7)

[a] This structure will be published in full elsewhere. [b] Data from ref. 11. [c] Planes: A, defined by atoms C(1)–C(5); B, C(6)–C(10); C, the phenyl group on the R′ moiety; D, C(10), C(11) and N.

The extent of the difference seems to be dependent on the nature of the other ligands on the Pd atom. The more electron withdrawing these ligands are the larger is the change in Δ. Compounds **41**–**48** all have PPh_3 and Cl as the other ligands on Pd in common with **40a**, so these are all internally comparable. Of these compounds **40**, **41**and **44**–**48** all show Δ values smaller than those of the unmetallated ferrocenyl Schiff bases. Compounds **40**, **46** and **47** all contain CH_2 groups (electron donating) between N and the R′ (Ph) ring. In the case of **40** the change in Δ is nearly twice those of **46** and **47** and may reflect the fact that this compound contains two CH_2 groups shielding the ferrocene (η^5-C_5H_4)Fe(η^5-C_5H_4) entity from the C_6H_5 group. This compound then shows the pure electron pulling power of the $Pd(PPh_3)Cl$ entity. Thus compounds **41** and **44**–**48** have this entity pulling, and the R′ group as well. The parent ligands **22**, **27**, **29**, **30**, **31** and **32** of these compounds can be ordered, **31** > **27** > **29** > **30** = **22** > **32** in the magnitude of their Δ values before bonding to $Pd(PPh_3)Cl$. The order of the Δ values for the bonding to $Pd(PPh_3)Cl$ is **45** > **48** > **47** > **46** > **44** ≈ **41** which is not compatible with just binding the group alone, but could be understood if conformation changes take place on binding Pd. Clearly there is only slight evidence for such changes in Tables 3 and 4 for the R = R′ = Ph structures (see for example the angles between planes B and C and B and D). The question that must now be addressed is: how do the $Pd(PPh_3)Cl$ units act as electron-pulling entities in these compounds?

There are three possible answers: (1) directly from the cyclopentadienyl ring, (2) *via* the N of the C=N unit or (3) a combination of (1) and (2). A partial answer for this can be found by considering aspects of structures of this type (Table 4). The C(11)–N bonds are longer in three of the structures than those in Table 3. Thus the addition of the $Pd(PPh_3)Cl$ or $Pd(PEt_3)Cl$ lengthens the C(11)–N bond, though this is not true for the R = Ph complex. However, this complex shows a longer overall C(10)–C(11)–N distance 4.185 Å (compare 4.176 Å). In addition, all three palladium structures in Table 4 have significantly longer N–C(18) bond lengths than those in Table 3, again suggesting electron depletion at N. Thus there is evidence of direct electron donation from N to Pd supporting answer (2) above, but we cannot rule out answer (3). The angle between planes B and C also changes in the palladium structure. Thus there are crystallographic data which can be interpreted as evidence that the $Pd(PX_3)Cl$ groups (X = Ph or Et) are electron withdrawing.

Table 5 Crystallographic data and details of the refinements for compounds **27** and **7***

	27	**7**
Formula	$C_{23}H_{19}FeN$	$C_{18}H_{16}FeN$
M	365.257	302.18
Crystal size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
a/Å	13.367(4)	10.481(2)
b/Å	11.100(2)	18.293(3)
c/Å	11.584(3)	7.426(1)
β/°	90.40(3)	103.92(1)
U/Å^3	1719(1)	1382.0(7)
D_c/g cm^{-3}	1.411	1.452
F(000)	760.0	628.0
μ(Mo-Kα)/cm^{-1}	9.05	11.07
No. of collected reflections	3535	2649
No. of reflections with $I \geqslant 2.5\sigma(I)$	2494	1727
Weighting scheme (k)	0.008	0.001
No. of hydrogens	17 located and 2 computed	All located
R	0.066	0.066
R'	0.069	0.076
No. of refined parameters	278	233
Maximum and minimum peaks/e Å^{-3}	+0.4, −0.3	+0.3, −0.3

* Details in common: monoclinic, space group $P2_1/c$; $\alpha = \gamma = 90°$; $Z = 4$; λ(Mo-Kα) = 0.710 69 Å; θ 2–30°; maximum shift/e.s.d. = 0.06.

Table 6 Final atomic coordinates (× 10^5) of complex **7**

Atom	X/a	Y/b	Z/c
Fe	20 459(7)	10 635(4)	7 928(10)
N	4 683(4)	1 541(2)	−2 072(7)
C(1)	492(5)	1 533(3)	1 411(8)
C(2)	1 268(6)	1 210(3)	3 002(8)
C(3)	2 467(6)	1 545(3)	3 337(8)
C(4)	2 428(6)	2 073(3)	1 954(9)
C(5)	1 211(5)	2 062(3)	760(9)
C(6)	3 309(6)	248(3)	739(9)
C(7)	2 086(6)	−24(3)	332(9)
C(8)	1 359(6)	329(3)	−1 262(9)
C(9)	2 183(5)	842(3)	−1 848(8)
C(10)	3 396(5)	799(3)	−590(7)
C(11)	4 539(5)	1 217(3)	−636(8)
C(12)	5 882(6)	1 922(4)	−1 926(10)
C(13)	6 648(5)	1 601(3)	−3 178(7)
C(14)	7 857(6)	1 861(3)	−3 063(9)
C(15)	8 613(6)	1 579(4)	−4 148(11)
C(16)	8 141(7)	1 036(4)	−5 392(10)
C(17)	6 936(6)	776(4)	−5 540(10)
C(18)	6 196(5)	1 056(4)	−4 451(8)

Conclusion

An interesting point that comes out of this work is that the C=N group itself is an acceptor, thus molecules like **10** of Table 1 are not D–π–A type but are in fact D–π–D where the π group is the acceptor. Of the 38 compounds in Table 1 only compound **11** is truly an D–π–A type. However **13** is D–σ–A in type.

Experimental

Crystal Structure Determination and Refinement.—Prismatic crystals of compounds **7** and **27** (sizes in Table 5) were selected and mounted on a Philips PW-110 diffractometer. In both cases, unit-cell parameters were determined from automatic centring of 25 reflections in the range 8 ⩽ θ ⩽ 16°, and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-Kα radiation using the ω–2θ scan technique. The number of reflections collected and the ranges are listed in Table 5. Three reflections were measured every 2 h as orientation and intensity control and no significant variations were observed in any of the cases. Lorentz polarization corrections, but not absorption, were made.

The structures were solved by the Patterson method using the SHELXS-program[30] and refined by full-matrix least squares with the SHELX 76 program.[31] The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + k|F_o|^2]^{-1}$. Values of f, f' and f'' were taken from ref. 32. The number of hydrogen atoms located, the final R and R' values, the number of refined parameters for each structure, as well as the maximum and minimum peaks in the final difference syntheses are also given in Table 5. Final atomic coordinates are given in Tables 6 and 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Preparation of Complexes.—The complexes reported in this work, **6**–**48**, were prepared by the methods described in the literature.[33–40] Specific references are listed in Table 8.

Iron-57 Mössbauer Spectra.—Mössbauer spectra were recorded using solid samples in aluminium holders. The

Table 7 Final atomic coordinates (× 10^5) of complex **27**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	12 840(7)	9 397(9)	−17 939(9)
N	1 788(5)	4 341(5)	−993(6)
C(1)	1 671(7)	−879(9)	−1 877(9)
C(2)	2 516(6)	−160(8)	−1 758(8)
C(3)	2 483(6)	547(8)	−692(8)
C(4)	1 520(7)	240(9)	−216(7)
C(5)	1 055(7)	−610(7)	−840(9)
C(6)	391(5)	2 434(7)	−1 638(7)
C(7)	−112(7)	1 547(8)	−2 268(8)
C(8)	453(6)	1 250(7)	−3 294(8)
C(9)	1 332(6)	1 986(6)	−3 257(6)
C(10)	1 324(5)	2 741(6)	−2 225(6)
C(11)	2 048(6)	3 628(7)	−1 839(7)
C(12)	3 040(5)	3 725(7)	−2 460(6)
C(13)	3 616(7)	2 698(8)	−2 682(9)
C(14)	4 515(6)	2 801(8)	−3 286(7)
C(15)	4 838(7)	3 923(9)	−3 654(8)
C(16)	4 311(7)	4 931(9)	−3 394(8)
C(17)	3 359(6)	4 850(7)	−2 838(7)
C(18)	2 468(5)	5 108(7)	−440(6)
C(19)	3 362(6)	4 749(8)	59(7)
C(20)	3 979(7)	5 536(9)	672(8)
C(21)	3 690(8)	6 761(9)	796(9)
C(22)	2 804(8)	7 118(9)	286(10)
C(23)	2 158(7)	6 367(7)	−342(8)

Table 8 Origin of sample preparations

Compound	Ref.
6	33, 40
7, **8**	11
9–**24**	36, 37
10, **25**, **44**–**48**	40
21	34
22, **23**, **41**–**43**	39
26	38
27–**32**	33, 40

samples were placed in the cryostat under dinitrogen, after quenching to 78 K or experiments were run at 298 K. The spectrometer (previously described)[41] 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.

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