Ferrocenyl Ligands. Part 1. An Analysis of the Structures of Substituted Ferrocenylphosphines to aid in the Understanding of the Ligand Bonding. The Crystal and Molecular Structure of Diferrocenylphenylphosphine†

Andrew Houlton, Roger M. G. Roberts,* and Jack Silver*
Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ
Michael G. B. Drew*
Department of Chemistry, University of Reading, Reading RG6 2AD

The crystal and molecular structure of diferrocenylphenylphosphine $PPh[C_5H_4Fe(C_5H_5)]_2$ has been determined. The central phosphorus atom is in a tetrahedral environment with CPC angles less than ideal as expected for the presence of a phosphorus lone pair. The average angle is ≈100°, which is smaller than the corresponding angle in PPh_3 and 1-(1′-dimethylaminoethyl)-2-(diphenylphosphino)ferrocene. The causes of such bond-angle distortions are discussed with reference to other related structures and also with respect to the effect on ^{31}P n.m.r. chemical shifts. The nature of the interaction between the phosphorus atom and the ferrocenyl moiety can be understood by considering Mössbauer spectra in conjunction with structural data for ferrocenylphosphines and their quaternised derivatives.

Recently we have reported the results of an ^{57}Fe Mössbauer and ^{13}C n.m.r. spectroscopic studies of ferrocenyl-amines and -phosphines.[1] The results highlighted the difference in the type of interaction of phosphorus and nitrogen with the ferrocene moiety. The lone pair of nitrogen is clearly involved in bonding to the ferrocenyl groups (resulting in a trigonal N atom in the case of triferrocenylamine),[2] whereas the phosphorus lone pair has no such interaction. Although no other crystal structures of ferrocenylamines exist, the structure of $[Fe(\eta^5\text{-}C_5H_4NEt_2)(CO)Br\{PhP(OEt)_2\}]$ has been determined[3] which contains the $(\eta^5\text{-}C_5H_4NEt_2)Fe$ fragment. Examination of this part of the structure reveals the nitrogen atom to be nearly coplanar with its substituents. The angle of this plane with that of the cyclopentadienyl ring is only 5.3°. The CNC angles average 119° (being 120.8, 121.3, and 117.8°). These features are again consistent with the delocalisation of the nitrogen lone pair over the whole $C_5H_4NEt_2$ moiety. The shorter $N\text{–}C(C_5H_4)$ distance of 1.332(4)[3] Å compared to 1.414(15) Å[2] for the same distance in triferrocenylamine perhaps reflects the electron-releasing effect of the ethyl groups.

In order to gain further insight into the bonding involved in these interesting phosphine ligands we have undertaken a structural study of diferrocenylphenylphosphine (**1**) the results of which form the basis of this report.

Experimental

Diferrocenylphenylphosphine (**1**) and ferrocenyldiphenylphosphine (**2**) were purchased from Aldrich Chemicals. Recrystallisation from acetone afforded crystals suitable for the analysis of (**1**). The compounds $[PPh\{C_5H_4Fe(C_5H_5)\}_2I][I_3]$ (**3**) and $[PPh_2\{C_5H_4Fe(C_5H_5)\}I][I_3]$ (**4**) were prepared according to literature methods.[4] Mössbauer data were recorded and fitted as previously described.[5]

Crystallography.—Crystals were prepared as described above.

Crystal data. $C_{16}H_{23}Fe_2P$, (**1**), $M = 347.7$, triclinic, space group $P\bar{1}$, $a = 9.339(8)$, $b = 12.133(12)$, $c = 11.283(13)$ Å, $\alpha = 118.6(1)$, $\beta = 78.0(1)$, $\gamma = 109.1(1)°$, $U = 1\,058.2$ Å^3, $D_m = 1.39$ g cm^{-3}, $Z = 2$, $D_c = 1.37$ g cm^{-3}, $F(000) = 352$, $\lambda = 0.7107$ Å, $\mu(Mo\text{–}K_\alpha) = 18.3$ cm^{-1}.

A crystal of approximate size 0.25 × 0.3 × 0.3 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable-width ω scans. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of (1.5 + sin μ/tan θ). 3 501 Independent reflections were measured of which 1 838 with $I > 3\sigma(I)$ were used in subsequent refinement. The structure was determined by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically. The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final *R* value was 0.082 ($R' = 0.083$). In the final cycle of refinement all shift/error ratios were $< 0.3\sigma$. The final difference Fourier map showed no peaks greater than 0.5e Å^{-3}. Calculations were carried out using SHELX 76[6] and some of our own programs on the Amdahl V7 at the University of Reading. Scattering factors and dispersion corrections were taken from ref. 7. Positional parameters are given in Table 1 and selected molecular dimensions in the co-ordination sphere in Table 2.

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

Results and Discussion

Mössbauer Data.—Mössbauer spectroscopic data are presented in Table 3.

As we previously reported,[1] the ferrocenylphenylphosphines all exhibit smaller quadrupole splittings (q.s.) than ferrocene indicating that electron density is withdrawn from the ferrocenyl groups by the phosphino group. This is perhaps unexpected bearing in mind the lower electronegativity of phosphorus compared to nitrogen. However, backbonding into the empty low-lying phosphorus *d* orbitals is a characteristic feature in the chemistry of phosphorus.

The interaction of ferrocenyl groups with phosphorus and the resulting effect on the reactivity of P has been examined by

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for $PPh[C_5H_4Fe(C_5H_5)]_2$

Atom	*x*	*y*	*z*
Fe(1)	5 325(2)	−1 620(2)	7 243(2)
Fe(2)	11 072(2)	2 682(2)	8 936(2)
P	8 162(3)	828(3)	6 816(3)
C(11)	12 318(15)	2 416(14)	7 138(14)
C(12)	12 907(14)	2 061(15)	7 951(18)
C(13)	13 331(17)	3 165(17)	9 160(18)
C(14)	12 979(14)	4 206(14)	9 178(15)
C(15)	12 354(14)	3 716(14)	7 930(14)
C(21)	9 617(15)	3 259(19)	10 615(14)
C(22)	9 948(16)	2 104(18)	10 367(18)
C(23)	9 458(15)	1 130(16)	9 084(17)
C(24)	8 851(12)	1 719(14)	8 513(13)
C(25)	8 984(13)	3 010(14)	9 476(12)
C(31)	5 349(12)	289(10)	8 456(11)
C(32)	3 835(15)	−506(13)	8 220(14)
C(33)	3 665(15)	−1 125(12)	6 820(15)
C(34)	5 078(12)	−761(11)	6 181(13)
C(35)	6 181(11)	157(10)	7 197(11)
C(41)	5 983(26)	−3 260(14)	5 901(16)
C(42)	4 617(23)	−3 568(13)	6 608(16)
C(43)	4 845(17)	−2 945(12)	7 981(14)
C(44)	6 354(19)	−2 241(14)	8 130(14)
C(45)	7 066(19)	−2 396(14)	6 825(17)
C(51)	8 051(13)	2 217(11)	6 613(11)
C(52)	6 840(13)	2 795(12)	7 150(13)
C(53)	6 851(16)	3 841(13)	6 987(14)
C(54)	8 056(17)	4 354(17)	6 304(16)
C(55)	9 241(18)	3 802(15)	5 731(17)
C(56)	9 208(15)	2 674(16)	5 864(14)

Table 2. Molecular dimensions (distances in Å, angles in °)

Fe(1)–C(31)	2.045(10)	Fe(2)–C(13)	2.031(15)
Fe(1)–C(32)	2.037(12)	Fe(2)–C(14)	2.054(13)
Fe(1)–C(33)	2.046(13)	Fe(2)–C(15)	2.026(12)
Fe(1)–C(34)	2.011(11)	Fe(2)–C(21)	2.052(13)
Fe(1)–C(35)	2.060(11)	Fe(2)–C(22)	2.023(15)
Fe(1)–C(41)	2.041(13)	Fe(2)–C(23)	2.042(14)
Fe(1)–C(42)	2.022(13)	Fe(2)–C(24)	2.044(12)
Fe(1)–C(43)	2.033(12)	Fe(2)–C(25)	2.029(11)
Fe(1)–C(44)	2.022(14)	P–C(24)	1.823(13)
Fe(1)–C(45)	2.004(13)	P–C(35)	1.812(10)
Fe(2)–C(11)	2.053(12)	P–C(51)	1.843(11)
Fe(2)–C(12)	1.999(12)		
C(24)–P–C(35)	100.0(5)	C(35)–P–C(51)	101.0(5)
C(24)–P–C(51)	98.6(5)		

Table 3. ^{57}Fe Mössbauer spectroscopic data (at 80 K)

Compound	δ/mm s^{-1}	Δ/mm s^{-1}	Ref.
(1) $PPh[C_5H_4Fe(C_5H_5)]_2$	0.52(1)	2.32(1)	1
(2) $PPh_2[C_5H_4Fe(C_5H_5)]$	0.52(1)	2.31(1)	1
(5) $[Fe(C_5H_4PPh_2)_2]$	0.53(1)	2.30(1)	1
(3) $[PPh\{C_5H_4Fe(C_5H_5)\}_2I][I_3]$	0.52(1)	2.27(1)	This work
(4) $[PPh_2\{C_5H_4Fe(C_5H_5)\}I][I_3]$	0.52(1)	2.25(1)	This work
$[Fe(C_5H_5)_2]$	0.54(1)	2.37(1)	1

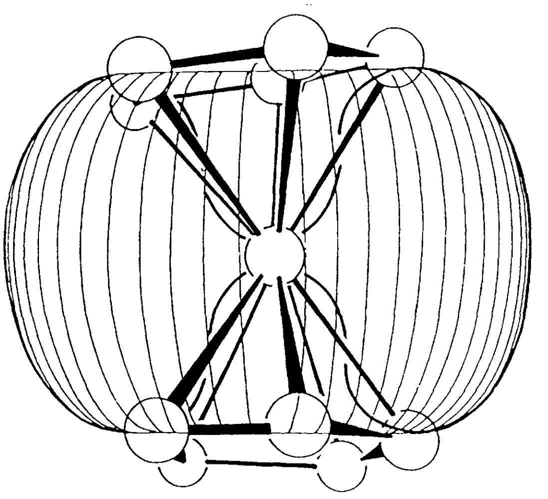


Figure 1. Ferrocenyl h_{ag} orbital. The 'cored apple' orbital

McEwen *et al.*[8,9] They reported the pronounced deactivating effect of a ferrocenyl group on an adjacent phosphorus atom in the alkaline hydrolysis of quaternary phosphonium salts. They cited this as evidence for strong interaction between the ferrocenyl group and the cationic phosphorus atom which decreased the electrophilic reactivity of the latter, steric effects having been ruled out. The decreased reactivity of the ferrocenylphosphonium hydroxides compared to the phenyl analogue was attributed mainly to the result of overlap of the h_{ag} molecular orbital of the ferrocenyl group with 3*d* orbitals on phosphorus. From their data the rate-depressing effect of a single ferrocenyl group was almost as great as that of two or three such groups implying that there was effective overlap of just one ferrocenyl h_{ag} orbital with a 3*d* orbital of phosphorus in the phosphonium cation, which seems to us surprising as there is no obvious orbital symmetry constraint for this.

The ferrocenyl h_{ag} orbital (Figure 1) is a molecular orbital (m.o.) that has largely been ignored by workers in the field since the calculations of Moffit.[10] The iron orbitals that contribute to this m.o. are 4*s* and $3d_{z^2}$ orbitals. Unfortunately, this orbital combination has not been considered for its contribution to the ^{57}Fe Mössbauer effect. As the only component orbital of the h_{ag} m.o. that can generate a field gradient is the d_{z^2} orbital, it could reasonably be assumed that removal of electron density from this orbital (due to overlap with P) would cause an increase in the q.s. since it has a negative contribution to the field gradient. Therefore based on the hypothesis of McEwen *et al.*, a reaction producing a cationic P should increase the q.s. This is not observed experimentally as can be seen from the parameters of $[PPh\{C_5H_4Fe(C_5H_5)\}_2I][I_3]$ (3) and $[PPh_2\{C_5H_4Fe(C_5H_5)\}I][I_3]$ (4) which show a decrease from the parent phosphine.

Structural Data.—The molecular structure of $PPh[C_5H_4Fe(C_5H_5)]_2$ (1) is shown in Figures 2 and 3 and consists of discrete units of the molecule. The two ferrocene groups have an eclipsed geometry (see Figure 2) with the two rings in each ferrocene approximately parallel (angles of 2.1° between rings 1 and 2 and 1.6° between rings 3 and 4).

The substituent ferrocenes are approximately perpendicular to each other with an angle of 86.9° between the molecular axes of the ferrocene moieties. There are no intramolecular distances significantly less than the sum of the van der Waals radii.

All bond lengths are typical of a substituted ferrocene[11] with Fe–C averaging 2.029(12) Å to the unsubstituted cyclopentadienyl rings and 2.039(12) Å to the substituted rings. The C–C bonds of the C_5H_5 rings are in the range 1.371—1.474 Å. However, the errors in the C–C bonds are such that it is impossible to differentiate average lengths between the substituted and unsubstituted rings unlike our findings in other ferrocene structures,[12] although a similar trend is apparent.

The central phosphorus is in a tetrahedral environment with CPC angles less than the ideal angle of 109.5°, being 101.0(5), 98.6(5), and 100.0(5), averaging to 100°. The phosphorus atom

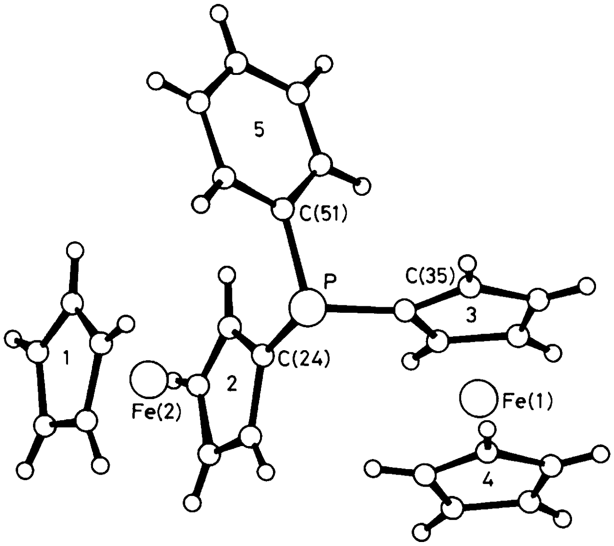


Figure 2. Drawing of the molecular structure of $PPh[C_5H_4Fe(C_5H_5)]_2$ (**1**) showing the numbering scheme

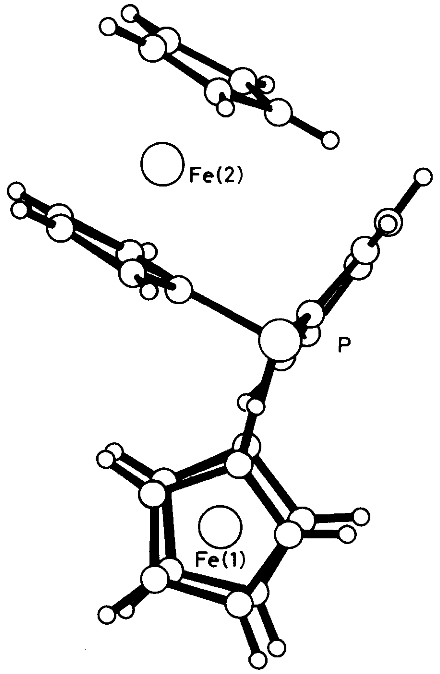


Figure 3. Molecular structure of compound (**1**) showing the eclipsed conformation of the ferrocenyl groups

is located (distance r_p) 0.85(1) Å from the plane of the three bonding carbon atoms.

The phosphorus is closely planar with the C_5H_4 ring to which it is attached, being 0.06(1) Å from ring 2 and 0.08(1) Å from ring 3.

Comparison of the structure of $PPh[C_5H_4Fe(C_5H_5)]_2$ *with related structures.* It can be seen from the figures that the general features of the structure of compound (**1**) are remarkably similar to those of 1-(1′-dimethylaminoethyl)-2-(diphenylphosphino)-ferrocene (**6**).[13] particularly with regard to the orientations of the phenyl and ferrocenyl groups. For the latter, the planes of the phenyl groups lie almost orthogonal to those of the cyclopentadienyl rings of the ferrocenyl substituent. In the case of (**1**), one ferrocenyl and one Ph group are approximately orthogonal to the second ferrocenyl group. Replacing one Ph by a ferrocenyl group has relatively little effect on the overall geometry.

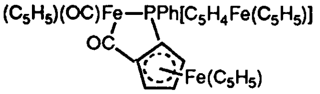
Table 4 lists selected bond lengths and angles for ferrocenylphosphines and related structures. The average P–C(ferrocene) distance of 1.817(11) Å in (**1**) compares with 1.802(7) Å for the corresponding distance in (**6**). The P–C(phenyl) distance of 1.843(11) Å compares with an average distance of 1.837(8) Å in (**6**). Both phosphines show P–C(ferrocene) distances shorter than P–C(phenyl) distances, and this latter distance increases with increasing ferrocenyl substitution {*cf.* mean values: PPh_3, 1.828; $PPh_2[C_5H_4Fe(C_5H_5)]$, 1.837; and $PPh[C_5H_4Fe(C_5H_5)]_2$, 1.843 Å}.

McEwen *et al.*[8] have reported the crystal structure of benzylferrocenyldiphenylphosphonium chloride. The P–C bond length to the ferrocenyl group, at 1.768(3) Å is shorter than the other P–C (aromatic) bond lengths, at 1.803(3) and 1.804(4) Å, in common with the ferrocenylphosphine derivatives discussed above. These workers suggested that this is due to a delocalisation of positive charge into the ferrocene system by overlap of the h_{ag} orbital with the d_{z^2} orbital on P. As discussed earlier, the Mössbauer studies do not support this theory. It is possible, however, to account for this difference from a knowledge of the difference in hybridisation of the phosphorus-bearing carbons in five- and six-membered rings. Simple calculations[14] indicate a 10% increase in *s* character of the P–C(ferrocene) bond compared with the P–C(phenyl) bond, which would account for a shortening of this magnitude ($\approx$0.02 Å). Evidence in support of this comes from a comparison of the $C–CH_3$ bond lengths in hexamethylbenzene[15] and decamethylferrocene[16] of 1.53 and 1.502 Å respectively. Complexation of a metal to a carbocyclic ring also causes some shortening of the exocyclic bonds as is shown by the $C–CH_3$ bond distances in $[Fe(\eta^6-C_6Me_6)_2][tcnq]$ (tcnq = tetracyanoquinodimethinide), 1.505(7) Å,[17] and $[Co(\eta^6-C_6Me_6)_2]PF_6$, 1.519(6) Å.[18] In view of this and the Mössbauer data for compounds (**3**) and (**4**) (from Table 3), it is more likely that donation of charge by the ferrocene moiety to the phosphorus is by ferrocenyl e_1 ring-based orbitals with concomitant increase in back bonding from Fe to C_5H_5 *via* e_2 orbitals. There is also the possibility of some direct overlap between iron e_2 and phosphorus *d* orbitals. It must be stated that the distance between Fe and P has a range of 3.397 Å [in (**8**)] to 3.581 Å [in (**9**)], and averages 3.425 Å in (**1**). These distances are clearly too long for a direct bonding overlap of P and Fe orbitals (*cf.* normal Fe–P bonds around 2.40 Å, although longer distances as high as 2.77 Å have been reported as bonding[19]) but could still allow some interaction.

For all the compounds (**1**) and (**6**)—(**9**) the phosphorus atom is in a distorted tetrahedral environment with angles (θ) less than the ideal angle of 109.5° and this is true for all the unco-ordinated phosphines in (**1**), (**6**), and (**7**). The average value of θ in these three compounds decreases with increasing ferrocenyl substitution, being reduced from 103.0° in (**7**) to 101.8° in (**6**) to 100.0° in (**1**). This trend may be explained on the basis of valence-shell electron-pair repulsion (VSEPR) theory. The phosphorus lone pair will repel the bonding-pair electrons to a greater extent than the bonding pairs repel one another. Thus increasing the lone-pair character present on the phosphorus causes the angles to be reduced from those of a perfect tetrahedron. The decrease in the CPC angle is in keeping with the electron-donating nature of the ferrocenyl group compared to phenyl in the solid state and is in keeping with Mössbauer data.[1] As phenyl groups are replaced by ferrocenyl groups, the phosphorus retains more lone-pair character and hence there will be an increase in the repulsion of the bonding pairs and a decrease in the CPC angle.

In addition, the ferrocenyl group has a greater electron density on its rings in the π cloud than the phenyl group. Thus

Table 4. Bond lengths (Å) and angles (°) of ferrocenylphosphines and relevant structures[a]

Compound	P–C(ferrocene)	P–C(phenyl)	C–P–C(mean)	Distance (r_p) from 3C plane(Å)	Fe–P	Ref.
(**7**) PPh_3	—	1.828[b]	102.96	0.785	—	*c*
(**6**) $PPh_2\{C_5H_4FeC_5H_4[CH(NMe_2)Me]\}$[d]	1.802(7)	1.837(8)[b]	101.8(4)	0.810	3.408(3)	13
(**1**) $PPh[C_5H_4Fe(C_5H_5)]$	1.817(11)[b]	1.843(11)	100.03	0.85	3.423(11) 3.427(11)	This work
(**8**) $[P\{C_5H_4Fe(C_5H_5)\}_3I][I_3]$	1.763[b]	—	110.93[b]	0.543	3.468 3.397 3 452	4
(**9**) 	1.805	1.816	106.2	0.691	3.506 3.581	30
$[PPh_2(CH_2Ph)\{C_5H_4Fe(C_5H_5)\}]Cl$	1.768[e]	1.804[e]	107.7[e]	—	3.449	8

[a] Data obtained from the Cambridge Crystallographic Structure Data Base except where indicated to the contrary. [b] Average. [c] J. J. Daly, *J. Chem. Soc.*, 1964, 3799. [d] 1-(1′-Dimethylaminoethyl)-2-(diphenylphosphino)ferrocene. [e] From ref. 8.

greater repulsion will occur between the phosphorus lone pair and the C_5H_5 group than that for the phenyl group though overall this will admittedly be small. The related distance of the displacement of the phosphorus from the plane of the three bonding carbon atoms is in accord with the observed θ values. This distance (r_p) is shorter for (**7**) at 0.785 Å and increases to 0.85 Å in (**1**). Using simple hybridisation arguments, increase in θ in going from compounds (**1**) to (**2**) to (**7**) should result in more *s* character in the P–C bonds and hence more *p* character in the lone pair.[20] This predicts that the ligand strengths should increase in the order $PPh_3 > PPh_2[C_5H_4Fe(C_5H_5)] \approx [Fe(C_5H_4PPh_2)_2] > PPh[C_5H_4Fe(C_5H_5)]_2$. This sequence has been verified experimentally using ligand displacement in $[Ni(acac)_3]$ (acac = acetylacetonate),[21] though the authors invoke steric hindrance as the dominant effect. Correlation of solid-state and solution structures is fraught with difficulty. However, evidence for such correlation can in some cases be obtained from n.m.r. spectroscopy. In this context, it is interesting to compare the values of θ with the ^{31}P n.m.r. chemical shift [δ(P)]. From a study of trialkylphosphines, Mann[22] concluded that an increase in θ resulted in deshielding of the P nucleus. However, Quinn and Breen[23] have argued that α,β, and γ substituent effects of an aliphatic chain also affect δ(P).[24] For the phosphine series PPh_3, $PPh_2[C_5H_4Fe(C_5H_5)]$, $PPh[C_5H_4Fe(C_5H_5)]_2$, none of these effects is present. The δ(P) values[1] are −7, −15, and −27 p.p.m. respectively (average values). The ground-state electronic properties of the ferrocenyl group are quite similar to those of the phenyl group.[25] This is apparent from the Mössbauer data quoted above and also from the almost identical ^{13}C n.m.r. chemical shifts for the C_5H_5 and Ph carbons in $PPh_2[C_5H_4Fe(C_5H_5)]$ and $PPh[C_5H_4Fe(C_5H_5)]_2$.[1] The values of θ must therefore be dominated by the stereoelectronic factors previously discussed. The variation of θ with δ(P) is linear for the above phosphine series, though of course more points are required to be statistically significant (particularly relevant would be data for triferrocenylphosphine which is not available at present). Nevertheless the trend supports Mann's postulate[22] that a decrease in θ causes an upfield shift of phosphorus resonance. This increased shielding can be rationalised in terms of increasing *s*-electron density in the lone pair on phosphorus. In this connection, it is also worth noting that the ^1J(P–C) values for the *ipso* phenyl carbons also increase with θ and it is tempting to explain this again as being due to increased *s* character in the P–C bonds. However, it has clearly been demonstrated that ^1J(P–C) for PPh_3 is negative[26,27] which poses serious difficulties for the Fermi-contact theory of coupling phenomena.[28,29] The overall evidence from n.m.r. data does however point towards a similarity in the relative geometries of these phosphines in the solution and solid phases.

As would be expected, on co-ordination the CPC angle increases since a lone pair becomes a bonding pair. This can be seen in the structures of compounds (**8**) and (**9**) (see Table 4) which have θ values of 110.9 and 106.2° respectively, *i.e.* closer to the ideal tetrahedral angle. In the latter compound the iron–acyl distance is considered to be normal[30] and hence it can be concluded that there is little strain caused by the presence of this structural feature. Hence compound (**9**) can be considered as a co-ordinated diferrocenylphenylphosphine. The displacement (r_p) of the phosphorus atom decreases from 0.85 Å in (**1**) to 0.691 Å in (**9**). Also the P–C(ferrocene) bond length decreases by ≈0.12 Å. This decrease on co-ordination appears to be quite general as can be seen from structures of 1,1′-bis(diphenylphosphino)ferrocene and its metal complexes.[31,32] As increased ferrocenyl substitution has been shown to increase the lone-pair character of the phosphorus, it would be interesting to solve the structure of triferrocenylphosphine which should exhibit the smallest CPC angles of all such derivatives.

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