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Homoleptic iron(II)–diphosphine and –diarsine complexes: syntheses, characterization and redox properties

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Treatment of methanol solutions of $[Fe(H_2O)_6](BF_4)_2$ with excess ligand gives low-spin $[Fe(L–L)_3](BF_4)_2$ where L–L = 1,2-$C_6H_4(AsMe_2)_2$, **1b**, $Me_2PCH_2PMe_2$, **2**, $Me_2PCH_2CH_2PMe_2$, **3** and $Et_2PCH_2CH_2PEt_2$, **4**. These complexes have been characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, microanalyses, mass spectrometry, infrared and visible spectroscopy. The crystal structure of **1b**·$0.5H_2O$ has been determined. Although the Fe–As bond lengths are not significantly longer than the mean for the (very limited) range of other known Fe–1,2-$C_6H_4(AsMe_2)_2$ complexes, there is some evidence, from compressed Me–As–Me and extended Fe–As–Me angles, of steric crowding. Nevertheless, cyclic voltammetry reveals that the complexes have a quasi-reversible Fe(II)/Fe(III) redox process at potentials approximately consistent with the Lever electrochemical ligand parameter (E_L) scheme. This is in marked contrast to their Ru(II) analogues. Complex **4** reacts with CH_3CN to give *trans*-$[Fe(depe)_2(CH_3CN)_2](BF_4)_2$, **5**, in near-quantitative yield.

Introduction

The study of homoleptic complexes can be useful in elucidating details of metal–ligand bonding in the absence of potentially complicating ligand–ligand interactions. We recently reported the synthesis and electrochemical investigation of a series of homoleptic Ru(II)–diphosphine and –diarsine complexes, $[Ru(L–L)_3]^{2+}$. These complexes were unusually stable towards oxidation to Ru(III), to an extent significantly greater than predicted on the basis of Lever's well-known electrochemical ligand parameters.[1] We therefore wished to examine the electrochemistry of analogous complexes $[Fe(L–L)_3]^{2+}$. The complex $[Fe(diars)_3](ClO_4)_2$ (diars = 1,2-bis[dimethylarsino]benzene) was isolated and characterized thirty years ago.[2] More recently, $[Fe(dmpm)_3]^{2+}$ (dmpm = $Me_2PCH_2PMe_2$) was characterized spectroscopically,[3] and $[Fe\{MeC(CH_2PMe_2)_3\}_2](BF_4)_2$ has been prepared and structurally characterized.[4] Interestingly, the Fe(II)/Fe(III) redox potential of $[Fe\{MeC(CH_2PMe_2)_3\}_2]^{2+}$ was determined. At +0.96 V *vs.* ferrocene/ferrocinium, it agrees well with the prediction of Lever's electrochemical ligand parameter scheme (E_L *ca.* +0.3 V for Me_2PR multidentates; for Fe(II)/Fe(III) [both low-spin], E_{obs} [*vs.* NHE] = 1.11 [ΣE_L] −0.43[1] = +1.57 V *vs.* NHE, or approximately +0.9 V *vs.* ferrocene/ferrocinium). Moreover, low-spin $[Fe(diars)_3]^{3+}$ was prepared by nitric acid oxidation of the Fe(II) complex,[5] whereas we found that when $[Ru(diars)_3](OTf)_2$ was dissolved in conc. nitric acid, there was no colour change, and the addition of 60% $HClO_4$ precipitated only $[Ru(diars)_3](ClO_4)_2$.[6] Stimulated by these observations, we have therefore explored the synthesis, characterization and electrochemistry of complexes $[Fe(L–L)_3]^{2+}$ (L–L = diars, dmpm, dmpe [$Me_2PCH_2CH_2PMe_2$] and depe [$Et_2PCH_2CH_2PEt_2$]), and report these results here.

Experimental

General considerations

Reactions were carried out under nitrogen using standard Schlenk line techniques. Dmf was anhydrous grade (≤0.005% water). Perdeuterated solvents for NMR studies were used as received. The ligands dmpm, dmpe and depe (Strem Chemicals) were used as received, and diars was prepared by a literature method.[7] Tetraethylammonium tetrafluoroborate (TEAT) was recrystallised from ethanol and dried at 60 °C *in vacuo*. General experimental and characterisation methods were as recently described.[8] Electrochemical experiments from −2.4 to +1.6 V (*vs.* ferrocene/ferrocinium) were conducted using an EcoChemie PGSTAT 20 system, using Au disc working electrodes; 0.2 M TEAT in CH_3CN was employed. The reference electrode was an aqueous SCE, but potentials are quoted with respect to the ferrocene/ferrocinium couple, which was routinely monitored after each set of voltammetric measurements to reduce errors due to junction potentials.

Syntheses

$[Fe(diars)_3](ClO_4)_2$ (1a). This complex was made by the literature method,[2] except that the crude product was recrystallized from MeCN–Et_2O. Yield 75%. **CAUTION!** A small sample of this complex exploded when touched with a nickel spatula; it is preferable to prepare the tetrafluoroborate salt. Anal. Calc. for $C_{30}H_{48}As_6Cl_2FeO_8$: C, 32.38; H, 4.35%. Found: C, 33.11; H, 4.41%. FAB MS: *m*/*z* 1014 (9) $[M - ClO_4]^+$, 914 (5) $[M - 2ClO_4 - H]^+$, 727 (58) $[M - diars - ClO_4]^+$, 627 (100) $[M - diars - 2ClO_4 - H]^+$. ^1H NMR data δ (d^6 dmso): 8.25 (br s, 6H, *o*-C_6H_4), 7.90 (br s, 6H, *o*-C_6H_4), 1.99 (s, 18H, As*Me*), 1.58 (s, 18H, As*Me*). $^{13}C\{^1H\}$ data δ (d^6 dmso): 140.5, 132.6, 130.0, 20.7, 17,7. The complex $[Fe(diars)_3](BF_4)_2$ (**1b**) was prepared, in 77% yield, by the method described below for $[Fe(dmpm)_3](BF_4)_2$ (**2**).

$[Fe(dmpm)_3](BF_4)_2$ (2). $[Fe(H_2O)_6](BF_4)_2$ (0.096 g, 0.284 mmol) was added to the ligand (0.18 g, 1.32 mmol) in MeOH (10 cm^3). The mixture was refluxed for 3 h, and the solvent was then removed *in vacuo*. The residue was recrystallised from EtOH–Et_2O, filtered off, washed with Et_2O and dried *in vacuo*. Yield 0.14 g, 80%. Anal. Calc. for $C_{15}H_{42}B_2F_8FeP_6$: C, 28.25; H, 6.64%. Found: C, 28.40; H, 6.70%. FAB MS: *m*/*z* 551 (16) $[M - BF_4]^+$, 463 (20) $[M - 2BF_4 - H]^+$. Electronic spectral data: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 25.00 (200), 29.24 (460). ^1H NMR data δ (CD_3OD): 3.50 (br m, 6H,

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PCH_2P), 1.79 (br s, 18H, PCH_3), 1.61 (s, 18H, PCH_3). $^{13}C\{^1H\}$ data δ (CD_3OD): 45.9 (br m, PCH_2P), 21.8 (br m, PCH_3), 20.7 (br m, PCH_3). $^{31}P\{^1H\}$ data δ (CD_3OD): −5.1 (s).

[Fe(dmpe)$_3$](BF$_4$)$_2$ (3). This was prepared as for **2**, from $[Fe(H_2O)_6](BF_4)_2$ (0.21 g, 0.612 mmol) and the ligand (0.28 g, 1.80 mmol) in MeOH (10 cm^3). Yield 0.23 g, 55%. Anal. Calc. for $C_{18}H_{48}B_2F_8FeP_6$: C, 31.80; H, 7.12%. Found: C, 30.00; H, 6.82%. FAB MS: *m*/*z* 593 (8) $[M - BF_4]^+$, 375 (87) $[FeF(dmpe)_2]^+$, 356 (52) $[Fe(dmpe)_2]^+$. Electronic spectral data: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 24.04 (245), 28.90 (345). ^1H NMR data δ (d^6 dmso): 1.90 (br m, 12H, PCH_2CH_2P), 1.56 (br s, 18H, PCH_3), 1.50 (br s, 18H, PCH_3). $^{13}C\{^1H\}$ data δ (d^6 dmso): 30.6 (br m, PCH_2CH_2P), 20.9 (br m, PCH_3), 19.9 (br m, PCH_3). $^{31}P\{^1H\}$ data δ (MeCN, d^6 acetone lock): 47.7 (s).

[Fe(depe)$_3$](BF$_4$)$_2$ (4). This was prepared as for **2**, from $[Fe(H_2O)_6](BF_4)_2$ (0.160 g, 0.346 mmol) and the ligand (0.30 g, 1.60 mmol) in MeOH (10 cm^3). The product was precipitated by the addition of Et_2O at −18 °C. Yield 0.23 g, 57%. Anal. Calc. for $C_{30}H_{72}B_2F_8FeP_6$: C, 42.50; H, 8.56%. Found: C, 41.20; H, 8.25%. FAB MS: *m*/*z* 761 (1) $[M - BF_4]^+$, 468 (43) $[Fe(depe)_2]^+$. Electronic spectral data: $E_{max}/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) (CH_3CN): 21.83 (250), 26.88 (345). ^1H NMR data δ (d^6 dmso): 1.95, 1.79, 1.59, (br m's, PCH_2, total 36H), 1.24 (br m, CH_3, 36H). $^{13}C\{^1H\}$ data δ (d^6 dmso): 28.6, 24.2, 20.4 (br, PCH_2), 11.8, 10.6 (br, PCH_3). $^{31}P\{^1H\}$ data δ (CD_3CN): 54.5 (s).

***trans*-[Fe(depe)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$ (5).** Complex **4** (0.040 g, 0.047 mmol) was dissolved in CH_3CN (12 cm^3), and the solution was refluxed for 3 h. Solvent was removed *in vacuo*, and the lemon yellow residue was recrystallised from CH_3CN–hexane. Yield 0.030 g, 97%. Anal. Calc. for $C_{24}H_{54}B_2F_8FeN_2P_4$: C, 39.83; H, 7.52; N, 3.87%. Found: C, 39.20; H, 7.52; N, 2.97%. FAB MS: *m*/*z* 673 (8) $[M - BF_4]^+$, 555 (12) $[M - 2CH_3CN - BF_4]^+$, 487 (100) $[FeF(depe)_2]^+$. IR (Nujol mull, cm^{-1}): 2263 (w) (coord. CH_3CN). $^{31}P\{^1H\}$ data δ (CD_3CN): 66.0 (s).

X-Ray crystallography

Crystals of **1b**·$0.5H_2O$ were grown by diffusion of Et_2O into an EtOH solution. Crystal data for **1b**·$0.5H_2O$: $C_{30}H_{49}As_6B_2F_8FeO_{0.5}$, MW = 1096.68, space group $P2_1/c$, $a = 12.0709(7)$ Å, $b = 16.5127(9)$ Å, $c = 38.986(2)$ Å, $\beta = 95.5350(10)°$, $V = 7734.6(7)$ Å^3, $Z = 8$, $T = 150(2)$ K, $D_C = 1.884$ g cm^{-3}, μ(Mo-Kα) 5.547 mm^{-1}, $F(000) = 4312$, $\lambda = 0.71070$ Å. Intensity data were collected using a STOE–IPDS image plate diffractometer (graphite monochromator) in the ϕ rotation scan mode. 48101 unique reflections were measured and used in the refinement. The structure was solved by direct methods with the SHELXS97 package and refined using full matrix least squares on F^2 (SHELXL97). Refinement converged to $R_1 = 0.0360$, wR_2 0.0815 for the 17812 reflections with $F^2 > 2\sigma(F^2)$.

CCDC reference number 185618.

See http://www.rsc.org/suppdata/dt/b2/b204533h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and spectroscopic characterisation

The coordination chemistry of Fe(II) with diphosphine ligands is surprisingly varied and complex. With aryldiphosphines, examples of high-spin, tetrahedral $[FeX_2(L–L)]$ (*e.g.* X = Cl, I; L–L = dppe),[9,10] high-spin, octahedral $[FeX_2(L–L)_2]$ (*e.g.* X = Cl, Br, I; L–L = 1,2-$C_6H_4\{PPh_2\}_2$),[10,11] low-spin, octahedral $[FeX_2(L–L)_2]$ (*e.g.* X = Cl; L–L = dppe),[12] and low-spin, five-coordinate $[FeI(1,2\text{-}C_6H_4\{PPh_2\}_2)_2]I$[10,11] are all known. Also pertinent to our study, substitution of halide ligands by MeCN gives mainly octahedral, low-spin *trans*-$[Fe(L–L)_2(MeCN)_2]^{2+}$ with these ligands.[10,11] Smaller alkyldiphosphines, which are better σ-donors, give low-spin octahedral $[FeX_2(L–L)_2]$ (*e.g.* X = Cl, I; L–L = dmpe, depe) which, on dissolution in CH_3CN, form low-spin $[Fe(L–L)_2(MeCN)_2]^{2+}$. Interestingly, bulkier alkyldiphosphines can also give high-spin tetrahedral $[FeX_2(L–L)]$. For example, protonation of [Fe(H)Cl(depe)$_2$] gives [FeCl$_2$(depe)],[9] $[FeX_2(^iPr_2PCH_2CH_2P^iPr_2)]$ (X = Cl, Br, I) have been isolated,[13] and the surprising high-spin $[FeR_2(^iPr_2PCH_2CH_2P^iPr_2)]$ (R = bulky alkyl) have been described.[13]

Table 1 10D_q and *B* values for $[Fe(L–L)_3]^{2+}$ complexes

Complex	10D_q/cm^{-1}	*B*/cm^{-1}
$[Fe(diars)_3](BF_4)_2$	24650	325
$[Fe(dmpm)_3](BF_4)_2$	27650	265
$[Fe(dmpe)_3](BF_4)_2$	27080	304
$[Fe(depe)_3](BF_4)_2$	24990	316

Spectra all recorded in CH_3CN. 10D_q and *B* values calculated on the basis that the energy of the $^1T_{1g}$ state is $10D_q - C$,[15] and that $C = 10B$, as for $[Fe(diars)_3]^{2+}$.[2]

Treatment of $[Fe(H_2O)_6](ClO_4)_2$ with excess diars in EtOH gave pure $[Fe(diars)_3](ClO_4)_2$ (**1a**) in good yield after recrystallization, as described by Feltham.[2] *However, we found that **1a** decomposed violently when scratched.* Since $[Fe\{MeC(CH_2PMe_2)_3\}_2](BF_4)_2$ was prepared, albeit in modest yield, by treatment of $FeCl_2$ with the ligand in MeOH, followed by ion exchange,[4] we likewise treated $[Fe(H_2O)_6]Cl_2$ with excess diars in EtOH. However, this almost immediately precipitated *trans*-$[FeCl_2(diars)_2]$.[14] Treatment of $[Fe(H_2O)_6](BF_4)_2$ with excess diars in MeOH gave $[Fe(diars)_3](BF_4)_2·2H_2O$ (**1b**) in good yield, and accordingly, the yellow–orange diphosphine complexes $[Fe(dmpm)_3](BF_4)_2$ (**2**), $[Fe(dmpe)_3](BF_4)_2$ (**3**) and $[Fe(depe)_3](BF_4)_2$ (**4**) were subsequently isolated in the same way. The complexes were characterized by microanalyses (C and H), fast atom bombardment mass spectrometry, multinuclear (^{13}C, ^1H, $^{31}P\{^1H\}$ and ^{19}F) NMR spectroscopy, IR and electronic spectroscopy. Additionally, a crystal structure determination was carried out on **1b** (see below).

One disadvantage of BF_4^- as a counter ion is that the C and H microanalyses of these salts were consistently low, although NMR spectroscopy and other data confirmed the identity and purity of the complexes. We encountered a similar problem with the Ru(II) analogs, isolated as triflate salts, and suspect that the relatively large fluoride content hinders complete combustion. The FAB mass spectra of **1**–**4** all showed clusters of peaks at the correct value for $[M - \text{counter ion}]^+$, and the tetrafluoroborates also showed clusters of peaks for $[M(L–L)_2F]^+$ (from F^- abstraction from BF_4^-) and $[M(L–L)_2]^+$. The $^{31}P\{^1H\}$ NMR spectra of **2**–**4** showed singlets as expected for $[Fe(diphosphine)_3]^{2+}$. The ^{13}C NMR spectra of **1**, **2** and **3** showed two singlets (**1**), or multiplets due to coupling to P (**2**, **3**), for the ligand methyl groups, and this is supported by the ^1H NMR spectra, which likewise show two equally intense resonances for **1**–**3**. As confirmed by the crystal structure determination (below), each donor atom is equivalent, and has one methyl substituent oriented towards the backbone of a neighbouring ligand, and the other oriented towards one of the two opposite triangular faces of the octahedron which include one donor from each of three different ligands. However, the resonances for the ethyl –CH_2– groups of depe in **4** overlap the complex multiplets due to the ligand backbone. The ^{19}F NMR spectra, which show a single resonance due to non-coordinated anion, and the IR spectra which show a single unsplit band around 1055 cm^{-1}, confirm that the BF_4^- anions remain non-coordinated both in solution and in the solid state in **1b**–**4**.

The electronic spectrum of **1a** was identical to that previously reported (Table 1), and the spectra of **2**–**4** were similar to that of **1a**. The two bands are assigned, in order of increasing

Table 2 Electrochemical data for $[Fe(L–L)_3]^{2+}$ complexes[a]

Complex	$E_{1/2}$/V	k^b/s^{-1}	Predicted $E_{1/2}{}^c$/V
$[Fe(diars)_3](BF_4)_2$	+1.03	0.02	+0.90
$[Fe(dmpm)_3](BF_4)_2$	+0.67	2.00	
$[Fe(dmpe)_3](BF_4)_2$	+0.82	0.02	+0.77
$[Fe(depe)_3](BF_4)_2$	+0.63	0.07	

[a] $E_{1/2}$ *vs.* ferrocene/ferrocinium. All oxidations are quasi-reversible. [b] Pseudo-first order rate constant for complex decomposition, assuming an EC process, calculated from the working curve in ref. 20. [c] Calculated from Lever's electrochemical ligand parameters in ref. 1.

energy, to the $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ transitions, expected for a pseudooctahedral low-spin d^6 complex.[15] Table 1 shows the values of $10D_q$ and B calculated from the data. The methyl-substituted diphosphines exert a somewhat larger ligand field than either the diarsine, or the bulkier ethyl-substituted depe.

Although we have isolated a complex which we formulated as $[Ru(dppm)_3](OTf)_2$ on the basis of spectroscopic data,[6] we have been unable to isolate any homoleptic Fe(II)–diphosphine or –diarsine complex with aryl-substituted ligands, such as dppm, dppe or $Ph_2As(CH_2)_nAsPh_2$ (n = 1, 2). Since homoleptic, low-spin Fe(II) complexes $[Fe(P\{OR\}_3)_6]^{2+}$ have been prepared,[16–18] and trialkylphosphites are even weaker σ-donors than arylphosphines, it is most likely that steric effects are responsible for our inability to prepare $[Fe(diphosphine)_3]^{2+}$ complexes with the aryl-substituted ligands.

While complexes **1**–**3** were stable in CD_3CN at room temperature over a period of days, complex **4** slowly reacted to give *trans*-$[Fe(NCCD_3)_2(depe)_2]^{2+}$ and free depe (monitored by $^{31}P\{^1H\}$ NMR spectroscopy). No intermediate species were detected. A sample of *trans*-$[Fe(NCCH_3)_2(depe)_2]^{2+}$ (**5**) was prepared in essentially quantitative yield by refluxing **4** in neat CH_3CN, and was fully characterized; **5** has also been prepared by treatment of $[FeX_2(depe)_2]$ with CH_3CN.[10,19] In view of the fact that a 1 : 1 complex, $[FeCl_2(depe)]$, is the product when $[Fe(H)Cl(depe)_2]^+$ reacts with HCl,[9] the ready loss of one ligand from the 3 : 1 complex **4** is not surprising. In contrast, no reaction was observed ($^{31}P\{^1H\}$ NMR spectroscopy) when $[Ru(depe)_3](OTf)_2$ (**6**)[6] was refluxed in CH_3CN for 48 h.

Treatment of $[Fe(H_2O)_6](BF_4)_2$ with excess PMe_3 in MeOH failed to yield $[Fe(PMe_3)_6](BF_4)_2$, although $[Fe(P\{OMe\}_3)_6](BPh_4)_2$ has been prepared from $[FeCl_2(thf)_n]$ and a very large excess of $P(OMe)_3$.[17] The reason is presumably the larger cone angle of the trialkylphosphine.

Electrochemistry

Complexes **1**–**4** showed a single, one-electron, quasi-reversible oxidation wave at 0.6–1.03 V (*vs.* internal ferrocene/ferrocinium) in 0.2 M TEAT–CH_3CN. The $E_{1/2}$ values are shown in Table 2, along with pseudo-first order rate constants for Fe(III) complex decomposition, calculated assuming an EC mechanism.[20] A typical cyclic voltammogram, for **4**, is shown in Fig. 1. Interestingly, whereas the analogous Ru(II) complexes show totally irreversible oxidation waves,[6] with formal potentials much more positive than those predicted by Lever's electrochemical ligand parameters (E_L),[1] the agreement between the Fe(II)/Fe(III) potentials calculated using the equation E_{obs} (*vs.* NHE) = 1.11 [ΣE_L] −0.43[1] appropriate for low-spin Fe(II) and Fe(III) partners, and our experimental Fe(II)/Fe(III) redox potentials, is excellent.

We also observed two (in some cases, three) irreversible reduction waves at $E_p \leq -1.4$ V. The variation of peak heights with scan rate suggests quite complex behaviour, and the analysis of the reductive electrochemistry (together with that of the corresponding Ru(II) complexes) will be discussed elsewhere.

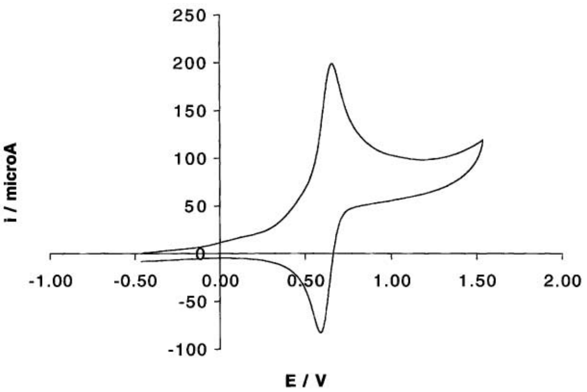

Fig. 1 Cyclic voltammogram (250 mV s^{-1}) of $[Fe(depe)_3]^{2+}$, freshly-dissolved in CH_3CN–0.2 M Et_4NBF_4. Au disk working electrode, SCE reference electrode, potential scale *vs.* internal ferrocene.

Structure of $[Fe(diars)_3](BF_4)_2$ (1b)

X-Ray quality single crystals of **1b**·$0.5H_2O$ were grown by solvent diffusion. We found that $[Ru(diars)_3]Cl_2$ showed evidence of considerable steric crowding.[6] In particular, the mean Ru–As bond (2.4468(15) Å) was significantly longer than the mean value for the 14 published structures containing the *trans*-$[Ru^{II}(diars)_2]$ moiety (2.425 Å). We suggested that this is the reason why the redox behaviour of these complexes deviates markedly from Lever's E_L scheme.

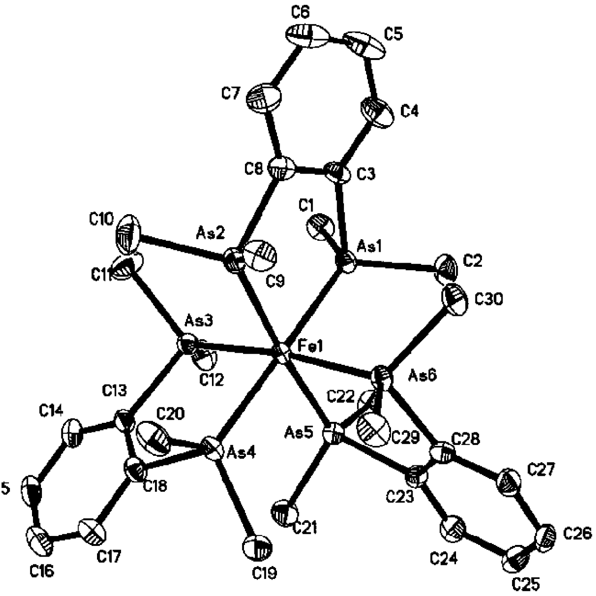

Fig. 2 ORTEP plot of one of the two slightly different cations in the asymmetric unit, from the crystal structure of $[Fe(diars)_3](BF_4)_2$·$0.5H_2O$.

The structure of the cation of **1b** is illustrated in Fig. 2, and Table 3 shows significant bond lengths and angles. The paucity of published data restricts comparison of **1b** with other complexes. The mean Fe–As bond length in **1b** (over the two slightly different molecules in the asymmetric unit) is 2.3598(7) Å. There are four published structures of iron–diars complexes which do not involve Fe(0)–carbonyl centres.[21] The mean value of the Fe–As bond length in these is 2.372 Å. It is tempting to speculate, on this basis, that the Fe(II)/Fe(III) redox potentials for **1**–**4** are in agreement with Lever's E_L scheme because steric crowding is less important for **1**–**4** than for the corresponding Ru(II) complexes; Ru(II) is a better π-donor than Fe(II). However, quite apart from the usual limitations on comparisons of this kind,[22] a note of caution should be

Table 3 Selected bond lengths (Å) and angles (°) for **1b**[a]

Fe(1)–As(1)	2.3661(6)	Fe(1)–As(2)	2.3666(6)
Fe(1)–As(3)	2.3843(6)	Fe(1)–As(4)	2.3484(6)
Fe(1)–As(5)	2.3547(6)	Fe(1)–As(6)	2.3632(6)
As–C(Me) (mean)	1.948(4)	As–C(aryl) (mean)	1.943(4)
As(1)–Fe(1)–As(2)	86.00(2)	As(3)–Fe(1)–As(4)	85.40(2)
As(5)–Fe(1)–As(6)	86.33(2)	As(1)–Fe(1)–As(4)	178.99(3)
As(2)–Fe(1)–As(5)	175.18(3)	As(3)–Fe(1)–As(6)	173.26(3)
Me–As–Fe(1) (mean)	122.39(14)	Me–As–Me (mean)	97.69(19)

[a] Two slightly different cations in asymmetric unit; data for one cation shown.

introduced. Of the four published structures, two ($[Fe(NO)(diars)_2](ClO_4)_2$ and $[Fe(NO)(NCS)(diars)_2](ClO_4)$[23] are nitrosyl complexes, in which the geometry is distorted by the very strong Fe–NO interaction in such a way as to lengthen the Fe–As bonds, and in the other two structures, the diars is *trans* to either one ($[Fe(Me)(CO)_2(PMe_3)(diars)]BF_4$)[24] or two ($[Fe(C\{O\}Me)(diars)(CO)_2(P\{OCH_2\}_3CEt)]BPh_4$)[25] carbonyl ligands, which might also be expected to lengthen the Fe–As bonds. Moreover, the mean Me–As–Me angle in **1b** (97.69(19)°) is significantly smaller than the mean for the published structures (102.5°) and the mean Me–As–Fe angle for **1b** (122.39(14)°) is wider than the mean (118.4°) for the published structures. Compressed Me–As–Me and extended Me–As–metal angles have been cited as indicators of steric crowding in diars complexes.[6,26] The *limited* evidence we have is therefore consistent with some steric crowding in **1b**, even though the redox potentials of these Fe(II) complexes are in agreement with predictions using Lever's E_L parameters. We are currently attempting to use theoretical methods to shed further light on the reasons for this apparent anomaly.

Conclusions

Treatment of Fe(II) salts of non-coordinating anions with an excess of diphosphine or diarsine, in a polar solvent, gives homoleptic $[Fe(L–L)_3]^{2+}$, providing that L–L is sufficiently small (methyl or, at most, ethyl-substituted ligands). These have been characterized by analyses, multinuclear NMR spectroscopy and, in one case, X-ray crystallography. In contrast to their Ru(II) analogues, the Fe(II) complexes undergo a quasi-reversible one-electron oxidation to Fe(III), at potentials in agreement with the values predicted by Lever's E_L parameters.

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