



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 $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ 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 $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ ($\text{R} = \text{H}$, 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 $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}]$ ($\text{R} = \text{H}$, 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 $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]\mu\text{-CH}_2(\text{CH}_2)_n\text{CH}_2\}$ 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 $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$ ($\text{R} = \text{H}, \text{CH}_3$)

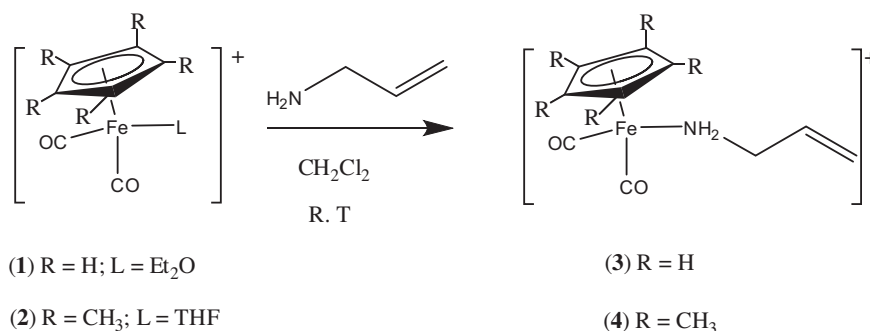
The reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{OEt}_2)]\text{BF}_4$, **1**, with an equimolar amount of 3-amino-1-propene at room temperature resulted in the formation of the allylamino complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2)]^+$, **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.

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