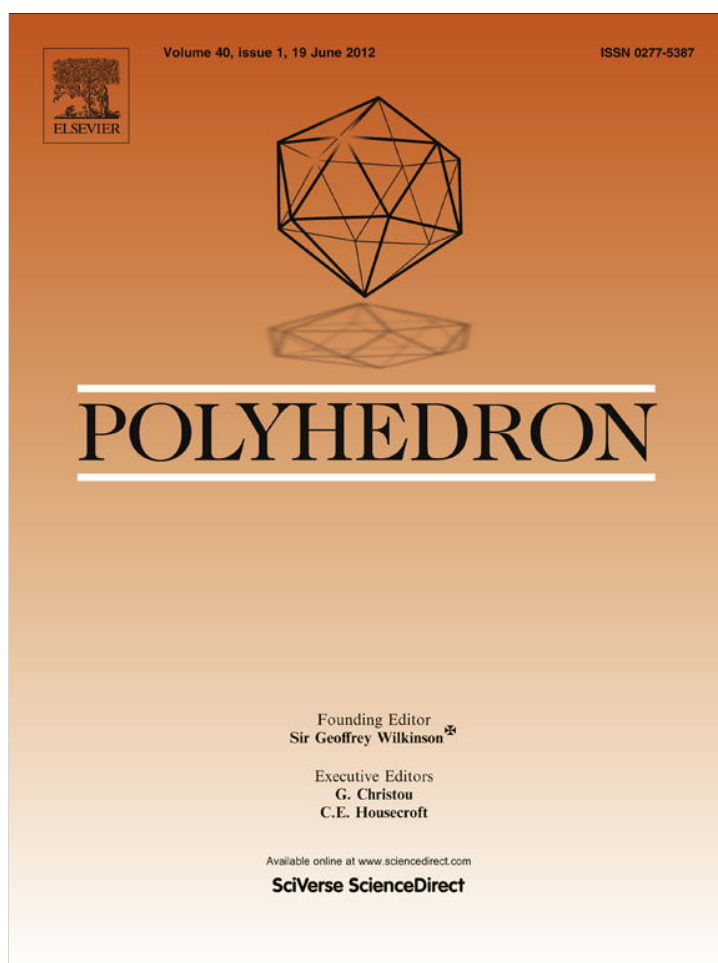


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Syntheses, structural elucidation and reactions of allylamino compounds of the type, $[\eta^5\text{-C}_5\text{R}_5(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$

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ABSTRACT

The reaction of 3-aminoprop-1-ene (allylamine) with the etherate complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{L})]^+$ ($\text{R} = \text{H}$; $\text{L} = \text{Et}_2\text{O}$; $\text{R} = \text{CH}_3$; $\text{L} = \text{THF}$) have been investigated and found to give air stable allylamino complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$ ($\text{R} = \text{H}$ (**3**) or CH_3 (**4**)) with the vinyl functionality pendant on the alkyl chain. These complexes have been isolated as the tetrafluoroborate salts. They undergo halogenation reactions on the pendant vinyl group to give high yields of the dihalopropylamino complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{\text{NH}_2\text{CH}_2\text{CH}(\text{X})\text{CH}_2\text{X}\}]^+$ ($\text{X} = \text{Cl}$ (**5**), Br (**6**)) and $[(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Fe}\{\text{NH}_2\text{CH}_2\text{CH}(\text{Br})\text{CH}_2\text{Br}\}]^+$, (**7**), respectively. Complexes **3** and **4** also react with the etherate complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{L})]^+$ to yield dinuclear complexes of the type, $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{R}'_5)]^{2+}$ (R not necessarily equal to R'), in which the two iron moieties are in different electronic environments. The NMR and IR data of the dinuclear complexes show that the allylamine ligand bridges the two metal systems. It is coordinated to the metal on one end via the nitrogen of the amine functionality in a η^1 -fashion and on the other end via the vinylic functionality in a η^2 -fashion forming a chiral metallacyclopropane type structure. The reaction of the dinuclear salt $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)\}(\text{BF}_4)_2$ with NaI in acetone gives $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{I}$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{I}$ indicating that the iodide displaces the η^2 -coordinated metal center. All these compounds have been fully characterized. The molecular structures of **[3][BF₄]**, **[4][BF₄]** and **[7][BF₄]** have been determined by single crystal X-ray diffraction.

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1. Introduction

The metal allyl and alkenyl complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ ($\text{R} = \text{H}, \text{CH}_3$; $n > 0$) have been known for a long time [1]. They are mainly synthesized by displacement of halides from haloalkenes by the anion $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]^-$ [2–7]. They form an important class of organometallic compounds from which other important compounds are prepared. For instance, the alkenyl complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ ($\text{R} = \text{H}, \text{CH}_3$; $n = 2\text{--}5$, **7**) have been shown to undergo an oxidative-hydroboration reaction to yield alkylalcohol complexes [8], while $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ ($n = 2\text{--}4$, **6**) reacts with Ph_3CPF_6 to give η^2 -(α,ω -diene) complexes [9].

The allyl complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CH}_2)]$ has been reported to undergo condensation with the cationic ethylene complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$ to give a dinuclear complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2)\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^+$ [6], as has the allyl complex with the carbenoid complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}_2]^+$ to give $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHCH}_2\text{CH}_2)\text{Fe}(\text{CO})_2$

$(\eta^5\text{-C}_5\text{H}_5)]^+$ [10]. The longer chain polymethylene complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{\text{CH}_2=\text{CH}(\text{CH}_2)_{n-1}\text{CH}_2\}\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^+$ ($n = 4\text{--}10$) have been prepared by β hydride abstraction from the neutral dinuclear polymethylene complexes $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2\{\mu\text{-CH}_2(\text{CH}_2)_n\text{CH}_2\}\}$ and these studies have clearly shown that the vinyl group is bonded to the metal in a η^2 -fashion [11,12].

The reaction of the metal allyl complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CH}_2)]$ with HCl was reported by Green and Nagy to yield the cationic complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CHCH}_2)]^+\text{Cl}^-$ [3]. However, the reaction of HCl with longer chain alkenyl complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ ($n = 2, 3$) was reported to yield the chlorido complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCl}]$ as well as their corresponding chloroalkenes [2]. Busetto et al. found that the σ -methoxyethyl complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}_2\text{OCH}_3)]$ reacts with HCl to give the cationic complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}_2)]^+$, rather than $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}_2\text{Cl})]$ [13]. The reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{\eta^1\text{-CH}_2\text{N}(\text{CH}_3)_2\}]$ with CH_3COCl has also been reported to occur via a carbon–nitrogen bond cleavage to produce $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{Cl})]$ [14]. This observation suggests that it is difficult to prepare secondary halide complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2)_n\text{CH}(\text{X})\text{CH}_3]$ by hydrohalogenation of metal alkenyl complexes. However, the primary halide

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complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}_2\text{X}\}]$ are well known and they are conveniently prepared by the reaction of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ with an equivalent of α,ω -dihaloalkanes [15–17].

Bromination of the allyl complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2\text{CH}=\text{CH}_2)]$, followed by deprotonation provides the compound $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{Br})]\text{PF}_6$ [18], which can alternatively be obtained from the reaction of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ with α,ω -dibromopropane followed by β hydride abstraction [19]. Other bromination products reported are $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2\text{CH}=\text{CHBr})]$ [1], $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{\eta^2\text{-CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Br}\}]$ [18] and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\eta^2\text{-CH}=\text{CHCHBrCH}_2\text{CH}_2)]\text{PF}_6$ [20]. It is also well established that molecular halogens cleave iron–carbon bonds leading to cyclopentadienyl(halo)iron dicarbonyl [21–25]. The dihaloalkyl complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}(\text{X})\text{CH}_2\text{X}\}]$ have not been reported, although the alkenyl complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ are well known [2,7]. Halogenation is an important chemical transformation, particularly in drug design, because it is known to enhance membrane binding and permeation [26].

Reactions of amines are characterized by high regioselectivity with respect to other electron donor systems such as those with π -bonds. They are good electron donors and therefore they bind strongly to the metal. This implies that aminoalkenes can be tethered to the metal center leaving the vinyl function free. Thus addition reactions, such as halogenations, could take place on the vinyl functionality without cleaving the metal–nitrogen bond and this would provide a route to a new class of organometallic compounds.

The chromium complexes, $[(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2]^+\text{I}^-$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ reported by Legzdins et al. [27], and the palladium complex $[\text{PdCl}_2(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2]$ reported by Hayes et al. [28] are examples of allylamino complexes that have appeared in literature. There are no reports whatsoever about allylamino complexes of iron and no reports about dihaloalkylamino metal complexes. Herein we report the new allylamino complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$ ($\text{R} = \text{H}, \text{CH}_3$) and on their reactions with electrophilic reagents.

2. Results and discussion

2.1. Preparation of the complexes $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$ ($\text{R} = \text{H}, \text{CH}_3$)

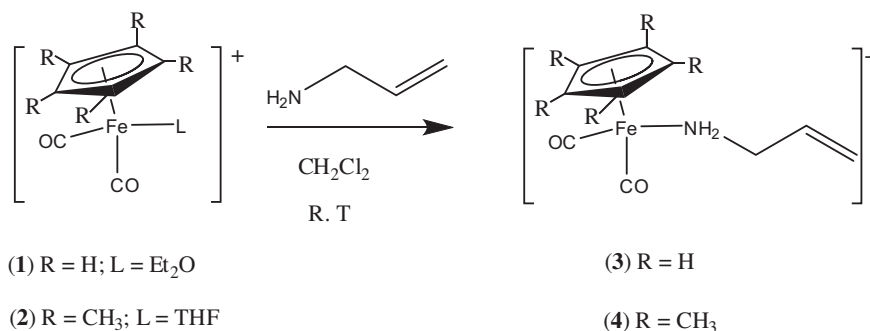
The reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{OEt}_2)]\text{BF}_4$, **1**, with an equimolar amount of 3-amino-1-propene at room temperature resulted in the formation of the allylamino complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$, **3**, in 98% yield (Scheme 1). The product is partially soluble in dichloromethane, causing it to crystallize out

from the solution after 6 h of reaction. It is easily isolated by filtration, contrary to the reported remarkable difficulty encountered in the isolation of neutral alkenyl complexes [4]. Complex **3** was obtained as a yellow microcrystalline solid which was insoluble in hexane and diethyl ether but very soluble in acetone, methanol, water and acetonitrile. It is relatively stable in the solid state and when in nitrogen saturated solutions. However, it undergoes slow photodecomposition when exposed to light to form a brown unidentified substance.

Similarly, the THF complex $\{[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{Fe}(\text{THF})\}^+$, **2**, reacted with one equivalent of 3-amino-1-propene to give $\{[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)\}^+$, **4**, in 78% yield. Unlike complex **3**, complex **4** exhibited high solubility in dichloromethane and stability in the solid state, as well as in solution. This is expected, owing to the presence of the electron releasing pentamethylcyclopentadienyl ligand. No evidence of the coordination occurring at the C=C bond was obtained. When two or more equivalents of the ether complex were used, mixtures of the mononuclear $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$ and the dinuclear complex $\{[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}]_2(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)\}^{2+}$ were formed. It was difficult to isolate the dinuclear complex in its pure form. However, an analytically pure sample of the dinuclear complex can be obtained from the reaction of $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$ with an equimolar amount of the ether compound $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{L})]\text{BF}_4$.

Complexes **3** and **4** resemble the neutral allyl complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ reported by various authors [2,4,5,7] in the sense that they have a terminal double bond on the alkyl chain. However, they are different in that the allylamino complexes are cationic and contain both amino and terminal double bond functionalities in the same molecule. Therefore, they can be regarded as ligand supported metal–nitrogen moieties in which the metal is σ -bonded to an aliphatic aminoalkyl group with a reactive pendant vinyl group. The pendant vinylic functionality is accessible to electrophiles through which various new iron–organometallic complexes can be synthesized. As will be seen in the following sections, allylamino complexes may react by addition of electrophiles across the double bond and by coordination of the C=C bond giving rise to new chiral complexes. The NMR, IR and elemental analysis characterization data for **3** and **4** are given in Section 4.

Complex **3** shows IR carbonyl bands at 2051 and 2004 cm^{-1} (cf. those of complex **4** observed at 2029 and 1983 cm^{-1}). This is a characteristic region for carbonyl compounds with auxiliary ligands that are strong electron donors such as amines [29–31], thiols [32] or phosphines [33]. Characteristic peaks assignable to N–H asymmetric and symmetric stretching modes were observed at ca. 3310 and 3279 cm^{-1} , respectively. A peak due to the N–H bending mode was observed at ca. 1605 cm^{-1} , while a characteristic weak band assignable to uncoordinated C=C stretching mode was



Scheme 1. Reactions of etherate complexes with allylamine.

observed at ca. 1640 cm^{-1} . Peaks assignable to $=\text{CH}$ out-of-plane bending vibrations were observed at 948 and 682 cm^{-1} [34] in the IR spectrum of complex **3** and at 927 and 663 cm^{-1} in the spectrum of complex **4**. These bands were absent in the infrared spectra of halogenated and olefin-coordinated compounds (Sections 2.2 and 2.3).

The ^1H NMR spectra of both complexes **3** and **4** show well resolved characteristic olefinic proton peaks. A multiplet assignable to the $\text{CH}=\text{}$ proton was observed at ca. 5.81 ppm and two doublets at 5.28 and 5.23 ppm, each integrating for one proton, assignable to two non equivalent $=\text{CH}_2$ protons. These values are within the range reported for alkenyl complexes [2,5,35]. The methylene protons alpha to the amine group exhibited a quartet at ca. 2.95 ppm with a coupling constant $^3J_{\text{HH}} = 6.51$ Hz. The ^{13}C NMR spectra of both compounds clearly show peaks corresponding to the vinylic carbon in the expected region above 115 ppm. All peaks assignable to allylamino protons slightly shifted upfield upon changing from $(\eta^5\text{-C}_5\text{H}_5)$ to $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$. However, no significant change was noted in the ^{13}C NMR spectra.

2.1.1. The molecular structures of compounds $[\mathbf{3}][\text{BF}_4]$ and $[\mathbf{4}][\text{BF}_4]$

Single crystal X-ray diffraction was used to determine the absolute structures of complexes **3** and **4**. Molecular diagrams for the two complexes are given in Figs. 1 and 2, respectively. Selected bond distances and angles are provided in Table 1, while the X-ray crystallographic data can be found in Table 2. $[\mathbf{3}][\text{BF}_4]$ crystallizes as brown blocks, while $[\mathbf{4}][\text{BF}_4]$ crystallizes as brown plates. The asymmetric units of both $[\mathbf{3}][\text{BF}_4]$ and $[\mathbf{4}][\text{BF}_4]$ contain the molecular cations $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$ and $\{[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$, respectively, and the counteranion, BF_4^- . Both compounds have the familiar “pseudo-octahedral three-legged piano stool” structures (see Figs. 1 and 2). The five cyclopentadienyl ring carbon atoms occupy the apical positions, while the two $\text{C}=\text{O}$ and allylamine ligands occupy the basal positions of the piano stool.

Coordination of the allylamine occurs via the nitrogen atom resulting in a formal σ -bond between the Fe atom and the allylamine N atom. The Fe–N bond distance in **3** is slightly shorter

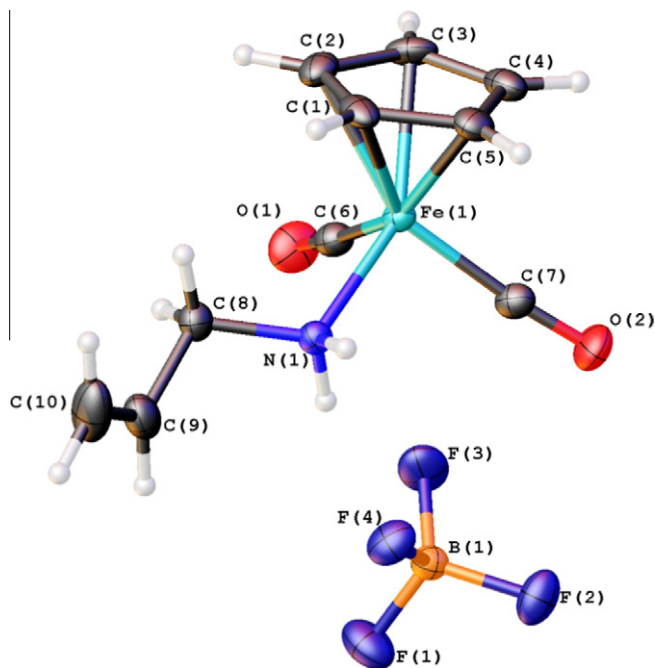


Fig. 1. The structure of compound $[\mathbf{3}][\text{BF}_4]$ showing the atom-numbering scheme. Displacement ellipsoids are drawn at 40% probability level and H atoms are shown as small spheres.

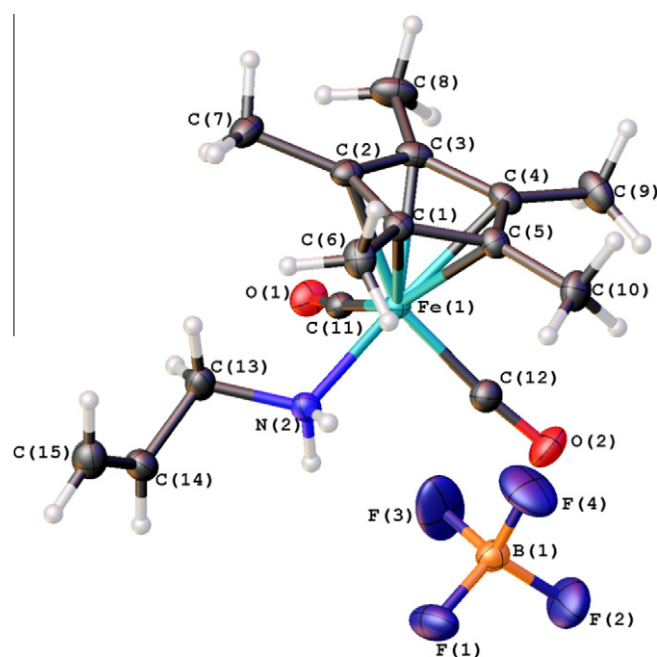


Fig. 2. The structure of $[\mathbf{4}][\text{BF}_4]$ showing the atom-numbering scheme. Displacement ellipsoids are drawn at 40% probability level and H atoms are shown as small spheres.

Table 1

Selected bond lengths and angles for $[\mathbf{3}][\text{BF}_4]$ and $[\mathbf{4}][\text{BF}_4]$ (\AA , $^\circ$).

	$[\mathbf{3}][\text{BF}_4]$	$[\mathbf{4}][\text{BF}_4]$	$[\mathbf{3}][\text{BF}_4]$	$[\mathbf{4}][\text{BF}_4]$
Fe–N	2.018(4)	2.029(1)	Fe–N–C	117.0(3)
Fe–C _{carbonyl}	1.780(5)	1.784(2)	N–C–C	112.3(4)
Fe–C _{carbonyl}	1.789(5)	1.793(2)	C–C=C	123.4(7)
C–O	1.138(6)	1.136(2)	C–Fe–C	95.0(2)
C–O	1.136(6)	1.133(2)	N–Fe–C	93.3(2)
N–C	1.484(8)	1.491(2)	N–Fe–C	94.1(2)
C=C	1.300(9)	1.320(3)	Cg...Fe–N	123.4
C–C _{allylamine}	1.496(8)	1.320(3)	Cg...Fe–C	121.9
Cg...Fe	1.715	1.726	Cg...Fe–C	121.6
				120.4

Cg1 and Cg2 are the centroid of the atoms forming the $(\eta^5\text{-C}_5\text{H}_5)$ and $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ rings, (C1, C2, C3, C4 and C5).

[2.0180(4) \AA] compared to the same distance in **4** [2.0294(14) \AA], but both are comparable to those of related aminocyclopentadienylirondicarbonyl complexes, 2.017(8) \AA for $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2(\text{CH}_2)_2\text{CH}_3)]\text{BF}_4$, 2.013(2) \AA for $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2(\text{CH}_2)_3\text{CH}_3)]\text{BF}_4$ [29] and 2.006(2) \AA for $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2[\mu\text{-NH}_2(\text{CH}_2)_2\text{NH}_2]\}(\text{BF}_4)_2$ [36], as well as those of amino pentamethylcyclopentadienylirondicarbonyl complexes, 2.022(15) \AA for $\{[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{Fe}(\text{NH}_2(\text{CH}_2)_2\text{CH}_3)]\text{BF}_4$ and 2.0202(14) \AA for $\{[\eta^5\text{-C}_5(\text{CH}_3)_5](\text{CO})_2\text{Fe}\}_2[\mu\text{-NH}_2(\text{CH}_2)_3\text{NH}_2]\}(\text{BF}_4)_2$ [31]. The Fe–C_{carbonyl} bond distances are similar in both complexes and are typical of most iron carbonyl complexes (1.78(3) \AA) [37]. The allylamine C=C (vinyl) bond distances are 1.300(9) and 1.320(3) \AA in $[\mathbf{3}][\text{BF}_4]$ and $[\mathbf{4}][\text{BF}_4]$, respectively. These are slightly shorter than a formal C=C double bond (1.34 \AA) [38,39] but close to calculated distances for a terminal C=C bond; 1.315 \AA for ethylene, 1.316 \AA for propene and 1.321 \AA for 2-methylpropene [40].

Figs. 3 and 4 are packing diagrams for $[\mathbf{3}][\text{BF}_4]$ and $[\mathbf{4}][\text{BF}_4]$, respectively. In the crystal of $[\mathbf{3}][\text{BF}_4]$, the cations and the anions are connected by two C–H...F intermolecular interactions [C(8)...F(3) and C(10)...F(1)] resulting in chains that run in the crystallographic a axis. These chains are connected by N–H...F intermolecular interactions [N(1)...F(4)] resulting in rings that can be

Table 2
Crystal data and structure refinement for compound [3][BF₄], [4][BF₄] and [7][BF₄].

Compound	[3][BF ₄]	[4][BF ₄]	[7][BF ₄]
Empirical formula	C ₁₀ H ₁₂ BF ₄ FeNO ₂	C ₁₅ H ₂₂ BF ₄ FeNO ₂	C ₁₅ H ₂₂ BBr ₂ F ₄ FeNO ₂
Formula weight	320.87	391.00	550.82
T (K)	173(2)	173(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$
<i>Unit cell dimension</i>			
a (Å)	15.250(3)	9.5051(2)	9.3954(10)
b (Å)	8.8443(17)	9.5487(3)	10.5527(11)
c (Å)	18.981(4)	11.0937(3)	11.0867(12)
α (°)	90	64.913(2)	88.6930(10)
β (°)	93.209(5)	84.663(2)	79.3410(10)
γ (°)	90	73.277(2)	66.3740(10)
V (Å ³)	2556.2(8)	872.84(4)	988.09(18)
Z	8	2	2
D _{calc} (mg m ⁻³)	1.668	1.488	1.851
Absorption coefficient (mm ⁻¹)	1.224	0.910	4.852
F(000)	1296	404	544
Crystal size (mm)	0.39 × 0.29 × 0.13	0.47 × 0.30 × 0.15	0.30 × 0.25 × 0.20
Theta range for data collection (°)	2.15–28.00	2.03–28.00	1.87–28.74
<i>Index ranges</i>			
h	−20 → 20	−12 → 12	−12 → 12
k	−11 → 11	−12 → 12	−13 → 13
l	−24 → 25	−14 → 11	−14 → 14
Reflections collected	9761	8448	11 875
Independent reflections	3083	4204	4698
Internal fit	R _{int} = 0.0618	R _{int} = 0.0366	R _{int} = 0.0206
Absorption correction	integration	integration	multi-scan
Transmission factor (T _{min} ; T _{max})	0.6469; 0.8571	0.6742; 0.8755	0.3238; 0.4436
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²
Parameters	172	222	276
Goodness-of-fit on F ²	1.113	1.029	1.091
Final R indices [I > 2σ(I)]	R ₁ = 0.0675, wR ₂ = 0.2098	R ₁ = 0.0322, wR ₂ = 0.0802	R ₁ = 0.0410, wR ₂ = 0.0909
R indices (all data)	R ₁ = 0.0840, wR ₂ = 0.2188	R ₁ = 0.0422, wR ₂ = 0.0849	R ₁ = 0.0475, wR ₂ = 0.0931
Largest difference in peak and hole (e Å ⁻³)	2.327 and −0.618	0.508 and −0.258	1.550 and −0.905

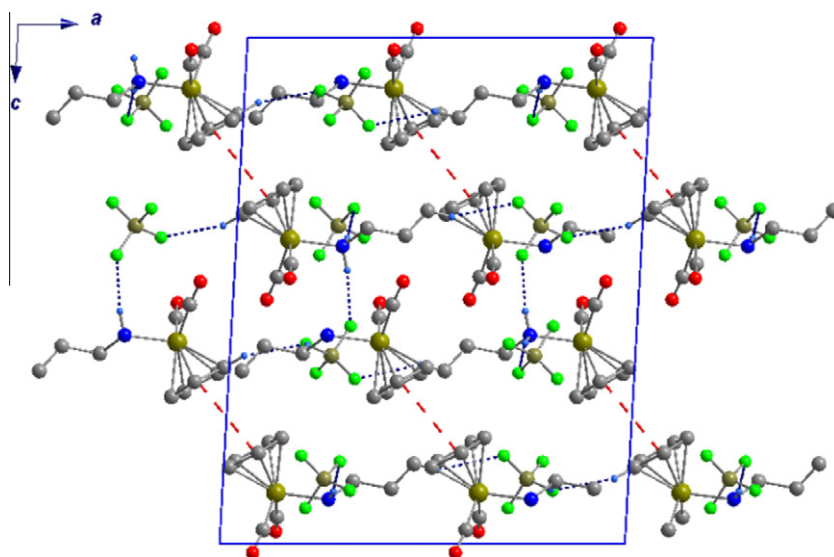


Fig. 3. Crystal packing of [3][BF₄] viewed down the crystallographic *b*-axis showing N–H...F, C–H...F and π ... π intermolecular interactions.

described by a R_4^4 graph set notation. The chains are further stabilized by N–H...F [N(1)...F(2)] and C–H...F [C(4)...F(3)] (Fig. 3) connecting the chains and rings in the *b* crystallographic direction, and π ... π intermolecular interactions [Cg1...Cg1 = 3.375(4) Å, symmetry code; $-x, y, \frac{1}{2} - z$]. This mode of packing is similar to that observed in the compound [(η^5 -C₅H₅)(CO)₂Fe{NH₂(CH₂)₂CH₃}]BF₄ [29].

In the crystal of [4][BF₄], the cations and anions are connected through a N–H...F, a C–H...F and two C–H...O intermolecular interactions (Table 3) resulting in chains that run diagonally through the unit. C(13)–H(13B)...O(1) connects two centrosymmetrically related cations with an inversion center between the two molecules. C(7)–H(7C)...O(1) also connects the same cations with the O atom being bifurcated. N(2)–H(2A)...F(2) and N(2)–H(2B)...F(3)

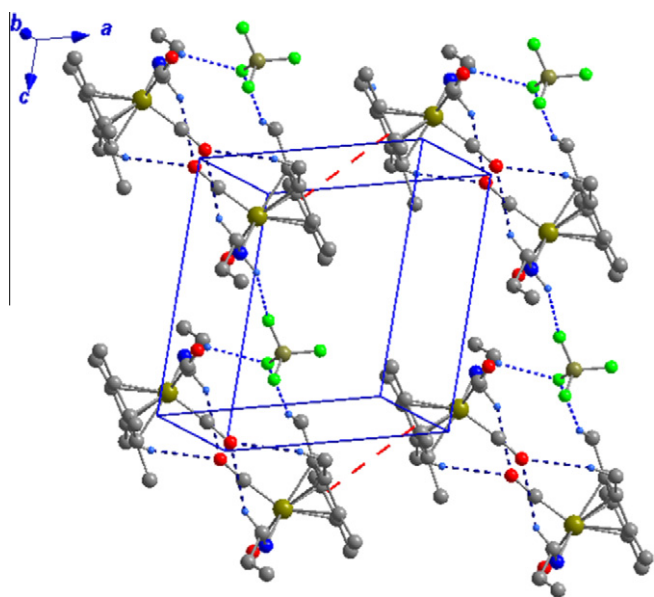


Fig. 4. A perspective of [4][BF₄] showing N–H...F, C–H...F, C–H...O and π – π intermolecular interactions as indicated by dashed and dotted lines.

Table 3
Intermolecular interactions geometry for compounds [3][BF₄] and [4][BF₄] (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A	Symmetry operator
[3][BF₄]					
N(1)–H(1A)...F(4)	0.92	2.13	3.027(5)	165	$x, 1 - y, \frac{1}{2} - z$
N(1)–H(1B)...F(2)	0.92	2.08	2.983(5)	166	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
C(4)–H(4)...F(3)	0.95	2.42	3.213(6)	141	$-x, y, \frac{1}{2} - z$
C(8)–H(8A)...F(3)	0.99	2.43	3.378(6)	159	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
C(10)–H(10B)...F(1)	0.95	2.55	3.407(9)	151	$1 - x, y, \frac{1}{2} - z$
[3][BF₄]					
N(2)–H(2A)...F(2)	0.92	2.27	3.0134	137	$-x, 1 - y, 1 - z$
C(7)–H(7C)...O(1)	0.98	2.60	3.5645	169	$-x, 2 - y, -z$
C(13)–H(13B)...O(1)	0.99	2.57	3.4824	152	$-x, 2 - y, -z$
C(8)–H(8B)...F(2)	0.98	2.52	3.3923	149	$x, 1 + y, -1 + z$

then connects the pairs of cations to complete the chains. The chains are then linked through weak π ... π intermolecular interactions [Cg ... Cg = 3.9994 Å, symmetry code; $1 - x, 1 - y, -z$] (Fig. 4).

2.2. Halogenation of complexes 3 and 4

The cationic allylamino complexes $[(\eta^5-C_5R_5)(CO)_2Fe(NH_2CH_2-CH=CH_2)]^+$ (R = H (3), CH₃ (4)) react readily with Cl₂ and Br₂ in CH₂Cl₂ to give the aminodihalopropane complexes $[(\eta^5-C_5R_5)(CO)_2Fe\{NH_2CH_2CH(X)CH_2X\}]^+$ (R = H; X = Cl (5), Br (6) and R = CH₃; X = Br (7)) as shown in Scheme 2. The compounds [5][BF₄], [6][BF₄] and [7][BF₄] were obtained as microcrystalline solids. The reaction of [4][BF₄] with chlorine gave a mixture of white and dark green sticky solids which showed no carbonyl bands in the IR spectrum. There was no evidence to suggest the formation of the halide complexes $[(\eta^5-C_5R_5)Fe(CO)_2X]$ in all these cases.

Halogenation is believed to proceed according to the mechanism illustrated in Scheme 3. Initially, the halogen molecule is polarized by pi bond electrons leading to the formation of halonium and halide ions [41]. Then the halide adds to the side opposite the carbon–halogen bond of the halonium ion in order to achieve the maximum overlap of the C–X σ^* antibonding molecular orbitals. In this way the two halogens add in an anti-addition fashion

resulting in a racemic mixture of (R) and (S) enantiomers as shown in Scheme 3. This is indeed further corroborated by the single crystal structure of compound [7][BF₄] (Fig. 5) and the NMR data discussed below.

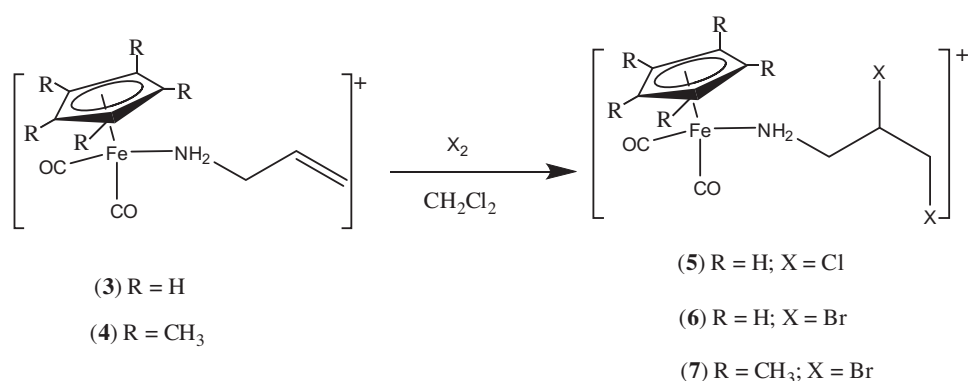
The success of the halogenation reactions of complexes 3 and 4 was marked by the disappearance of the strong IR band between 920 and 950 cm⁻¹ and weak IR bands at ca. 1640 cm⁻¹ which correspond to =CH out-of-plane bending and C=C stretching vibrations, respectively. The infrared spectrum of compound [5][BF₄] exhibited a characteristic band assignable to C–Cl at 746 cm⁻¹, while compound [6][BF₄] showed a vibration band corresponding to C–Br stretching at 652 cm⁻¹, which, as expected, is at a lower wavenumber than that corresponding to C–Cl. A similar peak was observed in the infrared spectrum of compound [7][BF₄] at 670 cm⁻¹. There was no significant variation in the carbonyl bands upon halogenation, indicating that the halogen atoms were added to the vinyl group which is far from the metal and therefore the electron density on the metal center was not significantly affected.

As expected for chiral molecules, the protons of the α -CH₂ group neighboring the chiral center CHX (Scheme 3) are diastereotopic and they show two well separated multiplets at around 3.00 and 2.77 ppm ($\Delta\delta \sim 0.2$ ppm), each integrating for one proton. The peaks corresponding to CHX and CH₂X were observed at around 4.28 and 3.86 ppm, respectively. This corresponds to an upfield shift of 1.54 and 1.38 ppm relative to the peaks due to CH= and =CH₂ of the starting material, respectively, indicating loss of anisotropy upon halogenation. The ¹³C NMR data for compounds [5][BF₄], [6][BF₄] and [7][BF₄] were assigned with the help of 2D NMR experiments. As expected, these data show that the position of the peaks due to CO and (η^5 -C₅H₅) are independent of the type of halide in the molecule. The ¹³C NMR spectrum of compound [6][BF₄] shows a peak assignable to the terminal carbon neighboring bromine at 31.2 ppm which is 15.1 ppm upfield relative to that of the similar carbon neighboring chlorine in the ¹³C NMR spectrum of compound [5][BF₄], as expected, because chlorine is significantly more electronegative than bromine.

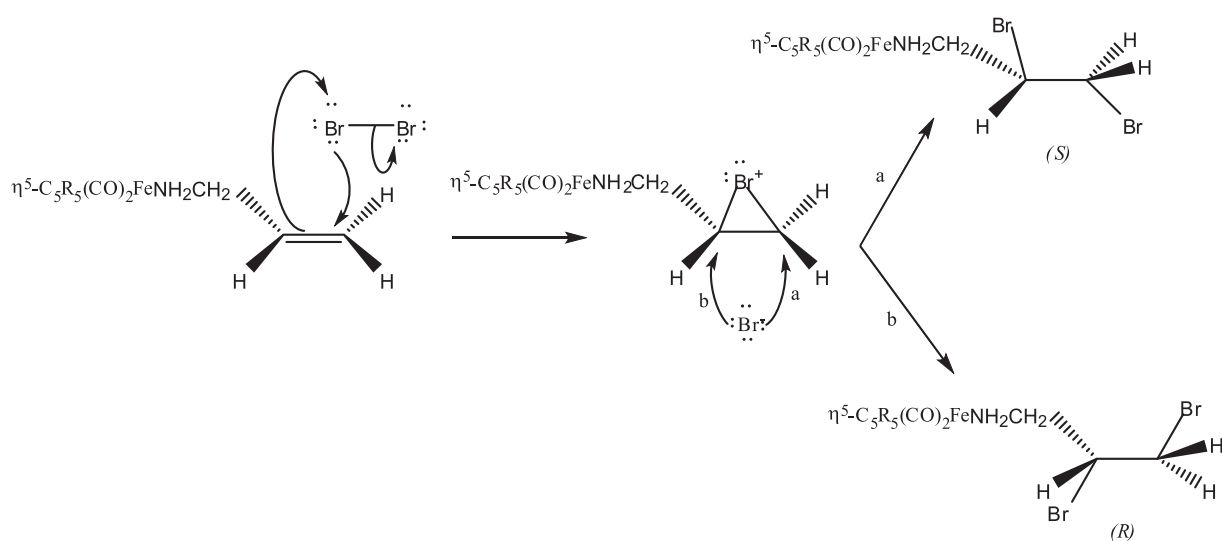
No reaction was noted between the allylamino complexes and formic acid or tetrafluoroacetic acid, even when a large excess of these reagents was used and the mixtures stirred for 24 h at room temperature or at refluxing temperatures. There was also no reaction between the allylamino complexes and hydrogen chloride gas. Interestingly, although amines are weak bases, the allylamino complexes were recovered intact at the end of the period by evaporating the mixture to dryness, followed by extraction using dichloromethane and precipitation by diethyl ether. The coordination of the amine functionality probably severely weakens the basic properties of the allylamine, thereby stabilizing the metal-coordinated compounds in acidic medium.

2.2.1. Crystal structure of $[(\eta^5-C_5(CH_3)_5)(CO)_2Fe\{NH_2CH_2CH(Br)CH_2Br\}]BF_4$, [7][BF₄]

Compound [7][BF₄] is a product of the bromination reaction of the allylamino compound [4][BF₄]. The compound crystallizes in $P\bar{1}$ space group as brown plates from a 1:6 v/v solution of dichloromethane and diethyl ether. The asymmetric unit consists of one cation and one anion. The structure shows an uncommon form of disorder in which two enantiomorphs with 50% occupancy are observed. Each molecular site is occupied with equal probability with only the C(1)–C(2)(Br1)–C(3)(Br2) arm of the molecule occupying different sites. Fig. 5 shows molecular structures of the two enantiomers R and S. Dibromoaminopropane coordinated to the metal differently as *gauche* or *anti* depending on the enantioface for this type of compound (in Scheme 3). In this compound, the bromine atoms adopt a *gauche*-conformation in the (R) enantiomer and an *anti*-conformation in the (S) enantiomer. The torsion angles Br2A–C15A–C14A–Br1A and Br1B–C14B–C15B–Br2B in the two



Scheme 2. Halogenation of allylamino complexes.



Scheme 3. Proposed mechanism for bromination of complexes 3 and 4.

enantiomers are considerably different, 69.0(4)° and 178.8(3)°, respectively, and this is probably due to packing and steric effects of the bulky $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ and Br atoms. Coordination is via the N atom resulting in “pseudo-octahedral three-legged piano stool” structures. The Fe–N bond distances are both 2.036(3) Å (Table 4), and are slightly longer than those observed in [4] [BF₄] [2.0294(14) Å], in $[\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{Fe}(\text{NH}_2(\text{CH}_2)_3\text{CH}_3)]\text{BF}_4$ [2.022(15) Å] [31] and in $[\{\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{Fe}\}_2(\mu\text{-NH}_2(\text{CH}_2)_3\text{NH}_2)](\text{BF}_4)_2$ [2.0182(16) and 2.0202(14) Å] [31]. Similarly, C(2)–C(3) is ca. 1.538 Å, significantly longer than the corresponding bond in 4 (C(14)–C(15)) by ca. 0.216 Å. The bond angles C1–C2–C3, C1–C2–Br1, Br1–C2–C3 and C2–C3–Br2 in both the enantiomers of compound [7][BF₄] are close to 109.5°, further confirming that the allylamine complex 4 reacts with bromine to form a saturated dibromoalkane complex.

In the crystal of [7][BF₄] (Fig. 6), the cations and anions are connected mainly through two C–H...F interaction and one N–H...F interaction (Table 5). These interactions are further stabilized by a C–H... π intermolecular interaction [C(14)–H(14A)...Cg(1); H(14A)...Cg = 2.61 and $\angle\text{C}(14)\text{--H}(14\text{A})\text{...Cg}(1) = 163^\circ$; symmetry code = $-x, 1 - y, -z$].

2.3. Metallation of 3 and 4

Although a wide variety of bridged metal complexes are reported, metal complexes bridged by ligands comprising of two

non equivalent binding sites are rare [42]. The reactions of the allylamine complexes 3 and 4 with molar equivalents of the etherate complexes 1 and 2 produced dinuclear complexes (Fig. 7) in which the two iron systems are in different electronic environments. Thus, the reaction of 3 with 1 and 2 in CH₂Cl₂ at room temperature gave the dinuclear complexes 8 and 9, respectively. Similarly, 4 reacts with 1 and 2 to give the dinuclear complexes 10 and 11, respectively. Complex 8 is insoluble in dichloromethane, hexane and diethyl ether, but soluble in acetone, methanol, water and acetonitrile. Thus it was easily isolated by filtration and purified by recrystallization from an acetone/diethyl ether mixture (1/3 v/v). Unlike 8, the other dinuclear complexes are very soluble in dichloromethane and they were precipitated from their solution by addition of diethyl ether. The isolated compounds were characterized by NMR, IR and elemental analysis and the characterization data are given in Section 4.

As expected, the infrared spectra of complexes 8 and 11 show four absorption bands assignable to the terminal carbonyls. The spectrum of complex 8 shows bands corresponding to the two carbonyls on the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2=\text{CH}$ - side of the molecule at 2078 and 2064 cm⁻¹ and another two bands assignable to the two terminal carbonyls on the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeNH}_2\text{CH}_2$ - side at 2041 and 2004 cm⁻¹. These data are in close agreement with those of the related olefin complexes with the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{-FeCH}_2=\text{CH}$ - moiety [6,9,11,12,43–45]. The infrared spectrum of complex 11 shows two peaks assignable to the two terminal

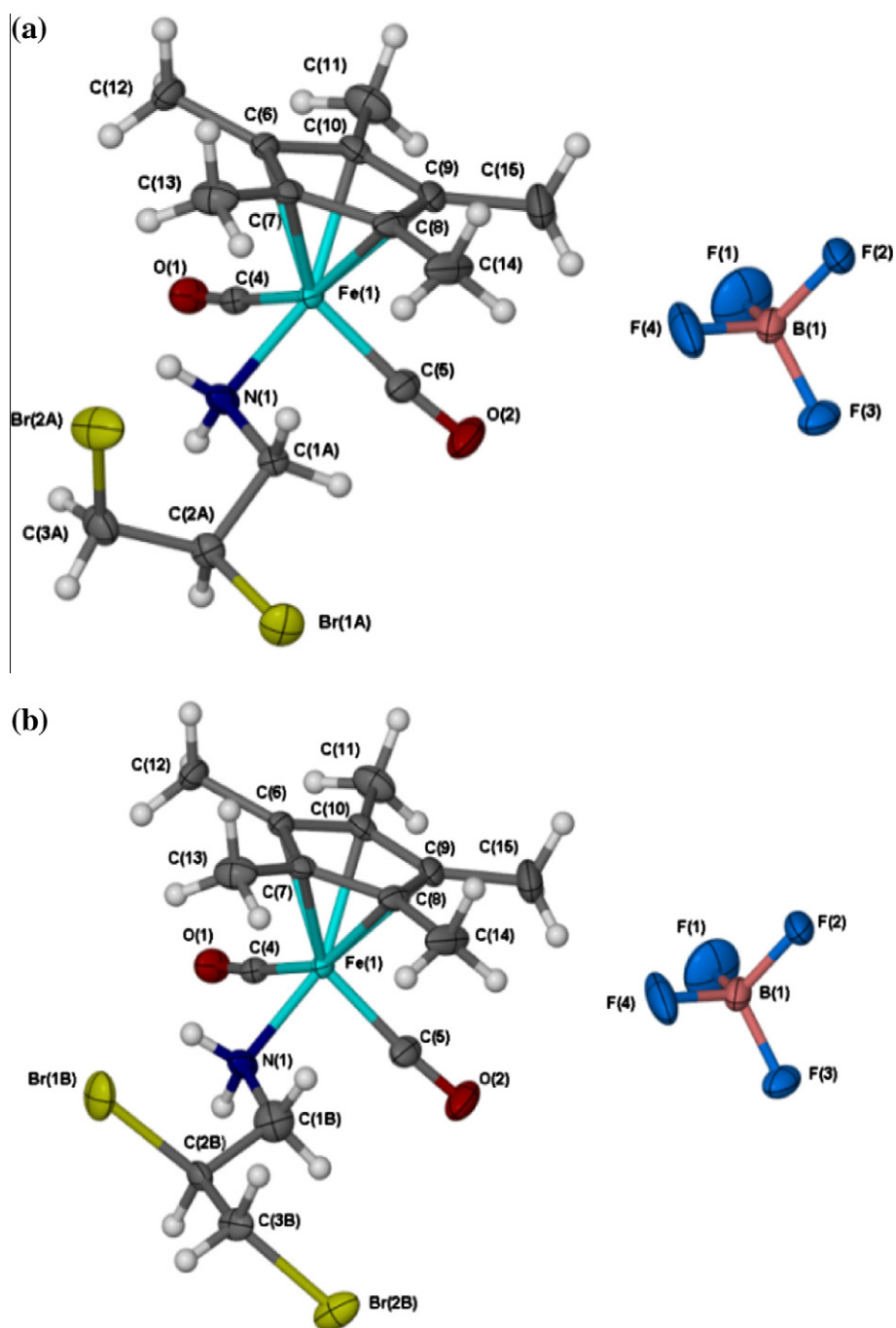


Fig. 5. Molecular structures of both enantiomers of $[7][BF_4]$ showing the numbering scheme of the atoms in (a) *R* and (b) *S*.

Table 4

Selected bond distances and bond angles in the two enantiomers of $[7][BF_4]$ (Å, °).

	<i>R</i>	<i>S</i>		<i>R</i>	<i>S</i>
Cg...Fe(1)	1.727	1.727	Cg–Fe(1)–N(1)	125.6(5)	125.6(5)
Fe(1)–C(4)	1.794(3)	1.794(3)	Cg–Fe(1)–C(4)	120.0(1)	120.0(1)
Fe(1)–C(5)	1.790(3)	1.790(3)	Cg–Fe(1)–C(5)	122.1(8)	122.1(8)
Fe(1)–N(1)	2.036(2)	2.36(2)	Fe(1)–N(1)–C(1)	115.4(2)	121.8(3)
C(4)–O(1)	1.133(4)	1.133(4)	C(4)–Fe(1)–C(5)	96.56(13)	96.56(13)
C(5)–O(2)	1.137(4)	1.137(4)	C(4)–Fe(1)–N(1)	91.29(11)	91.29(11)
C(1)–C(2)	1.537(2)	1.539(2)	C(5)–Fe(1)–N(1)	93.23(13)	93.23(13)
C(2)–C(3)	1.537(2)	1.539(2)	C(2)–C(1)–N(1)	111.4(4)	116.4(5)
C(2)–Br(1)	1.942(5)	1.956(7)	C(1)–C(2)–C(3)	115.4(5)	112.5(6)
C(3)–Br(2)	1.923(6)	1.967(7)	C(1)–C(2)–Br(1)	107.6(3)	109.0(5)
N(1)–C(1)	1.478(6)	1.494(8)	C(2)–C(3)–Br(2)	113.7(4)	109.5(5)

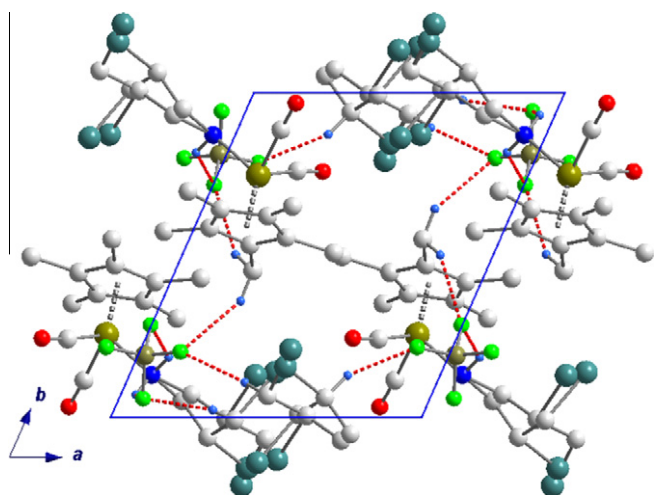


Fig. 6. Packing diagram for [7][BF₄] showing N...F and C...F intermolecular interactions as viewed down the crystallographic *c*-axis.

Table 5
Intermolecular interaction geometry for [7][BF₄] (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A	Symmetry operator
N(1)–H(1E)...F(3)	0.92	2.13	2.966(3)	150	– <i>x</i> , – <i>y</i> , 1 – <i>z</i>
C(2A)–H(2A)...F(1)	1.00	2.31	3.134(2)	139	– <i>x</i> , – <i>y</i> , 1 – <i>z</i>
C(12)–H(12C)...F(4)	0.98	2.51	3.392(3)	150	– <i>x</i> , 1 – <i>y</i> , 1 – <i>z</i>

carbonyls on the $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{FeCH}_2=\text{CH}-$ side at 2050 and 2014 cm^{-1} , which is in agreement with the reported data for related complexes [44,46]. The other two bands assignable to the two terminal carbonyls on the $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{FeNH}_2\text{CH}_2-$ side were observed at 1986 and 1955 cm^{-1} . These values are at considerably lower wavenumbers than the ca. 2023 and 1970 cm^{-1} found for the compound $[\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{Fe}\{\text{NH}_2(\text{CH}_2)_3\text{CH}_3\}]\text{BF}_4$ [31].

The infrared spectrum of complex **9** shows only two bands, while that of **10** shows three bands corresponding to the two sets of terminal carbonyls. The carbonyl bands of complexes **9** and **10** are strong and broad suggesting band overlap. All IR spectra of complexes **8–11** show two bands in the N–H stretching region at ca. 3308 and 3268 cm^{-1} , which are assignable to NH asymmetric and symmetric stretching, respectively. The medium band at ca. 1600 cm^{-1} can be assigned to NH bending. The peak at ca. 1640 cm^{-1} , as well as the peaks at ca. 938 cm^{-1} , which were assigned to C=C stretching and =CH wagging in the infrared spectra of the parent allylamino complexes, are absent.

The ¹H NMR data show that the allylamino molecule links the two metal centers using the amine on one end and the vinyl functionality on the other end. These two functionalities have different electronic effects and as a result the ¹H NMR spectra of complexes **8** and **11** gave two well separated characteristic peaks corresponding to protons of the two cyclopentadienyl ligands and pentamethylcyclopentadienyl ligands in the different electronic environments. In the ¹H NMR spectrum of **8**, two peaks were observed at 5.54 and 5.92 ppm and were assigned to the $(\eta^5\text{-C}_5\text{H}_5)$ groups of the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeN}$ and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeC}$ moieties, respectively. The ¹H NMR spectrum of complex **11** exhibited peaks at 1.89 and 2.01 ppm corresponding to the $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ group of the $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{FeN}-$ and $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{FeC}$ moieties, respectively. The peaks corresponding to the $(\eta^5\text{-C}_5\text{H}_5)$ and $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ ligands attached to the metal on the vinyl end appear downfield relative to those on the amine end. The downfield shift of these peaks upon olefin coordination has been previously attributed to the deshielding effects of the cationic metal center [9]. However, the influence of π -backdonation of electrons from the metal orbital to the vinylic carbons should not be ignored, since drawing of electrons from the metal increases its electrophilicity, which consequently would lead to deshielding of the $(\eta^5\text{-C}_5\text{H}_5)$ or $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ protons. For this reason, whereas both metal centers are cationic, the $(\eta^5\text{-C}_5\text{H}_5)$ or $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ protons neighboring the metal on the vinyl end appear at higher chemical shift values than those on the amine side.

The ¹H NMR spectra of the mixed ligand complexes **9** and **10**, which are structural isomers, show $(\eta^5\text{-C}_5\text{H}_5)$ peaks at 5.20 and 5.90 ppm, while $\{\eta^5\text{-C}_5(\text{CH}_3)_5\}$ peaks were observed at 2.01 and 1.90 ppm, respectively. Complexes **8** and **10** show characteristic sharp doublets at ca. 4.14 ppm ($J \sim 8.3$ Hz) and 3.62 ppm ($J \sim 14.24$ Hz) assignable to the diastereotopic methylene protons γ to NH₂ which are *cis* and *trans* to βCH . These values are in good agreement with data reported for related cyclopentadienyliron complexes [6,9,11,12,44,45]. Similar sharp doublets were observed in the ¹H NMR spectra of complexes **9** and **11** at ca. 3.01 ($J \sim 7.76$ Hz) and 3.55 ($J \sim 13.84$ Hz), also in agreement with data reported for the related pentamethylcyclopentadienyl complexes [44,46]. The αCH_2 protons are also diastereotopic, hence two separate multiplets assignable to these protons were observed at ca. 2.35 and 3.44 ppm. These observations confirm that complexes **8–11** have a rigid chiral structure which is maintained even in solution. The ¹³C NMR spectra of complexes **8–11** show peaks assignable to the carbon of the vinyl group coordinated to the metal at chemical shifts below 80 ppm. This is about 59 ppm upfield relative to the pendant vinyl groups in the starting materials (complexes **3** and **4**). This is a clear indication that the vinyl group of allylamino ligand links the second metal center in a η^2 -fashion.

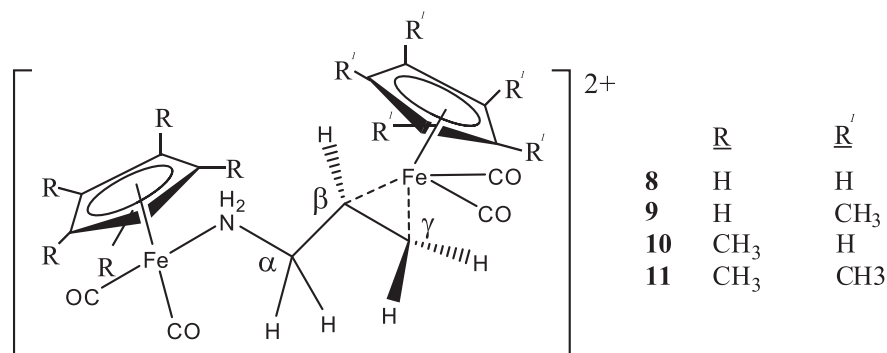
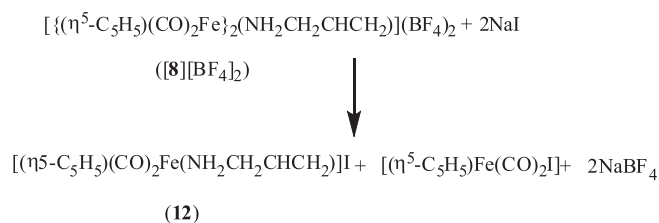


Fig. 7. The dinuclear complexes, $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{R}'_5)]^{2+}$.

2.4. Reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]_2(\mu\text{-NH}_2\text{CH}_2\text{CH}=\text{CH}_2)(\text{BF}_4)_2$, $[\mathbf{8}][\text{BF}_4]_2$ with NaI

It is well established that olefin complexes are demetallated when treated with excess NaI to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ and the corresponding olefin [12,45,47]. Haloalkene displacement when olefin complexes are treated with NaI or $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ has also been reported [19]. Contrary to these observations, the dinuclear salt $[\mathbf{8}][\text{BF}_4]_2$ reacts with NaI at room temperature in acetone to give the mononuclear compound $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{I}$ (**12**) and the known neutral iodo complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{I}$ [48] according to Eq. (1). There was no evidence of the formation of the dimeric complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ nor of Fe–N bond cleavage, even when the reaction was repeated at 35 °C. Compound **12** was obtained as a yellow microcrystalline solid upon treating the dichloromethane extract with diethyl ether. The iodo complex remained in the mother liquor and it was obtained as a gray crystalline solid upon evaporation.



The formation of complex **12** illustrates that the Fe–N bond in the allylamino complex is too strong to be cleaved by the iodide, I^- . The complex was characterized by elemental analysis, IR and NMR spectroscopy and the data are listed in Section 4.7. A similar pattern of the IR peaks was observed as for the BF_4^- salt, compound **3** $[\text{BF}_4]$, with the exception of the peaks at 999–1051 cm^{-1} (assigned to BF_4^-) and the finger-print region.

3. Conclusion

We have unequivocally shown that the etherate complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{OEt}_2)]^+$ and $[(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Fe}(\text{CO})_2(\text{THF})]^+$ react with 3-aminoprop-1-ene to give the new allylamino complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$, which in turn undergo electrophilic halogenation to form new chiral complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}(\text{X})\text{CH}_2\text{X})]^+$. The crystallographic data of compound $[(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}(\text{Br})\text{CH}_2\text{Br})]\text{BF}_4$ show that it exists as a mixture of (R) and (S) enantiomers. The reactions of the etherate complexes with the allylamino complexes is a convenient route to dinuclear complexes of the type $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{R}_5')]^{2+}$ in which the two metal fragments are bridged by the allylamino via the amine on one side and via the vinyl group on the other side. Coordination of the vinyl group occurs only after amine coordination, as expected.

4. Experimental

4.1. General

All experimental manipulations of organometallic compounds were carried out under inert atmosphere using standard Schlenk line procedures unless otherwise stated. Reagent grade THF, hexane and Et_2O were distilled from sodium/benzophenone and used immediately; acetone and MeCN were distilled from anhydrous CaCl_2 and stored under molecular sieves of porosity size 4;

CH_2Cl_2 was distilled from phosphorus(V) oxide and used immediately. Dry chlorine gas was generated according to literature method [49]. The other reagents were used as received from the suppliers without further purification. Melting points were recorded on an Ernst Leitz Wetzlar hot-stage microscope and are uncorrected. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer. Infrared spectra were recorded using an ATR PerkinElmer Spectrum 100 spectrophotometer between 4000 and 400 cm^{-1} . ^1H and ^{13}C NMR spectra were recorded using Bruker 400 MHz and 600 MHz spectrometers and chemical shifts are recorded in ppm. Correlations were confirmed through COSY and HSQC experiments. The deuterated solvents CDCl_3 (Aldrich, 99.8%), acetonitrile- d_3 (Merck, 99%), acetone- d_6 (Aldrich, 99.5%) and methanol- d_4 (Aldrich, 99.8%) were used as purchased. The precursors $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{OEt}_2)]\text{BF}_4$ [29] and $[(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_2\text{Fe}(\text{THF})]\text{BF}_4$ [50] were prepared by the literature methods.

4.2. Reaction of allylamine with one equivalent of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{OEt}_2)]\text{BF}_4$, $[\mathbf{1}][\text{BF}_4]$

Into a solution of compound **1** $[\text{BF}_4]$ (0.86 g, 2.54 mmol) in CH_2Cl_2 (10 ml), allylamine (0.19 ml) was added and the mixture stirred for 6 h under nitrogen at room temperature, after which a yellow precipitate was formed. The mixture was filtered into the pre-weighed Schlenk tube and the residue washed with a minimum amount of dichloromethane (2 ml) followed by diethyl ether (5 ml). A further crop of the compound was recovered from the filtrate by addition of diethyl ether and allowing the mixture to stand at room temperature for 1 h. The mother liquor was syringed off and the residue was washed with diethyl ether to give the yellow microcrystalline solid of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$, **3** $[\text{BF}_4]$. Yield 0.80 g, 98%. *Anal.* Calc. for $\text{C}_{10}\text{H}_{12}\text{BF}_4\text{FeNO}_2$: C, 37.38; H, 3.74; N, 4.36. Found: C, 37.86; H, 3.84; N, 3.99%. ^1H NMR (600 MHz, methanol- d_4): 5.36 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 3.81 (s, 2H, NH_2), 2.95 (q, $J_{\text{HH}} = 6.60$ Hz, 2H, $-\text{CH}_2$), 5.80 (m, 1H, $=\text{CH}$), 5.22 (d, $J_{\text{HH}} = 10.38$ Hz, 1H, $=\text{CH}$ cis), 5.26 (d, $J_{\text{HH}} = 17.22$ Hz, 1H, $=\text{CH}$ trans). ^{13}C NMR (600 MHz, methanol- d_4): 85.95 ($\eta^5\text{-C}_5\text{H}_5$), 53.88 ($-\text{CH}_2$), 134.99 ($\text{CH}=\text{}$), 117.81 ($=\text{CH}_2$), 211.05 (CO). IR (solid state) ν_{max} (cm^{-1}): 2051, 2004 (CO); 3307, 3277 (NH_2). Decomposes at temperature >120 °C.

4.3. Reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]\text{BF}_4$, **3** $[\text{BF}_4]$ with chlorine

A Schlenk tube equipped with a magnetic bar and charged with a solution of **3** $[\text{BF}_4]$ (0.16 g, 0.498 mmol) in CH_2Cl_2 (10 ml) was cooled to -78 °C (dry ice/acetone) and then chlorine gas condensed into the mixture. The mixture was stirred and allowed to warm slowly to room temperature for the excess chlorine gas to escape and then it was filtered into a pre-weighed Schlenk tube. Diethyl ether (25 ml) was added and the mixture was allowed to stand overnight, after which a yellow microcrystalline solid was found stuck on the walls of the Schlenk tube. The mother liquor was syringed off and the residue washed with diethyl ether (5 ml) and dried under reduced pressure gave 0.083 g (47%) of compound **5** $[\text{BF}_4]$. *Anal.* Calc. for $\text{C}_{10}\text{H}_{12}\text{BCl}_2\text{F}_4\text{FeNO}_2$: C, 30.66; H, 3.09; N, 3.58. Found: C, 30.82; H, 3.46; N, 3.09%. ^1H NMR (400 MHz, methanol- d_4): 5.39 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.14 (br, 1H, CHCl), 3.85 (br, 2H, NH_2), 3.82 (br, 2H, CH_2Cl), 2.87 (br, 1H, $\text{CH}_2\text{-N}$), 2.70 (br, 1H, $\text{CH}_2\text{-N}$). ^{13}C NMR (400 MHz, methanol- d_4): 87.63 ($\eta^5\text{-C}_5\text{H}_5$), 62.18 (CHCl), 56.71 ($\text{CH}_2\text{-N}$), 46.87 (CH_2Cl), 212.06 (CO). IR (solid-state) ν_{max} (cm^{-1}): 2052, 2001 (CO); 3306, 3274 (NH_2). M.p., 63–65 °C.

4.4. Reaction of compound **[3][BF₄]** with bromine

Liquid bromine (0.2 ml, 3.882 mmol) was added to a solution of compound **[3][BF₄]** (0.24 g, 0.732 mmol) in CH₂Cl₂ (20 ml) and the mixture stirred under nitrogen for 2 h at room temperature. Excess bromine was removed under vacuum and the mixture evaporated to ca. 7 ml under reduced pressure. Diethyl ether was added until a yellow precipitate was formed and then the mixture was allowed to stand at room temperature for 5 h in the dark. The mother liquor was removed and the yellow residue was washed with diethyl ether (2 × 10 ml). Drying the residue under reduced pressure gave 0.197 g (56% yield) of microcrystalline [(η⁵-C₅H₅)(CO)₂(NH₂CH₂CH(Br)CH₂Br)]BF₄, **[6][BF₄]**. *Anal. Calc.* for C₁₀H₁₂BBr₂F₄FeNO₂: C, 24.99; H, 2.52; N, 2.91. Found: C, 25.06; H, 2.27; N, 2.83%. ¹H NMR (400 MHz, methanol-*d*₄) 5.40 (s, 5H, η⁵-C₅H₅), 4.22 (m, 1H, CHBr), 3.88 (m, 1H, CH₂Br), 3.77 (m, 1H, CH₂-N), 3.00 (m, 1H, CH₂-N), 2.79 (m, 1H, CH₂). NH not observed. ¹³C NMR (400 MHz, methanol-*d*₄): 87.42 (η⁵-C₅H₅), 57.67 (CH₂-N), 52.85 (CHBr), 34.18 (CH₂Br), 212.04 (CO). IR (solid state) ν_{\max} (cm⁻¹): 2047, 1995 (CO); 3294, 3266 (NH₂). M.p., 109–110 °C.

4.5. Reaction of compound **[3][BF₄]** with compound **[1][BF₄]**

A mixture of compound **[1][BF₄]** (0.15 g, 0.440 mmol) in CH₂Cl₂ (10 ml) and that of compound **[3][BF₄]** (0.10 g, 0.31 mmol) in CH₂Cl₂ (15 ml) was stirred at room temperature for 1 h. An orange solid formed and was allowed to settle for 30 min after which the mother liquor was syringed off. The residue was washed with CH₂Cl₂ (2 × 5 ml) and dried under reduced pressure. The product was further purified by recrystallizing from acetone/diethyl ether (1/3 v/v) to give a bright yellow microcrystalline solid, [(η⁵-C₅H₅)(CO)₂Fe]₂(NH₂CH₂CH=CH₂)](BF₄)₂, **[8][BF₄]**₂. Yield. 0.130 g, 72%. *Anal. Calc.* for C₁₇H₁₇B₂F₈FeNO₂: C, 34.93; H, 2.93; N, 2.40. Found: C, 34.84; H, 3.40; N, 1.87%. ¹H NMR (400 MHz, acetone-*d*₆) 5.92 (s, 5H, η⁵-C₅H₅), 5.54 (s, 5H, η⁵-C₅H₅), 4.99 (m, 1H, CH), 4.12 (d, *J*_{HH} = 8.32 Hz, 1H, *cis* CH), 3.72 (d, *J*_{HH} = 14.20 Hz, 1H, *trans* CH), 3.57 (m, 1H, CH-N), 2.48 (m, 1H, CH-N), 3.76 (s br, 2H, NH₂). ¹³C NMR (400 MHz, acetone-*d*₆): 90.94 (η⁵-C₅H₅), 87.46 (η⁵-C₅H₅), 76.96 (CH), 57.42 (CH₂-Fe), 56.70 (CH₂-N), 211.81, 211.75, 210.59, 207.87 (CO). IR (solid state) ν_{\max} (cm⁻¹): 2078, 2064, 2041, 2004 (CO); 3309, 3270 (NH₂). Decomposes at temperature >129°C.

4.6. Reaction of compound **[3][BF₄]** with [(η⁵-C₅(CH₃)₅)Fe(CO)₂(THF)]BF₄, **[2][BF₄]**

To a stirred solution of compound **[3][BF₄]** (0.15 g, 0.467 mmol) in CH₂Cl₂ (10 ml), a solution of **[2][BF₄]** (0.19 g, 0.468 mmol) in CH₂Cl₂ (10 ml) was added within 30 s. The mixture was stirred for 12 h after which it was filtered into a pre-weighed Schlenk tube and diethyl ether added to the filtrate to give a yellow precipitate. The precipitate was allowed to stand undisturbed for 5 h and then the mother liquor was removed. Washing the residue with diethyl ether (10 ml) and drying it under reduced pressure afforded 0.128 g (42% yield) of the dinuclear mixed ligand complex [(η⁵-C₅H₅)(CO)₂Fe(NH₂CH₂CH=CH₂)Fe(CO)₂(η⁵-C₅(CH₃)₅)](BF₄)₂, **[9][BF₄]**₂. *Anal. Calc.* for C₂₂H₂₇B₂F₈Fe₂NO₄: C, 40.36; H, 4.16; N, 2.14. Found: C, 40.46; H, 3.89; N, 2.16%. ¹H NMR (400 MHz, acetone-*d*₆) 5.20 (s, 5H, (η⁵-C₅H₅)), 3.71 (m, 1H, CH), 3.54 (br, 1H, *cis* CH), 2.85 (br, 1H, *trans* CH), 3.40 (m, 1H, CH-N), 2.35 (m, 1H, CH-N), 2.01 (s, 15H, η⁵-C₅(CH₃)₅). ¹³C NMR (400 MHz, acetone-*d*₆): 87.49 (η⁵-C₅H₅), 77.50 (CH), 60.42 (CH₂-Fe), 56.95 (CH₂-N), 9.16 (η⁵-C₅(CH₃)₅), 103.85 (η⁵-C₅(CH₃)₅), 213.13, 212.38, 211.88, 211.82 (CO). IR (solid state) ν_{\max} (cm⁻¹): 2053, 2001br (CO); 3304, 3272 (NH). M.p., 40–42 °C.

4.7. Reaction of [(η⁵-C₅H₅)(CO)₂Fe]₂(μ-NH₂CH₂CH=CH₂)](BF₄)₂, **[8][BF₄]**₂, with NaI

To an acetone solution (25 ml) of compound **[8][BF₄]**₂ (0.33 g, 0.564 mmol) was added NaI (1.02 g, 6.80 mmol). The solution was stirred at 35 °C for 12 h, during which the solution turned from yellow to dark brown. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (30 ml). The extract was then concentrated to about one third of the initial volume. Addition of diethyl ether completed the precipitation of the allylamino complex [(η⁵-C₅H₅)(CO)₂Fe(NH₂CH₂CH=CH₂)]I, **12**, which was filtered off, washed with diethyl ether (2 × 10 ml) and dried under reduced pressure. It was purified further by recrystallization from acetone/diethyl ether 1:4 v/v. to give a bright yellow microcrystalline solid (0.114 g, 56%). *Anal. Calc.* for C₁₀H₁₂FeINO₂: C, 33.27; H, 3.35; N, 3.88. Found: C, 33.35; H, 3.54; N, 3.76%. ¹H NMR (600 MHz, acetone-*d*₆) 5.62 (s, 5H, η⁵-C₅H₅), 4.14 (s, 2H, NH₂), 3.09 (q, *J*_{HH} = 6.18 Hz, 2H, -CH₂), 6.01 (m, 1H, =CH), 5.15 (d, *J*_{HH} = 10.02 Hz, 1H, =CH *cis*), 5.28 (d, *J*_{HH} = 17.16 Hz, 1H, =CH *trans*). ¹³C NMR (600 MHz, acetone-*d*₆): 86.54 (η⁵-C₅H₅), 53.85 (-CH₂), 135.77 (CH=), 118.02 (=CH₂), 211.73 (CO). IR (solid state) ν_{\max} (cm⁻¹): 2042, 2002 (CO); 3152 br (NH₂). M.p., 130–131 °C.

The filtrate was evaporated to dryness to give a purple gray microcrystalline solid (0.53 g; 31% yield) which according to IR and NMR was found to be the known [(η⁵-C₅H₅)(CO)₂Fe]I **[51]**.

4.8. Reaction of allylamine with one equivalent of [(η⁵-C₅(CH₃)₅)Fe(CO)₂(THF)]BF₄, **[2][BF₄]**

3-Amino-1-propene (0.039 ml, 0.523 mmol), was added to a solution of compound **[2][BF₄]** (0.21 g, 0.517 mmol) in CH₂Cl₂ (10 ml) and the mixture stirred at room temperature for 12 h. The mixture was filtered into a pre-weighed Schlenk tube and diethyl ether added to the filtrate. The mixture was allowed to stand in the dark at room temperature for 18 h after which yellow-brown crystals stuck on the walls of the Schlenk tube. The mother liquor was syringed off and the crystals washed with diethyl ether (2 × 5 ml) after which it was dried under reduced pressure to give 0.158 g (78%) of compound **[4][BF₄]**. *Anal. Calc.* for C₁₅H₂₂B₂F₄FeNO₂: C, 46.08; H, 5.67; N, 3.58. Found: C, 45.93; H, 6.03; N, 3.39%. ¹H NMR (400 MHz, acetone-*d*₄) 1.93 (s, 15H, η⁵-C₅(CH₃)₅), 3.23 (br, 2H, NH₂), 3.08 (q, *J*_{HH} = 6.80 Hz, 2H, -CH₂), 5.84 (m, 1H, =CH), 5.21 (d, 1H, *J*_{HH} = 17.17 Hz, =CH₂), 5.15 (d, 1H, *J*_{HH} = 10.33 Hz, =CH₂). ¹³C NMR (400 MHz, acetone-*d*₆): 9.26 (η⁵-C₅H₅), 98.71 (η⁵-C₅(CH₃)₅), 55.10 (-CH₂), 136.57 (CH=), 118.86 (=CH₂), 214.42 (CO). IR (solid state) ν_{\max} (cm⁻¹): 2029, 1983 (CO); 3212, 3280 (NH₂). M.p., 131–132 °C.

4.9. Reaction of [(η⁵-C₅(CH₃)₅)(CO)₂Fe(NH₂CH₂CH=CH₂)]BF₄, **[4][BF₄]** with bromine

To a solution of compound **[4][BF₄]** (0.21 g, 0.537 mmol) in CH₂Cl₂ (10 ml), bromine (0.05 ml, 1.048 mmol) was added and the mixture stirred for 5 h. The solvent was removed resulting in a yellow solid which was recrystallized from dichloromethane/diethyl ether (1:6 v/v) to give an orange microcrystalline solid of [(η⁵-C₅(CH₃)₅)(CO)₂Fe(NH₂CH₂CH(Br)CH₂Br)]BF₄, **[7][BF₄]**. Yield, 0.145 g, 49%. *Anal. Calc.* for C₁₅H₂₂B₂F₄Br₂FeNO₂: C, 32.71; H, 4.03; N, 2.54. Found: C, 32.41; H, 4.06; N, 2.23%. ¹H NMR (400 MHz, acetone-*d*₆) 4.47 (m, 1H, CHBr), 3.94 (m, 2H, CH₂Br), 3.15 (m, 1H, CH-N), 2.83 (m, 1H, CH-N), 3.34 (br, 2H, NH₂), 1.97 (s, 15H, η⁵-C₅(CH₃)₅). ¹³C NMR (400 MHz, acetone-*d*₆): 54.31 (CHBr), 57.07 (CH₂N), 35.16 (CH₂Br), 9.47 (η⁵-C₅(CH₃)₅), 98.83 (η⁵-C₅(CH₃)₅), 213.87, 213.70 (CO). IR (solid state) ν_{\max} (cm⁻¹): 2034, 1978 (CO); 3296, 3268 (NH). M.p., 111–112 °C.

4.10. Reaction of compound [4][BF₄] with compound [1][BF₄]

To a solution of compound [4][BF₄] (0.12 g, 0.307 mmol) in CH₂Cl₂ (10 ml), a solution of [1][BF₄] (0.11 g, 0.325 mmol) was added and the mixture stirred overnight. The mixture was filtered and diethyl ether was added into the filtrate to form an orange suspension. The mixture was kept at 0° for 8 h after which it was filtered and the residue washed with diethyl ether (2 × 5 ml) to give an orange-yellow solid. This was dissolved in a minimum of dichloromethane and precipitated using diethyl ether and then filtered. This process was repeated three times to give the pure mixed-ligand compound $[\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}(\text{BF}_4)_2$, [10][BF₄]. Yield 0.091 g, 45%. *Anal. Calc.* for C₂₂H₂₇B₂F₈Fe₂NO₄: C, 40.36; H, 4.16; N, 2.14. Found: C, 40.26; H, 4.19; N, 2.13%. ¹H NMR (400 MHz, acetone-*d*₆) 5.90 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 5.18 (m, 1H, CH), 4.15 (d, *J*_{HH} = 8.20 Hz, 1H, *cis* CH), 3.58 (d, *J*_{HH} = 14.28 Hz, 1H, *trans* CH), 3.50 (m, 1H, CH–N), 2.31 (m, 1H, CH–N), 1.90 (s, 15H, $\eta^5\text{-C}_5(\text{CH}_3)_5$). ¹³C NMR (400 MHz, acetone-*d*₆): 91.03 ($\eta^5\text{-C}_5\text{H}_5$), 76.52 (CH), 57.99 (CH₂–Fe), 57.02 (CH₂–N), 9.18 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 98.76 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 213.90, 213.81, 210.72, 208.31 (CO). IR (solid state) ν_{max} (cm^{–1}): 2080, 2027, 1971 (CO); 3311, 3265 (NH). M.p., 33–35 °C.

4.11. Reaction of compound [4][BF₄] with compound [2][BF₄]

To a solution of compound [2][BF₄] (0.02 g, 0.049 mmol) in CH₂Cl₂ (10 ml), a solution of compound [4][BF₄] (0.02 g, 0.051 mmol) in CH₂Cl₂ (10 ml) was added. The mixture was stirred at room temperature for 16 h after which diethyl ether was added until a yellow precipitate was formed. This was allowed to settle for 20 min and the mother liquor was removed. The residue was washed with diethyl ether and dried under reduced pressure to give 0.018 g of the dinuclear complex $[\{\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{CO})_2\text{Fe}\}_2(\mu\text{-NH}_2\text{CH}_2\text{CH}_2\text{CH}_2)](\text{BF}_4)_2$, [11][BF₄]. Yield 51%. *Anal. Calc.* for C₂₇H₃₇B₂F₈Fe₂NO₄: C, 44.74; H, 5.14; N, 1.93%. Found: C, 45.12; H, 5.29; N, 1.97%. ¹H NMR (400 MHz, acetone-*d*₆) 4.11 (m, 1H, CH), 3.55 (d, *J*_{HH} = 13.85 Hz, 1H, *trans* CH), 3.18 (d, *J*_{HH} = 7.76 Hz, 1H, *cis*CH), 3.28 (m, 1H, CH–N), 2.24 (m, 1H, CH–N), 2.01 (s, Cp*–CH₂) 1.89 (s, 15H, Cp*–N). ¹³C NMR (400 MHz, acetone-*d*₆): 78.08 (CH), 60.99 (CH₂–Fe), 57.27 (CH₂–N), 9.19 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 9.27 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 98.74 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 103.87 ($\eta^5\text{-C}_5(\text{CH}_3)_5$), 213.92, 213.05, (CO). IR (solid state) ν_{max} (cm^{–1}): 2050, 2014, 1986, 1955 (CO); 3309, 3259 (NH). Decomposes at temperature >140 °C.

4.12. Single crystal X-ray diffraction

Crystals of compounds [3][BF₄], [4][BF₄] and [7][BF₄] suitable for single crystal X-ray diffraction were obtained by the liquid diffusion method of crystal growth. A nitrogen-saturated solution of each compound in dichloromethane was layered with diethyl ether and kept in the dark at room temperature for a period of one week. The X-ray diffraction data of [3][BF₄] and [4][BF₄] were collected on a Bruker Apex-II CCD area detector diffractometer with graphite monochromated Mo K α radiation (50 kV, 30 mA) using the APEX2 [52] data collection software, while that of [7][BF₄] was collected on SMART APEX CCD diffractometer, also using Mo K α radiation. The structures were solved and refined using SHELXS-97 and SHELXL-97 [53] while molecular graphics were generated using OLEX2 [54]. The crystallographic data and structural refinement information for compounds [3][BF₄], [4][BF₄] and [7][BF₄] are summarized in Table 2.

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Appendix A. Supplementary data

CCDC 851117, 851115 and 851116 contains the supplementary crystallographic data for compounds [3][BF₄], [4][BF₄] and [7][BF₄], respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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