



# Synthesis and characterization of amine complexes of the cyclopentadienyliron dicarbonyl complex cation, $[\text{Cp}(\text{CO})_2\text{Fe}]^+$

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## ABSTRACT

The organometallic Lewis acid,  $[\text{CpFe}(\text{CO})_2]^+\text{BF}_4^-$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) reacts with excess dry diethyl ether at low temperatures to form the labile complex  $[\text{CpFe}(\text{CO})_2(\text{Et}_2\text{O})]^+\text{[BF}_4]^-$  (**1**) which is stable at low temperatures and has been fully characterized. Complex **1** in turn reacts with 1-aminoalkanes and  $\alpha,\omega$ -diaminoalkanes to form new complexes of the type  $[\text{CpFe}(\text{CO})_2\text{NH}_2(\text{CH}_2)_n\text{CH}_3]\text{BF}_4$  ( $n = 2\text{--}6$ ) (**2**) and  $[\{\text{CpFe}(\text{CO})_2\}_2\mu\text{-(NH}_2(\text{CH}_2)_n\text{NH}_2)\}(\text{BF}_4)_2$  ( $n = 2\text{--}4$ ) (**3**), respectively. These complexes have been fully characterized and the mass spectral patterns of complexes **2** are reported. The structures of compounds **2a** ( $n = 2$ ) and **2b** ( $n = 3$ ) have been confirmed by single crystal X-ray crystallography. The single crystal X-ray diffraction data show that complex **2a**,  $[\text{CpFe}(\text{CO})_2\text{NH}_2(\text{CH}_2)_2\text{CH}_3]\text{BF}_4$ , crystallizes in a triclinic  $P\bar{1}$  space group while **2b**,  $[\text{CpFe}(\text{CO})_2\text{NH}_2(\text{CH}_2)_3\text{CH}_3]\text{BF}_4$ , crystallizes in an orthorhombic  $Pca2_1$  space group with two crystallographically independent molecular cations in the asymmetric unit. Furthermore, the reaction of **1** with 1-alkenes gives the  $\eta^2$ -alkene complexes in high yield.

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## 1. Introduction

The cationic complexes of type,  $[\text{CpFe}(\text{CO})_2\text{L}]^+$  ( $\text{L}$  = labile ligand) [1–4] are an important class of transition metal compounds that have been extensively utilized in synthesis [2,4–21] and catalysis [3,14,22–33]. A particular example is the ethereal complex,  $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$  [34] in which the labile tetrahydrofuran (THF) is coordinated to the metal centre through the oxygen atom. This complex has been proven to be an essential precursor in the synthesis of various cyclopentadienyliron complexes [4,10–13,15–20,35], as well as catalysts in various organic syntheses such as the [2+2] cycloaddition of alkenes [36], Diels–Alder reactions [37,38], cyclopropanation [27,31–33], epoxidation [29,30] and aziridination [25–28], among others [3,22–24,27,29,39]. In all these reactions THF is easily displaced by the desired substrate to form either the desired intermediate or desired end product.  $[\text{CpFe}(\text{CO})_2(\text{acetone})]^+$  is another complex with an oxygen-bonded ligand which has also been extensively used in the synthesis of both neutral and cationic complexes based on the  $\text{CpFe}(\text{CO})_2$  moiety [2,5–9,21,40,41].

Although diethyl ether has a higher donor number (0.49) than acetone (0.44) [42,43], the analogous diethyl ether complex,  $[\text{CpFe}(\text{CO})_2(\text{OEt}_2)]^+$  has not been previously reported. However,

the phosphine complex,  $[\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{Et}_2\text{O})][\text{BAR}'_4]$  ( $\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ) has been synthesized by protonation of  $[\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CH}_3]$  using  $\text{H}(\text{OEt}_2)\text{BAR}'_4$  at  $-80^\circ\text{C}$  [44]. The dimethyl ether complex,  $[\text{CpFe}(\text{CO})_2(\text{OMe}_2)]\text{BF}_4$ , and its reaction with acetonitrile to give  $[\text{CpFe}(\text{CO})_2(\text{NCCH}_3)]\text{BF}_4$  has also been reported [1].  $[\text{CpFe}(\text{CO})_2(\text{OMe}_2)]\text{BF}_4$  degraded within a few hours even when stored under vacuum at  $-20^\circ\text{C}$ . This thermal instability made the complex difficult to handle, leading to its limited application as a starting material for  $\text{CpFe}(\text{CO})_2$  complexes. Diethyl ether complexes of other cyclopentadienylmetal carbonyls such as Mn [45], Re [45], Mo [46], and W [46] are known.

There have been very few reports on aminoalkane complexes of cyclopentadienyliron dicarbonyl in which the aminoalkane is coordinated to the metal *via* the nitrogen atom. Reported cases include a reaction between  $[\text{CpFe}(\text{CO})_2(\eta^2\text{-Et-C}\equiv\text{C-Et})]\text{BF}_4$  and 2-amino-propane,  $(\text{NH}_2\text{Pr}^i)$ , to yield the black solid  $[\text{CpFe}(\text{CO})_2(\text{NH}_2\text{Pr}^i)]^+$  [47]. This is in sharp contrast to the yellow solid complex  $[\text{CpFe}(\text{CO})_2(\text{NH}_2\text{Pr}^n)]^+$  reported herein. The reaction between  $[\text{CpFe}(\text{CO})_2(\eta^2\text{-Ph-C}\equiv\text{C-Ph})]\text{BF}_4$  and 2-amino-2-methylpropane to give  $[\text{CpFe}(\text{CO})_2(\text{NH}_2\text{Bu}^t)]^+$  was also reported [47] but no physical or analytical details were given.

Cyclopentadienyliron dicarbonyl complexes of secondary [48], tertiary [35] and cyclic [49] amines are established. Reaction of the acetone complex  $[\text{CpFe}(\text{CO})_2(\text{acetone})]^+$  with half a molar equivalent of either di(tertiary phosphine) [9,50], 2,5-dithiahexane or pyrazine [9] have been reported to yield bimetallic complexes in which the ligand acts as a bridge between two metal centers.

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However, to our knowledge, there are no reports on diaminoalkane complexes of iron in which the diaminoalkane links two iron centers.

Hence, in this paper we report the synthesis and characterization of  $[\text{CpFe}(\text{CO})_2(\text{Et}_2\text{O})][\text{BF}_4]^-$  **1** and its reactions with a series of 1-aminoalkanes, and  $\alpha,\omega$ -diaminoalkanes to form new complexes,  $[\text{CpFe}(\text{CO})_2\text{NH}_2(\text{CH}_2)_n\text{CH}_3]\text{BF}_4$  ( $n = 2-6$ ) (**2**) and  $[\{\text{CpFe}(\text{CO})_2\}_2\mu\text{-(NH}_2(\text{CH}_2)_n\text{NH}_2)\}(\text{BF}_4)_2$  ( $n = 2-4$ ) (**3**), respectively.

## 2. Results and discussion

### 2.1. Synthesis of $[\text{CpFe}(\text{CO})_2(\text{Et}_2\text{O})]\text{BF}_4$ (**1**)

Reaction of  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$  with a large excess of diethyl ether at low temperatures results in the immediate formation of the diethyl ether complex **1** in excellent yield. The product precipitates and is easily isolated by filtration under inert atmosphere. Reaction of  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$  with two equivalents of diethyl ether in  $\text{CH}_2\text{Cl}_2$  gave low yields (20%) of **1** and was difficult to isolate in pure form. It thus appears that the rate of reaction is partially dictated by the amount of diethyl ether present.

Compound **1** is a moisture sensitive red powder, insoluble in hexane, sparingly soluble in chloroform, but very soluble in acetone and dichloromethane. The complex can be stored in anhydrous atmosphere at  $-6^\circ\text{C}$  for at least three months without any degradation.

#### 2.1.1. Characterization

The IR spectrum of the complex **1** shows two carbonyl absorption peaks at 2063 and  $2010\text{ cm}^{-1}$ . These suggest a weak synergic interaction between the iron center and the carbonyl due to reduced electron density on the metal centre which is as a result of the coordination of the ethereal group. A medium and two weak intensity bands due to the symmetrical and asymmetrical C–H stretching modes were observed in the region between 2990 and  $2850\text{ cm}^{-1}$ . Two other medium intensity bands due to C–H rocking and C–O stretching were observed at 1392 and  $1286\text{ cm}^{-1}$ , respectively.

The  $^1\text{H}$  NMR spectrum of **1** recorded in  $\text{CD}_2\text{Cl}_2$  at  $-26^\circ\text{C}$  exhibited a Cp peak at 5.42 ppm and a characteristic quartet at 3.47 ppm and a triplet at 1.09 ppm assignable to  $\text{CH}_2$  and  $\text{CH}_3$ , respectively, of the two identical ethyl groups in coordinated diethyl ether. The distinct quartet at 3.43 ppm and a triplet at 1.15 ppm assignable to the  $\text{CH}_2$  and  $\text{CH}_3$  protons, respectively, of the two identical ethyl groups in uncoordinated diethyl ether were also observed. The free diethyl ether was displaced from **1** by water molecules in the  $\text{CD}_2\text{Cl}_2$  leading to the more stable aqua complex,  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{OH}_2)]^+$  [51]. The aqua complex is responsible for a Cp resonance peak observed at 5.28 ppm and a peak due to coordinated water observed at 2.33 ppm.

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$  at  $-26^\circ\text{C}$ ) spectra also showed separate resonance peaks corresponding to coordinated and uncoordinated diethyl ether. The carbons of the coordinated diethyl ether methylene and methyl groups appear at 78.93 and 13.38 ppm, respectively, while resonance peaks corresponding to uncoordinated diethyl ether were observed at 65.97 and 15.23 ppm, respectively. The spectrum exhibited two Cp peaks at 85.95 and 85.26 ppm corresponding to the Cp carbons of the etherate and aqua complexes, respectively. The carbonyl peak of the etherate complex was observed at 209.59 ppm while that of the aqua complex appeared at 209.10 ppm. The assignment was done by comparing the spectrum with that of the isolated aqua complex.

Similarly, the proton NMR spectrum of compound **1** recorded in acetone- $\text{d}_6$  at  $-30^\circ\text{C}$  gave a quartet at 3.67 and a triplet at 1.16 ppm assignable to the  $\text{CH}_2$  and  $\text{CH}_3$  protons of the identical

ethyl groups in coordinated diethyl ether, respectively. Separate resonance peaks corresponding to the protons of the methylene and methyl groups of uncoordinated diethyl ether were observed at 3.39 and 1.10 ppm, respectively. The uncoordinated diethyl ether in this case had been displaced from the coordination center by acetone, leading to the known acetone complex,  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{OCMe}_2)]^+$  [52]. The chemical shift due to the Cp protons of the etherate complex was observed at 5.78 ppm, while a separate resonance peak assignable to the Cp protons of the acetone complex was observed at 5.71 ppm. When wet acetone- $\text{d}_6$  was used, a peak due to the Cp protons of the aqua complex,  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{OH}_2)]^+$ , was observed at 5.23 ppm.

The intensity of the peaks at 5.78, 3.67 and 1.16 ppm corresponding to the etherate complex diminished as the temperature was raised from  $-30$  to  $-10^\circ\text{C}$  and eventually disappeared at higher temperature. Conversely, the intensity of the resonance peaks at 5.71, 3.39 and 1.10 corresponding to the acetone complex increased and dominated at  $-5^\circ\text{C}$ . In general, the proton NMR spectrum of compound **1** shows that diethyl ether is coordinated to the metal centre in the coordination sphere and is not just a solvent molecule trapped within the crystal lattice.

### 2.2. Reaction studies

The poor electron donating nature of diethyl ether makes complex **1** very electrophilic and thus it reacts with a wide range of nucleophiles.

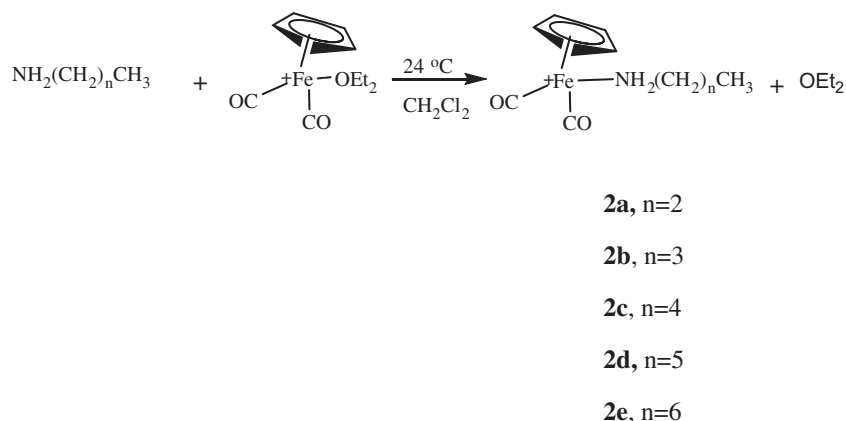
#### 2.2.1. Reactions of **1** with *n*-aminoalkanes

Equimolar quantities of **1** and 1-aminoalkanes react smoothly at room temperature in  $\text{CH}_2\text{Cl}_2$  to give a series of the new complexes, **2**, via displacement of diethyl ether according to Scheme 1.

The reaction time of **1** with 1-aminoalkanes at room temperature is chain length dependent. The longer aminoalkanes, though stronger Lewis bases than the shorter ones, required longer reaction times, probably due to steric effects. For example, while the reactions of **1** with 1-aminopropane and 1-aminobutane took less than 2 h, its reaction with longer aminoalkanes took 3–6 h. All these complexes were obtained in good yields as yellow crystalline solids after purification by recrystallization. However, the yield diminished as the aminoalkane chain became longer with concomitant increase in  $[\text{CpFe}(\text{CO})_2]_2$  as side product. The complexes are soluble in chlorinated solvents, methanol, acetone, acetonitrile and water, but sparingly soluble in hexane and diethyl ether. Thus they were easily purified by recrystallization from either hexane or diethyl ether without a significant change in yield. They are moderately air stable, both in solid state and solution for short periods of time. Their melting points were sharp and generally decreased with increase in alkyl chain length.

**2.2.1.1. Characterization.** The aminoalkane complexes have been fully characterized by elemental analysis, IR spectroscopy,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy (Sections 4.3–4.7), as well as mass spectroscopy. The crystal structures of **2a** and **2b** have also been determined by single crystal X-ray crystallography.

The IR spectra of the aminoalkane complexes show two very strong absorption bands in the  $\nu(\text{CO})$  region in the range 1993– $2061\text{ cm}^{-1}$ , which are assignable to the two terminal carbonyls. The positions of the  $\nu(\text{CO})$  absorption bands are at lower wavenumbers relative to those of **1**. This is consistent with the increase in electron density on the iron center (caused by the coordinated aminoalkane group), which results in increased back-bonding to the carbonyl groups, and hence a lower  $\nu(\text{CO})$  absorption frequency. A slight shift towards lower wavenumbers is observed as the carbon chain becomes longer because the nucleophilicity of aminoalkanes increases with increase in chain length [53,54].



**Scheme 1.** Preparation of aminoalkane complexes.

The complexes also show a medium split absorption band in the  $\nu(\text{N-H})$  region in the range  $3278\text{--}3313\text{ cm}^{-1}$  assignable to the N-H stretching mode. A single absorption band due to the N-H bending mode is observed in the range  $1605\text{--}1620\text{ cm}^{-1}$ .

The  $^1\text{H}$  NMR data for the aminoalkane complexes were recorded in  $\text{CDCl}_3$  and the assignments made by help of 2D NMR spectra. The proton spectrum of each complex shows a characteristic singlet assignable to the two amine protons at *ca.* 2.90 ppm, which is a down-field shift by *ca.* 1.80 ppm relative to free aminoalkane (1.10 ppm). This shift can be attributed to the deshielding of the amine proton as nitrogen donates its lone pair to the metal and partially to the presence of a hydrogen bond as found in the structure determinations of compounds **2a** and **2b**. The spectra also exhibited a sharp singlet at *ca.* 5.27 ppm due to the five equivalent cyclopentadienyl protons. As the chain becomes longer the resonance peaks due to the  $\gamma$ ,  $\delta$ ,  $\epsilon$  and  $\omega$  carbon protons (Fig. 1) overlapped at *ca.* 1.20 ppm suggesting that the influence of the amine group attached to the metal on the chain end is minimal or absent.

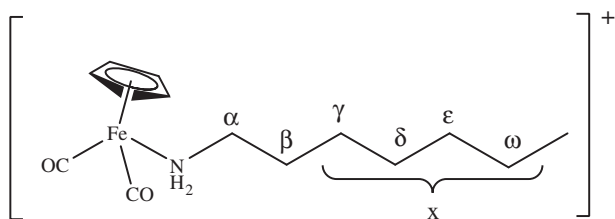
The  $^{13}\text{C}$  NMR spectra for these complexes were recorded in  $\text{CDCl}_3$  and assignments made by comparison with the data reported for the cationic complexes,  $[\text{CpM}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHR})]^+$  [13] and  $[\{\text{CpM}(\text{CO})_2\}_2(\text{CH}_2=\text{CH}(\text{CH}_2)_n)]^+$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) [55] as well as HSQC and HMBC experiments. The Cp singlets of these complexes at ca. 86 ppm are not affected by the increase of the polymethylene chain length of the aminoalkane. Similarly, chain

length does not appear to affect the position of the CO peaks. However, there is a slight down-field shift of the methylene and methyl resonances as the chain grows longer. This is probably due to a deshielding effect caused by increased charge transfer by the alkyl group to the amine group.

The electrospray mass spectra of the series **2a–2e** were recorded and are summarized in Table 1. All these complexes show a similar fragmentation pattern. Thus loss of BF<sub>4</sub> leads to the base peak of each aminoalkane complex ion, [ $\eta^5$ -CpFe(CO)<sub>2</sub>(NH<sub>2</sub>(CH<sub>2</sub>)<sub>*n*</sub>-CH<sub>3</sub>)]<sup>+</sup> (parental molecular ion without counteranion), followed by successive loss of the carbonyl groups to give [CpFe(NH<sub>2</sub>(CH<sub>2</sub>)<sub>*n*</sub>-CH<sub>3</sub>)]<sup>+</sup>. Peaks due to [CpFe(CO)<sub>2</sub>]<sup>+</sup> (*m/e* 177) or [CpFe]<sup>+</sup> (*m/e* 121) were not observed. However, peaks due to the protonated aminoalkane were observed and their intensity increased with hydrocarbon chain length. This is not unexpected since aminoalkanes are strong Lewis bases due to inductive and polarization stabilization effects of the alkyl group directly bonded to the nitrogen atom [53,54].

**2.2.1.2. Structural analysis of 1-aminoalkane complexes.** Single crystal X-ray diffraction data were obtained for complexes **2a** and **2b**. Crystals of both complexes were grown from CHCl<sub>3</sub> solutions layered with hexane. Complex **2a** crystallized in a triclinic *P1* space group, with one molecular cation and a counterion in each asymmetric unit, while **2b** crystallized as orange needles in the orthorhombic *Pca*2<sub>1</sub> space group, with two independent molecular cations and two anions in each asymmetric unit. The molecular structures of **2a** and **2b** are shown in Figs. 2 and 3, respectively. In both structures the Fe atom is coordinated in pseudo-octahedral 3-legged piano-stool fashions, with the η<sup>5</sup>-coordinated cyclopentadienyl ligand occupying three apical positions while the two carbonyl groups and the alkylamine ligand occupy basal positions. Crystal data and structure refinement information for compounds **2a** and **2b** are summarized in Table 2.

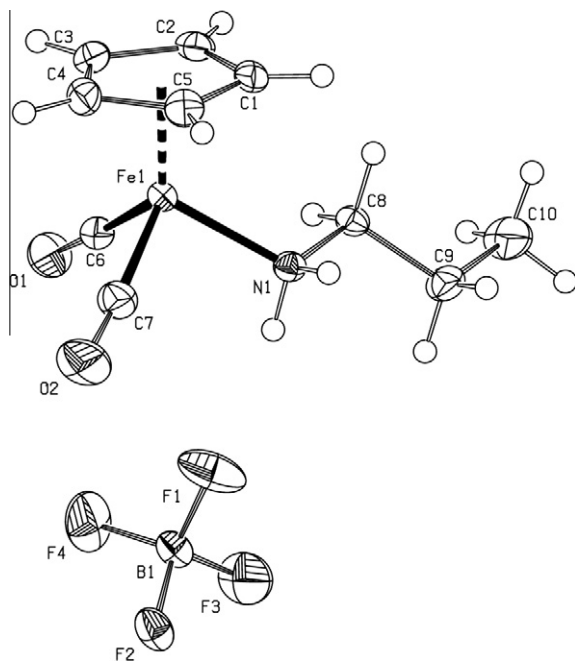
The coordination by alkylamine occurs *via* a single  $\sigma$ -bond through donation of the electron pair on the  $sp^3$ -hybridized orbital of nitrogen to the metal. In the crystal, both **2a** and **2b** adopt



**Fig. 1.** General structure of the aminoalkane complexes ( $n = 6$  in this instance).

**Table 1**  
Mass spectral data for aminoalkane complexes  $[\text{CpFe}(\text{CO})_2(\text{NH}_2(\text{CH}_2)_n\text{CH}_3)]\text{BF}_4$  ( $n = 2-6$ ).

Ion	Relative intensity (%)				
	<b>2a</b> ( <i>m/e</i> )	<b>2b</b> ( <i>m/e</i> )	<b>2c</b> ( <i>m/e</i> )	<b>2d</b> ( <i>m/e</i> )	<b>2e</b> ( <i>m/e</i> )
M <sup>+</sup>	100 (235.7)	100 (249.7)	100 (263.8)	57.5 (277.7)	13.7 (291.7)
[M–CO] <sup>+</sup>	15.4 (207.7)	16.2 (221.7)	19.4 (235.8)	6.8 (249.7)	0
[M–2CO] <sup>+</sup>	23.1 (179.7)	23.0 (193.7)	37.0 (207.8)	37.0 (221.7)	5.5 (235.6)
[(M–Fp)+H] <sup>+</sup>	0.0	2.7 (73.8)	19.4 (87.8)	100 (101.7)	100 (115.7)



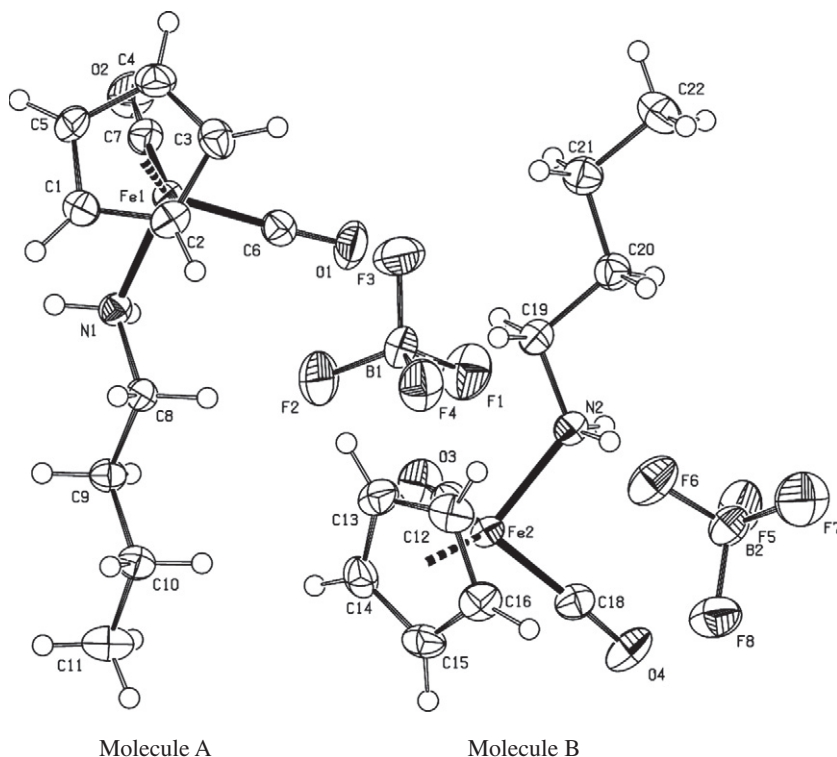
**Fig. 2.** The molecular structure of **2a** showing atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

energetically favoured gauche type conformation (Fig. 4a and b) in which the  $\alpha$ -carbon of the alkylamine lies in a conformation between a CO ligand and the cyclopentadienyl ring. This is in agreement with the IR data that shows two peaks for the symmetric and anti-symmetric stretches of the two nominally *cis*-CO ligands. Fig. 5a and b show crystal packing and hydrogen bonds in the crystals of **2a** and **2b**, in which molecules are arranged in layers.

Alkyl chains of molecules of **2a** are oriented in the same direction within each layer, while those of **2b** are oriented in opposite direction within the same layer as well as in alternating layers. This mode of packing is observed in related structures [47,56] which aims to minimize steric repulsion. Hence, a set of molecules in a layer of **2a** are related to the subsequent layer via a screw axis, while **2b** favored a packing arrangement in which the bulky Cp ligands of subsequent layers occupy the spaces created due to the mutual repulsion of the flexible alkyl chains of adjacent neighboring molecules.

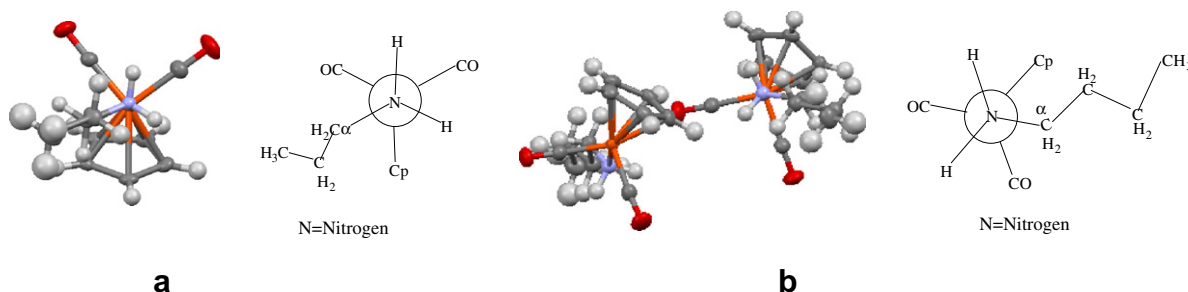
The Fe–N bonds were found to be 2.018, 2.013 and 2.006 Å which is in close agreement with 2.015 Å observed for the same bond in the complex  $[\text{CpFe}(\text{CO})_2\text{NH}_2\text{CH}(\text{CH}_3)_2]^+$  [47]. The N–C bond length was found to fall in the range 1.479–1.491 Å, slightly longer than the C–N bond (1.47 Å) observed for free methylamine [57] and shorter than the N–C bond length (1.502 Å) observed for  $[\text{CpFe}(\text{CO})_2\text{NH}_2\text{CH}(\text{CH}_3)_2]^+$  [47]. The C–C bond lengths in the alkyl chain of the alkylamine fall within the range 1.511–1.527 Å which is in close agreement with that of typical C–C bond lengths (1.53 Å) of alkane chains, indicating that the alkylamine suffered no distortion. Selected bond lengths and angles in molecules of compounds **2a** and **2b** are given in Table 3.

In both crystals the molecules are held together by strong inter-molecular hydrogen bonds and charge-assisted van der Waals forces of attraction. The hydrogen bonding occurs between the fluoride of the counter anion,  $\text{BF}_4^-$ , and the hydrogen, as well as the carbonyl oxygen of the complex cation. Formation of the hydrogen-bond results in an electron density shift from the hydrogen atoms to the more electronegative nitrogen [58], leaving the hydrogen atom with a significant positive charge which leads to a coulombic interaction with the fluorine atoms. The down-field shift of the resonance peak due to the coordinated amine proton relative to uncoordinated amine observed in the  $^1\text{H}$  NMR spectra of complexes **2** may partially be as a result of this electron density transfer. The N–H $\cdots$ F bonds are in the range between 2.07 and



**Table 2**Crystal data and structure refinement information for **2a** and **2b**.

Compound	<b>2a</b>	<b>2b</b>
Empirical formula	C <sub>10</sub> H <sub>14</sub> BF <sub>4</sub> FeNO <sub>2</sub>	C <sub>11</sub> H <sub>16</sub> BF <sub>4</sub> FeNO <sub>2</sub>
Formula weight	322.88	336.91
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pca</i> 2 <sub>1</sub>
Unit cell dimensions		
<i>a</i> (Å)	8.8559(12), $\alpha = 108.727(3)$	18.4242(3), $\alpha = 90^\circ$
<i>b</i> (Å)	8.9932(12), $\beta = 92.219(3)$	8.88960(10), $\beta = 90^\circ$
<i>c</i> (Å)	8.9932(12), $\gamma = 92.219(3)$	17.4545(3), $\gamma = 90^\circ$
Volume (Å <sup>3</sup> )	676.83(16)	2858.76(7)
<i>Z</i>	2	8
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.584	1.566
Absorption coefficient (mm <sup>-1</sup> )	1.156	1.098
<i>F</i> (0 0 0)	328	1376
Crystal size (mm <sup>3</sup> )	0.43 × 0.30 × 0.25	0.45 × 0.17 × 0.05
$\theta$ Range for data collection (°)	2.30–28.00	2.21–27.99
Index ranges	$-11 \leq h \leq 11$ $-10 \leq k \leq 10$ $-11 \leq l \leq 11$	$-24 \leq h \leq 24$ $-11 \leq k \leq 11$ $-23 \leq l \leq 20$
Reflections collected	8250	31377
Independent reflections	3252 [ <i>R</i> <sub>int</sub> = 0.0394]	6794 [ <i>R</i> <sub>int</sub> = 0.0499]
Completeness to $\theta$ limit%	99.9	100
Absorption correction	Integration	Integration
Maximum and minimum transmission	0.7610 and 0.6363	0.9471 and 0.6378
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3252/0/173	6794/1/364
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.179	1.026
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0377, <i>wR</i> <sub>2</sub> = 0.0967	<i>R</i> <sub>1</sub> = 0.0306, <i>wR</i> <sub>2</sub> = 0.0635
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0413, <i>wR</i> <sub>2</sub> = 0.1031	<i>R</i> <sub>1</sub> = 0.0401, <i>wR</i> <sub>2</sub> = 0.0658
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.423 and -1.178	342 and -0.465

**Fig. 4.** Molecular structure of **2a** (a) and **2b** (b) showing staggered gauche type conformation.

2.53 Å, shorter than N–H...F (2.62 Å) in hydrazinium difluoride [59], while the N–H...O bond lengths fall in the range between 3.02 and 3.08 Å which is significantly shorter than simple van der Waals (3.50 Å) interactions. Tables 4 and 5 show the hydrogen bonding data for compounds **2a** and **2b**, respectively.

### 2.2.2. Reactions of $\alpha,\omega$ -diaminoalkanes with two equivalents of **1**

Complex **1** was found to undergo facile displacement of Et<sub>2</sub>O by diaminoalkanes at room temperature when reacted with half equivalents of  $\alpha,\omega$ -diaminoalkanes, affording symmetric bridged bimetallic complexes **3a–3d** in good yields (Scheme 2).

These complexes were isolated as yellow microcrystalline solids by precipitation with diethyl ether. They are soluble in water, acetone and acetonitrile but insoluble in chlorinated solvents, hexane and diethyl ether, making them easily separated by filtration under nitrogen. In all cases [CpFe(CO)<sub>2</sub>]<sub>2</sub> was obtained as a side product, the yield of which increased as the diaminoalkane chains became longer. The stability of complexes **3** in acetone varied with chain

length. For example, whereas **3a** was purified by recrystallization from an acetone/diethylether mixture, the decomposition of **3c** and **3d** was rapid even in nitrogen-saturated acetone. However, **3c** and **3d** are moderately stable in air and in nitrogen-saturated acetonitrile. They decompose without melting in the range 120–183 °C, with the decomposition temperature increasing with increase in alkyl chain length.

### 2.3. Characterization

The diaminoalkane complexes have been fully characterized by elemental analysis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy (Sections 4.8–4.11).

Their IR spectra exhibited two strong absorption bands in the  $\nu$ (CO) region in the range 1991–2057 cm<sup>-1</sup>, which characterize identical cationic CpFe(CO)<sub>2</sub> groups [9,55]. Again, the positions of the  $\nu$ (CO) absorption bands are at lower wavenumbers relative to those of **1** for similar reasons given in Section 2.2.1.1. The



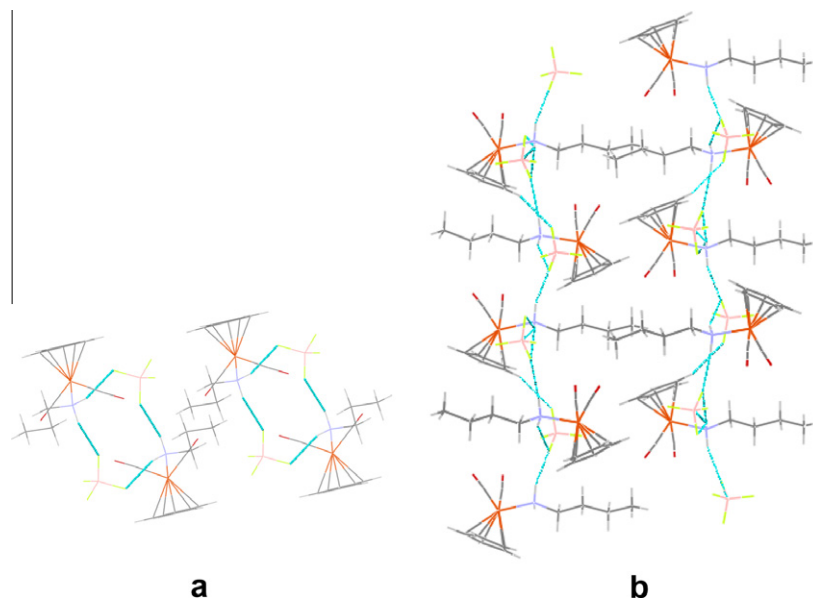


Fig. 5. Crystal structures of compound **2a** (a) and **2b** (b) showing hydrogen bonds.

Table 3

Selected bond lengths and angles for compound **2a** and **2b**.

	Bond length (Å)			Bond angle (°)		
	<b>2a</b>	<b>2b</b>		<b>2a</b>	<b>2b</b>	
		A	B		A	B
Cent–Fe1*	1.721(7)	1.717(4)		Cent–Fe1–C6	123.7(6)	122.9(4)
(Cent–Fe2)			1.714(1)	(Cent–Fe2–C17)		123.5(2)
C6–Fe1	1.776	1.795(2)		Cent–Fe1–C7	121.8(8)	122.1(1)
(C17–Fe2)			1.790(2)	(Cent–Fe2–C18)		121.0(6)
C7–Fe1	1.793(2)	1.791(3)		Cent–Fe1–N1	122.5(8)	122.4(6)
(C18–Fe2)			1.789(3)	(Cent–Fe2–N2)		123.0
N1–Fe1	2.017(8)	2.013(2)		C6–Fe1–C7	93.4(10)	96.2(11)
(N2–Fe2)			2.006(2)	(C17–Fe2–C18)		95.8(11)
C6–O1	1.139(3)	1.132(3)		C6–Fe1–N1	93.9(8)	93.0(11)
(C17–O3)			1.138(3)	(C17–Fe2–N2)		94.1(10)
C7–O2	1.142(3)	1.134(3)		C7–Fe1–N1	93.2(8)	92.2(10)
(C18–O4)			1.33(3)	(C18–Fe2–N2)		91.4(10)
N1–C8	1.489(2)	1.492(3)		Fe1–N1–C8	118.0(11)	117.4(15)
(N2–C19)			1.479(3)	(Fe2–N2–C19)		120.4(17)
C8–C9	1.527(3)	1.514(3)		N1–C8–C9	111.4(16)	112.1(2)
(C19–C20)			1.527(4)	(N2–C19–C20)		110.3(2)

\* Cent is the centroid of the atoms forming the Cp ring, (e.g. C1, C2, C3, C4 and C5).

complexes also show two medium absorption bands in the  $\nu(\text{N-H})$  region in the range  $3276\text{--}3315\text{ cm}^{-1}$ , assignable to the symmetric and anti-symmetric N–H stretching mode.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for **3a** and **3b** were recorded in acetone- $\text{d}_6$ , while those of **3c** and **3d** were recorded in acetonitrile- $\text{d}_3$ . The assignments were made by help of 2D NMR spectra and by comparison with data reported by Peng et al., for the bridged diphosphine complexes,  $[\{\text{CpFe}(\text{CO})_2\}_2\mu\text{-(Ph}_2\text{P}(\text{CH}_2)_n\text{-}$

$\text{PPh}_2\text{)]}^{2+}$  ( $n = 1\text{--}4$ ) [50]. The proton NMR spectra of **3a** and **3b** exhibited characteristic peaks assignable to the Cp protons at *ca.* 5.50 ppm, while this resonance peak was observed at *ca.* 5.26 ppm for **3c** and **3d** recorded in acetonitrile- $\text{d}_3$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR data suggested a symmetrical structure (Fig. 6), which is also evidence that the diaminoalkane bridges the two metal centers.

Table 4

Hydrogen bonds and angles for compound **2a**.

D–H...A	[d(D–H) Å]	[d(H...A) Å]	[d(D...A) Å]	[<(DHA) °]
N(1)–H(1A)...F(1)#1	0.92	2.62	3.319(2)	132.8
N(1)–H(1A)...F(2)#1	0.92	2.07	2.954(2)	159.4
N(1)–H(1B)...F(1)	0.92	2.08	2.973(2)	164.2
N(1)–H(1B)...O(1)	0.92	3.02	3.537(2)	117.0

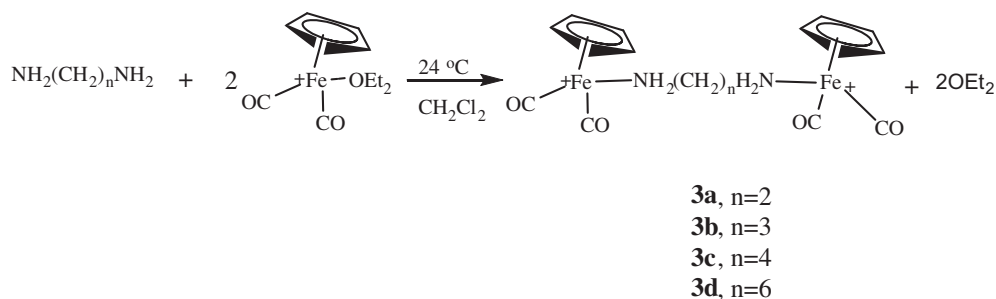
Symmetry transformations used to generate equivalent atoms: #1  $-x, -y + 1, -z + 1$ .

Table 5

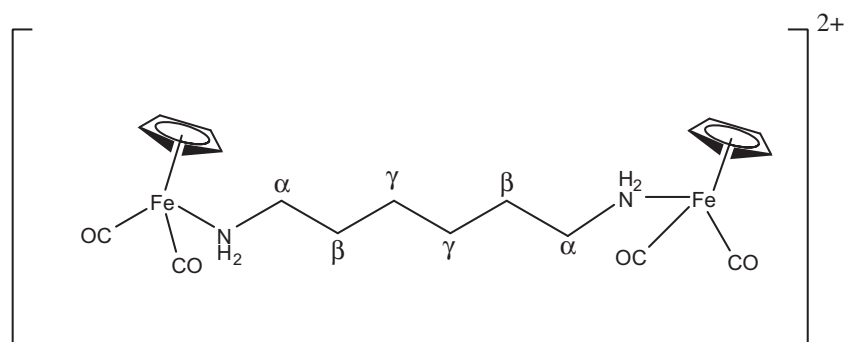
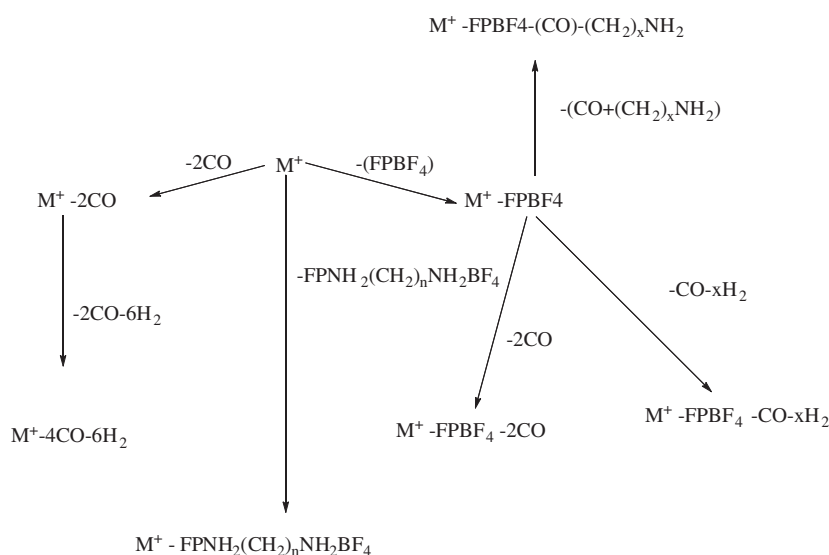
Hydrogen bonds and angles for compound **2b**.

D–H...A	[d(D–H) Å]	[d(H...A) Å]	[d(D...A) Å]	[<(DHA) °]
N(1)–H(1A)...F(1)	0.92	2.53	3.178(3)	122.1
N(1)–H(1A)...F(4)	0.92	2.31	3.178(3)	156.7
N(1)–H(1B)...F(6)	0.92	2.16	3.077(2)	173.2
N(1)–H(1B)...O(3)	0.92	3.08	3.702(2)	126.3
N(2)–H(2A)...F(5)	0.92	2.23	3.003(3)	140.8
N(2)–H(2A)...F(6)	0.92	2.33	3.195(3)	157.2
N(2)–H(2B)...F(2)#1	0.92	2.45	3.363(3)	171.9
N(2)–H(2B)...F(4)#1	0.92	2.42	3.116(3)	132.5

Symmetry transformations used to generate equivalent atoms: #1  $x - 1/2, -y + 1, z$ .



Scheme 2. Preparation of bridged diaminoalkane complexes.

Fig. 6. General structure of the diaminoalkane complexes ( $n = 6$ , in this instance).Scheme 3. Fragmentation of diaminoalkane complexes (FP = CpFe(CO)<sub>2</sub>).

For instance, the <sup>1</sup>H NMR spectrum of compound **3b** shows a triplet resonance peak at 1.74 ppm ( $J_{\text{HH}} = 7.20$  Hz) and a quintet at 2.51 ( $J_{\text{HH}} = 7.12$  Hz) assignable to two  $\beta$ -methylene protons and four  $\alpha$ -methylene protons, respectively.

The <sup>13</sup>C NMR spectrum shows four resonance peaks at 36.41, 50.73, 87.45 and 212.23 ppm corresponding to the  $\beta$ -carbon, two identical  $\alpha$ -carbons, five equivalent Cp carbons and four identical carbonyls, respectively.

The electrospray mass spectra of the four diaminoalkane complexes, **3a–3d** were obtained. Unlike aminoalkane complexes, the fragmentation of diaminoalkane complexes is influenced by the two metal ends and therefore are more complicated (Scheme 3). First BF<sub>4</sub> is lost leading to parental molecular ion M<sup>+</sup>

(i.e. (CpFe(CO)<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub>BF<sub>4</sub>) of weak intensity. Loss of the second counter anion is accompanied by loss of a Fp fragment forming M<sup>+</sup>–FPBF<sub>4</sub> which was of the strongest intensity peak for the diaminoethane and diaminopropane complexes, but decreased with increase in bridge length. Carbonyl ligands were lost in either of five ways as follows: M<sup>+</sup>–2CO, M<sup>+</sup>–4CO–6H<sub>2</sub>, M<sup>+</sup>–FPBF<sub>4</sub>–CO–xH<sub>2</sub>, M<sup>+</sup>–FPBF<sub>4</sub>–2CO or M<sup>+</sup>–FPBF<sub>4</sub>–CO–(CH<sub>2</sub>)<sub>x</sub>NH<sub>2</sub> ( $x = 1, 2, 5$  for diaminoethane, diaminopropane and diaminohexane, respectively).

### 2.3.1. Reactions of **1** with 1-alkenes, and triphenylphosphine

The ether complex **1** reacts with terminal alkenes and triphenyl phosphine to give known complexes of the type [CpFe(CO)<sub>2</sub>L]BF<sub>4</sub> (L = CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, PPh<sub>3</sub>) as air stable yellow

solids. The IR and NMR spectroscopy data obtained are identical to reported data [13,60]. The alkene complexes had been previously prepared by either hydride abstraction from their respective alkyl complexes, ligand substitution reactions using Fe–THF or Fe–isobutene complexes or *in situ* reaction of alkenes with the reactive complex  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$ . In cases where isobutene has been used, low yields are reported because isobutene is not easily displaced by the incoming olefin ligand. Normally heat is used to induce the dissociation but this also leads to the formation of side products, such as the iron dimer, thus lowering the yield. In reactions where the THF complex has been used,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  is added to remove THF from the system. The disadvantage of using  $\text{BF}_3$  is that it is a highly corrosive gas and catalyses polymerization of some olefins [61], thus making the method difficult. An *in situ* reaction of the alkene with  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$  generated by iodide abstraction from  $\text{CpFe}(\text{CO})_2\text{I}$  using  $\text{AgBF}_4$  leads to low yields of alkene complexes due to formation of an iodo bridged complex,  $[\text{CpFe}(\text{CO})_2]_2\text{IBF}_4$  as a side product [51]. Contrary to these reactions, the diethyl ether complex **1** reacts smoothly with alkenes and triphenylphosphine at room temperature to give excellent yields of the alkene and triphenylphosphine complexes, respectively (Sections 4.12 and 4.13).

### 3. Conclusion

The diethyl ether complex,  $[\text{CpFe}(\text{CO})_2(\text{Et}_2\text{O})]\text{BF}_4$  has been successfully synthesized, isolated and shown to be an excellent precursor for the synthesis of a range of cationic cyclopentadienyl-iron dicarbonyl complexes. Its reaction with 1-aminoalkanes and  $\alpha,\omega$ -diaminoalkanes leads to formation of novel compounds of type  $[\text{CpFe}(\text{CO})_2(\text{NH}_2(\text{CH}_2)_n\text{CH}_3)]\text{BF}_4$  and  $[\{\text{CpFe}(\text{CO})_2\}_2\mu\text{-(NH}_2(\text{CH}_2)_n\text{NH}_2)(\text{BF}_4)_2]$ , respectively. The structures of some of these compounds have been determined by single crystal X-ray crystallography.

### 4. Experimental

#### 4.1. General

All manipulations were carried out under inert atmosphere (UHP or HP nitrogen) using Schlenk line techniques. Nitrogen gas was dried over phosphorus(V) oxide. Reagent grade THF, hexane and  $\text{Et}_2\text{O}$  were distilled from sodium/benzophenone and stored over sodium wire; acetone,  $\text{CH}_2\text{Cl}_2$  and MeCN were distilled from anhydrous  $\text{CaCl}_2$ . The other chemical reagents were obtained from the suppliers shown in parentheses: dicyclopentadiene, iron pentacarbonyl, aminoheptane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, tetrafluoroboric acid diethyl ether, iodomethane, mercury (Aldrich), aminopropane, aminopentane, aminohexane 1,2-diaminoethane, silver tetrafluoroborate (Merck), aminobutane (BDH), sodium (Fluka) and iodine (Unilab) were used as supplied. Melting points were recorded on an Ernst Leitz Wetzlar hot-stage microscope and are uncorrected. Elemental analyses were performed on LECO CHNS-932 elemental analyzer. Infrared spectra were recorded using an ATR Perkin–Elmer Spectrum 100 spectrophotometer between 4000 and  $400\text{ cm}^{-1}$ , in the solid state. Mass spectra were recorded on an Agilent 1100 series LC/MSD trap with electrospray ionization (ESI) source and quadrupole ion trap mass analyzer by direct infusion and ESI operated in the positive mode. Acetonitrile (100%) was used as mobile phase and  $10\text{ }\mu\text{L}$  of the sample injected at  $0.3\text{ ml/min}$  flow rate. NMR spectra were recorded on Bruker topspin 400 and 600 MHz spectrometers. The deuterated solvents  $\text{CDCl}_3$  (Aldrich, 99.8%), acetonitrile- $\text{d}_3$  (Merck, 99%) and acetone- $\text{d}_6$  (Aldrich, 99.5%), were used as purchased. Solutions for NMR spectroscopy were prepared under nitrogen

using nitrogen-saturated solvents. The precursors  $[\text{CpFe}(\text{CO})_2]_2$  [62],  $\text{CpFe}(\text{CO})_2\text{I}$  [63],  $\text{CpFe}(\text{CO})_2\text{CH}_3$  [22] and  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$  [51], were prepared by the literature methods. The reactions between **1** and aminoalkanes were monitored by IR spectroscopy, and stopped after all of **1** was consumed as indicated by the complete shift in the  $\nu(\text{CO})$  peak from 2063 to lower wavenumbers.

#### 4.2. Preparation of $[\text{Cp}(\text{CO})_2(\text{Et}_2\text{O})]\text{BF}_4$ (**1**)

The complex was prepared from  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$  made by either iodide abstraction using  $\text{AgBF}_4$  or by methyl abstraction using  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ . These two routes and an *in situ* reaction of diethyl ether with  $[\text{CpFe}(\text{CO})_2]\text{BF}_4$  are described below.

##### 4.2.1. Iodide complex route

A foil-wrapped 100 ml Schleck tube was charged with  $\text{CpFe}(\text{CO})_2\text{I}$  (0.213 g, 0.70 mmol) and  $\text{AgBF}_4$  (0.196 g, 1.00 mmol). The mixture was dried under reduced pressure for at least 6 h to remove any water absorbed by  $\text{AgBF}_4$  during transfer. Dichloromethane (20 ml) was then added and the mixture stirred in the dark for 45 min. The reaction mixture was cooled to  $-78^\circ\text{C}$  and stirred for 30 min. The resulting wine red-colored solution was canula filtered into a Schleck tube previously flushed with nitrogen and filled with ice-cooled dry nitrogen-saturated diethyl ether (30 ml, 290 mmol). Immediately a red precipitate formed and the mixture was cooled to  $-78^\circ\text{C}$  and maintained there for at least 2 h. The mother liquor was removed by the use of a canula under nitrogen to leave a red solid residue. The solid was dried under reduced pressure at  $0^\circ\text{C}$  for at least 6 h resulting in a red-orange moisture sensitive microcrystalline solid. It was purified further by recrystallization from a dichloromethane/diethyl ether mixture (1:1 ratio). Brief exposure to air caused conversion to the known aqua complex,  $[\text{CpFe}(\text{CO})_2(\text{OH}_2)]\text{BF}_4$  [51]. However, the solid product was stored at  $-6^\circ\text{C}$  under nitrogen atmosphere for three months without noticeable decomposition. The mother liquor was evaporated and dried under similar conditions to give a thick brown oil which was found to be a decomposition product as suggested by  $^1\text{H}$  NMR due to the presence of numerous Cp resonance peaks. Yield: 0.175 g, 74%.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  5.42 (s, 5H, Cp), 3.47 (q,  $J_{\text{HH}} = 6.54\text{ Hz}$ , 4H), 1.09 (t,  $J_{\text{HH}} = 6.54\text{ Hz}$ , 6H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  85.95 (Cp), 78.93 (O–CH<sub>2</sub>), 13.38 (CH<sub>3</sub>), 209.59 (CO). IR (solid state):  $\nu(\text{CO})$  2063, 2010  $\text{cm}^{-1}$ .

##### 4.2.2. Methyl complex route

A pre-weighed 100 ml Schlenk tube was charged with a solution of  $\text{CpFe}(\text{CO})_2\text{CH}_3$  (0.949 g, 4.94 mmol) in freshly distilled  $\text{CH}_2\text{Cl}_2$  (20 ml) followed by  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  (1 ml, 7.29 mmol) added dropwise while stirring. The mixture was stirred for 10 min and then cooled to  $-78^\circ\text{C}$  for 10 min, after which 15 ml of diethyl ether was added, resulting in a red precipitate. This was allowed to warm up to a temperature of  $-6^\circ\text{C}$ , cooled and allowed to stand at  $-78^\circ\text{C}$  for at least 10 min. Filtration through a canula and drying the residue at  $0^\circ\text{C}$  for 8 h provided a red microcrystalline solid identical to the one obtained through the iodide complex route. Yield: 1.503 g, 90%.

##### 4.2.3. *In situ* reaction of diethyl ether with $[\text{CpFe}(\text{CO})_2]\text{BF}_4$

A nitrogen-saturated solution of  $\text{CpFe}(\text{CO})_2\text{CH}_3$  (0.286 g, 1.47 mmol) in dry diethyl ether (20 ml) in a 50 ml Schleck tube was cooled to  $-78^\circ\text{C}$  and 0.4 ml of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  added dropwise while stirring. No reaction was observed at this temperature. On warming the mixture to ca.  $-6^\circ\text{C}$ , evolution of methane gas began and a red precipitate started to form. The mixture was then cooled further to  $-78^\circ\text{C}$ , separated and purified as explained in (i) and (ii) above. Yield: 0.343 g, 69%.



#### 4.3. Reaction of **1** with 1-aminopropane

Aminopropane (0.12 ml, 1.46 mmol) was added dropwise to a stirred solution of the diethyl ether complex, **1** (0.460 g, 1.36 mmol) in dry dichloromethane (10 ml). This resulted in an immediate change of color from red to brown. The mixture was stirred for 3 h and then dry diethyl ether added until a yellow precipitate formed. The mixture was allowed to stand for 10 min, after which the mother liquor was removed using canula. Washing the residue with diethyl ether (2 × 10 ml) and drying under reduced pressure provided 0.383 g (87% yield) of yellow-orange solid. *Anal.* Calc. for  $C_{10}H_{14}BF_4FeNO_2$ : C, 37.15; H, 4.33; N, 4.33. Found: C, 37.13; H, 4.47; N, 4.13%.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  5.27 (s, 5H, Cp), 2.95 (s, 2H,  $-NH_2$ ), 2.19 (m,  $J_{HH} = 7.38$  Hz, 2H,  $\alpha CH_2$ ), 1.52 (m,  $J_{HH} = 7.34$  Hz, 2H,  $\beta CH_2$ ), 0.82 (t,  $J_{HH} = 7.38$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  86.06 (Cp), 55.31 ( $\alpha C$ ), 25.74 ( $\beta C$ ) 10.82 ( $CH_3$ ), 210.06 (CO). IR (solid state):  $\nu(CO)$  2057, 2000  $cm^{-1}$ ;  $\nu(NH)$  3311, 3281  $cm^{-1}$ . M.p., 102–103 °C.

#### 4.4. Reaction of **1** with 1-aminobutane

To **1** (0.960 g, 2.84 mmol) in a Schleck tube, freshly distilled dichloromethane (20 ml) was added followed by 1-aminobutane (0.30 ml, 3.05 mmol). The mixture was stirred for 3 h when the reaction was judged complete using IR (appearance of absorption band at 2055  $cm^{-1}$  and disappearance of absorption band at 2066  $cm^{-1}$ ). On addition of diethyl ether to the mixture and allowing it to stand for 1 h, yellow flake-like crystals formed. The mixture was filtered *via* canula and the solid washed with 2 × 20 ml diethyl ether, dried under reduced pressure and purified further by recrystallisation from a dichloromethane–diethyl ether mixture to give 0.909 g (95% yield) yellow solid. *Anal.* Calc. for  $C_{11}H_{16}BF_4FeNO_2$ : C, 39.17; H, 4.75; N, 4.15. Found: C, 39.75; H, 4.44; N, 4.35%.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  5.27 (s, 5H, Cp), 2.91 (s, 2H,  $-NH_2$ ), 2.23 (m, 2H,  $\alpha CH_2$ ), 1.47 (m, 2H,  $\beta CH_2$ ), 1.24 (m, 2H,  $\gamma CH_2$ ), 0.83 (t,  $J_{HH} = 7.35$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  86.07 (Cp), 53.35 ( $\alpha C$ ), 34.42 ( $\beta C$ ), 19.62 ( $\gamma C$ ) 13.53 ( $CH_3$ ), 210.62 (CO). IR (solid state):  $\nu(CO)$  2055, 2000  $cm^{-1}$ ;  $\nu(NH)$  3307, 3279  $cm^{-1}$ . M.p., 58–60 °C.

#### 4.5. Reaction of **1** with 1-aminopentane

1-Aminopentane (0.16 ml, 1.39 mmol) was added dropwise, while stirring, into a solution of **1** (0.440 g, 1.30 mmol) in dichloromethane (20 ml). The solution turned from red to light brown. The mixture was stirred overnight and then hexane was added to precipitate the product as a yellow solid. The mixture was then treated similarly to that of the 1-aminobutane complex to give 0.324 g (71% yield) of yellow solid. On evaporation of the filtrate under reduced pressure, purple needle-like crystals were obtained and identified as  $[CpFe(CO)_2]_2$  by IR,  $^1H$  NMR and  $^{13}C$  NMR spectroscopy. *Anal.* Calc. for  $C_{12}H_{18}BF_4FeNO_2$ : C, 41.03; H, 5.13; N, 3.99. Found: C, 40.87; H, 4.95; N, 4.13%.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  5.27 (s, 5H, Cp), 2.90 (s, 2H,  $-NH_2$ ), 2.22 (m, 2H,  $\alpha CH_2$ ), 1.50 (m, 2H,  $\beta CH_2$ ), 1.18 (m, 2H,  $(CH_2)_2$ ), 0.82 (t,  $J_{HH} = 6.96$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  86.07 (Cp), 53.62 ( $\alpha C$ ), 32.15 ( $\beta C$ ), 28.54 ( $\gamma C$ ) 22.14 ( $\delta C$ ), 13.80 ( $CH_3$ ), 210.60 (CO). IR (solid state):  $\nu(CO)$  2061, 1993  $cm^{-1}$ ;  $\nu(NH)$  3312, 3282  $cm^{-1}$ . M.p., 83–85 °C.

#### 4.6. Reaction of **1** with 1-aminohexane

This reaction procedure was executed as described above for aminopentane with the following quantities of reagents: **1** (1.47 g, 4.35 mmol), 1-aminohexane (0.6 ml, 4.54 mmol). A yellow solid was obtained, 1.13 g (71% yield). *Anal.* Calc. for  $C_{13}H_{20}BF_4FeNO_2$ : C, 42.74; H, 5.48; N, 3.84. Found: C, 42.51; H, 5.25; N, 4.47%.

$^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  5.27 (s, 5H, Cp), 2.90 (s, 2H,  $-NH_2$ ), 2.22 (m, 2H,  $\alpha CH_2$ ), 1.49 (m, 2H,  $\beta CH_2$ ), 1.20 (m, 2H,  $(CH_2)_3$ ), 0.82 (t,  $J_{HH} = 10.44$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  86.08 (Cp), 53.72 ( $\alpha C$ ), 32.58 ( $\beta C$ ), 31.30 ( $\gamma C$ ) 26.21 ( $\delta C$ ) 22.48 ( $\epsilon C$ ), 14.00 ( $CH_3$ ), 210.68 (CO). IR (solid state):  $\nu(CO)$  2048, 1994  $cm^{-1}$ ;  $\nu(NH)$  3309, 3277  $cm^{-1}$ . M.p., 61–62 °C.

#### 4.7. Reaction of **1** with 1-aminoheptane

The reaction procedure was executed as described for aminopentane with the following quantities of reagents: **1** (0.87 g, 2.57 mmol), 1-aminoheptane (0.4 ml, 2.70 mmol). A yellow solid was obtained, 0.575 g (59% yield). *Anal.* Calc. for  $C_{14}H_{22}BF_4FeNO_2$ : C, 44.32; H, 5.80; N, 3.69. Found: C, 44.61; H, 6.29; N, 3.43%.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  5.27 (s, 5H, Cp), 2.88 (s, 2H,  $-NH_2$ ), 2.23 (m, 2H,  $\alpha CH_2$ ), 1.49 (m, 2H,  $\beta CH_2$ ), 1.19 (m, 2H,  $(CH_2)_4$ ), 0.82 (t,  $J_{HH} = 6.84$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  86.06 (Cp), 53.64 ( $\alpha C$ ), 32.46 ( $\beta C$ ), 31.57 ( $\gamma C$ ) 28.74 ( $\delta C$ ) 26.45 ( $\epsilon C$ ), 22.47 ( $\omega C$ ), 13.96 ( $CH_3$ ), 210.55 (CO). IR (solid state):  $\nu(CO)$  2055, 2020  $cm^{-1}$ ;  $\nu(NH)$  3304, 3269  $cm^{-1}$ . M.p., 40–41 °C.

#### 4.8. Reaction of **1** with 1,2-diaminoethane

1,2-Diaminoethane (0.05 ml, 0.75 mmol) was added dropwise to a solution of **1** (0.500 g, 1.48 mmol) in  $CH_2Cl_2$  (15 ml) at 0 °C and the mixture stirred rapidly for 10 min. The mixture was then allowed to stand at room temperature for 6 h during which a brown precipitate formed. The mother liquor was removed through a canula and the residue washed with 2 × 10 ml portions of  $CH_2Cl_2$  and dried under reduced pressure to give yellow solid. This solid was extracted with 10 ml of dry acetone and dry diethyl ether added to the extract until yellow precipitate formed. Filtration of the precipitate, followed by drying under reduced pressure provided a yellow microcrystalline solid. This was purified further by recrystallization from an acetone–diethyl ether mixture. Yield: 0.339 g, 78%; *Anal.* Calc. for  $C_{16}H_{18}B_2F_8Fe_2N_2O_4$ : C, 32.65; H, 3.06; N, 4.76. Found: C, 32.96; H, 3.28; N, 5.02%.  $^1H$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  5.48 (s, 5H, Cp), 3.33 (s, 4H,  $NH_2$ ), 2.58 (s, 4H,  $CH_2$ ).  $^{13}C$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  87.43 (Cp), 54.50 ( $CH_2$ ), 211.92 (CO). IR (solid state):  $\nu(CO)$  2054, 2001  $cm^{-1}$ ;  $\nu(NH)$  3315, 3276  $cm^{-1}$ . Decomposes at temperature >120 °C.

#### 4.9. Reaction of $[CpFe(CO)_2(Et_2O)]BF_4$ with 1,3-diaminopropane

To a solution of **1** (0.520 g, 1.54 mmol) in  $CH_2Cl_2$  (20 ml), 1,3-diaminopropane (0.06 ml, 0.72 mmol) was added dropwise at room temperature and stirred for 12 h. The mixture was filtered, the residue washed with 2 × 10 ml portion of  $CH_2Cl_2$  to give a yellow solid. The yellow solid was extracted with 10 ml of dry nitrogen-saturated acetonitrile and dry nitrogen-saturated diethyl ether added to the extract until a yellow precipitate formed. Filtration, followed by drying of the residue under reduced pressure provided a yellow microcrystalline solid. Yield: 0.310 g, 67%; *Anal.* Calc. for  $C_{17}H_{20}B_2F_8Fe_2N_2O_4$ : C, 33.89; H, 3.32; N, 4.65. Found: C, 33.95; H, 3.86; N, 4.80%.  $^1H$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  5.50 (s, 5H, Cp), 3.43 (s, 4H,  $NH_2$ ), 2.51 (m,  $J_{HH} = 7.12$  Hz, 4H,  $\alpha CH_2$ ), 1.74 (t,  $J_{HH} = 7.20$  Hz, 4H,  $\beta CH_2$ ).  $^{13}C$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  87.45 (Cp), 50.73 ( $\alpha C$ ), 36.41 ( $\beta C$ ), 212.23 (CO). IR (solid state):  $\nu(CO)$  2051, 1997  $cm^{-1}$ ;  $\nu(NH)$  3307, 3280  $cm^{-1}$ . Decomposes at temperature >160 °C.

#### 4.10. Reaction of **1** with 1,4-diaminobutane

To a solution of **1** (0.45 g, 1.33 mmol) in 15 ml of  $CH_2Cl_2$ , 1,4-diaminopropane (0.06 ml, 0.60 mmol) was added dropwise at room temperature while stirring. Stirring was continued for 5 h

and then the mixture was allowed to stand at room temperature overnight. The rest of the procedure was executed as described in Section 4.9 for 1,3-diaminopropane complex to provide yellow microcrystalline solid: Yield: 0.283 g, 69%; *Anal. Calc.* for  $C_{18}H_{22}B_2F_8Fe_2N_2O_4$ : C, 35.06; H, 3.57; N, 4.55. Found: C, 35.58; H, 3.61; N, 4.27%.  $^1H$  NMR (600 MHz,  $CD_3CN$ ):  $\delta$  5.26 (s, 5H, Cp), 2.61 (s, 4H,  $NH_2$ ), 2.23 (m, 4H,  $\alpha CH_2$ ), 1.34 (m, 4H,  $\beta CH_2$ ).  $^{13}C$  NMR (400 MHz,  $CD_3CN$ ):  $\delta$  86.24 (Cp), 52.04 ( $\alpha C$ ), 29.08 ( $\beta C$ ), 211.15 (CO). IR (solid state):  $\nu(CO)$  2057, 1991  $cm^{-1}$ ;  $\nu(NH)$  3310, 3281  $cm^{-1}$ . Decomposes at temperature  $>180^\circ C$ .

#### 4.11. Reaction of **1** with 1,6-diaminohexane

This reaction procedure was executed as described above for the diaminobutane complex with the following quantities of reagents: **1** (0.470 g, 1.39 mmol), 1,6-diaminohexane (0.09 ml, 0.69 mmol). A yellow solid was obtained, 0.313 g (70% yield). *Anal. Calc.* for  $C_{20}H_{26}B_2F_8Fe_2N_2O_4$ : C, 37.27; H, 4.04; N, 4.35. Found: C, 37.56; H, 4.58; N, 4.23%.  $^1H$  NMR (400 MHz,  $CD_3CN$ ):  $\delta$  5.26 (s, 5H, Cp), 2.61 (s, 4H,  $NH_2$ ), 2.26 (m, 4H,  $\alpha CH_2$ ), 1.58 (m, 4H,  $\beta CH_2$ ), 1.18 (m, 4H,  $\gamma CH_2$ ).  $^{13}C$  NMR (400 MHz,  $CD_3CN$ ):  $\delta$  85.93 (Cp), 52.33 ( $\alpha C$ ), 31.88 ( $\beta C$ ), 25.21 ( $\gamma C$ ), 210.90 (CO). IR (solid state):  $\nu(CO)$  2052, 2004  $cm^{-1}$ ;  $\nu(NH)$  3327, 3285  $cm^{-1}$ . Decomposes at temperature  $>183^\circ C$ .

#### 4.12. Reaction of **1** with 1-alkenes

The procedure for the reaction of **1** with 1-pentene is described as an illustration of the general procedure followed in the reactions with 1-alkenes. To a solution of **1** (0.246 g, 0.73 mmol) in 10 ml dichloromethane, 1-pentene (2 ml, 18.31 mmol) was added and the mixture stirred for 10 min and then allowed to stand overnight at room temperature. The resulting mixture was filtered and dry diethyl ether added to the filtrate. Although a yellow precipitate formed immediately, the mixture was allowed to stand for 5 h to allow its settling. The precipitate was then filtered off, washed with  $3 \times 5$  ml portions of diethyl ether and dried under reduced pressure. A yellow solid was obtained and purified by recrystallization from a dichloromethane–diethyl ether mixture (1:2 volume ratio), yield: 0.221 g, 91%. *Anal. Calc.* for  $C_{12}H_{15}BF_4FeO_2$ : C, 43.11; H, 4.49. Found: C, 42.67; H, 5.03%.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  5.62 (s, 5H, Cp), 5.17 (m, 1H,  $=CH$ ), 4.06 (d,  $J_{HH} = 7.68$  Hz, 1H,  $=CH_2$ , *cis*), 3.28 (d,  $J_{HH} = 14.7$  Hz, 1H,  $=CH_2$ , *trans*), 2.43 (m, 1H,  $=CHCH$ ) 1.57 (m, 3H,  $CHCH_2$ ) 0.95 (t,  $J_{HH} = 12.96$  Hz, 3H,  $-CH_3$ ).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  88.95 (Cp), 85.62 ( $\beta C$ ), 54.56 ( $\alpha C$ ), 38.88 ( $\gamma C$ ), 25.63 ( $\delta C$ ), 13.51 ( $CH_3$ ). 208.16, 209.23 (CO). IR (solid state):  $\nu(CO)$  2073, 2032  $cm^{-1}$ .

$[CpFe(CO)_2(CH_2CH(CH_2)_3CH_3)]BF_4$  was synthesized in a similar way to the pentene analogue, by reacting **1** (0.368 g; 1.09 mmol) with 1-hexene (2 ml; 15.48 mmol). Yield: 0.368 g, 97%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  5.62 (s, 5H, Cp), 5.17 (m, 1H,  $=CH$ ), 4.05 (d,  $J_{HH} = 7.8$  Hz, 1H,  $=CH_2$ , *cis*), 3.27 (d,  $J_{HH} = 14.9$  Hz, 1H,  $=CH_2$ , *trans*), 2.42 (m, 1H,  $=CHCH$ ) 1.56 (m, 5H,  $CHCH_2CH_2$ ) 0.87 (t,  $J_{HH} = 12.9$  Hz, 3H,  $-CH_3$ ). IR (solid state):  $\nu(CO)$  2075, 2033  $cm^{-1}$ .

#### 4.13. Reaction of **1** with $PPh_3$

A solution of **1** (0.352 g, 1.041 mmol) in 20 ml of dry diethyl ether was treated with 0.620 g (2.37 mmol) of triphenylphosphine and the mixture stirred overnight at room temperature. Then the mixture was filtered and dry diethyl ether added to the filtrate until a yellow precipitate formed. The mother liquor was syringed off and the solid residue washed with  $3 \times 5$  ml diethyl ether to yield a yellow solid. Yield: 0.520 g, 95%. *Anal. Calc.* for  $C_{25}H_{20}BF_4FePO_2$ : C, 57.03; H, 3.80. Found: C, 56.41; H, 4.03%.  $^1H$  NMR (400 MHz,  $CD_3NO$ ):  $\delta$  5.41 (s, 5H, Cp), 7.62 (m, 15H).  $^{13}C$  NMR (400 MHz,

$CDCl_3$ ):  $\delta$  88.97 (Cp), 132.57 (m, phenyl), 210.38 (CO). IR (solid state):  $\nu(CO)$  2048, 2013  $cm^{-1}$ .

#### 4.14. X-ray crystal structure determinations of complexes **2a** and **2b**

Crystals of compounds **2a** and **2b** suitable for single crystal X-ray diffraction studies were grown by liquid diffusion method. Solutions of the compounds in dry chloroform were layered with *ca.* fourfold of excess hexane and allowed to stand undisturbed in the dark at room temperature for 6 weeks. Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K $\alpha$  radiation (50 kV, 30 mA) using the APEX2 [64] data collection software. The collection method involved  $\omega$ -scans of width  $0.5^\circ$  and  $512 \times 512$  bit data frames. Data reduction was carried out using the program SAINT+ [65] and face indexed absorption corrections were made using XPREP [65].

The crystal structure was solved by direct methods using SHELXTL [66]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on  $F^2$  using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTL, platon [67] and ORTEP-3 [68]. Table 2 summarizes crystal data and structure refinement information while selected bond length and angles are given in Tables 3–5.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.10.018.

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