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Full Paper

# Metal Template Synthesis of a Tripodal Tris(bipyridyl) Receptor that Encapsulates a Proton and an Iron(II) Centre in a Pseudo Cage\*

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The Fe(II) template synthesis of the first member of a new category of tripodal tris-bipyridine ligands incorporating a nitrogen bridgehead is reported. The X-ray structure of the reaction product shows that the ligand adopts a pseudo cage-like structure that encapsulates both a proton and an Fe(II) ion in its cavity. The complex shows an extended helical arrangement that is effectively 'capped' at its open end by a hydrogen bonded  $PF_6^-$  counter ion that is symmetrically aligned with the 3-fold axis of the helix. A <sup>1</sup>H NMR study demonstrated that the encapsulated proton can be reversibly exchanged under acid/base conditions in CD<sub>3</sub>CN.

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## Introduction

In a previous study our group investigated the metal template synthesis of  $Mn(\pi)$ ,  $Co(\pi)$ ,  $Fe(\pi)$ , and  $Cu(\pi)$  complexes of fully closed tris-bipyridyl cages of type **1** (Fig. 1) that adopt extended helical structures on binding to the metal ion.<sup>[1]</sup> The encapsulation procedure involved a series of reductive amination reactions involving three molecules of the dialdehyde precursor of type **2** (Fig. 1) and ammonium acetate (as a source of ammonia), together with sodium cyanoborohydride, as reactants. The procedure was carried out either as a one-pot reaction in the presence of the metal ion or in a two-step fashion involving initial isolation of the corresponding octahedral  $[ML_3]^{2+}$  (L = **2**) precursor as its hexafluorophosphate salt followed by reaction with excess ammonium acetate and sodium cyanoborohydride.

As an extension of this study we were interested in applying the above general procedure to the synthesis of the corresponding Fe(II) complex of the related tripodal ligand **3** (Fig. 2), hence giving rise to a pseudo-cage derivative in which the expected triple helix would have one end 'open'; in part, a motivation for this study was to act as a foundation for further synthesis aimed at producing new anion receptors related to those reported previously based on tris-bipyridine ligand derivatives.<sup>[2]</sup> Nevertheless, it was realized that the synthesis of a complex of the above type could well be less than straight forward since the use of an unsymmetrical mono-aldehyde analogue of **2** might be expected to give rise to *fac*- and *mer*-isomers of the intermediate tris-ligand, mono-aldehyde derivative complex. Clearly if both isomers are initially formed, it was of interest to probe whether isomerization, possibly associated with dynamic covalent imine chemistry,<sup>[3]</sup> might occur to yield the resulting pseudo-cage product in reasonable yield. To this end, Fe(II) was chosen as the templating metal because of its well established propensity to yield strong, low-spin (diamagnetic) complexes incorporating a tris-bipyridyl coordination environment<sup>[4]</sup> and thus allowing ready investigation of the reaction outcome by <sup>1</sup>H NMR. The moderate kinetic inertness associated with the use of low-spin Fe(II) ( $d^6$  electronic configuration) was not expected to significantly impede such a rearrangement within the timescale of the synthetic procedure.

## **Results and Discussion**

### Ligand Precursors

An outline of the synthesis of the mono-aldehyde precursor **6** starting from 5,5'-dimethyl-2,2'-bipyridine is given in Scheme 1; precursor 5-trimethylsilylmethyl-5'-methyl-2,2'-bipyridine (**4**) was prepared by a literature procedure.<sup>[5]</sup> Silane **4** was then converted to 5-chloromethyl-5'-methyl-2,2'-bipyridine

<sup>\*</sup>Dedicated to Roger Bishop – a fine supramolecular chemist.

(5) in 85% yield by reaction with  $Cl_3CCCl_3$  and  $CsF.^{[6]}$  A Williamson condensation of 5 with salicylaldehyde in dimethylformamide resulted in the target mono-aldehyde 6 whose <sup>1</sup>H NMR spectrum is given in Fig. 3a.



Fig. 1. Structures of compounds 1 and 2.



Fig. 2. Structure of compound 3.

#### Metal-Template Preparation of Pseudo Cage 3

The protonated cation,  $[Fe(HL)_3]^{3+}$  (L = 6) (see below), was prepared in a one pot procedure involving the initial interaction of three equivalents of mono-aldehyde 6 with Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in refluxing acetonitrile. To monitor the progress of the reaction, a small aliquot of the reaction solution was removed and the product isolated as its PF<sub>6</sub><sup>-</sup> salt; the <sup>1</sup>H NMR spectrum (Fig. 3b) of this product in CD<sub>3</sub>CN was consistent with the formation of [FeL<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (L = 6) as a mixture of its *mer/fac* isomers. The latter is most clearly illustrated by the observation of four signals for the aldehyde protons of 6 in the <sup>1</sup>H NMR spectrum of the product (see expanded region of the spectrum in Fig. 3b).

Reductive amination of the bulk solution then involved addition of NH4OAc followed by excess NaCNBH3 to the stirred red solution at 0°C for 2 h; the solution was then allowed to warm to room temperature and stirring was continued overnight. The product was isolated as its PF<sub>6</sub><sup>-</sup> salt and further purified by chromatography on silica gel and the product reisolated as its PF<sub>6</sub> salt to afford [Fe(HL)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>·CH<sub>3</sub>CN (L=3) as a purplish red crystalline solid in 55% yield. The microanalysis and HRMS data are in accord with the above formulation (see Experimental). As anticipated, the <sup>1</sup>H NMR spectrum of this product was markedly simplified (see Fig. 3c) relative to the mono-aldehyde precursor complex,  $[FeL_3]^{2+}$ (L = 6) and is again consistent with the formation of an Fe(II) complex of the above stoichiometry. In particular, the spectrum shows AB spin systems centred at 3.97 and 5.07 ppm in the aliphatic region that correspond to proton resonances for methylene groups adjacent to the nitrogen bridgehead atom and the benzyl ethers, respectively. The <sup>1</sup>H NMR spectrum of the deprotonated form of the above complex, namely [Fe(L)]  $(PF_6)_2$  (L = 3) is shown in Fig. 3d. Deprotonation was achieved by treatment of the NMR sample of  $[Fe(HL)](PF_6)_3$  (L = 3) in CD<sub>3</sub>CN with K<sub>2</sub>CO<sub>3</sub>; interestingly, no colour change was observed on deprotonation. The aforementioned AB spin system peaks are significantly further resolved in the <sup>1</sup>H NMR spectrum of the deprotonated species, consistent with a decreased equivalence of the respective geminally related protons. As might be expected, proton resonances corresponding to the methylene groups adjacent to the nitrogen bridgehead atom are now shifted upfield by 0.82 ppm to be centred at 3.15 ppm.

<sup>1</sup>H NMR evidence also indicates that reprotonation of the above species is readily achieved. Thus addition of two equivalents of trifluoroacetic acid to the above NMR solution results in



Scheme 1. Synthesis of precursors for pseudo cage 3.

regeneration of the spectrum of the protonated  $[Fe(HL)_3]^{3+}$  species. The <sup>1</sup>H NMR spectral differences between the methylene and aromatic resonances in  $[Fe(HL)_3](PF_6)_3$  (L = 3) and  $[Fe(L)_3](PF_6)_2$  (L = 3) are in keeping with a significant conformational rearrangement of the tertiary amine capping unit occurring in generating the latter species.

## X-Ray Structure and Modelling Studies

Slow diffusion of diethyl ether into an acetonitrile solution of the product obtained from the template synthesis yielded purplishred crystals suitable for X-ray diffraction. The structure determination of  $[Fe(HL)](PF_6)_3$  (L = 3) (Fig. 4) confirmed that



**Fig. 3.** <sup>1</sup>H NMR spectrum of (a) mono-aldehyde 6 in CDCl<sub>3</sub>, (b) mixture of *mer* and *fac* isomers of  $[Fe(6)_3](PF_6)_2$  in CD<sub>3</sub>CN, (c)  $[Fe(HL)](PF_6)_3$  (L = 3) in CD<sub>3</sub>CN and (d)  $[Fe(L)](PF_6)_2$  (L = 3) in CD<sub>3</sub>CN.

C. R. K. Glasson et al.



**Fig. 4.** X-ray structure of  $[Fe(HL)](PF_6)_3$  (L = 3). Left: view approximately perpendicular to the  $C_3$ -axis (two anions removed for clarity). Right: view of the cationic section down the  $C_3$ -axis. Dashed lines indicate hydrogen bonds, dotted lines  $CH_{methyl}$ -F interactions.

protonation of the bridgehead nitrogen had occurred. The complex crystallizes in the centric trigonal space group  $R\overline{3}$  with onethird of the molecule in the asymmetric unit. The optically active metal centres are, as expected, coordinated in a fac tris-chelate fashion to the three 2,2'-bipyridine units resulting in an octahedral configuration showing typical Fe-N bond lengths of 1.977(4) Å and 1.974(4) Å and a bite angle of 81.68(16)°. The twist angle of  $52^{\circ}$  is also similar to that observed (54°) in tris(5,5'-dimethyl-2,2'-bipyridine)iron(II).<sup>[1]</sup> The protonated bridgehead nitrogen is arranged endo towards the metal centre - an arrangement stabilized by hydrogen bonding between this proton and the three adjacent ether oxygen atoms (N-H...O 2.44(5)Å, 117(3)°) (Fig. 4). A related arrangement has been observed in metal complexes of zwitterionic polyphenolic ligands<sup>[7]</sup> but not previously observed for phenol-ethers.

The presence of the metal-ion imparts a helical twist on the ligand that extends  $\sim$ 13.3 Å down the length of the molecule.<sup>[1,8]</sup> The helical twist experienced by the ligand along this distance is 131° implying a pitch length of 36.5 Å, which is a similar pitch length to both mononuclear and dinuclear bipyridine-containing helicates and tetrahedra previously reported by our group,<sup>[1,8–10]</sup> in keeping with the degree of chiral twist experienced by all these complexes being a function of the metal chelate twist angle. The extension of this twist results in the methyl groups at the termini of the ligand being arranged  $\sim 6.4$  Å apart producing a binding pocket which is a good size and shape match for a face of the hexafluorophosphate anions present. Indeed, a  $PF_6^-$  anion (containing atom P(1)) is located in a position to take advantage of weak CH<sub>methyl</sub>... fluorine interactions, with each methyl group interacting with two fluorines to form bifurcated hydrogen bonds with CH···F distances of 2.70 Å and 2.95 Å (Fig. 4). There are therefore a total of six such interactions between each cation and the face of the anion binding to it; a similar arrangement is observed in a dinuclear ruthenium(II) complex formed from quaterpyridine ligands.[9]

While there are several weak offset face-to-face  $\pi$ - $\pi$  (C<sub>pyridyl</sub>-C<sub>pyridyl</sub> distances of 3.3 Å) and methylene- $\pi$  interactions (CH<sub>methylene</sub>-C<sub>phenyl</sub> distances of ~2.9 Å) present between molecules in the lattice, the packing is dominated by CH…F interactions that result in a complicated three-dimensional network. For example, in addition to the methyl-fluorine interaction described above, each P(1)-containing anion interacts

with four adjacent  $[Fe(HL)]^{3+}$  (L = 3) cations through six  $CH_{phenylene} \cdots F$  or  $CH_{pyridyl} \cdots F$  contacts of less than 2.9 Å, while the P(2)-containing anion undergoes two similar interactions of 2.3 Å, as well as several weaker methylene  $\cdots F$  contacts and also two anion- $\pi$  interactions with the comparatively electron poor pyridyl rings (indicated by a F $\cdots$ ring centroid distance of 2.9 Å).<sup>[11]</sup>

In order to investigate the possibility of encapsulation of other guest species, the volume of the cavity of  $[Fe(HL)](PF_6)_3$ (L = 3) was estimated using the X-ray crystallographic data. The phenoxy oxygens were treated as the limits to the cavity size in these calculations. The average oxygen to oxygen distance is 3.77 Å. Consideration of the van der Waals radius of oxygen  $(1.52 \text{ Å})^{[12]}$  results in an equilateral triangle (for which the apices are represented by the three phenoxy-oxygen atoms) with side length of 0.73 Å. Using Euclidean geometry the diameter of a sphere representative of the cavity volume was calculated to be 0.84 Å (volume = 0.31 Å<sup>3</sup>). The effect of deprotonation of  $[Fe(HL)](PF_6)_3$  (L = 3) was then investigated using an energy minimized model generated via the semi-empirical PM3 method.<sup>[13]</sup> The structure was optimized with atom coordinates for the donor atoms and the Fe(II) metal centre fixed at their X-ray values. The oxygen to oxygen distances increased to an average of 4.07 Å. Consideration of van der Waals radii of oxygen now resulted in an equilateral triangle side length of 1.03 Å, allowing the diameter of the sphere representing the cavity volume to be calculated as 1.18 Å (volume =  $0.86 \text{ Å}^3$ ). Clearly this is in accord with the encapsulated proton being a snug fit for the cavity of the  $[Fe(L)](PF_6)_2$  (L = 3) host. Interestingly, the model gives clear evidence of a significant conformational change of the tris-salicyloxyamine capping unit consistent with the NMR spectral changes observed upon deprotonation of  $[Fe(HL)](PF_6)_3$  (L = 3).

## Conclusion

The results presented in this report are in accordance with a mixture of *fac/mer* isomers present in the intermediate monoaldehyde Fe(II) complex, [FeL<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (L = **6**), undergoing significant isomerization from *mer* to *fac* during the course of the reductive amination reaction. Although not specifically identified for the present system, it seems likely that the Fe(II) template isomerization process may be associated with some degree of dynamic imine exchange behaviour. The result is the Fe(II) complex of a new tripodal (pseudo cage) ligand showing an extended helical structure. Further, in the solid state the arrangement is effectively 'capped' through symmetrical hydrogen bond interactions with an axially aligned  $PF_6^-$  counter ion.

#### Experimental

All reagents were of analytical grade unless otherwise indicated. Chromatography grade solvents were distilled through a fractionation column packed with glass helices. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-300 or a Varian Mercury 300 MHz spectrometer (300.133 MHz) at 298 K. NMR of organic species was recorded in CDCl<sub>3</sub> and for metal complexes in CD<sub>3</sub>CN. <sup>1</sup>H and <sup>13</sup>C NMR resonance are quoted in ppm and the coupling constants (J) in Hertz (Hz). <sup>1</sup>H NMR spectra were referenced according to residual proton resonances for CDCl<sub>3</sub> (7.24 ppm) and CD<sub>3</sub>CN (1.94 ppm). <sup>13</sup>C NMR spectra were referenced to solvent peaks for CDCl<sub>3</sub> (77.0 ppm) and CD<sub>3</sub>CN (1.39 ppm). Positive ion electrospray ionization high resolution (ESI-HR): Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) measurements were obtained on a Bruker BioAPEX 47e mass spectrometer equipped with an Analytica of Branford electrospray ionization (ESI) source. Microanalyzes were performed by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin.

#### 5-Trimethylsilylmethyl-5'-methyl-2,2'-bipyridine (4)

Lithium diisopropylamide (LDA) was prepared by adding 1.5 M *n*-BuLi  $(4.4 \text{ cm}^3)$  dropwise to a stirred solution of dry diisopropylamine (0.758 g, 7.5 mmol) in THF ( $15 \text{ cm}^3$ ) at  $-78^{\circ}$ C. This solution was stirred for a further 0.5 h and allowed to warm to 0°C for 10 min. The resulting LDA solution was cooled to -78°C and a solution of 5,5'-dimethyl-2,2'-bipyridine (552 mg, 3 mmol) in THF was added dropwise. The reaction was allowed to continue for 2 h and Me<sub>3</sub>SiCl (760 mg, 7 mmol) was then added rapidly and the reaction was guenched with  $3 \text{ cm}^3$  of MeOH after 3 min. The solvent was then removed under vacuum and the resulting paste was taken up in dichloromethane and the solution filtered. The dichloromethane was then removed under vacuum and the solid that remained was purified by chromatography on deactivated silica gel with 60 % petroleum and 40 % ethyl acetate as eluent to afford the product as a waxy white solid (614 mg, 80 %).  $\delta_{\rm H}$  0.02 (s, 9H), 2.11 (s, 2H), 2.38 (s, 3H), 7.44 (dd,  ${}^{3}J8.3, {}^{4}J2.1, 1$ H), 7.61 (ddd,  ${}^{3}J8.1, {}^{4}J2.1, {}^{5}J0.6, 1$ H), 8.22 (d,  ${}^{3}J8.3, 1$ H), 8.24 (d,  ${}^{3}J8.1, 1$ H), 8.34 (d,  ${}^{4}J2.1, 1$ H), 8.48 (dd,  ${}^{4}J2.1, {}^{5}J0.6, 1$ H),  $\delta_{\rm C}$  –1.79, 18.55, 24.21, 120.44, 120.64 133.12, 136.46, 136.65, 137.81, 148.47, 149.57, 152.27, 153.80.

#### 5-Chloromethyl-5'-methyl-2,2'-bipyridine (5)

A solution of 5-trimethylsilylmethyl-5'-methyl-2,2'-bipyridine (475 mg, 1.85 mmol), hexachloroethane (876 mg, 3.70 mmol) and anhydrous CsF (562 mg, 3.70 mmol) in acetonitrile (20 cm<sup>3</sup>) was heated at 60°C with stirring for 6 h. The acetonitrile was removed and replaced with dichloromethane (50 cm<sup>3</sup>) and the resulting mixture was filtered. The filtrate was washed with water (30 cm<sup>3</sup>) then brine (30 cm<sup>3</sup>) and was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the solid that remained was chromatographed on silica gel with dichloromethane (97.5%), MeOH (2%) and saturated NH<sub>3</sub> (0.5%) as eluent to afford the pure product (344 mg, 85%) as a white crystalline solid.  $\delta_{\rm H}$  2.37 (s, 3H), 4.62 (s, 2H), 7.62 (ddd, <sup>3</sup>J 8.1, <sup>4</sup>J 1.8, <sup>5</sup>J 0.6, 1H), 7.82 (dd, <sup>3</sup>J 8.1, <sup>4</sup>J 2.4, 1H), 8.27 (d, <sup>3</sup>J

8.1, 1H), 8.36 (d,  ${}^{3}J$  8.1, 1H), 8.48 (dd,  ${}^{4}J$  1.8,  ${}^{5}J$  0.6, 1H), 8.63 (d,  ${}^{4}J$  2.4, 1H).  $\delta_{\rm C}$  18.60, 43.36, 120.98, 121.07, 133.10, 134.05, 137.39, 137.93, 149.15, 149.70, 153.05, 156.27. *m/z* (ESI-HRMS) Calc. for  $[M + {\rm H}]^+ = 219.0683$ , found 219.0676; calc. for  $[M + {\rm Na}]^+ = 241.0503$ , found = 241.0497.

## 2-((5'-Methyl-[2,2'-bipyridin]-5-yl)methoxy) benzaldehyde (**6**)

A DMF (10 cm<sup>3</sup>) solution of salicylaldehyde (230 mg, 1.88 mmol) and 5-chloromethyl-5'-methyl-2,2'-bipyridine (343 mg, 1.57 mmol) in the presence of  $K_2CO_3$  (650 mg, 4.7 mmol) was stirred at room temperature for 10 h. H<sub>2</sub>O  $(20 \,\mathrm{cm}^3)$  was then added to the reaction mixture, and the resulting precipitate was filtered off and washed with water followed by a minimum volume of chilled MeOH. The crude product was purified by chromatography on silica gel with dichloromethane (98.75%), MeOH (1%) and saturated NH<sub>3</sub> (0.25%) as eluent to afford the product (477 mg, 94%) as a white solid.  $\delta_{\rm H}$  2.41 (s, 3H), 5.27 (s, 2H), 7.06 (d, <sup>3</sup>*J* 8.4 Hz, 1H), 7.13 (dd, <sup>3</sup>*J*7.8, <sup>3</sup>*J*7.2, 1H), 7.56 (ddd, <sup>3</sup>*J*8.4, <sup>3</sup>*J*7.8, <sup>4</sup>*J*1.8, 1H), 7.67 (dd, <sup>3</sup>*J* 8.1, <sup>4</sup>*J* 1.5, 1H), 7.88 (dd, <sup>3</sup>*J* 7.8, <sup>4</sup>*J* 1.8, 1H), 7.93 (dd, <sup>3</sup>*J* 8.1, <sup>4</sup>*J* 2.1, 1H), 8.31 (d, <sup>3</sup>*J* 8.1, 1H), 8.45 (d, <sup>3</sup>*J* 8.1, 1H), 8.53 (d, <sup>4</sup>J1.5, 1H), 8.75 (d, <sup>4</sup>J2.1, 1H), 10.55 (s, 1H).  $\delta_{\rm C}$  18.64, 68.19, 113.01, 121.24, 121.27, 121.68, 125.42, 129.02, 131.77, 134.31, 136.18, 136.55, 138.46, 148.39, 149.32, 152.76, 155.88, 160.73, 189.62. m/z (ESI-HRMS) Calc. for  $[M + Na]^+ =$ 327.1104, found = 327.1117.

## $[FeHL](PF_6)_3 \cdot CH_3 CN \ (L = 3)$

A stirred solution of 2-(5'-methyl-[2,2']bipyridinyl-5-ylmethoxy)benzaldehyde 6 (61 mg, 0.2 mmol) and  $Fe(BF_4)_2 \cdot 6H_2O$  (23 mg, 0.067 mmol) in acetonitrile  $(10 \text{ cm}^3)$  was refluxed for 40 min(for the <sup>1</sup>H NMR spectrum of  $[Fe(6)_3](BF_4)_2$ , see Fig. 3b). The reaction mixture was cooled to room temperature and further acetonitrile (90 cm<sup>3</sup>) added. To this, NH<sub>4</sub>OAc (77 mg, 1.0 mmol) was added and the resulting mixture stirred for 0.5 h. The reaction mixture was then cooled to 0°C in an ice bath followed by the addition of NaCNBH<sub>3</sub> (124 mg, 2.0 mmol). After 2 h the reaction mixture was allowed to warm to room temperature and stirred overnight and the solvent volume was reduced under vacuum to  $\sim 5 \text{ cm}^3$  and excess KPF<sub>6</sub> in H<sub>2</sub>O (15 cm<sup>3</sup>) was added. The resulting precipitate was isolated by filtration and washed with H<sub>2</sub>O and a minimum volume of cold MeOH then purified by chromatography on silica gel with CH<sub>3</sub>CN, H<sub>2</sub>O, and saturated KNO<sub>3</sub> (7:1:0.5) as eluent. The product was then isolated as its PF<sub>6</sub> salt (see above) affording a purplish red solid (51 mg, 55 %).  $\delta_{\rm H}$  2.24 (s, 9H), 3.94 (d, <sup>2</sup>J13.2, 3H), 4.01 (d, <sup>2</sup>*J* 13.2, 3H), 5.04 (d, <sup>2</sup>*J* 12.0, 3H), 5.09 (d, <sup>2</sup>*J* 12.0, 3H), 7.05 - 7.20 (m, 12H), 7.41 (br s, 3H), 7.54 (ddd,  ${}^{3}J7.5$ ,  ${}^{3}J$ 7.5,  ${}^{4}J$  1.8, 3H), 7.80 (br s, 3H), 7.98 (d,  ${}^{3}J$  8.3, 3H), 8.02 (d,  ${}^{3}J$ 8.3, 3H), 8.44 (d,  ${}^{3}J$  8.3, 3H), 8.49 (d,  ${}^{3}J$  8.3, 3H).  $\delta_{\rm C}$  18.11, 51.64, 67.20, 112.37, 121.90, 123.74, 123.97, 132.70, 133.88, 136.52, 138.05, 138.88, 139.47, 152.29, 154.44, 156.45, 157.45, 157.42, 159.53. m/z (ESI-HRMS) Calc. for  $[M-3PF_6]^{3+}$  = 312.7822, found = 312.7834. Anal. Calc. for  $C_{57}H_{52}FeN_7O_3P_3F_{18}$ . CH<sub>3</sub>CN: C 50.08, H 3.92, N 7.92. Found: C 50.15, H 4.03, N 8.02.

The deprotonated form of this compound was obtained by treatment of the CD<sub>3</sub>CN NMR sample with K<sub>2</sub>CO<sub>3</sub>.  $\delta_{\rm H}$  2.20 (s, 9H), 3.08 (d, <sup>2</sup>*J* 11.4, 3H), 3.21 (d, <sup>2</sup>*J* 11.4, 3H), 4.92 (d, <sup>2</sup>*J* 12.7, 3H), 5.14 (d, <sup>2</sup>*J* 12.7, 3H), 6.87 – 6.99 (m, 9H), 7.09 (d, <sup>4</sup>*J* 0.9, 3H), 7.94 (dd, <sup>3</sup>*J* 8.3, <sup>4</sup>*J* 1.8, 6H), 8.00 (br s, 3H), 8.41 (d, <sup>3</sup>*J* 

8.3, 3H), 8.45 (d,  ${}^{3}J$  8.3, 3H). m/z (ESI-HRMS) Calc. for  $[M - PF_6]^+ = 1082.3041$ , found = 1082.3004; calc. for  $[M - 2PF_6]^{2+} = 468.6697$ , found 468.6699.

#### X-Ray Structure Determination

Data were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Ka radiation generated from a rotating anode (0.71073 Å) with  $\omega$ and  $\psi$  scans to ~56° 20 at 150(2) K. Data integration and reduction were undertaken with SAINT and XPREP.<sup>[14]</sup> Subsequent computations were carried out using the WinGX-32 graphical user interface.<sup>[15]</sup> The structure was solved by direct methods using SIR97.<sup>[16]</sup> Multi-scan empirical absorption corrections were applied to the dataset using the program SADABS.<sup>[17]</sup> Data were refined and extended with SHELXL-97.<sup>[18]</sup> Non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Nitrogen bound hydrogen atoms were first located in the difference Fourier map before refinement. There is a small amount of thermal motion evident in the fluorine atoms of the anions and subsequently the thermal parameters of these atoms on the opposite sides of the molecule were restrained to be equal. CCDC 855907 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# Crystallographic Data

Formula C<sub>57</sub>H<sub>52</sub>F<sub>18</sub>FeN<sub>7</sub>O<sub>3</sub>P<sub>3</sub>, *M*1373.82, trigonal, space group  $R\bar{3}$ (#148), *a* 14.7878(9), *b* 14.7878(9), *c* 45.461(6) Å, *g* 120.00°, *V* 8609.5(14) Å<sup>3</sup>, *D*<sub>c</sub> 1.590 g cm<sup>-3</sup>, *Z* 6, crystal size 0.250 by 0.150 by 0.100 mm, colour purplish red, habit prism, T 150(2) K, *l*(MoKa) 0.71073 Å, *m*(MoKa) 0.458 mm<sup>-1</sup>, *T*(SADABS)<sub>min,max</sub> 0.6494, 0.7457,  $2q_{max}$  50.00, *hkl* range -17 17, -16 17, -52 54, *N* 20775, *N*<sub>ind</sub> 3381(*R*<sub>merge</sub> 0.0654), *N*<sub>obs</sub> 2480(*I* > 2*s*(*I*)), *N*<sub>var</sub> 267, residuals<sup>A</sup> *R*1(*F*) 0.0793, *wR*2(*F*<sup>2</sup>) 0.2291, GoF(all) 1.094, *Dr*<sub>min,max</sub> -1.118, 1.603 e<sup>-</sup>Å<sup>-3</sup>.

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Aust. J. Chem. Juli www.publish.csiro.au/journals/ajc

 $<sup>{}^{</sup>A}R1 = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| \text{ for } F_{o} > 2\sigma(F_{o}); wR2 = (\sum w(F_{o}^{2} - F_{c}^{2})2 / \sum (wF_{c}^{2})^{2})^{1/2} \text{ all reflections } w = 1/[\sigma^{2}(F_{o}^{2}) + (0.1085P)^{2} + 86.3000P] \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3.$