

Note

Unexpected isolation and structural characterization of a redox-active Fe(II) piano-stool complex with an η^1 -dppe ligand

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Abstract

A new cationic complex $[(\eta^2\text{-bipy})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\eta^1\text{-dppe})][\text{BPh}_4]$ featuring a pendant free diphenylphosphine arm has been isolated in good yield after reaction of 2,2'-bipyridine with the known chloro precursor complex $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeCl}$ in presence of NaBPh_4 . This complex which can be envisioned as a new redox-active building-block has been structurally characterized.

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1. Introduction

The study of redox families obtained from dinuclear complexes where two redox-active “ $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C}-$ ” endgroups are connected together via an unsaturated organic bridge brings decisive information about the capability of the central spacer to convey electrons [1–3]. In the hope of isolating a new family of such dinuclear compounds featuring a 2,2'-bipyridyl unit in the bridge like **A** (Scheme 1) we have reacted the corresponding diethynyl-2,2'-bipyridine (**1**) with 2 equiv. of the $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeCl}$ complex (**2**) in presence of KPF_6 or NaBPh_4 and a strong base under various conditions [2,3]. However, instead of obtaining the expected alkynyl complex, only mixtures of unidentified compounds were obtained in each case, some of which being paramagnetic [4]. Thus, much to our surprise, this usually well

behaved reaction proved unselective in this instance and led to mixtures of several unidentified compounds. In order to rationalize the unexpected course of this reaction, we have subsequently performed several control experiments. We thereby could evidence that the reaction between the starting $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeCl}$ complex (**2**) and neat 2,2'-bipyridine (**3**) in presence of NaBPh_4 led quantitatively to the formation of the new compound **4** $[\text{BPh}_4]$ in which the dppe ligand adopts a rather rare η^1 -coordination mode. We report in the following the characterization of this new complex.

2. Experimental

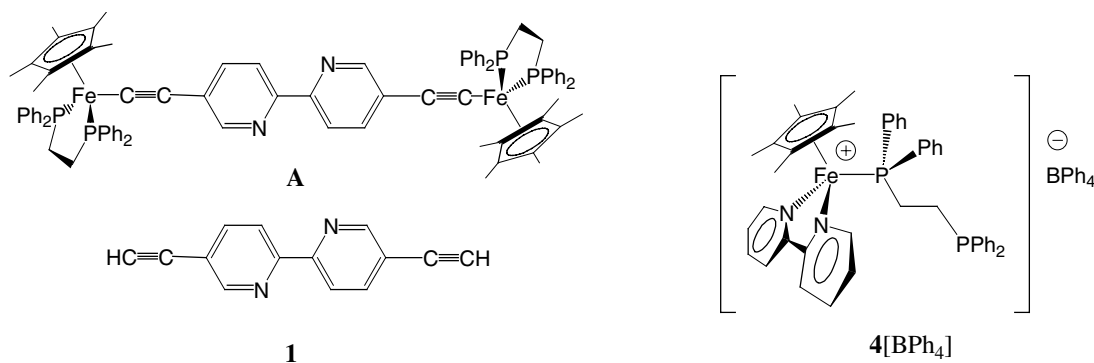
All manipulations were carried out under inert atmospheres using Schlenk techniques. Transmittance-FTIR spectra were recorded using a Bruker IFS28 spectrometer (400–4000 cm^{-1}). UV-Vis spectra were recorded on an UVIKON XL spectrometer. NMR spectra were recorded on AVANCE 200 MHz and 500 MHz spectrometers and were calibrated against the deuterated solvent used as internal reference. Elemental analyses were performed at the “Centre Régional de Mesures Physiques de l'Ouest” (CRMPO, University of Rennes).

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Scheme 1.

2.1. Synthesis of $[(\eta^2\text{-bipy})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\eta^1\text{-dppe})][\text{BPh}_4]$ ($4[\text{BPh}_4]$)

In a Schlenk tube, 0.125 g of 2,2'-bipyridine (**3**; 0.80 mmol) and 0.274 g of NaBPh_4 (0.80 mmol) were added to 0.505 g of $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeCl}$ (**2**; 0.80 mmol) in 30 mL of methanol. The reaction mixture was stirred for ca. 20 h during which time a deep red powder precipitated in the reaction medium. The later was recovered by filtration and washed with methanol several times, before being dried in vacuo, providing the new complex $4[\text{BPh}_4]$ as a deep red solid (0.600 g, 70%). This compound could be crystallized by slow diffusion of *n*-pentane in a dichloromethane solution of the crude material previously isolated (total yield: 60%). MS (ESI⁺, *m*-NBA) m/z 745.2565 ($[\text{M}]^+$, 100%), m/z calc for $[\text{C}_{46}\text{H}_{47}\text{N}_2\text{P}_2^{56}\text{Fe}]^+ = 745.22564$. Anal. Calc. for $\text{C}_{70}\text{H}_{67}\text{BFeN}_2\text{P}_2$: C, 78.95; H, 6.34; N, 2.63. Found: C, 79.00; H, 6.35; N, 2.70%. FT-IR (KBr/Nujol, ν in cm^{-1}) 1578 cm^{-1} , (m, bipy). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3 , δ_p in ppm) 60.0 ppm (s, dppe). ^1H NMR (200 MHz, CDCl_3 , δ_H in ppm) 8.22 (m, 2H, H_{bipy}); 7.60–7.00 (m, 46H, aromatics); 1.60–1.10 (m, 19H, $\text{C}_5\text{Me}_5 + 2\text{CH}_2$). UV–Vis. (CH_2Cl_2) λ_{max} ($\epsilon/10^3 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$) 228 (sh, 58); 298 (27.4); 356 (sh, 3.9); 486 (2.5); 518 (2.6). CV (CH_2Cl_2 , 0.1 M *n*-Bu₄N⁺, PF₆⁻, 20 °C, 0.1 V s⁻¹) E_0 (ΔE_p , i_a/i_c) 0.34 V (0.06, 1).

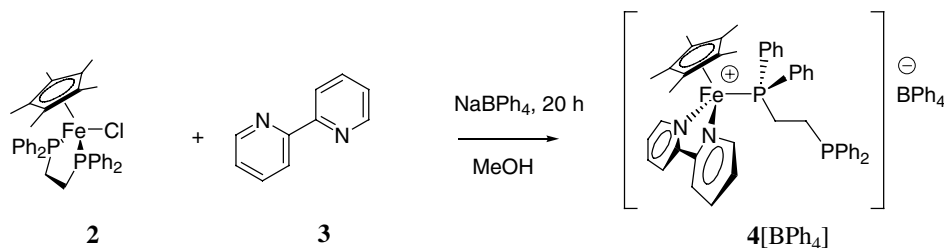
2.2. Crystallography

X-ray data were collected on a NONIUS Kappa CCD with graphite monochromatized Mo K α radiation. The cell parameters were obtained with Denzo and Scalepack [5] with 10 frames (psi rotation: 1° per frame) on a 0.22 × 0.12 × 0.08 mm crystal. The data collection ($2\theta_{\text{max}} = 54^\circ$,

154 frames via 2.0° omega rotation and 80 s per frame) provided 38 115 reflections for $4[\text{BPh}_4]$, from which 13 394 were unique [6]. Subsequent data reduction with Denzo and Scalepack [5] gave 10 428 independent reflections [$I > 2\sigma(I)$]. The structure was solved with SIR-97 which revealed the non-hydrogen atoms [7]. After anisotropic refinement, the remaining atoms were found in Fourier difference maps. The complete structure was next refined with SHELXL97 [8] by the full-matrix least-square technique (use of F square magnitude; x, y, z, β_{ij} for Fe, P, C, N and/or O atoms, x, y, z in riding mode for H atoms with 716 variables for 10 428 observations and $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = [F_o^2 + F_c^2]/3$ with $a = 0.0587$ and $b = 2.3717$). Atomic scattering factors were taken from the literature [9]. ORTEP views of 4^+ were realized with PLATON98 [10].

3. Results and discussion

This new complex $4[\text{BPh}_4]$ was formed overnight by reaction of 1 equiv 2,2'-bipyridine (**3**) with the known Fe(II) chloride precursor **2** in presence of NaBPh_4 (Scheme 2) [11]. Dark red crystals of this compound, which constitutes the unique product of the reaction according to mass spectrometry (MS-ESI), were obtained by slow diffusion of *n*-pentane into a saturated CH_2Cl_2 solution of the above complex. The quite quantitative formation of $4[\text{BPh}_4]$ reveals the high affinity of the cationic Fe(II) centre for diimine-like ligands. Actually, the complex formation takes most likely place after reaction of 2,2'-bipyridine (**3**) with the 16e intermediate $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}][\text{BPh}_4]$ ($5[\text{BPh}_4]$) transiently generated after abstraction of the chloride ligand from **2** by the sodium salt in methanol. Likewise, the coordination of the bipyridyl site of **1** on 5^+ is possibly at the origin



Scheme 2.

Table 1
Crystal data, data collection, and refinement parameters for $4[\text{BPh}_4] \cdot \text{CH}_2\text{Cl}_2$

Empirical formula	$\text{FeP}_2\text{C}_{46}\text{H}_{47}\text{N}_2\text{BCl}_2 \cdot \text{CH}_2\text{Cl}_2$
Formula weight	1150.79
T (K)	120(1)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.8235(2)
b (Å)	13.9849(2)
c (Å)	19.3985(3)
α (°)	94.919(1)
β (°)	106.535(1)
γ (°)	105.172(1)
V (Å ³)	2922.88(8)
Z	2
Absorption coefficient (mm ⁻¹)	0.450
θ Range (°)	2.47–25.52
Index ranges	$0 \leq h \leq 15$; $-18 \leq k \leq 17$; $-25 \leq l \leq 23$
Final R indices	$R = 0.047$; $R_w = 0.117$
R indices (all data)	$R = 0.067$; $R_w = 0.130$
Goodness of fit/ $F^2(S_w)$	1.022

of the unselective course taken by the previous reactions between 4,4'-diethynyl-2,2'-bipyridine (**1**) and **2** under similar conditions [12].

As shown by the solid state structure of $4[\text{BPh}_4]$ (Table 1), the 2,2'-bipyridyl ligand is essentially planar, with an inter-cycle torsion angle of ca. 5° (Fig. 1). This ligand has replaced the chloride ion in the coordination sphere as well as one of the diphenylphosphine arms of the dppe ligand. However, in solution at 25 °C, the dppe ligand appears fluxional, as evidenced by the observation of a single peak near 60 ppm and by a much broader peak near -11 ppm in ³¹P NMR, sometimes quite difficult to detect. Also, fluxionality is suggested by broad CH₂ signals, which partly merge with the methyl signals of the cyclopentadienyl ligand on the ¹H NMR spectrum. Note that this fluxional motion is apparently frozen when an excess 2,2'-bipyridine (**3**) is introduced in the solution, since a clean AX system (³ $J_{\text{PP}} = 24$ Hz) can then be observed by ³¹P NMR [13]. The ESI-MS spectrum of the crude isolated product **4**⁺, while confirming the mononuclear structure proposed, did not allow for observation of other species. The other experimental characterizations (see experimental part) are also consistent with the diamagnetic organoiron(II) formulation of $4[\text{BPh}_4]$ [3]. Such η^1 -ligated dppe piano-stool complexes are however quite unusual for electron-rich Fe(II) centres. To our knowledge, related electron-rich Fe(II) complexes featuring a η^1 -dppe ligand with a pendant free diphenylphosphine arm are not ubiquitous species and were reported only in seldom cases [14–18]. Notably, cyclic voltammetry indicates that $4[\text{BPh}_4]$ undergoes a chemically reversible oxidation at 0.34 V vs. ECS i.e. slightly lower than the oxidation potential of ferrocene [19].

In conclusion, we have shown here that diimine ligands like 2,2'-bipyridine are able to displace one phosphine group of the dppe ligand and the halogen ligand in the iron chloride complex **2** to give the cationic complex $4[\text{BPh}_4]$ in

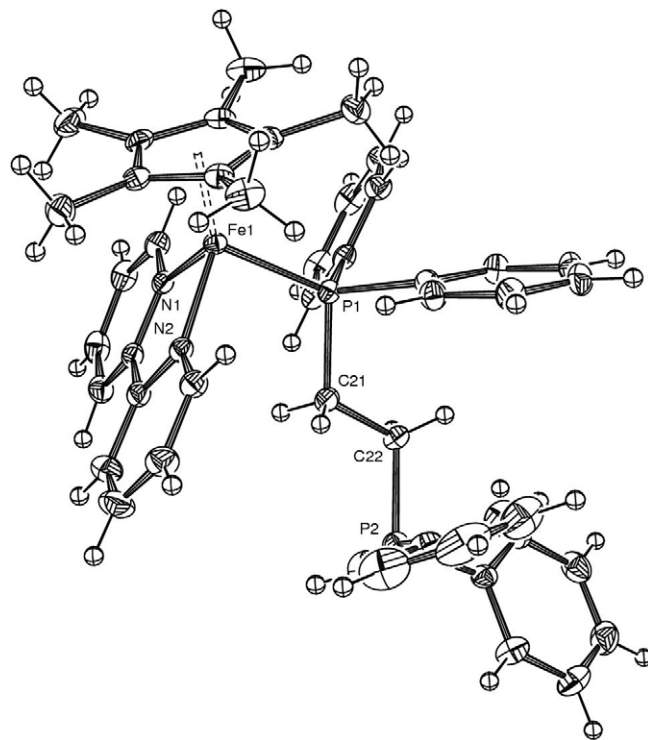


Fig. 1. ORTEP representations of the cation in $4[\text{BPh}_4] \cdot \text{CH}_2\text{Cl}_2$ at 50% probability level. Selected bond distances (Å): Fe1–(Cp*)_{centroid}, 1.740; Fe1–P1, 2.2571(6); Fe1–P2, 6.104; Fe1–N1, 1.9602(18); Fe1–N2, 1.9642(17) (Cp* = pentamethylcyclopentadienyl ligand). Selected bond angles (deg): N1–Fe1–N2, 80.84(7); P1–Fe1–N1, 87.87(5); P1–Fe1–N2, 92.59(5).

good yields. Although initially unwanted, this new redox-active complex presents an available coordinating site (i.e. the free diphenylphosphino unit) and exhibits a reversible oxidation. Likewise to **A**, it might therefore also constitute an appealing building block for the realization of polynuclear assemblies using simple complexation reactions [17,20], provided its fluxional behaviour in solution can be properly understood. Efforts in this direction shall be pursued. Coming back to the failure to isolate the complex **A** (Scheme 1) from the diethynyl-2,2'-bipyridyl ligand **1**, it seems that prior protection of the diimine site constitutes an important requirement when (poly)ethynyl 2,2'-bipyridine ligands are to be reacted with the iron(II) chloride precursor **2**. Work along these lines is currently underway in our group in order to selectively synthesize the target compound **A**.

Acknowledgement

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Appendix A. Supplementary material

CCDC 619568 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.047.

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- [13] Until yet, we were unable to rationalize the role played by the bipyridine ligand in this equilibrium by running ^1H and ^{31}P variable temperature experiments. Upon suggestion from a referee, we have nevertheless verified that the bipyridine ligand does not simply act as a base in the medium. Thus, the spectrum of **4**[BPh₄] in chloroform is quite unchanged upon addition of triethylamine, a stronger base than 2,2'-bipyridine.
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