



Regioselective reactions of electrophilic iron dicarbonyl cations, $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]^+$ ($\text{R} = \text{H}, \text{CH}_3$) with heterofunctional amine ligands

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ABSTRACT

The reactions of the ether salts $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(E)]\text{BF}_4$, ($\text{R} = \text{H}, E = \text{Et}_2\text{O}$; $\text{R} = \text{CH}_3, E = \text{THF}$) with various ligands possessing two different coordination sites have been investigated. It was established that $[(\text{Cp}(\text{CO})_2\text{Fe}(\text{OEt}_2))\text{BF}_4$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), **1**, and $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{THF})]\text{BF}_4$ ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$), **2**, react with 1-aminopropanol, 4-methoxybenzylamine and 3-aminopropyltriethoxysilane to give only mononuclear complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{L})]^+$, irrespective of the reactant ratios. On the other hand, the reaction of **1** with one equivalent of 4-aminobenzonitrile (ABN) furnished both mononuclear and dinuclear complexes, $[\text{Cp}(\text{CO})_2\text{Fe}(\text{ABN})]^+$ and $[(\text{Cp}(\text{CO})_2\text{Fe})_2(\mu\text{-ABN})]^{2+}$ isolated as tetrafluoroborate salts, with the mononuclear complex being the major product. The reaction of $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(E)]\text{BF}_4$ with 1,4-phenylenedimethanamine (PDA) afforded only the dinuclear complex $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]_2(\mu\text{-PDA})^{2+}$ regardless of the reactant ratios. The reaction of **2** with one equivalent of the compound $[\text{Cp}(\text{CO})_2\text{Fe}(\text{ABN})]\text{BF}_4$ gave the mixed ligand salt $[\text{Cp}(\text{CO})_2\text{Fe}(\text{ABN})\text{Fe}(\text{CO})_2\text{Cp}^*](\text{BF}_4)_2$. The reactions of dipropylamine with $[\text{Cp}(\text{CO})_2\text{Fe}(\text{OEt}_2)]\text{BF}_4$ gave the dipropylamine salt $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{NH}(\text{CH}_2\text{CH}_2\text{CH}_3)_2\}]\text{BF}_4$. All these compounds are reported for the first time and have been fully characterized by ¹H NMR, ¹³C NMR, IR spectroscopy and elemental analysis. Molecular structures of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{NH}(\text{CH}_2\text{CH}_2\text{CH}_3)_2\}]\text{BF}_4$, $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\text{NH}_2(\text{CH}_2)_2\text{CH}_2\text{OH}\}]\text{BF}_4$ and $[\text{Cp}^*(\text{CO})_2\text{Fe}(\text{NH}_2\text{C}_6\text{H}_4\text{OCH}_3)]\text{BF}_4$ have been confirmed by single crystal X-ray crystallography.

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1. Introduction

Despite the great role played by the amine functionality in catalysis [1–5], pharmacology [6–15] and physiology [16–19], the coordination of simple amine ligands to transition metals is an area in chemistry that appears to be relatively ignored. We recently embarked on the study of the reactions of substitutionally unsaturated ether salts $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(E)]\text{BF}_4$ ($\text{R} = \text{H}: E = \text{Et}_2\text{O}$; $\text{R} = \text{Me}: E = \text{THF}$) with various types of amine ligands and we have reported a number of nitrogen-containing complexes [20–23]. We found that these complexes are stable and the majority are soluble in water. Very recently we reported on organometallic compounds of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$ and showed that the cationic moiety $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]^+$ selectively binds to the amine functionality of the allylamine. It was also found that these compounds can be used as precursors in syntheses of chiral organometallic compounds, since the pendant vinyl group is capable of undergoing addition reactions such as halogenation or

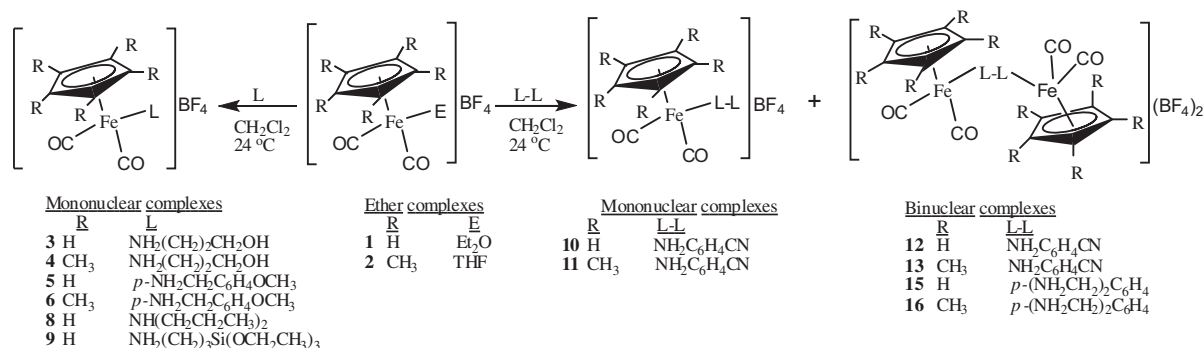
coordination [24]. In this paper we report on amine complexes of iron in which the amine ligand contains a second donor group such as oxygen, cyanide, etc. competing for the metal centre with the amine moiety. The complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_3\text{Si}(\text{OCH}_3)\}]$ ($\text{R} = \text{H}, \text{CH}_3$) [25], $[\text{Cp}(\text{CO})_2\text{Fe}\{(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3\}]$ [26], $[\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_6\text{H}_5\text{OCH}_3)]$ [27] and $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}_2\text{OH}\}]$ ($\text{R} = \text{H}, \text{CH}_3$) [28] resemble, to a degree, some of the compounds reported in this paper.

2. Results and discussion

The reactions of the ether salts $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(E)]\text{BF}_4$ ($\text{R} = \text{H}: E = \text{Et}_2\text{O}$ (**1**); $\text{R} = \text{Me}: E = \text{THF}$ (**2**)) with heterofunctional amine ligands (1-aminopropanol, 4-methoxybenzylamine, 3-aminopropyltriethoxysilane and 4-aminobenzonitrile) proceeded at room temperature with coordination to the amine functionality as shown in Scheme 1. Except for compound **3**, which was obtained as an oil, all other compounds were obtained as yellow moderately air stable solids which are soluble in polar solvents such as water, acetonitrile, methanol and acetone. All of the dinuclear complexes (**12–16**) precipitated out from their reaction mixtures and were

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Scheme 1. Reactions of ether complexes with heterofunctional amine ligands.

easily separated by filtration. Unlike the dinuclear complexes, all of the mononuclear complexes (**3–11**) are also soluble in dichloromethane and they were precipitated from their solution by addition of diethyl ether. The mononuclear complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{ABN})]^+$ (ABN = 4-aminobenzonitrile; R = H, CH₃) are transformed into the dinuclear complexes $\{[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]_2(\mu\text{-ABN})\}^{2+}$ by reaction with the appropriate etherate complex. All of these complexes are new and have been fully characterized by IR and NMR spectroscopy and elemental analysis. The molecular structures of **4**, **6** and **8** have been established by single crystal X-ray diffraction. Generally, the melting points or decomposition temperatures of the Cp* complexes are higher than those of their corresponding Cp analogues.

2.1. Synthesis of $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{FeL}]\text{BF}_4$ (**3–9**)

The novel compounds $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{FeL}]\text{BF}_4$ (R = H, CH₃; L = NH₂(CH₂)₂CH₂OH, NH₂CH₂C₆H₄OCH₃) and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeL}]\text{BF}_4$ (L = NH₂(CH₂)₃Si(OCH₂CH₃)₃, NH(CH₂CH₂CH₃)₂) were obtained in medium to high yields by direct displacement of the ether molecule of the etherate salts $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe(E)}]\text{BF}_4$ with the appropriate ligands as shown in Scheme 1. Their elemental analysis, infrared spectra and NMR data is summarized in the experimental.

In the IR spectra of compounds **3–9**, the $\nu(\text{CO})$ bands are in the expected range for terminal carbonyl groups of amine-coordinated iron dicarbonyl complexes [20,22]. The infrared spectra of the Cp* complexes **4** and **6** show the $\nu(\text{CO})$ bands at lower frequencies than their Cp counterparts due to the electron releasing ability of the pentamethylcyclopentadienyl ligand which consequently increases the metal \rightarrow carbon back donation. With the exception of the dipropylamine complex **8**, the infrared spectra of other complexes show two characteristic absorption bands in the range 3315–3210 cm⁻¹ which correspond to NH₂ symmetrical and asymmetrical stretching modes (c.f. 3358–3285 observed for the amino group in the free ligand). The low-frequency shift occurs due to coordination of the amine functionality to the metal and also probably due to the participation of the hydrogen atoms of the NH₂ group in the hydrogen bonding as evidenced by crystal structures of **4** and **6** as shown in Figs. 1b and 2b, respectively). Compound **8** shows one band in this region which is assignable to NH symmetrical stretching.

In the ¹H NMR spectra of compounds **3–9**, the regioselective coordination of the metal fragment to NH₂ is unambiguously indicated by downfield shifts of amine protons relative to those of the free ligands. For example, a resonance peak in the ¹H NMR spectrum assigned to the amine protons of the coordinated NH₂CH₂C₆H₄OCH₃ appeared downfield by ca. 2.18 ppm relative to free ligand, while that of the coordinated NH₂(CH₂)₂CH₂OH shows a downfield shift of ca. 0.64 ppm. Further evidence for amine

coordination is a ca. 10.9 ppm downfield shift of the peaks corresponding to the carbon of the methylene group alpha to the amine functionality relative to that of the similar carbon in uncoordinated NH₂CH₂C₆H₄OCH₃ and NH₂(CH₂)₂CH₂OH, indicating a strong influence of the metal on the amine side. These effects diminish towards the oxygen side, such that the chemical shift of the carbon neighbouring the oxygen does not significantly vary from that of the free ligand. Moreover, the Fe–N bond distances found in the molecular structures of compounds **4**, **6** and **8** (Section 2.1.1) fall within the range 2.020–2.058 Å observed for related amine coordinated iron complexes [20–22,29]. This further confirms that coordination of these ligands occurs *via* the nitrogen atom of the amine group. Although 3-aminopropanol is known to act as a bidentate ligand, whereby N and O are involved in coordination in Ni(NCS)₂(NH₂CH₂CH₂CH₂OH)₂ [30], in the iron complexes **3** and **4** it acts as a monodentate ligand binding *via* nitrogen only. This is not unusual given that bases donating a lone pair of electrons through nitrogen atoms are softer than bases donating through an oxygen atom. It therefore follows that amines would form stronger dative covalent bonds with soft Lewis acids such as $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]^+$ than alcohols would do.

The 4-methoxybenzylamine salts, **5** and **6**, were found to be stable in the aqueous media. For example 75% of compound **5** was recovered from its aqueous solution by extraction using dichloromethane and found to be unchanged after 24 h in aqueous solution as judged by IR, NMR and elemental analysis. The stability of compound **5** in water was further demonstrated by the counter anion exchange reaction with NaBPh₄ in deionized water to form $[\text{Cp}(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3)]\text{BPh}_4$ (**7**) which was also fully characterized. Assignment of ¹H NMR and ¹³C NMR data of compounds **3–9** was done with the help of COSY and HSQC experiments, as well as comparison with the data reported for $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{OH}\}]$ [28], $[\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_6\text{H}_4\text{OCH}_3)]$ [31], $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{CH}_2(\text{CH}_2)_n\text{CH}_3\}]\text{BF}_4$ [20] and $[\text{Cp}^*(\text{CO})_2\text{Fe}\{\text{CH}_2(\text{CH}_2)_n\text{CH}_3\}]\text{BF}_4$ [22].

Compound **8** was obtained in high yield (73%) by direct displacement of diethyl ether from compound **1** with an equivalent of dipropylamine at room temperature. Similar compounds, $[\text{Cp}(\text{CO})_2\text{Fe}(\text{NHR}_2)]\text{PF}_6$ (R = Et, Me, SiMe₃) have been obtained in low yield (10–35%) from the reaction of $[\text{CpFe}(\text{CO})_2\text{Cl}]$ with the corresponding amine and NaPF₆ [32].

The infrared spectrum of **8** shows two strong IR bands in the $\nu(\text{CO})$ region at 2061 and 2005 cm⁻¹ assignable to two terminal carbonyl ligands and a characteristic single, medium band centred at 3260 cm⁻¹ assignable to $\nu(\text{NH})$ stretching. The results are in good agreement with the data reported for similar salts, $[\text{Cp}(\text{CO})_2\text{Fe}(\text{NHR}_2)]\text{PF}_6$ (R = Et, Me, SiMe₃) [32]. The ¹H NMR spectrum of **8** in CDCl₃ shows a characteristic triplet, integrating for 6H, at 0.88 ppm ($J_{\text{HH}} = 7.28$ Hz) corresponding to the two methyl groups. Two

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