

Synthesis, redox properties, and crystal structures of the diphenylphosphinomethaneiron(II) complexes $[\text{FeCp}(\text{dppm})(\text{L})]^+ \text{PF}_6^-$ (L = CO and CH_3CN)

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Abstract

Photolysis of $[\text{FeCp}(\text{C}_6\text{H}_5\text{CH}_3)]^+ \text{PF}_6^-$ ($\mathbf{1}^+$), (Cp = $\eta^5\text{-C}_5\text{H}_5$) with visible light in acetonitrile in the presence of 1 equiv. dppm gives $[\text{FeCp}(\eta^2\text{-dppm})(\text{CH}_3\text{CN})]^+ \text{PF}_6^-$ ($\mathbf{2}^+$) (dppm = 1,2-bis(diphenylphosphino)methane) and photolysis in dichloromethane in the presence of 2 equiv. dppm gives $[\text{FeCp}(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^+ \text{PF}_6^-$ ($\mathbf{3}^+$). Complex $\mathbf{3}^+$ is converted into $\mathbf{2}^+$ in acetonitrile upon reflux or irradiation. Complex $\mathbf{2}^+$ reacts under 5–10 atm of CO at 20°C in acetone in the dark to give $[\text{FeCp}(\text{dppm})(\text{CO})]^+ \text{PF}_6^-$ ($\mathbf{4}^+$), which upon irradiation with visible light in acetonitrile is reconverted into $\mathbf{2}^+$. The $\mathbf{2}^+/\mathbf{4}^+$ pair is a photochromic system. Complex $\mathbf{2}^+$ is reversibly oxidized (cyclic voltammetry) and complex $\mathbf{4}^+$ is irreversibly reduced (1 F) at an Hg cathodic pool or Na/Hg to give $[\{\text{FeCp}(\mu_2\text{-CO})\}_2(\mu_2\text{-dppm})]$ ($\mathbf{5}$). The efficient photolytic and electrocatalytic exchanges of arene by P donors in $\mathbf{1}^+$ are compared. The crystal structures of $\mathbf{2}^+$ and $\mathbf{4}^+$ (as their PF_6^- salts) are reported.

Introduction

1,2-Bis(diphenylphosphino)methane, abbreviated as dppm, has received considerable attention in organo-transition metal chemistry [1]. It behaves (i) as a bridging bidentate ligand supporting metal–metal bonding in the so-called “A-frame” type complexes (ii) as a chelating ligand for a single metal centre (“small bite”) [2], and (iii) as a monodentate ligand in a few cases, in which it is referred to as a dangling ligand [3]. Of these three coordination modes, the A-frame is the most stable, the

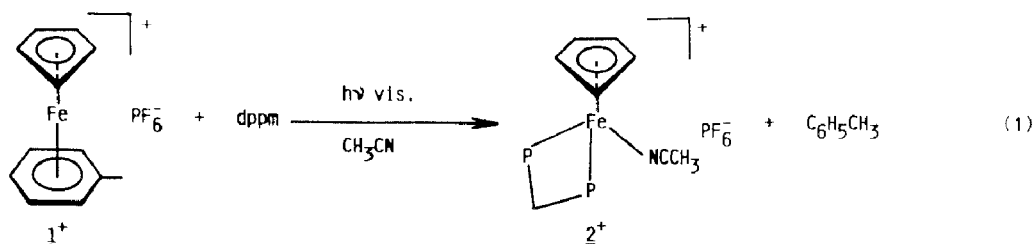
small bite four-atom ring being strained (PMP angles in the range of 67° to 74° , with the PCP angle about 95° compared with normal angles of 90° and 109° , respectively) [1].

In the present study, we describe Fe^{II} complexes of dppm involving all three modes, and crystal structures of the chelated complexes $[\text{FeCp}(\text{dppm})(\text{L})]^+ \text{PF}_6^-$, $\text{L} = \text{CO}$ and CH_3CN . These compounds were made by photochemical irradiation of $[\text{FeCp}(\text{C}_6\text{H}_5\text{R})]^+ \text{PF}_6^-$ ($\text{R} = \text{H}$ or CH_3) with visible light. This route is well known [4–6] although the dppm complexes are new. One of us previously reported photochemical preparations of dppe analogues by the same route [5]. Many complexes of the type $[\text{FeCp}(\text{dppe})(\text{X})]$ or $[\text{FeCp}(\text{dppe})(\text{L})]^+$ have been prepared previously by thermal reactions of $[\text{FeCp}(\text{CO})_2(\text{X})]$ [7–9].

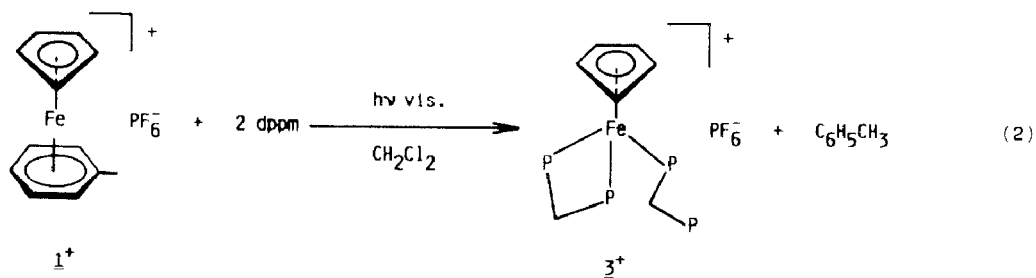
Results and discussion

1. Photochemical syntheses of the piano-stool dppm complexes

The photolysis of $[\text{FeCp}(\text{C}_6\text{H}_5\text{CH}_3)]^+ \text{PF}_6^-$ with visible light in the presence of dppm proceeds rapidly. As usual, the reactions were carried out in dichloromethane or acetonitrile. The choice of the solvent and of the stoichiometry of dppm is important in determining the nature of the final product; in acetonitrile and with only 1 equivalent of dppm the mixed dppm- CH_3CN complex is formed (eq. 1), and the solution progressively turns from yellow to red.



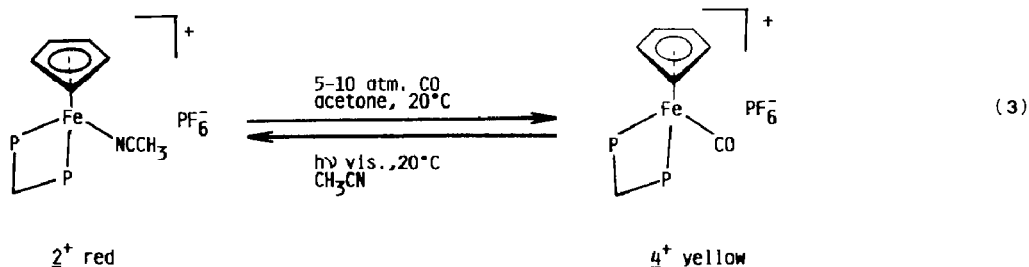
On the other hand, in dichloromethane and with 2 equivalents of dppm, a dark orange complex, containing a dangling dppm ligand in addition to the chelated one (eq. 2), is formed.



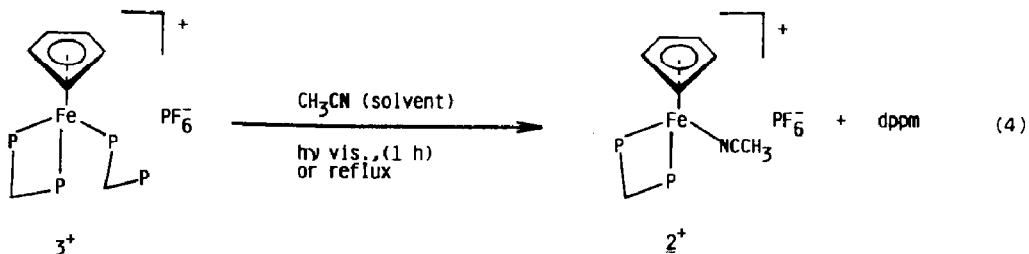
The nature of the arene ligand in 1^+ is not very important except that it should not be C_6Me_6 if visible light is used because $[\text{FeCp}(\text{C}_6\text{Me}_6)]^+$ only undergoes photolysis with UV light [6b], though acetone can be used as a sensitizer under visible light [6a]. Toluene was chosen because 1^+ is obtained in high yield; it is very soluble, and toluene is easily removed in the work up.

II. Ligand exchange in the piano-stool dppm complexes

The red complex 2^+ reacts at 20°C in acetone under 5–10 atm of CO with displacement of its CH_3CN ligand by CO. This gives the yellow carbonyl complex 4^+ . This reaction is similar to that previously reported for the dppe complexes $[\text{Fe}(\text{C}_5\text{R}_5)(\text{dppe})(\text{CH}_3\text{CN})]^+$ with $\text{R} = \text{H}$ [5] or CH_3 [10]. The reverse reaction takes place when complex 4^+ is irradiated in CH_3CN at 20°C with visible light, regenerating 2^+ . Thus, this is a photochromic system [11] (eq. 3).



Complex 3^+ is unstable because of the dangling dppm ligand. This ligand can be replaced by CH_3CN thermally (reflux) or photolytically, to give 2^+ (eq. 4). The exchange takes place slowly even at 20°C .



III. Spectroscopic properties

Whereas 2^+ and 3^+ show a single ^{31}P NMR resonance in CD_3COCD_3 at ca. 30 ppm (Table 1), 3^+ shows three ^{31}P resonances at 26.2 ppm (presumably from the P_2 bite), 61.1 ppm (presumably the coordinated P of the dangling dppm), and -21.3 ppm (free P). In the ^1H and ^{13}C NMR spectra the Cp signal is shifted upfield upon replacement of the strong π -acceptor CO by the σ -donor CH_3CN : $\Delta\delta$ 0.65 ppm (^1H), 6.6 ppm (^{13}C) and 8.7 ppm (^{31}P) [12].

IV. Crystal structures of the complexes 2^+ and 4^+

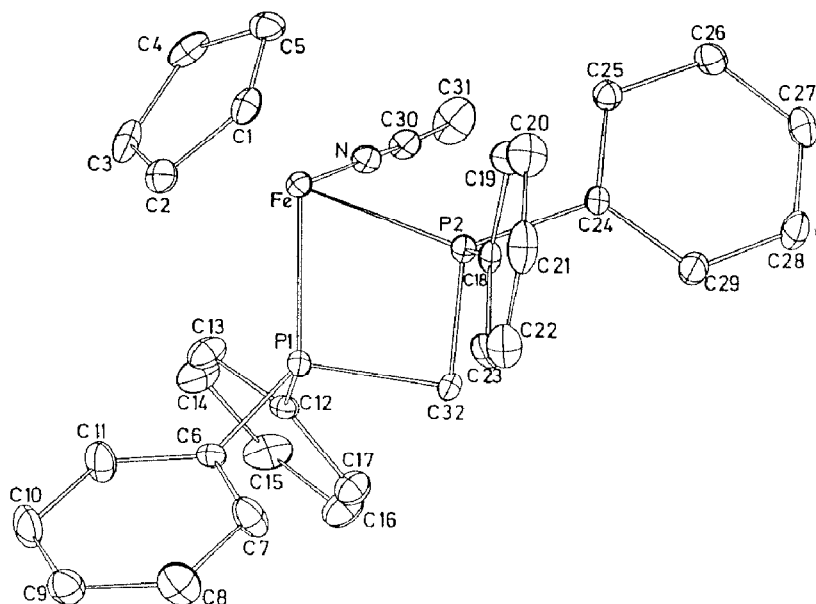
The crystal structures of the analogous dppe complexes have been reported [8c,d,e], as has that of the BPh_4^- salt of 2^+ [8f]. The ORTEP drawing of the X-ray crystal structures of complexes 2^+ and 4^+ are shown in Fig. 1 and 2 and the data are summarized in Table 2. The locations of the tripods with regard to the cyclopentadienyl ligand are shown in Fig. 3 for 2^+ and in Fig. 4 for 4^+ . The Fe–Cp distances in 2^+ and 4^+ (1.70 Å) are slightly shorter than those in the analogous dppe complexes (1.715 Å). This difference can be tentatively accounted for in terms of the bite effect of dppm increasing the acceptor property of the frontier orbital of the tripod. Similarly the Fe–P bonds are shorter in the dppm than in the dppe complexes, as are the Fe–Cp distances. The characteristics of 2^+ and 4^+ are summarized in Tables 3 and 4. A more detailed comparison of 2^+ and 4^+ is available [8e].

(continued on p. 314)

Table 1

Multinuclear NMR data for complexes 2^+ – 4^+ (Chemical shifts (δ) in ppm to high frequency of SiMe_4 for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and to high frequency of 85% H_3PO_4 for $^{31}\text{P}\{^1\text{H}\}$ NMR. Measurements at ambient temperature in $(\text{CD}_3)_2\text{CO}$.)

Compound	^1H NMR (δ)	$^{13}\text{C}\{^1\text{H}\}$ (δ)					$^{31}\text{P}\{^1\text{H}\}$ (δ)	
		CO	Ph	C=N	C_5H_5	<i>gem</i> - CH_2		CH_3
2^+	4.62 (s,5H,Cp)		132.90	127.39	76.50	28.60	3.5	+ 38.41
	AMX ₂ pseudo 1st ord.		132.18					η^2 -dppm
	5.21 (d,1H, CH_2)		131.39					
	4.18 (d,1H, CH_2)		129.82					
	1.74 (t,3H, CH_3)							
	7.70 (m,20H,Ph)							
3^+	7.45–6.76 (m,40H)		133.75		79.22	28.50		+ 61.14. d.
	4.76 (q,5H,Cp)		131.88					η^1 -P-dppm
	<i>J</i> (P–H) 1.75 Hz		128.73					+ 26.22. d.
	5.11 (m,2H, <i>gem</i> - CH_2)		127.74					2-dppm
	3.90 (m,2H, <i>gem</i> - CH_2)							– 21.28. d.
							P-dppm	
4^+	7.8–7.60 (m,20H,Cp)	203.73	131.82		83.11	28.10		+ 29.68
	5.3 (t,5H,Cp)		131.21					η^2 -dppm
	<i>J</i> (P–H) 1.47 Hz		130.10					
	5.4–4.5 (double t,2H CH_2 , ABX ₂ system)		129.40					
	<i>J</i> (H_A – H_B) 16 Hz							
	<i>J</i> (P–H) 13.3 Hz							

Fig. 1. Ortep view of 2^+ .

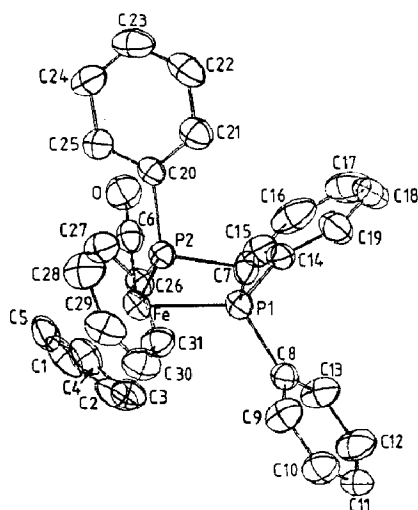
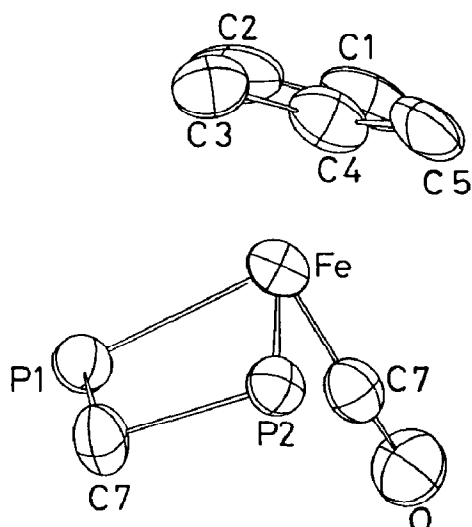
Fig. 2a. Ortep view of 4^+ .Fig. 2b. Ortep view of the piano stool shape of 4^+ without the phenyl groups.

Table 2

Crystal data for $[\text{FeCp}(\eta^2\text{-dppm})(\text{CH}_3\text{CN})] (2^+)$ and $[\text{FeCp}(\eta^2\text{-dppm})(\text{CO})] (4^+)$

Compound	$[\text{C}_5\text{H}_5\text{Fe}(\text{dppm})(\text{CO})]\text{PF}_6$	$[\text{C}_5\text{H}_5\text{Fe}(\text{dppm})(\text{NCCH}_3)]\text{PF}_6$
Formula	$\text{FeP}_3\text{F}_6\text{C}_{31}\text{OH}_{27}$	$\text{FeP}_3\text{F}_6\text{NC}_{32}\text{H}_{30}$
<i>M</i>	678.32	691.36
Space group	$P2_1/n$, monoclinic	$P2_1/c$, monoclinic
<i>a</i> (Å)	12.397(11)	9.346(9)
<i>b</i> (Å)	14.829(7)	18.886(9)
<i>c</i> (Å)	16.516(15)	17.850(9)
β (°)	98.85(4)	99.76(4)
<i>U</i> (Å ³)	3000(3)	3185(3)
<i>Z</i>	4	4
<i>D</i> _c (g cm ⁻³)	1.502	1.479
<i>F</i> (000)	1384	1416
<i>T</i> (K)	291	291
Crystal size (mm)	0.46 × 0.18 × 0.08	0.56 × 0.12 × 0.05
μ (mm ⁻¹)	0.719	0.695
Diffractometer type	Four circle, Nonius CAD 4	Four circle, Nonius CAD 4
2θ range (°)	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
Wavelength (Å)	0.71073	0.71073
Scan technique	$\omega-2\theta$	$\omega-2\theta$
Scan width (°)	$(1.0 + 0.35 \tan \theta)^\circ$	$(1.0 + 0.35 \tan \theta)^\circ$
Reflections measured	5270	6535
Reflections observed	2673	3041
Range of <i>hkl</i>	From 0,0, -19 to 14,17,19	From 0,0, -21 to 11,22,21
Goodness of fit (G.O.F.)	1.164	1.929
<i>R</i> ^a	0.034	0.059
<i>R</i> _w ^b	0.041	0.072
<i>P</i>	0.06	0.04
Largest shift/error in last full matrix refinement	0.04	0.14

^a $R = \sum(|F_o| - |F_c|) / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ with $\frac{1}{w} = \sigma_{(F)}^2 = \frac{1}{4}(\sigma_{(I)}^2 + (pI)^2) / I$ and $F_o^2 > 3\sigma(F_o^2)$.

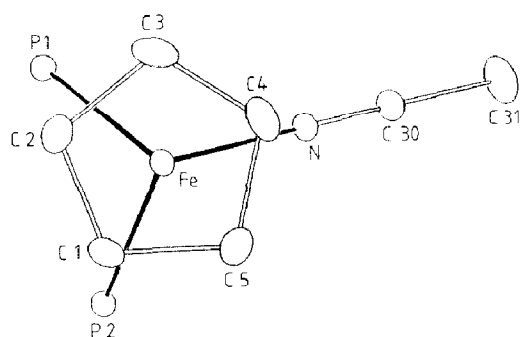


Fig. 3. Ortep view of the projection of the tripod of 2^+ on the cyclopentadienyl ring.

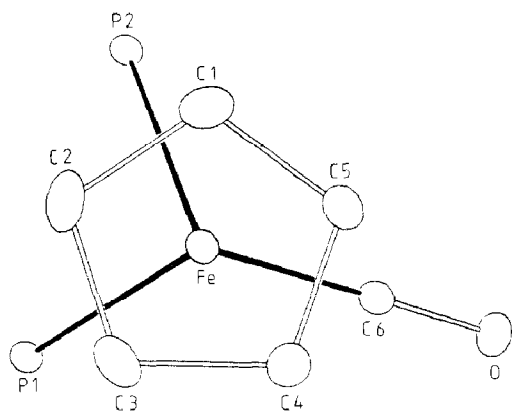


Fig. 4. Ortep view of the projection of the tripod of 4^+ on the cyclopentadienyl ring.

Table 3

Main distances (Å) for 2^+ and 4^+

Complexes	Fe–P(1)	Fe–P(2)	Fe–N(C)	Fe–Cp centroid	C=O
2^+	2.198(1)	2.208(1)	1.892(4)	1.697	1.135(7)
4^+	2.214(1)	2.210(1)	1.744(5)	1.708	1.145(5)

Table 4

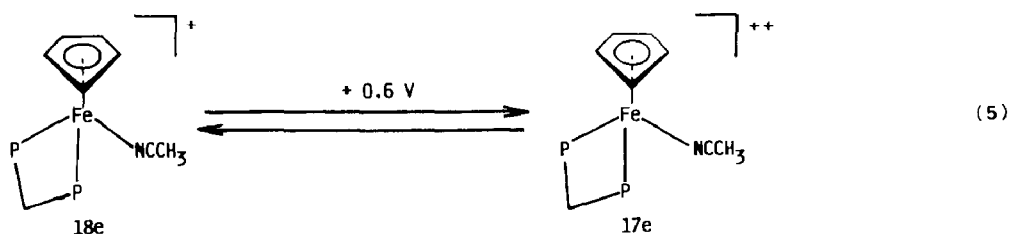
Main angles (°) for 2^+ and 4^+

Complexes	P(1)–Fe–P(2)	P(1)–Fe–N(C)	P(2)–Fe–N(C)	Fe–N≡C(C=O)	N≡C–C
2^+	74.63(5)	90.6(1)	90.9(1)	179.5(6)	178.1(8)
4^+	75.20(4)	94.2(1)	94.2(1)	176.7(4)	

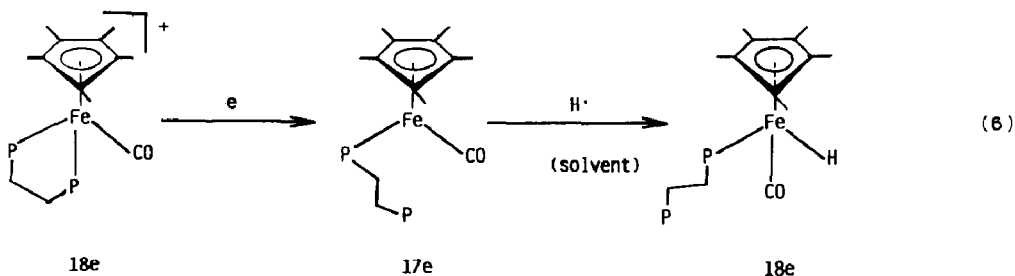
V. Redox processes of the complexes 2^+ and 4^+

The great difference in electronic properties between the CO and CH_3CN ligands which affects both the NMR chemical shifts of 2^+ and 4^+ and their UV-vis spectra (λ_{max} 4^+ 380 nm; 2^+ 480 nm) is also reflected in the electrochemical data. The

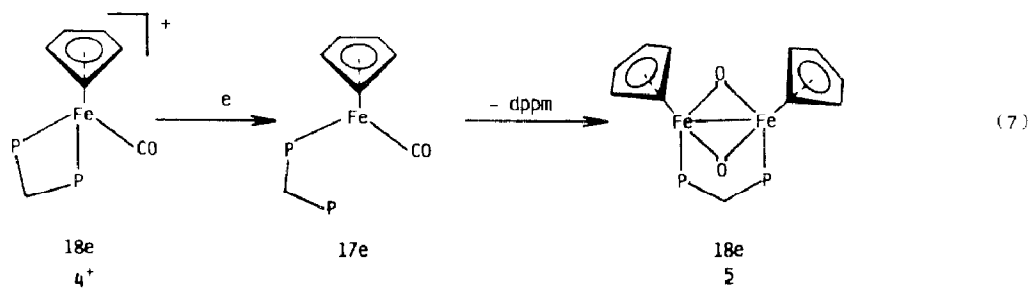
carbonyl complex 4^+ is easily reduced (-1.34 V vs. SCE, irreversibly) but difficult to oxidize (no oxidation below 1.5 V vs. SCE), whereas the acetonitrile complex is reduced irreversibly at more negative potentials but easily and reversibly oxidized at $+0.67$ V vs. SCE (ΔE_p 0.60 V, eq. 5). This behaviour is similar to that of the dppe complexes [13]. The reversible oxidation of complexes of the type $[\text{FeCp}(\text{dppe})(\text{X})]$ has been noted by Treichel [14,15], who reported the isolation of several 17e complexes $\text{FeCp}(\text{dppe})(\text{X})^+ \text{PF}_6^-$, the E° values for which were found to be close to 0 V vs. SCE. Complex 2^+ is cationic and more difficult to oxidize. In coulometric experiments, the solution slowly decomposed after passage of 1 F and attempts to isolate 2^{2+} failed. However, it is probable that the reversible oxidation is as shown in eq. 5.



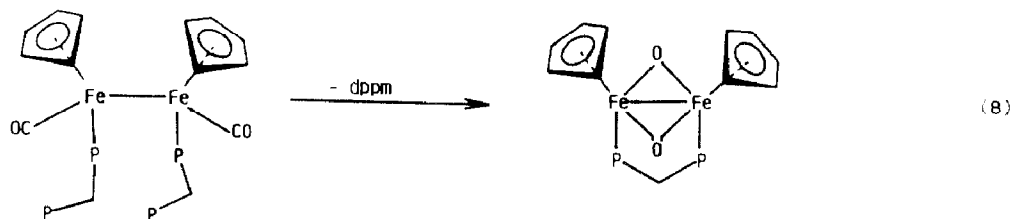
On the other hand, both electrochemical and chemical reductions of 4^+ have been carried out. We know that the Na/Hg or LiAlH_4 reduction of the C_5Me_5 -dppe analogue $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})(\text{CO})]^+ \text{PF}_6^-$ gives a hydride via a 17e or 19e radical, for which an ESR spectrum was observed [16] (eq. 6).



The electroreduction of 4^+ on Hg in $\text{CH}_2\text{Cl}_2/\text{THF}$ (1/2) at -1.40 V vs. SCE consumed 0.95 F/mol and produced a green species which was also more conveniently obtained by Na/Hg reduction in THF at 20°C . The complex was obtained in 75% yield by the latter method and appeared to be the known dimer **5b** in the case of dppe [17]. Both the dppe and dppe complexes **5a** and **5b** were analyzed and showed analogous dimeric structures. Although **5a** was previously known, the earlier synthesis was by a completely different method. The dimerization occurred by formation of a metal-metal bond from 17e iron-centered radicals analogous to that postulated in the reaction of the C_5Me_5 analogue. The monoelectronic reduction of 4^+ can give a 19e species which then releases a phosphorus atom from the metal centre to form the 17e intermediate. Alternatively the P decoordination may be concomitant with the electron transfer, which forms this 17e intermediate directly (eq. 6 and 7). However, there is no evidence in favour of either hypothesis, as was the case for eq. 6.



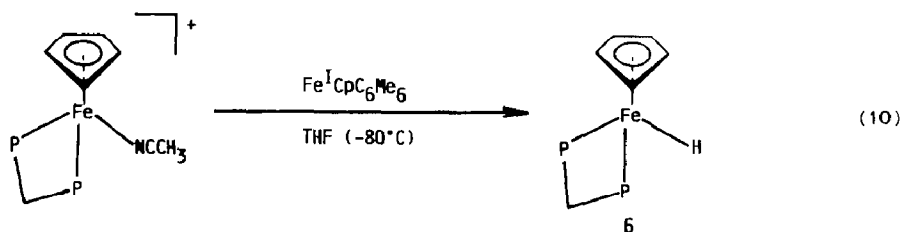
We note that a phosphorus atom rather than the CO ligand is detached upon electron-transfer and that 1 dppm is absent from the final product. Structure **5** is obviously more satisfactory than that of a dimer of the precursor **17e** radical with two dangling dppm ligands. It is probable that such a dimer is formed, however, but has a short lifetime owing to rapid entropy-driven displacement of a dangling dppm by the free P of the other dppm (eq. 8). An alternative mechanism involving decooordination of a dangling dppm from a **17e** radical to generate a **15e** radical is much less probable.



The chemical reduction of 2^+ was more difficult because extensive decomposition occurred during this type of reaction. The classical Na/Hg reduction at 20°C gave much decomposition, and was not further examined. Thus we carried out the reduction of 2^+ PF_6^- with naphthyl sodium at -80°C or with the mild electron reservoir complex $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$ [**6b**, **17e**]. Electron-transfer by the latter is possibly endergonic by 200 mV (the E° value of $2^+/2$ is not known since the reduction of 2^+ is totally irreversible). However, electron transfer occurs because the endergonicity is not too large, and the ET reaction is followed by reactions which remove **2**:



The decomposition is not so extensive when the reactions are carried out at low temperature but cannot be totally avoided. It can be detected by ^1H NMR spectroscopy by the observation of the signal from polycyclopentadiene at δ 1–2 ppm in C_6D_6 . Some ferrocene is also formed in small amounts. The major reaction product is the hydride $[\text{FeCp}(\text{dppm})(\text{H})]$ (**6**) (eq. 10), a type of complex which is often found in the chemistry of the **17e** and **19e** radicals $\text{Fe}^{\text{I}}\text{CpL}_2$ and $\text{Fe}^{\text{I}}\text{CpL}_3$ [**17f**] ($\text{L} = \text{PR}_3$). For instance, this complex was also formed in the reaction of the **19e** complex $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_5\text{CH}_3)]$ with dppm. The **17e** intermediate species FeCpL_2 abstracts an H atom from the medium.



The great difference in the behavior between two 19e radicals $[\text{Fe}^{\text{I}}\text{Cp}(\text{dpmm})(\text{L})]$ is noteworthy. With $\text{L} = \text{CO}$, a P ligand is decoordinated, whereas with $\text{L} = \text{CH}_3\text{CN}$, L is decoordinated rather than a P ligand. The order of decoordination ability in 19e piano-stool complexes is thus $\text{CO} < \text{PR}_3 < \text{CH}_3\text{CN}$, which suggests that the acceptor character stabilizes the 19e state. The properties of 17e and 19e piano-stool organo-iron radicals will be more extensively described elsewhere [17f].

VI. Comparison between the photolytic and electrocatalytic arene exchange in 1^+

Another way of replacing the arene ligand in 1^+ by three two-electron ligands L is to catalyze the reaction with small amounts of a reducing reagent such as the 19e complex **1** [18]. The reaction can be effected in a THF suspension, and gives $[\text{FeCp}(\text{L})_3]^+$ in the presence of 3 equivalents of a P ligand [17f]. If the reaction is carried out in homogeneous solution in CH_3CN , 2^+ can also be isolated. This can be understood in terms of the ligand exchange behaviour described in this paper. Both the photolytic and the electrocatalytic ligand exchange reactions of 1^+ give quantitative yields.

The question thus arises of whether there is a connection between these two equally facile processes. Indeed, it is well known that the redox ability of a photoexcited state is much greater than that of the ground state [19]. The photoexcited state of $[\text{FeCp}(\text{arene})]^+$ has been shown to reduce methylviologen and oxidize dimethylaniline [20]. Wrighton has shown that PPh_3 can act both as a reducing agent for the excited state of $[\text{Re}(\text{phen})(\text{CO})(\text{CH}_3\text{CN})]^+$, and as a ligand which replaces CH_3CN in the 19e neutral complex [21].

We carried out such a photoelectrocatalytic experiment with dpmm in the absence or presence of various sacrificial amines but without success. It is probable that the photoexcited state is not sufficiently long-lived to allow efficient electron-transfer. An external sensitizer could also be used, but its excited state would have to be able to reduce $[\text{FeCp}(\text{toluene})]^+$ rapidly, and thus would have to have $E^\circ < -1.2 \text{ V}$ vs. SCE (which is not the case for $[\text{Ru}(\text{bipy})_3]^{2+}$).

Experimental

General data

All manipulations were carried out under argon by Schlenk techniques. Microanalyses were carried out at the Centre for Microanalyses of the CNRS at Lyon-Villeurbanne. IR spectra were recorded on a Perkin-Elmer 567 grating spectrometer (Nujol or KBr disks). Some NMR spectra were recorded on a Varian XL-100 (^1H) instrument; high resolution NMR spectra were recorded on a Bruker WM-250 spectrometer (^1H , $^{13}\text{C}\{^1\text{H}\}$) or on a Bruker WP-80 spectrometer ($^{31}\text{P}\{^1\text{H}\}$), shifts are in ppm relative to SiMe_4 (^1H , ^{13}C) or 85% H_3PO_4 external (^{31}P). The compounds

$[\text{FeCp}(\text{arene})]^+ \text{PF}_6^-$, (arene = naphthalene, benzene, toluene), were prepared by published methods [22]. Photolyses were performed with a tungsten lamp (200 W) or a halogen lamp (500 W) with an Oriel filter (400 nm) in a Pyrex thermostated cell. Cyclic voltammograms were obtained by use of an EPL 2 Tacussel three-electrode instrument with a saturated calomel reference electrode (SCE). Controlled-potential electrolysis was carried out with a Wenking EVI-80 coulometer. The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode. A platinum mesh electrode (105 cm²) was used for controlled-potential electrolysis. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium hydroxide (Aldrich) and perchloric acid as previously described [23]. High-purity solvents both for photolytical reactions and electrochemical determinations were obtained and checked by standard procedures [23].

Photochemical synthesis of $[\text{FeCp}(\eta^2\text{-dppm})(\text{CH}_3\text{CN})]^+ \text{PF}_6^- (2^+ [\text{PF}_6]^-)$

Method (a): A solution containing 179 mg (0.50 mmol) of $[\text{FeCp}(\text{C}_6\text{H}_5\text{CH}_3)]^+ \text{PF}_6^-$, 250 mg (0.65 mmol) of dppm in a mixture of 5 ml of acetonitrile and 10 ml of dichloromethane was irradiated in a Pyrex cell under argon at 0 °C for 3 h. The solution was then concentrated and the product precipitated with ether to yield 225 mg (65%) of the red salt $2^+ [\text{PF}_6]^-$. Crystallization in a mixture acetonitrile/ether at low temperature gave red crystals. IR (KBr): 2260(w) cm⁻¹. UV-vis: λ_{max} 480 nm; ϵ 600 dm³ mol⁻¹ cm⁻¹. Anal. Found: C, 55.36; H, 4.52; P, 13.53; Fe, 8.01; N, 1.91. C₃₂H₃₀FeNP₃F₆ calcd.: C, 55.60; H, 4.37; P, 13.44; Fe, 8.07; N, 2.03%.

Method (b): A solution of 169 mg (0.1 mmol) of $[\text{FeCp}(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^+ \text{PF}_6^-$, in 5 ml of acetonitrile was irradiated at room temperature for 1 h or refluxed (in the dark) for 30 min. The initial orange colour of the solution changed to red. Precipitation by ether gave the red crystalline PF_6^- salt of 2^+ . Yields: 86% under photochemical conditions and 81% under thermal ones.

Method (c): A pale yellow solution containing 136 mg (0.2 mmol) of the PF_6^- salt carbonyl cationic complex 4^+ in 5 ml of acetonitrile was irradiated under argon for 1 h at 20 °C to give a red solution. The product was then precipitated with ether and recrystallized from acetonitrile/ether. Yield: 93% of a red crystalline solid.

Synthesis of $[\text{FeCp}(\eta^2\text{-dppm})(\text{CO})]^+ \text{PF}_6^- (4^+ [\text{PF}_6]^-)$

(This compound was previously obtained by refluxing $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{SC}_2\text{H}_5)]^+ \text{BPh}_4^-$ with dppm in acetone [8f]). A solution of 200 mg (0.29 mmol) of **1** in acetone (7 ml) was kept under carbon monoxide (Matheson) in a Carius tube (ca. 5 atm) in the dark for 3 days. The initially deep-red solution changed slowly to yellow. The product was precipitated by addition of cold ether at -20 °C to give a 70% yield of yellow crystals. IR (KBr): 1975(w) cm⁻¹. UV-vis: λ_{max} 380 nm; ϵ 714 dm³ mol⁻¹ cm⁻¹. Anal. Found: C, 54.40; H, 3.98; P, 13.15. C₃₁H₂₇FeOP₃F₆ calcd.: C, 54.90; H, 4.01; P, 13.70%.

Synthesis of $[\text{FeCp}(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^+ \text{PF}_6^- (3^+ [\text{PF}_6]^-)$

Irradiation at 0 °C of a yellow solution containing 179 mg (0.50 mmol) of $[\text{FeCp}(\text{C}_6\text{H}_5\text{CH}_3)]^+ \text{PF}_6^-$ and 375 mg (0.97 mmol) of dppm in 15 nml of dichloromethane for 3 h gave a dark orange solution. After removal of the solvent in vacuo, the solid residue was washed with toluene and ether under argon, and was then dissolved at low temperature (0 °C) in 3 ml of dichloromethane. The solution was

filtered, and the product crystallized by slow diffusion of ether into the solution, in the dark at 0 °C, to give 202 mg of dark orange crystals (yield 48%). Anal. Found: C, 63.40; H, 4.53; P, 14.53; Fe, 5.73. $C_{55}H_{49}P_5F_6$ calcd.: C, 63.85; H, 4.53; P, 14.97; Fe, 5.40%.

Reductive dimerization of $[FeCp(CO)(\eta^2-dppm)]^+ PF_6^-$ ($4^+ [PF_6]^-$)

(a) *Chemical reduction.* A suspension of 4^+ , (339 mg, 0.50 mmol) in 50 ml of dry THF was added through a cannula to 1% sodium amalgam under argon. An olive-green colour developed immediately. The mixture was stirred at 0 °C for 2 h, then the mixture was warmed to 20 °C and stirred for a further hour at 20 °C. After filtration under argon, the green solution evaporated to dryness in vacuo. The residual solid was washed with a toluene/pentane mixture to remove the free dppm, then recrystallized from a chloroform/pentane mixture. The green crystals of **4** were identified by comparison with literature data [17a–d]. The yield was 75%.

(b) *Electroreduction of $4a^+$:* A bulk electrolysis of 4^+ was carried out in THF/dichloromethane (2/1), with TEAP (0.1 M) as supporting electrolyte on a mercury pool as working electrode at –1.40 V vs. SCE. Electrochemical instrumentation and devices were as described by Peltier and Moinet [25]. This electrosynthesis consumed 0.95 F and gave a green solution. The IR spectrum (Nujol) consisted of bands at 1920(w) and 1671(s) cm^{-1} , in accordance with the literature data for $[{FeCp(\mu-CO)}_2(\mu_2-dppm)]$. The latter was isolated by rotary evaporation of THF followed by extraction with water/ether, evaporation of the organic layer, and recrystallization of the product from a chloroform/pentane solution. The C, H analyses and 1H NMR spectra agree with the assigned formulation.

Chemical reduction of $[FeCp(\eta^2-dppm)(CH_3CN)]^+ PF_6^-$ ($2^+ [PF_6]^-$)

A solution of 2^+ (346 mg, 0.50 mmol) in 50 ml of dry THF at –80 °C was stirred with $[Fe^1Cp(C_6Me_6)]$ (0.142 mg, 0.50 mmol). The green solution turned red-brown with the formation of a yellow precipitate of $[FeCp(C_6Me_6)]^+ PF_6^-$. THF was then removed in vacuo and the crude product was extracted with 3×20 ml of pentane. Concentration of the solvent gave 136 mg (54% yield) of orange microcrystals of $[FeCp(\eta^2-dppm)(H)]$ (**6**) [17f].

Crystallographic studies [28]*

Crystals of 2^+ and 4^+ suitable for X-ray diffraction were irradiated at room temperature. Data were collected on an Enraf–Nonius CAD4 diffractometer. For each compound cell constants were obtained by least-square refinements of the setting angles of 25 reflections in the range shown in Table 2, which also gives other crystallographic information. All data reduction and computing calculation were carried out using the S.D.P. program package [26]. The positions of the metal atoms and P atoms in each structure were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-square refinement and difference electron density syntheses. Atomic scattering terms were taken from the usual tabulations [27]. Hydrogen atoms were placed at calculated positions and kept fixed during refinements.

Atomic coordinates are listed in Tables 5 and 6, and bond lengths and angles in Tables 7 and 8. Supplementary material is available [28*].

(continued on p. 325)

Table 5

Atomic coordinates (with e.s.d.'s) for $[\text{FeCp}(\eta^3\text{-dppm})(\text{CH}_3\text{CN})] (\mathbf{2}^+)$

Atom	x	y	z	B (\AA^2)	Atom	x	y	z	B (\AA^2)
Fe	-0.01934(9)	0.1682(5)	0.52603(5)	2.89(2)	C(28)	0.4802(8)	0.3576(4)	0.5393(5)	5.5(2)
P(1)	-0.0031(2)	0.19026(9)	0.64779(9)	3.12(3)	C(29)	0.3438(8)	0.3446(4)	0.5568(4)	4.8(2)
P(2)	0.0799(2)	0.27303(8)	0.54164(9)	3.00(3)	C(30)	0.2770(7)	0.0976(4)	0.5548(4)	4.2(2)
P(3)	0.3016(2)	0.0790(1)	0.3024(1)	4.56(4)	C(31)	0.4170(9)	0.0639(5)	0.5659(6)	7.5(3)
F(1)	0.1729(8)	0.0637(4)	0.2392(4)	13.3(2)	C(32)	0.1067(7)	0.2714(3)	0.6457(4)	3.6(1)
F(2)	0.3672(8)	0.1087(5)	0.2391(4)	16.6(3)	H(1)	-0.2110	0.2404	0.4246	5 ^a
F(3)	0.4326(8)	0.0951(4)	0.3635(4)	14.8(2)	H(2)	-0.3065	0.1782	0.5297	5
F(4)	0.230(1)	0.0517(5)	0.3647(4)	19.2(3)	H(3)	-0.2011	0.0549	0.5422	5
F(5)	0.3553(9)	0.0055(3)	0.2941(5)	16.4(3)	H(4)	-0.0471	0.0421	0.4439	5
F(6)	0.243(1)	0.1529(4)	0.3106(4)	17.6(3)	H(5)	-0.0378	0.1581	0.3720	5
N	0.1661(5)	0.1238(3)	0.5440(3)	3.5(1)	H(6)	-0.1422	0.3163	0.6948	5
C(1)	-0.1868(7)	0.1933(4)	0.4413(4)	4.4(2)	H(7)	-0.3502	0.3401	0.7429	5
C(2)	-0.2407(7)	0.1587(4)	0.4996(4)	4.8(2)	H(8)	-0.5037	0.2479	0.7647	5
C(3)	-0.1834(8)	0.0907(4)	0.5066(4)	5.9(2)	H(9)	-0.4343	0.1327	0.7442	5
C(4)	-0.0970(8)	0.0043(4)	0.4522(4)	5.9(2)	H(10)	-0.2183	0.1104	0.6976	5
C(5)	-0.0926(8)	0.1482(4)	0.4112(4)	5.1(2)	H(11)	0.0143	0.0419	0.6594	5
C(6)	-0.1618(7)	0.2116(3)	0.6896(3)	3.4(1)	H(12)	0.1637	-0.0405	0.7314	5
C(7)	-0.2023(9)	0.2787(4)	0.7046(5)	6.0(2)	H(13)	0.3353	-0.0018	0.8325	5

C(8)	-0.3271(9)	0.2924(4)	0.7328(5)	7.0(2)	H(14)	0.3568	0.1173	0.8614	5
C(9)	-0.4154(8)	0.2381(5)	0.7466(4)	5.7(2)	H(15)	0.2144	0.2001	0.7872	5
C(10)	-0.3754(9)	0.1717(5)	0.7338(5)	7.7(2)	H(16)	0.2550	0.2153	0.4386	5
C(11)	-0.2480(8)	0.1586(4)	0.7052(5)	6.4(2)	H(17)	0.4849	0.2397	0.4090	5
C(12)	0.1010(6)	0.1297(3)	0.7140(3)	3.3(1)	H(18)	0.6257	0.3286	0.4739	5
C(13)	0.0862(9)	0.0581(4)	0.7000(4)	5.3(2)	H(19)	0.5395	0.3936	0.5658	5
C(14)	0.173(1)	0.0090(4)	0.7436(5)	6.8(2)	H(20)	0.3088	0.3708	0.5950	5
C(15)	0.273(1)	0.0319(4)	0.8024(4)	6.7(2)	H(21)	-0.0009	0.3302	0.3978	5
C(16)	0.2876(9)	0.1018(5)	0.8186(4)	6.1(2)	H(22)	-0.1333	0.4262	0.3432	5
C(17)	0.2026(8)	0.1513(4)	0.7754(4)	4.9(2)	H(23)	-0.2391	0.5030	0.4163	5
C(18)	-0.0216(6)	0.3516(3)	0.5064(3)	3.3(1)	H(24)	-0.2090	0.4874	0.5465	5
C(19)	-0.0423(9)	0.3624(4)	0.4290(4)	5.1(2)	H(25)	-0.0686	0.3930	0.6038	5
C(20)	-0.121(1)	0.4190(4)	0.3968(5)	6.8(2)	H(26)	0.2050	0.2657	0.6690	5
C(21)	-0.1833(9)	0.4645(4)	0.4392(5)	6.7(2)	H(27)	0.0666	0.3115	0.6671	5
C(22)	-0.1642(8)	0.4556(4)	0.5159(5)	6.4(2)	H(28)	0.4490	0.0567	0.6189	5
C(23)	-0.0830(8)	0.3984(4)	0.5497(4)	4.7(2)	H(29)	0.4097	0.0197	0.5405	5
C(24)	0.2583(6)	0.2912(3)	0.5190(3)	3.4(1)	H(30)	0.4838	0.0935	0.5463	5
C(25)	0.3123(7)	0.2525(3)	0.4645(4)	3.7(1)					
C(26)	0.4495(7)	0.2664(4)	0.4473(4)	4.6(2)					
C(27)	0.5314(7)	0.3192(4)	0.4854(4)	5.3(2)					

^a H atoms B_{iso} .

Table 6
Atomic coordinates (with e.s.d.'s) for $[\text{FeCp}(\eta^2\text{-dppm})(\text{CO})]^+ (4^+)$

Atom	x	y	z	B (\AA^2)	Atom	x	y	z	B (\AA^2)
Fe	0.52206(4)	0.50308(4)	0.20107(3)	2.86(1)	C(26)	0.6973(3)	0.4024(3)	0.3642(2)	2.97(8)
P(1)	0.38870(7)	0.49708(8)	0.27596(6)	2.78(2)	C(27)	0.7788(3)	0.3391(3)	0.3644(3)	4.1(1)
P(2)	0.57147(8)	0.39559(7)	0.29188(6)	2.73(2)	C(28)	0.8751(4)	0.3467(3)	0.4199(3)	5.4(1)
P(3)	0.7270(1)	0.78505(9)	0.51298(8)	4.56(3)	C(29)	0.8885(4)	0.4159(3)	0.4747(3)	4.8(1)
F(1)	0.6142(3)	0.8331(3)	0.5143(2)	8.8(1)	C(30)	0.8097(4)	0.4792(3)	0.4755(3)	4.5(1)
F(2)	0.6718(3)	0.6917(2)	0.5288(2)	9.2(1)	C(31)	0.7147(3)	0.4731(3)	0.4197(3)	3.9(1)
F(3)	0.8391(3)	0.7361(3)	0.5130(2)	8.8(1)	H(1)	0.7424	0.5335	0.2290	^a
F(4)	0.7181(3)	0.3763(2)	0.0022(2)	10.4(1)	H(2)	0.6225	0.6309	0.3034	
F(5)	0.2581(3)	0.6991(3)	0.1080(2)	8.9(1)	H(3)	0.4624	0.6794	0.2007	
F(6)	0.6954(3)	0.7681(3)	0.4191(2)	7.73(9)	H(4)	0.4814	0.6119	0.0656	
O	0.4192(2)	0.3825(2)	0.0750(2)	4.61(7)	H(5)	0.6549	0.5210	0.0826	
C(1)	0.6757(4)	0.5610(3)	0.2055(3)	5.4(1)	H(6)	0.4132	0.3606	0.3521	
C(2)	0.6094(4)	0.6153(3)	0.2470(3)	5.8(1)	H(7)	0.4777	0.4371	0.4022	
C(3)	0.5206(4)	0.6418(3)	0.1900(3)	5.3(1)	H(8)	0.4953	0.5978	0.4159	
C(4)	0.5312(4)	0.6046(3)	0.1151(3)	4.4(1)	H(9)	0.4448	0.7155	0.4941	
C(5)	0.6275(4)	0.5540(3)	0.1244(3)	4.5(1)	H(10)	0.2755	0.7830	0.4607	
C(6)	0.4583(3)	0.4292(3)	0.1265(2)	3.34(9)	H(11)	0.1581	0.7346	0.3468	

C(7)	0.4559(3)	0.4134(3)	0.3488(2)	3.30(9)	H(12)	0.2060	0.6165	0.2683
C(8)	0.3540(3)	0.5920(3)	0.3361(2)	2.95(8)	H(13)	0.2531	0.5065	0.1196
C(9)	0.4252(3)	0.6244(3)	0.4021(3)	4.4(1)	H(14)	0.0794	0.4535	0.0656
C(10)	0.3956(4)	0.6948(3)	0.4481(3)	4.5(1)	H(15)	-0.0208	0.3705	0.1459
C(11)	0.2962(4)	0.7350(3)	0.4282(3)	4.1(2)	H(16)	0.0488	0.3396	0.2811
C(12)	0.2268(4)	0.7059(3)	0.3615(3)	5.1(1)	H(17)	0.2242	0.3891	0.3358
C(13)	0.2550(3)	0.6356(3)	0.3152(3)	4.4(1)	H(18)	0.5039	0.2290	0.3574
C(14)	0.2566(3)	0.4522(3)	0.2329(2)	3.15(9)	H(19)	0.4994	0.0786	0.3150
C(15)	0.2127(3)	0.4719(3)	0.1529(3)	4.0(1)	H(20)	0.5521	0.0412	0.1907
C(16)	0.1091(4)	0.4407(3)	0.1210(3)	5.6(1)	H(21)	0.6209	0.1503	0.1120
C(17)	0.0497(4)	0.3917(4)	0.1685(4)	6.6(1)	H(22)	0.6278	0.3001	0.1550
C(18)	0.0910(4)	0.3729(3)	0.2480(4)	5.9(1)	H(23)	0.7693	0.2902	0.3267
C(19)	0.1951(4)	0.4028(3)	0.2806(3)	4.6(1)	H(24)	0.9316	0.3035	0.4195
C(20)	0.5653(3)	0.2787(3)	0.2596(2)	2.81(8)	H(25)	0.9539	0.4199	0.5129
C(21)	0.5276(3)	0.2132(3)	0.3073(3)	3.9(1)	H(26)	0.8196	0.5273	0.5138
C(22)	0.5243(4)	0.1242(3)	0.2819(3)	4.6(1)	H(27)	0.6601	0.5182	0.4193
C(23)	0.5570(4)	0.1021(3)	0.2090(3)	4.9(1)				
C(24)	0.5966(4)	0.1666(3)	0.1619(3)	4.2(1)				
C(25)	0.6006(3)	0.2551(3)	0.1875(3)	3.38(9)				

^a H atoms B_{iso} 4.5 (\AA^2).

Table 7

Bond lengths (Å) and bond angles (°) for 2^+ . Numbers in parentheses are estimated standard deviations in the least significant digits

<i>Distances</i>					
Fe–P(1)	2.198(1)	C(1)–C(2)	1.394(7)	C(16)–C(17)	1.376(9)
Fe–P(2)	2.208(1)	C(1)–C(5)	1.395(10)	C(18)–C(19)	1.376(8)
Fe–N	1.892(4)	C(2)–C(3)	1.389(8)	C(18)–C(23)	1.363(9)
P(1)–C(6)	1.815(7)	C(3)–C(4)	1.370(8)	C(19)–C(20)	1.368(7)
P(1)–C(12)	1.809(5)	C(4)–C(5)	1.414(8)	C(20)–C(21)	1.342(6)
P(1)–C(32)	1.848(5)	C(6)–C(7)	1.362(9)	C(21)–C(22)	1.361(7)
P(20)–C(18)	1.816(7)	C(6)–C(11)	1.344(10)	C(22)–C(23)	1.397(8)
P(2)–C(24)	1.814(6)	C(7)–C(8)	1.370(9)	C(24)–C(25)	1.378(8)
P(2)–C(32)	1.831(5)	C(8)–C(9)	1.363(9)	C(24)–C(29)	1.389(9)
P(3)–F(1)	1.536(4)	C(9)–C(10)	1.340(10)	C(25)–C(26)	1.393(7)
P(3)–F(2)	1.485(5)	C(10)–C(11)	1.395(8)	C(26)–C(27)	1.366(7)
P(3)–F(3)	1.526(4)	C(12)–C(13)	1.379(9)	C(27)–C(28)	1.354(10)
P(3)–F(4)	1.486(5)	C(12)–C(17)	1.381(9)	C(28)–C(29)	1.385(10)
P(3)–F(5)	1.491(5)	C(13)–C(14)	1.382(8)	C(30)–C(31)	1.438(8)
P(3)–F(6)	1.517(5)	C(14)–C(15)	1.355(7)		
N–C(30)	1.135(7)	C(15)–C(16)	1.353(8)		
<i>Angles</i>					
P(1)–Fe–P(2)	74.63(5)	F(4)–P(3)–F(5)	87.4(5)	C(14)–C(15)–C(16)	120.5(5)
P(1)–Fe–N	90.6(1)	F(4)–P(3)–F(6)	91.6(5)	C(15)–C(16)–C(17)	121.0(6)
P(2)–Fe–N	90.9(1)	F(5)–P(3)–F(6)	178.4(5)	C(12)–C(17)–C(16)	119.8(6)
C(6)–P(1)–C(12)	105.2(3)	C(2)–C(1)–C(5)	109.5(5)	P(2)–C(18)–C(19)	116.4(5)
C(6)–P(1)–C(32)	108.6(3)	C(1)–C(2)–C(3)	108.5(5)	P(2)–C(18)–C(23)	125.4(5)
C(12)–P(1)–C(32)	107.2(2)	C(2)–C(3)–C(4)	106.4(5)	C(19)–C(18)–C(23)	118.2(6)
C(18)–P(2)–C(24)	102.4(3)	C(3)–C(4)–C(5)	111.3(6)	C(18)–C(19)–C(20)	120.8(6)
C(18)–P(2)–C(32)	109.8(3)	C(1)–C(5)–C(4)	104.2(6)	C(19)–C(20)–C(21)	121.2(5)
C(24)–P(2)–C(32)	104.9(3)	P(1)–C(6)–C(7)	124.2(5)	C(20)–C(21)–C(22)	119.4(5)
F(1)–P(3)–F(2)	83.4(4)	P(1)–C(6)–C(11)	118.6(5)	C(21)–C(22)–C(23)	120.0(5)
F(1)–P(3)–F(3)	178.2(4)	C(7)–C(6)–C(11)	117.1(6)	C(18)–C(23)–C(22)	120.4(6)
F(1)–P(3)–F(4)	95.0(4)	C(6)–C(7)–C(8)	122.0(6)	P(2)–C(24)–C(25)	121.2(4)
F(1)–P(3)–F(5)	89.2(3)	C(7)–C(8)–C(9)	120.3(6)	P(2)–C(24)–C(29)	120.2(5)
F(1)–P(3)–F(6)	89.6(3)	C(8)–C(9)–C(10)	118.5(6)	C(25)–C(24)–C(29)	118.6(6)
F(2)–P(3)–F(3)	94.8(4)	C(9)–C(10)–C(11)	120.6(6)	C(24)–C(25)–C(26)	121.1(5)
F(2)–P(3)–F(4)	177.1(5)	C(6)–C(11)–C(10)	121.5(6)	C(25)–C(26)–C(27)	119.1(5)
F(2)–P(3)–F(5)	95.0(5)	P(1)–C(12)–C(13)	118.2(4)	C(26)–C(27)–C(28)	120.6(6)
F(2)–P(3)–F(6)	85.9(5)	P(1)–C(12)–C(17)	123.6(4)	C(27)–C(28)–C(29)	120.9(7)
F(3)–P(3)–F(4)	86.8(4)	C(13)–C(12)–C(17)	118.1(5)	C(24)–C(29)–C(28)	119.6(7)
F(3)–P(3)–F(5)	90.8(3)	C(12)–C(13)–C(14)	121.5(6)	N–C(30)–C(31)	178.1(8)
F(3)–P(3)–F(6)	90.4(3)	C(13)–C(14)–C(15)	119.0(5)	P(1)–C(32)–P(2)	93.1(2)

Table 8

Bond lengths (Å) and bond angles (°) for 4⁺. Numbers in parentheses are estimated standard deviations in the least significant digits

<i>Distances</i>					
Fe–P(1)	2.214(1)	P(3)–F(3)	1.568(3)	C(14)–C(19)	1.387(5)
Fe–P(2)	2.210(1)	P(3)–F(4)	1.552(5)	C(15)–C(16)	1.390(6)
Fe–C(1)	2.080(4)	P(3)–F(5)	1.575(3)	C(16)–C(17)	1.365(8)
Fe–C(2)	2.065(4)	P(3)–F(6)	1.560(3)	C(17)–C(18)	1.363(8)
Fe–C(3)	2.066(4)	O–C(6)	1.145(5)	C(18)–C(19)	1.392(7)
Fe–C(4)	2.084(4)	C(1)–C(2)	1.404(7)	C(20)–C(21)	1.377(5)
Fe–C(5)	2.096(4)	C(1)–C(5)	1.383(6)	C(20)–C(25)	1.376(5)
Fe–C(6)	1.744(5)	C(2)–C(3)	1.391(7)	C(21)–C(22)	1.382(6)
	1.744(5)	C(3)–C(4)	1.379(6)	C(22)–C(23)	1.369(6)
P(1)–C(7)	1.837(4)	C(4)–C(5)	1.398(6)	C(23)–C(24)	1.370(6)
P(1)–C(8)	1.811(4)	C(8)–C(9)	1.379(5)	C(24)–C(25)	1.378(6)
P(1)–C(14)	1.808(4)	C(8)–C(13)	1.383(5)	C(26)–C(27)	1.379(5)
P(2)–C(7)	1.850(4)	C(9)–C(10)	1.373(6)	C(26)–C(31)	1.388(5)
P(2)–C(20)	1.811(4)	C(10)–C(11)	1.364(6)	C(27)–C(28)	1.394(6)
P(2)–C(26)	1.816(4)	C(11)–C(12)	1.359(6)	C(28)–C(29)	1.361(6)
P(3)–F(1)	1.574(3)	C(12)–C(13)	1.370(6)	C(29)–C(30)	1.357(6)
P(3)–F(2)	1.584(3)	C(14)–C(15)	1.381(5)	C(30)–C(31)	1.381(6)
<i>Angles</i>					
P(1)–Fe–P(2)	75.20(4)	C(22)–C(23)–C(24)	120.8(4)	F(1)–P(3)–F(2)	89.2(2)
P(1)–Fe–C(6)	94.2(1)	C(23)–C(24)–C(25)	119.3(4)	F(1)–P(3)–F(3)	179.0(2)
P(2)–Fe–C(6)	94.2(1)	C(20)–C(25)–C(24)	120.5(4)	F(1)–P(3)–F(4)	91.1(2)
C(9)–C(10)–C(11)	120.5(4)	P(2)–C(26)–C(27)	121.3(3)	F(1)–P(3)–F(5)	90.0(2)
C(10)–C(11)–C(12)	119.4(4)	P(2)–C(26)–C(31)	120.5(3)	F(1)–P(3)–F(6)	89.9(2)
C(11)–C(12)–C(13)	120.7(4)	C(27)–C(26)–C(31)	118.3(4)	F(2)–P(3)–F(3)	90.0(2)
C(8)–C(13)–C(12)	120.6(4)	C(26)–C(27)–C(28)	120.0(4)	F(2)–P(3)–F(4)	179.6(2)
P(1)–C(14)–C(15)	119.9(3)	C(27)–C(28)–C(29)	120.2(4)	F(2)–P(3)–F(5)	90.7(2)
P(1)–C(14)–C(19)	121.0(3)	C(28)–C(29)–C(30)	120.9(4)	F(2)–P(3)–F(6)	88.5(2)
C(15)–C(14)–C(19)	119.0(4)	C(29)–C(30)–C(31)	119.4(4)	F(3)–P(3)–F(4)	89.6(2)
C(14)–C(15)–C(16)	119.8(5)	C(26)–C(31)–C(30)	121.3(4)	F(3)–P(3)–F(5)	89.3(2)
C(15)–C(16)–C(17)	120.6(5)	C(7)–P(1)–C(8)	106.7(2)	F(3)–P(3)–F(6)	90.8(2)
C(16)–C(17)–C(18)	120.4(5)	C(7)–P(1)–C(14)	107.5(2)	F(4)–P(3)–F(5)	89.1(2)
C(17)–C(18)–C(19)	119.7(5)	P(1)–C(8)–C(13)	120.2(3)	F(4)–P(3)–F(6)	91.7(2)
C(14)–C(19)–C(18)	120.5(5)	C(9)–C(8)–C(13)	118.0(4)	F(5)–P(3)–F(6)	179.2(2)
P(2)–C(20)–C(21)	120.7(3)	C(8)–C(9)–C(10)	120.7(4)	C(2)–C(1)–C(5)	108.6(5)
P(2)–C(20)–C(25)	119.6(3)	C(8)–P(1)–C(14)	103.0(2)	C(1)–C(2)–C(3)	107.0(4)
C(21)–C(20)–C(25)	119.7(4)	C(7)–P(2)–C(20)	106.6(2)	C(2)–C(3)–C(4)	108.7(5)
C(20)–C(21)–C(22)	119.8(4)	C(7)–P(2)–C(26)	108.1(2)	C(3)–C(4)–C(5)	108.3(4)
C(21)–C(22)–C(23)	119.8(4)	C(20)–P(2)–C(26)	103.8(2)	C(1)–C(5)–C(4)	107.5(4)
				Fe–C(6)–O	176.7(4)
				P(1)–C(7)–P(2)	94.1(2)
				P(1)–C(8)–C(9)	121.8(3)

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