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Paul Hamon, Loic Toupet, Thierry Roisnel, Jean-René Hamon, Claude Lapinte. Preparation and Characterization of the Triflate Complex [Cp*(dppe)FeOSO₂CF₃]: A Convenient Access to Labile Five- and Six-Coordinate Iron(I) and Iron(II) Complexes. *European Journal of Inorganic Chemistry*, Wiley-VCH Verlag, 2020, 2020 (1), pp.84-93. 10.1002/ejic.201901086 . hal-02434627

HAL Id: hal-02434627

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Preparation and characterization of the triflate complex [Cp*(dppe)FeOSO₂CF₃]: a convenient access to labile five- and six-coordinate Fe(I) and Fe(II) complexes

Paul Hamon,^[a] Loic Toupet,^[b] Thierry Roisnel,^[a] Jean-René Hamon,^{*[a]} and Claude Lapinte,^{*[a]}

This article is dedicated to our friend and colleague Dr. Jean-François Halet on the occasion of his 60th birthday, and recognizes his scientific achievements in the field of molecular and solid-state theoretical chemistry.

Abstract: Treatment of the iron hydride [Cp*(dppe)FeH] (**1**) with methyltriflate (CH₃OSO₂CF₃) yielded the iron triflate adduct [Cp*(dppe)FeOSO₂CF₃] (**4**, 85 %). In the solid state, the triflate is coordinated at the iron center as shown by XRD ($d_{\text{Fe-O}} = 2.118(4)\text{\AA}$) and IR spectroscopy ($\nu_{\text{SO}} = 1305\text{ cm}^{-1}$). In solution, **4** is in equilibrium with the 16-electron species [Cp*(dppe)Fe]OSO₂CF₃ (**5(OSO₂CF₃)**), **4** / **5(OSO₂CF₃)** = 2:1). The CV of **4** displays two waves ($E_1 = -0.74\text{ V}$, $E_2 = 0.24\text{ V}$ vs SCE) assigned to the [Cp*(dppe)Fe(I)]/[Cp*(dppe)Fe(II)]⁺ and [Cp*(dppe)Fe(II)]⁺/[Cp*(dppe)Fe(III)]²⁺ redox couples. Reduction of **4** with Cp₂Co provided the complex [Cp*(dppe)Fe(I)] (**6**, 95 %) and oxidation of **6** with [Cp₂Fe]PF₆ gave [Cp*(dppe)Fe]PF₆ (**5(PF₆)**, 98 %). XRD established the pseudo-trigonal bipyramidal geometry for the five-coordinated cation **5***. The reactivity of **5(PF₆)** and **6** toward small molecules (CH₂Cl₂, H₂O, CO, H₂, N₂) is reported.

Introduction

Incorporation of the Cp*(dppe)Fe or, more generally, Cp*(P₂)Fe {Cp* = η⁵-C₅(CH₃)₅, P₂ = bis-monodentate or chelating bidentate phosphine} moieties in various unsaturated organic architectures led to the realization of a wealth of interesting molecules for molecular electronics.^[1-3] The development of this synthetic chemistry allowing selective and easy introduction of the organoiron units in various organic environments has been based on the reactivity of the chloro complex [Cp*(dppe)FeCl] {dppe = 1,2-bis(diphenylphosphanyl)ethane} with alkynes.^[4, 5] Despite a rather strong Fe-Cl bond, the rich chemistry of [Cp*(dppe)FeCl] with terminal alkynes and terminal polyalkynes comes from the 1,2-migration of the terminal hydrogen atom which constitutes the driving force for the irreversible formation of the corresponding vinylidene complexes.^[6]

Interestingly, the complex [Cp*(dppe)FeCl] can be handled in air in the solid state.^[4] The chloride ligand is displaced by bromide and iodide.^[4] It can also be quickly displaced by molecular white phosphorus,^[7] and good two-electron ligands like nitriles, in the presence of salts with a large counter anions (i.e. PF₆⁻, BPh₄⁻, ...), to give [Cp*(dppe)Fe(NC-R)]PF₆. The complex [Cp*(dppe)FeCl] does not react with KF and small molecules such as H₂, N₂, or H₂O.^[8] The chloride ligand of the

complex [Cp*(dppe)FeCl] is less labile than in many other related iron(II) complexes. Indeed, it has been shown that the chloride atom can be abstracted with sodium tetraphenylborate in the case of many iron(II) chloro complexes like *trans*-[(depe)₂Fe(H)Cl], *trans*-[(dmpe)₂FeCl₂], [Cp(dippe)FeCl], [Cp*(dippe)FeCl] (depe = 1,2-bis(diethylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane; dippe = 1,2-bis(diisopropylphosphino)ethane) allowing the generation of the corresponding 16-electron species which can be eventually stabilized by labile ligands like dihydrogen or dinitrogen.^[9, 10]

Many years ago we found that the protonation of the hydride complex [Cp*(dppe)FeH] (**1**) with HBF₄·O(C₂H₅)₂ occurs at the Fe-H bond and gives the η²-H₂ complex [Cp*(dppe)Fe(η²-H₂)]BF₄ (**2(BF₄)**) faster than the protonation at the metal atom, as it had been predicted previously.^[11, 12] The dihydrogen adduct was isolated, stored as lemon yellow microcrystals for several weeks at -50 °C, and characterized. The presence of the coordinated η²-H₂ ligand was definitively established by the determination of the hydrogen-deuterium coupling constant ($J_{\text{HD}} = 27\text{ Hz}$) for the isotopomer [Cp*(dppe)Fe(η²-HD)]BF₄.^[11] As soon as the temperature increases above -50 °C, the color becomes orange indicating that the dihydrogen complex is converted into the iron(IV) dihydride [Cp*(dppe)Fe(H)₂]BF₄ (**3(BF₄)**).

In a previous papers, we briefly reported that the triflate complex [Cp*(dppe)FeOSO₂CF₃] (**4**) available from its chloro relative in two steps constitutes a valuable precursor to the coordinatively unsaturated complex [Cp*(dppe)Fe]PF₆ (**5(PF₆)**) and an alternative to [Cp*(dppe)FeCl] for the coordination of alkynyl ligands containing carbon-silicon bonds.^[13, 14] We also found that compound **4** opened the route to the iron(I) 17-electron derivative [Cp*(dppe)Fe] (**6**).^[15] We now report the full characterization and some reactivity of **4**, a convenient access to **5** and **6** together with their basic chemical properties including

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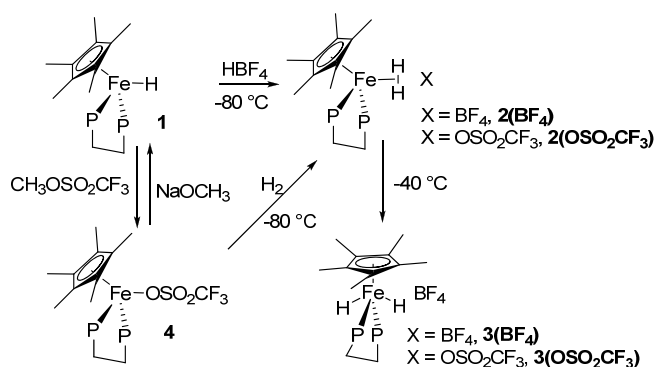
the preparation of the water complex $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{OH}_2)]\text{PF}_6$ (**12**), and the nitrogen adduct $[\text{Cp}^*(\text{dppe})\text{Fe}(\eta^1\text{-N}_2)]\text{PF}_6$ (**13**).

Results and Discussion

1. Synthesis and reactivity of $[\text{Cp}^*(\text{dppe})\text{FeOSO}_2\text{CF}_3]$ (**4**)

Treatment of the iron hydride $[\text{Cp}^*(\text{dppe})\text{FeH}]$ (**1**) with 1.1 equiv of methyl triflate ($\text{CH}_3\text{OSO}_2\text{CF}_3$) at -80°C causes the formation of a yellow suspension which quickly turns green even if the temperature is maintained at -80°C . The solid material isolated by filtration and purified by crystallization from a THF/pentane mixture was identified as the iron triflate adduct $[\text{Cp}^*(\text{dppe})\text{FeOSO}_2\text{CF}_3]$ (**4**, 85 % yield, Scheme 1). When the reaction is performed at 20°C , the yellow intermediate is still briefly observed and the yield of the reaction is unchanged. We assumed that the transient yellow intermediate could be the η^2 -methane adduct, but the very short lifetime of this putative intermediate precluded the collection of any experimental evidence. This reaction is reminiscent with the reaction of the hydride **1** with acidic reagents ($\text{HBF}_4 \cdot (\text{C}_2\text{H}_5)_2$ or HOSO_2CF_3) which also gave yellow intermediates identified as the $\eta^2\text{-H}_2$ complex $[\text{Cp}^*(\text{dppe})\text{Fe}(\eta^2\text{-H}_2)]\text{X}$ (**2(X)**).^[11] However, the final product is different here, since the oxidative addition of methane was not observed.

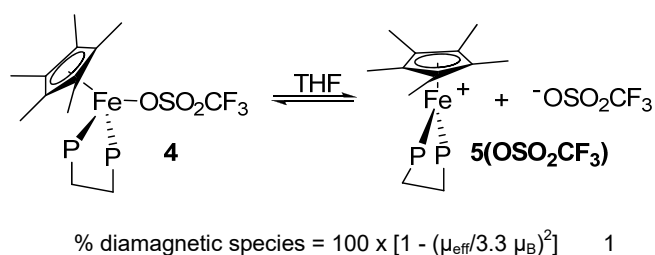
The IR spectrum of **4** (KBr disk, Figure S4, Supporting Information) displays a series of bands below 1300 cm^{-1} characteristic of the presence of triflate anion. However, these bands are useless to establish the existence of a Fe-O bond between the anion and the metal center. Interestingly, the presence of the sulfonyl stretching mode at 1305 cm^{-1} can be regarded as the spectroscopic signature of coordinated triflate. In this respect, it can be noted that the IR spectrum of the closely related complex $[\text{Cp}^*(\text{dppp})\text{Fe}]\text{OSO}_2\text{CF}_3$ (dppp = 1,2-bis(diphenylphosphanyl)propane) in which the triflate is not bound to the iron atom, does not show this sulfonyl stretching mode.^[16] The triflate anion was definitely demonstrated to be coordinated to the metal by an X-ray diffraction analysis on



single crystal (see Section 6).

Scheme 1. Synthesis of complex $[\text{Cp}^*(\text{dppe})\text{FeOSO}_2\text{CF}_3]$ (**4**) (The phenyl groups of the dppe ligand have been omitted for clarity).

As expected for 18-electron iron(II) complexes, **4** is diamagnetic. This was confirmed by the SQUID measurement of the corrected molar magnetic susceptibility of a powdered sample of **4**. In the range 4-300 K, the plot of the product $\chi_M T$ vs T is linear and the intercept is very close to zero, in agreement with the diamagnetic nature of the complex.^[17] In solution, the ^1H NMR spectrum of a d_8 -THF solution of **4** shows three broad bands at $\delta = 26.3$ ($W_{1/2} = 375\text{ Hz}$), 22.3 ($W_{1/2} = 375\text{ Hz}$), and 0.9 ($W_{1/2} = 250\text{ Hz}$) ppm ($W_{1/2}$ = half-height width). Based on their relative intensities, the signals can be assigned to the CH_2 , CH_3 , and phenyl resonances, respectively (Figure S1, Supporting Information). The broadness of the bands and the chemical shifts indicate a paramagnetic behavior of the solution. Accordingly, the chemical shifts strongly vary with the temperature and move to positions expected for diamagnetic derivatives as the temperature decreases. Thus, at 193 K, the resonances of the phenyl, CH_2 , and CH_3 groups are found at $\delta = 7.3$, 3.7 , and 2.6 ppm, respectively. The magnetic moment determined in solution by the Evans method ($\mu_{\text{eff}} = 1.9\ \mu_B$, d_8 -THF, 307 K)^[18] is much smaller than the value expected for a complex carrying two unpaired electron ($S = 1$, $2.83\ \mu_B$).^[19] Based on this result, one can assume that the triflate ligand is partially dissociated in solution, providing an equilibrium between the 18-electron neutral complex **4** and the paramagnetic 16-electron salt $[\text{Cp}^*(\text{dppe})\text{Fe}]\text{OSO}_2\text{CF}_3$ (**5(OSO}_2\text{CF}_3)) (Scheme 2). Indeed, as a consequence of its pseudo trigonal-bipyramidal geometry, complex **5(OSO}_2\text{CF}_3) has a triplet ground state ($S = 1$, see below). The percentage of diamagnetic triflate complex **4** present in the THF solution at 307 K can be calculated using the relationship proposed by Puerta *et al.* (eq 1).^[20] In eq. 1, the value of $3.3\ \mu_B$ corresponds to the magnetic moment determined for pure $[\text{Cp}^*(\text{dppe})](\text{PF}_6)$ (see below). Thus, one can estimate that THF solution of **4** contains 67 % of the triflate adduct in equilibrium with 33 % of the salt **5(OSO}_2\text{CF}_3).******



Scheme 2. Dissociation of the triflate complex **4** in solution (The phenyl groups of the dppe ligand have been omitted for clarity).

The partial dissociation of **4** in THF solution was also validated by a series of ^1H NMR spectra of **4** in THF with increasing quantities of lithium triflate. For instance, the methyl resonances of the Cp^* ligand are observed at $\delta = 22.3$, 19.7 , 15.4 , and 14.8 ppm with 0, 1, 10, and 20 equiv of lithium triflate, respectively.

Assuming that the 16-electron cation **5*** can be easily reduced into its 17-electron counterpart $[\text{Cp}^*(\text{dppe})\text{Fe}]$ (**6**) by a base, and subsequently quenched by a good hydrogen atom

donor like methanol, the iron triflate complex **4** was reacted with one equiv of sodium methoxyde in methanol. As expected, the reaction gives back the starting iron hydride **1** almost quantitatively (Scheme 1). The 16-electron complex **5**(OSO₂CF₃) can also be quenched in situ by dihydrogen. To a THF solution of **5**(OSO₂CF₃) a pressure of 0.1 bar of dihydrogen was introduced at -80 °C. Readily, a lemon yellow color characteristic of the dihydrogen complex [Cp*(dppe)Fe(η²-H₂)]OSO₂CF₃ (**2**(OSO₂CF₃)) appears and persists until the temperature increases above -50 °C. Then, the color turns progressively orange indicating the formation of dihydride complex **3**(OSO₂CF₃) (Scheme 1).

2. Redox properties of [Cp*(dppe)FeOSO₂CF₃] (**4**) in THF

The initial scan in the cyclic voltammetry (CV) of **4** was run from -1.2 V to 0.8 V [vs. a standard calomel electrode (SCE)] in THF at 20 °C. The cyclic voltammogram displays two mono-electronic waves and one additional wave in the reduction process (Figure 1). The potentials for the two redox couples are found at E₁ = -0.74 and E₂ = +0.24 V. The two redox systems originate from the dissociation of the triflate complex **4** in THF, the redox active species being the [Cp*(dppe)Fe]⁺ cation and not complex **4**. Indeed, it has been invariably observed that all mononuclear complexes with the general formula [Cp*(dppe)FeX] show a unique reversible oxidation wave in their CV between -1V and +1 V vs SCE.^[2-4]

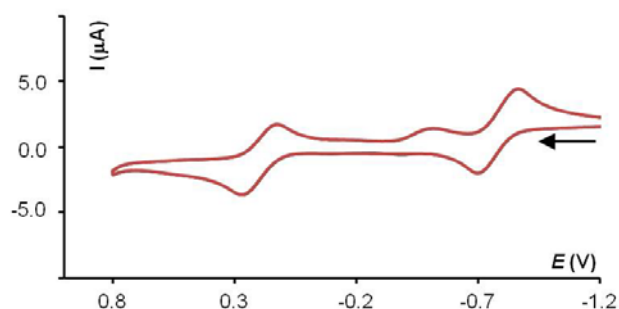


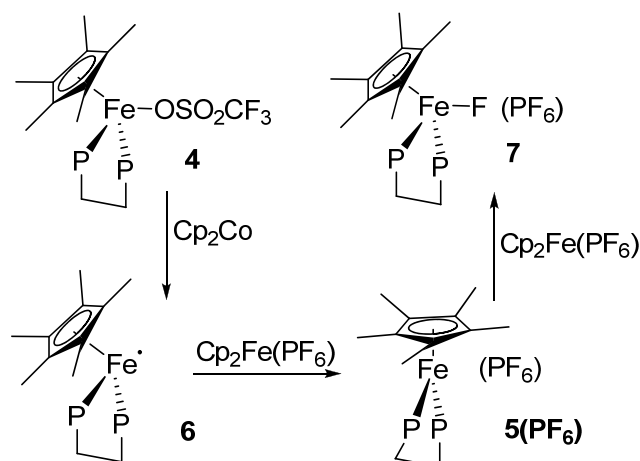
Figure 1. Cyclic voltammogram of **4** (THF, 0.1 M [*n*-Bu₄N]PF₆, 20 °C, platinum electrode, sweep rate = 0.1 V s⁻¹, potentials in V vs SCE; the ferrocene-ferrocenium couple (0.56 V vs SCE)^[21] was used as an internal reference.

The two electrochemical processes can be assigned to the redox couples [Cp*(dppe)Fe(I)]/[Cp*(dppe)Fe(II)]⁺ and [Cp*(dppe)Fe(II)]/[Cp*(dppe)Fe(III)]²⁺, respectively. The ratio of the anodic and cathodic peak current (*i*_{pa}/*i*_{pc} = 1) establishes the thermal stability at 20 °C of the redox species [Cp*(dppe)Fe(I)]/[Cp*(dppe)Fe(II)]⁺ at the platinum electrode. In the case of the second redox event which corresponds to the [Cp*(dppe)Fe(II)]/[Cp*(dppe)Fe(III)]²⁺ system, the current peak ratio is less than one (*i*_{pa}/*i*_{pc} = 0.8) indicating that the 15-electron dicationic iron(III) species is not chemically stable at the platinum electrode. The measured peak-to-peak separations (ΔE_{p1} = 0.16 V, ΔE_{p2} = 0.15 V) which are larger than the value expected for reversible electrochemical processes (ΔE_p = 0.060

V) indicate that both electron transfers are associated with significant reorganizations of the coordination sphere around the metal center.^[2] From the CV data, the preparation of the [Cp*(dppe)Fe(I)] constitutes a viable synthetic target, while the isolation of the product resulting from the chemical evolution of [Cp*(dppe)Fe(III)]²⁺ can also be expected. It is assumed that the additional wave observed in reduction (E_p = -0.48 V) constitutes the electrochemical signature of the in situ generated species (Figure 1).

3. Reduction and oxidation of **4**

Thus, complex **4** was reacted with 1 equiv of cobaltocene in THF at -80 °C (Scheme 3). As the reaction proceeds, the original dark green color turns orange in less than one hour. After work up, the 17-electron iron(I) complex **6** was isolated in pure form as very air and moisture sensitive orange crystals (95 % yield) from cold pentane. The molecular structure of **6** was confirmed by X-ray diffraction study.^[15]



Scheme 3. Preparation of **5**(PF₆) via **6**, and **7**, from **4** (The phenyl groups of the dppe ligand have been omitted for clarity).

Complex **6** was first characterized by CV analysis. As expected, its cyclic voltammogram was found identical to that of **4**. The characterization of **6** by ¹H and ³¹P NMR was not successful. However, the presence of an odd electron in **6** was probed by the measurement of the magnetic moment in solution by ¹H NMR using the Evans method.^[18] The effective magnetic moment (μ_{eff} = 1.48 ± 01 μ_B, C₆D₆) is not far from the theoretical spin-only value (μ_B = 1.73). The X-band ESR spectrum for **6** run at 77 K in a pentane glass displays three features (*g*₁ = 1.9934; *g*₂ = 2.1911; *g*₃ = 2.1971) in accord with its pseudo octahedral geometry. The iron(I) complex **6** was also characterized in the solid state by ⁵⁷Fe Mössbauer spectroscopy. The Mössbauer spectrum run for samples stored at 20 °C for several weeks under argon atmosphere exhibits a single doublet confirming the thermal stability of this 17-electron iron(I) species. The Mössbauer parameters and their analysis are given below in the Mössbauer section.

The neutral complex **6** was oxidized with 1 equiv of ferrocenium hexafluorophosphate in THF at -40 °C for 2 h

(Scheme 3). Its 16-electron counterpart $[\text{Cp}^*(\text{dppe})\text{Fe}]\text{PF}_6$ (**5(PF₆)**) was quantitatively isolated (98 % yield) as air and moisture sensitive red-orange crystals after recrystallization from a THF/pentane mixture. It is interesting to note that in the closely related series $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Fe}]^+$,^[22] and $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Fe}]^+$,^[23] THF coordinates to the metal and the corresponding THF adducts were isolated. The molecular structure of **5(PF₆)** was definitely established by an X-ray diffraction analysis on single crystal (see Section 6). In accord with its pseudo C_{2v} symmetry, the 16-electron cation shows a magnetic moment $\mu_{\text{eff}} = 3.3 \pm 0.2 \mu_B$ (THF, 307 K, Evans method) not far from the value expected for a transition metal ion bearing two unpaired electron ($\mu_{\text{eff}} = 2.83 \mu_B$).^[19] The ESR spectrum of **5(OSO₂CF₃)** was obtained from a frozen THF solution of **4**. The spectrum displayed three well resolved features ($g_1 = 2.0677$, $g_2 = 2.1051$, $g_3 = 2.3730$) with an hyperfine splitting due to the coupling with the two phosphorus nuclei of the dppe ligand for the low field tensor g_3 ($a_3 = 21$ G). Furthermore, the $\Delta m_s = 2$ transition characteristic of the triplet state was found at $g = 4.264$.

The ¹H NMR spectrum of **5(PF₆)** run at 300 K in d₈-THF exhibits two broad resonances at $\delta = 67.6$ ($W_{1/2} = 990$ Hz), 56.5 ($W_{1/2} = 720$ Hz), and a broad multiplet at $\delta = 10.2$ ppm which can be assigned to the CH₂, CH₃ and phenyl groups of the Cp* and dppe ligands. The ³¹P NMR spectrum shows one well resolved resonance at $\delta = 85.1$ ppm corresponding to the phosphorus nuclei of the dppe ligand. Surprisingly enough, the ¹³C NMR spectrum is well resolved and displays resonances corresponding to the two ligands bound to the metal (see Exp. Sect. and Figures S5-S7 in Supporting Information).

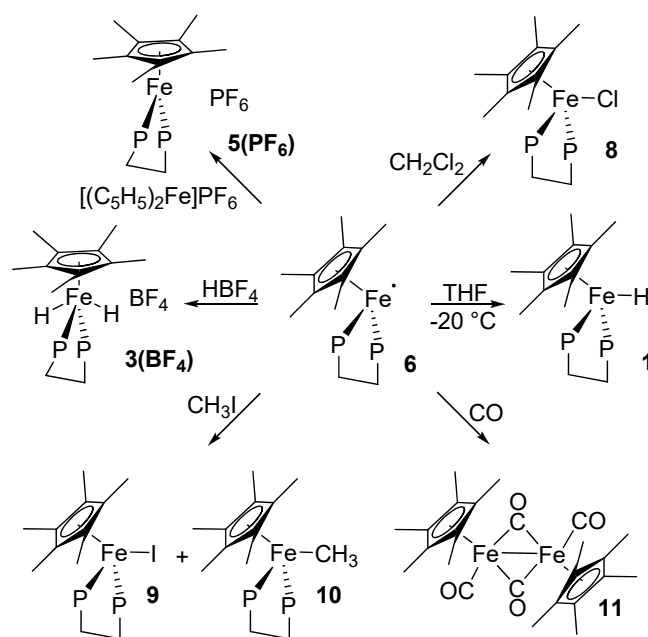
In accord with its redox potential, complex **5(PF₆)** can easily be oxidized by treatment of a THF solution at -80 °C with 1 equiv of $[\text{Cp}_2\text{Fe}]\text{PF}_6$ (Scheme 3). After warming up to 20 °C, the mixture is filtered and the obtained red liquor is evaporated to dryness to give the known iron(III) fluoride complex $[\text{Cp}^*(\text{dppe})\text{Fe-F}]\text{PF}_6$ (**7**, 90 % yield).^[24] In agreement with the observation made in cyclic voltammetry (see above), the in situ generated 15-electron species $[\text{Cp}^*(\text{dppe})\text{Fe}]^{2+}$ activates the PF₆⁻ counter anion by capturing a fluoride anion. It can also be noted that this very reactive intermediate does not react with the THF and no trace of polymerization of the solvent was detected.

4. Reactivity of $[\text{Cp}^*(\text{dppe})\text{Fe}]$ (**6**)

Microcrystals of the complex **6** can be stored at 20 °C for days under vacuum or argon pressure. In solution, it behaves as a highly reactive species as expected for a 17-electron iron(I) radical. For instance, it can be stored in THF at -50 °C for a while, but as the temperature reached -20 °C, it readily abstracts a hydrogen atom from the solvent to give back the iron hydride **1** (Scheme 4). Complex **6** also reacts with CH₂Cl₂ to afford quantitatively and specifically the iron chloride $[\text{Cp}^*(\text{dppe})\text{FeCl}]$ (**8**). Treatment of a cold THF solution of **6** with an excess of CH₃I under similar conditions, immediately results in the quantitative formation of a 1:1 mixture of $[\text{Cp}^*(\text{dppe})\text{FeI}]$ (**9**) and $[\text{Cp}^*(\text{dppe})\text{FeCH}_3]$ (**10**).^[4] Probably, in the first step of these two reactions, the Fe(I) complex **6** abstracts a halide atom from CH₃I

or CH₂Cl₂. The methyl radical might be stable enough under the experimental conditions to be quenched by a second molecule of **6**. In contrast, the radical $\cdot\text{CH}_2\text{Cl}$ probably reorganizes by itself instead of reacting with a second molecule of **6**.

The addition by syringe of 1 equiv of $\text{HBF}_4 \cdot (\text{O}(\text{C}_2\text{H}_5)_2)_2$ to a pentane solution of **6** cooled at -80 °C produces the immediate formation of a lemon-yellow solid which slowly precipitates. This color is characteristic of the dihydrogen complex $[\text{Cp}^*(\text{dppe})\text{Fe}(\eta^2\text{-H}_2)]\text{BF}_4$ (**2(BF₄)**) which is stable at -80 °C as previously obtained from the protonation of the hydride **1**.^[11] Above -50 °C, the precipitate turns orange indicating the dihydrogen derivative is converted to the Fe(IV) dihydride counterpart $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{H})_2]\text{BF}_4$ (**3(BF₄)**). After work up, the dihydride **3(BF₄)** is isolated in 95 % yield and identified by its characteristic sharp triplet ($\delta = -7.89$ ppm, $^2J_{\text{PH}} = 68$ Hz) in the ¹H NMR spectrum. It is surprising that **6** can be converted in **3(BF₄)** with only one equiv of $\text{HBF}_4 \cdot (\text{O}(\text{C}_2\text{H}_5)_2)_2$. The proton is probably reduced by **6** to generate the 16-electron species **5*** and one hydrogen atom. It is possible that H⁺ catches another hydrogen atom from the diethyl ether in the solvent cage to form one molecule of H₂ which instantaneously reacts with the 16-electron **5*** to form the dihydrogen complex **3(BF₄)**.



Scheme 4. Some examples of the reactivity of **6** (The phenyl groups of the dppe ligand have been omitted for clarity).

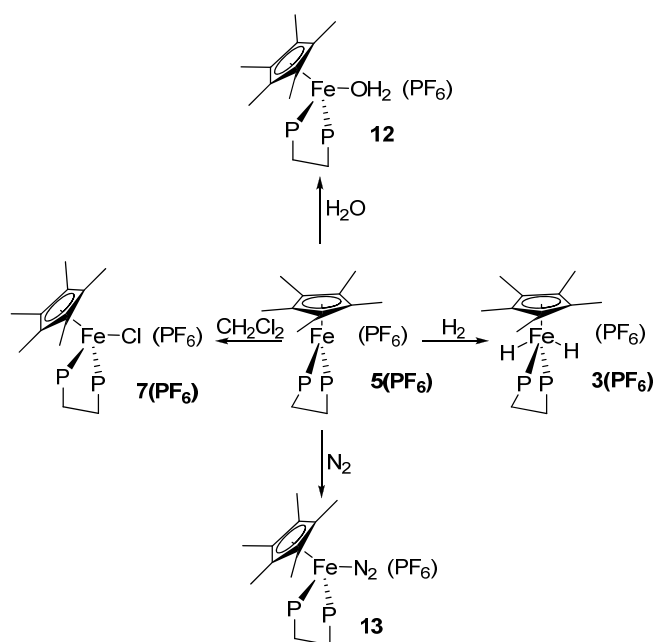
The Fe(I) complex **6** also reacts very quickly with CO. Indeed, when an excess of carbon monoxide was introduced in a Schlenk tube containing an orange pentane solution of **6**, immediately the color turned to dark purple. After work up, the binuclear complex $[\text{Cp}^*(\text{CO})_2\text{Fe}]_2$ (**11**) was isolated as a purple powder and identified by IR and NMR spectroscopy.^[25] It can be assumed that the 17-electron species **6** reacts with CO to generate the 19-electron intermediate $[\text{Cp}^*(\eta^2\text{-dppe})\text{Fe}(\text{CO})]^\cdot$ which can easily relaxes by decoordination of one phosphorus atom of the dppe ligand, generating $[\text{Cp}^*(\eta^1\text{-dppe})\text{Fe}(\text{CO})]^\cdot$ as a

17-electron second intermediate. Reaction with a second molecule of CO liberates the diphosphane from the metal and dimerization of the $[\text{Cp}^*\text{Fe}(\text{CO})_2]^+$ species gives **11**. It is interesting to observe that a sequence of 17-electron and 19-electron intermediates easily produces the displacement of the chelating dppe by CO.

5. Reactivity of $[\text{Cp}^*(\text{dppe})\text{Fe}]\text{PF}_6$ (**5**(PF_6))

The coordinatively unsaturated complex **5**(PF_6) behaves as a strong Lewis acid. It reacts cleanly and quickly with small molecules like water, dihydrogen, dinitrogen, and methylene dichloride as well (Scheme 5). As **4** is in equilibrium with **5**(OSO_2CF_3) (Scheme 2), the reactivity of **4** and **5**(PF_6) are absolutely identical. Depending on the reactions and the experimental conditions, the isolation of the products as triflate or hexafluorophosphate salts can lead to different yields of the isolated pure products. As a general rule, better yields are obtained in the hexafluorophosphate series, and the reactions reported below are described in this series.

Similarly to **4**, **5**(PF_6) reacts with H_2 and provides the dihydride derivative $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{H})_2]\text{PF}_6$ (**3**(PF_6)), 95 % yield, Scheme 5). The reaction of **5**(PF_6) with CH_2Cl_2 is also very quick and specific, leading to the formation of the iron(III) chloride $[\text{Cp}^*(\text{dppe})\text{FeCl}]\text{PF}_6$ (**7**(PF_6)), Scheme 5) that was isolated in 92 % yield after crystallization.^[4]



Scheme 5. Some examples of the reactivity of **5**(PF_6) (The phenyl groups of the dppe ligand have been omitted for clarity).

Although the 16-electron complex does not coordinate THF in contrast with its $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Fe}]^+$ and $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]^+$ relatives,^[22, 23] it can nevertheless give adduct with oxygenated molecules. For instance, it was shown that **5**(PF_6) gives a stable adduct with acetone.^[13] It can be mentioned here, that the acetone adduct

$[\text{Cp}^*(\text{dppe})\text{Fe}(\text{O}=\text{C}(\text{CH}_3)_2)]\text{OSO}_2\text{CF}_3$ (**14**) was reported to be paramagnetic.^[13] A careful reinvestigation of the dependence of the magnetic susceptibility with temperature have shown that the bulk crystalline samples of **14** is a diamagnetic material polluted by a paramagnetic impurity containing two unpaired electrons ($S = 1$). Examination of crystalline samples of **14** with microscope allowed to found few red small crystals among the dark green bulk material. Further investigation were not carried out.

It was also found that upon addition of water to an orange THF solution of $[\text{Cp}^*(\text{dppe})\text{Fe}]\text{PF}_6$ (**5**(PF_6)) the color turned dark green, immediately. Slow diffusion of pentane into this mixture provides green crystals identified by an X-ray diffraction analysis as the water complex $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{H}_2\text{O})]\text{PF}_6$ (**12**) as a solvate with two molecules of THF (see Section 6). The presence of the water molecule is evidenced by the observation of a ν_{OH} band in the IR spectrum at 3402 cm^{-1} (KBr disk). Analytically pure microcrystalline samples of the 18-electron complex **12** were found diamagnetic. The determination of the magnetic moment in d_8 -THF at 307 K by the Evans method ($\mu_{\text{eff}} = 0.4\ \mu_B$) showed that the complex **12** is partially dissociated in solution (See Figure S8-S10, Supporting Information). According to eq. 1, the solution contains 88 % of the water adduct in equilibrium with 12 % of 16-electron complex **5**(PF_6). In solution, the water adduct is more stable than the triflate complex **4**, in accord with a shorter FeO bond distance in the former derivative (see Section 6). The ^1H NMR spectrum (d_8 -THF, 25 °C) of **12** resembles that of **4** with three broad resonances at $\delta = 8.2, 6.4$ and 5.9 ppm assigned to the CH_2 , CH_3 , and phenyl resonances, respectively. The protons of the water molecule could not be found. A single resonance is observed in the ^{31}P NMR spectrum ($\delta = 89.6\text{ ppm}$ (d_8 -THF, 25 °C)).

It is now well recognized that dinitrogen molecule can act as a ligand to a transition metal complex.^[26] In particular, a large variety of iron-dinitrogen complexes have been reported. They all display an η^1 , or end-on, binding geometry.^[27] Upon exposure to nitrogen gas, an orange THF solution of **5**(PF_6) turns progressively to yellow. After work up, the new salt $[\text{Cp}^*(\text{dppe})\text{Fe}(\eta^1\text{-N}_2)]\text{PF}_6$ (**13**) was isolated as yellow microcrystals in 92 % yield. The dinitrogen complex **13** is thermally stable when stored under argon or under vacuum. The $[\text{Cp}^*(\text{dppe})\text{Fe}]^+$ framework of this compound was characterized by ^1H , ^{31}P , and ^{13}C NMR. The presence of the N_2 molecule attached to the iron nucleus was probed by elemental analysis and IR spectroscopy (Figure S11, Supporting Information).

The IR spectrum displays a relatively intense ν_{N_2} stretching band at 2120 cm^{-1} , characteristic of a mononuclear complex end-bonded to a molecule of dinitrogen.^[27] The IR frequency compares well with those found for the iron(II) complexes as for examples $[(\text{dppe})_2\text{Fe}(\eta^1\text{-N}_2)]\text{BPh}_4$ (2130 cm^{-1}), $[(\text{dmpe})_2\text{Fe}(\text{H})(\eta^1\text{-N}_2)]\text{BPh}_4$ (2112 cm^{-1} , $d_{\text{NN}} = 1.13\ \text{\AA}$), and $[\text{Cp}(\text{dippe})\text{Fe}(\text{H})(\eta^1\text{-N}_2)]\text{BPh}_4$ (2112 cm^{-1} , $d_{\text{NN}} = 1.13\ \text{\AA}$).^[10, 27, 28] It is worthy to note that the bulky Cp^* ligand plays here a decisive role on the specificity of the reaction. Indeed, it has been shown that the binuclear complex $[(\text{C}_5\text{H}_5)(\text{dppe})\text{Fe}-\text{NN}-\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)](\text{PF}_6)_2$ is formed when the C_5 ring is not methylated.^[29] The cyclic voltammogram of **13** recorded in THF between -1.0 V and $+1.0$

V does not show any wave. This result clearly indicates that the nitrogen ligand is well-coordinated to the iron atom and its dissociation in THF does not occur.

6. Molecular structures of **4**, **5(PF₆)**, and **12·2(C₄H₈O)**

Slow diffusion of pentane into concentrated THF solutions of the triflate adduct **4**, the 16-electron Fe(II) complex **5(PF₆)** and the water complex **12·2(C₄H₈O)** provided suitable crystals for X-ray analyses. Diffraction parameters for these compounds are available in Table S1 (Supporting Information). ORTEP views are given in Figure 2, while pertinent bond lengths and angles for these three complexes are collected in Table 1. The structures of the six-coordinated complexes **4** and **12·2(C₄H₈O)** show for the iron centers the expected pseudo-octahedral geometry with three sites occupied by the Cp* ligand, two sites by the chelating bis-phosphane; the triflate or the water molecules being coordinated at the remaining sixth position. The Fe-C and Fe-P bond distances, and the bond angles are in the previously established ranges for cationic iron(II) derivatives of this series.^[2-4]

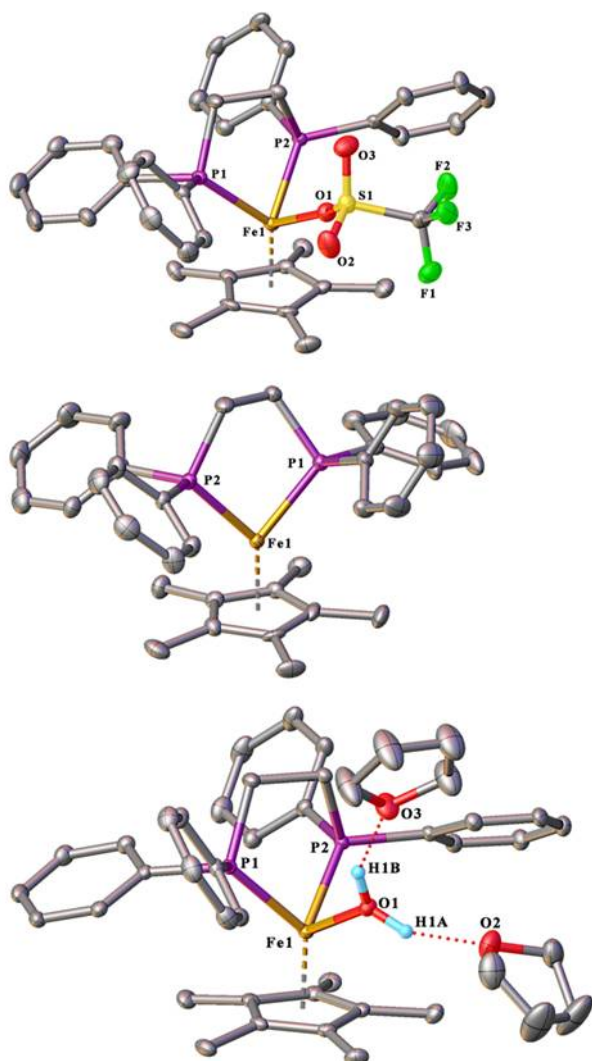


Figure 2. Molecular structures of the triflate adduct **4** (top), the cationic 16-electron Fe(II) complex **5(PF₆)** (middle), and the water complex **12·2(C₄H₈O)** (bottom) with their respective partial numbering scheme. Hydrogen atoms, except those involved in H-bonding interactions in **12·2(C₄H₈O)**, and counter anions have been omitted for clarity. Thermal ellipsoids are drawn at 20 % probability.

However, these bonds are slightly longer than that determined for the closely related complex [Cp*(dppe)Fe(O=C(CH₃)₂)]PF₆ (**14**) ($d_{\text{Fe-O}} = 2.031(4)$ Å) and significantly longer than those reported for other iron complexes like [(η⁵-C₅Me₄Et)(CO)₂Fe(OH₂)]BF₄ ($d_{\text{Fe-O}} = 2.022(9)$ and $2.043(9)$ Å).^[23]

The X-ray analysis of **12·2(C₄H₈O)** also revealed the presence of two molecules of solvent per cation with hydrogen bonding interactions between the protons of the water molecule and the oxygen atoms of the molecules of THF (Table 2). The hydrogen atoms of the water ligand were not located or refined. The Fe-O...OC₄H₈ distances are 2.710(4) Å and 2.781(4) Å. The Fe-O bond length determined for **4** (2.118(4) Å) and **12·2(C₄H₈O)** (2.077(2) Å) are much shorter than the sum of the van der Waals radii (2.67 Å),^[30, 31] and very close to the average of the distances reported in the literature showing that the triflate and water ligands are well bound to the metal atom.^[31, 32]

Table 1. Selected bond distances [Å] and angles [°] for **4**, **5(PF₆)**, and **12·2(C₄H₈O)**.

	4	5(PF₆)	12·2(C₄H₈O)
Bond lengths			
Fe(1)-O(1)	2.118(4)	-	2.077(2)
Fe(1)-P(1)	2.2682(17)	2.233(3)	2.2339(11)
Fe(1)-P(2)	2.2238(17)	2.256(3)	2.2219(14)
Fe(1)-C _{Cp*} av.	2.129(6)	2.134(10)	2.112(3)
Fe-Cp* _{cent}	1.748	1.770	1.793
Bond angles			
P(1)-Fe(1)-O(1)	94.22(13)	-	89.84(8)
P(2)-Fe(1)-O(1)	84.29(13)	-	86.61(8)
P(1)-Fe(1)-P(2)	84.20(6)	86.39(11)	85.01(4)

The view of **5(PF₆)** in Figure 2 clearly shows that the iron atom is in a formally five-coordinate environment and the data does not reveal any indications of stabilization by means of intra- or intermolecular agostic interaction. The Cp* ring is pentahapto bonded and the plane defined by the phosphorus nuclei of dppe ligand and the iron atom is almost perpendicular to the Cp* plane. The molecule is close to the C_{2v} symmetry. The angle defined by the ring centroid, the Fe atom, and the centroid of the P(1) - P(2) segment is close to 180° (175.2°) in accord with the pseudo-trigonal bipyramidal geometry for the coordination of the complex cation. The bond distances and angles found for **5(PF₆)** compare well with those found for the related X-ray characterized 16-electron species [Cp*(dippe)Fe]BPh₄ and [(pentadienyl)(PEt₃)₂Fe]PF₆.^[33]

Table 2. Hydrogen bond interaction parameters for **12·2(C₄H₈O)**

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]
O1-H1A...O2	0.93	1.84	2.710(4)	156

O1-H1B...O3	0.94	1.94	2.781(4)	149
C12-H12A...O3	0.97	2.58	3.511(5)	162

7. ⁵⁷Fe Mössbauer Spectroscopy of 4-6, 12 and 14

The ⁵⁷Fe Mössbauer spectra of the complexes **4-6**, **12**, and **14** were run at 80 K and least-square fitted with Lorentzian line shapes.^[34] The spectra of all complexes show a single doublet which clearly establishes the spectroscopic purity of the samples and the chemical stability of these complexes over weeks. The isotropic shift (IS) and quadrupole splitting (QS) are reported in Table 3. The line broadening (Γ) are in line with the value observed for half sandwich iron complexes, except in the case of the five-coordinated complex **5(PF₆)**. Probably, relaxation phenomenon due to the magnetic properties of this complex ($S = 1$) is at the origin of the broad lines.^[35]

The Mössbauer parameters depend on several factors including the oxidation and the spin states, the atoms coordinated at the Mössbauer nucleus, and the coordination numbers.^[35, 36] In the present case, only the comparison of IS and QS between the iron(II) with oxygen ligands **4**, **12**, and **14** makes sense. In this series of complexes, the IS and QS parameters decrease in the order **4**, **12**, **14** while the iron-oxygen bond distances decrease continuously. It is interesting to note that the strength of the Fe-O bond determined in the solid state is in line with the thermodynamic stability of the complexes in solution. It can also be noted that, the five-coordinated complexes **5(PF₆)** and **6** display much smaller values for both the IS and QS parameters.^[2]

Table 3. ⁵⁷Fe Mössbauer data for the new and some closely related complexes (80 K)

Cmpd	IS (mm/s)	QS (mm/s)	Γ (mm/s)	$d_{\text{Fe-O}}$ (Å)
1 ^[4]	0.20	2.08	0.13	
4	0.713	2.336	0.124	2.128(4)
5(PF₆)	0.499	1.728	0.257	
6	0.436	1.241	0.136	
12	0.591	2.233	0.118	2.076(2)
14 ^[13]	0.567	2.191	0.128	2.031(4)
15 ^[16]	0.553	1.752	0.130	not bound
14 = [Cp*(dppe)Fe(O=C(CH ₃) ₂)]OSO ₂ CF ₃ ,				15 = [Cp*(dppp)Fe]OSO ₂ CF ₃

Conclusions

In this contribution, we described the synthesis, spectroscopic and structural characterization, and redox properties of the triflate adduct [Cp*(dppe)FeOSO₂CF₃] (**4**). The triflate anion is well coordinated at the iron nucleus in the solid state, but partially dissociates in solution to liberate the highly reactive cationic 16-electron [Cp*(dppe)Fe]⁺ (**5**⁺). As a result, the 17-electron iron(I) derivative [Cp*(dppe)Fe] (**6**) is accessible by a one electron reduction with Cp₂Co, and the 15-electron iron(III) counterpart [Cp*(dppe)Fe](PF₆)₂ can be generated by a one electron oxidation with [Cp₂Fe]PF₆. However, the dication reacts with the PF₆⁻ anion to yield [Cp*(dppe)FeF]PF₆ (**7**). The reactivity of **4** is richer than that of its precursor [Cp*(dppe)FeCl] (**8**). In contrast

with **8**, complexes **4** and **5(PF₆)** react with small molecules like dihydrogen, dinitrogen, carbon monoxide, and water. Further synthetic efforts from our group are in progress to take advantage of the rich reactivity of **4** for the elaboration of new molecular architectures.

Experimental Section

General Data: Manipulations of air-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in a argon-filled Jacomex 532 drybox. All glassware was oven-dried and vacuum or argon flow-degassed before use. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were dried and deoxygenated by distillation from sodium/benzophenone ketyl. Dichloromethane was distilled under argon from P₂O₅ and then from Na₂CO₃. [Cp*(dppe)FeH] (**1**),^[4] [Cp*(dppe)FeCl] (**8**),^[4] and ferricinium hexafluorophosphate [Fe(η⁵-C₅H₅)₂]PF₆^[21] were prepared following published procedures. Methyl triflate (CH₃O₃SCF₃) and ammonium hexafluorophosphate were commercially available and used as received without further purification. **Caution:** Methyl trifluoromethanesulfonate is toxic and a suspected carcinogen, and must be handled in a well-ventilated fume hood. FT-IR spectra were recorded using a Bruker IFS28 spectrophotometer (range 4000-400 cm⁻¹) as solids dispersed in KBr pellets. ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker DPX200 NMR multinuclear spectrometer at 298 K, unless otherwise noted. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) for ¹H and ¹³C NMR spectra, external 85 % H₃PO₄ for ³¹P NMR spectra, and external CFC₃ for ¹⁹F spectra. Coupling constants (J) are reported in hertz (Hz), and integrations are reported as number of protons. EPR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer. Magnetic susceptibility measurements were conducted in solution according to the Evans' method.^[18] Mössbauer spectra were recorded with a 2.5 x 10⁻² C (9.25 x 10⁸ Bq) ⁵⁷Co source using a symmetric triangular sweep mode. Computer fitting of the Mössbauer data to Lorentzian line shapes was carried out with a previously reported computer program.^[34] The isomer shift values are reported relative to iron foil at 298 K. The electrochemical analyses were performed with use of an EG&G-PAR Model 263 potentiostat/galvanostat. Cyclic voltammetry (CV) measurements were performed at room temperature (ca. 20 °C) with a normal three-electrode configuration consisting of a Pt-disk ($d = 1.0$ mm) working electrode, a saturated calomel reference electrode (SCE), and a platinum-wire counter electrode. The ferrocene/ferrocenium redox couple ($E^{1/2} = 0.560$ V in THF) was used as an internal calibrant for the potential measurements.^[21] Elemental analyses were conducted on a Thermo-Finnigan Flash EA 1112 CHNS/O analyser by the Microanalytical Service of the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) at the University of Rennes 1, France.

[Cp*(dppe)FeOSO₂CF₃] (4**):** A Schlenk tube was loaded with 0.590 g (1.0 mmol) of [Cp*(dppe)FeH], 150 mL of diethyl ether and a magnetic stirbar. Methyl triflate (125 μ L, 1.1 mmol) was then added by syringe to the red-orange solution. A yellow suspension appeared immediately which quickly gave a green precipitate. The dark solid was filtered by cannula, washed with 3 x 20 mL portion of pentane and dried under vacuum. Recrystallization from THF/pentane mixture provided 0.630 g (85 % yield) of [Cp*(dppe)FeOSO₂CF₃] as air and moisture sensitive dark-green crystals. A crystal from this crop was used for an X-ray structure determination. Anal. Calcd for C₃₇H₃₉F₃FeO₃P₂S: C, 60.17; H, 5.32. Found : C, 59.82; H, 5.33%. FT-IR (KBr): $\nu = 1305, 1267, 1234, 1169, 1153, 1094, 1032$ cm⁻¹. μ_{eff} (d₈-THF, 307 K) = 1.9 μ B. ¹H NMR (200 MHz, d₈-THF, 300 K): $\delta = 26.3$ (br s, CH₂, $w_{1/2} = 375$ Hz); 22.3 (br s,

C_5Me_5 , $w_{1/2} = 375$ Hz); 0.9 (br s, Ph) ppm. ^{13}C NMR (50 MHz, d_8 -THF, 193 K): $\delta = 137.7$ -129.3 (m, Ph), 95.1 (br s, C_5Me_5), 34.2 (br s, CH_2), 8.5 (s, C_5Me_5) ppm. ^{31}P NMR (81 MHz, d_8 -THF, 193 K): $\delta = 89.8$ (s, dppe) ppm. ^{19}F NMR (188 MHz, d_8 -THF): $\delta = -72.5$ (s, CF_3O_2SO) ppm.

Preparation of the hydride 1 from 4: A Schlenk tube was charged with 0.738 g (1 mmol) of **4**, 30 mL of methanol and a stirbar. The solution was cooled to -80 °C before adding $NaOCH_3$ (0.065 g, 1.2 mmol). The solution changed slowly from green to orange while the temperature was allowed to increase to 20 °C. The solvent was removed under reduced pressure, and the solid residue extracted with 3 x 15 mL portion of pentane. After removal of the solvent and drying under vacuum, the complex $[Cp^*(dppe)FeH]$ (**1**) was isolated (0.56 g, 95 % yield), and identified by 1H nmr spectroscopy with its characteristic triplet at $\delta = -16.8$ ppm ($^2J_{HP} = 67$ Hz) with comparison with an authentic sample.^[4]

$[Cp^*(dppe)Fe]$ (6**):** A Schlenk tube cooled to -80 °C was loaded with 0.738 g (1.0 mmol) of $[Cp^*(dppe)FeOSO_2CF_3]$, 30 mL of THF and a magnetic stirbar. Cobaltocene (0.170 g, 0.9 mmol) was then added in one go to the green solution. The color slowly turned orange and at -20 °C the solvent was removed under vacuum. At room temperature, the solid residue was extracted with 3 x 10 mL portion of pentane. Crystallization from cold pentane gave 0.50 g (95 % yield) of $[Cp^*(dppe)Fe]$ as a very air and moisture sensitive orange microcrystalline solid. Anal. Calcd for $C_{36}H_{39}FeP_2$: C, 73.35; H, 6.67. Found : C, 72.87; H, 6.65. μ_{eff} (C_6H_6 , 307 K) = 1.48 ± 0.1 μ_B .

$[Cp^*(dppe)Fe]PF_6$ (5(PF₆)**):** A Schlenk tube cooled to -40 °C was charged with 1.35 g (2.3 mmol) of $[Cp^*(dppe)Fe]$, 20 mL of THF and a magnetic stirbar. Ferricinium hexafluorophosphate (0.685 g, 2.07 mmol) was then added in one go to the orange solution. The reaction mixture was stirred for 2 h while it slowly warmed up to 20 °C. The solvent was evaporated under vacuum and the solid residue washed with 5 x 50 mL portion of a pentane/diethyl ether mixture (1:1, v/v). Recrystallization from THF/pentane mixture provided 1.50 g (98 % yield) of $[Cp^*(dppe)Fe]PF_6$ as very air and moisture sensitive orange-red crystals. A crystal from this crop was used for an X-ray structure determination. Anal. Calcd for $C_{36}H_{39}F_6FeP_2$: C, 58.87; H, 5.35. Found : C, 58.55; H, 5.63. μ_{eff} (THF, 307 K) = 3.3 ± 0.2 μ_B . 1H NMR (200 MHz, d_8 -THF, 297 K): $\delta = 67.6$ (br s, CH_2 , $w_{1/2} = 990$ Hz), 56.5 (br s, CH_3 , $w_{1/2} = 720$ Hz), -10.2 (br s, *o*-Ph) ppm. ^{31}P NMR (81 MHz, d_8 -THF, 297 K): $\delta = 85.1$ (s, dppe), -140.6 (sept., PF_6) ppm. ^{19}F NMR (188 MHz, d_8 -THF, 297 K): $\delta = -69.5$ (d, $J_{P-F} = 714$ Hz, PF_6) ppm.

Chemical oxidation of $[Cp^*(dppe)Fe]PF_6$ (5(PF₆)**):** To a 50 mL orange THF solution of **5(PF₆)** (0.734 g, 1.0 mmol), cooled at -80 °C, was added in one go a solid sample of ferrocenium hexafluorophosphate (0.320 g, 0.97 mmol). The color turned immediately dark red, and stirring was continued while the mixture was allowed to warm to room temperature. The solvent was evaporated under reduced pressure and the solid material extracted with 5 x 20 mL portion of acetone. The extracts were combined and evaporated to dryness. The dark red residue was washed with 2 x 20 mL portion of diethyl ether to remove the ferrocene. Crystallization from acetone/pentane mixture afforded 0.601 g (90 % yield based on $[Cp_2Fe]PF_6$) of $[Cp^*(dppe)FeF]PF_6$ (**7**) isolated as a thermally air stable dark red powder. Complex **7** was authenticated by comparison of its ^{19}F NMR (CD_2Cl_2) broad signal at $\delta_{Fe-F} = -60.0$ ($w_{1/2} = 360$ Hz) ppm with literature data.^[24]

Reaction of **6 with CH_2Cl_2 :** In a Schlenk tube containing 20 mL of CH_2Cl_2 under argon was added 0.290 g (0.5 mmol) of $[Cp^*(dppe)Fe]$ (**6**) at 20 °C. The solution turned instantaneously green, and the stirring was maintained for 15 min. The solvent was removed under reduced pressure and the dark green solid was extracted with 2 x 10 mL portions

of diethyl ether. The extracts were taken to dryness and $[Cp^*(dppe)FeCl]$ (**8**) was collected in 95 % yield as a pure microcrystalline powder. The compound was identified by comparison of its 1H NMR and CV data with those of an authentic sample.^[4]

Reaction of **6 with CH_3I :** A Schlenk tube was charged with 0.290 g (0.5 mmol) of $[Cp^*(dppe)Fe]$ (**6**) and 10 mL of THF. The solution was cooled to -80 °C and 4 μL of CH_3I (0.6 mmol) was added by syringe. The solvent was then removed at 20 °C. The solid residue was extracted with 2 x 10 mL portions of pentane. The extract taken to dryness contained $[Cp^*(dppe)FeI]$ (**9**) and $[Cp^*(dppe)FeCH_3]$ (**10**) formed in the 1:1 ratio and quantitative yield. The products were identified by 1H , ^{31}P NMR and cyclic voltammetry (CV) and comparison of the data with those of authentic samples.^[4]

Reaction of **6 with $HBF_4 \cdot OEt_2$:** A Schlenk tube was loaded with 0.590 g (1.0 mmol) of $[Cp^*(dppe)Fe]$ (**6**) and 20 mL of pentane at -80 °C. Then, 150 μL (1.1 mmol) of $HBF_4 \cdot OEt_2$ were added by syringe. Immediately, a lemon-yellow solid precipitated. The resulting solid was filtered off, washed with 2 x 10 mL portions of diethyl ether and dried under vacuum at 20 °C. The complex $[Cp^*(dppe)Fe(H)_2]BF_4$ (**3(BF₄)**) was recovered as a yellow powder (0.64 g, 95 % yield), and identified by comparison of its characteristic 1H NMR spectrum ($\delta_{Fe-H} = -7.9$ ppm (t, $^2J_{HP} = 68$ Hz) with that of an authentic sample.^[11]

Reaction of **6 with CO:** A Schlenk tube was charged with 0.590 g (1.0 mmol) of $[Cp^*(dppe)Fe]$ (**6**) and 20 mL of pentane at 20 °C. The glassware was purged under reduced pressure and refilled with 2 bars of CO. The orange solution became instantaneously purple. The stirring was continued for 15 min. The solvent was then removed under reduced pressure and the solid residue washed with 3 x 10 mL portion of diethyl ether to remove free dppe that was identified by 1H and ^{31}P NMR spectroscopy. The remaining purple residue was dried under vacuum to provide 0.38 g (98 % yield) of $[Cp^*(CO)_2Fe]_2$ (**11**). Complex **11** was identified spectroscopically (IR and NMR) by comparison with literature data.^[25]

Reaction of **5(PF₆) with H_2 :** A Schlenk tube was charged with 0.734 g (1.0 mmol) of $[Cp^*(dppe)Fe]PF_6$ and 30 mL of THF at 20 °C. The argon atmosphere was partially removed under reduced pressure before introducing 1.2 bar of H_2 . The orange solution turned immediately yellow. The solution was stirred for 15 min and the solvent was removed under reduced pressure. The solid residue was washed with 3 x 20 mL portion of pentane. The complex $[Cp^*(dppe)Fe(H)_2]PF_6$ (**3(PF₆)**) was recovered as a yellow powder (0.64 g, 95% yield) and identified by comparison of its characteristic 1H NMR spectrum with that of an authentic sample.^[11]

Reaction of **5(PF₆) with CH_2Cl_2 :** A Schlenk tube was charged with 0.734 g (1.0 mmol) of $[Cp^*(dppe)Fe]PF_6$ and 15 mL of CH_2Cl_2 at 20 °C. The resulting solution was stirred for 10 min and the solvent was removed under reduced pressure. The solid residue was washed with 3 x 15 mL portion of pentane and dried under vacuum. The complex $[Cp^*(dppe)FeCl]PF_6$ (**8(PF₆)**) was recovered as red garnet crystals (0.710 g, 92 % yield) and identified by comparison with an authentic sample.^[4]

Reaction of **5(PF₆) with H_2O :** A Schlenk tube was loaded with 0.734 g (1.0 mmol) of $[Cp^*(dppe)Fe]PF_6$, 30 mL of THF and a magnetic stirbar. Degassed water (0.09 g, 5.0 mmol) was then added by syringe to the orange solution. The reaction mixture was stirred for 15 min during which time the color changed to dark green. The solvent was removed under reduced pressure, the solid residue washed with 3 x 20 mL portion of pentane, and dried under vacuum to provide 0.76 g (85% yield) of $[Cp^*(dppe)FeOH_2 \cdot 2THF]PF_6$ (**12**) as an air sensitive black powder.

Single crystals suitable for X-ray analysis were grown by slow diffusion of pentane into a THF solution. Anal. Calcd for $C_{44}H_{57}F_6FeO_3P_3$: C, 58.94; H, 6.41; P, 10.36. Found: C, 58.97; H, 6.49; P, 9.50. μ_{eff} (d_8 -THF, 307 K) = 0.4 μ_B . FT-IR (KBr): $\nu_{\text{OH}} = 3402 \text{ cm}^{-1}$. ^1H NMR (200 MHz, d_8 -THF, 298 K): $\delta = 8.2$ (br s, CH_2), 6.4 (br s, $w_{1/2} = 150 \text{ Hz}$, CH_3), 5.9 (br s, $w_{1/2} = 50 \text{ Hz}$, o -Ph) ppm. ^{13}C NMR (50 MHz, d_8 -THF, 298 K): $\delta = 179.0$ - 146.0 (Ph), 132.0 (C_5Me_5), 51.9 (CH_2), 0.5 (C_5Me_5) ppm. ^{31}P NMR (81 MHz, d_8 THF, 193 K): $\delta = 89.6$ (s, dppe) ppm.

Reaction of 5(PF₆) with N₂: A Schlenk tube was charged with 0.734 g (1.0 mmol) of $[\text{Cp}^*(\text{dppe})\text{Fe}]\text{PF}_6$ and 30 mL of THF at 20 °C. The argon atmosphere was partially removed under reduced pressure before introducing 1.2 bar of N₂. The orange solution turned immediately yellow. The solution was stirred for 15 min and the solvent was removed under reduced pressure. The solid residue was washed with 3 x 20 mL portion of pentane. The complex $[\text{Cp}^*(\text{dppe})(\text{Fe}(\text{N}_2))]\text{PF}_6$ (**13**) (0.705 g, 92 % yield) was recovered as yellow microcrystals. Anal. Calcd for $\text{C}_{36}\text{H}_{39}\text{F}_6\text{FeN}_2\text{P}_3$: C, 56.71; H, 5.16; N, 3.67. Found: C, 56.92; H, 5.13; N, 3.55. ^1H NMR (200 MHz, CD_3COCD_3 , 300 K): $\delta = 8.26$ - 7.41 (m, 20H, Ph dppe), 2.07-1.99 (2m, 4H, CH_2 , dppe), 1.61 (s, 15H, C_5Me_5) ppm. ^{13}C NMR (50 MHz, CD_3COCD_3 , 300 K): $\delta = 133.9$ - 129.7 (m, Ph dppe), 92.5 (s, C_5Me_5), 28.6 (tm, CH_2 dppe, $^1J_{\text{CH}} 136 \text{ Hz}$), 9.3 (q, CH_3 , $^1J_{\text{CH}} = 128 \text{ Hz}$) ppm. ^{31}P NMR (81 MHz, CD_3COCD_3 , 300 K): $\delta = 85.5$ (s, dppe) ppm. FT-IR (KBr): $\nu_{\text{NN}} = 2120 \text{ cm}^{-1}$.

X-ray Crystal Structure Determinations: A suitable X-ray single crystal of compound **4**, **5(PF₆)** and **12·2(C₄H₈O)** obtained as described above, was mounted with epoxy cement on the tip of a glass fiber. The three compounds were studied on an automatic CAD4 NONIUS diffractometer with graphite monochromatized MoK radiation ($\lambda = 0.71073 \text{ \AA}$).^[37] The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{\text{max}} = 54^\circ$, scan $\omega/2\theta = 1$, $t_{\text{max}} = 60 \text{ s}$) gave independent reflections (Table S1, Supporting Information). The structures were solved with SIR-97 which revealed the non-hydrogen atoms.^[38] After anisotropic refinement, the remaining atoms were found in Fourier difference maps. The complete structures were then refined with SHELXL97 by the full-matrix least-squares procedures on reflection intensities (F^2).^[39] The absorption was not corrected. The non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as idealized contributions. Atomic scattering factors were taken from the literature.^[40] In addition, the contribution of the disordered solvents to the calculated structure factors of **5(PF₆)** and **12·2(C₄H₈O)** were estimated following the BYPASS algorithm,^[41] implemented as the SQUEEZE option in PLATON.^[42] Then, a new data set, free of solvent contribution, was used in the final refinement. Crystal data, details of data collection and structure refinement parameters for **4**, **5(PF₆)** and **12·2(C₄H₈O)** are summarized in Table S1. ORTEP views were drawn using OLEX2 software.^[43] CCDC 1957164 (for **4**), 1957165 (for **5(PF₆)**), and 1957166 (for **12·2(C₄H₈O)**) contain 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.

Keywords: Iron • triflate adduct • N, O ligands • X-ray diffraction • coordination modes

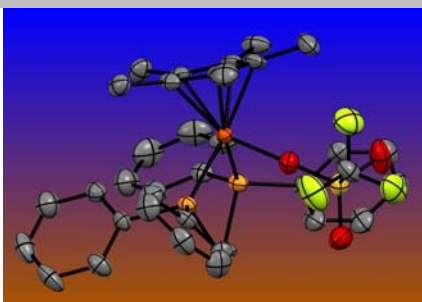
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FULL PAPER

The new complex $[\text{Cp}^*(\text{dppe})\text{FeOSO}_2\text{CF}_3]$ was prepared by treatment of the hydride $[\text{Cp}^*(\text{dppe})\text{FeH}]$ with $\text{CH}_3\text{OSO}_2\text{CF}_3$ (85 % yield). This compound dissociates in THF opening the route to the five-coordinated complexes $[\text{Cp}^*(\text{dppe})\text{Fe}]$, and $[\text{Cp}^*(\text{dppe})\text{Fe}]\text{PF}_6$, and to the six-coordinated derivatives $[\text{Cp}^*(\text{dppe})\text{Fe-L}]\text{PF}_6$ (L = CO, H₂, N₂, H₂O).



Key Topic*: Organoiron complexes

Paul Hamon, Loic Toupet, Thierry Roisnel, Jean-René Hamon, Claude Lapinte**

Page No. – Page No.

Preparation and characterization of the triflate complex

$[\text{Cp}^*(\text{dppe})\text{FeOSO}_2\text{CF}_3]$: a convenient access to labile five- and six-coordinate Fe(I) and Fe(II) complexes