Iron-57 Mössbauer Spectroscopic Studies on 1,1'-Bis(diphenylphosphino)-ferrocene Metal Complexes. The Influence of Metal-ion Geometry on the Hyperfine Interactions†

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^{57}Fe Mössbauer spectroscopic data for a series of 1,1'-bis(diphenylphosphino)ferrocene metal complexes $[Fe(\eta\text{-}C_5H_4PPh_2)_2MX_n]$ (X = halide or CO, *n* = 2 or 4) are reported. An approximately linear correlation was found between the isomer shift (δ) and the quadrupole splitting (Δ). Moreover, complexes of like co-ordination geometry fell within exclusive domains on a plot of δ *vs.* Δ. The results of an analysis of available crystal-structure data are consistent with these observations. The Mössbauer hyperfine interactions are discussed in relation to the geometry of the co-ordinated metal.

Organometallic ligands provide a convenient route to producing bimetallic complexes. Ferrocenyl ligands, particularly the ferrocenylphosphines, have received considerable investigation in this respect.[1] 1,1'-Bis(diphenylphosphino)ferrocene complexes have been widely studied, due to their activity as catalysts in Grignard cross-coupling reactions,[1–3] hydrogenation reactions,[1–3] and more recently for their possible anti-tumour activity.[4] A large number of *X*-ray structures of such complexes[3–10] have been reported as well as work on their physiochemical properties, including ^{57}Fe Mössbauer data.[11]

Here we report ^{57}Fe Mössbauer data for a series of these complexes together with an analysis of the known structural features. The results of this analysis enable the Mössbauer hyperfine interactions to be rationalised.

Experimental

All compounds were prepared by literature methods.[12] Mössbauer data were collected at 80 K unless otherwise stated, on a spectrometer previously described[13] and isomer shift δ is referred to natural iron at room temperature as zero shift. Crystal-structure data were obtained from the Cambridge Crystallographic database. Data thus derived do not include errors on the calculated distances. However, all structures have very good *R* factors (see Table 2) and so high confidence can be placed in the differences between these distances.

Results and Discussion

The ^{57}Fe Mössbauer data for $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ and the metal complexes studied are presented in Table 1 together with some recent literature results.[11] Unfortunately there are discrepancies in the Δ values for some of our complexes and in this report,[11] particularly the value for ferrocene itself at 80 K (2.42 compared to the more typical value of 2.37 mm s^{-1})[14] is large. Also in this report the Δ value for the platinum complex is far more temperature dependent between 80 K and room temperature (δΔ = 0.06 mm s^{-1}) than for any of the other complexes. Furthermore, the value of 2.29 mm s^{-1} at 80 K is higher than would have been expected from the results and discussion presented here. The room-temperature value is more in keeping with our values and it is this value that is used in the discussion. There is close agreement, however, between our results and those reported by Corain *et al.*[11] for the complexes of Co and Ni.

Table 1. ^{57}Fe Mössbauer data (mm s^{-1}) for $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ and its metal complexes[a]

	δ	Δ	$\Gamma_{\frac{1}{2}}$
$[Fe(\eta\text{-}C_5H_4PPh_2)_2]$	0.53(1)	2.30(1)	0.15(1)
$FeCl_2$	0.56(1)	2.29(1)	0.16(1)
	0.70(1)	2.79(1)	0.17(1)
$CoCl_2$	0.56(1)	2.35(1)	0.20(1)
$NiCl_2$	0.57(1)	2.29(1)	0.16(1)
$NiBr_2$	0.55(1)	2.31(1)	0.18(1)
NiI_2	0.58(1)	2.33(1)	0.15(1)
$Cr(CO)_4$	0.52(1)	2.23(1)	0.18(1)
$W(CO)_4$	0.54(1)	2.23(1)	0.15(1)
$Mo(CO)_4$	0.52(1)	2.27(1)	0.16(1)
$PdCl_2$	0.50(1)	2.14(1)	0.19(1)
$CoCl_2$[b]	0.55	2.34	
$NiCl_2$[b]	0.54	2.29	
$PdCl_2$[b]	0.49	2.21	
$PtCl_2$[b]	0.50	2.29	
	0.41[c]	2.23[c]	
$ZnCl_2$[b]	0.55	2.35	
$CdCl_2$[b]	0.51	2.27	
$HgCl_2$[b]	0.56	2.36	

[a] Data measured at 80 K unless otherwise stated. [b] Data from ref. 11. [c] Data measured at room temperature.

The compound $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ itself exhibits a reduced Δ value compared to ferrocene (2.30, *cf.* 2.37 mm s^{-1}) in keeping with the results for other ferrocenylphosphines which we have recently reported and discussed.[14] On complexation the electronic environment of the ferrocenyl iron is perturbed, and new values for δ and Δ are observed. The ranges of δ and Δ for the complexes studied here are 0.50—0.58 and 2.14—2.35 mm s^{-1} respectively. The former range spans the δ values reported by Corain *et al.*[11] and only one of their complexes gives a Δ value outside of our range. This is the mercury complex which has a splitting of 2.36 mm s^{-1}.

At this point it is worthwhile reviewing the factors that may influence the Mössbauer parameters in ferrocenyl derivatives: (1) direct metal-to-iron bonding or interaction; (2) substituent effects; (3) ring-tilt or variations in iron-to-ring distance; and (4) ring conformation. Although it is convenient to isolate these

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factors for discussion, we do not imply that they are necessarily independent.

(1) *Direct Metal-to-iron Bonding Interactions.*—Morrison and Hendrickson[15] first reported the reaction of ferrocene with mercury(II) halides, proposing a structure involving a direct iron–mercury bond. Evidence in support of this structure for ferrocene and ferrocenophanes came from Mössbauer spectroscopy, very large Δ values, *i.e.* > 3.0 mm s^{-1}, being observed.[16,17] An analogous case for interaction at the ferrocenyl iron causing increases in Δ (and also decreases in δ) has been reported for frozen solutions of ferrocene with CF_3SO_3H and also $HAlCl_4$.[18] As can be seen from the data in Table 1 there are no Δ values approaching 3.0 mm s^{-1} and this confirms there to be no direct metal-to-iron bonding in these complexes in agreement with the known crystal structures.[3–10] A typical iron-to-metal distance of ≈4.3 Å is found in the structure of $Fe(\eta\text{-}C_5H_4PPh_2)_2PtCl_2]$.[8] The $[Fe(\eta\text{-}C_5H_4PPh_2)_2HgCl_2]$ complex with $\Delta = 2.36$ mm s^{-1} obviously is in keeping with Hg–P bonds and no Hg–Fe interactions.

(2) *Substituent Effects.*—The variations in δ and Δ for a series of substituted ferrocene derivatives are relatively small and δ is often assumed to be constant.[19] The relatively small changes in Δ values is a consequence of the fact that the electric field gradient at the nucleus arises largely from the π-bonded ligands. These are not greatly influenced by changes in the σ bonding of the ring substituents. Despite this, variations of Δ with the nature of the substituent group do occur. We have reported[20] the correlation of Hammett-type substituent constants and oxidation potentials with Δ for a series of mono- and di-substituted ferrocenes. However, these relationships are disrupted whenever ring tilt is present in the structure.

(3) *The Effect of Ring Tilt on the Mössbauer Parameters.*—The effect of ring tilt in ferrocene derivatives on the hyperfine interactions as displayed in the Mössbauer spectra has been investigated by Hillman and co-workers.[21–25] They showed there to be a linear correlation between the iron-to-ring distances and the observed change in δ and Δ, with decreases in both with decreasing distance. They concluded that the ring tilt was important only in that it caused this distance to change. This in turn is dependent on the type of ring tilt exhibited (the reader is directed to ref. 25 for a discussion).

Trautwein *et al*[26] have calculated Mössbauer parameters for some bridged ferrocene complexes. They found a ring tilt of 6° to have a negligible effect on the parameters, concluding that the tilting brings some carbons closer to the iron atom and others further away, averaging to an overall effect of zero. However, despite the impressive agreement between calculated and observed Mössbauer parameters, the increasing availability of crystallographic data for bridged ferrocene compounds shows that even for singularly bridged ferrocenes a simple description of tilting is difficult.

(4) *Ring Conformation.*—Trautwein *et al.*[26] calculated the Δ values for the fully eclipsed and fully staggered conformations of ferrocene and found that they may differ by ≈0.04 mm s^{-1}

Of the four factors listed above we have eliminated direct metal–iron bonding as a possible influence on the hyperfine interactions in the complexes studied here.

We now turn to simple substituent effects in these compounds. The substituent groups may be classified in two ways: (*i*) as the PPh_2 groups alone (although this would not offer an understanding of the differences observed) or (*ii*) the entire group including the metal atom and its ligands. Hammett constants are not available for the substituent groups in this series of compounds. However, crude estimates of group electronegativity (*i.e.* the sum of the electronegativities of the component elements) can be made. Where the metal ions had the same co-ordinating groups (P_2Cl_2), as in the cases of the tetrahedral and square-planar complexes, only the metal electronegativities were considered. There was no general correlation with the crude estimates of group electronegativity and Δ. For instance, the later transition metals, platinum and palladium, have lower electronegativities than the first-row transition metals like iron, nickel, and cobalt. In these complexes all the metals are bound to two P and two Cl atoms and yet the platinum and palladium complexes show the lowest δ and Δ values. Interestingly, for the $[Fe(\eta\text{-}C_5H_4PPh_2)_2NiX_2]$ complexes, where X = Cl, Br, or I, Δ decreased with increasing electronegativity in X, as may be expected. Overall, there was no apparent correlation between the Δ and electronegativity. Thus simple substituent effects alone cannot explain the observed changes in the Mössbauer parameters so we now turn to a discussion of structure to assess the roles played by the final two factors.

Structural Analysis.—Table 2 lists structural parameters for $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ and some of its metal complexes.

The structures of $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ ligated to metals that have been determined to date include examples of four different metal co-ordination geometries, square-planar (Pt^{II} and Pd^{II}),[6,7,10] octahedral (Mo^0 and Re^I),[6,9] tetrahedral (Ni^{II}),[5,6] and linear (Au^I).[4] The last configuration represents a unique case as each P is bound to a different metal ion and must be considered separately. The fact that $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ can bind to and satisfy such different co-ordination geometries indicates its versatility and flexibility as a ligand.

Although ring tilt is present in all the structures of $[Fe(\eta\text{-}C_5H_4PPh_2)_2]$ bound to metal ions in a bidentate manner, it is always small. The largest reported is that of the palladium complex which has a tilt of 6.2° which is only just outside the 6° range reported by Trautwein *et al.*[26] as having a negligible effect on the quadrupole splitting.

The magnitude of the ring tilt is not correlated to the Mössbauer parameters and so ring tilt *per se* is not the important factor influencing the Mössbauer parameters.

In the $PdCl_2$[6] complex the cyclopentadienyl rings are staggered by a rotation of 39.5° from a fully eclipsed conformation and tilted by 6.2°. The inter-ring spacing towards the substituent phosphines is decreased. This compares well with the similar square-planar $PtCl_2$[8] structure in which the rings are staggered, tilted by 5.9° and the spacing between the phosphorus atoms is also decreased.

By contrast, the octahedral geometry of Mo in the $Mo(CO)_4$ complex[6] produces different distortions to the ferrocenyl group. Again the rings are staggered (a rotation of 41.9° from an eclipsed geometry) and the inter-ring spacing decreases towards the phosphine groups, but here the ring tilt is reduced at 2.2°. Very recently Wrighton and co-workers[9] have reported the crystal structure of $[Fe(\eta\text{-}C_5H_4PPh_2)_2Re(CO)_3Cl]$ which also exhibits octahedral co-ordination around the Re atom. Again the cyclopentadienyl rings are staggered (15° from eclipsed) and the two rings are tilted with respect to each other, being 3° from parallel.

The tetrahedral site in the $NiBr_2$ complex[6] is distorted from the ideal P–Ni–P angle of 109.5 to 102.5°. However, the same angle in the $NiCl_2$ complex[5] is much closer to the ideal angle at 105°. This difference suggests that there are steric repulsions between the phenyl groups and the bromine atoms in the former complex. In this structure the cyclopentadienyl rings are 6.5° from an eclipsed configuration and the ring tilt is 6.2°. The inter-ring spacing towards the phosphine substituent is increased. Likewise similar distortions of the ferrocenyl moiety exist in the case of the $NiCl_2$ complex (see Table 2).

Table 2. Selected bond distances (Å) and tilt angles (°) for [Fe(η-$C_5H_4PPh_2)_2$] and some of its metal complexes[a]

	C_{cp}–P	C_{Ph}–P	Fe–P	Fe–ring	Conformation[b]	Tilt[b]	Ref.	*R* factor
[Fe(η-$C_5H_4PPh_2)_2$]	1.819(5)	1.835(4)	3.46	—	Staggered	0	5	0.043
$PdCl_2$(CH_2Cl_2 solvate)	1.809	1.827 1.827	3.378	1.638	Staggered (39.5°)	6.2	6	0.029
	1.805	1.825 1.809	3.352	1.634				
$PdCl_2$($CHCl_3$ solvate)	1.794	1.822 1.827	3.379	1.629	Staggered (39.5°)	6.2	7	0.036
	1.804	1.832 1.825	3.375	1.632				
$PtCl_2$[b]	—	—	—	—	Staggered	5.9	8	0.052
$NiBr_2$	1.810	1.816 1.809	3.499	1.660	6.5° from eclipsed	6.2	6	0.069
	1.831	1.837 1.808	3.417	1.672				
$NiCl_2$[b]	1.836(4)	1.842(4) 1.832(4)		1.651(3)	9° from eclipsed	4.5	5	0.043
	1.822(4)	1.816(5) 1.829(5)		1.654(3)				
$Mo(CO)_4$	1.821	1.841 1.837	3.432	1.647	Staggered (41.9°)	2.2	6	0.033
	1.805	1.838 1.834	3.395	1.646				
$Re(CO)_3Cl$[b]	—	—	—	1.654 1.646	Staggered (14.8°)	—	9	0.032
[{Fe(η-$C_5H_4PPh_2)_2$PtO}$_2$]	1.813	1.797 1.851	3.350	1.645	Staggered	—	10	0.064
	1.773	1.823 1.815	3.299	1.638				
$(AuCl)_2$[b] (Molecule A)	1.79(1)	1.81(1) 1.82(1)			Staggered		4	0.042
(Molecule B)	1.81(1) 1.79(1)	1.82(1) 1.82(1) 1.82(1)			Staggered			

[a] All data derived from the Cambridge Crystallographic database unless otherwise stated. [b] Data from the original reference.

A comparison of the C–P bond lengths (in an attempt to categorise the different types of co-ordination) is inconclusive, though Fe–P and the Fe–ring distances are more revealing. In the square-planar complexes (*i.e.* of Pt and Pd) these distances are shortest. Although few data are available, the octahedral complexes of Mo and Re have distances intermediate between those of the square-planar and tetrahedral complexes.

Thus it is evident from the above discussion that each type of co-ordination geometry produces specific demands on the ligand to adopt a particular geometry.

In the [Fe(η-$C_5H_4PPh_2)_2$] complexes the iron-to-ring distances and the conformations of the two cyclopentadienyl rings with respect to each other (*i.e.* the extent to which they are staggered or eclipsed) also differ depending on the metal ion bound. The iron-to-ring distances vary slightly (from 1.629 Å in the $PdCl_2$ complex to 1.672 Å in the $NiBr_2$ complex). The shortest distances [range 1.629—1.638, average 1.633, standard deviation (s.d.) 0.003 Å] are found in the square-planar complexes of palladium, which also exhibit the lowest δ and Δ values. (The [{Fe(η-$C_5H_4PPh_2)_2$PtO}$_2$] complex[10] was excluded since this has a distorted square-planar geometry.) The next shortest distances (1.646—1.654, average 1.648, s.d. 0.004 Å) are found in the octahedral complexes. These have intermediate Mössbauer parameters. Both the largest distances (1.651—1.672, average 1.659, s.d. 0.009 Å) and values of δ and Δ occur in the tetrahedral complexes. These findings are in keeping with the results and ideas of Hillman and Nagy (see earlier).[25]

So it appears that the metal co-ordination geometry dominates, perhaps to the point of dictation, the structure of the ligand and this as a consequence influences the electronic environment of the ferrocenyl-iron atom. This is manifested in the Mössbauer data.

In the tetrahedral complexes studied here Δ is in the range 2.29—2.35 mm s^{-1} and δ in the range 0.55—0.58 mm s^{-1}. Octahedral complexes have Δ 2.23—2.27 mm s^{-1} with δ 0.52—0.54 mm s^{-1}. The remaining square-planar $PdCl_2$ complex has $\delta = 0.50$ mm s^{-1} and $\Delta = 2.14$ mm s^{-1}. A plot of δ *vs.* Δ for our complexes is reasonably linear [$n = 9$, $r = 0.84$, slope 2.02(3)] but more apparent is the grouping of complexes of like metal–iron co-ordination. A similar plot of the data of Corain *et al.*[11] yields a better linear correlation [$n = 7$, $r = 0.97$, slope 2.08(1)] but contains fewer data. The relative lack of data in the latter work makes the grouping of complexes of like co-ordination less obvious. A plot of all the data again gives a reasonably straight line [$n = 15$, $r = 0.76$, slope 1.82(3)] and this is shown in the Figure. This plot again clearly shows the grouping of complexes exhibiting the same co-ordination geometry. The grouping for tetrahedral complexes (mainly first-row transition-metal halide complexes) has the highest δ and Δ values and also includes the mercury complex.[11] It is suggested here, from the Mössbauer data, that the latter complex is tetrahedral.

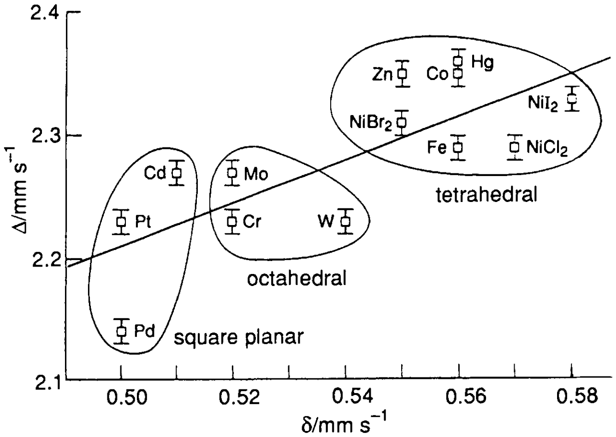

Figure. Plot of δ *versus* Δ for [Fe(η-$C_5H_4PPh_2)_2$] complexes

The octahedral carbonyl complexes of Cr, Mo, and W have δ values that are more typical of ferrocene (0.52—0.54 mm s^{-1}) and Δ values lower than for the tetrahedral complexes. The square-planar complexes of Pt (of Corain *et al.*[11]) and Pd show the lowest combination of δ and Δ values. Of particular interest is the fact that the cadmium complex, prepared for the first time by Corain *et al.*,[11] also appears in this region. This is unusual as the other complexes of the group (Zn and Hg) are tetrahedral as expected. However, Corain *et al.*[11] reported that the ^{31}P n.m.r. spectrum of the cadmium complex exhibited a broad singlet and a low shift of −8.68 p.p.m. (compared to the shift of ≈20 p.p.m. for all the other metal complexes, other than that of Zn which also showed a low shift). They attributed this broadening to phosphine exchange at 27 °C (the temperature at which the n.m.r. data were collected). Although this implies that the complex is fluxional, this is likely to be a phenomenon of the solution only. In support of this is the lack of anything unusual about the room-temperature Mössbauer measurements. It is suggested here that the cadmium complex is not tetrahedral in the solid state and may approach a square-planar co-ordination.

While there is certainly a similarity between the results here and those of Hillman and Nagy[25] for the ferrocenophanes a note of caution must be added. A plot of these latter data gives a straight line that is quite different [*n* = 13, *r* = 0.97, slope 3.1(3)] to those obtained here.

This correlation of high δ values pairing high Δ values is in keeping with the fact that back bonding will reduce the positive contribution to the quadrupole splitting and also decrease the shielding of the *s* electrons (hence a decrease in δ would be expected).

The gold(I) complex (δ = 0.50, Δ 2.30 mm s^{-1} at 50 K)[4] does not fit the above discussion in that when included in the plot it does not lie near the line of best fit. This perhaps should be expected due to the unbridged configuration of this complex. However, again this demonstrates the fact that different co-ordination geometries produce changes in the hyperfine interactions.

These results are only the second example of a series of ferrocene derivatives to show a systematic change in both δ and Δ. In general, the back bonding in ferrocene is controlled by the substituent groups on the cyclopentadienyl rings. The more electronegative these groups are the more back bonding will occur. As previously mentioned, there was an absence of correlation between, the albeit crude, estimates of group electronegativity and Δ. This demonstrates that the changes in the electric field gradient experienced by the ferrocenyl-iron atom in these complexes are predominantly a consequence of the structural demands made by the ligated metal ion and cannot be explained by any single factor as has been possible previously.[25]

Conclusion

This series of ferrocenyl complexes is only the second to show a linear correlation between δ and Δ. It is interesting that both of these series contain bridged ferrocenyl structures [excluding the gold(I) derivative]. More importantly however, the plot of δ *vs.* Δ divides easily into three domains for the three structural types (Figure).

The analysis of the crystal structures shows the changes in iron–ring distance are in keeping with the previous findings of Hillman and Nagy.[25] However, the changes in Δ were not sufficiently large as to attribute this as the sole cause of the effect, since the configuration of the cyclopentadienyl rings can also influence Δ.

As more data become available, it will be interesting to ascertain whether a plot of δ *vs.* Δ can consistently establish the geometry of the P-bound metal ion. The ^{57}Fe nuclei of the ferrocenyl ligands would then provide a probe for the co-ordination of the metal to which they are bound.

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