



Coordination and reactivity of white phosphorus and tetraphosphorus trisulphide in the presence of the fragment CpFe(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane]

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ABSTRACT

The reaction of [CpFe(dppe)Cl] (**1**) [dppe = 1,2-bis(diphenylphosphino)ethane] with one equivalent of P₄ or P₄S₃ in the presence of a chloride scavenger, TlPF₆ or AgOTf (OTf = triflate, OSO₂CF₃), affords the complexes [CpFe(dppe)(η¹-P₄)]PF₆ (**2**) and [CpFe(dppe)(η¹-P_{basal}-P₄S₃)]OTf (**3**) which contain the tetrahedral P₄ and the mixed P₄S₃ cage molecule η¹-bound to the metal. Both P₄ and P₄S₃ yield furthermore the dimetal compounds [(CpFe(dppe))₂(μ,η^{1:1}-P₄)](PF₆)₂ (**4**) and [(CpFe(dppe))₂(μ,η^{1:1}-P_{apical}-P_{basal}-P₄S₃)](OTf)₂ (**5**), which contain the tetrahedral P₄ or the mixed-cage P₄S₃ molecule tethering two ruthenium fragments *via* two phosphorus atoms. All the compounds have been characterized by elemental analyses and NMR measurements. The crystal structure of **4** has been determined by X-ray diffraction methods. The complexes readily react with excess water under mild reaction conditions and the outcoming products have been identified.

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1. Introduction

It has been recently found that P₄ [1–5], AsP₃ [6] and P₄S₃ [7–9] readily bind to 16e fragments yielding mono- and bimetallic compounds which contain the intact cage molecules either η¹ coordinated to the metal or tethering two metal fragments. Such complexes, at variance with the few unstable P₄ and P₄S₃ compounds previously described [10–17], possess good stability and most of them are easily obtained in gram amounts; accordingly, they are potentially useful for investigating the reactivity of the coordinated molecules. Among all compounds, the cyclopentadienyl mono-[CpM(PPh₃)₂(η¹-P₄)]Y (M = Ru [2], Os [5]; Y = PF₆, CF₃SO₃) and bimetallic [(CpRu(PPh₃)₂)₂(μ,η^{1:1}-P₄)](PF₆)₂ and [(CpRu(PPh₃)₂)₂(μ,η^{1:1}-P_{apical}-P_{basal}-P₄S₃)](OTf)₂ [4] complexes have been found to undergo hydrolysis in exceedingly mild conditions exhibiting a spectacular change in reactivity of the coordinated molecules with respect to the free molecules. The hydrolysis of the monometal P₄ derivatives yields PH₃ and phosphorus oxygenated species which are the final products along the degradation pathway of the P₄ molecule [2,3]. The hydrolysis of the bimetallic compounds has been found to be particularly interesting for the metal platform(s) stabilize molecules that are intermediate species along the P₄ and P₄S₃ degradation. The hydrolysis of the

P₄S₃ derivative yields thiophosphinous acid, PH₂SH [4], and the P₄ dimetal compound yields diphosphane, P₂H₄ [4], 1-hydroxotriphosphane, PH(OH)PHPH₂ [18] and 1,1,4-tris(hydroxy)tetraphosphane, P(OH)₂PHPHPH(OH) [19], according to the relative amounts of the complex and water employed. It is worthwhile to point out that such molecules, which are stabilized through coordination to the metal fragments, are either unknown as free entities or very difficult to be obtained [20]; the outcomings furthermore allow to trace some hypotheses on the steps of the degradation process [19].

The above results have shown that the reactivity of coordinated P₄ and P₄S₃ is highly affected by the electronic and/or steric properties of both the metal and its coligands [1]. With the aim to obtain more information in this field, we have investigated the behaviour of the cage molecules in the presence of the CpFe(dppe) fragment (dppe = 1,2-bis(diphenylphosphino)ethane), which bears ligands analogous to those employed with the ruthenium and osmium moieties and, in view of the easy access of iron to different oxidation states, could promote red-ox reactions of the coordinated molecules in the course of their degradation.

2. Results and discussion

The reaction of the dppe iron complex [CpFe(dppe)Cl] (**1**) [dppe = 1,2-bis(diphenylphosphino)ethane] with one equivalent of P₄ or P₄S₃ in the presence of a chloride scavenger (TlPF₆ or

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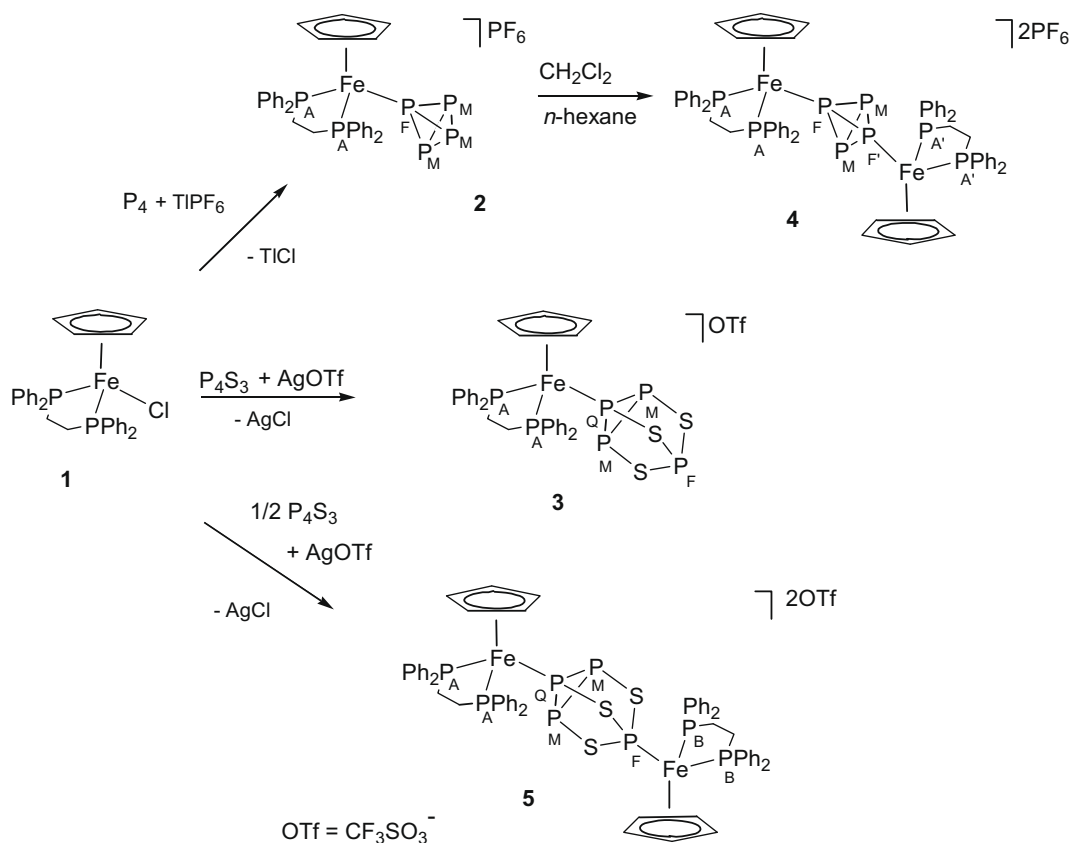
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AgCF₃SO₃ = AgOTf) readily yields the compounds [CpFe(dppe)(η¹-P₄)]PF₆ (**2**) and [CpFe(dppe)(η¹-P_{basal}-P₄S₃)]OTf (**3**) with a good yield (Scheme 1). Compounds **2** and **3** are stable under an inert atmosphere and in this regard they behave as the related [CpM(PPh₃)₂(η¹-P₄)]Y (M = Ru [2], Os [5]) and [CpRu(dppe)(η¹-P₄)]Y derivatives [3]. The complexes are soluble in common organic solvents; **2** dissolved in CH₂Cl₂ undergoes transformation to afford the dimetallic compound [(CpFe(dppe))₂(μ,η^{1:1}-P₄)](PF₆)₂ (**4**), see below. The ³¹P NMR spectrum of **2** in (CD₃)₂CO yields a first-order A₂FM₃ spin pattern (see Scheme 1 for labels). The four phosphorus atoms of the cage yield the FM₃ part of the resonances which are downfield shifted with respect to the signal of the free P₄. This shift, as found for the analogous ruthenium and osmium [CpM(PPh₃)₂(η¹-P₄)]Y (M = Ru, Os) derivatives [2,5], is particularly enhanced for the atom bound to the metal centre; furthermore, both signals are significantly downfield shifted with respect to the corresponding ones of the ruthenium and osmium derivatives. The ³¹P NMR spectrum of **3** in (CD₃)₂CO yields an A₂FM₂Q spin system, see Scheme 1 for labels; the signals of dppe occur in the expected region and the four phosphorus atoms of the heptatomic cage form the FM₂Q part of the spin system. The coordinated phosphorus, P_Q, exhibits a notable downfield shift with respect to the three equivalent P atoms of the free cage, whereas the P_M and P_F are only moderately deshielded. Other metal complexes containing one P₄S₃ cage coordinated to one 16e metal fragment have been described by our group and they present invariably a pair of coordination isomers which differ for the bonding mode of the P₄S₃ molecule to the metal, i.e. through the apical or through one of the basal P atoms; furthermore, the relative amounts of each isomer are significantly affected by the geometry and the electronic properties of the metal fragments [7–9]. The NMR data of **3** are consistent with the formation of one isomer where the cage is

coordinated through one of the basal phosphorus atoms. The present iron fragment accordingly appears to be highly regioselective for the basal phosphorus of the P₄S₃.

A CH₂Cl₂ solution of **2** overnight yields **4**, which crystallizes with CH₂Cl₂ and toluene solvate molecules; the complex is stable under an inert atmosphere as the related homo- [(CpRu(PPh₃)₂)₂(μ,η^{1:1}-P₄)]Y₂ (Y = PF₆, OTf) [4] and hetero-bimetallic [(CpRu(PPh₃)₂){CpOs(PPh₃)₂}(μ,η^{1:1}-P₄)](OTf)₂ derivatives [5]. The complex is soluble in common organic solvents. The ³¹P NMR spectrum of **4** in (CD₃)₂CO yields, as the ruthenium bimetallic derivative [(CpRu(PPh₃)₂)₂(μ,η^{1:1}-P₄)]Y₂ [4], an A₂A'₂FF'M₂ spin pattern (Scheme 1 for labels); where A and A' are the dppe phosphorus atoms, F and F' are the P₄ atoms bound to the metal and M the two atoms of the tetraphosphorus tetrahedron not involved in the coordination. The signals of the coordinated atoms are significantly downfield shifted with respect to that of the free molecule and such shift is similar to those observed for the previous homo- and hetero-bimetallic compounds [4,5].

The structure of compound **4** comprises dimetallic cations, PF₆⁻ anions and solvate toluene and dichloromethane molecules, the latter being disorderly arranged. The overall coordination geometry (Fig. 1) is grossly similar to that found for the dimetal cations [(CpRu(PPh₃)₂)₂(μ,η^{1:1}-P₄)]²⁺ [4] and [(CpRu(PPh₃)₂){CpOs(PPh₃)₂}(μ,η^{1:1}-P₄)]²⁺ [5], although there are differences due to the presence of the bidentate phosphane ligand in **4** instead of a pair of monodentate PPh₃ ligands and to lower crowding around the dimetal core in **4** than in the other two structures, due to a smaller number of phenyl groups in **4**. The metal–phosphorus distances in **4** (Table 1) are ca. 0.13 Å shorter, in the mean, than those in the diruthenium or in the mixed ruthenium–osmium dication, in line with the differences between covalent metal radii [20,21]. The differences between the metal–Cp(centroid) distances in **4** (1.713 Å, mean value) and those



Scheme 1.

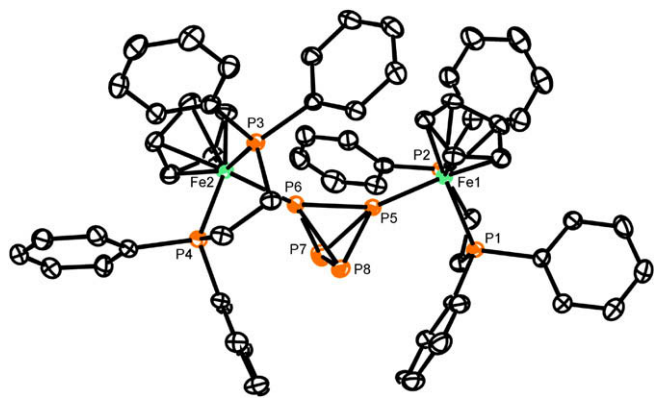


Fig. 1. A view of the dication in the structure of **4**, with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **4**.

Fe1–P1	2.224(1)	Fe2–P3	2.213(1)
Fe1–P2	2.223(1)	Fe2–P4	2.237(1)
Fe1–P5	2.151(1)	Fe2–P6	2.174(1)
P5–P6	2.160(2)	P7–P8	2.229(2)
P5–P7	2.185(2)	P6–P7	2.193(2)
P5–P8	2.186(2)	P6–P8	2.190(2)
P1–Fe1–P2	85.74(5)	P3–Fe2–P4	85.62(5)
P1–Fe1–P5	90.91(5)	P3–Fe2–P6	92.43(5)
P2–Fe1–P5	99.14(5)	P4–Fe2–P6	93.45(5)
Fe1–P5–P6	153.16(7)	Fe2–P6–P5	157.33(7)

of the other two cations (1.878 Å [4], 1.880 Å [5]) are still larger than the above difference between the metal–phosphorus distances. The P_4 cage exhibits the type of distortion already found for the other two structures, where the P–P bond between the atoms bound to the metals is the shortest of those in the cage and the P–P bond between the other two atoms is the longest one. The Fe1–P5–P6–Fe2 8.1(3)° torsion angle differs from those (–27.4(6)° [4], –26.9(6)° [5]) of the other two compounds, possibly as a result of the release of steric hindrances in **4** between the ligands on the two sides of the cation.

Compound **5** is obtained in a good yield (Scheme 1) by reacting **1** in THF/ CH_2Cl_2 with half equivalent of P_4S_3 in the presence of AgOTf. The complex, poorly soluble in common organic solvents, is stable under an inert atmosphere. The $^{31}P\{^1H\}$ NMR spectrum of **5** in $(CD_3)_2CO$ yields a first-order $A_2B_2FM_2Q$ spin system, see the Scheme 1 for labels. Both the chemical shifts and the coupling constants of P_A and P_B nuclei show values in the range expected for cationic iron half-sandwich compounds. The four phosphorus atoms of the cage form the FM_2Q part of the spectrum: all resonances are downfield shifted with respect to the free P_4S_3 molecule, and such shift is consistent with the trend observed for the cations $\{[(triphos)Re(CO)_2]_2(\mu,\eta^{1:1}-P_{apical}-P_{basal}-P_4S_3)\}^{2+}$ [7], $\{[Cp^*Ru(L_2)]_2(\mu,\eta^{1:1}-P_{apical}-P_{basal}-P_4S_3)\}^{2+}$ [9] and $\{[CpRu(PPh_3)]_2(\mu,\eta^{1:1}-P_{apical}-P_{basal}-P_4S_3)\}^{2+}$ previously described, which contain the P_4S_3 bridging ligand [4].

Compounds **2**, **3**, **4** and **5** in $(CH_3)_2CO$ or THF undergo readily transformation at room temperature in the presence of an excess amount of water (1:100). $^{31}P\{^1H\}$ NMR measurements have shown that reactions carried out on different batches are reproducible both with respect to the amount and to the nature of the products obtained; also, the gaseous phase does not contain phosphorus compounds and the solid obtained after removing the solvent is a mixture of several compounds.

Compounds **3** and **5** complete their transformation within 2–3 h, whereas **2** and **4** require ca. one day for completion of the hydrolysis.

The P_4S_3 derivatives **3** and **5** yield basically the same products i.e. free phosphorous, H_3PO_3 , and hypophosphorous, H_3PO_2 , acids and the new cations $[CpFe(dppe)\{RP(OH)_2\}]^+$ ($R = H$ (**6**), OH (**7**)) where the unstable $HP(OH)_2$ and $P(OH)_3$ tautomers of the two acids are bound to the metal fragment. The cationic species have been characterized by comparing the 1H and ^{31}P NMR data of the hydrolysed mixture with those of the pure samples that have been independently synthesized (see below). The outcomings of the P_4 derivatives **2** and **4** are characterized by the presence of a large amount of free P_4 (ca. 80% of that in the parent complex) and of the cations $[CpFe(dppe)\{H-P(OH)_2\}]^+$ **6** and $[CpFe(dppe)(PH_3)]^+$ **8**, the latter containing phosphine coordinated to the iron moiety.

The $[CpFe(dppe)\{RP(OH)_2\}]OTf$ [$R = H$ (**6**), OH (**7**)] and $[CpFe(dppe)(PH_3)]OTf$ (**8**) derivatives are easily obtained by reacting **1** and the chloride scavenger with the appropriate molecule (PH_3 , H_3PO_2 and H_3PO_3). All the complexes yield a $^{31}P\{^1H\}$ NMR A_2F spin system where A and F are the phosphorus atoms of the dppe and of the added molecule, respectively. The resonances of the biphosphane occur in the typical region of pseudooctahedral $CpFe(dppe)$ moieties; the shifts and the coupling constants (P–P and P–H) of the coordinated molecules parallel those observed for the analogous ruthenium and osmium derivatives [4,5,22]. Accordingly they are assigned the same geometry where the phosphorus atom of each molecule, PH_3 , H_3PO_2 or H_3PO_3 , is bound to the metal fragment. As found for the ruthenium [22] and osmium derivatives [5], the phosphane tautomers of hypophosphorous and phosphorous acid, i.e. $HP(OH)_2$ and $P(OH)_3$, are stabilized through coordination.

The above results show that the present $CpFe(dppe)$ fragment is suitable to bind the cage molecules. The reactivity of P_4S_3 is significantly modified, upon coordination, with respect to that of the free molecule. The P_4 compounds are characterized by the easy detachment of the coordinated molecule. At variance with the outcomings from the hydrolysis of the ruthenium derivatives, the products contain one atom from the parent coordinated P_4 and P_4S_3 ; thus only the species which are at the final step of the degradation of the molecules are observed.

3. Experimental

3.1. General

All reactions and manipulations were performed under an atmosphere of dry oxygen-free nitrogen. The solvents were purified according to standard procedures [23]. The 1H , ^{19}F and ^{31}P NMR spectra were run on a Bruker Avance 400 plus spectrometer. ^{19}F and ^{31}P chemical shifts are relative to external $CFCl_3$ and to 85% H_3PO_4 , respectively. 1H chemical shifts are relative to tetramethylsilane as external reference and were calibrated against the residual solvent resonance. Downfield values are reported as positive, coupling constants are in Hertz. ^{19}F NMR spectra of the triflate derivatives yielded a singlet at –75.5 ppm for the anion. Coupling constants of **4** were obtained from 1D $^{31}P\{^1H\}$ NMR spectrum with the aid of computer simulation using the $gNMR$ program [24]. Microanalyses were done by the Microanalytical Laboratory of the Department of Chemistry of the University of Firenze. $[CpFe(dppe)Cl]$ **1** was prepared according to the literature method [25].

3.2. Synthesis of the complexes

3.2.1. $[CpFe(dppe)(\eta^1-P_4)]PF_6$ (**2**)

Neat $[CpFe(dppe)Cl]$ **1** (280 mg, 0.50 mmol), $TIPF_6$ (175 mg, 0.50 mmol) and P_4 (75 mg, 0.6 mmol) were suspended in a mixture of CH_2Cl_2 (20 cm^3) and THF (30 cm^3) and the resulting slurry was

stirred for 4 h; the precipitated TiCl_4 was filtered off and the solvent evaporated under reduced pressure. The dark red solid was washed twice with toluene (10 cm^3), *n*-hexane and dried. Yield: 310 mg (80%). Anal. Calc. for $\text{C}_{31}\text{H}_{29}\text{F}_6\text{FeP}_7$: C, 47.23; H, 3.71; P, 27.10. Found: C, 47.10; H, 3.82; P, 26.90%. ^1H NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$]: 7.80–7.20 (20H, m, Ph), 4.94 (5H, s, Cp), 2.81 (4H, m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$], spin system of the anion A_2FM_3 : 90.5 (2P, d, $^2J(\text{P}_A-\text{P}_F) = 55.0$, P_A), -147.3 (1P, sept, $^1J(\text{P}-\text{F}) = 711.5$, PF_6^-), -317.4 (1P, tq, $^1J(\text{P}_F-\text{P}_M) = 233.0$, P_F), -492.7 (3P, d, P_M).

3.2.2. $[\text{CpFe}(\text{dppe})(\eta^1\text{-P}_{\text{basal}}\text{-P}_4\text{S}_3)]\text{OTf}$ (**3**)

The complex was prepared through the same procedure to obtain **2** by adding to the slurry of $[\text{CpFe}(\text{dppe})\text{Cl}]$ **1** (280 mg, 0.50 mmol) and AgOTf (128 mg, 0.50 mmol) the stoichiometric amount of P_4S_3 dissolved in toluene. Yield: 270 mg (60%). Anal. Calc. for $\text{C}_{32}\text{H}_{29}\text{F}_3\text{FeO}_3\text{P}_6\text{S}_4$: C, 43.26; H, 3.29; P, 20.91. Found: C, 43.08; H, 3.40; P, 20.30%. ^1H NMR [δ , CD_2Cl_2 , 20 $^\circ\text{C}$]: 7.80–7.20 (20H, m, Ph), 4.70 (5H, s, Cp), 3.02 (4H, m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , CD_2Cl_2 , 20 $^\circ\text{C}$], spin system of the anion $\text{A}_2\text{FM}_2\text{Q}$: 92.2 (2P, d, $^2J(\text{P}_A-\text{P}_Q) = 41.5$, P_A), 86.5 (1P, dt, $^2J(\text{P}_F-\text{P}_Q) = 42.0$, $^2J(\text{P}_F-\text{P}_M) = 67.5$, P_F), 48.8 (1P, tq, $^1J(\text{P}_Q-\text{P}_M) = 235.5$, P_Q), -138.5 (2P, dd, P_M).

3.2.3. $[\{\text{CpFe}(\text{dppe})\}_2(\mu, \eta^{1:1}\text{-P}_4)](\text{PF}_6)_2 \cdot 0.6\text{CH}_2\text{Cl}_2 \cdot 0.6\text{C}_7\text{H}_8$ (**4**)

$[\text{CpFe}(\text{dppe})(\eta^1\text{-P}_4)]\text{PF}_6$ **2** (390 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and the solution stratified under toluene (40 cm^3). Red crystals of **4**, suitable for X-ray analysis, were obtained overnight. The solid was filtered, washed with *n*-hexane and dried. Yield: 120 mg (30%). Anal. Calc. for $\text{C}_{67.3}\text{H}_{64.6}\text{Cl}_{1.3}\text{F}_{12}\text{Fe}_2\text{P}_{10}$: C, 51.52; H, 4.15; P, 19.75. Found: C, 51.10; H, 4.22; P, 19.13%. ^1H NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$]: 7.90–7.10 (43H, m, Ph), 5.61 (0.6H, s, CH_2Cl_2), 4.75 (10H, s, Cp), 2.75 (8H, mbr, CH_2), 2.30 (0.6H, s, $\text{CH}_3\text{C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$], spin system of the anion $\text{A}_2\text{A}'_2\text{FF}'\text{M}_2$: 89.3 (4P, $^2J(\text{P}_A-\text{P}_F) = ^2J(\text{P}_A'-\text{P}_F') = 50.5$, $^3J(\text{P}_A-\text{P}_F) = ^3J(\text{P}_A'-\text{P}_F') = -2.0$, $^3J(\text{P}_A-\text{P}_M) = ^3J(\text{P}_A'-\text{P}_M) = 3.0$, P_A and P_A'), -147.3 (2P, sept, $^1J(\text{P}-\text{F}) = 711.5$, PF_6^-), -265.5 (2P, $^1J(\text{P}_F-\text{P}_F') = 210.0$, $^1J(\text{P}_F-\text{P}_M) = ^1J(\text{P}_F'-\text{P}_M) = 153.5$, P_F and P_F'), -488.2 (2P, P_M).

3.2.4. $[\{\text{CpFe}(\text{dppe})\}_2(\mu, \eta^{1:1}\text{-P}_{\text{apical}}\text{-P}_{\text{basal}}\text{-P}_4\text{S}_3)](\text{OTf})_2$ (**5**)

The complex was prepared through the same procedure to obtain **3** by adding to the slurry of $[\text{CpFe}(\text{dppe})\text{Cl}]$ **1** (280 mg, 0.50 mmol) and AgOTf (128 mg, 0.50 mmol) half equivalent of P_4S_3 dissolved in toluene. Yield: 290 mg (75%). Anal. Calc. for $\text{C}_{64}\text{H}_{58}\text{F}_6\text{Fe}_2\text{O}_6\text{P}_8\text{S}_5$: C, 49.37; H, 3.76; P, 15.91. Found: C, 49.02; H, 3.60; P, 15.20%. ^1H NMR [δ , CD_2Cl_2 , 20 $^\circ\text{C}$]: 7.90–7.20 (40H, m, Ph), 4.69 (5H, s, Cp), 4.33 (5H, s, Cp), 2.52 (8H, m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , CD_2Cl_2 , 20 $^\circ\text{C}$], spin system of the anion $\text{A}_2\text{B}_2\text{FM}_2\text{Q}$: 178.5 (1P, dtt, $^2J(\text{P}_F-\text{P}_Q) = 24.0$, $^2J(\text{P}_F-\text{P}_M) = 38.0$, $^2J(\text{P}_F-\text{P}_B) = 40.0$, P_F), 89.8 (2P, d, $^2J(\text{P}_A-\text{P}_Q) = 42.0$, P_A), 88.7 (2P, d, P_B), 40.5 (1P, dtt, $^1J(\text{P}_Q-\text{P}_M) = 206.0$, P_Q), -129.6 (dd, 2P, P_M).

3.2.5. $[\text{CpFe}(\text{dppe})\{\text{RP}(\text{OH})_2\}]\text{OTf}$ [$\text{R} = \text{H}$ (**6**), OH (**7**)] and $[\text{CpFe}(\text{dppe})(\text{PH}_3)]\text{OTf}$ (**8**)

The complexes were prepared through the same procedure to obtain **2** by adding to the slurry of $[\text{CpFe}(\text{dppe})\text{Cl}]$ **1** (280 mg, 0.50 mmol) and TiOTf (175 mg, 0.50 mmol) the stoichiometric amount of the acid (H_3PO_2 or H_3PO_3) or by bubbling PH_3 through the suspension. Pure complexes were obtained after recrystallization from CHCl_3 and *n*-hexane with a ca. 40% yield. Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{F}_3\text{FeO}_5\text{P}_3\text{S}$ (**6**): C, 52.33; H, 4.39. Found: C, 52.10; H, 4.50%. ^1H NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$]: 8.20 (1H, dt, $^3J(\text{H}-\text{P}_A) = 5$, HP), 7.90–7.20 (20H, m, Ph), 4.62 (5H, s, Cp), 2.88 (4H, m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$], spin system of the anion A_2F : 171.5 (1P, t, $^2J(\text{P}_F-\text{P}_A) = 85.0$, P_F), 100.7 (2P, d, P_A). Anal. Calc. for

Table 2

Crystal data and structure refinement parameters for $[\{\text{CpFe}(\text{dppe})\}_2(\mu, \eta^{1:1}\text{-P}_4)](\text{PF}_6)_2 \cdot 0.66(\text{C}_7\text{H}_8) \cdot 0.64(\text{CH}_2\text{Cl}_2)$ (**4**).

Empirical formula	$\text{C}_{67.29}\text{H}_{64.59}\text{Cl}_{1.28}\text{F}_{12}\text{Fe}_2\text{P}_{10}$
M_r	1568.01
Crystal system	Monoclinic
Space group	$P2_1/c$
T (K)	173(2)
a (Å)	20.4944(2)
b (Å)	14.7927(2)
c (Å)	23.7333(3)
β ($^\circ$)	90.768(1)
V (Å 3)	7194.5(2)
Z	4
d_{calcd} (g cm^{-3})	1.448
Absorption coefficient (mm $^{-1}$)	6.386
$F(0\ 0\ 0)$	3200
θ Range ($^\circ$)	4.12–65.08
Reflections measured	45 725
Independent reflections	12 256
Observed reflections ($I > 2\sigma(I)$, R_{int})	8835, 0.0439
No. of parameters/restraints	886/135
Final R indices ($I > 2\sigma(I)$) R_1 , wR_2	0.0579, 0.1681
Final R indices (all data) R_1 , wR_2	0.0836, 0.1839
Goodness-of-fit (GOF) on F^2	1.083
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å $^{-3}$)	1.049, -0.532

$\text{C}_{32}\text{H}_{32}\text{F}_3\text{FeO}_6\text{P}_3\text{S}$ (**7**): C, 51.22; H, 4.30. Found: C, 51.10; H, 4.40%. ^1H NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$]: 7.90–7.20 (20H, m, Ph), 4.67 (5H, s, Cp), 2.92 (4H, m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$], spin system of the anion A_2F : 165.6 (1P, t, $^2J(\text{P}_F-\text{P}_A) = 95.0$, P_F), 100.1 (2P, d, P_A). Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{F}_3\text{FeO}_3\text{P}_3\text{S}$ (**8**): C, 54.72; H, 4.60. Found: C, 54.40; H, 4.55%. ^1H NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$]: 7.90–7.20 (20H, m, Ph), 4.75 (5H, s, Cp), 4.60 (3H, dt, $^3J(\text{H}-\text{P}_A) = 6$, HP), 2.78 (4H, m, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR [δ , $(\text{CD}_3)_2\text{CO}$, 20 $^\circ\text{C}$], spin system of the anion A_2F : 96.5 (2P, d, $^2J(\text{P}_A-\text{P}_F) = 59.5$, P_A), -81.9 (1P, t, $^1J(\text{P}_A-\text{H}) = 347.5$, P_F).

3.3. X-ray crystallography of (**4**)

X-ray diffraction data for **4**, as dichloromethane and toluene solvate, were collected on an Oxford Diffraction Xcalibur PX Ultra CCD diffractometer equipped with Enhance Ultra optics, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). Crystal data and the main data collection and structure refinement parameters are given in Table 2. Lattice constants were obtained from the setting angles of 22 649 reflections in the θ range 4.11–72.13 $^\circ$. Intensity data were corrected for absorption by a multi-scan procedure [26]. The structures were solved by direct methods, with SIR-97 [27], and were refined by full-matrix least-squares on F^2 values [28]. All non-hydrogen atoms were refined anisotropically. All hydrogens bound to carbons were placed in idealized positions, each riding on the respective carrier atom, with its temperature factor linked to the isotropic equivalent U of the latter. Acceptable temperature factors for atoms of the solvate molecules were only attained if the molecules were assigned fractional occupancy factors; the values of these were refined. The highly disordered dichloromethane molecule was modelled as being distributed over two positions; restraints on geometry and thermal parameters of both solvate molecules were imposed. Too close approaches between a fraction of CH_2Cl_2 and the toluene molecule could be excluded in view of the fractional occupancy factors. Programs used in the crystallographic calculations included WINGX [29] and ORTEP [30] for graphics.

4. Supplementary material

CCDC 755705 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from The Cam-

bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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