Mössbauer and Preparative Studies of Some Iron(II) Complexes of Diphosphines†

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Analytical and Mössbauer spectral data show that $Ph_2PCH_2CH_2PPh_2$ (dppe) forms adducts $[FeCl_2(dppe)]$ and $[FeI_2(dppe)]$, and that $[FeCl_2(dppe)_2]$ does not exist. The phosphine 1,2-$C_6H_4(PPh_2)_2$ (opdp) forms adducts $FeX_2(opdp)_2$, which exists in one form (high-spin, *trans* octahedral) for X = Cl, and in two isomeric forms for X = Br or I. One isomer for X = I is high-spin, *trans* octahedral, and the other is ionic low-spin, and five-co-ordinate. A comparison is made of these structures and of their Mössbauer spectra with those of derivatives of $Me_2PCH_2CH_2PMe_2$, $Et_2PCH_2CH_2PEt_2$, $Pr^i_2PCH_2CH_2Pr^i_2$, and $Ph_2PCH_2PPh_2$.

There has been a considerable amount of work on adducts of iron(II) halides and diphosphines such as $Ph_2PCH_2CH_2PPh_2$ (dppe), [1–4] $Et_2PCH_2CH_2PEt_2$ (depe),[3] and $Me_2PCH_2CH_2PMe_2$ (dmpe).[5] Although iron(II) is not considered to be a particularly good Lewis base for phosphines, several stable complexes (with varying degrees of dioxygen sensitivity) have been isolated. These have the formulae $[FeX_2(\text{diphosphine})]$ or $[FeX_2(\text{diphosphine})_2]$ (X = halide), although reasons for the two different classes are not clear.

We have been interested in ascertaining whether iron can support the same kind of dinitrogen-residue chemistry which we have established for molybdenum and tungsten. This is because iron rather than molybdenum or vanadium may be the active element at the active site of certain nitrogenases. Several dinitrogen complexes of iron are known, [6] although only a very few, containing very reduced iron [iron(0) or even iron(−II)], contain dinitrogen activated with respect to its protonation. Iron compounds containing groups such as $=NNH_2$ and $=NNR_2$ (R = alkyl or aryl) are rare,[7] although the molybdenum and tungsten homologues are well established.

Our intention was to explore the chemistry of these groups when bound to iron. Since, formally, a hydrazide(2−) residue should impose at least two units of oxidation state above zero on an iron to which it is bound, any subsidiary ligands should be neutral, or confer only one unit of negative charge in all, otherwise the overall oxidation state of iron will be IV or more. We chose to use tertiary phosphines because of our prior experience with them, and we report here our investigations of the reactions of selected diphosphines with FeX_2 (X = Cl, Br, or I).

The diphosphines depe and dmpe react with $FeCl_2$ to form complexes of formula $[FeCl_2(\text{diphosphine})_2]$,[3,5] although recently a complex $[FeCl_2(depe)]$ has been obtained by an indirect route.[8] Green $[FeI_2(dmpe)_2]$ was observed to lose diphosphine and turn yellow on standing,[3] although no products were identified. Iron(II) chloride and dppe are reported by one group of workers to give rise to white crystalline $[FeCl_2(dppe)_2]$ [1] whereas others report that these reactants yield products which were not well defined and readily dissociated.[3] Nevertheless, Mössbauer evidence has been adduced by yet another group to show that both $[FeCl_2(dppe)]$ and $[FeCl_2(dppe)_2]$ are produced by the reaction of $[Fe(C_2H_4)(dppe)_2]$ with $SiMeCl_2H$.[4] To add to the confusion, $FeCl_2\cdot 4H_2O$ and dppe are reported to yield green $[FeCl_2(dppe)]$ [the bromide analogue yields $FeBr_2(dppe)(H_2O)]$[2] and $[FeH(N_2)(dppe)_2]^+$ is said to react with HCl to yield white $[FeCl_2(dppe)]$.[8] Finally, $[FeI_2(dppe)]$ has been isolated from the reaction of $[FeH(C_6H_4PPhCH_2CH_2PPh_2)(dppe)]$ with iodine.[9]

In contrast to this apparent duality of behaviour, the diphosphines $Ph_2PCH{=}CHPPh_2$ (dppen) and $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$ (bdpp) form complexes of the type $[FeX_2(\text{diphosphine})_2]$. These are high-spin iron(II) compounds.[10,11] For bdpp, the structures have been shown to be *trans* octahedral, with a terminal phosphorus of each bdpp being unco-ordinated.[10] $[FeCl_2(dppen)_2]$ undergoes a transition to a low-spin form on cooling, and $[FeCl_2(dppen)_2]\cdot 2Me_2CO$ has been structurally characterized as a high-spin form at 250 K and low-spin at 130 K,[11] with a spin-crossover at an intermediate temperature. These materials, and related structures determined by us, will be discussed in a following paper.

We decided to carry out a systematic study of some of these complexes. The aims were to establish oxidation state, geometry, and co-ordination number. We also investigated some iron(II) chemistry of $Ph_2PCH_2PPh_2$ (dppm) because of its restricted bite, 1,2-$C_6H_4(PPh_2)_2$ (opdp) because of the geometry imposed by the *o*-phenylene ring, and $Pr^i_2PCH_2CH_2PPr^i_2$ (dippe) because of its bulk.

Some information on related systems based upon $Me_2PCH_2PMe_2$ (dmpm) has already appeared,[12] and complexes $[FeX_2(dippe)]$ (X = Cl, Br, or I) have been referred to, but not described in detail.[13,‡]

In this paper we report the results of our Mössbauer spectroscopic and magnetic studies.

Results and Discussion

The complexes discussed are presented in Table 1 together with their colours, analytical data, magnetic moments, and conductivities. Their Mössbauer parameters are presented in Table 2. It is noteworthy that adducts of iron(II) halides with opdp, dppe, dippe, or dppm are often of high-spin, though they all contain strong-field phosphorus ligands.

Complexes containing dppe.—Both anhydrous $FeCl_2$ and anhydrous FeI_2 react with one molar equivalent of dppe in

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† *Non-S.I. unit employed:* mmHg ≈ 13.6 × 9.8 Pa.

‡ *Note added at proof:* The structure of $[FeCl_2(dippe)]$ has now been described in detail, and confirms our inferences from Mössbauer data (A. R. Hermes and G. S. Girolami, *Inorg. Chem.*, 1988, **27**, 1775).

Table 1. Characterization of iron(II) compounds

Complex	Colour	Analysis[a] (%) C	H	N	Yield (%)	Magnetic moment/B.M.[b] (solid state, 295 K)	Conductivity/ ohm^{-1} cm^2 mol^{-1}
(1) [$FeCl_2$(dppe)]	White	59.3 (59.5)	4.7 (4.6)	0.0 (0.0)	72	Paramagnetic[c]	*d*
(2) [FeI_2(dppe)]	Yellow	43.0 (44.1)	3.6 (3.4)	0.0 (0.0)	68	5.2	74[e]
(6) [FeI_2(dmpe)$_2$]	Green	23.6 (23.6)	5.0 (5.2)	0.0 (0.0)	85	Diamagnetic	0[f]
(10) [FeI_2(dppm)$_2$]	Green	50.4 (50.0)	3.8 (3.9)	0.0 (0.0)	30	5.23	0[f]
(11) [$FeCl_2$(opdp)$_2$]	Yellow	69.9 (70.6)	4.9 (4.7)	0.0 (0.0)	70	5.02	0[f]
(12) [$FeBr_2$(opdp)$_2$]	Yellow	64.3 (65.0)	4.6 (4.3)	0.0 (0.0)	42	5.13	0[f]
(13) [FeI_2(opdp)$_2$]	Yellow	59.1 (59.9)	4.3 (4.0)	0.0 (0.0)	—	6.36	0[f]
(15) [FeI(opdp)$_2$]I·2CH_2Cl_2	Red	53.7 (54.2)	4.1 (3.8)	0.0 (0.0)	40	Diamagnetic	37[f]
(16) [Fe(MeCN)$_2$(dppe)$_2$]I_2	Pink	56.1 (56.5)	4.5 (4.6)	2.2 (2.4)	52	—	115[e]
(17) [Fe(MeCN)$_2$(depe)$_2$]I_2	Yellow	37.6 (35.8)	6.8 (6.7)	4.5 (3.5)	53	Diamagnetic	173[e]
(18) [Fe(MeCN)$_2$(dmpe)$_2$]I_2	Yellow	27.4 (27.8)	5.5 (5.5)	3.9 (4.1)	70	Diamagnetic	175[g]
(19) [Fe(MeCN)$_2$(opdp)$_2$]I_2	Red	57.7 (59.8)	4.6 (4.2)	2.0 (2.2)	100	—	132[e]
(20) [Fe(MeCN)$_2$(dppm)$_2$]I_2	Pink	56.1 (55.9)	4.3 (4.3)	2.4 (2.4)	—	—	174[g]
(21) [Fe(MeCN)$_2$(dppm)]I_2	Red	45.8 (45.8)	3.7 (3.6)	3.2 (3.6)	—	—	153[g]

[a] Required values in parentheses. [b] B.M = 9.274×10^{-24} J T^{-1}. [c] A value of 5.1 B.M. is quoted in ref. 8. [d] Too insoluble. [e] In nitromethane, 295 K. [f] In dichloromethane, 295 K. [g] In acetonitrile, 295 K.

Table 2. Mössbauer parameters of some iron(II) derivatives at *ca.* 77 K

Compound		δ/mm s^{-1}	Q.s./mm s^{-1}	Γ*/mm s^{-1}
(1) [$FeCl_2$(dppe)]		0.74(1)	2.54(1)	0.16(1)
(2) [FeI_2(dppe)]		0.67(1)	3.14(1)	0.16(1)
$FeCl_2$ + 2dppe	60%	0.75	2.54	0.21(1)
	40%	1.22	0.95	0.15(1)
[$FeCl_2$(dppe)] + dppe		0.75	2.54	0.17(4)
[$FeCl_2$(dppe)$_2$]'	30%	0.71(1)	2.53(1)	0.14(1)
	70%	1.01(2)	2.54(2)	0.21(2)
$FeCl_2$	91%	1.22(1)	0.95(1)	0.15(1)
	8%	1.23(2)	2.61(1)	0.14(1)
(3) [$FeCl_2$(dippe)]		0.72(1)	2.98(1)	0.20(1)
(4) [FeI_2(dippe)]		0.87(1)	3.09(1)	0.21(1)
(5) [$FeCl_2$(dmpe)$_2$]		0.37(1)	1.70(1)	0.14(1)
(6) [FeI_2(dmpe)$_2$]		0.40(1)	1.74(2)	0.20(1)
(7) [$FeCl_2$(depe)$_2$]	Ref. 18	0.41	1.42	
	This work	0.37(1)	1.44(1)	0.16(1)
(8) [$FeBr_2$(depe)$_2$]	Ref. 18	0.47	1.45	
(9) [FeI_2(depe)$_2$]	Ref. 18	0.48	1.38	
(10) [FeI_2(dppm)$_2$]		0.67(1)	3.13(1)	0.19(1)
(11) [$FeCl_2$(opdp)$_2$]		0.95(1)	2.26(1)	0.14(1)
(12) [$FeBr_2$(opdp)$_2$]		0.96(1)	2.48(1)	0.14(1)
(13) [FeI_2(opdp)$_2$]		0.96(1)	2.29(1)	0.21(1)
(14) FeI_2(opdp)$_3$	77%	0.45(1)	0.80(1)	0.26(1)
	14%	0.48(1)	2.49(1)	0.14(1)
	8%	1.3(1)	2.6(2)	0.20(2)
(15) [FeI(opdp)$_2$]I·2CH_2Cl_2		0.49(1)	2.43(1)	0.14(1)
(16) [Fe(MeCN)$_2$(dppe)$_2$]I_2		0.38(1)	0.35(1)	0.16(1)
(17) [Fe(MeCN)$_2$(depe)$_2$]I_2		0.23(1)	1.00(1)	0.15(1)
(18) [Fe(MeCN)$_2$(dmpe)$_2$]I_2		0.39(1)	0.36(1)	0.18(1)
(19) [Fe(MeCN)$_2$(opdp)$_2$]I_2		0.38(1)	0.00(1)	0.22(1)
(20) [Fe(MeCN)$_2$(dppm)$_2$]I_2		0.26(1)	0.73(1)	0.18(1)
(21) [Fe(MeCN)$_2$(dppm)]I_2		0.28(1)	0.81(2)	0.19(2)

* Width at half height.

refluxing benzene, toluene, or dichloromethane to form white products which analyse as 1:1 adducts. The product [$FeCl_2$(dppe)] **(1)** appears identical to the material recently reported by Henderson[8] although satisfactory analyses were not obtained.

The reaction of iron(II) chloride with dppe in 1:2 molar ratio in benzene at reflux is reported[1] to give [$FeCl_2$(dppe)$_2$], though in other hands the product was not characterizable.[3] In order to clarify this, we prepared off-white crystalline materials by reaction of anhydrous $FeCl_2$ with dppe in various molar ratios (1.0:0.5, 1.0:1.0, 1.0:1.5, or 1.0:2.0) in refluxing benzene. We found that it is indeed possible to obtain a material analysing as [$FeCl_2$(dppe)$_2$] starting with a 1:2 molar ratio. However, Mössbauer spectroscopy revealed that this product is a mixture, the only iron-containing species being [$FeCl_2$(dppe)] and $FeCl_2$, anhydrous or hydrated (see below and Table 2). Further, a comparison of the Mössbauer parameters of our product with the values assigned to [$FeCl_2$(dppe)$_2$] and [$FeCl_2$(dppe)] by

Parish and Riley,[4] and to [$FeCl_2$(dppe)] by Baker and Lutz[2] leaves little doubt that [$FeCl_2$(dppe)] is a distinct species, whereas the existence of [$FeCl_2(dppe)_2$] as described spectroscopically by Parish and Riley[4] cannot be confirmed. The parameters reported by them for [$FeCl_2(dppe)_2$] are not consistent with our data, although this may be because their values were obtained by deconvolution of spectra of mixtures, of which [$FeCl_2(dppe)_2$] constituted at best *ca.* 50%.

To check further the existence of [$FeCl_2(dppe)_2$], we showed that heating dppe with [$FeCl_2$(dppe)] in refluxing benzene produces no new iron-containing species. We conclude that, despite the fact that both [$FeH_2(dppe)_2$] and [FeHCl$(dppe)_2$] are known,[1] and that $FeCl_2(dppe)_2$, although a mixture, can be reduced by Li[AlH_4] to the former dihydride, [$FeCl_2(dppe)_2$] does not exist.

The complex [FeI_2(dppe)] (**2**) prepared by us corresponds to the material isolated from the reaction of [$FeH(C_6H_4PPhCH_2CH_2PPh_2)$(dppe)] with iodine.[9] Not surprisingly, in view of our experience with $FeCl_2$, we found no evidence for the existence of [$FeI_2(dppe)_2$]. It is tempting to assume that the reason that only one dppe co-ordinates to the small iron(II) is steric. However, as discussed below, the situation is more complex. For example, it is not at all clear why a high-spin form of [$FeCl_2(dppe)_2$] does not exist.

Complexes [$FeCl_2$(dppe)] (**1**)[2,8] and [FeI_2(dppe)] (**2**) (Table 1) are high-spin and paramagnetic. Their Mössbauer parameters at 80 K fall into the range expected of tetrahedral iron(II). The isomer shift and quadrupole splitting (q.s.) of [$FeCl_2$(dppe)] do not, however, exhibit the temperature dependence considered typical of tetrahedral iron(II) complexes,[14] and, in fact, they do not change significantly between 80 K and room temperature (Table 2, but see also ref. 2). This lack of temperature dependence has been ascribed to distortion from idealized tetrahedral symmetry,[2] and we suggest that the replacement of chloride by phosphorus splits $d_{x^2-y^2}$ and d_{z^2} such that the thermal populations do not change significantly in the temperature range investigated. It should be noted that the temperature dependence of the Mössbauer spectra of tetrahedral iron(II) complexes was observed in anionic complexes,[14] not neutral complexes such as those under consideration here.

The assignment of tetrahedral structures to the two dppe complexes is supported by the chemistry of the recently reported[13] complexes [FeX_2(dippe)] (X = Cl, Br, or I). In addition, the structure of [$Fe(CH_2Ph)_2$(dippe)] has been shown by *X*-ray structure analysis to be tetrahedral.[13] The Mössbauer data in Table 2 are clearly consistent with high-spin tetrahedral structures for [FeX_2(dippe)] [X = Cl (**3**) or I (**4**)].

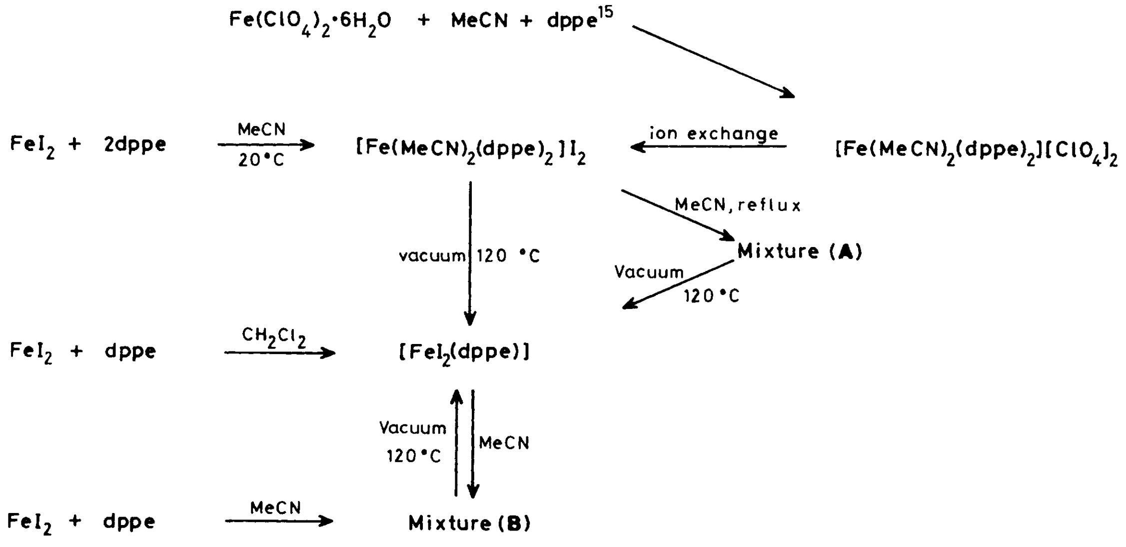
We were also able to prepare a complex containing two dppe molecules, [$Fe(MeCN)_2(dppe)_2]I_2$,[14] by direct reaction of FeI_2 with dppe in MeCN. The complex [$Fe(MeCN)_2(dppe)_2]^{2+}$ has been previously prepared[15] from the reaction of $Fe(ClO_4)_2\cdot 6H_2O$ with dppe, and characterized in considerable detail. We found that the chemistry it displays is dominated by the ready loss of a dppe molecule, presumably due to the small size of iron and the weakness of the iron–phosphorus bonds. The interconversions observed are shown in the Scheme. The products (**A**) and (**B**) were provisionally identified as FeI_2(MeCN)(dppe) (orange) and $FeI_2(MeCN)_2$(dppe) (pink), respectively. However, the analyses corresponding to these compositions were not reproducible, and the Mössbauer spectra showed unequivocally that they are mixtures of two or three species, one component of (**B**) being [$Fe(MeCN)_2(dppe)_2]^{2+}$ and another possibly [FeI_2(dppe)].

These findings led us to investigate two further bulky phosphines, dppm and opdp.

Complexes containing dppm.—We found no reports in the literature of iron halide adducts with dppm, although the methyl analogue, dmpm, forms complexes such as *cis*-[$FeMe_2(dmpm)_2$], [$Fe(dmpm)_3$] in which one dmpm is monodentate, and [$Fe(dmpm)_3]I_2$.[12]

We were not able to isolate any characterisable product from the reactions of $FeCl_2$ with dppm, and Mössbauer spectroscopy showed that the materials obtained were mixtures. On the other hand, we were able to isolate [$FeI_2(dppm)_2$] (**10**), with a Mössbauer spectrum (Table 2) not very different in form and behaviour from that of [FeI_2(dppe)] (**2**). Presumably the former has an analogous tetrahedral high-spin structure. A tetrahedral geometry implies that the dppm ligands are monodentate in this case. This is rationalized in terms of the excessive strain which would be imposed on bidentate dppm bound to iron(II).

The reaction of FeI_2 with an excess of dppm in acetonitrile produces mixtures. Careful crystallization of the product enabled us to isolate compounds analysing as [$Fe(MeCN)_2(dppm)_2]I_2$ (**20**) and [$Fe(MeCN)_2(dppm)]I_2$ (**21**), both 1:2 electrolytes in MeCN (Table 1). Their Mössbauer spectra are not very different, but [$Fe(MeCN)_2(dppm)_2]I_2$ would appear to be of the same structure as the other bis(acetonitrile)bis(diphos-



Scheme.

phine) adducts which implies a strained PCPFe ring. Compound **(21)** may also contain octahedral iron(II) in the solid state, even if not in solution. This is not a very easy system to analyse, and by far the major part of the product material was never properly characterized.

Complexes containing opdp.—The diphosphine opdp has only become available in quantity relatively recently,[16] and no adducts with iron(II) halides have been reported. The product obtained by us is a function of X in FeX_2. For FeI_2, the immediate product is a dark brown material analysing for $FeI_2(opdp)_3$ **(14)**, which, judging from the Mössbauer spectrum, is a mixture of one major constituent (*ca.* 75%) and two minor (*ca.* 15 and 10%). None has been characterized, but recrystallization from dichloromethane yields red crystals unambiguously identified by *X*-ray crystal structure analysis as $[FeI(opdp)_2]I\cdot 2CH_2Cl_2$ **(15)**. The structure will be described in detail in the following paper.[17] On one occasion we were able to obtain a yellow form by recrystallization from a very dilute solution in dichloromethane. This appears to be a non-conducting isomer, and, by analogy with the structure of $[FeCl_2(opdp)_2]$ (see below) and by Mössbauer spectroscopy, has a *trans*-octahedral structure.

Reaction of $FeBr_2$ with opdp gives a product analysing as $[FeBr_2(opdp)_2]$ **(12)** which apparently exists in two isomeric forms, yellow and red. The red form, which seems to be obtained preferentially from dichloromethane, is probably analogous to the five-co-ordinate iodide, and the yellow form, to judge from the Mössbauer spectrum, conductivity and magnetic moment, is presumably six-co-ordinate.

Iron(II) chloride gives rise to one form only, the yellow six-co-ordinate species. Recrystallization of $[FeI(opdp)_2]I\cdot 2CH_2Cl_2$ **(15)** from MeCN gives rise to $[Fe(MeCN)_2(opdp)_2]I_2$ **(19)**. This is six-co-ordinate and has a structure, as determined by *X*-ray structure analysis, precisely analogous to that of the dppe homologue.[17] The diphosphine opdp thus exhibits rather different properties from those of dppm, and, more especially, dppe. The sizes of dppe and opdp are not very different, and their steric requirements are rather similar. Yet opdp can still bind to iron in the ratio 2:1, if necessary losing a halide from the co-ordination sphere. The loss of halide is less favoured as the size of the halide decreases. The consequence is five-co-ordination. In contrast, dppe complexes retain both halides and hence only one dppe can bind. At this stage, we cannot decide whether this represents the effect of relative Fe–P bond strengths, or relative steric requirements.

Complexes containing dmpe and depe.—The diphosphines dmpe and depe are relatively small, strong donors, and have similar behaviour. Green $[FeCl_2(dmpe)_2]$ **(5)** has been prepared by others, and has a *trans* structure,[10] and $[FeX_2(depe)_2]$ [X = Cl **(7)**, Br **(8)**, or I **(9)**] are already known.[3,18] We have synthesized $[FeI_2(dmpe)_2]$ **(6)** (green) to compare it with $[FeI_2(depe)_2]$ (yellow) **(9)**. The former turns yellow after standing under dinitrogen for some months at room temperature. Perhaps this is an an isomerization, although we now know that yellow $[FeI_2(depe)_2]$ has a *trans*-octahedral structure[17] which also characterizes $[FeCl_2(dmpe)_2]$.

The chloro complexes with these two diphosphines react with MeCN, but on attempting to isolate the products, all MeCN is lost, regenerating the green chlorides. However, both iodides dissolve completely in MeCN, yielding pink solutions. We were able to obtain pink solids from such solutions, but they apparently contained less than one nitrogen per iron. In general, the pink solutions gave rise to yellow crystalline solids with analyses corresponding to $[Fe(MeCN)_2(depe)_2]I_2$ **(17)** and $[Fe(MeCN)_2(dmpe)_2]I_2$ **(18)**. These results presumably reflect the poorer donor power of I^- compared to both MeCN and Cl^-. The stereochemistry of these bis(acetonitrile) materials is probably *trans* octahedral {*cf.* yellow, *trans*-octahedral $[Fe(MeCN)_2(dmpe)_2]^{2+}$, and pink $[FeCl(MeCN)(dmpm)_2]^{+}$ [19]}.

Despite the differences in colour, all the $[FeX_2(depe)_2]$ and $[FeX_2(dmpe)_2]$ compounds would appear to have the *trans* configuration, demonstrated by *X*-ray structure analyses for $[FeCl_2(dmpe)_2]$ [10] and $[FeI_2(depe)_2]$,[17] and by dipole moment data for $[FeCl_2(depe)_2]$.[3] Bancroft *et al.*[18] also used quadrupole splittings to make predictions of *cis* and *trans* stereochemistries because, in general, a *cis* stereochemistry would be expected to produce a less symmetrical field than a *trans* stereochemistry. Our results show that the difference in q.s. between dmpe (these are all *ca.* 1.70 mm s^{-1}) and depe (all *ca.* 1.40 mm s^{-1}) complexes of the type $[FeX_2(diphosphine)_2]$ cannot be a reflection of different stereochemistries. The Mössbauer data are best interpreted in terms of the very extensive series of compounds studied by Bancroft *et al.*[18] some years ago. Our data for $[FeX_2(dmpe)_2]$ [X = Cl **(5)** or I **(6)**], fall into the pattern they reported for $[FeX_2(depe)_2]$ [X = Cl **(7)**, Br **(8)**, or I **(9)**] namely that the isomer shifts are in the region expected for low-spin iron(II) in an octahedral environment. In addition, $[FeCl_2(dmpe)_2]$ has also been shown to be diamagnetic.[5] Bancroft *et al.*[18] also reported a series of 'partial shift' values as follows: Cl^-, 0.10; Br^-, 0.13; I^-, 0.13; depe/2, 0.06; dmpe/2, 0.05 (all ±0.01 mm s^{-1}). The difference in shifts between $[FeCl_2(dmpe)_2]$ and $[FeI_2(dmpe)_2]$ is perhaps rather less than one might expect from comparison with the depe compounds. Comparison of corresponding depe and dmpe complexes suggests that the partial shift for dmpe/2 is *ca.* 0.04 mm s^{-1}. This can reasonably be interpreted in terms of dmpe being a better σ donor than depe. However, the octahedral MeCN adducts do not fit this pattern, since the isomer shift of the depe compound is less than that of the dmpe derivative. Presumably MeCN is a better π acceptor in the former compound, or else a less good σ donor. The second possibility seems to fit the case better.

Conclusions

The structural observations discussed above will be rationalized here in terms of the Mössbauer data. Quadrupole splittings are a measure of the electronic asymmetry at the nucleus. In ^{57}Fe spectroscopy, they arise from a combination of the ligand field, and the distribution of electrons in the iron orbitals. In low-spin complexes, it therefore depends predominantly on the nature of the ligands and their geometrical arrangement in the first co-ordination sphere. Since replacement of halide by MeCN leads to a drop in quadrupole splitting, this is taken to mean that the donor properties of MeCN are much more akin to those of phosphine than of halide. The fact that the quadrupole splitting in $[Fe(MeCN)_2(opdp)_2]I_2$ is zero implies that the donor–acceptor properties of MeCN are very similar to those of an opdp phosphorus atom. If we assume that the behaviour of MeCN does not change very much wherever it is co-ordinated, then the relative quadrupole splittings in the compounds $[Fe(MeCN)_2(diphosphine)_2]^{2+}$ can give the order of donor power of the diphosphines. In addition, dppen forms $[FeCl_2(dppen)_2]$ which is high-spin at 295 K and low-spin at 130 K,[11] and may dissociate to give $[FeCl_2(dppen)]$ in solution {$[FeBr_2(dppen)]$ has been partially characterized in the solid state[20]}. Because $[FeCl_2(opdp)_2]$ is still high-spin at liquid-nitrogen temperature (Mössbauer spectrum), we can include dppen in the series of donor power below dppe. The near equivalence of dmpe and dppe may, at first sight, seem somewhat surprising: MeCN, opdp < dppen < dppe, dmpe < dppm < depe, but clearly any difficulty in accommodating dppe due to its bulk does not make it appreciably weaker a donor than dmpe. It is not necessary that the phosphines which provoke high-spin should contain phosphorus atoms which are conjugated, since two which cause high-spin (opdp and dppen) do contain conjugated phosphorus atoms and a further two which cause high-spin (dppe and bdpp) do not. Also, the situation is clearly balanced quite critically since [FeHCl(opdp)$_2$][21] has a typical octahedral low-spin Mössbauer spectrum [shift 0.36(1) mm s^{-1}, q.s. 0.75(1) mm s^{-1}]. However, a comparison of shifts in [Fe(MeCN)$_2$(diphosphine)$_2$]$^{2+}$ along the series dmpe 0.39, dppe 0.38, opdp 0.38, dppm 0.26, depe 0.23 mm s^{-1}, although not incompatible with the series inferred from quadrupole splittings, should warn against a superficial interpretation of the data in the light of relative steric or electronic effects. Nevertheless, the relative donor powers of the diphosphines in the above series can explain the principal spin states of their complexes of iron(II) as found in this work.

The strongest donors, depe and dmpe, always produce low-spin complexes. The medium-strength donors, dppe and dppm, form high-spin tetrahedral complexes when one of them is present in a complex, but low-spin octahedral complexes when two are present. Steric influences make dippe a medium-strength donor rather than a strong donor. The weakest donors, opdp and dppen, form high-spin iron(II) complexes at room temperature.

Lastly, we consider the opdp compounds (**11**)—(**14**). The yellow complexes [FeX$_2$(opdp)$_2$] have similar high-spin, octahedral structures, as discussed above. Our data argue for considerable ionic character in the bonds. This may be a consequence of steric crowding and the consequent long bonds. However, the compounds are non-conductors in solution in nitromethane, and have magnetic moments equivalent to the spin-only value, making due allowance for experimental error. On the other hand, [FeI(opdp)$_2$]I·2CH$_2$Cl$_2$ retains its field asymmetry and has a typical low-spin isomer shift. There is no obvious precedent for comparison with this five-co-ordinate structure, although the co-ordination is not unique for iron(II) {*cf.* [FeI(bdpp)$_2$]BPh$_4$[10]}. On the basis of the shift alone, the opdp iodide could be an $S = 1$ compound. It is not obvious why the loss of one iodide from the co-ordination sphere of [FeI$_2$(opdp)$_2$] should provoke a change from high-spin to low-spin. This observation merits further investigation.

Finally, we note that our spectrum of FeCl$_2$, made by the method of Kovacic and Brace,[22] has Mössbauer parameters that are significantly different from those reported previously.[23] We suspect that since anhydrous FeCl$_2$ is very hygroscopic, the older data may have been spoiled by the presence of moisture as well as by the instrumental instability characteristic of the earlier spectrometers.

Experimental

All manipulations were carried out under dry dinitrogen using dried solvents. Iron(II) iodide was made by reaction of metallic iron with iodine,[24] but using MeOH rather than MeCN, and anhydrous iron(II) chloride by dehydration of commercial hydrated iron(II) chloride.[21] The ligands opdp,[16] dppe, dppm, dmpe,[25] dippe,[25] and depe[25] were prepared by standard methods.

Mössbauer spectra were recorded on powdered samples compressed into aluminium holders. The samples were placed in the holders under dinitrogen, quenched to 78 K and transferred to a cryostat. The spectrometer (previously described)[26] was calibrated with a natural iron absorber 25-μm thick, and this was used as zero for the isomer shift measurements. The spectra were computer fitted.[26]

Magnetic moments were determined by the Faraday method using Hg[Co(CNS)$_4$] as standard.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*di-iodoiron*.—Iron(II) iodide (2.10 g, 6.8 mmol) and dmpe (2.03 cm^3, 13.5 mmol) were stirred in CH$_2$Cl$_2$ (25 cm^3) for several hours. The solution was taken to dryness at 10^{-3} mmHg and the *residue* washed thoroughly with diethyl ether. Yield: 3.5 g.

Bis(*acetonitrile*)*bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*iron Di-iodide*.—Iron(II) iodide (0.97 g, 3.1 mmol) and dmpe (0.94 cm^3, 6.3 mmol) in MeCN (25 cm^3) were stirred for 2 h, producing a red solution. The volume was reduced to *ca.* 10 cm^3 at 10^{-3} mmHg, which produced a *yellow solid*. This was filtered off, washed with diethyl ether, and dried at 10^{-3} mmHg. Further yellow solid could be obtained by cooling the filtrate further and by reducing the volume. Yield: 1.5 g.

Bis(*acetonitrile*)*bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*iron Di-iodide*.—Iron(II) iodide (0.89 g, 2.9 mmol) was stirred in MeCN (25 cm^3) for 1 h, and the solution then taken to dryness at 10^{-3} mmHg. The dark brown residue was dissolved in acetone (25 cm^3) and depe (12 mmol) added. Upon addition of MeCN (*ca.* 5 cm^3) a *yellow solid* precipitated out. This was filtered off and dried at 10^{-3} mmHg. Yield 1.2 g.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dichloroiron*.—Iron(II) chloride (0.53 g, 4.2 mmol) and dppe (1.70 g, 4.3 mmol) were heated together in toluene under reflux for *ca.* 24 h. The pale off-white *microcrystalline solid* was filtered off, washed with toluene (10 cm^3), and dried at 10^{-3} mmHg. Yield 1.6 g.

The product was heavily contaminated with iron(II) chloride as shown by the Mössbauer spectrum and consistent with the low carbon analysis. A sample of material prepared by Henderson's method[6] had the required analyses and showed itself to be a single iron-containing species identical with the material which is not iron(II) chloride in the product prepared as above from toluene.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*di-iodoiron*.—Iron(II) iodide (0.90 g, 2.9 mmol) and dppe (1.16 g, 2.9 mmol) were stirred at 20 °C in CH$_2$Cl$_2$ (20 cm^3). After 0.5 h the yellow mixture was filtered, washed with CH$_2$Cl$_2$ (20 cm^3), and dried at 10^{-3} mmHg. Yield: 1.4 g. Alternative preparations of this material are indicated in the Scheme. They involve heating acetonitrile-containing materials to 120 °C *in vacuo*. The material can also be obtained from the iodide and dppe, in 1:1 or 1:2 mol ratios, in tetrahydrofuran (thf) as well as in CH$_2$Cl$_2$. The identity of the iron-containing product was always the same, as judged by Mössbauer spectroscopy, even where the analyses were not altogether consistent with the formulation. For example, products obtained by heating [Fe(MeCN)$_2$(dppe)$_2$]I$_2$ *in vacuo* at 120 °C always contained an excess of dppe, not easily removed by sublimation.

Bis(*acetonitrile*)*bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*iron Di-iodide*.—Iron(II) iodide (1.15 g, 3.7 mmol) was mixed with MeCN (15 cm^3), and dppe (2.95 g, 7.4 mmol) added. The mixture was stirred for 15 h at 20 °C. The pink solid was filtered off, washed with diethyl ether, and dried at 10^{-3} mmHg. Yield: 2.3 g.

Bis[*bis*(*diphenylphosphino*)*methane*]*di-iodoiron*.—Iron(II) iodide (0.42 g, 1.35 mmol) and dppm (1.04 g, 2.71 mmol) were stirred together in thf (25 cm^3) at 20 °C for 2 h. A small amount of unreacted material was filtered off, diethyl ether (20 cm^3) added, and the mixture held at −20 °C for 18 h. The solution turned green. The *solid green product* was filtered off, washed with diethyl ether, and dried at 10^{-3} mmHg. Yield: 0.44 g.

Bis(*acetonitrile*)[*bis*(*diphenylphosphino*)*methane*]*iron*(II) *Di-iodide and Bis*(*acetonitrile*)*bis*[*bis*(*diphenylphosphino*)*methane*]-*iron*(II) *Di-iodide*.—Iron(II) iodide (0.71 g, 2.29 mmol) and dppm (1.76 g, 4.58 mmol) were stirred in MeCN for 2 h at 20 °C. The resulting brown solid (0.95 g) was filtered off and was never satisfactorily characterized. After 1 week at 20 °C, the filtrate deposited large deep red crystals, and subsequently smaller light red crystals. These analysed as $[Fe(MeCN)_2(dppm)]I_2$ and $[Fe(MeCN)_2(dppm)_2]I_2$, respectively.

Dichlorobis[o-*phenylenebis*(*diphenylphosphine*)]*iron*.—Iron(II) chloride was treated with anhydrous tetrahydrofuran (thf) and the mixture taken to dryness. Some of the residue (0.44 g, 1.9 mmol) reckoned as $FeCl_2(thf)_{1.5}$ was mixed with acetone (*ca.* 25 cm^3) and opdp (1.69 g, 3.7 mmol). The mixture turned yellow, and was stirred at 20 °C for 24 h. The yellow *solid* was filtered off, washed with diethyl ether, and dried at 10^{-3} mmHg. Yield: 1.4 g.

Dibromobis[o-*phenylenebis*(*diphenylphosphine*)]*iron*.—Iron(II) bromide (0.38 g, 1.8 mmol) and opdp (1.37 g, 3.1 mmol) were allowed to react as for the chloride. The solid product was extracted with CH_2Cl_2 in a Soxhlet extractor, yielding yellow *crystals* which were filtered off and dried at 10^{-3} mmHg. Yield: 0.81 g.

A red crystalline form of this material, presumably $[FeBr(opdp)_2]Br$, was obtained the first time we undertook this preparation. The amount was not sufficient for characterization and the red material was not obtained in the two subsequent preparations.

Iodobis[o-*phenylenebis*(*diphenylphosphine*)]*iron Iodide–Dichloromethane* (1/2).—Iron(II) iodide (0.61 g, 2.0 mmol) and opdp (1.76 g, 4.0 mmol) were allowed to react in acetone (*ca.* 25 cm^3) as above. The reddish orange solid (1.76 g) analysed repeatedly for $FeI_2(opdp)_3$. Soxhlet extraction with dichloromethane yielded the *product* as red crystals. Yield: 0.95 g.

Di-iodobis[o-*phenylenebis*(*diphenylphosphine*)]*iron*.—On one occasion the Soxhlet extraction from the previous preparation was observed to give a mixture of red and yellow crystals. On drying at 10^{-3} mmHg the yellow material apparently increased in proportion. The product turned red upon mechanical grinding. On storage for several weeks in daylight at 20 °C, the mixed crystals became uniformly yellow. The formulation is based upon analysis and Mössbauer data.

Bis(*acetonitrile*)*bis*[o-*phenylenebis*(*diphenylphosphine*)]*iron Di-iodide*.—The iodoiron iodide with opdp was treated with MeCN giving a pink solution and a pink solid. The saturated solution was cooled to −20 °C for 5 d, giving a crop of deep red needle-shaped *crystals*. Yield apparently quantitative.

Bis[1,2-*bis*(*di-isopropylphosphino*)*ethane*]*dichloroiron*(II).[13]—The thf adduct of $FeCl_2$ (0.89 g, 3.4 mmol) and dippe (0.89 cm^3, 3.4 mmol) were stirred in thf (25 cm^3) for 1 h. Diethyl ether (20 cm^3) was then added and the solution stood at −20 °C for 12 h. The off-white crystals were filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*. Yield: 0.45 g (35%) (Found: C, 43.5; H, 10.9; Cl, 18.5; N, 0.0; P, 13.8. $C_{14}H_{32}Cl_2FeP_4$ requires C, 43.2; H, 8.2; Cl, 18.3; N, 0.0; P, 13.8%).

Bis[1,2-*bis*(*di-isopropylphosphino*)*ethane*]*di-iodoiron*(II).[13]—Iron(II) iodide (0.41 g, 1.32 mmol) and dippe (0.35 cm^3, 1.33 mmol) were stirred in CH_2Cl_2 (25 cm^3) for 1 h. Diethyl ether (10 cm^3) was then added, and the solution stood at −20 °C for 12 h. A pale brown solid was filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*. Yield: 0.21 g (28%) (Found: C, 28.6; H, 7.3; N, 0.0. $C_{14}H_{32}FeI_2P_4$ requires C, 29.4; H, 5.6; N, 0.0%).

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