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## NEW ENTRY TO PIANO-STOOL ELECTRON RICH (PENTAMETHYL CYCLOPENTADIENYL) IRON COMPLEXES

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### ABSTRACT

A new route to the electron rich pentamethylcyclopentadienyl iron complexes ( $n^5\text{-C}_5\text{Me}_5\text{)=Cp}^*$ ) starting from the commercially available dimer  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ , is presented. Reaction of the dimer with  $\text{I}_2$  in  $\text{CH}_2\text{Cl}_2$  affords the mononuclear carbonyl complex  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}$  which in turn reacts with bis(diphenylphosphinoethane) in toluene under UV irradiation to give  $\text{Cp}^*\text{Fe}(\text{dppe})\text{I}$ . Treatment of  $\text{Cp}^*\text{Fe}(\text{dppe})\text{I}$  with the neutral ligands L (L =  $\text{CH}_3\text{CN}$ ,  $\text{PPh}_3$ ,  $\text{SEt}_2$ ) in the presence of  $\text{TIPF}_6$  affords the cationic derivatives  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{L}]\text{PF}_6$ , while that the reaction with  $\text{S}_2(\text{CH}_2\text{C}_6\text{H}_5)_2$  in  $\text{CH}_3\text{OH}$  yields the thiolate complex  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{S-CH}_2\text{C}_6\text{H}_5]\text{PF}_6$ . The unusual magnetic properties of these complexes are discussed. Extended Hückel OM calculation confirmed the most electron rich character of the  $\text{Cp}^*\text{Fe}(\text{dppe})^+$  derivatives than their unsubstituted  $\text{CpFe}(\text{dppe})^+$ . Electrochemical as well as Mössbauer data are in agree with this.

**KEYWORDS:** *pentamethylcyclopentadienyl iron, electron rich fragments, OM calculation, organometallic*

### RESUMEN

Se presenta una nueva ruta de síntesis para compuestos complejos pentametilciclopentadienilo-hierro(II) usando como precursor el dímero  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ .

La reacción de este dímero con  $\text{I}_2$  en  $\text{CH}_2\text{Cl}_2$  produce el compuesto  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}$  el cual a su vez reacciona con bis(difenilfosfinoetano) en tolueno para dar el complejo  $\text{Cp}^*\text{Fe}(\text{dppe})\text{I}$ .

La reacción de éste con ligandos neutros L (L =  $\text{CH}_3\text{CN}$ ,  $\text{PPh}_3$ ,  $\text{SEt}_2$ ) en presencia de  $\text{TIPF}_6$  produce los derivados cationicos  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{L}]\text{PF}_6$  mientras que la reacción con  $\text{S}_2(\text{CH}_2\text{C}_6\text{H}_5)_2$  en  $\text{CH}_3\text{OH}$  genera el complejo tiolato  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{S-CH}_2\text{C}_6\text{H}_5]\text{PF}_6$ . Se discuten las propiedades inusuales paramagnéticas de los complejos. Cálculos de orbitales moleculares Hückel extendido confirman la más alta densidad electrónica de los derivados  $\text{Cp}^*\text{Fe}(\text{dppe})^+$  respecto de los correspondientes no sustituidos  $\text{CpFe}(\text{dppe})^+$ .

Estudios electroquímicos y de espectrometría Mössbauer están de acuerdo con estos resultados.

**PALABRAS CLAVES:** *pentametilciclopentadienilo-hierro(II), fragmentos con alta densidad electrónica, cálculos de OM, organometalico*

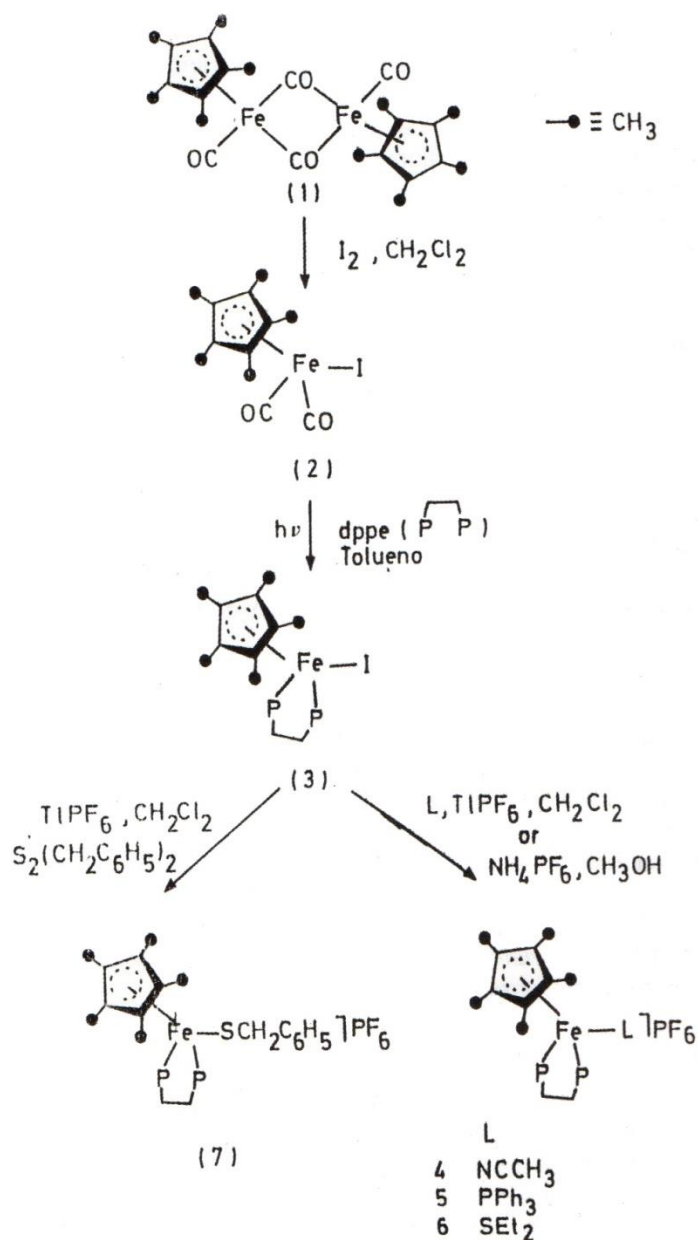
### INTRODUCTION

Whereas the cyclopentadienyl iron dicarbonyl series is one of the most widely studied organometallic families, [1] pentamethyl cyclopentadienyl ( $n^5\text{-C}_5\text{Me}_5\text{)=Cp}^*$ ) homologues have been less studied [2] Green et al. reported the first synthetic route to this series by metal vapor synthesis [2c]. Subsequently Lehmkühl [1f] et al. proposed another entry to bis(monophosphine) iron complexes of the type  $\text{Cp}^*\text{Fe}[(\text{P}(\text{CH}_3))_n(\text{C}_6\text{H}_5)_3]_2\text{Cl}$   $n = 0-3$ . More recently Astruc [2a,b] and Bercaw [2e] proposed a new route to pentamethyl cyclopentadienyl complexes starting from  $\text{CpFe}(\text{acac})$ , which can be obtained from  $\text{Fe}(\text{acac})_2$  and  $\text{Cp}^*\text{Li}$  [2d]. The last reported method to the series  $\text{Cp}^*\text{Fe}(\text{dppe})\text{X}$  involves the reaction of  $\text{Fe}(\text{dppe})\text{Cl}_2$  with  $\text{Cp}^*\text{Li}$

[2a] or with  $C_5Me_5H$  [2g] to give  $Cp^*Fe(dppe)Cl$ . Here we report a new synthetic entry to iron pentamethylcyclopentadienyl compounds and a general discussion about the influence of the methyl substitution ring using experimental and OM calculations.

## RESULTS AND DISCUSSION

We have previously reported [3] the synthesis of  $CpFe(dppe)I$  from  $CpFe(CO)_2I$  and dppe under Uv - radiation in toluene as solvent and also of their cationic  $[CpFe(dppe) L]PF_6$  from treatment with L in  $CH_2Cl_2$  in presence of  $TiPF_6$  [4]. An analogous treatment of  $Cp^*Fe(CO)_2I$  (1) with dppe in toluene under Uv - irradiation affords  $Cp^*Fe(dppe)I$  [2a] (2) which was conveniently isolated in 72 %, see Scheme 1.



The precursor (2) in spite of that has been used previously as starting reactive for to introduce the  $\text{Cp}^*\text{Fe}(\text{CO})_2$  fragment [5], surprisingly its has been poorly characterized [6]. The original cite of their synthesis by Moro- Oko Akita et al. [6] does not include an adequate characterization of this complex. Treatment of the commercially available  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$  with a excess of  $\text{I}_2$  in  $\text{CH}_2\text{Cl}_2$  at room temperature followed by elimination of excess of  $\text{I}_2$  with  $\text{Na}_2\text{S}_2\text{O}_3$  affords (2) as a black - red powder, which was recrystallized from a n-hexane/ $\text{CH}_2\text{Cl}_2$  solution as dark red crystals in a 91%. As expected two carbonyl bands were observed in their Ir spectrum, at 2000 and 1953  $\text{cm}^{-1}$ . The  $^{13}\text{C}$ -NMR exhibit the  $\text{Cp}^*$  signal at 97.9 ppm while that the carbonyl signal was clearly observed at 217 ppm. The signal methyl group of  $\text{Cp}^*$  ligand signal appears at 11.15 ppm.

The complex  $\text{Cp}^*\text{Fe}(\text{dppe})\text{I}$  react with neutral ligand L ( $\text{L} = \text{CH}_3\text{CN}, \text{PPh}_3, \text{SEt}_2$ ) in  $\text{CH}_2\text{Cl}_2$  and in presence of  $\text{TiPF}_6$  to give the series of complexes  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{L}]\text{PF}_6$ . The complex  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{N}(\text{CCH}_3)_3]\text{PF}_6$  have been previously prepared by reaction of  $[\text{Cp}^*\text{Fe}(\text{CH}_3\text{CN})_3]^+$  with dppe [2b] and starting from  $\text{Cp}^*\text{Fe}(\text{dppe})\text{Cl}$  [2a].

On the other hand the reaction of  $\text{Cp}^*\text{Fe}(\text{dppe})\text{I}$  with  $\text{S}_2(\text{CH}_2\text{C}_6\text{H}_5)_2$  in  $\text{CH}_3\text{OH}$  and in presence of  $\text{NH}_4\text{PF}_6$  yield the new iron(III)-thiolate  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{S}-\text{CH}_2\text{C}_6\text{H}_5]\text{PF}_6$ .

The new complexes  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{SEt}_2]\text{PF}_6$ ,  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{PPh}_3]\text{PF}_6$  are paramagnetic and were characterized by elemental analysis, Ir, Uv-visible and magnetic method.  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra of the complexes give rise to broad (almost missing in some cases) and/or shifted signal. As example in figure 1

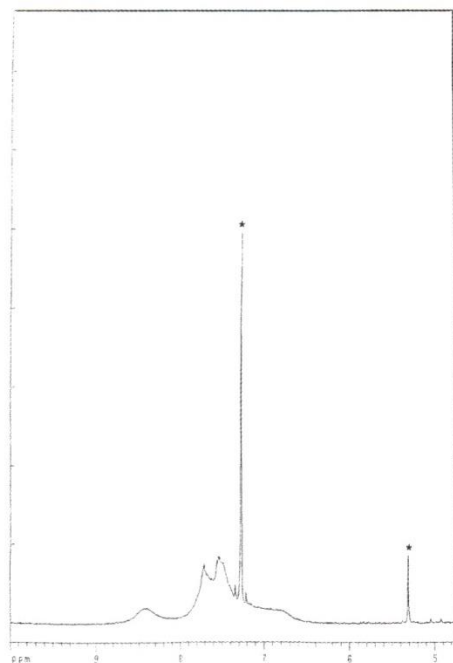
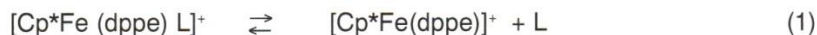


Figure 1.  $^1\text{H}$ -NMR spectrum of  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{SEt}_2]\text{PF}_6$  in the aromatic region in  $\text{CDCl}_3$  solution. The asterisk denote the signal of  $\text{CDCl}_3$  and of the  $\text{CH}_2\text{Cl}_2$  of crystallization.

in shown the  $^1\text{H}$ -NMR spectrum of  $[\text{Cp}^*\text{Fe}(\text{dppe})(\text{SEt}_2)]\text{PF}_6$ . On the other hand their  $^{31}\text{P}$ -NMR spectrum exhibits the dppe signal shifted at 28.95 ppm respect to the normal position for  $\text{Cp}^*\text{Fe}(\text{dppe})\text{X}$  or  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{L}]\text{PF}_6$  around 90 ppm [2a]. The signal of  $\text{PF}_6$  appears very weak (due to broadening probably) at - 142 ppm. The rare paramagnetism exhibit by 18 electron  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{L}]^+$  species in solution have been attributed to the equilibrium.



to generate the 16e specie  $\text{Cp}^*\text{Fe}(\text{dppe})^+$  which is known to be paramagnetic [8]. Recent theoretical calculation [9] found a triplet ground state for  $\text{Cp}^*\text{Fe}(\text{dppe})^+$  species. However the solid state paramagnetism exhibit by the 18e complexes  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{SEt}_2]\text{PF}_6$  and  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{PPh}_3]\text{PF}_6$ , neither the previously



reported  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{OCMe}_2]\text{PF}_6$  and  $\text{Cp}^*\text{Fe}(\text{dppe})\text{OSO}_2\text{CF}_3$  can not be explained by the theoretical results. The paramagnetic behavior exhibit by the complexes  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{PPh}_3]\text{PF}_6$  and  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{SEt}_2]\text{PF}_6$  in solution can be explained by the equilibrium (eq.1); however the origin of the paramagnetism in solid state is not clear. The paramagnetism exhibited by these species it appears to be associated in same unclear manner to the presence of pentamethylcyclopentadienyl groups because  $[\text{CpFe}(\text{dppe})\text{L}]\text{PF}_6$  complexes are generally diamagnetic. Consistently with this, the complex  $[\text{CpFe}(\text{dippe})\text{NCCH}_3]\text{PF}_6$  is diamagnetic while the complex  $[\text{Cp}^*\text{Fe}(\text{dippe})\text{NCCH}_3]^+$  is paramagnetic dippe = 1,2 Bis (diisopropylphosphine) ethane.

The high magnetic moment exhibits by the complex  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{SCH}_2\text{C}_6\text{H}_5]\text{PF}_6$  can be due to a ground state of Fe(III) high spin situation. In contrast the complexes  $[\text{Cp}^*\text{Fe}(\text{dppe})\text{SR}]\text{PF}_6$  are paramagnetic ( $\mu = 1,6\text{-}2,4\text{BM}$ ) with a low spin ground state Fe(III). Most detailed temperature variable susceptibility measurements for all the paramagnetic complexes are in course.

Uv-visible spectra of the complexes (2)-(7) exhibit a similar absorption patterns to that  $\text{Cp}^*\text{Fe}(\text{PMe}_3)_2\text{CH}_3$  and  $\text{Cp}^*\text{Fe}(\text{PMe}_3)_2\text{Cl}$  previously assigned [2e], however a less defined maximal were observed. The band around 450nm and some unresolved band in the range 450-600nm were observed.

#### Comparison of the $\text{CpFe}(\text{dppe})$ and $\text{Cp}^*\text{Fe}(\text{dppe})$ fragments.

Several experimental evidences have pointed the most electron donor character of the  $\text{C}_5\text{Me}_5$  ring than the  $\text{C}_5\text{H}_5$ , leading to most electron rich character to  $\text{C}_5\text{Me}_5\text{Fe}(\text{dppe})^+$  fragment than  $\text{C}_5\text{H}_5\text{Fe}(\text{dppe})^+$ . In fact as is shows in Table I the half wave potential oxidation is lower for the  $\text{C}_5\text{Me}_5$  series than the unsubstituted  $\text{C}_5\text{H}_5$ , indicating an iron with greatest electron density.

TABLE I

Comparison of Oxidation Potential for  $\text{CpFe}(\text{dppe})^+$  and their Methylated Analogue  $\text{Cp}^*\text{Fe}(\text{dppe})^+$

Complex	E°p <sup>a</sup>			
	Cp	Reference	Cp*	Reference
Fe (dppe)Cl	0.08	10	- 0.28	2 a
Fe (dppe) I	0.15	10	- 0.22	2 a
Fe (dppe) H	-0.08	10	- 0.43	2 a
Fe (dppe)CH <sub>3</sub>	-0.26	10	- 0.58	2 a
Fe (dppe) Ph	0.08	11	- 0.13	11
Fe (dppe) Bu <sup>t</sup>	-0.06	11	- 0.28	11

<sup>a</sup> in  $\text{CH}_2\text{Cl}_2$  solution, using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Values Vs SCE.

On the other, hand Mössbauer data also indicate a most high electron density on the iron atom for the Cp\* derivative compared with their Cp counter parts. As shown in Table II, the Cp\* derivative produces a most lower isomeric shifts which can be interpreted as a most high electron density around the iron atom.

TABLE II

Comparison of Mössbauer Parameters for CpFe(dppe)+ and Cp\*Fe(dppe)+

Complex	$\sigma^a$ ; $\Delta E_q^b$	$\sigma$ ; $\Delta E_q$	Reference
	Cp	Cp*	
Fe (dppe) H	0.50 - 1.86	0.20 ; 2.08	2 a
Fe (dppe) CH <sub>3</sub>	0.53 - 1.82	0.15 ; 1.95	2 a

a isomeric shift,  $\sigma$  in mm/s, relative to sodium nitropruside at room temperature.

b quadrupole splitting,  $\Delta E_q$  in mm/s.

For to confirm this we have performed extended Hückel (EH) calculation on the models Cp\*Fe(PH<sub>3</sub>)<sub>2</sub><sup>+</sup> and CpFe(PH<sub>3</sub>)<sub>2</sub><sup>+</sup>. As in shown in figure 2 the main changes on going from Cp to Cp\* iron derivatives are the increasing in the HOMO - LUMO level, the HOMO-LUMO gap as well as the increasing of the electron density from - 0.5 to - 1.4.

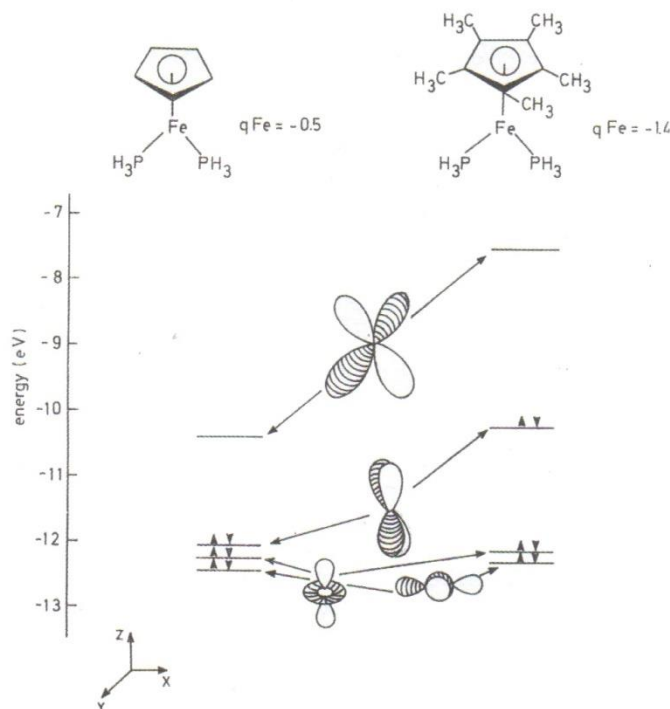


Figure 2. OM diagram and atomic charges for the fragment models CpFe(PH<sub>3</sub>)<sub>2</sub><sup>+</sup> and Cp\*Fe(PH<sub>3</sub>)<sub>2</sub><sup>+</sup>



## EXPERIMENTAL

All reactions were carried out under purified N<sub>2</sub> or Ar using standard Schlenk techniques and the solvent used (methanol, dichloromethane, diethyl ether and n-hexane) were appropriately distilled and dried before use. [Cp\*Fe(CO)<sub>2</sub>]<sub>2</sub> (Strem), I<sub>2</sub>, [NBu<sub>4</sub>]<sub>2</sub>PF<sub>6</sub>, NH<sub>4</sub>PF<sub>6</sub> and dppe (Aldrich) were used as received. TlPF<sub>6</sub> (caution! Thallous salts are very poisonous and should be handled with precaution) was prepared from Tl<sub>2</sub>CO<sub>3</sub> and HPF<sub>6</sub>. IR spectra were recorded as KBr pellets on a FT-Bruker 66V spectrometer. NMR spectra were run in CD<sub>2</sub>Cl<sub>2</sub> or (CD<sub>2</sub>)<sub>2</sub>CO solution at room temperature on a Bruker AMX 300 spectrometer with TMS(H) δ = 0.0 ppm as internal standard or 85% H<sub>3</sub>PO<sub>4</sub> and downfield positive to the reference as external standard for the <sup>31</sup>P measurements. UV-Visible spectra were run on a Varian DMS-9 spectrophotometer with 1 cm optical path cuvettes. Magnetic measurements were carried out by a Gouy's method at room temperature (25°C) using a Johnson Matthey Balance, using mercury tetrathiocyanate cobaltate(II) as calibrant.

### Reaction of [Cp\*Fe(CO)<sub>2</sub>]<sub>2</sub> with I<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

A mixture of 0.5 g (1.0 mmol) of [Cp\*Fe(CO)<sub>2</sub>]<sub>2</sub> and I<sub>2</sub> 1.0 g (3.9 mmol) in 50 ml dichloromethane was stirred at room temperature for 1h. The solution was filtered and washed three times with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2.5g in 50ml H<sub>2</sub>O) and the organic phase was treated with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered through celite. The red solution was then evaporated to dried under reduced pressure. The resulting solid was recrystallized from of a n-hexane-diethyl ether 1:1 mixture to give (2) as red-dark crystal. Yield 0.69 g; 91%. Anal. Found.: C 37.42, H 3.93. Calc. for C<sub>12</sub>H<sub>21</sub>O<sub>2</sub>Fe C 38.52, H 4.01. Ir(KBr, pellets): ν(CO):2000, 1953

### Reaction of Cp\*Fe(CO)<sub>2</sub>I with dppe in Toluene.

A solution of Cp\*Fe(CO)<sub>2</sub>I 0.5 g (1.33mmol) and dppe 0.6 g (0.15mmol) were irradiated in toluene(50ml) for 8hr. After this, the solution was filtered through celite and the solution evaporated to dried in a rotavapor. The resulting red dark solid was redissolved in a n-hexane-diethyl ether 1:1 mixture and placed in the freezer for overnight to give (3) as red-brown solid. Yield 0.62 g, 72%. The complex Cp\*Fe(dppe)I was characterized by Ir and NMR spectroscopy by comparison with an authentically sample [2a].

### Reaction of Cp\*Fe(dppe)I with CH<sub>3</sub>CN in presence of NH<sub>4</sub>PF<sub>6</sub>.

Cp\*Fe(dppe)I 0.08 g (0.11 mmol) was stirred with 10ml of a mixture CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> in presence of NH<sub>4</sub>PF<sub>6</sub> 0.04 g (0.2 mmol) were stirred for 22h. at room temperature. The solution was evaporated under vacuum and the solid residue extracted with dichloromethane and filtered through Celite. Then the solution was evaporated and the red solid washed with diethyl ether. and dried under reduced pressure. Yield 0.05g 63%. The complex [Cp\*Fe(dppe)(CH<sub>3</sub>CN)]PF<sub>6</sub> was characterized by Ir and NMR spectroscopy by comparison with an authentically sample [2a,b].

### Reaction of Cp\*Fe(dppe)I with CH<sub>3</sub>CN in presence of TlPF<sub>6</sub>.

Cp\*Fe(dppe)I 0.08 g (0.11 mmol) was stirred with 10ml of CH<sub>3</sub>CN in presence of TlPF<sub>6</sub> 0.08g (0.22 mmol) were stirred for 27h. at room temperature. The solution was filtered through Celite and the solvent was evaporated to dried. The red solid washed with diethyl ether. and dried under reduced pressure. Yield 0.05g 63%. The complex [Cp\*Fe(dppe)(CH<sub>3</sub>CN)]PF<sub>6</sub> was characterized by Ir and NMR spectroscopy by comparison with an authentically sample [2a,b]

### Reaction of Cp\*Fe(dppe)I with PPh<sub>3</sub> in presence of NH<sub>4</sub>PF<sub>6</sub>.

Cp\*Fe(dppe)I 0.11g (0.15 mmol) and 0.08g (0.3mmol) PPh<sub>3</sub> in presence of NH<sub>4</sub>PF<sub>6</sub> 0.02 g (0.24 mmol) in CH<sub>3</sub>OH (20 ml) were stirred for 21 h. The solvent was evaporated under vacuum and the solid residue extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through celite. The solvent was eliminated and the solid residue washed with ether and dried under reduced pressure give (5) as a red -brown solid. Yield 0.08g 53% μ<sub>eff</sub>=1.58 BM. Anal. Found.: C 62.72, H 4.96. Calc. for C<sub>61</sub>H<sub>54</sub>F<sub>6</sub>P<sub>4</sub>Fe•3CH<sub>2</sub>Cl<sub>2</sub> C 61.41, H 4.79.

Ir(KBr, pellets): 1117 δ(CH)<sub>p</sub>: 695 δ(CH)<sub>op</sub>: 843 (PF<sub>6</sub>).



**Reaction of Cp\*Fe(dppe)I with PPh<sub>3</sub> in presence of TlPF<sub>6</sub>.**

Cp\*Fe(dppe)I 0.14g (0.19 mmol) and 0.08g (0.3mmol) PPh<sub>3</sub> in presence of TlPF<sub>6</sub> 0.14 g (0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) were stirred for 19 h. The solution was filtered through celite and the solvent was evaporated under vacuum and the solid residue washed with ether and dried under reduced pressure. Yield 0.08g, 53%. Spectroscopic data were similar to that obtained for the complex [Cp\*Fe(dppe)PPh<sub>3</sub>][PF<sub>6</sub>] obtained by the above method.

**Reaction of Cp\*Fe(dppe)I with S(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> in presence of TlPF<sub>6</sub>.**

Cp\*Fe(dppe)I 0.10g (0.13mmol) and 0.08g (0.93mmol) S(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> in presence of TlPF<sub>6</sub> 0.14 g (0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) were stirred for 22 h. The red solution was filtered through celite and the solvent was evaporated under vacuum and the solid residue washed with ether and dried under reduced pressure to give (6) as brown solid. Yield 0.05g 56%.  $\mu_{\text{eff}} = 1.34$  BM. Anal. Found.: C 50.57, H 4.51. Calc. for C<sub>40</sub>H<sub>49</sub>F<sub>6</sub>S P<sub>3</sub>Fe • 2CH<sub>2</sub>Cl<sub>2</sub> C 50.72, H 4.93.

Ir(KBr, pellets): 1120  $\delta(\text{CH})_{\text{ip}}$ , 695  $\delta(\text{CH})_{\text{op}}$ , 843 (PF<sub>6</sub>).

**Reaction of Cp\*Fe(dppe)I with S<sub>2</sub>(CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> in presence of TlPF<sub>6</sub>.**

Cp\*Fe(dppe)I 0.1g (0.14 mmol) and 0.05g (0.2 mmol) S<sub>2</sub>(CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> in presence of TlPF<sub>6</sub> 0.02 g (0.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) were stirred for 22 h at room temperature. The solution was filtered through celite, and the solvent eliminated in vacuum. The solid residue was washed with ether and dried under reduced pressure, to give (6) as a gray-brown solid. Yield 0.09 g, 75%.  $\mu_{\text{eff}} = 6.36$  BM Ir(KBr, pellets) 1123  $\delta(\text{CH})_{\text{ip}}$ , 695  $\delta(\text{CH})_{\text{op}}$ , 843 (PF<sub>6</sub>).

**Calculations.** EH. MO calculations were carried out using the modified Wolfsberg-Helmholz formula [13]. The atomic parameters for the elements involved in our calculations have been previously reported [14]. The bonding distances used in the models CpFe(PH<sub>3</sub>)<sub>2,3</sub><sup>+</sup> and Cp\*Fe(PH<sub>3</sub>)<sub>2</sub><sup>+</sup> were similar to those for the crystal structure of [CpFe(dppe)L]<sup>+</sup> as well as [Cp\*Fe(dppe)]<sup>+</sup> derivatives [8,9]. For the two fragments the basic parameters were: bond distances Fe-P 2.17 Å, Fe-C 2.08 Å, bond angle P-Fe-P 98.9°. MO drawing were generated with the use of the program CACAO [15].

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