Partial Mössbauer quadrupole splittings in low-spin iron(II) compounds: properties of bidentate phosphine ligands and possibilities to forecast when complexes can be prepared for octahedral low-spin iron(II)

Jack Silver

Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ (U.K.)

Abstract

The Mössbauer spectroscopic quadrupole splittings (QS) for a series of six-coordinate low-spin iron(II) complexes containing bidentate phosphine ligands are discussed. Partial quadrupole splittings (*p.q.s.*) are used to assign *cis* and *trans* geometries to several of the complexes. From the invariance of the *p.q.s.* value for $Et_2PCH_2CH_2PEt_2$ (depe) it is suggested that this ligand does not vary its bonding to low-spin iron(II) irrespective of the other monodentate ligands present. The *p.q.s.* values for the bidentate phosphine ligands are refined and ordered. A correlation between small *p.q.s.* values and large cone angles is found and put into context. The bidentate phosphine ligands have bonding properties (both electronic and steric) that lie between those of triorganic phosphines and triorganic phosphites of similar sterochemistry around the phosphorus atoms. The range of QS values in the low-spin complexes is found to span from -1.84 to $+1.8$ mm s^{-1}. Some hypothetical complexes whose predicted QS lies within the QS range and which should not be unstable on steric grounds are listed.

Introduction

Many studies have demonstrated that point-charge parameters [1], partial quadrupole splittings [2–4], or partial field gradients [5] can be used to correlate Mössbauer spectroscopic quadrupole splittings (QS) with the geometry of iron(II) compounds [2], iron($-$II) compounds [6] and tin(IV) compounds [1, 7, 8]. To date all such work has been based on explaining observed QS values, where the signs of the QS in several of these of key compounds were established. To derive a self-consistent set of partial quadrupole splittings (*p.q.s.*) for a range of ligands, knowledge of the signs of the QS of some of the compounds is important [2, 3].

Recently, we reported Mössbauer parameters for a range of iron(II) complexes of diphosphines [9]. We found that five different diphosphine ligands all gave rise to low-spin iron(II) complexes of the general formula $[Fe(MeCN)_2(diphosphine)_2]^{2+}$. Four diphosphines in the formula $[FeX_2(diphosphine)_2]$ (where X = Cl, Br or I) gave stable complexes. Of these, two were low-spin, one was high-spin, the fourth was tetrahedral (with the diphosphine ligands acting as monodentate ligands) and the fifth was not stable in that formulation but gave a high-spin tetrahedral complex of formulae [FeX₂(diphos-

phine)] (X = Cl or I) [9]. In this paper we report on the application of point-charge models to these complexes.

To carry out this work it was necessary to use previously published values for partial quadrupole splittings (*p.q.s.*). The values we chose mainly follow the work of Bancroft *et al.* [2, 3, 10–12]. These *p.q.s.* values may be used to forecast the sign of the observed QS values for proposed compounds. This work also addresses the problem of assigning accurate *p.q.s.* values to chelating ligands [12]. By making assumptions about the signs of the observed QS, it was possible to assign *p.q.s.* values to the bidentate phosphine. From these and from knowledge of the range of QS values observed to date for six-coordinate low-spin iron(II) complexes, it is shown in this work that simple point-charge calculations can be used to predict whether such low-spin iron(II) complexes of hypothetical formulae might be stable.

Discussion

Derivation of p.q.s. values

We take the *p.q.s.* value for chloride as -0.30 mm s^{-1} at 295 K (from refs. 3 and 12). In addition, we take a *p.q.s.* value for 1/2 depe

($Et_2PCH_2CH_2PEt_2$ = depe) from ref. 3 as the value of -0.62 mm s^{-1} at 295 K better fits all the data than the value of -0.65 mm s^{-1} these authors use later [12]. It should be noted that the QS values do show some small temperature dependence as observed in the data presented in ref. 2, thus there should be a slight temperature dependence on the $p.q.s.$ values, *vide infra*. This work will be confined to *trans*-Fe^{II}A$_2$B$_4$ octahedra, *trans*-Fe^{II}ACB$_4$ and *cis*-Fe^{II}A$_2$B$_4$ octahedra complexes. The QS can be expressed either by use of a point-charge or molecular orbital model as:

$$QS_{trans} = +4[A] - 4[B] \tag{1}$$

$$QS_{trans} = +2[A] + 2[C] - 4[B] \tag{2}$$

$$QS_{cis} = -2[A] + 2[B] \tag{3}$$

where [A], [B] and [C] are $p.q.s.$ values for ligands A, B and C, respectively [3, 4].

[Fe(MeCN)$_2$(diphosphine)$_2$] structures

Using the $p.q.s.$ values for 1/2 depe (-0.62 mm s^{-1}) [3] and MeCN (-0.43 mm s^{-1}) [12], then the calculated QS (for a *trans* structure) for compound 1 (Table 1) is $+0.76$ mm s^{-1}, this is just outside the range which we would say is good. Calculated QS values are judged to be satisfactory if they are within ± 0.20 mm s^{-1} of the observed value [12]. If a *trans* structure is assumed for compound 2 (Table 1), a QS of 1.08 mm s^{-1} is calculated. This is clearly unsatisfactory. If a *cis* structure is assumed, then the calculated value becomes -0.54 mm s^{-1} which

is in the correct range. The complex must have a *cis* structure in the solid state. It may reorganise when dissolved as it gives [13] a ^{31}P NMR spectrum which indicates a *trans* geometry.

Compound 3 contains the 1,2-C$_6$H$_4$(PPh$_2$)$_2$ (opdp) ligand. The $p.q.s.$ value for 1/2 opdp must be close to that of MeCN (-0.43 mm s^{-1}) to satisfy the observed QS. In fact, this compound is known to have a *trans* structure [14]. Compound 4 is a complex of the ligand Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe), and from the calculations it has a *cis* structure. This is reasonable in view of the *cis* structure of [FeH$_2$(dppe)$_2$] [15]. The fifth compound (5) contains the Ph$_2$PCH$_2$PPh$_2$ ligand (dppm). This can act as a bidentate ligand but with strained rings [16]; it could conceivably act as a bridging ligand between octahedral units.

It is possible thus to derive two different $p.q.s.$ values for 1/2 dppm. A *trans* structure gives a $p.q.s.$ value of -0.61 mm s^{-1} whereas a *cis* structure yields a value of -0.79 mm s^{-1}. Comparing the values to those for other phosphine ligands [12], it is observed that PPh$_2$Me has a $p.q.s.$ value of -0.58 mm s^{-1}. This is close to -0.61 mm s^{-1} for the *trans* structure for dppm. Thus we assign a *trans* structure to compound 5. From the $p.q.s.$ values given in Table 2 it is possible to order the complexing power of these phosphine ligands in a more reasonable way than we previously achieved if we make a simple assumption based on established literature [2, 3, 14–20]. From the work of Bancroft *et al.* [2, 3] $p.q.s.$ values become more positive with increasing π-backbonding

TABLE 1. ^{57}Fe Mössbauer data for low-spin six-coordinate iron(II) complexes used in this work

Compound	T (K)	δ (mm s^{-1})[a]	QS (mm s^{-1})	QS_{calc} (mm s^{-1})	Reference[b]
[Fe(MeCN)$_2$(depe)$_2$]I$_2$ (1)	77	0.23(1)	1.00(1)	+0.76	9
[Fe(MeCN)$_2$(dmpe)$_2$]I$_2$ (2)	77	0.39(1)	0.36(1)	−0.54	9
[Fe(MeCN)$_2$(opdp)$_2$]I$_2$ (3)	77	0.38(1)	0.00(1)	0.16	9
[Fe(MeCN)$_2$(dppe)$_2$]I$_2$ (4)	77	0.38(1)	0.35(1)	−0.34	9
[Fe(MeCN)$_2$(dppm)$_2$]I$_2$ (5)	77	0.26(1)	0.73(1)	+0.72	9
[FeCl$_2$(depe)$_2$] (6)	80	0.39	1.42	+1.40	2b
	295	0.39	1.29	+1.28	2b
[FeBr$_2$(depe)$_2$] (7)	80	0.45	1.45	+1.44	2b
	295	0.39	1.37	+1.36	2b
[FeI$_2$(depe)$_2$] (8)	80	0.46	1.38	+1.36	2b
	295	0.38	1.33	+1.32	2b
[FeCl$_2$(dmpe)$_2$] (9)	77	0.37	1.70(1)	+1.72	9
[FeI$_2$(dmpe)$_2$] (10)	77	0.40	1.74(1)	+1.68	9
[FeHCl(depe)$_2$] (11)	80	0.18	⩽0.13	−0.14	2b
	295	0.11	⩽0.12	−0.20	2b
[FeHI(depe)$_2$] (12)	80	0.16	⩽0.19	−0.16	2b
	295	0.12	∼0.0	−0.18	2b
[FeH(N$_2$)(depe)$_2$]BPh$_4$ (13)	295	0.05	0.33	−0.34	18
[FeH(CO)(depe)$_2$]BPh$_4$ (14)	295	−0.13	1.00	−1.08	18

[a]All relative to natural Fe at 295 K. [b]Mössbauer data reference.

TABLE 2. Partial quadrupole splittings (mm s^{-1}) used in this work

	~77 K	~295 K
Cl	−0.27[a]	−0.30[b]
Br	−0.26[a]	−0.28[b]
I	−0.28[a]	−0.29[b]
N$_2$	−0.37[c]	−0.37[d]
MeCN	−0.43[c]	−0.43[d]
1/2opdp	−0.47[a]	−0.47[d]
1/2depb	−0.59[c]	−0.59[d]
1/2dppe	−0.60[c]	−0.60[d]
1/2dppm	−0.61[a]	−0.61[d]
1/2depe	−0.62[d]	−0.62[b]
1/2dmpe	−0.70[c]	−0.70[d]
CO	−0.74[e]	−0.74[e]
CN	−0.84[d]	−0.84[b]
H	−1.04[b]	−1.04[d]

[a]Calculated this work. [b]Values taken from ref. 3 room temperature data. Note some of these values were amended in ref. 12. We have used ref. 3 data except where otherwise stated, see text. [c]Value from ref. 12. [d]Assumed not to vary with temperature. [e]Assumed not to vary with temperature and calculated from cis-H$_2$Fe(CO)$_4$. Ref. 2b note not used in ref. 12, see also discussion on CO, ref. 12.

but more negative with increasing σ-bonding. The P–Fe bond lengths in known low-spin iron(II) compounds are not constant and vary with the phosphorous ligand (Table 3 and discussion in following sections). This means that the bond strength varies in these compounds, if this observation is not due to steric repulsions. The result of this is that both σ-donation and π-backbonding may be expected to vary. If the p.q.s. values of the P ligands are examined (Table 2) and the assumption is made that P ligands that contain no phenyls but only aliphatic ligands will be poor π-acceptors, then we can order the ligands in ascending donor power; opdp < depb < dppe ~ dppm < depe < dmpe. The ligand depb = 1,2-C$_6$H$_4$(PEt$_2$) fits into the series [2, 12]

close to opdp as expected. We have not yet included Ph$_2$PCH=CHPPh$_2$ (dppen) as though it would be stronger than opdp for reasons previously discussed [9], it is now not apparent where it would lie. In this new order dmpe and dppe are nearly equivalent [9], so our earlier comments regarding difficulties in accommodating dppe due to its bulk not making it an appreciably weaker donor than dmpe are still pertinent.

[FeX$_2$(diphosphine)$_2$] structures

Surprisingly it is not now obvious why dppe does not form [9] a low-spin complex of the formula [FeCl$_2$(dppe)$_2$]. However, we have shown that the complex [Fe(MeCN)$_2$(dppe)$_2$]$^{2+}$ is cis, the known structure of [Fe(H)$_2$(dppe)$_2$] [15] is cis and a cis structure has been demonstrated for [Fe(NCS)$_2$(dppe)$_2$] [9]. There are other known cis structures containing phosphine ligands but three [17] of these contain the tripod ligand P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$ with axial halide ion. The average Fe–P bond lengths increase only slightly with halide size [17], being 2.265 Å for the Cl$^-$ compound, 2.27 Å for the Br$^-$ and 2.29 Å for the I$^-$. This shows that the steric bulk of the other ligands has little effect upon the Fe–P bond length. The fourth cis structure, [FeH$_2$(PhP(OEt)$_2$)$_4$], has short Fe–P bond lengths in the range 2.12–2.15 Å. In [Fe(H)$_2$(dppe)$_2$] the Fe–P bonds are also short (compound 9, Table 3) compared to those of the trans low-spin iron(II) diphosphine structures (compounds 1–3, 4a and 8, Table 3) [14, 18–20]. It therefore appears that the cis structures allow short Fe–P bonds (except for complexes of P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$ which might not be able to form shorter Fe–P bonds because of its own internal steric problems), even for ligands such as dppe. Clearly the ligand dppe could not form such short bonds in a trans structure. This can be seen by looking

TABLE 3. Selected bond lengths (Å) in octahedral iron(II) phosphine complexes

Compound	Fe–P1	Fe–P2	Fe–X	P1...P2	Reference
[FeI$_2$(depe)$_2$] (1)	2.295(1)	2.323(1)	2.706(1)	3.075	14
[FeCl$_2$(depe)$_2$] (2)	2.260(2)	2.268(3)	2.349(2)	3.04	18
[FeCl$_2$(dmpe)$_2$] (3)	2.241(1)	2.230(1)	2.352(1)	3.02	19
[FeCl$_2$(dppen)$_2$]·2Me$_2$CO (4) 130 K	2.312(8)	2.289(3)	2.329(6)	3.01	20
295 K	2.592(2)	2.576(2)	2.363(2)	3.24	20
[FeCl$_2$(dppen)$_2$] (5)	2.675(1)	2.532(1)	2.347(1)	3.28	20
[FeCl$_2$(bdpp)$_2$·2Me$_2$CO (6)	2.713(3)	2.665(3)	2.354(3)	3.36	19
[FeCl$_2$(opdp)$_2$]·thf (7)	2.612(3)	2.622(4)	2.348(3)	3.165	14
[Fe(MeCN)$_2$(opdp)$_2$]I$_2$ (8)	2.337(1)	2.343(1)	1.894(4)	3.042	14
[FeH$_2$(dppe)$_2$][a] (9)	2.18	2.16		3.02	15

[a]This compound is the only cis compound in the above list. The Fe–P1 distance is the mean of four in which P1 is trans to H. The Fe–P2 distance is similar for P2 trans to P.

at the results for compounds 1–3, 4a and 8 (Table 3) where the Fe–P bond lengths increase in the order: dmpe < depe < dppen < opdp. This is the reverse of the donor power order derived above and enables dppen to be included. It is clear that dppe is almost as good a donor as dmpe but is restricted from forming *trans* complexes of this type by its own steric bulk. Although opdp and dppen have similar P1...P2 distances (Table 3), they have different cone angles and are weaker donors. The cone angles for these ligands [21] are 107° (dmpe), 114° (depe), 121° (dppm) and 125° (dppe). The angle for opdp has not been calculated but is expected to be much larger than dppe [9, 14].

The question that now remains is can two dppe ligands exist in a *trans* structure around iron(II) Fe in the solid state. The results and discussion of Parish and Riley [22] are pertinent here; these data are summarised in Table 4 (along with the other information for the dppe ligands). These authors have assigned *trans* structures to compounds 5–9 (Table 4). Their arguments appear sound and this geometry must be forced by the steric bulk of the Si ligands. As noted earlier, we find that the $p.q.s.$ value suggested by Bancroft and Libbey [12] for dppe of −0.68 mm s^{-1} is not quite good enough to fit all the data (within ±0.20 mm s^{-1}) as compound 7 is outside, Table 4. The lower value of −0.64 mm s^{-1} [22] is better but now compounds 1 and 7 (Table 4) are not in allowable limits. We calculate a value of −0.60 mm s^{-1} to be better still but compound 1 is still poor. The last value requires slightly lower $p.q.s.$ values for the Si ligands than those previously calculated [22] but these are still reasonable. Although in these *trans* compounds the Fe–P bonds must be longer than in the *cis* compounds, it has not been necessary to assign different $p.q.s.$ values for dppe

in *cis* or *trans* structures. This suggests that the mode of bonding of the ligand is similar, but steric forces cause the change in geometry to favour the *trans* structure.

More extreme factors cause the compound [FeCl$_2$(opdp)$_2$] to be high-spin. The cone angle for opdp is likely to be at least as big as that of dppe and most probably larger. As the bulk of the axial ligand increases on passing from MeCN to Cl, the dppe ligands are forced back and the compound is consequently high-spin [9, 14].

Temperature dependence of $p.q.s.$ values

As $p.q.s.$ values are relative, it should not matter what temperature is used for the measurements providing it is consistent. However, where there are temperature-dependent QS values and the $p.q.s.$ values come from more than one source, to finalise a consistent set it is necessary to take account of any such dependence.

The temperature dependence of the QS values for low-spin six-coordinate iron(II) complexes is apparent from the data presented in Table 3 taken from ref. 2a. Temperature dependent $p.q.s.$ values for the halide ions are used to calculate the QS values. The justification in allowing the $p.q.s.$ values for the halide ions to vary with temperature and not those of the phosphine ligands is as follows. The crystal structure data (Table 3) of compound 4 (130 K) and compounds 2 and 3 indicate an increase in the Fe–Cl bond length of ~0.02 Å in ~165 K. The phosphine bond lengths in compound 4 (at 130 K) are similar to those in compound 1 (Table 3) and so the inference is that they have little temperature dependence.

TABLE 4. Observed and calculated quadrupole splittings for different $p.q.s.$ values

Fe(dppe)$_2$X$_2$ X$_2$	QS obs. (mm s^{-1})	QS calc. (mm s^{-1}) at $p.q.s.$ dppe			Reference[a]
		0.68 (mm s^{-1})	0.64 (mm s^{-1})	0.60 (mm s^{-1})	
cis-H$_2$ (1)	0.57	+0.72	+0.80	+0.88	3
cis-(NCS)$_2$ (2)	0.33	−0.38	−0.30	−0.22	3
cis-(MeCN)$_2$ (3)	0.35	−0.50	−0.42	−0.34	9
cis-(Cl)(SiCl$_3$) (4)	0.42	−0.53	−0.53	−0.53	22
trans-(Si(OEt)$_3$)$_2$ (5)	0.75	−0.49[b]	−0.45[b]	−0.41[b]	22
trans-(SiMeCl$_2$)$_2$ (6)	0.85	+0.72	+0.84	+1.00	22
trans-(SiCl$_3$)$_2$ (7)	0.88	+0.48	+0.64	+0.80	22
trans-H(SiCl$_3$) (8)	0.48	−0.56[b]	−0.48[b]	−0.40[b]	22
trans-H(SiMeCl$_2$) (9)	0.37	−0.50[b]	−0.43[b]	−0.35[b]	22

[a]Ref. for QS obs. [b]$p.q.s.$ value (not QS value) for Si ligand based on specific $p.q.s.$ dppe values at top of column. These $p.q.s.$ values then used to calculate QS values where ligand occurs again in that column.

Bonding properties of bidentate phosphine ligands

In Fig. 1, the QS values for the known six-coordinate bis(bidentate phosphine) low-spin iron(II) complexes [2b, 9, 12, 22–24] are plotted against the $p.q.s.$ [12] value of the non-phosphorus ligand (if two different ligands are present the average value is used). The values for the sixteen depe compounds all fall close to one line (linear regression $R = 0.9943$). This is not, of course, surprising as the equation relating QS values to $p.q.s.$ values is linear. However, this indicates the depe ligand does not vary its bonding to the iron(II) centre irrespective of the other ligands present. Although there are only three points on the depb line, this line is nearly parallel to that for the depe compounds. In all these compounds the non-phosphine ligands are *trans*. Similarly the two complexes for opdp also lie on a line close to these lines. All the lines must be parallel if the $p.q.s.$ values are additive, however; Fig. 1 is included to show how good the data are. Thus, although the lines are not exactly parallel, they show the derived $p.q.s.$ values are good. The dmpe complexes behave differently. The two halide complexes (**9** and **10**, Table 1) are *trans* and lie in the top right hand corner of the plot near the halide complexes of the other *trans* ligands. The compound $[Fe(MeCN)_2(dmpe)_2]^{2+}$ (complex **2**, Table 1) lies on the left of the plot next to the dppe *cis* complexes coinciding with one of them. The *cis* $[FeX_2(dppe)_2]$ complexes are included to indicate the negative slope a plot of *cis* compounds

would show. (Note the slope is twice as steep, as *cis* complexes show half the QS values expected for *trans* complexes [4].)

Two important points emerge from observations on our data and that of Bancroft *et al.* [2, 3, 10–12]. Firstly, for the bidentate phosphines (where two such ligands are present in the six-coordinate low-spin iron(II) complex), there are apparently no complexes where both *cis* and *trans* isomers exist in the solid state. This is undoubtedly due to the phosphorus cone angle which dictates the geometry. Secondly, of such complexes so far studied using Mössbauer spectroscopy, dppe and dmpe are the only bidentate ligands found in both *cis* and *trans* geometries in the solid state (though not with the same other ligands). Presumably the change from *trans* to *cis* occurs because of bonding changes going from $[FeCl_2(dmpe)_2]$ to $[FeH_2(dmpe)_2]$ rather than steric factors. The depe complexes are all *trans*, and the dppe complexes are only *trans* for larger axial ligands (and do not appear to exist for two axial halide ions [22] in a low-spin iron(II) form).

Bancroft *et al.* [2b] found that the more negative the $p.q.s.$ value the better the σ-donor power of the ligand. The bidentate phosphine ligands tend to have more negative $p.q.s.$ values than the equivalent monodentate ligands, and hence their effective σ-bonding appears stronger. This is probably a manifestation of the chelate effect. The apparent exception to this is opdp which has the smallest $p.q.s.$
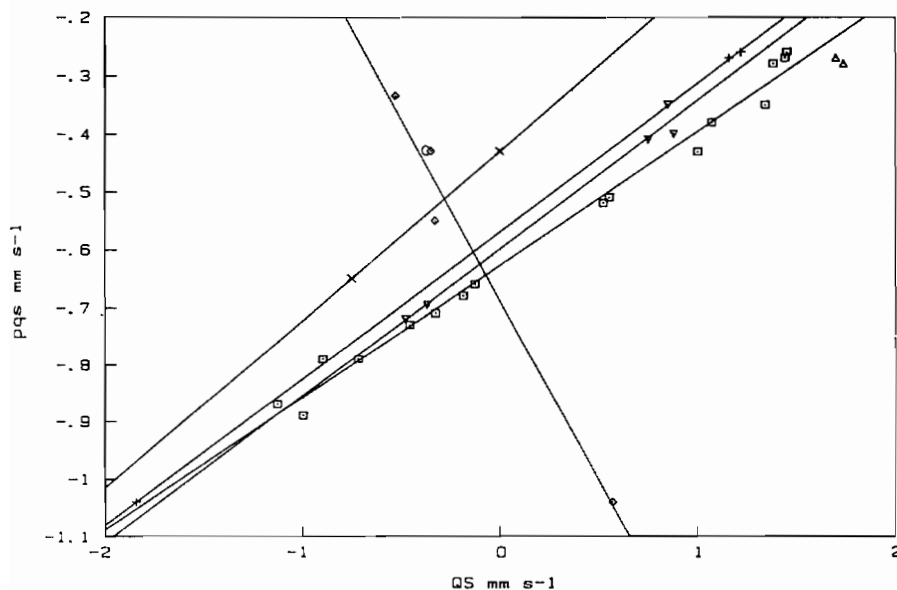

Fig. 1. Plot of $p.q.s.$ (mm s^{-1}) data against observed QS (mm s^{-1}) data for six-coordinate low-spin iron(II) complexes. dmpe complexes △ *trans*, ○ *cis*, QS data from ref. 9; □ *trans* depe complexes, QS data from refs. 2b, 9, 23; ▽ *trans* dppe complexes, ◇ *cis* dppe complexes, QS data from refs. 9, 12, 22, 24; × *trans* depb complexes, QS data from ref. 2b; + *trans* opdp complexes, QS data from ref. 9. The $p.q.s.$ data for the monodentate ligands are taken from ref. 12 and this work (see 'Discussion'); straight lines are linear regression fits.

value of the phosphorus ligands, but this has the greatest steric bulk [9, 14].

Stability of the trans low-spin iron(II) complexes

For the *trans* six-coordinate low-spin iron(II) complexes, the range of observed QS therefore spans -1.84 to $+1.8$ mm s^{-1}. It might therefore be concluded from this that any hypothetical complex whose calculated QS value lies within this range might be stable provided other factors did not interfere. Previously we reported that we failed to prepare the complex [FeCl$_2$(dppe)$_2$] [9]. We also noted that the species [FeCl$_2$(opdp)$_2$] is a high-spin iron(II) complex. As both these complexes have calculated *trans* six-coordinate low-spin iron(II) QS values in the above range, we conclude that it is steric forces that prevent their formation. We note [FeCl$_2$(dppe)$_2$] has been claimed to exist but has not been isolated in a pure form [9, 22].

Table 5 presents calculated QS values for some hypothetical *trans* low-spin iron(II) six-coordinate complexes and predicts their possible existence both on steric and point charge considerations.

CO as a ligand

The value adopted in this work for the *p.q.s.* for CO is -0.74 mm s^{-1}. This is taken from QS of *cis*-[FeH$_2$(CO)$_4$], ref. 2b. The derived value is different to that used by the earlier workers [2b, 12]. It has been pointed out that different values of *p.q.s.* for CO might be deployed depending on whether it is in *cis* or *trans* coordination [12]. The values suggested for CO$_{trans}$ and CO$_{cis}$ were -0.53 and -0.60 mm s^{-1}, respectively. Neither of these values agrees with ours, from which we calculated a reasonable QS for [FeH(CO)(depe)$_2$]$^+$[BPh$_4$]$^-$ [18] (compound 14, Table 1). It has been claimed that the additivity model for *p.q.s.* values may breakdown for strong π-acceptors [25]. It therefore seems reasonable that the CO ligand varies its *p.q.s.* depending on the nature of its surrounding ligands. It should be appreciated that the CO ligand can accept electron density both from iron(II) and the ligands *cis* to it. Clearly, *cis* ligands that are electron rich and have orbitals capable of π-bonding to CO will aid stronger π-acceptance by it. This will be manifested by the need for more positive CO *p.q.s.* values to fit the observed QS.

TABLE 5. All calculations use *p.q.s.* data from Table 3 and are assumed to be *trans*-octahedral complexes

| Compound	Temperature (K)	QS calc. (mm s^{-1})	Comments
[FeCl$_2$(opdp)$_2$] (1)	77	$+0.80$	compound is high spin, ref. 9
[FeCl$_2$(dppe)$_2$] (2)	77	$+1.32$	compound could not be isolated, ref. 9
[FeCl$_2$(dppm)$_2$] (3)	77	$+1.36$	compound could not be isolated, ref. 9
[FeCl(N$_2$)(depe)$_2$]$^+$ (4)	77	$+1.20$	should be possible
[FeCl(N$_2$)(dmpe)$_2$]$^+$ (5)	77	$+1.52$	should be possible
[FeCl(N$_2$)(opdp)$_2$]$^+$ (6)	77	$+0.60$	should be possible
[FeCl(N$_2$)(dppm)$_2$]$^+$ (7)	77	$+1.16$	should be possible
[FeCl(N$_2$)(dppe)$_2$]$^+$ (8)	77	$+1.12$	should be possible
[FeCl(CO)(dmpe)$_2$]$^+$ (9)	77	$+0.78$	should be possible
[FeCl(CO)(opdp)$_2$]$^+$ (10)	77	-0.14	should be possible
[FeCl(CO)(dppe)$_2$]$^+$ (11)	77	$+0.38$	should be possible
[FeCl(CO)(dppm)$_2$]$^+$ (12)	77	$+0.42$	should be possible
[FeH(N$_2$)(dmpe)$_2$]$^+$ (13)	295	-0.02	should be possible
[FeH(N$_2$)(opdp)$_2$]$^+$ (14)	295	-0.94	should be possible
[FeH(N$_2$)(dppe)$_2$]$^+$ (15)	295	-0.42	should be possible
[FeH(N$_2$)(dppm)$_2$]$^+$ (16)	295	-0.38	should be possible
[Fe(CN)(N$_2$)(depe)$_2$]$^+$ (17)	295	$+0.06$	should be possible
[Fe(CN)(N$_2$)(dmpe)$_2$]$^+$ (18)	295	$+0.38$	should be possible
[Fe(CN)(N$_2$)(opdp)$_2$]$^+$ (19)	295	-0.54	should be possible
[Fe(CN)(N$_2$)(dppe)$_2$]$^+$ (20)	295	-0.02	should be possible
[Fe(CN)(N$_2$)(dppm)$_2$]$^+$ (21)	295	$+0.02$	should be possible
[Fe(CO)$_2$(depe)$_2$]$^{2+}$ (22)	295	-0.48	should be possible
[Fe(CO)$_2$(dmpe)$_2$]$^{2+}$ (23)	295	-0.16	should be possible
[Fe(CO)$_2$(opdp)$_2$]$^{2+}$ (24)	295	-1.08	should be possible
[Fe(CO)$_2$(dppm)$_2$]$^{2+}$ (25)	295	-0.52	should be possible
[Fe(CO)$_2$(dppe)$_2$]$^{2+}$ (26)	295	-0.56	should be possible
[Fe(N$_2$)$_2$(depe)$_2$]$^{2+}$ (27)	295	$+1.00$	should be possible
[Fe(N$_2$)$_2$(dmpe)$_2$]$^{2+}$ (28)	295	$+1.32$	should be possible
[Fe(N$_2$)$_2$(opdp)$_2$]$^{2+}$ (29)	295	$+0.40$	should be possible
[Fe(N$_2$)$_2$(dppe)$_2$]$^{2+}$ (30)	295	$+0.92$	should be possible
[Fe(N$_2$)$_2$(dppm)$_2$]$^{2+}$ (31)	295	$+0.96$	should be possible
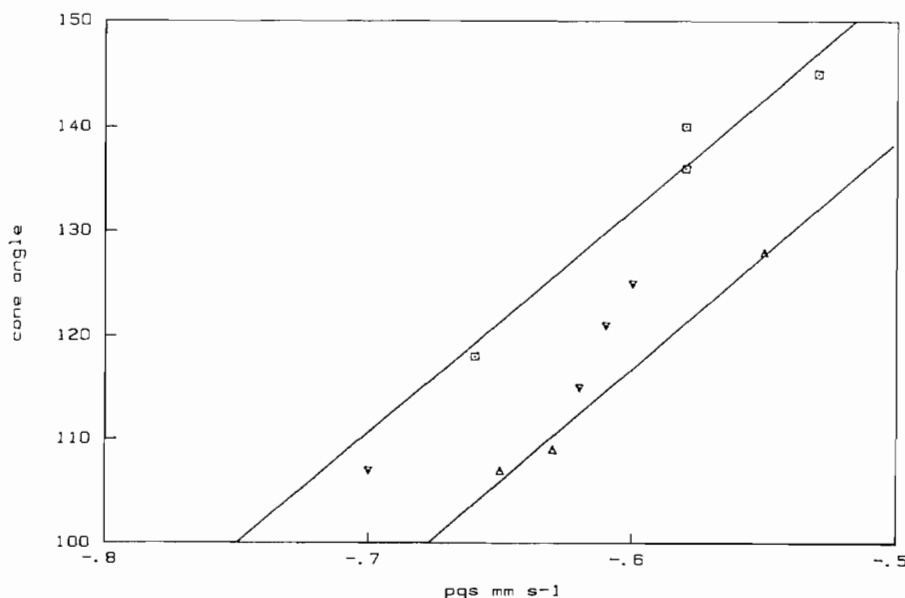
Fig. 2. Plot of *p.q.s.* (mm s^{-1}) against their cone angle data for the phosphine and phosphite ligands given in Table 6. □ phosphines, △ phosphites, ▽ bidentate phosphines. Straight lines are linear regression fits.

TABLE 6. *p.q.s.* data and cone angles for phosphorus ligands

Ligand	*p.q.s.* (mm s^{-1})[a]	Cone angle (°)[b]
PPh$_3$	−0.53	145
PPh$_2$Et	−0.58	140
PPh$_2$Me	−0.58	136
PMe$_3$	−0.66	118
P(OPh)$_3$	−0.55	128
P(OEt)$_3$	−0.63	109
P(OMe)$_3$	−0.63	107
1/2dppe	−0.60	125
1/2depe	−0.62	115
1/2dmpe	−0.70	107
1/2dppm	−0.61	121

[a]*p.q.s.* data from refs. 3, 12 or this work. [b]Cone angle data from ref. 21.

p.q.s. values and cone angles

If the cone angles [21] are plotted against the *p.q.s.* values [12] for the phosphorus ligands a trend emerges (Fig. 2, data Table 6). The smaller *p.q.s.* values correlate with the greater cone angles (steric bulk).

The calculation of cone angle assumes a set phosphorus to metal distance of 2.28 Å [21, 26]. This is satisfactory for low-spin iron(II) complexes (Table 3). Increasing the angles between phosphorus substituents decreases s-electron character in the phosphorus lone pair [21]. In reality, changing the substituents on the P atom modifies its electronegativity and will affect bond angles and distances [21]. Although it is difficult to separate electronic and steric factors, the cone angle calculations are essentially steric. The *p.q.s.* values show only charge effects but ligand size affects geometry and some steric effect will be hidden in the values. So the cone angles and the *p.q.s.* values will already each carry some information in common. Nevertheless, the trend does allow a tentative comment on the chemistry. The bidentate phosphine ligands have bonding properties (both electronic and steric) that lie between those of triorganic phosphines and triorganic phosphites of similar stereochemistry around the phosphorus atoms.

Conclusions

The bonding of bidentate phosphine ligands to iron(II) has been rationalised by using *p.q.s.* values derived from Mössbauer spectroscopic quadrupole splittings.

Low-spin *trans*-A$_2$B$_2$Fe(II) (B = bidentate phosphine) complexes have QS values in the range −1.84 to +1.8 mm s^{-1}. Compounds yet to be prepared but having QS values in this range may well be stable provided steric factors do not interfere.

The *p.q.s.* values for the phosphorus ligands have been shown to correlate with the cone angles (high *p.q.s.* values going with small cone angles). The bidentate phosphines are better σ-donors than the monodentate phosphines · but not as good as monodentate phosphites with comparable cone angles.

The ligand dppe only forms $trans$[FeX$_2$(dppe)$_2$] complexes if the anionic ligands are too large to form cis species. If the ligands are larger still, the complexes are unstable with respect to tetrahedral complexes, e.g. [FeX$_2$(dppe)$_2$] (X = Cl, Br, I).

The $p.q.s.$ value derived in this work for CO provides further evidence for the ability of this ligand to vary its bonding properties [12].

Acknowledgement

References

1 R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, (1969) 2145.

2 (a) G. M. Bancroft, M. J. Mays and B. E. Prater, *Discuss. Faraday Soc.*, *47* (1969) 136; (b) *J. Chem. Soc. A*, (1970) 956.

3 G. M. Bancroft, R. E. B. Garrod and A. G. Maddock, *J. Chem. Soc. A*, (1971) 3165.

4 R. R. Berrett and B. W. Fitzsimmons, *J. Chem. Soc. A*, (1967) 525.

5 M. G. Clark, *Mol. Phys.*, *20* (1971) 257.

6 R. A. Mazak and R. L. Collins, *J. Chem. Phys.*, *51* (1969) 3220.

7 J. Ensling, P. Gütlich, K. M. Hasselbach and B. W. Fitzsimmons, *J. Chem. Soc. A*, (1971) 1940.

8 R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, *4* (1970) 65.

9 J. E. Barclay, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc., Dalton Trans.*, (1988) 2865.

10 G. M. Bancroft, K. D. Butler and E. T. Libbey, *J. Chem. Soc., Dalton Trans.*, (1972) 2643.

11 G. M. Bancroft, M. J. Mays and B. E. Prater, *J. Chem. Soc., Chem. Commun.*, (1968) 1575.

12 G. M. Bancroft and E. T. Libbey, *J. Chem. Soc., Dalton Trans.*, (1973) 2103.

13 G. J. Leigh, personal communication.

14 J. E. Barclay, A. Hills, D. L. Hughes and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, (1988) 2871.

15 E. B. Lobkovskii, M. V. Antipin, A. P. Borisov, V. D. Makhaev, K. N. Simenenko and Yu. T. Strukov. *Koord. Khim.*, *6* (1960) 1267.

16 R. J. Puddephatt, *Chem. Soc. Rev.*, *12* (1983) 99.

17 M. Antberg and L. Dahlenburg, *Inog. Chim. Acta*, *104* (1985) 51.

18 See ref. 13 of ref. 19 below.

19 M. Di Vaira, S. Midollini and L. Sacconi, *Inorg. Chem.*, *20* (1981) 3430.

20 F. Cecconi, M. Di Vaira, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chem. 20* (1981) 3423.

21 C. A. Tolman, *Chem. Rev.*, *77* (1977) 344.

22 R. V. Parish and N. F. Riley, *J. Chem. Soc., Dalton Trans.*, (1974) 482.

23 G. M. Bancroft, M. J. Mays and B. E. Prater, *J. Chem. Soc., Chem. Commun.*, (1969) 585.

24 G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays and B. E. Prater, *J. Am. Chem. Soc.*, *94* (1972) 647.

25 M. G. Clark, A. G. Maddock and R. H. Platt, *J. Chem. Soc., Dalton Trans.*, (1972) 281.

26 C. A. Tolman, *J. Am. Chem. Soc.*, *92* (1970) 2956.