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Transformations of bridging ligands in diiron complexes: unconventional routes to new functionalized multisite bound organic frames

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Table of contents

CHAPTER I

Introduction.....1

References.....6

CHAPTER II

C-C bond formation through olefin-thiocarbyne coupling in diiron complexes.....9

References.....26

CHAPTER III

Olefin-aminocarbyne coupling in diiron complexes:

Synthesis of new bridging aminoallylidene complexes.....29

References.....54

CHAPTER IV

Coupling of allenes with μ-alkylidyne ligands in diiron complexes:

Synthesis of novel bridging thio and aminobutadienylidene complexes.....57

References.....85

CHAPTER V

Functionalized μ-vinyliminium complexes as organometallic ligands.....87

References.....111

CHAPTER VI

Functionalised ferrocenes from [3+2] cycloadditions in bridging vinylalkylidene

diiron complexes.....115

References.....136

CHAPTER VII

Alkyne insertion into the Pd-C bond of cyclopalladated compounds
containing [C(sp^2, ferrocene),N,S] tridentate ligands.....139
References.....152

CHAPTER VIII

Conclusions.....155

List of publications.....161

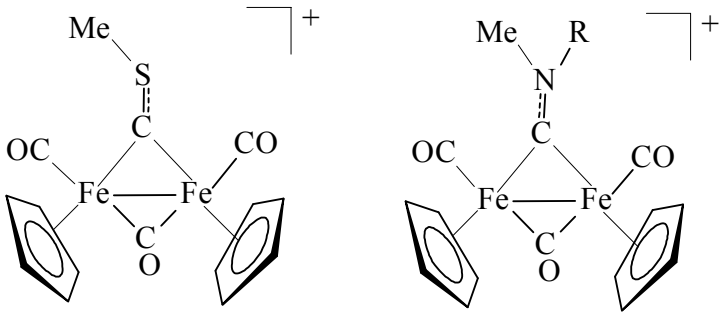
CHAPTER I

INTRODUCTION

Introduction

Organometallic transition metal compounds play a key role in a wide range of reactions, both catalytic and stoichiometric, leading to the formation of new C-C bonds. These synthetic methodologies find applications in industrial processes, as well as in organic synthesis. [1] Most of these reactions are promoted by mononuclear species; however, di- or poly-nuclear transition metal complexes, providing multisite interactions between the metal atoms and the coordinated molecules, offer new possibilities of substrate activation, which cannot be expected in mononuclear complexes. In particular, dinuclear complexes with adjacent metal centers allow bridging coordination, opening new perspectives in the field of metal-assisted transformation of small organic molecules. [2]

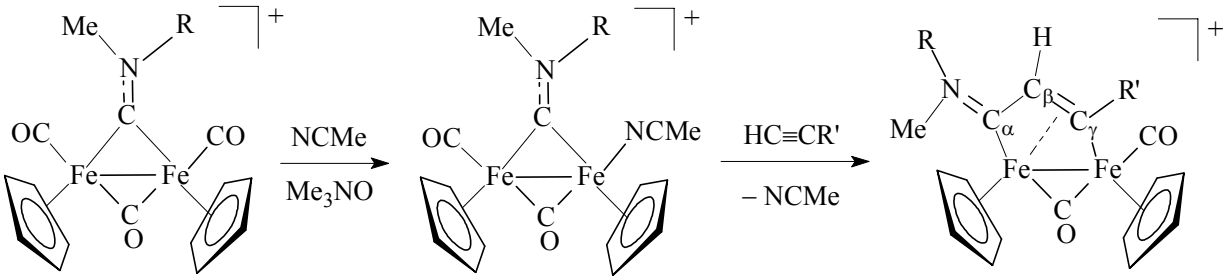
Within this field, the attention of the research group in which I have carried out the Ph.D. has been focused on the chemistry of diiron complexes containing bridging carbene and carbyne ligands. [3] Among these, the μ-thiocarbyne complex $[Fe_2\{\mu\text{-}CS(Me)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1**) (Chart 1.1) has offered a number of new C-C bond forming reactions, which take advantage of the strong electrophilic character of the bridging carbyne ligand and are based on the addition of carbon nucleophiles (e.g. organo-lithium, organocopper, and Grignard reagents). [4]



1 **2**

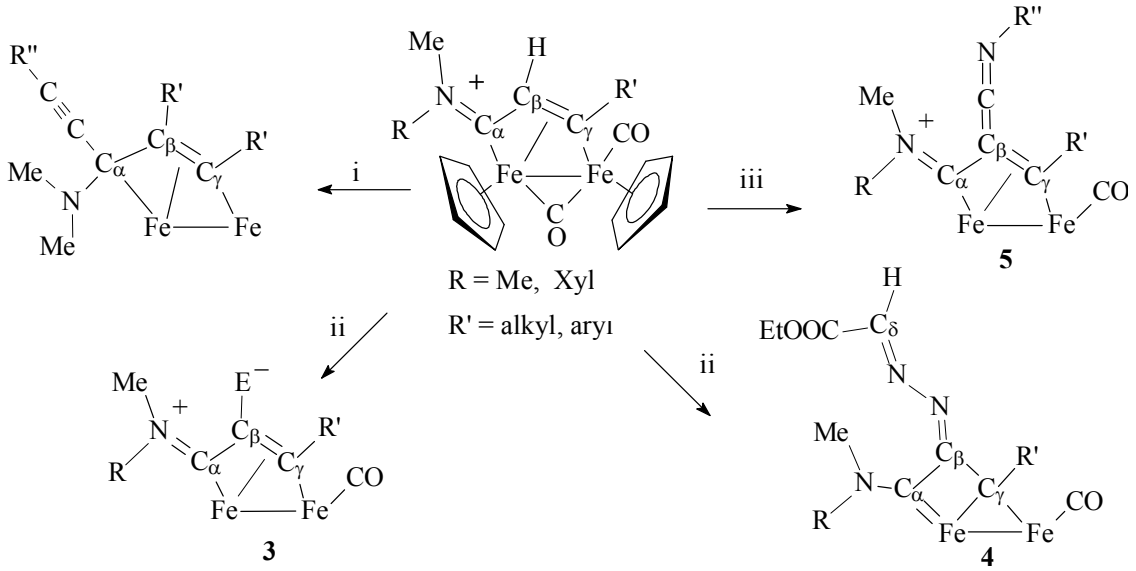
Chart 1.1

On the other hand, studies on the related μ-aminocarbyne complex $[Fe_2\{\mu\text{-}CN(Me_2)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**2**) (Chart 1.1) have revealed a further possibility to generate C-C bonds and transform the C_1 into a C_3 bridging frame, consisting in the insertion of alkynes in the metal-carbyne bond (Scheme 1.1). [5] The reaction can be generalized to a variety of substituents both on the alkyne and on the aminocarbyne nitrogen.



Scheme 1.1

The reaction leads to the formation of a bridging vinyliminium ligand, which exhibits a remarkable reactivity due to the combination of multisite coordination and activation effects owing to the presence of the iminium group. [6] This combination results in unconventional reaction routes, which lead to the transformation of the bridging vinyliminium ligand into new multifunctional coordinated species. Two major approaches have been followed: (a) nucleophilic additions at the bridging ligand, which exploit its electrophilic character, [7] and (b) replacement of the C_β-H hydrogen of the bridging frame with appropriate functionalities. This latter approach, which takes advantage of the acidic character of the C_β-H, consists in the proton removal in the presence of trapping reagents. These include group 16 elements, diazocompounds, and isocyanides, and the corresponding products are the zwitterionic complexes **3**, [8] the diazine bis-alkylidenes **4**, [9] and the ketenimine complexes **5**, [10] as shown in Scheme 1.2.



i: LiCCR" (R' = Me, Et); ii: NaH, E (E = O,S, Se); iii: NaH, $N_2CH(COOEt)$; iv: NaH, CNR".

Scheme 1.2

All the reactions reported in Scheme 1.2 allow to increase the complexity of the bridging organic frame, and take advantage of the specific reactivity pattern due to multisite coordination. Noteworthy, these reactions are promoted by diiron complexes. The chemistry of coordination and organometallic compounds of iron has encountered a great revival in the past five years. Indeed, increased attention to sustainability, under economical and environmental point of view, has resulted in a resurrection of interest in iron compounds. Given its ready availability, low price and environmentally friendly character, iron is an attractive and often advantageous alternative to other transition metal in homogeneous catalysis as well as in organic synthesis. [11]

Scope of the thesis

Starting from the above reported important results in the field of the metal-assisted transformation of small organic molecules, the main scope of this Ph.D. thesis has concerned the possible transformations of bridging ligands in diiron complexes, in order to explore unconventional routes to the synthesis of new functionalized multisite bound organic frames, taking into consideration the following guidelines:

- We have explored the possibility of extending these coupling reactions, which represent valuable routes to the selective formation of new C-C bonds, to other unsaturated species, such as olefins and allenes. In particular, we have studied the coupling of alkenes and thio- and aminocarbyne (Chapter II and III, respectively). Then, we have extended the study to allenes (Chapter IV).
- The above mentioned reactions allow the introduction of functional groups characterized by the presence of heteroatoms, such as N and S (see in particular Scheme 1.2). These functionalities should be exploited to coordinate unsaturated metal fragments and, consequently, further increase the complexity of the bridging frame. Thus, we have investigated the possible use of bridging C_3 organic frames as 'organometallic ligands' (Chapter V).
- As shown before, the assembling of small organic molecules and bridging carbyne ligands in diiron complexes leads to the formation of variously functionalized C_3 organic frames. In this assembling process the activation/stabilization effects induced by the dimetal frame on the organic ligand play a key role. On the other hand, the possibility of releasing the organic frame from the bridging coordination appears

particularly appealing in the direction of a metal-assisted organic synthesis. Within this field, we have investigated the possibility of involving the C_3 bridging ligand in cycloaddition reactions with alkynes, with the aim of generating variously functionalized five-membered cycles (Chapter VI).

- Furthermore, I have spent a research period of about six months at the Department of Inorganic Chemistry of the Barcelona University, under the supervision of Prof. Concepción López, with the aim of studying the chemistry of polydentate ferrocenyl ligands and their use in organometallic synthesis (Chapter VII).

References

[1] Abel, E.W.; Stone, F.G.A.; Wilkinson, G. *"Transition metal Organometallics in organic Chemistry" vol 12*, *"Comprehensive Organometallic chemistry II"*, 1995, Ed. Pergamon.

[2] (a) Braunstein, P.; Rosé, J. In *Metal Cluster in Chemistry*; Braunstein, P., Oro, L.A., Raithby, P.R., Eds.; Wiley-VCH: Weinheim, 1999; p 616.

(b) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R.A., Cotton, F.A., Eds.; Wiley-VCH: New York, 1998.

(c) Adams, R.D.; Captain, B. *J. Organomet. Chem.* **2004**, *689*, 4521.

(d) Qin, J.C.; Gavrilova, A.; Bosnich, B. *Pure Appl. Chem.* **2001**, *73*, 221.

(e) Van Den Beuken, E.K.; Feringa, B.L. *Tetrahedron* **1998**, *54*, 12985.

(f) Severin, K. *Chem. Eur. J.* **2002**, *8*, 1514.

(g) Trepanier, S.J.; Dennett, J.N.L.; Sterenberg, B.T.; McDonald, R.; Cowie, M. *J. Am. Chem. Soc.* **2004**, *126*, 8046.

[3] Busetto, L.; Zanotti, V. *J. Organomet. Chem.* **2005**, *690*, 5430.

[4] (a) Albano, V.G.; Bordoni, S.; Busetto, L.; Monari, M.; Zanotti, V. *Organometallics* **1995**, *14*, 5455;

(b) Bordoni, S.; Busetto, L.; Camiletti, C.; Zanotti, V.; Albano, V.G.; Monari, M.; Prestopino, F. *Organometallics* **1997**, *16*, 1224;

(c) Albano, V.G.; Bordoni, S.; Busetto, L.; Camiletti, C.; Monari, M.; Palazzi, A.; Prestopino, F.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1997**, 4665.

[5] (a) Albano, V.G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *Organometallics* **2003**, *22*, 1326;

(b) Albano, V.G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2004**, *689*, 528;

(c) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2006**, *691*, 2424.

[6] (a) Erkkilä, A.; Majander, I.; Pihko, P.M. *Chem. Rev.* **2007**, *107*, 5416;

(b) Mukherjee, S.; Yang, J.W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471;

(c) List, B. *Acc. Chem. Res.* **2004**, *37*, 548;

(d) Lelais, G.; MacMillan, D.W.C. *Aldrichimica Acta* **2006**, *39*, 79.

[7] (a) Albano, V.G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *Organometallics* **2004**, *23*, 3348;

(b) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Eur. J. Inorg. Chem.* **2007**, 1799.

[8] Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Organometallics* **2006**, *25*, 4808.

[9] Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Organometallics* **2007**, *26*, 3577.

[10] Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Organometallics* **2008**, *27*, 5058.

[11] (a) *Iron Catalysis in Organic Chemistry; Reactions and Applications*; Plietker, B., Ed.; Wiley-VCH: Weinheim, 2008;

(b) Correa, A.; García Mancheño, O.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108;

(c) Gaillard, S.; Renaud, J. *ChemSusChem* **2008**, *1*, 505.

CHAPTER II

C-C BOND FORMATION THROUGH OLEFIN-THIOCARBYNE COUPLING IN DIIRON COMPLEXES

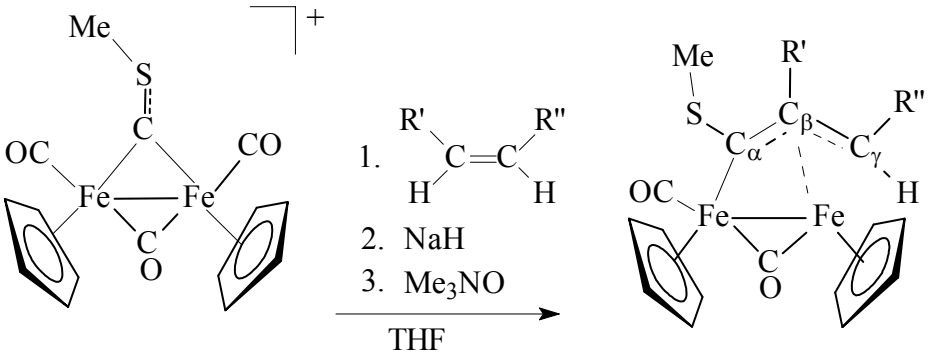
Abstract

The bridging diiron thiocarbyne complex $[Fe_2\{\mu\text{-}CS(Me)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1**) reacts with activated olefins (methyl acrylate, acrylonitrile, styrene, diethyl maleate), in the presence of Me_3NO and NaH, to give the corresponding μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R'' = CO_2Me, R' = H, **3.2a**; R'' = CN, R' = H, **3.2b**; R'' = C_6H_5, R' = H, **3.2c**; R'' = R' = CO_2Et, **3.2d**). The coupling reaction of olefin with thiocarbyne is regio- and stereospecific, leading to the formation of only one isomer. C-C bond formation occurs between the less substituted alkene carbon and the thiocarbyne. Moreover, olefinic hydrogens of the bridging ligands are mutually *trans*.

The reactions of **3.2a-b** with $MeSO_3CF_3$ result, selectively, in the formation of the cationic μ-sulphonium allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CO_2Me, **4.2a**; R = CN, **4.2b**). Compound **4.2a** undergo displacement of the SMe_2 group by nucleophiles such as $NaBH_4$, NBu_4CN and NaOMe, affording the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(R)C_\beta(H)C_\gamma(H)(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = H, **5.2a**; R = CN, **5.2b**; R = OMe, **5.2c**), respectively. The molecular structures of **3.2a** and **5.2a** have been determined by X ray diffraction studies.

Results and discussion

The bridging diiron thiocarbyne complex **1** reacts with olefins (methyl acrylate, acrylonitrile, styrene, diethyl maleate), in the presence of Me_3NO and NaH, to give the μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R'' = CO_2Me, R' = H, **3.2a**; R'' = CN, R' = H, **3.2b**; R'' = C_6H_5, R' = H, **3.2c**; R'' = R' = CO_2Et, **3.2d**) (Scheme 2.1). The reactions were carried out in THF solution at room temperature; **3.2a-d** were purified by chromatography on alumina and isolated in about 80 % yield.



1	R''	R'	
	CO_2Me	H	**3.2a**
	CN	H	**3.2b**
	C_6H_5	H	**3.2c**
	CO_2Et	CO_2Et	**3.2d**

Scheme 2.1

Compounds **3.2a-d** were characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structure of **3.2a**, determined by the X-ray diffraction, is reported in Figure 2.1. The main bond lengths and bond angles are reported in Table 2.1. The molecule is composed by a *cis*-$[Fe_2(\mu\text{-}CO)(CO)(Cp)_2]$ moiety to which a bridging $\mu\text{-}\eta^1\text{:}\eta^3$-C(SMe)CHCH($CO_2Me$) ligand is coordinated. The latter closely resembles other organic unsaturated fragments previously found, coordinated to diiron frames and obtained by addition of nucleophiles (*i.e.* hydride, cyanide, acetylides) to vinyliminium complexes [2]. All these ligands have been usually described as a result of the contribution of a bridging allylidene (Structure A in Chart 2.1) and a bridging vinylalkylidene (B) form. Depending on the substituents present on the ligand, one of the two forms can be predominant. In the present case, since both the C-C bonds within the ligand [C(13)-C(14) 1.415(4) Å, C(14)-C(15) 1.422(4) Å] and the Fe-C interactions

between the ligand and the diiron frame [Fe(1)-C(13) 2.049(3) Å, Fe(1)-C(14) 2.026(3) Å, Fe(1)-C(15) 2.068(3) Å] are very similar, it seems reasonable to conclude that the ligand can be mainly described as a bridging allylidene (A). It is noteworthy that the two hydrogen atoms within the ligand, *i.e.* H(14) and H(15), are in mutually *trans* position.

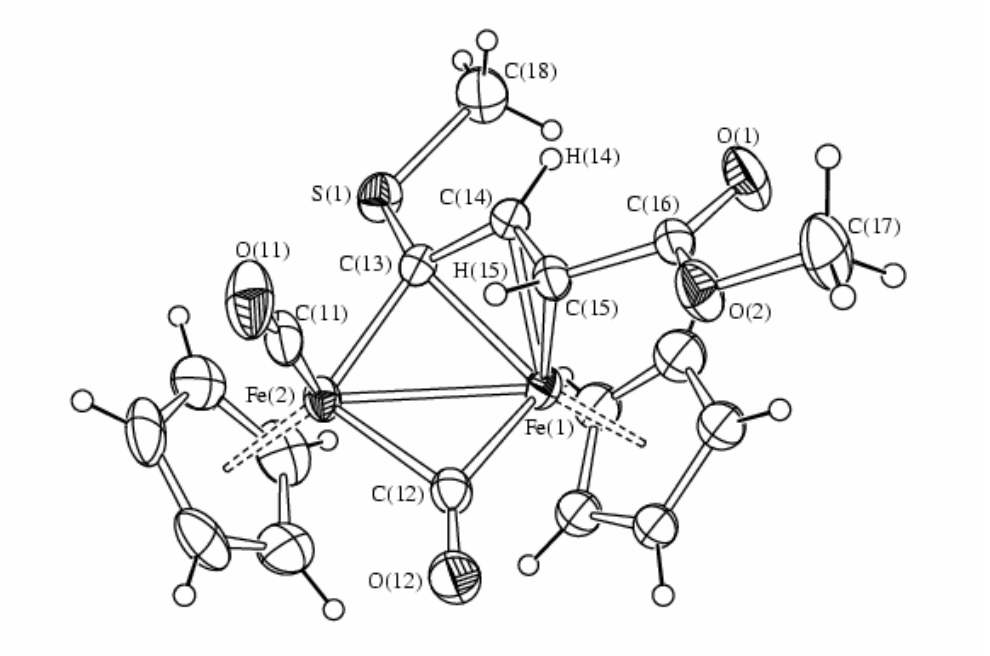


Figure 2.1 Molecular structure of **3.2a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level. Only the main image of the Cp ligand bonded to Fe(1) is drawn.

Table 2.1 Selected bond lengths (Å) and angles (deg) for **3.2a**.

Fe(1)-Fe(2)	2.5502(5)	C(12)-O(12)	1.165(4)
Fe(2)-C(11)	1.756(3)	C(13)-C(14)	1.415(4)
Fe(1)-C(12)	1.870(3)	C(14)-C(15)	1.422(4)
Fe(2)-C(12)	1.982(3)	C(13)-S(1)	1.758(3)
Fe(2)-C(13)	1.955(3)	S(1)-C(18)	1.802(4)
Fe(1)-C(13)	2.049(3)	C(15)-C(16)	1.471(4)
Fe(1)-C(14)	2.026(3)	C(16)-O(1)	1.204(4)
Fe(1)-C(15)	2.068(3)	C(16)-O(2)	1.341(4)
C(11)-O(11)	1.142(4)	O(2)-C(17)	1.450(4)
Fe(1)-C(12)-Fe(2)	82.87(12)	C(13)-C(14)-C(15)	121.1(3)
Fe(1)-C(13)-Fe(2)	79.09(10)	C(14)-C(15)-C(16)	117.9(3)
Fe(2)-C(13)-C(14)	123.5(2)	C(13)-S(1)-C(18)	107.02(16)

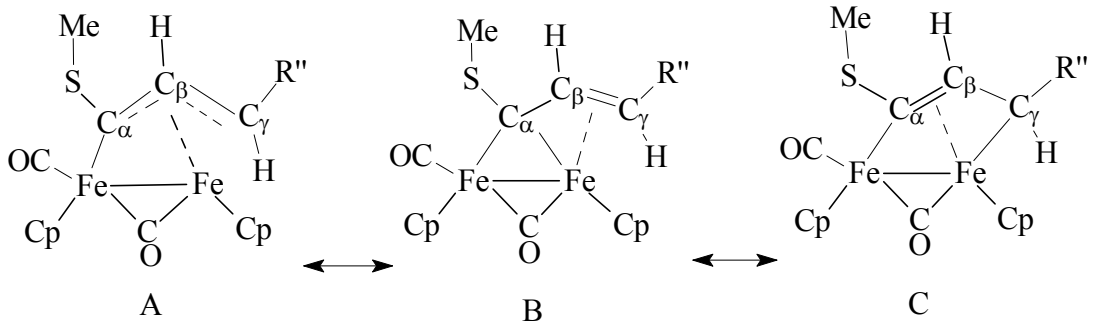


Chart 2.1

The IR spectra of **3.2a-d** (in CH_2Cl_2 solution) show the typical ν–CO band pattern consisting of one absorption for the terminal carbonyl (*e.g.* at 1960 cm^{-1} for **3.2a**) and one for the bridging carbonyl (*e.g.* at 1785 cm^{-1} for **3.2a**). Additional bands are observed in the case of **3.2a** and **3.2d**, due to the carboxylate (*e.g.* at 1698 cm^{-1} for **3.2a**), or attributable to the CN group (at 2209 cm^{-1} for **3.2b**).

For the complexes **3.2a-d** several isomeric forms are in theory possible. Indeed, complexes obtained by reaction with non-symmetric alkenes might exhibit two regio-isomers, depending on which of the two non equivalent alkene carbons forms the C-C bond with the thiocarbyne ligand. Moreover, when the coupling involves the CH_2 termination of the olefin, each of the two geminal hydrogens should undergo deprotonation. Therefore, the C_β-H and C_γ-H hydrogens in type **3.2** complexes, might result on the same or on the opposite side of the C_β-C_γ double bond, generating *E* or *Z* isomers. Finally, as for other complexes containing the $Fe_2Cp_2(\mu\text{-CO})$ framework, further isomers should arise from possible *cis-trans* isomerization (*cis* and *trans* are referred in this case to the mutual Cp position). In spite of these possibilities the ^1H NMR spectra of **3.2a-d** (in $CDCl_3$) evidence the presence of a single isomer, indicating that the olefin addition to the bridging ligand is both regio- and stereo-specific. The NMR data evidence that **3.2a-d**, in solution, adopt the same geometry observed in the solid. In particular, the C-C bond formation occurs between the less substituted alkene carbon and the thiocarbyne ligand. Indeed, the spectra of **3.2a-c** show two doublets, attributable to the $C_\beta H$ and $C_\gamma H$ protons, respectively, with coupling constant (*e.g.* 8.2 Hz for **3.2a** – see Figure 2.2) which indicates that these hydrogens are mutually *trans*, as found in the X-ray structure of **3.2a**. Likewise, NOE investigations on **3.2a-d** reveal that the Cp rings are *cis*. Finally, $C_\gamma H$ proton resonance is shifted to low frequencies (*e.g.* -0.79 ppm for **3.2a** – see Figure 2.2), accordingly to the proximity and the shielding effect exerted by the metal centre.

Relevant feature in the ^{13}C NMR spectra include the typical resonances due to the C_α, C_β and C_γ of the bridging allylidene (*e.g.* for **3a**, at 189.2, 74.8 and 43.1 ppm, respectively).

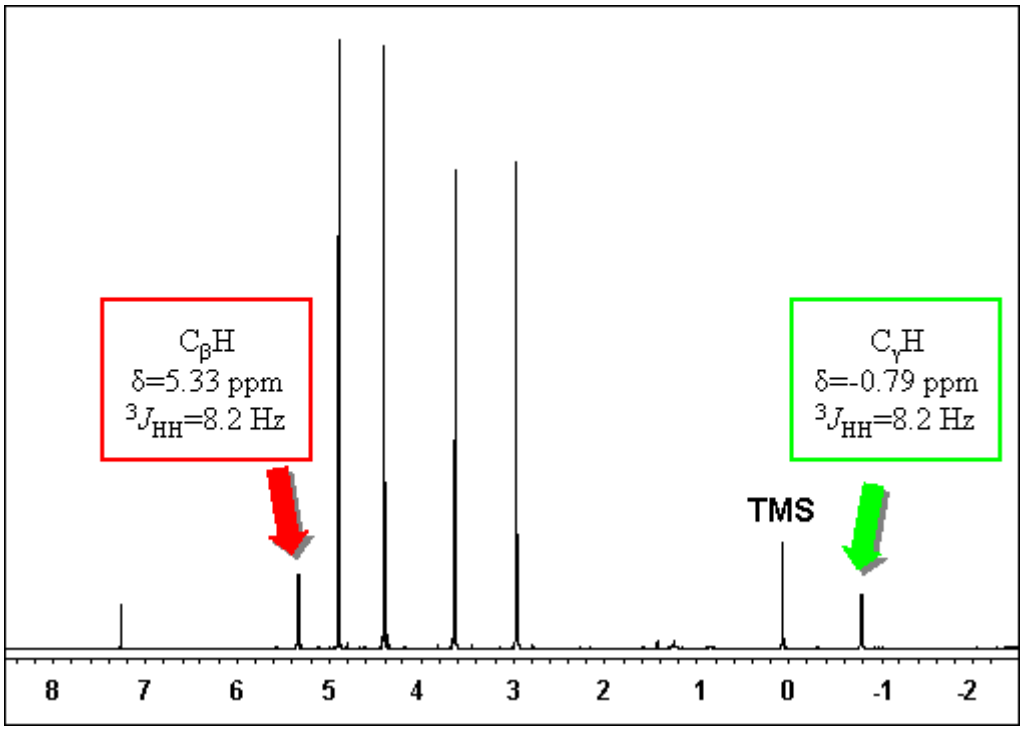


Figure 2.2

Consistently with their nature, the bridging ligands in **3.2a-d** (Chart 2.1) can be considered as the result of a nucleophilic addition of a vinyl group to the bridging carbyne carbon (Chart 2.1, **B**) or, alternatively, as derived from olefin insertion into the metal bridging carbyne ligand (Chart 2.1, **C**). This latter point has to be remarked because olefin insertion in the metal-carbon bond, which is a relevant step in various important catalytic cycles [3], is rarely observed in bridging ligands. Indeed, there are few examples of reactions involving olefins and bridging alkylidyne [4] and alkylidene ligands [5]. In particular, the formation of **3.2a-d** closely resembles the reaction between the μ-ethylidyne complex $[Ru_2\{\mu\text{-}C(Me)\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ and $MeCH{=}CH_2$, which also required photolytic conditions and deprotonation in order to form the bridging allylidene complex $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)C(Me)CH_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [4a].

Several bridging allylidene dinuclear complexes, analogous to **3.2a-d**, are known, but these compounds are normally obtained by reactions of bridging alkylidenes with alkynes [6] rather than be formed from alkenes.

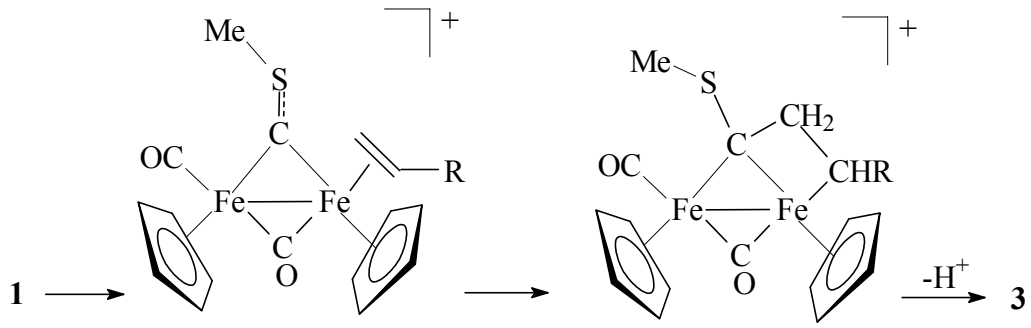
Some aspects concerning the reaction of the thiocarbyne **1** with olefins should be pointed out. First, the reaction requires the displacement of a CO ligand, which is accomplished by the use of Me_3NO. The generation of a vacant coordination site is presumably necessary to allow olefin coordination as initial reaction step. This is consistent with the fact that related insertion reactions

of alkynes into the metal carbon bond of bridging ligands require photolytic conditions or the presence of labile ligands, in order to provide a vacant coordination site [1, 6].

A second requirement is the presence of a base (NaH) in order to remove a proton from the olefin. Strictly related to this point is the observation that the reaction proceeds only with olefins activated by electron-withdrawing groups. In fact, yields are high (80-90%) with olefins activated by CO_2R or CN groups, and lower in the case of styrene (50% yield), whereas non-activated olefins, both linear (2-butene) and cyclic (cyclopentene, cyclohexene) are completely unreactive. Moreover, it has to be noticed that attempts to obtain **3.2b** by treatment of $[Fe_2\{\mu\text{-}CS(Me)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ with the vinyl anion, generated by treatment of CH_2=CHCN with BuLi, were unsuccessful. This further suggests that a preliminary olefin coordination is necessary to promote the reaction.

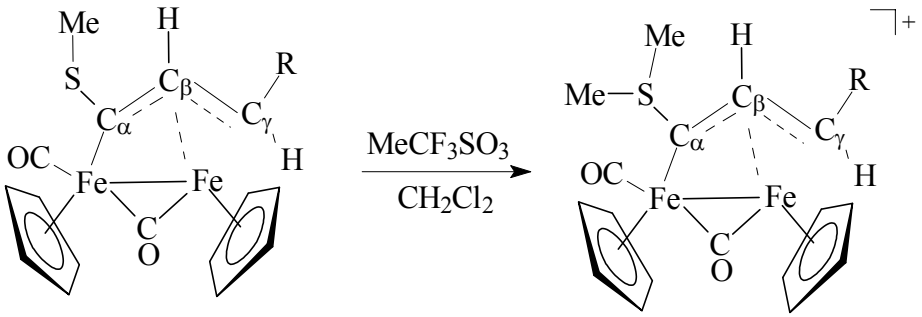
Interestingly, the reaction of **1** with diethyl maleate generates **3.2d** in high yield, whereas the corresponding reaction with diethyl fumarate does not take place, evidencing that steric effects have also to be considered.

These findings suggest that the reaction sequence should include, as initial step, the η^2-olefin coordination at the site made available by CO removal. Consequent olefin-thiocarbyne coupling might proceed by formation of a metallacyclobutane intermediate (Scheme 2.2), as proposed by Knox to explain the formation of $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Me)C(Me)CH_2\}(\mu\text{-}CO)(CO)(Cp)]$ [4a]. The following deprotonation and rearrangement steps could directly involve the metallacyclobutane intermediate, or take place by a different sequence, like the β-elimination route suggested by Knox for the diruthenium compound. However, other possibilities can not be excluded. Indeed, deprotonation could take place on the coordinated olefin and the resulting vinyl intermediate should rearrange and undergo intramolecular coupling with the thiocarbyne ligand.



Scheme 2.2

The reactivity of complexes of type **3.2** was then investigated. In particular, we have found that the reaction of compounds **3.2a-b** with methyl triflate results selectively in the S-methylation, with formation of the cationic μ-sulphonium allylidene complexes **4.2a-b**, in nearly quantitative yields (Scheme 2.3). The reaction is carried out in dichloromethane solution at room temperature.



	R	
3.2a	CO_2Me	**4.2a**
3.2b	CN	**4.2b**

Scheme 2.3

Compounds **4.2a-b** have been purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis.

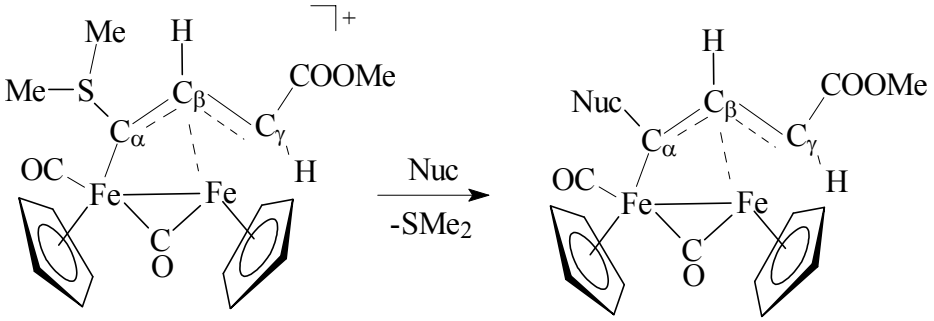
The IR spectra (in CH_2Cl_2 solution) of **4.2a-b** exhibit absorptions due to the terminal and bridging carbonyls (*e.g.* at 1989 and 1823 cm^{-1} for **4.2a**). Additional bands are observed, for **4.2a**, due to the CO_2Me (at 1708 cm^{-1}) and, for **4.2b**, attributable to a CN group (at 2220 cm^{-1}).

The ^1H NMR spectra ($CDCl_3$) of **4.2a-b** show only one set of resonances. In particular, the SMe_2 group gives rise to one singlet signal in both ^1H and ^{13}C NMR spectra (*e.g.* for **4.2a** at δ 3.67 and 52.0 ppm, respecively). The equivalence of the two Me groups is due to the free rotation of the SMe_2 unit around the μ-C-S bond.

Methylation at the S atom does not modify significantly the ^{13}C NMR resonance pattern for the carbons of the C_3 bridging group: C_α gives rise to a low field resonance (194 ppm for **4.2a**), whereas C_β and C_γ resonances occur in 85 – 30 ppm range.

Bridging sulphonium alkylidene complexes of the type $[Fe_2\{\mu\text{-}C(SMe_2)(X)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (X = CN, H) have been previously described [7]. These compounds have been shown to act as precursors of a variety of bridging alkylidene complexes *via* the displacement of SMe_2 by nucleophiles including: amines, alcohols, thiols, phosphines and carbon nucleophiles [8]. Therefore, we have investigated the reactivity of **4.2a** towards nucleophilic reagents, in order to demonstrate the possibility to accomplish further modifications of the bridging C_3 frame, *via*

nucleophilic displacement of SMe_2. Unfortunately, the complex **4.2a** appeared considerably less reactive compared to the sulphonium alkylidene complexes mentioned above. SMe_2 displacement has been observed only in the reactions with $NaBH_4$ or NBu_4^nCN which afforded the complexes **5.2a** and **5.2b**, respectively (Scheme 2.4).



	Nuc	Reactive	
4.2a	H^-	$NaBH_4$	**5.2a**
4.2a	CN^-	NBu_4^nCN	**5.2b**
4.2a	MeO^-	MeONa	**5.2c**

Scheme 2.4

Similarly, the reaction with MeONa in methanol yields the complex **5.2c** (Scheme 2.4). However, this latter is obtained in low yield because the nucleophilic substitution is accompanied by demethylation, leading to the formation of the parent compound **3.2a**. Demethylation becomes even more evident in the reactions with amines (e.g. pyrrolidine, pyrimidine, triethylamine), which almost quantitatively reverse the reaction with $MeSO_3CF_3$. Finally, attempts to replace the SMe_2 group by other carbon nucleophiles (acetylides, organolithium and Grignard reagents), failed to generate the expected complexes and yielded mixtures of decomposition products.

Compounds **5.2a-c** have been purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the X ray structure of **5.2a** has been determined.

The IR spectra of **5.2a-c** (in CH_2Cl_2 solution), show absorptions attributable to the terminal and bridging CO (*e.g.* for **5.2a** at 1960 and 1781cm^{-1}, respectively) and bands due to the COOMe (*e.g.* at 1700 cm^{-1} for **5.2a**), or, in the case of **5.2b**, attributable to the CN group (at 2160 cm^{-1}).

The ^{1}H NMR spectra of **5.2a-c** (in $CDCl_3$) indicate the presence of a single isomeric form, which, presumably, maintains the same conformation of the parent complex **4.2a**. In fact, only one set of resonances is observed and the signals generated by $C_\beta H$ and $C_\gamma H$ protons present, again, a value for $^3J_{HH}$ typical of olefin protons mutually *trans* (*e.g.* 8.0 Hz for **5.2a** – see Figure 2.3).

Interestingly, in compound **5.2a**, each carbon of the C_3 bridging chain displays a hydrogen substituent, characterized by a well distinct resonance. In fact, signals are observed at 12.04, 5.68 and -0.73 ppm, corresponding to C_α-H, C_β-H and C_γ-H, respectively. Finally, NOE investigations indicate the presence, in solution, of only the *cis* isomer: indeed a significant NOE effect has been revealed between the Cp resonances.

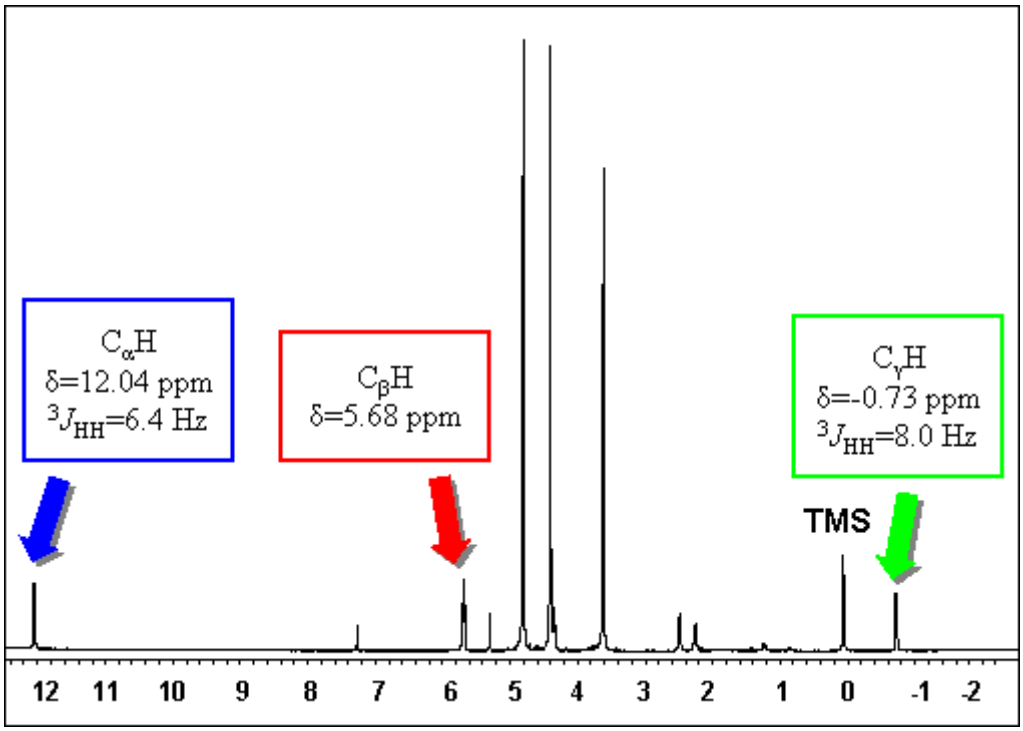


Figure 2.3

The molecular structure of **5.2a** is reported in Figure 2.4, whereas the main bond lengths and bond angles are summarised in Table 2.2. The bonding parameters of **5.2a** closely resembles the ones described for **3.2a** and, therefore, also this molecule can be mainly described as a bridging allylidene diiron complex. The hydrogen atoms H(13) and H(14) are in mutual *cis* position, whereas H(14) and H(15) are *trans*, as found in **3.2a**.

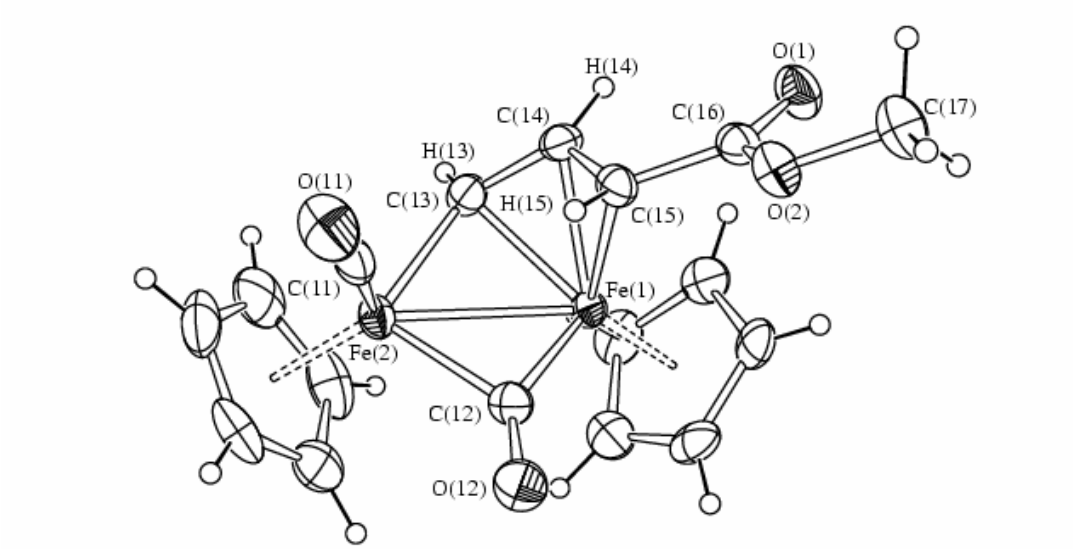


Figure 2.4 Molecular structure of **5.2a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level.

Table 2.2 Selected bond lengths (Å) and angles (deg) for **5.2a**.

Fe(1)-Fe(2)	2.5423(6)	C(11)-O(11)	1.148(4)
Fe(2)-C(11)	1.741(3)	C(12)-O(12)	1.168(3)
Fe(1)-C(12)	1.868(3)	C(13)-C(14)	1.396(4)
Fe(2)-C(12)	1.987(3)	C(14)-C(15)	1.415(4)
Fe(2)-C(13)	1.926(3)	C(15)-C(16)	1.470(4)
Fe(1)-C(13)	2.006(3)	C(16)-O(1)	1.213(3)
Fe(1)-C(14)	2.033(3)	C(16)-O(2)	1.333(4)
Fe(1)-C(15)	2.101(3)	O(2)-C(17)	1.445(4)
Fe(1)-C(12)-Fe(2)	82.47(12)	C(13)-C(14)-C(15)	121.4(3)
Fe(1)-C(13)-Fe(2)	80.53(11)	C(14)-C(15)-C(16)	117.9(3)
Fe(2)-C(13)-C(14)	126.9(2)		

Conclusions

The bridging thiocarbyne ligand in **1** reacts with olefins generating a bridging allylidene ligand. The reactions are regio- and stereospecific and represent a rare example of olefin incorporation into a bridging ligand producing a C_1 to C_3 chain growth. Since proton removal is required in order to accomplish the reaction, this latter is limited to olefins containing electron-withdrawing groups.

The study has evidenced that the bridging C_3 frame, obtained by alkene-carbyne coupling, can be further modified by methylation of the S atom and displacement of the SMe_2 group. This approach provides a route for replacing the μ–C-S bond with a μ–C-C or μ–C-H bond.

Experimental details

General

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and $^{1}H,^{13}C$ correlation through gs-HSQC and gs-HMBC experiments [9]. NOE measurements were recorded using the DPFGSE-NOE sequence [10]. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compound **1** was prepared by published methods [11].

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ *(R″ =* CO_2Me*, R′ = H,* ***3.2a****; R″ = CN, R′ = H,* ***3.2b****; R″ =* C_6H_5*, R′ = H,* ***3.2c****; R″ = R′ =* CO_2Et*,* ***3.2d****)*

To a solution of **1** (534 mg, 1.0 mmol) in THF (20 mL) were successively added: methyl acrylate (0.9 mL, 10 mmol), NaH (120 mg, 5.0 mmol), and Me_3NO (100 mg, 1.5 mmol). The mixture was stirred at room temperature for 15 min and then filtered on a celite pad. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, afforded a green/brown solid, corresponding to **3.2a**. Crystals suitable for X ray analysis were obtained by a dichloromethane solution, layered with petroleum ether, at –20 °C. Yield: 390 mg, 89%. Anal. Calc. for $C_{18}H_{18}Fe_2O_4S$: C, 48.87; H, 4.10. Found: C, 48.91; H, 4.08%. IR (CH_2Cl_2) ν(CO) 1960 (vs), 1785 (s), 1698 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.33 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz, $C_\beta H$); 4.89 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.63 (s, 3H, CO_2Me); 2.96 (s, 3H, S*Me*); -0.79 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz, $C_\gamma H$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 264.9 (μ-CO); 213.8 (CO); 189.2 (C_α); 162.4 (CO_2Me); 88.3 (Cp); 85.5 (Cp); 74.8 (C_β); 51.4 (CO_2Me); 43.1 (C_γ); 21.0 (S*Me*).

Compounds **3.2b-d** were prepared with the same procedure described for **3.2a**, by reacting **1** with NaH, Me_3NO and the appropriate olefin.

3.2b (yield: 85%; colour: green). Anal. Calc. for $C_{17}H_{15}Fe_2NO_2S$: C, 49.88; H, 3.70. Found: C, 49.84; H, 3.73%. IR (CH_2Cl_2) ν(CN) 2209 (w), ν(CO); 1965 (vs), 1797 (s) cm^{-1}. ^{1}H NMR

($CDCl_3$) δ 5.01 (d, 1H, $^3J_{HH}$ = 7.8 Hz, $C_\beta H$); 4.91 (s, 5H, Cp); 4.55 (s, 5H, Cp); 2.93 (s, 3H, S*Me*); -1.41 (d, 1H, $^3J_{HH}$ = 7.8 Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 264.3 (μ-CO); 213.1 (CO); 189.6 (C_α); 124.9 (CN); 88.7 (Cp); 86.3 (Cp); 74.3 (C_β); 22.2 (C_γ); 21.0 (S*Me*).

3.2c (yield: 51%; colour: green/brown). Anal. Calc. for $C_{22}H_{20}Fe_2O_2S$: C, 57.39; H, 4.38. Found: C, 57.33; H, 4.41%. IR (CH_2Cl_2) ν(CO) 1949 (vs), 1775 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.21-7.07 (m, 5H, Ph); 5.36 (d, 1H, $^3J_{HH}$ = 9.6 Hz, $C_\beta H$); 4.87 (s, 5H, Cp); 4.17 (s, 5H, Cp); 3.01 (s, 3H, S*Me*); 1.06 (d, 1H, $^3J_{HH}$ = 9.6 Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 264.5 (μ-CO); 213.5 (CO); 189.4 (C_α); 131.6 (C_{ipso}); 128.7 (C_{orto}); 125.9 (C_{meta}); 125.3 (C_{para}); 88.2 (Cp); 85.9 (Cp); 73.2 (C_β); 37.5 (C_γ); 21.1 (S*Me*).

3.2d (yield: 84%; colour: brown). Anal. Calc. for $C_{22}H_{24}Fe_2O_6S$: C, 50.00; H, 4.58. Found: C, 49.96; H, 4.53%. IR (CH_2Cl_2) ν(CO) 1980 (vs), 1810 (s), 1716 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.88 (s, 5H, Cp); 4.80 (s, 5H, Cp); 4.27-3.74 (m, 4H, $CO_2CH_2CH_3$); 2.26 (s, 3H, S*Me*); 1.49-1.10 (m, 6H, $CO_2CH_2CH_3$); -0.74 (s, 1H, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.0 (CO); 191.2 (C_α); 162.4 ($CO_2CH_2CH_3$); 162.6 ($CO_2CH_2CH_3$); 91.3 (Cp); 88.2 (Cp); 86.5 (C_β); 59.2 ($CO_2CH_2CH_3$); 58.7 ($CO_2CH_2CH_3$); 34.5 (C_γ); 21.1 (S*Me*); 14.7 ($CO_2CH_2CH_3$); 14.5 ($CO_2CH_2CH_3$).

*Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CO_2Me, **4.2a**; R = CN, **4.2b**)*

Methyl triflate (0.13 mL, 1.1 mmol) was added to a solution of **3.2a** (442 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) and the resulting solution was stirred at room temperature for 4h. Removal of the volatile material under reduced pressure and chromatography of the residue on an alumina column, with methanol as eluent, afforded a dark brown solid, corresponding to **4.2a**. Yield: 527 mg, 87%. Anal. Calc. for $C_{20}H_{21}F_3Fe_2O_7S_2$: C, 39.61; H, 3.49. Found: C, 39.68; H, 3.46%. IR (CH_2Cl_2) ν(CO) 1989 (vs), 1823 (s), 1708 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.57 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.2 Hz); 5.13 (s, 5H, Cp); 4.75 (s, 5H, Cp); 3.67 (s, 6H, SMe_2); 3.52 (s, 3H, CO_2Me); -0.65 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.4 (CO); 194.1 (C_α); 162.5 (CO_2CH_3); 88.9 (Cp); 85.5 (Cp); 83.7 (C_β); 52.0 (SMe_2); 46.5 (C_γ); 39.7 (CO_2CH_3).

Compound **4.2b** was prepared with the same procedure described for **4.2a**, by treating **3.2b** with methyl triflate in dichloromethane solution.

4.2b (yield: 86%; colour: dark brown). Anal. Calc. for $C_{19}H_{18}F_3Fe_2NO_5S_2$: C, 39.80; H, 3.17. Found: C, 39.81; H, 3.14%. IR (CH_2Cl_2) ν(CN) 2220 (w), ν(CO) 1993 (vs), 1829 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.26 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 7.8 Hz); 5.15 (s, 5H, Cp); 4.92 (s, 5H, Cp); 3.68 (s, 6H,

S*Me₂*); -1.20 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.5 (CO); 195.0 (C_α); 125.3 (*C*N); 89.1 (Cp); 86.5 (Cp); 84.1 (C_β); 52.4 (S*Me₂*); 28.8 (C_γ).

Synthesis of [Fe_2{μ-η^1:η^3-$C_\alpha(R)C_\beta(H)C_\gamma(H)(CO_2Me)$}(μ-CO)(CO)$(Cp)_2$] (R = H, ***5.2a****; R = CN,* ***5.2b****; R = OMe,* ***5.2c****)*

Complex **4.2a** (605 mg, 1.0 mmol) was dissolved in THF (20 mL) and treated with $NaBH_4$ (190 mg, 5.0 mmol). The mixture was stirred at room temperature for 30 min and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, afforded a green/brown solid, corresponding to **5.2a**. Yield: 355 mg, 90 %. Anal. Calcd. for $C_{17}H_{16}Fe_2O_4$: C, 51.52; H, 4.07. Found: C, 51.50; H, 4.01%. IR (CH_2Cl_2): ν 1960 vs (t-CO); 1781 s (μ-CO); 1700 m (CO_2Me) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 12.04 (d, 1H, $^3J_{HH}$ = 6.4 Hz, $C_\alpha H$); 5.68 (t, 1H, $^3J_{HH}$ = 7.2 Hz, $C_\beta H$); 4.80 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.62 (s, 3H, CO_2Me); -0.73 (d, 1H, $^3J_{HH}$ = 8.0 Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 267.5 (μ-CO); 213.7 (t-CO); 176.2 (CO_2Me); 174.4 (C_α); 87.4 (C_β); 87.1 (Cp); 83.4 (Cp); 51.4 (CO_2Me); 44.3 (C_γ).

Compounds **5.2b** and **5.2c** were prepared with the same procedure described for **5.2a**, by treating **4.2a** with NBu_4^nCN and MeONa, respectively. Sodium methoxyde was freshly obtained from Na and MeOH. For both **5.2b** and **5.2c** longer reaction time (4h) were required.

5.2b (yield: 84%; colour: green/brown). Anal. Calc. for $C_{18}H_{15}Fe_2NO_4$: C, 51.31 %; H, 3.59 %; N, 3.33 %. Found: C, 51.25 %; H, 3.65 %; N, 3.31 %. IR (CH_2Cl_2): ν 2160 w (CN); 1964 vs (t-CO); 1785 s (μ-CO); 1704 m (CO_2Me) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 5.86 (d, 1H, $^3J_{HH}$ = 7.6 Hz, $C_\beta H$); 4.80 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.68 (s, 3H, CO_2Me); -0.90 (d, 1H, $^3J_{HH}$ = 7.6 Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 267.5 (μ-CO); 213.5 (t-CO); 174.0 (CO_2Me); 150.4 (C_α); 135.1 (CN); 89.6 (C_β); 87.5 (Cp); 85.3 (Cp); 52.2 (CO_2Me); 44.9 (C_γ).

5.2c (yield: 34%; colour: brown). Anal. Calc. for $C_{18}H_{18}Fe_2O_5$: C, 50.71; H, 4.26. Found: C, 50.64; H, 4.25%. IR (CH_2Cl_2): ν 1961 vs (t-CO); 1783 s (μ-CO); 1702 m (CO_2Me) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 5.72 (d, 1H, $^3J_{HH}$ = 7.6 Hz, $C_\beta H$); 4.80 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.86 (s, 3H, O*Me*); 3.60 (s, 3H, CO_2Me); -0.82 (d, 1H, $^3J_{HH}$ = 7.6 Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 267.5 (μ-CO); 213.5 (t-CO); 168.8 (CO_2Me); 164.0 (C_α); 88.7 (C_β); 87.9 (Cp); 84.6 (Cp); 63.5 (O*Me*); 50.9 (CO_2Me); 43.7 (C_γ).

X-ray Crystallography for 3.2a and 5.2a

Crystal data for **3.2a** and **5.2a** were collected at room temperature on a Bruker APEX II CCD diffractometer using graphite monochromated Mo-Kα radiation. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [12]. Crystal data are listed in Table 2.3. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except position of H(14) and H(15) in **3.2a** and H(13), H(14) and H(15) in **5.2a** which were located in the Fourier map. H-atoms were treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom. The crystals of **3.2a** are racemically twinned with a refined Flack parameter of 0.144(16) [13]. The TWIN routine of SHELX97 was used during the refinement. The Cp ring bonded to Fe(1) in **3.2a** is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

Table 2.3 Crystal data and experimental details for **3.2a** and **5.2a**.

Complex	**3a**	**5a**
Empirical formula	$C_{18}H_{18}Fe_2O_4S$	$C_{17}H_{41}ClFe_2N_2O_2$
F*w*	442.08	396.00
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$
a, Å	13.3520(8)	9.8980(10)
b, Å	12.3123(7)	19.741(2)
c, Å	11.6974(7)	8.0365(8)
β, °	112.1770(10)	80.57(3)
Cell volume, Å^3	1780.72(18)	96.248(2)
Z	4	4
D_c, g cm^{-3}	1.649	1.685
μ, mm^{-1}	1.766	1.875
F(000)	904	808
Crystal size, mm	0.32×0.26×0.22	0.23×0.20×0.16
θ limits, °	2.23-27.10	2.06-27.00
Reflections collected	9533	16920
Independent reflections	3891 [R_{int} = 0.0151]	3406 [R_{int} = 0.0396]
Data/restraints/parameters	3891/ 50 / 231	3406 / 3 / 218
Goodness on fit on F^2	1.094	1.116
R_1 ($I > 2\sigma(I)$)	0.0284	0.0356
wR_2 (all data)	0.0758	0.0821
Largest diff. peak and hole, e.Å^{-3}	0.460 / -0.486	0.311 / -0.341

References

[1] (a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, Organometallics 22 (2003) 1326;

(b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 689 (2004) 528;

(c) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, J. Organomet. Chem. 691 (2006) 2424.

[2] (a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, Organometallics 23 (2004) 3348;

(b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 690 (2005) 837;

(c) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 691 (2006) 4234;

(d) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Eur. J. Inorg. Chem. (2006) 285.

[3] A. Yamamoto, J. Chem. Soc., Dalton Trans. (1999) 1027.

[4] (a) A. F. Dyke, J. E. Guerchais, S. A. R. Knox, J. Roué, R. L. Short, G. E. Taylor, P. Woodward, J. Chem. Soc. Chem. Comm. (1981) 537;

(b) C. P. Casey, P. J. Fagan, J. Am. Chem. Soc. 104 (1982) 4950;

(c) C. P. Casey, M. W. Meszaros, S. R. Marder, P. J. Fagan, J. Am. Chem. Soc. 106 (1984) 3680;

(d) C. P. Casey, M. W. Meszaros, P. J. Fagan, R. K. Bly, S. R. Marder, E. A. Austin, J. Am. Chem. Soc. 108 (1986) 4043;

(e) C. P. Casey, M. W. Meszaros, P. J. Fagan, R. K. Bly, R. E. Colborn, J. Am. Chem. Soc. 108 (1986) 4053;

(e) C. P. Casey, M. W. Meszaros, S. R. Marder, R. K. Bly, P. J. Fagan, Organometallics (1986), 5, 1873-9.

[5] (a) J. A. K. Howard, S. A. R. Knox, N. J. Terrill, M. I. Yates, J. Chem. Soc., Chem. Commun. (1989) 640;

(b) J. Levisalles, F. Rose-Munch, H. Rudler, J. C. Daran, Y. Dromzee, Y. Jeannin, J. Chem. Soc., Chem. Commun. (1981) 152;

(c) C. E. Sumner Jr., J. A. Collier, R. Pettit, Organometallics 1 (1982) 1350.

[6](a) A. F. Dyke, S. A. R. Knox, P. J. Naish, G. E. Taylor, J. Chem. Soc., Chem. Commun. (1980) 803;

(b) P. Q. Adams, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, P. J. Woodward, Chem. Soc. Chem. Commun. (1983) 222;

(c) R. E. Colburn, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, A. G. Orpen, J. Chem. Soc., Dalton Trans. (1989) 1799;

(d) Knox, S. A. R. J. Organomet. Chem. 1990, 400, 255;

(e) B. D. Rowsell, R. McDonald, M. J. Ferguson, M. Cowie, Organometallics 2003, 22, 2944-2955.

[7] (a) V. G. Albano, S. Bordoni, D. Braga, L. Busetto, A. Palazzi, V. Zanotti, Angew Chem. Int. Ed. Engl. 30 (1991) 847;
(b) L. Busetto, V. Zanotti, S. Bordoni, L. Carlucci, V. G. Albano, D. Braga, J. Chem. Soc., Dalton Trans. (1992) 1105;
(c) S. Bordoni, F. Mazza, V. Zanotti, Inorg. Chim. Acta 223 (1994) 31.

[8] (a) V. Zanotti, S. Bordoni, L. Busetto, L. Carlucci, A. Palazzi, R. Serra, V. G. Albano, M. Monari, F. Prestopino, F. Laschi, P. Zanello, Organometallics, 14 (1995) 5232;
(b) L. Busetto, L. Carlucci, V. Zanotti, V. G. Albano, M. Monari, Chem. Ber. 125 (1992) 1125;
(c) L. Busetto, M. C. Cassani, V. Zanotti, V. G. Albano, D. Braga, J. Organomet. Chem. 415 (1991) 395;
(d) S. Bordoni, L. Busetto, M. C. Cassani, A. Palazzi, V. Zanotti, Inorg. Chim. Acta 291 (1999) 333.

[9] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, Magn. Reson. Chem. 31 (1993) 287.

[10] K. Stott, J. Stonehouse, J. Keeler, T. L. Hwang, A. J. Shaka, J. Am. Chem. Soc. 117 (1995) 4199.

[11] M. H. Quick, R. J. Angelici Inorg. Chem. 20 (1981) 1123.

[12] G. M. Sheldrick, SHELX97, Program for crystal structure determination, University of Göttingen, Germany, 1997.

[13] H. D. Flack, Acta Crystallogr., Sect A, 39 (1983) 876.

CHAPTER III

OLEFIN-AMINOCARBYNE COUPLING IN DIIRON COMPLEXES: SYNTHESIS OF NEW BRIDGING AMINOALLYLIDENE COMPLEXES

Abstract

The bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **2a**; Xyl, **2b**; 4-C_6H_4OMe, **2c**; Xyl = 2,6-$Me_2C_6H_3$) react with acrylonitrile or methyl acrylate, in the presence of Me_3NO and NaH, to give the corresponding μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)(R))C_\beta(H)C_\gamma(H)(R')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Me, R' = CN, **3.3a**; R = Xyl, R' = CN, **3.3b**; R = 4-C_6H_4OMe, R' = CN, **3.3c**; R = Me, R' = CO_2Me, **3.3d**; R = 4-C_6H_4OMe, R' =CO_2Me, **3.3e**). Likewise, **2a** reacts with styrene or diethyl maleate, under the same reaction conditions, affording the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R' = H, R'' = C_6H_5, **3.3f**; R' = R'' = CO_2Et, **3.3g**). The corresponding reactions of $[Ru_2\{\mu\text{-}CN(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**2d**) with acrylonitrile or methyl acrylate afford the complexes $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)(CH_2Ph))C_\beta(H)C_\gamma(H)(R')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R' = CN, **3.3h**; CO_2Me, **3.3i**), respectively.

The coupling reaction of olefin with the carbyne carbon is regio- and stereospecific, leading to the formation of only one isomer. C-C bond formation occurs selectively between the less substituted alkene carbon and the aminocarbyne, and the C_β-H, C_γ-H hydrogen atoms are mutually *trans*.

The reactions with acrylonitrile, leading to **3.3a-c** and **3.3h** involve, as intermediate species, the nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NC\text{-}CH{=}CH_2)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Me, **4.3a**; M = Fe, R = Xyl, **4.3b**; M = Fe, R = 4-C_6H_4OMe, **4.3c**; M = Ru, R = $CH_2C_6H_5$, **4.3d**).

Compounds **3.3a**, **3.3d** and **3.3f** undergo methylation (by $CH_3SO_3CF_3$) and protonation (by HSO_3CF_3) at the nitrogen atom, leading to the formation of the cationic complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)_3)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **5.3a**; R = CO_2Me, **5.3b**; R = C_6H_5, **5.3c**) and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(H)(Me)_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **6.3a**; R = CO_2Me, **6.3b**; R = C_6H_5, **6.3c**), respectively.

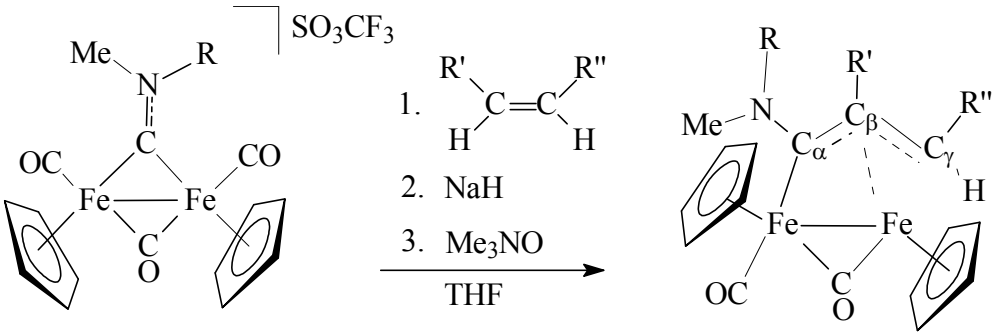
Complex **3.3a**, adds the fragment $[Fe(CO)_2(THF)(Cp)]^+$, through the nitrile functionality of the bridging ligand**,** leading to the formation of the complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CNFe(CO)_2Cp)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**9.3**).

In an analogous reaction, **3.3a** and $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$, in the presence of Me_3NO, are assembled to give the tetrameric species $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CN[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2])\}(\mu\text{-}CO)(CO)(Cp)_2])][SO_3CF_3]$ (R = Me, **10.3a**; R = Xyl, **10.3b**; R = 4-C_6H_4OMe, **10.3c**).

The molecular structures of **3.3a** and **3.3b** have been determined by X-ray diffraction studies.

Results and discussion

The bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **2a**; Xyl, **2b**; 4-C_6H_4OMe, **2c**; Xyl = 2,6-$Me_2C_6H_3$) react with olefins (methyl acrylate, acrylonitrile, styrene, diethyl maleate), in THF solution at room temperature, in the presence of Me_3NO/NaH, to give the corresponding μ-allylidene complexes **3.3a-g** in 70-80 % yields (Scheme 3.1).



	R	R'	R''	
2a	Me	H	CN	**3.3a**
2b	Xyl	H	CN	**3.3b**
2c	4-C_6H_4OMe	H	CN	**3.3c**
2a	Me	H	CO_2Me	**3.3d**
2c	4-C_6H_4OMe	H	CO_2Me	**3.3e**
2a	Me	H	C_6H_5	**3.3f**
2a	Me	CO_2Et	CO_2Et	**3.3g**

Scheme 3.1

The reaction parallels that of the thiocarbyne complex **1** with olefins (Chapter II): in both cases the carbyne-alkene coupling requires the displacement of a CO ligand and the presence of NaH in order to remove a proton from the olefin. However, significant differences have been evidenced in the stereochemistry of the reaction products, which concern the mutual orientation of the Cp ligands and will be discussed later.

Compounds **3.3a-g** were purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structures of **3.3a** and **3.3b** have been determined by X-ray diffraction. The ORTEP diagrams are shown in Figures 3.1 and 3.2, while the main bond lengths and angles are reported in Table 3.1.

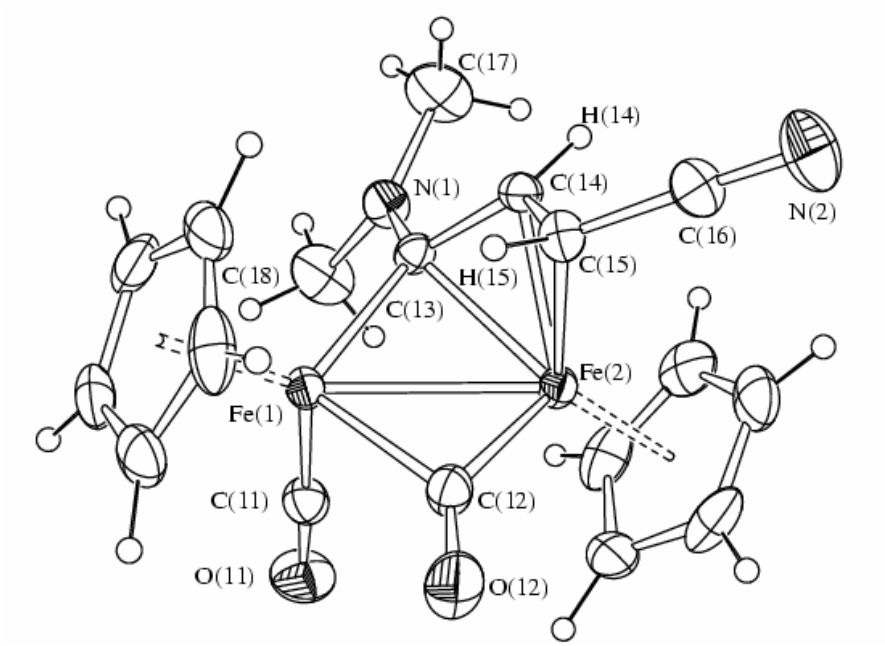


Figure 3.1 Molecular structure of **3.3a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level.

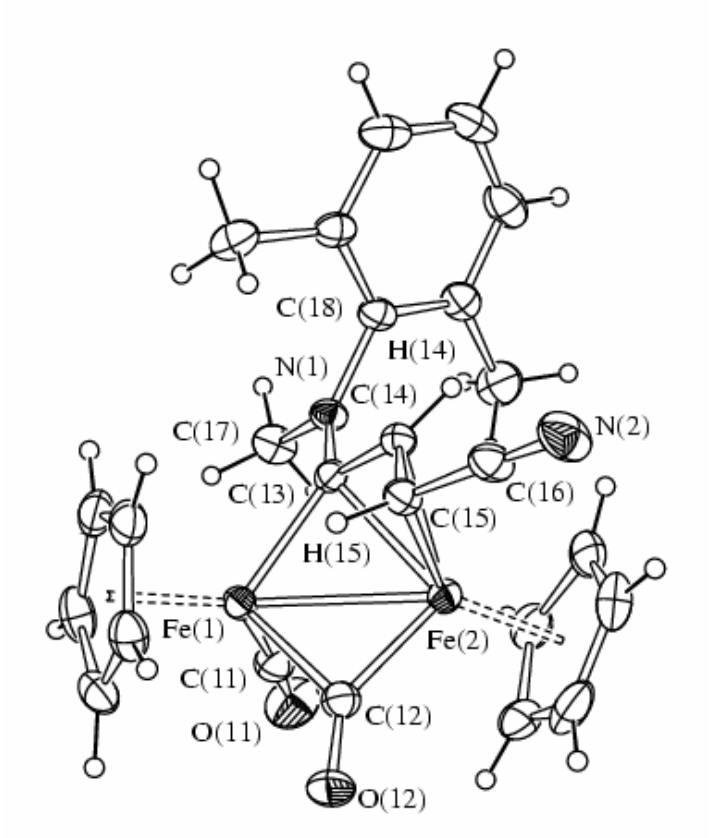


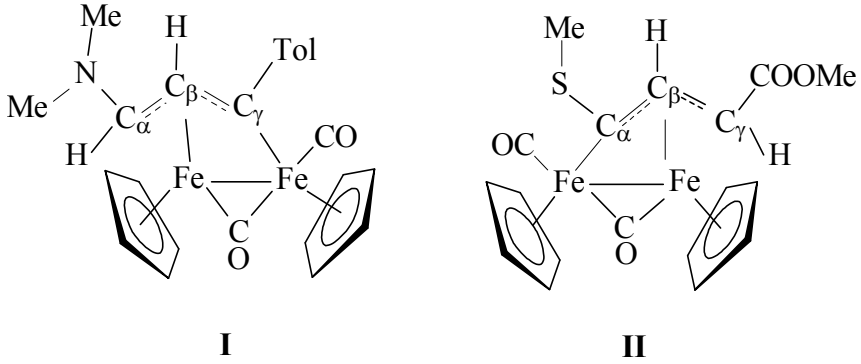
Figure 3.2 Molecular structure of **3.3b**, with key atoms labelled. Displacement ellipsoids are at 30% probability level.

Table 3.1

Selected bond lengths (Å) and angles (deg) for **3.3a** and **3.3b**.

	3.3a	**3.3b**
Fe(1)-Fe(2)	2.5602(5)	2.5812(5)
Fe(1)-C(11)	1.731(3)	1.733(3)
Fe(1)-C(12)	1.959(3)	1.991(2)
Fe(2)-C(12)	1.884(3)	1.867(2)
Fe(2)-C(13)	2.094(3)	2.179(2)
Fe(1)-C(13)	1.971(3)	1.967(2)
Fe(2)-C(14)	2.012(3)	2.023(2)
Fe(2)-C(15)	2.051(3)	2.058(2)
C(11)-O(11)	1.156(3)	1.155(3)
C(12)-O(12)	1.170(3)	1.173(3)
C(13)-C(14)	1.434(4)	1.416(3)
C(14)-C(15)	1.432(4)	1.435(3)
C(15)-C(16)	1.435(4)	1.440(3)
C(16)-N(2)	1.149(4)	1.137(3)
C(13)-N(1)	1.368(3)	1.375(3)
Fe(1)-C(12)-Fe(2)	83.54(11)	83.93(10)
Fe(1)-C(13)-Fe(2)	78.01(9)	76.82(8)
Fe(1)-C(13)-C(14)	118.09(19)	118.53(16)
C(13)-C(14)-C(15)	120.7(3)	121.5(2)
C(14)-C(15)-C(16)	117.8(3)	117.6(2)
C(15)-C(16)-N(2)	178.2(4)	178.6(3)
C(13)-N(1)-C(17)	122.7(3)	123.17(19)
C(13)-N(1)-C(18)	121.2(3)	121.34(19)
C(17)-N(1)-C(18)	115.1(3)	115.39(19)

The bonding parameters of the bridging ligand can be evaluated with respect to other C_3-bridging ligands present in closely related diiron complexes (Table 3.2). In particular, **3.3a-b** have to be compared with the μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Tol)CH{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [1] (Chart 3.1, **I**), and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(SMe)C(H)C(H)(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (Chapter II) (Chart 3.1, **II**). This analysis points out a close similarity in the bonding situation of **3.3a-b**, **I**, and **II** indicating that the $\mu\text{-}\eta^1\text{:}\eta^3$-C(N(Me)(R))C(H)C(H)(CN) [R = Me, **3.3a**; Xyl, **3.3b**] ligand acts mainly as a bridging allylidene, as inferable also from the fact that both the C-C bonds within the ligand [C_α-C_β 1.434(4) Å, C_β-C_γ 1.432(4) Å in **3.3a**; C_α-C_β 1.416(3) Å, C_β-C_γ 1.435(3) Å in **3.3b**] and the Fe-C interactions between the ligand and the diiron frame [Fe(2)-C(13) 2.094(3), Fe(2)-C(14) 2.012(3), Fe(2)-C(15) 2.051(3) in **3.3a**; Fe(2)-C(13) 2.179(2), Fe(2)-C(14) 2.023(2), Fe(2)-C(15) 2.058(2) in **3.3b**] are very similar. It is noteworthy that in **3.3a-b** the two hydrogen atoms within the ligand, *i.e.* H(14) and H(15), are in mutual *trans* position.



I **II**

Chart 3.1

Table 3.2 Comparison between the bonding parameters (Å) of C_3 units in different diiron complexes.

	3.3a	**3.3b**	**I**	**II**
Fe_a-C_{bridge} [(a)]	1.971(3)	1.967(2)	1.977(6)	1.955(3)
Fe_b-C_α	2.094(3)	2.179(2)	2.299(6)	2.049(3)
Fe_b-C_β	2.012(3)	2.023(2)	2.070(6)	2.026(3)
Fe_b-C_γ	2.051(3)	2.058(2)	1.979(6)	2.068(3)
C_α-C_β	1.434(4)	1.416(3)	1.408(9)	1.415(4)
C_β-C_γ	1.432(4)	1.435(3)	1.441(8)	1.422(4)
C_α-X [(b)]	1.368(3)	1.375(3)	1.375(8)	1.758(3)

[(a)] C_{bridge} = C_α in **3.3a-b** and **II**; C_{bridge} = C_γ in **I**.

[(b)] X = N in **3.3a-b** and **I**; X = S in **II**.

One of the most striking features of the complexes **3.3a-b** is that the Cp ligand are mutually *trans*, whereas most of analogous dinuclear complexes (including the μ-allylidene complexes **I** and **II**) are *cis*, with few exceptions [2].

Steric arguments offer a possible explanation for the observed differences. In complexes **3.3a-b** the C_α carbon displays a significant bridging alkylidene character (as emphasized in Chart 3.2), which forces the steric demanding N(Me)(R) substituent to reside closer to the metal centres than in the species **I**. In these latter, the C_γ assumes a μ-alkylidene character, leaving the N(Me)(R) moiety far apart. Thereby, when the steric demanding N(Me)(R) is closer to the dimetal centre (like in **3.3a-b**) a *trans* configuration for the Cp ligands is favoured.

Analogous considerations can be drawn comparing **3.3a-b** with the bridging thiomethylallylidene complexes (Chart 3.2, **II**). The coordination mode of the bridging ligand is the same, but the nature of the C_α substituents is different in the two cases [N(Me)(R) or SMe]. Presumably, the steric demand of the thiomethyl is not so relevant to force the Cp ligands to assume a *trans* configuration.

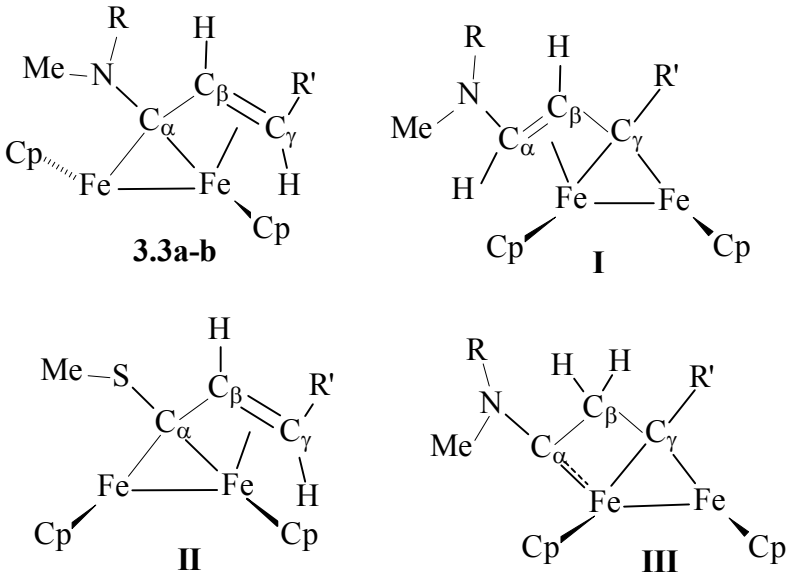


Chart 3.2 CO ligands are omitted for seek of clarity.

It should also be noted that the species **3.3a-b** and **I** exhibit the same hydrocarbyl chain: (Me)(R)N-C_α-C_β(H)-C_γ(R') plus an hydrogen atom, which is bonded to C_γ or C_α, respectively. A third possibility, in which the H atom is bonded to the C_β carbon, corresponds to the previously reported bis-alkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(R)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (Chart 3.2, **III**) [1]. These species are not true isomers, since R and R' are different, however they evidence that the dinuclear $Fe_2(CO)_2Cp_2$ frame is very effective and flexible in accommodating C_3 bridging

organic molecules of different nature. One of the reasons for this adaptability is the simplicity in which ancillary ligands can rearrange their coordination geometry around the dimetal centre to respond to different steric demands of the bridging organic frame.

Finally, it should be outlined that the different, but strictly related C_3 bridged frames (in **3.3a-b**, **I** and **III**) do not interconvert, and are exclusively obtained by distinct reaction routes: **3.3a-b** derive from μ-aminocarbyne-alkene coupling plus proton abstraction (Scheme 3.1), whereas **I** and **II** result from aminocarbyne-alkyne coupling, followed by hydride addition, which can be selectively directed to the C_α or C_β carbon, respectively [1].

The spectroscopic data of **3.3a-f** are consistent with the structures observed in the solid. In particular, the NMR data of **3.3a**, **3.3c-e** and **3.3g** reveal the presence, in solution, of a single isomeric form, in which the Cp ligands are mutually *trans*. Conversely, both *cis* and *trans* isomers of **3.3b** and **3.3f** are observed, with prevalence of the *trans* isomers. The presence of an isomeric mixture in the case of **3.3b** and **3.3f** was clearly indicated, in the NMR spectra, by the presence of two sets of resonances, and in the IR spectra (in CH_2Cl_2 solution) by the observation of two absorptions due to the terminally bonded CO ligand (*e.g.* at 1958 and 1932 cm^{-1} for *cis*-**3.3b** and *trans*-**3.3b**, respectively). The *cis* and *trans* isomeric forms were identified by NMR, since NOE effect is detected between the Cp resonances for the *cis* isomers, but not for the *trans* (*e.g.* for cis-**3.3b** NOE effect was revealed between the Cp signals at δ 4.71 and 4.41 ppm).

Interestingly, both *cis*-**3.3b** and *cis*-**3.3f** are quantitatively converted into the corresponding *trans* isomers upon heating for *ca.* 4 h in refluxing toluene. On the other hand, solutions containing only the *trans* forms are stable upon heating in refluxing toluene. This behavior, which is opposite to previously observed *trans* to *cis* isomerizations [2], indicates that the *trans* isomer is, in this case, thermodynamically more stable, and that the *cis* isomer is a kinetic product rather that being in equilibrium with the *trans*.

Concerning the stereochemistry of this reaction it has to be emphasised that beside *cis* and *trans* no other isomeric form was observed in solution. This leads to the important conclusion that the aminocarbyne-olefin coupling reactions are regio- and stereospecific. Indeed, the incorporation of asymmetric olefins should generate, in theory, two regioisomers. Conversely, the ^1H NMR spectra of **3.3a-g** evidence that the C-C bond formation occurs selectively between the less substituted alkene carbon and the aminocarbyne ligand. Likewise, the $C_\beta H$ and $C_\gamma H$ protons of the bridging ligand in **3.3a-f** result placed exclusively on opposite sides of the C_β-C_γ double bond interaction (*E* isomer). This is evidenced, in the ^1H NMR spectra, by the occurrence of two doublets, attributable to the $C_\beta H$ and $C_\gamma H$ protons, respectively, with a coupling constant that corresponds to *trans* olefin hydrogen atoms (*e.g.* 8.0 Hz for **3.3d** – see Figure 3.3). Moreover, $C_\gamma H$

proton resonance is shifted to low frequencies (*e.g.* -0.29 ppm for **3.3d** – see Figure 3.3), accordingly to the proximity and the shielding effect exerted by the metal centre. Thus, the structure of the complexes in solution is the same of that observed in the solid (X-ray structure of **3.3a-b**). Moreover, the regio- and stereoselective character of the olefin-aminocarbyne coupling is almost identical to that found in the corresponding reaction with thiocarbyne (Chapter II).

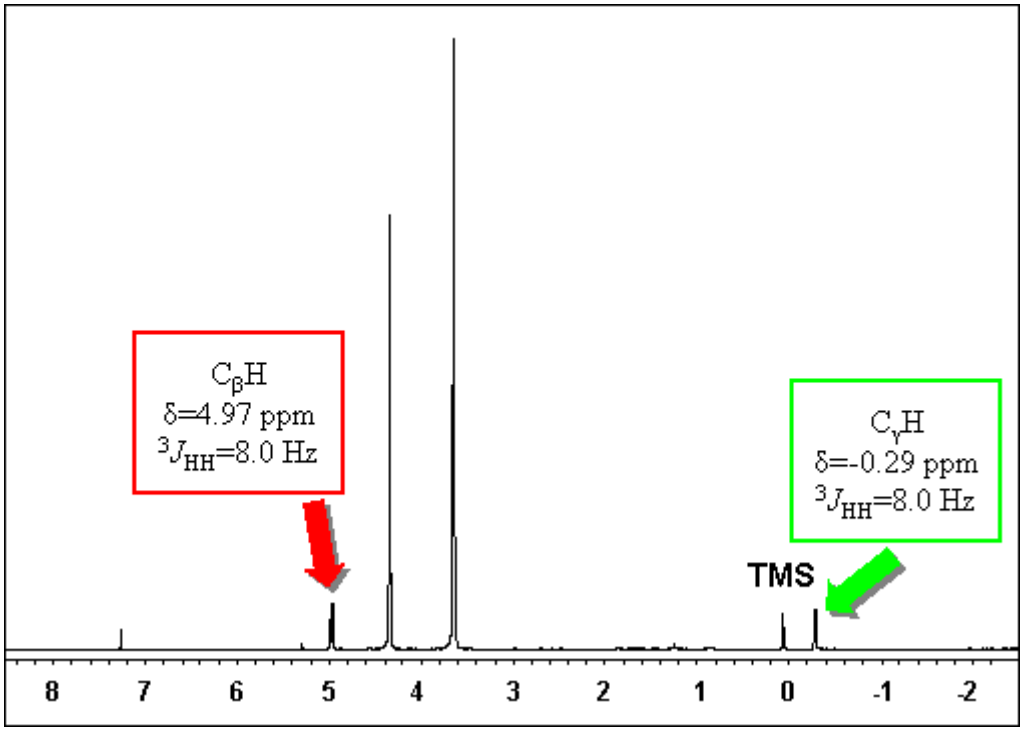


Figure 3.3

The ^{13}C NMR spectra show the resonances due to the C_α, C_β and C_γ of the bridging allylidene (*e.g.* for **3.3a**, at 203.9, 59.8 and 21.5 ppm, respectively).

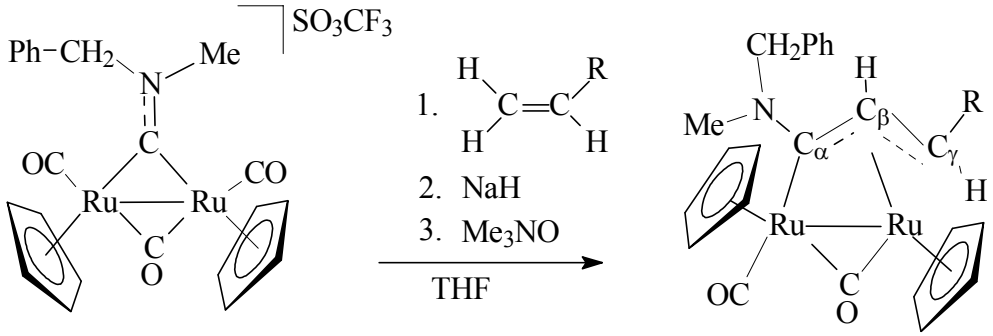
Finally, for complexes **3.3a**,**d**,**f** and **g** the N-methyls give rise to a single resonance in both ^1H and ^{13}C NMR spectra (*e.g.* for **3.3a**, at 3.62 ppm and 46.5 ppm, respectively). The equivalence of the N-methyls is consistent with the loss of double bond character in the C_α-N interaction consequent to the aminocarbyne-alkene coupling.

The aminocarbyne-olefin coupling has not a general character. The reaction is limited to olefins activated by electron withdrawing groups, which favour the deprotonation step. The conformation of the olefin is also important, in that **2a** reacts with diethyl maleate but not with diethyl fumarate.

The nature of the N(Me)R substituents in the μ-aminocarbyne ligand also exhibits some influence on the reaction rate. We observed that **2a** (R = Me) and **2c** (R = 4-C_6H_4OMe) display

comparable reactivity, whereas **2b** (R = Xyl) is significantly less reactive and only with acrylonitrile it gives appreciable yields.

Finally, the reactions involving the diruthenium complex **2d**, analogue to **2a-c**, do not evidence any effect due to the nature of the metal atoms. The presence of ruthenium in the place of iron does not produce any relevant change in the reaction path. Thus, reactions with acrylonitrile or methyl acrylate afford the corresponding bridging allylidene complexes **3.3h** and **3.3i**, respectively (Scheme 3.2).



	R	
2d	CN	**3.3h**
2d	CO_2Me	**3.3i**

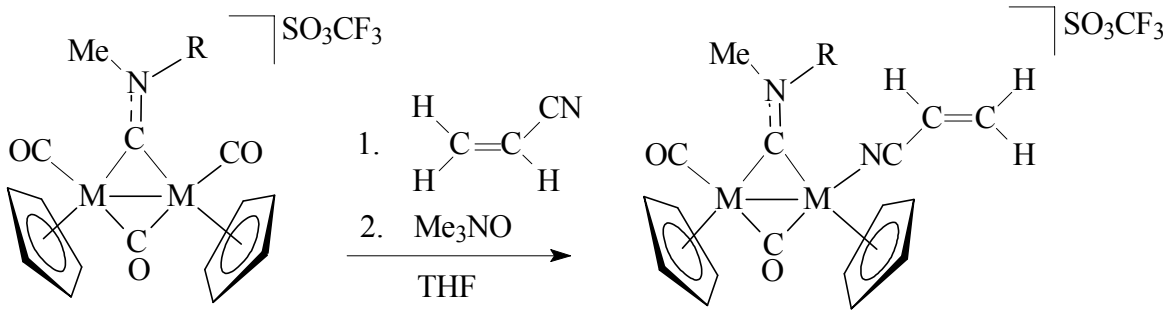
Scheme 3.2

Under the same reaction conditions, **2d** is less reactive than the diiron compounds **2a** and **2c** and the reactions yields are consequently lower. Moreover, the reaction products consist of a mixture of the *cis* and *trans* isomers, with predominance of the *trans*. Also in this case, the *cis* isomer is converted into the *trans* upon heating at reflux in THF.

As expected, the spectroscopic data of the diruthenium complexes **3.3h** and **3.3i** closely resemble those of the analogous diiron species described above, and do not deserve further comments.

The reaction described in the Schemes 3.1 and 3.2 are among the few examples of coupling between bridging carbyne ligands and olefins [3]. Among these, the most remarkable reactivity was exhibited by the μ-methylidyne complex $[Fe_2(\mu\text{-CH})(\mu\text{-CO})(CO)_2(Cp)_2]^+$, in which the methylidyne-olefin coupling was described as 'hydrocarbation reaction', because of the analogies with the hydroboration reaction [3c-g]. Less reactive bridging carbyne ligands, like the μ-ethylidyne complex $[Ru_2(\mu\text{-CMe})(\mu\text{-CO})(CO)_2(Cp)_2]^+$ [3a] and the thiocarbyne complex **1** (Chapter II) undergo coupling with olefins but require the presence of a base in order to remove a proton from the olefin.

Concerning the reaction mechanism, the conclusions we can draw are very similar to those reported for the olefin-carbyne coupling reactions involving the μ-ethylidyne complex $[Ru_2(\mu\text{-}CMe)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ [3a] or the thiocarbyne complex **1** (Chapter II). The reaction sequence should include, as preliminary step, the η^2-olefin coordination at the site made available by CO removal. This is accomplished, in our case, by the use of Me_3NO. Without this reagent the reaction does not take place. Subsequent steps include intramolecular coupling, which might entail a metallacyclobutane ring, and deprotonation. Unfortunately, none of the supposed intermediates have been detected. Even the initial η^2-olefin intermediate appears very elusive. Only in one case, namely in the reactions with acrylonitrile, it was possible to isolate intermediate species which were identified as the nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NC\text{-}CH{=}CH_2)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Me, **4.3a**; M = Fe, R = Xyl, **4.3b**; M = Fe, R = 4-C_6H_4OMe, **4.3c**; M = Ru, R = $CH_2C_6H_5$, **4.3d**) (Scheme 3.3). Coordination of acrylonitrile through the nitrile, rather than with the olefin functionality, is in a good agreement with the demonstrated reactivity of type **2** complexes towards nitriles [4]. Obviously, the nitrile complexes **4.3a-d** can be obtained in better yields upon treatment of **2a-d** with acrylonitrile and Me_3NO without NaH. The observation that the nitrile complexes **4.3a-d** are transformed into **3.3a-c** and **3.3h**, respectively, upon treatment with NaH, indicate that they are effective reaction intermediates.

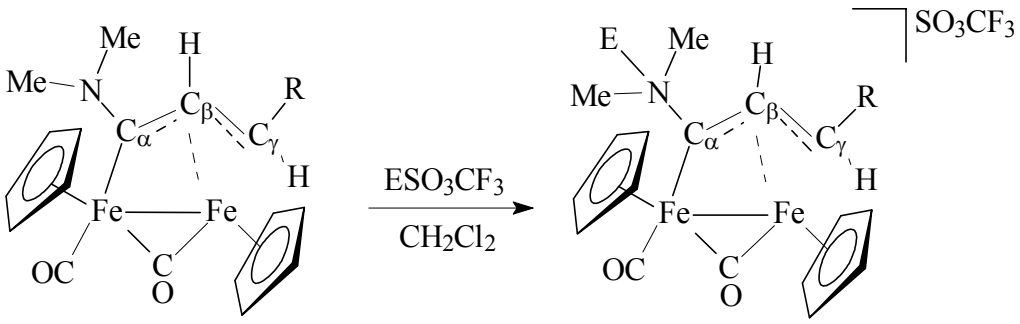


	M	R	
2a	Fe	Me	**4.3a**
2b	Fe	Xyl	**4.3b**
2c	Fe	4-C_6H_4OMe	**4.3c**
2d	Ru	$CH_2C_6H_5$	**4.3d**

Scheme 3.3

Compounds **4.3a-d** have been characterized by IR and NMR spectroscopy, and elemental analysis (see Experimental). Their spectroscopic data closely resemble those of analogous diiron and diruthenium nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCR')(Cp)_2][SO_3CF_3]$ reported in the literature [4, 5]. In particular these compounds are characterized, in the ^{13}C NMR spectra, by the typical low field resonance of the bridging aminocarbyne carbon, in the 330-340 ppm range (*e.g.* at 331.0 ppm for **4.3a**). Also consistent is the observation that **4.3a**, in which the substituents at the N atom are both methyls, displays a single isomeric form, whereas complexes **4.3b-d** are a mixture of two isomers. These are due to the different orientations that Me and R (R = Xyl, 4-C_6H_4OMe, $CH_2C_6H_5$) can assume with respect to the non-equivalent metal atoms, and are consequence of the double bond character of the μ-C=N interaction (*E* and *Z* isomerism).

The reactivity of complexes of type **3.3** was then investigated. In particular, we have found that compounds **3.3a**,**d** and **f** undergo methylation (by $CH_3SO_3CF_3$) and protonation (by HSO_3CF_3) at the NMe_2 group, affording, in nearly quantitative yields, the cationic species $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)_3)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **5.3a**; R = CO_2Me, **5.3b**; R = C_6H_5, **5.3c**) and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(H)(Me)_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **6.3a**; R = CO_2Me, **6.3b**; R = C_6H_5, **6.3c**), respectively (Scheme 3.4). The reactions were carried out in CH_2Cl_2 solution at room temperature.



	R	E	
3a	CN	CH_3^+	**5a**
3d	CO_2Me	CH_3^+	**5b**
3f	C_6H_5	CH_3^+	**5c**
3a	CN	H^+	**6a**
3d	CO_2Me	H^+	**6b**
3f	C_6H_5	H^+	**6c**

Scheme 3.4

Compounds **5.3** and **6.3** have been purified by filtration on celite and characterized by IR and NMR spectroscopy, and elemental analysis.

The IR spectra (in CH_2Cl_2 solution) of **5.3a-c** exhibit absorptions due to the terminal and bridging carbonyls (*e.g.* at 1986 and 1815 cm^{-1} for **5.3a**). Additional bands are observed for **5.3a**, due to the CN group (at 2205 cm^{-1}), and for **5.3b**, attributable to the CO_2Me (at 1710 cm^{-1}). As expected, the CO bands are shifted to higher frequencies (ca. 30 cm^{-1}) compared to the parent complexes, as effect of the positive charge in **5.3a-c**.

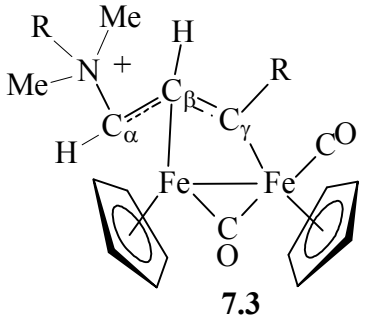
Analogous considerations concern the protonation reaction. In addition, the IR spectra of **6.3a-c** (in KBr pellets) show the typical NH absorption around 3200 cm^{-1} (*e.g.* at 3215 cm^{-1} for **6.3a**).

The ^1H NMR spectra (in CD_3CN solution) of compounds **5.3** and **6.3** indicate the presence of a single isomer, since only one set of resonances is observed. In particular, the N-methyls give rise to one singlet signal in both ^1H and ^{13}C NMR spectra (*e.g.* for **5.3a** at 3.12 and 58.8 ppm, respectively), indicating free rotation around the C_α-NMe_3 bond. Moreover, NOE investigations revealed that **5.3-6.3** retain the *trans* configuration of the Cp ligands, shown by their parent species **3.3**.

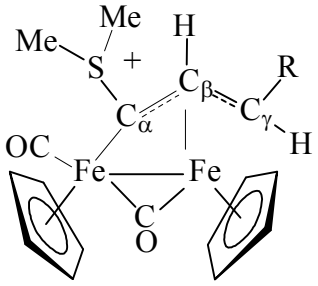
The electrophilic addition at the aminic nitrogen atom does not modify significantly the ^{13}C NMR resonance pattern for the C_3 bridging ligand: C_α gives rise to a low frequency resonance (180 ppm for **5.3a**), whereas C_β and C_γ signals occur in 80-20 ppm range.

The protonation reactions, which lead to **6.3a-c** are reversible and the parent complexes are restored upon treatment with bases (e.g. NaH), whereas methylation reactions are not.

The complexes **5.3a-c** present several similarities with the ammonium and the sulphonium complexes **7.3** [6] and **8.3** (Chapter II) (Chart 3.3), respectively.



7.3

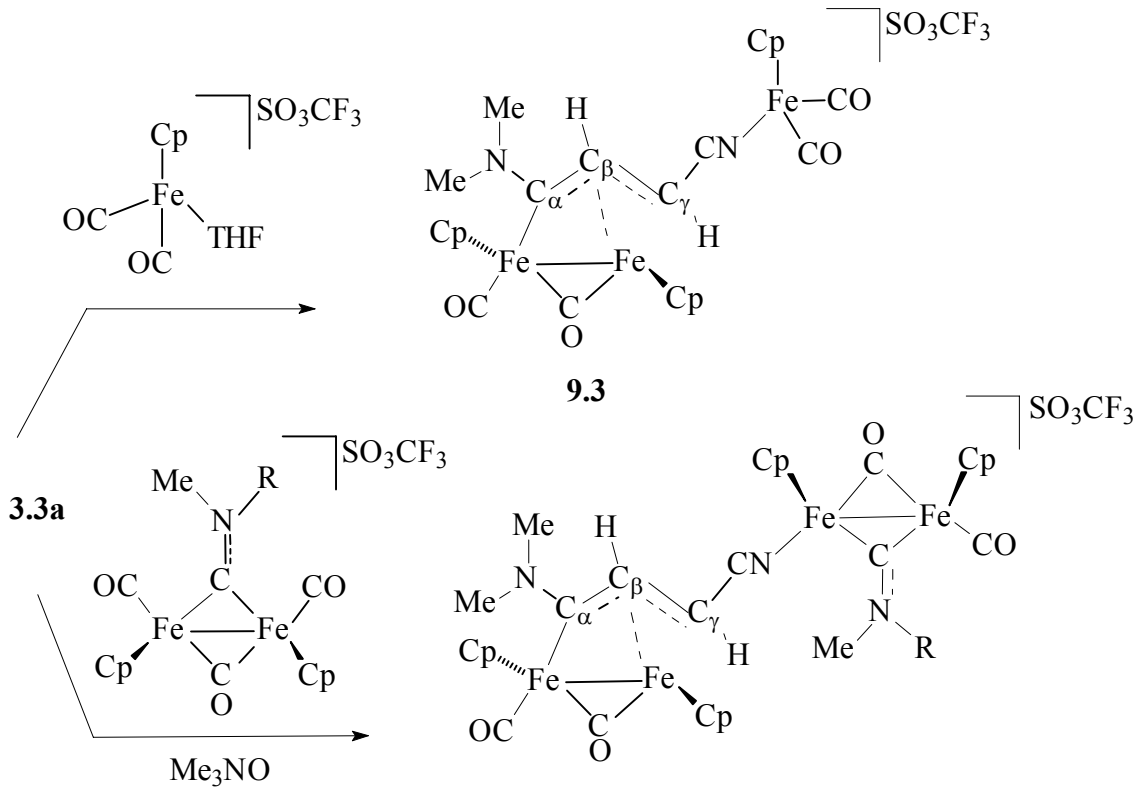


8.3

Chart 3.3

Also **7.3** and **8.3** were obtained by methylation (with $MeSO_3CF_3$) of the heteroatom in their corresponding neutral precursors. The main difference between the ammonium complexes **5.3** and **7.3** with respect to the sulphonium **8.3** is that the SMe_2 group can be displaced by nucleophiles like hydride ($NaBH_4$) and cyanide (NBu_4CN) (Chapter II), whereas, under similar reaction conditions, neither **7.3** nor **5.3** release the NMe_3 group. Thereby, the ammonium allylidene ligand in **5.3** fails to become the precursor of other bridging C_3 frames via NMe_3 displacement.

Beside the protonation and methylation reactions, the presence of nitrogen functional groups (NMe_2 and CN), potential able to act as ligands, could be exploited to coordinate further metal complexes. Thereby, we have investigated the reaction of **3.3a** with $[Fe(CO)_2(THF)(Cp)]^+$, generated by treatment of $[Fe_2(CO)_4(Cp)_2]$ with $AgSO_3CF_3$. The reaction, carried out in THF, leads to the formation of the trinuclear complex **9.3** in good yields (Scheme 3.5).



R = Me, **10.3a**; Xyl, **10.3b**; 4-C_6H_4OMe **10.3c**

Scheme 3.5

Likewise, the reaction of **3.3a** with $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **2a**; Xyl, **2b**; 4-C_6H_4OMe, **2c**) affords the corresponding tetranuclear adducts **10.3a-c**, respectively, in about 70% yield (Scheme 3.5). The reaction requires the presence of Me_3NO in order to generate a vacant coordination site on the aminocarbyne complexes and promote the nitrile coordination.

By contrast with the methylation and protonation, which occur at the NMe_2 group of **3.3a**, the addition of the iron frame takes place selectively through the nitrile coordination. The preference for the nitrile coordination is consistent with previous observations which evidenced that nitriles, better than amines, displace the CO ligand in the aminocarbyne complexes **2a-c** [4].

Compounds **9.3** and **10.3a-c** have been isolated by chromatography on alumina and characterized by IR and NMR spectroscopy and elemental analysis.

The IR spectra of **10.3a-c** (in CH_2Cl_2 solution) show two absorptions for the terminal carbonyls (*e.g.* at 1981 cm^{-1} and 1940 cm^{-1} for **10.3a**) and two for the bridging ones (*e.g.* at 1812 cm^{-1} and 1785 cm^{-1} for **10.3a**). Moreover, the μ-CN band is observed (*e.g.* at 1586 cm^{-1} for **10.3a**).

The corresponding NMR spectra (in $CDCl_3$) exhibit resonances consistent with those of the parent compounds **3.3a** and **2a-c**. In particular, the ^1H NMR spectra show the $C_\gamma H$ proton resonance, shifted to low frequencies (*e.g.* -1.35 ppm for **10.3a**), accordingly to the shielding effect exerted by the metal centre. On the other hand, the ^{13}C NMR spectra exhibit the signals due to the C_α, C_β and C_γ of the bridging allylidene (*e.g.* for **10.3a**, at 203.1, 53.1 and 19.6 ppm, respectively) and the typical downfield resonance of the bridging aminocarbyne carbon, (*e.g.* at 331.2 ppm for **10.3a**). Interestingly, each of the compounds **10.3a-c** exists in a single isomeric form. In particular, NOE investigations pointed out that the Cp rings of the aminocarbyne fragment are mutually *cis*, whereas those of the allylidene moiety are *trans*, as in their parent species **2a-c** and **3.3a**, respectively.

Conclusions

The bridging aminocarbyne complexes **2a-d** react with olefins generating bridging allylidene ligands. This result, together with those previously reported on related thiocarbyne complexes (Chapter II), show that the coupling between activated olefin and heteroatom substituted μ-carbynes has a general character, and that the reactions proceed as well with diiron and diruthenium complexes characterized by the $M_2(CO)_2(Cp)_2$ frame. This latter effectively supports the bridging allylidene ligand, in that it can easily arrange the coordination geometry of the ancillary CO and Cp (*e.g. cis trans* isomers) to better respond to the steric requirements of the bridging ligand.

Olefin incorporation into the aminocarbyne ligand is regio- and stereospecific. It represents a valuable example of bridging hydrocarbyl transformation (specifically: C_1 to C_3 chain growth). Further modifications of the bridging frame are feasible due to the presence nitrogen functional groups. These reactions include electrophilic additions at the NR_2 functional group, or assembling with unsaturated organometallic iron complexes through the nitrile functionality.

Experimental details

General

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^{1}H,^{13}C correlation through gs-HSQC and gs-HMBC experiments [7]. NOE measurements were recorded using the DPFGSE-NOE sequence [8]. NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds **2a,b** [9], **2c** [10] and **2d** [11] were prepared by published methods.

*Synthesis of $[M_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)(R))C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (M = Fe, R = Me, R′ = H, R″ = CN, **3.3a**; M = Fe, R = Xyl, R′ = H, R″ = CN, **3.3b**; M = Fe, R = 4-C_6H_4OMe, R′ = H, R″ = CN, **3.3c**; M = Fe, R = Me, R′ = H, R″ = CO_2Me, **3.3d**; M = Fe, R = 4-C_6H_4OMe, R′ = H, R″ = CO_2Me, **3.3e**; M = Fe, R = Me, R′ = H, R″ = C_6H_5, **3.3f**; M = Fe, R = Me, R′ = CO_2Et, R″ = CO_2Et, **3.3g**; M = Ru, R = $CH_2C_6H_5$, R′ = H, R″ = CN, **3.3h**; M = Ru, R = $CH_2C_6H_5$, R′ = H, R″ = CO_2Me, **3.3i**).*

To a solution of **2a** (531 mg, 1.0 mmol) in THF (20 mL) were successively added: acrylonitrile (0.4 mL, 10 mmol), NaH (120 mg, 5.0 mmol), and Me_3NO (110 mg, 1.5 mmol). The mixture was stirred at room temperature for 2 hours and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, afforded a green solid, corresponding to **3.3a**. Yield: 78%. Anal. Calc. for $C_{18}H_{18}Fe_2N_2O_2$: C, 53.20; H, 4.47; N, 6.90. Found: C, 53.09; H, 4.44; N, 6.96%. IR (CH_2Cl_2) ν(CN) 2204 (w); ν(CO) 1933 (vs), 1777 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.60 (d, 1H, $C_\beta H$, $^{3}J_{HH}$ = 8.0 Hz); 4.49 (s, 5H, Cp); 4.32 (s, 5H, Cp); 3.62 (s, 6H, NMe_2); –0.92 (d, 1H, $C_\gamma H$, $^{3}J_{HH}$ = 8.0 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 269.3 (μ-CO); 213.0 (CO); 203.9 (C_α); 126.3 (C≡N); 89.4 (Cp); 86.5 (Cp); 59.8 (C_β); 46.5 (NMe_2); 21.5 (C_γ).

Compounds **3.3b-i** were prepared with the same procedure described for **3.3a**, by reacting **2a-d** with NaH, Me_3NO and the appropriate olefin.

3.3b (yield: 38%). Anal. Calc. for $C_{25}H_{24}Fe_2N_2O_2$: C, 60.48; H, 4.88; N, 5.65. Found: C, 60.40; H, 4.92; N, 5.67 %. IR (CH_2Cl_2) ν(CN) 2204 (w), ν(CO) 1958 (vs), 1932 (vs), 1791 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.34-6.86 (m, 3H, $C_6H_3Me_2$); 4.71, *4.65* (s, 5H, Cp); 4.67, *4.17* (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); *4.44*, 4.41 (s, 5H, Cp); *3.83*, 3.55 (s, 3H, NMe); 2.63, *2.61* (s, 3H, C_6H_3Me); *2.23*, 2.19 (s, 3H, C_6H_3Me); *–0.80*, –0.92 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). *Trans*/*cis* ratio 2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ *265.4*, 265.0 (μ-CO); *213.1*, 213.0 (CO); *205.9*, 203.8 (C_α); 148.4, *148.3* ($C_{ipso\ Xyl}$); *129.0*, 126.5 (C≡N); 134.0-128.6 (C_{arom}); *88.2*, 87.7, 85.2, *84.9* (Cp); *59.0*, 58.3 (C_β); *48.3*, 46.1 (NMe); *20.2*, 19.3 (C_γ); *18.4*, 17.9 ($Me_2C_6H_3$); *17.5*, 17.2 ($Me_2C_6H_3$).

3.3c (yield: 75%). Anal. Calc. for $C_{24}H_{22}Fe_2N_2O_3$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.75; H, 4.52; N, 5.67%. IR (CH_2Cl_2) ν(CN) 2203 (w), ν(CO) 1935 (vs), 1779 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.36-6.78 (m, 4H, C_6H_4OMe); 4.68 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.49 (s, 5H, Cp); 4.43 (s, 5H, Cp); 3.85 (s, 3H, NMe); 3.75 (s, 3H, C_6H_4OMe); –0.92 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.0 (CO); 205.0 (C_α); 150.0, 128.5, 128.0, 115.0, 114.1 (C_{arom}); 126.0 (C≡N); 88.0, 85.8 (Cp); 59.6 (C_β); 56.1 (C_6H_4OMe); 46.6 (NMe); 21.5 (C_γ).

3.3d (yield: 80%). Anal. Calc. for $C_{19}H_{21}Fe_2NO_4$: C, 51.93; H, 4.82; N, 3.19. Found: C, 51.87; H, 4.75; N, 3.28%. IR (CH_2Cl_2) ν(CO) 1933 (vs), 1777 (s), 1693 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.97 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.34 (br s, 10H, Cp); 3.64 (s, 9H, NMe_2 + CO_2Me); –0.29 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 261.5 (μ-CO); 213.7 (CO); 204.6 (C_α); 175.9 (CO_2Me); 87.6, 84.2 (Cp); 60.2 (C_β); 51.3 (CO_2Me); 46.7 (NMe_2); 43.1 (C_γ).

3.3e (yield: 78%). Anal. Calc. for $C_{25}H_{25}Fe_2NO_5$: C, 56.49; H, 4.74; N, 2.64. Found: C, 56.59; H, 4.75; N, 2.56%. IR (CH_2Cl_2) ν(CO) 1930 (vs), 1773 (s), 1694 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.41-6.82 (m, 4H, C_6H_4OMe); 5.02 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.46 (s, 5H, Cp); 4.37 (s, 5H, Cp); 3.88 (s, 6H, NMe + C_6H_4OMe); 3.57 (s, 3H, CO_2Me); –0.32 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.1 (μ-CO); 212.9 (CO); 204.1 (C_α); 176.0 (CO_2Me); 150.0, 128.5, 128.0, 115.0, 114.1 (C_{arom}); 89.1 (Cp); 87.7, 68.5 (C_β); 56.1 (C_6H_4OMe); 51.4 (CO_2Me); 46.5 (NMe); 43.3 (C_γ).

3.3f (yield: 56%). Anal. Calc. for $C_{23}H_{23}Fe_2NO_2$: C, 60.39; H, 5.07; N, 3.06. Found: C, 60.46; H, 5.00; N, 3.05%. IR (CH_2Cl_2) ν(CO) 1958 (vs), 1938 (vs), 1767 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.43-6.95 (m, 5H, C_6H_5); 4.85, *4.45* (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.74, *4.70* (s, 5H, Cp); *4.66*, 4.64 (s, 5H, Cp); *3.95*, 3.65 (s, 6H, NMe_2); -0.87,-*1.13* (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). *Trans*/*cis* ratio 1.5:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) 265.0, *264.1* (μ-CO); 213.0, *212.2* (CO); 206.0, *204.0* (C_α); 131.5-125.2 (C_{arom}); *90.1*, 89.6, 87.0, *86.6* (Cp); *60.1*, 58.3 (C_β); *52.6*, 51.4 (NMe_2); *21.7*, 21.0 (C_γ).

3.3g (yield: 74%). Anal. Calc. for $C_{23}H_{27}Fe_2NO_6$: C, 52.57; H, 5.18; N, 2.67. Found: C, 52.49; H, 5.24; N, 2.65%. IR (CH_2Cl_2) ν(CO) 1939 (vs), 1780 (s), 1716 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.90 (s, 5H, Cp); 4.83 (s, 5H, Cp); 4.30-3.60 (m, 4H, $CO_2CH_2CH_3$); 3.70 (s, 6H, NMe_2); 1.50-1.08 (m, 6H, $CO_2CH_2CH_3$); –0.56 (s, 1H, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.0 (CO); 199.3 (C_α); 170.4 ($CO_2CH_2CH_3$); 90.1, 88.0 (Cp); 68.5 (C_β); 59.9, 58.0 ($CO_2CH_2CH_3$); 46.4 (NMe_2); 33.8 (C_γ); 14.5, 14.1 ($CO_2CH_2CH_3$).

3.3h (yield: 41%). Anal. Calc. for $C_{24}H_{22}N_2O_2Ru_2$: C, 50.18; H, 3.86; N, 4.88. Found: C, 50.08; H, 3.91; N, 4.83%. IR (CH_2Cl_2) ν(CN) 2202 (w), ν(CO) 1960, (vs), 1931 (vs), 1762 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.49-7.18 (m, 5H, $CH_2C_6H_5$); 5.23, *5.11* (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.98, *4.89* (s, 5H, Cp); *4.75*, 4.66 (s, 5H, Cp); 3.73-3.55 (m, 2H, $CH_2C_6H_5$); 3.75, *3.69* (s, 3H, NMe); *1.32*, 1.19 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). *Trans*/*cis* ratio 1.2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 246.0, *245.8* (μ-CO); 206.1, *205.5* (CO); *170.1*, 168.9 (C_α); 140.5-127.0 (C_{arom} + C≡N); 96.0, *94.7* (C_γ); 88.8, *88.2 85.6*, 84.1 (Cp); 68.1, *67.5* (C_β); *61.2*, 61.0 ($CH_2C_6H_5$); 48.3, *47.1* (NMe).

3.3i (yield: 36%). Anal. Calc. for $C_{25}H_{25}NO_4Ru_2$: C, 49.42; H, 4.15; N, 2.31. Found: C, 49.51; H, 4.66; N, 2.33%. IR (CH_2Cl_2) ν(CO) 1932 (vs), 1765 (s), 1695 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 7.55-7.11 (m, 5H, $CH_2C_6H_5$); 5.23, *5.02* (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.91, *4.82* (s, (s, 5H, Cp); *4.65*, 4.59 (s, 5H, Cp); 3.99-3.49 (m, 2H, $CH_2C_6H_5$); 3.77, *3.72* (s, 3H, NMe); 3.67, *3.59* (s, 3H, CO_2Me); *1.74*, 1.39 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). *Trans*/*cis* ratio 1.3:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 246.2, *245.8* (μ-CO); 206.6, *205.8* (CO); 177.5, *175.9* (CO_2Me); 170.9, *169.5* (C_α); 140.5-127.0 (C_{arom}); *88.6*, 88.0, 84.9, *84.1* (Cp); 68.8, *67.3* (C_β); 61.4, *60.9* ($CH_2C_6H_5$); 47.6, *46.5* (NMe).

Synthesis of [M_2{μ-CN(Me)(R)}(μ-CO)(CO)(NC-CH=CH_2)(Cp)$_2$][SO_3CF_3] (M = Fe, R = Me, ***4.3a****; M = Fe, R = Xyl,* ***4.3b****; M = Fe, R = 4-C_6H_4OMe,* ***4.3c****; M = Ru, R = $CH_2C_6H_5$,* ***4.3d****).*

To a solution of **2a** (531 mg, 1.0 mmol) in THF (20 mL) were successively added acrylonitrile (0.4 mL, 10 mmol) and Me_3NO (110 mg, 1.5 mmol). The mixture was stirred at room temperature for 15 min, and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with methanol as eluent, afforded a brown solid, corresponding to **4.3a**. Yield: 94%. Anal. Calc. for $C_{19}H_{19}F_3Fe_2N_2O_5S$: C, 41.01; H, 3.44; N, 5.04. Found: C, 40.96; H, 3.47; N, 5.05%. IR (CH_2Cl_2) ν(CO) 1983 (vs), 1814 (s), ν(CN) 1585 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.78 (d, 1H, $^3J_{HH}$ = 12.0 Hz, NCCH=CH_2); 5.68 (d, 1H, $^3J_{HH}$ = 16.0 Hz, NCCH=CH_2); 5.42 (dd, 1H, NCCH=CH_2); 4.90 (s, 5H, Cp); 4.78 (s, 5H, Cp); 4.46 (s, 3H, NMe); 4.16 (s, 3H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 331.0 (μ-CN); 265.8 (μ-CO); 211.0 (CO); 140.1 (NCCH=CH$_2$); 129.3 (NCCH=CH_2); 106.5 (NCCH=CH_2); 88.7, 87.3 (Cp); 54.0, 53.3 (NMe).

Compounds **4.3b-d** were prepared with the same procedure described for **4.3a**, by reacting **2b-d** with acrylonitrile and Me_3NO.

4.3b (yield: 95%). Anal. Calc. for $C_{26}H_{25}F_3Fe_2N_2O_5S$: C, 48.30; H, 3.90; N, 4.34. Found: C, 48.26; H, 3.91; N, 4.35%. IR (CH_2Cl_2) ν(CO) 1985 (vs), 1815 (s), ν(CN) 1521 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.37-7.23 (m, 3H, $C_6H_3Me_2$); 5.97-5.86 (m, 2H, NCCH=CH_2); 5.78-5.69 (m, 1H, NCCH=CH_2); 5.10, *5.03* (s, 5H, Cp); 4.85, *4.80* (s, 3H, NMe); 4.50, *4.43* (s, 5H, Cp); 2.69, *2.65* (s, 3H, C_6H_3*Me*); 2.14, *2.08* (s, 3H, C_6H_3*Me*). *E:Z* ratio 1.3:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 338.8, *338.6* (μ-CN); 264.5, *263.8* (μ-CO); 211.6, *211.4* (CO); 148.4, *148.3* ($C_{ipso\ Xyl}$); 140.3, *140.1* (NCCH=CH$_2$); 134.3-128.5 (C_{arom}); 129.4, *129.3* (NCCH=CH_2); 107.3, *107.1* (NCCH=CH_2); 88.6, *88.5* (Cp); 88.4, *88.3* (Cp); 54.6, *54.4* (NMe); 18.5, *18.2*, 17.6, *17.3* ($Me_2C_6H_3$).

4.3c (yield: 92%). Anal. Calc. for $C_{25}H_{23}F_3Fe_2N_2O_6S$: C, 46.30; H, 3.58; N, 4.32. Found: C, 46.33; H, 3.64; N, 4.35%. IR (CH_2Cl_2) ν(CO) 1985 (vs), 1817 (s), ν (CN) 1527 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.61-7.16 (m, 4H, C_6H_4OMe); 5.94-5.80 (m, 2H, NCCH=CH_2); 5.60 (m, 1H, NCCH=CH_2); 5.08, *4.99* (s, 5H, Cp); 4.46, *4.35* (s, 5H, Cp); 4.87, *4.79* (s, 3H, NMe); 3.90, *3.86* (s, 3H, OMe). *E:Z* ratio 1.2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 336.4, *336.2* (μ-CN); 265.1, *264.8* (μ-CO); 211.7, *211.0* (CO); 159.7, *159.3*, 144.2, *143.6*, 126.5, *125.9*, 115.0, *114.6* (C_{arom}); 140.5, *140.2* (NCCH=CH$_2$); 129.2, *129.1* (NCCH=CH_2); 107.0, *106.7* (NCCH=CH_2); 88.6, *88.3* (Cp); 87.9, *87.5* (Cp); 56.5, *56.0* (NMe); 55.6, *55.4* (OMe).

4.3d (yield: 90%). Anal. Calc. for $C_{25}H_{23}F_3N_2O_5Ru_2S$: C, 41.44; H, 3.20; N, 3.87. Found: C, 41.50; H, 3.20; N, 3.83%. IR (CH_2Cl_2) ν(CO) 1980 (vs), 1817 (s), ν (CN) 1574 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.49-7.30 (m, 5H, $CH_2C_6H_5$); 6.01-5.94 (m, 2H, NCCH=CH_2); 5.80-5.53 (m, 3H, C$H_2C_6H_5$ + NCCH=CH_2); 5.28, *5.25* (s, 5H, Cp); 4.98, *4.90* (s, 5H, Cp); 3.88, *3.83* (s, 3H, NMe). *E:Z* ratio 1.5:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 305.0, *304.7* (μ-CN); 238.1, *237.5* (μ-CO); 201.1, *200.3* (CO); 140.5-106.9 (C_{arom} + $C_{acrylonitrile}$); 89.8, 87.9 (Cp); 51.0, *49.9* (NMe).

Synthesis of [$Fe_2\{\mu$-η^1:η^3-$C_\alpha(N(Me)_3)C_\beta(H)C_\gamma(H)(R)\}(\mu$-CO)(CO)$(Cp)_2$][$SO_3CF_3$] (R = CN, ***5.3a****; R = CO_2Me,* ***5.3b****; R = C_6H_5,* ***5.3c****).*

$CH_3SO_3CF_3$ (0.13 mL, 1.1 mmol) was added to a solution of **3.3a** (406 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) and the resulting solution was stirred at room temperature for 4 hours. Removal of the volatile material under reduced pressure and chromatography of the residue on an alumina column, with methanol as eluent, afforded a dark brown solid, corresponding to **5.3a**. Yield: 87%. Anal. Calc. for $C_{20}H_{21}F_3Fe_2N_2O_5S$: C, 42.11; H, 3.71; N, 4.91. Found: C, 42.02; H, 3.66; N, 4.97%. IR (CH_2Cl_2) ν(CN) 2205 (w), ν(CO) 1986 (vs), 1815 (s) cm^{-1}. ^1H NMR (CD_3CN) δ 6.07 (d, 1H, C$_\beta H$, $^3J_{HH}$ = 8.2 Hz); 5.15 (s, 5H, Cp); 4.98 (s, 5H, Cp); 3.12 (s, 9H, NMe_3); –0.77 (d, 1H, C$_\gamma H$, $^3J_{HH}$ = 8.2 Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) δ 267.0 (μ-CO); 213.5 (CO); 180.1 (C_α); 126.5 (CN); 87.3, 85.2 (Cp); 75.0 (C_β); 58.8 (NMe_3); 38.7 (C_γ).

Compounds **5.3b-c** were prepared with the same procedure described for **5.3a**, by treating **3.3d** and **3.3f** with $CH_3SO_3CF_3$ in CH_2Cl_2 solution.

5.3b (yield: 86%). Anal. Calc. for $C_{21}H_{24}F_3Fe_2NO_7S$: C, 41.79; H, 4.01; N, 2.32. Found: C, 41.79; H, 3.96; N, 2.30%. IR (CH_2Cl_2) ν(CO) 1988 (vs), 1817 (s), 1710 (m) cm^{-1}. ^1H NMR (CD_3CN) δ 6.01 (d, 1H, C$_\beta H$, $^3J_{HH}$ = 7.8 Hz); 5.36 (s, 5H, Cp); 5.23 (s, 5H, Cp); 3.62 (s, 3H, CO_2Me); 3.12 (s, 9H, NMe_3); –0.56 (d, 1H, C$_\gamma H$, $^3J_{HH}$ = 7.8 Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) δ 266.7 (μ-CO); 213.3 (CO); 181.2 (C_α); 174.4 (CO_2Me); 89.1, 87.1 (Cp); 71.4 (C_β); 55.4 (NMe_3); 52.4 (CO_2Me); 39.1 (C_γ).

5.3c (yield: 87%). Anal. Calc. for $C_{25}H_{26}F_3Fe_2NO_5S$: C, 48.31; H, 4.22; N, 2.25. Found: C, 48.40; H, 4.18; N, 2.24%. IR (CH_2Cl_2) ν(CO) 1986 (vs), 1817 (s) cm^{-1}. ^1H NMR (CD_3CN) δ 7.41-7.01 (m, 5H, C_6H_5); 5.99 (d, 1H, C$_\beta H$, $^3J_{HH}$ = 8.2 Hz); 5.48 (s, 5H, Cp); 5.33 (s, 5H, Cp); 3.10 (s, 9H, NMe_3);

–0.74 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.2 Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) δ 266.5 (μ-CO); 213.0 (CO); 179.7 (C_α); 132.0-125.0 (C_{arom}); 89.9 (Cp); 86.0 (Cp); 73.4 (C_β); 56.7 (NMe_3); 35.4 (C_γ).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(H)(Me)_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, ***6.3a****; R = CO_2Me,* ***6.3b****; R = C_6H_5,* ***6.3c****).*

A solution of **3.3a** (406 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) was treated with HSO_3CF_3 (0.10 mL, 1.1 mmol). The resulting solution was stirred at room temperature for 1 hour. Removal of the volatile material under reduced pressure and filtration of the residue on a celite pad afforded a dark brown solid, corresponding to **6.3a**. Yield: 90%. Anal. Calc. for $C_{19}H_{19}F_3Fe_2N_2O_5S$: C, 41.01; H, 3.44; N, 5.04. Found: C, 40.90; H, 3.50; N, 4.97%. IR (CH_2Cl_2) ν(CN) 2206 (w), ν (CO) 1987 (vs), 1814 (s) cm^{-1}. ^1H NMR (CD_3CN) δ 6.04 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 5.22 (s, 5H, Cp); 4.85 (s, 5H, Cp); 3.49 (s, 6H, NMe_2); -1.36 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). *NH not observed*. $^{13}C\{^1H\}$ NMR (CD_3CN) δ 267.0 (μ-CO); 213.5 (CO); 182.4 (C_α); 125.9 (CN); 88.9, 85.9 (Cp); 78.3 (C_β); 52.3 (NMe_2); 33.4 (C_γ).

Compounds **6.3b-c** were prepared with the same procedure described for **6.3a**, by treating **3.3d** and **3.3f** with HSO_3CF_3 in CH_2Cl_2 solution.

6.3b (yield: 88%). Anal. Calc. for $C_{20}H_{22}F_3Fe_2NO_7S$: C, 40.75; H, 3.76; N, 2.38. Found: C, 40.79; H, 3.86; N, 2.30%. IR (CH_2Cl_2) ν(CO) 1988 (vs), 1816 (s), 1712 (m) cm^{-1}. ^1H NMR (CD_3CN) δ 5.91 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 5.41 (s, 5H, Cp); 5.05 (s, 5H, Cp); 3.75 (s, 3H, CO_2Me); 3.43 (s, 6H, NMe_2); –0.61 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). *NH not observed*. $^{13}C\{^1H\}$ NMR (CD_3CN) δ 266.5 (μ-CO); 213.1 (CO); 183.7 (C_α); 175.0 (CO_2Me); 89.2, 85.8 (Cp); 79.0 (C_β); 51.7 (NMe_2); 51.2 (CO_2Me); 43.5 (C_γ).

6.3c (yield: 87%). Anal. Calc. for $C_{24}H_{24}F_3Fe_2NO_5S$: C, 47.45; H, 3.98; N, 2.31. Found: C, 47.40; H, 4.07; N, 2.24%. IR (CH_2Cl_2) ν(CO) 1987 (vs), 1815 (s) cm^{-1}. ^1H NMR (CD_3CN) δ 7.37-7.03 (m, 5H, C_6H_5); 5.88 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.2 Hz); 5.51 (s, 5H, Cp); 5.28 (s, 5H, Cp); 3.40 (s, 6H, NMe_2); –0.70 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.2 Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) δ 267.1 (μ-CO); 213.5 (CO); 178.9 (C_α); 132.0-125.0 (C_{arom}); 90.1, 87.3 (Cp); 78.4 (C_β); 52.0 (NMe_2); 35.1 (C_γ).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CNFe(CO)_2Cp)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ *(**9.3**).*

A solution of **3.3a** (406 mg, 1.0 mmol) in THF (20 mL) was treated with $[Fe(CO)_2(THF)(Cp)][SO_3CF_3]$, freshly prepared by treatment of $[Fe_2(CO)_4(Cp)_2]$ (213 mg, 0.6 mmol) with $AgSO_3CF_3$ (180 mg, 0.7 mmol). The mixture was stirred at room temperature for 1 hour and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with methanol as eluent, afforded a green-brown solid, corresponding to **9.3**. Yield: 76%. Anal. Calc. for $C_{26}H_{23}F_3Fe_3N_2O_7S$: C, 42.63; H, 3.17; N, 3.83. Found: C, 42.71; H, 3.13; N, 3.70%. IR (CH_2Cl_2) ν(CO) 2079 (vs), 2035 (vs), 1939 (vs), 1780 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.35 (s, 5H, Cp); 4.56 (s, 5H, Cp); 4.34 (s, 5H, Cp); 4.18 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 3.64 (s, 6H, NMe_2); −1.14 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.8 (μ-CO); 211.9, 210.5, 209.8 (CO); 204.2 (C_α); 125.0 (C≡N); 90.9, 87.9, 85.8 (Cp); 52.0 (C_β); 46.0 (NMe_2); 19.1 (C_γ).

Synthesis of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)([Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)_2)C_\beta(H)C_\gamma(H)(CN)\}(\mu\text{-}CO)(CO)(Cp)_2])(Cp)_2][SO_3CF_3]$ *(R = Me, **10.3a**; R = Xyl, **10.3b**; R = 4-*C_6H_4OMe*, **10.3c**).*

To a solution of **2a** (531 mg, 1.0 mmol) in THF (20 mL) were successively added **3.3a** (406 mg, 1.0 mmol) and Me_3NO (110 mg, 1.5 mmol). The mixture was stirred at room temperature for 1 hour and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with methanol as eluent, afforded a brown solid, corresponding to **10.3a**. Yield: 70%. Anal. Calc. for $C_{34}H_{34}F_3Fe_4N_3O_7S$: C, 44.89; H, 3.77; N, 4.62. Found: C, 45.00; H, 3.73; N, 4.60%. IR (CH_2Cl_2) ν(CO) 1981 (vs), 1940 (vs), 1812 (s), 1785 (s), ν(CN) 1586 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.31 (s, 5H, Cp); 5.02 (s, 5H, Cp); 4.51 (s, 5H, Cp); 4.32 (s, 5H, Cp); 4.25 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.67 (s, 3H, NMe); 4.32 (s, 3H, NMe); 3.52 (s, 6H, NMe_2); −1.35 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 331.2 (μ-CN); 266.4 (μ-CO); 265.7 (μ-CO); 213.0 (CO); 211.5 (CO); 203.1 (C_α); 125.3 (C≡N); 90.1 (Cp); 88.9 (Cp); 87.3 (Cp); 86.1 (Cp); 54.0 (NMe); 53.3 (NMe); 53.1 (C_β); 46.5 (NMe_2); 19.6 (C_γ).

Compounds **10.3b-c** were prepared with the same procedure described for **10.3a**, by reacting **2b-c** with **3.3a** and Me_3NO.

10.3b (yield: 66%). Anal. Calc. for $C_{41}H_{40}F_3Fe_4N_3O_7S$: C, 49.25; H, 4.04; N, 4.21. Found: C, 49.30; H, 4.13; N, 4.30%. IR (CH_2Cl_2) ν(CO) 1985 (vs), 1938 (vs), 1819 (s), 1788 (s), ν (CN) 1525 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.40-7.03 (m, 3H, $Me_2C_6H_3$); 5.15 (s, 5H, Cp); 4.89 (s, 5H, Cp); 4.51 (s, 5H, Cp); 4.34 (s, 5H, Cp); 4.27 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.80 (s, 3H, NMe); 3.52 (s, 6H, NMe_2); 2.70 (s, 3H, $Me_2C_6H_3$); 2.20 (s, 3H, $Me_2C_6H_3$); −1.32 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 338.6 (μ-CN); 265.9, 265.0 (μ-CO); 213.0, 212.1 (CO); 203.6 (C_α); 148.0-125.1 (C_{arom} + C≡N); 89.2, 88.7, 87.0, 86.5 (Cp); 54.5 (NMe); 52.8 (C_β); 46.5 (NMe_2); 20.7-18.5 (C_γ + $Me_2C_6H_3$).

10c (yield: 73%). Anal. Calc. for $C_{40}H_{38}F_3Fe_4N_3O_8S$: C, 47.95; H, 3.83; N, 4.20. Found: C, 48.03; H, 3.77; N, 4.24%. IR (CH_2Cl_2) ν(CO) 1983 (vs), 1940 (vs), 1819 (s), 1786 (s), ν(CN) 1530 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.60-7.10 (m, 4H, C_6H_4OMe); 5.08 (s, 5H, Cp); 4.86 (s, 5H, Cp); 4.50 (s, 5H, Cp); 4.37 (s, 5H, Cp); 4.30 (d, 1H, $C_\beta H$, $^3J_{HH}$ = 8.0 Hz); 4.79 (s, 3H, NMe); 3.90 (s, 3H, C_6H_4OMe); 3.52 (s, 6H, NMe_2); −1.30 (d, 1H, $C_\gamma H$, $^3J_{HH}$ = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 336.5 (μ-CN); 265.9, 265.0 (μ-CO); 213.0, 210.9 (CO); 203.5 (C_α); 159.5-115.0 (C_{arom} + C≡N); 89.5, 88.9, 87.4, 87.0 (Cp); 56.5 (NMe); 55.1 (C_6H_4OMe); 53.0 (C_β); 46.5 (NMe_2); 20.1 (C_γ).

X-ray Crystallography for 3.3a and 3.3b

Crystals of **3.3a** and **3.3b** suitable for X ray analysis were obtained by a CH_2Cl_2 solution, layered with petroleum ether, at –20°C.

Crystal data for **3.3a** and **3.3b** were collected at room temperature on a Bruker APEX II CCD diffractometer using graphite monochromated Mo-Kα radiation. Structures were solved by direct methods and structures refined by full-matrix least-squares based on all data using F^2[12]. Crystal data are listed in Table 3.3. Non-H atoms were refined anisotropically. H-atoms were placed in calculated positions, except position of H(14) and H(15) in both **3.3a** and **3.3b** which were located in the Fourier map. H-atoms were treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom.

Table 3.3

*Crystal data and experimental details for **3.3a** and **3.3b***

Complex	**3.3a**	**3.3b**
Empirical formula	$C_{18}H_{18}Fe_2N_2O_2$	$C_{25}H_{24}Fe_2N_2O_2$
F*w*	406.04	496.16
T, K	293(2)	295(2)
λ, Å	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a, Å	7.4182(5)	8.0777(5)
b, Å	14.3307(9)	15.2350(10)
c, Å	15.8838(10)	18.0168(11)
β, °	90	101.5300(10)
Cell volume, Å^3	1688.58(19)	2172.5(2)
Z	4	4
D_c, g cm^{-3}	1.597	1.517
μ, mm^{-1}	1.730	1.360
F(000)	832	1024
Crystal size, mm	0.22×0.16×0.13	0.23×0.16×0.14
θ limits, °	1.91-28.69	1.77-27.00
Reflections collected	19654	23749
Independent reflections	4116 [R_{int} = 0.0417]	4728 [R_{int} = 0.0462]
Data/restraints/parameters	4116/ 2 / 225	4728 / 2 / 289
Goodness on fit on F^2	1.051	1.018
R_1 ($I > 2\sigma(I)$)	0.0322	0.0342
wR_2 (all data)	0.0675	0.0851
Largest diff. peak and hole, e.Å^{-3}	0.417 / -0.290	0.420 / -0.230

References

[1] V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, Organometallics 23 (2004) 3348.

[2] (a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 689 (2004) 528;
(b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 690 (2005) 837;
(c) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Inorg. Chim. Acta 358 (2005) 1204.

[3] (a) A. F. Dyke, J. E. Guerchais, S. A. R. Knox, J. Roue, R. L. Short, G. E. Taylor, P. Woodward, J. Chem. Soc., Chem. Commun. (1981) 537;
(b) J. Hein, J. C. Jeffery, F. Marken, F. G. A. Stone, Polyhedron 6 (1987) 2067;
(c) C. P. Casey, P. J. Fagan, J. Am. Chem. Soc. 104 (1982) 4950;
(d) C. P. Casey, M. W. Meszaros, S. R. Marder, P. J. Fagan, J. Am. Chem. Soc. 106 (1984) 3680;
(e) C. P. Casey, M. W. Meszaros, P. J. Fagan, R. K. Bly, S. R. Marder, E. A. Austin, J. Am. Chem. Soc. 108 (1986) 4043;
(f) C. P. Casey, M. W. Meszaros, P. J. Fagan, R. K. Bly, R. E. Colborn, J. Am. Chem. Soc. 108 (1986) 4053;
(g) C. P. Casey, M. W. Meszaros, S. R. Marder, R. K. Bly, P. J. Fagan, Organometallics 5 (1986) 1873.

[4] (a) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, E. Zoli, J. Organomet. Chem. 690 (2005) 1959;
(b) V. G. Albano, L. Busetto, M. Monari, V. Zanotti, J. Organomet. Chem. 606 (2000) 163.

[5] (a) K. Boss, C. Dowling, A. R. Manning, J. Organomet. Chem. 509 (1996) 197;
(b) K. Boss, M. G. Cox, C. Dowling, A. R. Manning, J. Organomet. Chem. 612 (2000) 18.

[6] V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 690 (2005) 4666.

[7] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, Magn. Reson. Chem. 31 (1993) 287.

[8] K. Stott, J. Stonehouse, J. Keeler, T. L. Hwang, A. J. Shaka, J. Am. Chem. Soc. 117 (1995) 4199.

[9] G. Cox, C. Dowling, A. R. Manning, P. McArdle, D. Cunningham, J. Organomet. Chem. 438 (1992) 143.

[10] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Organometallics 25 (2006) 4808.

[11] V. G. Albano, L. Busetto, C. Camiletti, M. Monari, V. Zanotti, J. Organomet. Chem. 563 (1998) 153.

[12] G. M. Sheldrick, SHELX97, Program for crystal structure determination, University of Göttingen, Germany, 1997.

CHAPTER IV

COUPLING OF ALLENES WITH μ-ALKYLIDYNE LIGANDS IN DIIRON COMPLEXES: SYNTHESIS OF NOVEL BRIDGING THIO- AND AMINOBUTADIENYLIDENE COMPLEXES

Abstract

The diiron aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Xyl, **2a**; R = 4-C_6H_4OMe, **2b**; R = Me, **2c**; Xyl = 2,6-$Me_2C_6H_3$) react with allenes of the type $CH_2=C=CR'R''$, in the presence of Me_3NO/Et_3N, to give the novel butadienylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha N(R)(Me)C_\beta(H)C_\gamma C_\delta(R')(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Xyl, R' = R'' = Me, **3.4a**; R = Xyl, R' = Me, R'' = H, **3.4b**; R = Xyl, R' = CO_2Et, R'' = H, **3.4c**; R = 4-C_6H_4OMe, R' = CO_2Et, R'' = H, **3.4d**; R = R' = R'' = Me, **3.4e**; R = Me, R' = CO_2Et, R'' = H, **3.4f**), in high yields.

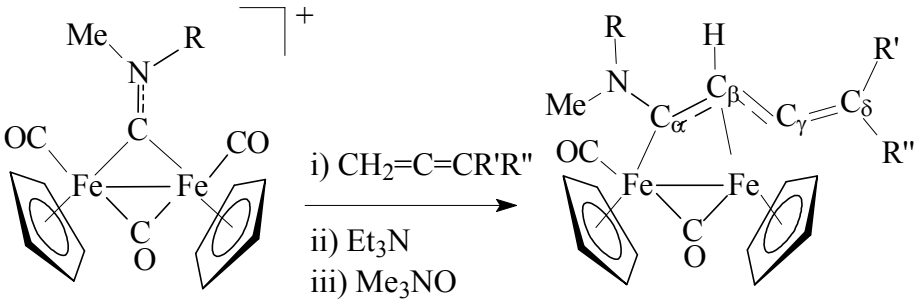
Analogously, the diiron thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$, (**1**) reacts with $CH_2=C=CR'R''$, in the presence of Me_3NO/Et_3N, affording the compounds $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha S(Me)C_\beta(H)C_\gamma C_\delta(R')(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R' = R'' = Me, **4.4a**; R' = CO_2Et, R'' = H, **4.4b**; R' = $SiMe_3$, R'' = Me, **4.4c**). Complexes **3.4**-**4.4** exist in solution as mixtures of *cis* and *trans* isomers.

Compounds **3.4a** and **3.4e**, upon treatment with HSO_3CF_3, are transformed into the corresponding vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(C_\delta HMe_2)C_\beta HC_\alpha N(R)(Me)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, **5.4a**; R = Me, **5.4b**], in nearly quantitative yields. Conversely, compounds **4.4a-b** undergo methylation (by $CH_3SO_3CF_3$) at the sulfur, giving the cationic complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma C_\delta(R')(R'')\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R' = Me, R'' = Me, **7.4a**; R' = CO_2Et, R'' = H, **7.4b**]. Protonation of **3.4a** is not reversible: treating **5.4a** with sodium hydride results in formation of the 1-metalla-2-amino-cyclopenta-1,3-dien-5-one species $[Fe(Cp)(CO)\{CN(Me)(Xyl)CHC(CHMe_2)C(O)\}]$ (**6.4**).

The molecular structures of *cis*-**3.4a,** *cis*-**4.4b**, **5.4a[CF_3SO_3]·CH_2Cl_2** and **7.4a[CF_3SO_3]·0.5CH_2Cl_2** have been determined by X-ray diffraction studies.

Results and discussion

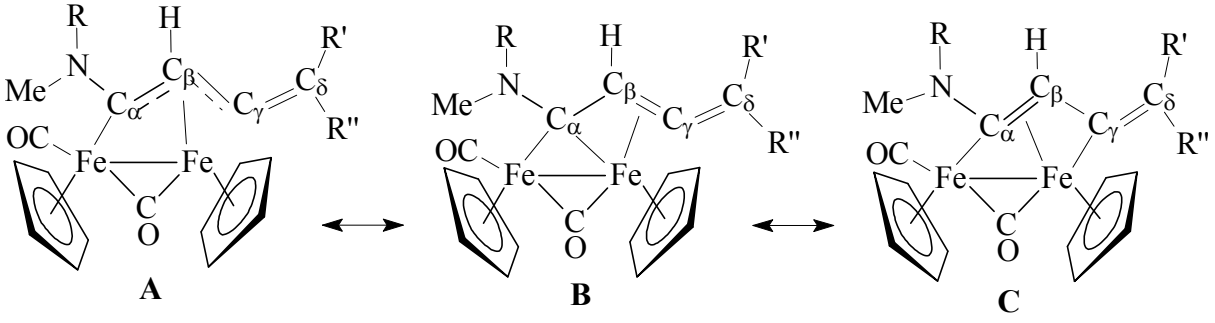
The diiron aminocarbyne complexes **2a-c** react, in THF solution, with allenes, in the presence of Me_3NO and Et_3N, affording the complexes **3.4a-f** in 70-80% yields (Scheme 4.1).



	R	R'	R''	
2a	Xyl	Me	Me	**3.4a**
2a	Xyl	Me	H	**3.4b**
2a	Xyl	CO_2Et	H	**3.4c**
2b	4-C_6H_4OMe	CO_2Et	H	**3.4d**
2c	Me	Me	Me	**3.4e**
2c	Me	CO_2Et	H	**3.4f**

Scheme 4.1

Compounds **3.4a-f** have been purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the X-ray structure of *cis*-**3.4a** has been determined (Figure 4.1 and Table 4.1). The molecule is composed by a *cis*-[$Fe_2(\mu$-$CO)(CO)(Cp)_2$] core to which is coordinated an allenylidene {μ-η^1:η^3-$C_\alpha N(Xyl)(Me)C_\beta(H)C_\gamma C_\delta(Me)_2$} ligand. The latter can be described by using three different resonance forms (Scheme 4.2).



Scheme 4.2

The fact that all three C(13), C(14) and C(15) carbon atoms (corresponding to C_α, C_β and C_γ, respectively) are coordinated to Fe(1) [Fe(1)-C(13) 2.0648(17) Å; Fe(1)-C(14) 2.0452(17) Å; Fe(1)-C(15) 1.9647(17) Å] with relatively similar bond distances and both C(13)-C(14) [1.431(2) Å] and C(14)-C(15) [1.407(2) Å] display some π-character is in agreement with the allyl like coordination displayed in (**A**). At the same time, Fe(1)-C(15) [1.9647(17) Å] is sensibly shorter than Fe(1)-C(13) [2.0648(17) Å] and Fe(1)-C(14) [2.0452(17) Å], which are almost equal, suggesting some contribution also from the 1-amino-1,3-butadienylidene form (**C**). Finally, the fact that C(14)-C(15) [1.407(2) Å] is shorter than C(13)-C(14) [1.431(2) Å] indicates that even the aminoallenyl alkylidene form (**B**) must be considered. In agreement with all the three structures **A**-**C**, the C(15)-C(16) interaction [1.317(3) Å] is an almost pure double bond, whereas C(13)-N(1) [1.395(2) Å] is quite elongated suggesting a limited π-interaction. All these considerations point to the fact that the coordination of such an unsaturated ligand to a bimetallic frame originates a highly delocalised and complex electronic structure which can not be simply described in an unequivocal way. On the other hand, this complex system of σ- and π-interactions is probably the origin of the stabilisation of the highly unsaturated organic fragments, by bridging coordination.

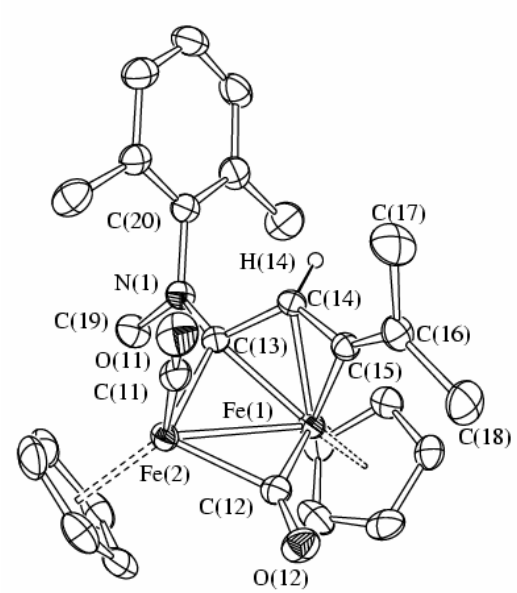


Figure 4.1 ORTEP drawing of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha N(Xyl)(Me)C_\beta(H)C_\gamma C_\delta(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (*cis*-**3.4a**) (all H-atoms, except H(14), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

Table 4.1. Selected bond lengths (Å) and angles (°) for $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha N(Xyl)(Me)C_\beta(H)C_\gamma C_\delta(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$, *cis*-**3.4a**.

Fe(1)-Fe(2)	2.5595(4)	C(11)-O(11)	1.153(2)
Fe(1)-C(12)	1.8702(18)	C(12)-O(12)	1.182(2)
Fe(2)-C(12)	1.9537(19)	C(13)-C(14)	1.431(2)
Fe(2)-C(11)	1.745(2)	C(14)-C(15)	1.407(2)
Fe(1)-C(13)	2.0648(17)	C(15)-C(16)	1.317(3)
Fe(2)-C(13)	2.0032(17)	C(13)-N(1)	1.395(2)
Fe(1)-C(14)	2.0452(17)	N(1)-C(19)	1.449(2)
Fe(1)-C(15)	1.9647(17)	N(1)-C(20)	1.440(2)
Fe(2)-C(13)-Fe(1)	77.96(6)	C(15)-C(16)-C(18)	123.21(19)
C(14)-C(13)-Fe(2)	117.16(12)	C(15)-C(16)-C(17)	120.96(19)
C(15)-C(14)-C(13)	120.66(16)	C(18)-C(16)-C(17)	115.78(19)
C(14)-C(15)-Fe(1)	72.57(10)	C(13)-N(1)-C(20)	120.82(14)
C(16)-C(15)-C(14)	141.06(18)	C(13)-N(1)-C(19)	123.88(15)
C(16)-C(15)-Fe(1)	145.96(15)	C(20)-N(1)-C(19)	115.04(15)

The spectroscopic data reveal that, in solution, **3.4a-d** consist of a mixture of *cis* and *trans* isomers, (*cis* and *trans* are referred to the mutual position of the Cp ligands with respect to the Fe-Fe bond). Similar *cis*-*trans* isomeric mixtures were previously observed in the complexes obtained by alkene-aminocarbyne coupling (Chapter III). These latter complexes were found to undergo rearrangements of the configuration of the ancillary Cp and CO ligands (*cis*-*trans* isomerization) to better respond to changes in the steric demand of the bridging organic frame.

The IR spectra of **3.4a-d** (in CH_2Cl_2 solution) display two adsorptions for the terminal CO, in agreement with presence of the two isomers (1946 and 1921 cm^{-1} for *cis*-**3.4a** and *trans*-**3.4a**, respectively), while one absorption (at *ca.* 1770 cm^{-1}) accounts for the bridging carbonyl of both isomers.

The NMR spectra show two sets of resonances. NOE investigations allow to assign the resonances to each isomer: indeed a significant NOE effect is detected between the Cp resonances in the case of the *cis*, but not for the *trans* isomer. In spite of the fact that **3.4a** exhibits a *cis* configuration in solid, the *trans* isomers generally prevail in solution and **3.4e-f** have been observed

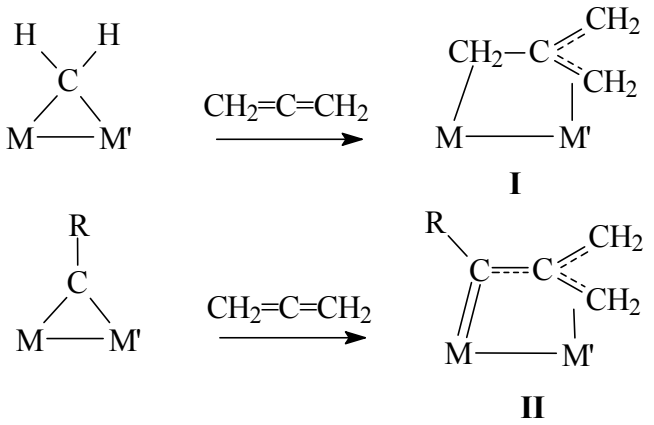
exclusively as *trans* isomers. Moreover, the composition of the isomeric mixture changes upon heating at reflux temperature in toluene, with conversion of *cis* into *trans*.

Beside *cis* and *trans* isomers, no other isomeric forms were observed. Indeed, the reactions with CH_2=C=C(H)CO_2Me should, in theory, produce two regioisomers, depending on which of the two terminal allene carbon forms the C-C bond with the μ-aminocarbyne. Conversely, the observed carbyne-allene coupling reactions are regioselective and C-C bond formation exclusively involves the CH_2 end of the allene unit.

Notably, complexes **3.4a** and **3.4e**, obtained from dimethyl allene, show distinct resonances in both ^{1}H and ^{13}C NMR spectra, for the two methyl groups bound to the terminal C_δ carbon of the bridging frame. This indicates that, at room temperature, there is no exchange between these groups and the bridging C_4 chain is tightly connected to the metal centres. By contrast, the N-methyls of **3.4e-f** give raise to a single resonance in both ^{1}H and ^{13}C NMR spectra, and their equivalence is attributable the loss of double bond character in the C_α-N interaction.

Finally, ^{13}C NMR spectra evidence the resonances due to C_γ and C_δ (δ = 158.9 and 118.6 ppm, respectively for *trans*-**3.4a**), in the range typical of olefin carbons, and the C_α resonance (δ = 203.5 ppm for *trans*-**3.4a**), which suggests a partial aminocarbene character.

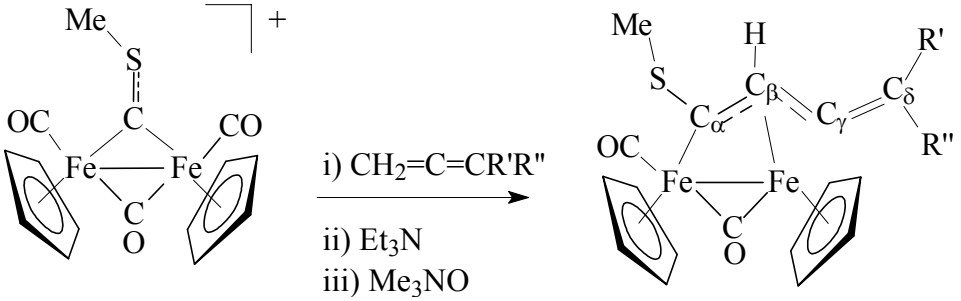
Some aspects concerning the reactions of complexes of the type **2** with allenes should be pointed out. First, the reaction outcome is different from the insertion through the secondary carbon of the allene, reported in Scheme 4.3. [1-4] By contrast, the assembly of **2** with allenes is the result of an allenyl addition at the μ-alkylidyne. Therefore it implies a deprotonation step, and the C-C bond formation involves the terminal carbon of the cumulene. It should be remarked that no reaction takes place between **2a-c**, allenes and Me_3NO in the absence of NEt_3 (or a different base like NaH). Thus, the coupling of **2** with allenes rather resembles the corresponding reaction with alkenes (Chapter III), which occurs under very similar conditions.



Scheme 4.3

A second observation is that, beside the deprotonation, a further requirement is the removal of a CO ligand in order to create a vacant coordination site. Most of the coupling reactions involving bridging ligands and olefins or alkynes, which have been mentioned in the introduction, proceed only in the presence of labile ligands (acetonitrile) or under photolytic conditions. The reason is that preliminary coordination of the unsaturated molecules to one metal centre is necessary to promote an intramolecular coupling between ligands. This might be also the case of the reaction of **2** with allenes. Removal of CO from **2**, accomplished upon treatment with Me_3NO, is presumably crucial in allowing coordination of the cumulene at one Fe atom in the very initial step of the reaction sequence. Thus, the observed assembling should be the result of an intramolecular coupling rather than of a direct nucleophilic allenyl attack at the bridging alkylidyne ligand. Theoretical studies indicate that the μ-alkylidyne - allene coupling involving the complex $[L_2W(\mu\text{-}CSiMe_3)]_2$ [4] (Scheme 4.3), proceeds through the formation of an allene adduct. [5] Likewise, the reactions of the di-iridium complexes $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)][SO_3CF_3]$ with allenes have been shown to occur by initial η^2-allene coordination, which is followed by intramolecular rearrangements. [6] In spite of these considerations, our attempts to detect and isolate possible η^2-allene intermediates have been unsuccessful. Our efforts included: i) low temperature reaction conditions (-40C°), ii) reaction of **2a** with $Me_2C{=}C{=}CMe_2$, which does not contain removable hydrogen atoms, iii) creation of the coordinative unsaturation by chloride abstraction from $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$, upon treatment of with $AgSO_3CF_3$.

Then, investigations have been extended to the thiocarbyne complex $[Fe_2\{\mu\text{-}CS(Me)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1**) in order to compare the reactivity of the thio- and amino-alkylidyne ligands and evidence a possible influence of the heteroatom (S or N). The reactions of **1** with allenes ($H_2C{=}C{=}CR'R''$), under analogous conditions to those described for the aminocarbyne complexes, result in formation of the neutral complexes **4.4a-c** (Scheme 4.4), which have been purified by chromatography on alumina, and characterized by spectroscopy. In addition, the molecular structure of *cis*-**4.4b** has been determined by X-ray diffraction (Figure 4.2 and Table 4.2).



	R'	R''	
1	Me	Me	**4.4a**
	CO_2Et	H	**4.4b**
	$SiMe_3$	Me	**4.4c**

Scheme 4.4

The molecular structure of *cis*-**4.4b** is very similar to that previously described for *cis*-**3.4a**, apart the different substituents on C(13) and C(16) (corresponding to C_α and C_δ). Also in this case, the $[Fe_2(\mu\text{-}CO)(CO)(Cp)_2]$ core possesses a *cis* geometry and the coordination of the $\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha S(Me)C_\beta(H)C_\gamma C_\delta(H)(CO_2Et)\}$ can be described by resonance forms analogous to those depicted in Scheme 4.2, even though the different nature of the substituents present on C(13) and C(16) makes their relative weights different. In particular, the C(13)-C(14) [1.369(9) Å] and C(14)-C(15) [1.381(9) Å] bond lengths are inverted compared to *cis*-**3.4a** [1.431(2) Å and 1.407(2) , respectively], more in agreement with the 1-thio-1,3-butadienylidene form (**C**), and with an allyl-like coordination (**A**). More importantly, the Fe(1)-C(15) interaction [1.906(6) Å] is considerably shorter than Fe(1)-C(13) [2.003(7) Å] and Fe(1)-C(14) [2.036(7) Å] indicating that the corresponding interactions can be more appropriately described as nearly σ for Fe(1)-C(15), whereas the C(13) C(14) are π-bonded in an olefinic fashion to Fe(1). Therefore, the bonding structure of *cis*-**4.4b** can be very well described by the 1-thio-1,3-butadienylidene form (**C**). It is very difficult to say whether the slightly different bonding situation in *cis*-**3.4a** and *cis*-**4.4b** is due to substitution at C(13) (amino *vs.* thio), or by the different groups present on C(16) (electron donating in *cis*-**3.4a** *vs.* electron withdrawing in *cis*-**4.4b**), or to both of them. Nonetheless, it is possible to conclude that the coordination of these unsaturated C_4 carbon chains to the $[Fe_2(\mu\text{-}CO)(CO)(Cp)_2]$ core is very flexible and sensible to minor variations in the electronic properties even of groups not directly coordinated to the metal framework.

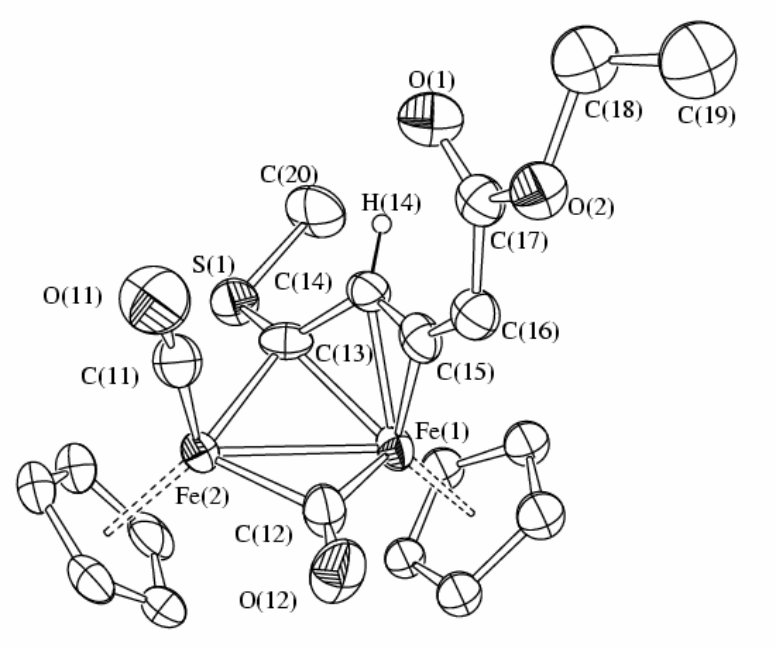


Figure 4.2 ORTEP drawing of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha S(Me)C_\beta(H)C_\gamma C_\delta(H)(CO_2Et)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (*cis*-**4.4b**) (all H-atoms, except H(14), have been omitted for clarity). Only the main images of the disordered Cp ligand bonded to Fe(2) and the OEt group bonded to C(17) are drawn. Thermal ellipsoids are at the 30% probability level.

Table 4.2. Selected bond lengths (Å) and angles (°) for $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha S(Me)C_\beta(H)C_\gamma C_\delta(H)(CO_2Et)\}(\mu\text{-}CO)(CO)(Cp)_2]$, *cis*-**4.4b**.

Fe(1)-Fe(2)	2.5221(10)	C(11)-O(11)	1.133(9)
Fe(1)-C(12)	1.872(7)	C(12)-O(12)	1.174(8)
Fe(2)-C(12)	1.950(7)	C(13)-C(14)	1.369(9)
Fe(2)-C(11)	1.753(8)	C(14)-C(15)	1.381(9)
Fe(1)-C(13)	2.003(7)	C(15)-C(16)	1.360(9)
Fe(2)-C(13)	2.002(7)	C(13)-S(1)	1.771(6)
Fe(1)-C(14)	2.036(7)	S(1)-C(20)	1.788(8)
Fe(1)-C(15)	1.906(6)	C(16)-C(17)	1.409(10)
O(1)-C(17)	1.217(8)	C(17)-O(2)	1.365(10)
Fe(2)-C(13)-Fe(1)	78.0(2)	C(15)-C(16)-C(17)	121.7(7)
C(14)-C(13)-Fe(2)	121.5(5)	O(1)-C(17)-O(2)	121.0(7)

C(15)-C(14)-C(13)	119.4(6)	O(1)-C(17)-C(16)	126.4(7)
C(14)-C(15)-Fe(1)	74.6(4)	O(2)-C(17)-C(16)	111.9(7)
C(16)-C(15)-C(14)	142.6(7)	C(17)-O(2)-C(18)	109.0(10)
C(16)-C(15)-Fe(1)	142.3(6)	C(13)-S(1)-C(20)	105.1(4)

The similarity between complexes of the type **3.4** and **4.4** is reflected in their spectroscopic properties, which are also similar (see experimental part). In particular, compounds **4.4a** and **4.4b** are to be compared to **3.4a** and **3.4c**, respectively, in that they are identical except for having the SMe group in place of the NMe(Xyl) substituent. Likewise **3.4a-d**, complexes **4.4a-b** exist in solution as *cis* and *trans* isomers, however the isomeric composition is different and the *cis* isomers prevail in complexes **4.4**. In particular *trans* to *cis* conversion is observed upon heating at reflux temperature in THF, which is opposite to what found in the case of type **3.4** complexes. These results are consistent with the *cis/trans* isomeric compositions observed in the complexes obtained by coupling of olefins with **1** and **2** (see Chapter II-III).

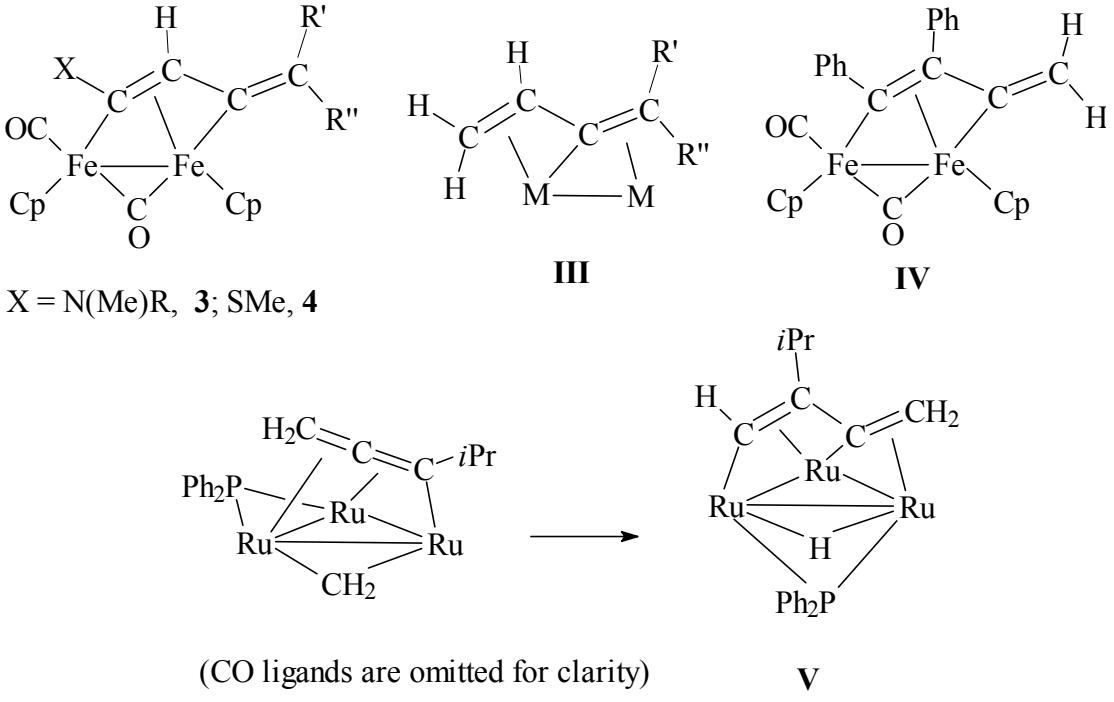
NOE investigations have been performed on complex **4.4c**, in order to establish the orientation of the Me and $SiMe_3$ substituents on the C_δ carbon of the bridging chain. Thus, irradiation of the resonance due to C_δ*Me* (δ = 2.23 ppm) resulted in significant enhancements of the signals due to $C_\delta Si$*Me*$_3$ (δ = –0.12 ppm) and to one Cp ring (δ = 4.55 ppm). In addition, irradiation of the resonance at –0.12 ppm ($C_\delta Si$*Me*$_3$) has revealed NOE effects with the resonances attributable to C_δ*Me* and C_βH (δ = 3.87 ppm). These observations indicate that C_δ-*Me* group is located anti to C_β-*H*, and that the more hindered C_δ-*SiMe*$_3$ is pointing far, from the bulky Cp ligand, as expected.

Both **3.4** and **4.4** display a bridging C_4 carbon chain, which is linear (not branched) as a consequence of the fact that C-C bond formation has occurred between the μ-alkylidyne and the primary carbon of the allene. Moreover, the C_4 bridging carbon chain displays an extended π– bond which is consequence of μ-alkylidyne-allenyl coupling and of the extension of the unsaturated character of cumulene to the bridging carbyne carbon.

Analogous linear C_4 fragments bridging two adjacent metal centers are known. They include, for example, μ-η^2:η^3-2-butadienyl ligands (Scheme 4.5, **III**) in diruthenium [7] and in diiron complexes. [8] A more appropriate comparison is with the complex [Fe_2{μ-η^1:η^3-C(Ph)C(Ph)C=CH_2)}(μ-CO)(CO)(Cp)$_2$] [9] (Scheme 4.5, **IV**), which exhibits a bridging C_4 ligand very similar to that of **3.4** and **4.4**, except for the fact that it does not contain heteroatoms. The bridging C_4 frame can be described as a bridging allenylcarbene, or as μ-η^1:η^3-butadienylidene

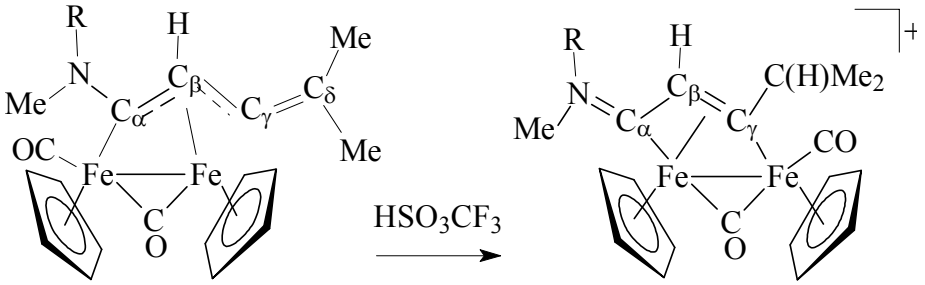
complexes. The representations of **3.4-4.4** and **IV**, shown in Scheme 4.5, emphasize the butadienylidene nature of the bridging ligands. It should be noted that the bridging ligand in **IV**, although similar to **3.4-4.4**, is the result of a different synthetic approach, in that it comes from the coupling between two C_2 units: a bridging ethylidene and a diphenylacetilene.

A further example of bridging butadienylidene ligand is found in the triruthenium complex $[Ru_3(CO)(\mu_3\text{-}\eta^4\text{-}CH_2{=}CC(i\text{Pr}){=}CH)(\mu\text{-}PPh_2)(\mu\text{-}H)]$ [10] (Scheme 4.5, **V**). The coordination mode of the butadienylidene ligand in **V**, involving three metal atoms, is similar but not identical to that found in **3.4-4.4**. However, in this case the analogy concerns the synthetic route. As shown in Scheme 4.5, the C_4 ligand in **V** was obtained upon intramolecular coupling of allenyl and bridging methylidene ligands, accompanied by hydrogen abstraction and coordination as bridging hydride. [11]



Scheme 4.5

The multisite bound unsaturated C_4 fragment in **3.4** and **4.4** is potentially susceptible of electrophilic additions, as well as of a number of other transformations. As an example, we have investigated the reactivity of **3.4-4.4** with HSO_3CF_3 and $CH_3SO_3CF_3$. Compounds $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha N(R)(Me)C_\beta(H)C_\gamma C_\delta(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Xyl, **3.4a**; R = Me, **3.4e**) react with HSO_3CF_3 affording the vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(C_\delta HMe_2)C_\beta HC_\alpha N(R)(Me)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, **5.4a**; R = Me, **5.4b**], in nearly quantitative yields (Scheme 4.6).



	R
3.4a	Xyl
3.4e	Me

5.4a
5.4b

Scheme 4.6

Complexes **5.4a-b** have been characterized by spectroscopy and elemental analysis. Moreover, the X-ray structure of **5.4a** has been determined (Figure 4.3 and Table 4.3). The cationic complex **5.4a** can be described as a vinyliminium cation and all relevant bonding parameters perfectly parallel the ones described in the literature for analogous complexes. [12] Moreover, the molecule displays a *cis* geometry for the Cp ligands, and the *E* conformation for the iminium group, as normally found for similar complexes which present a Me and a Xyl group at iminium moiety and a hydrogen atom at C_β.

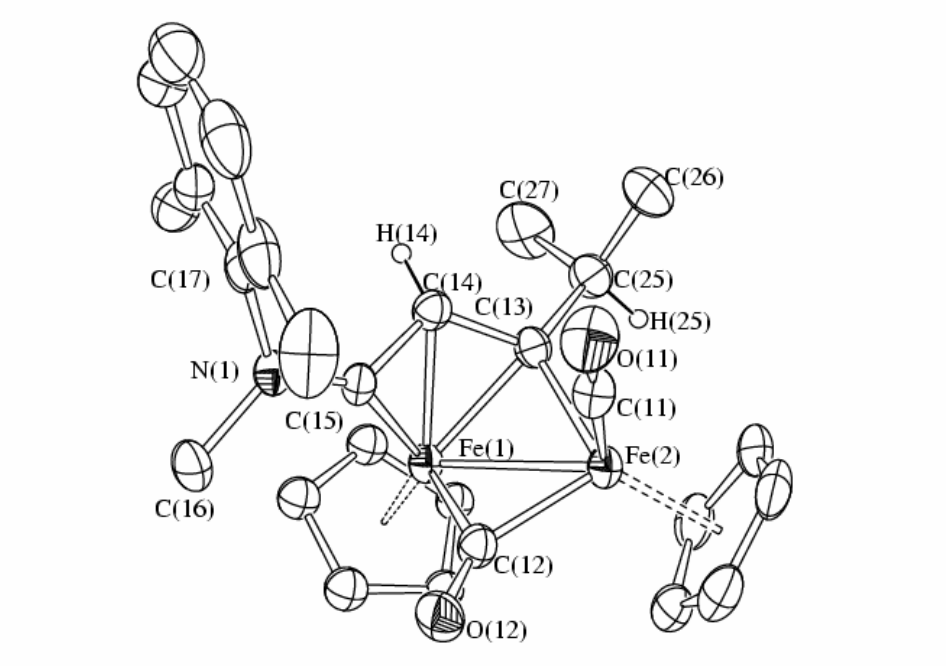


Figure 4.3 ORTEP drawing of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(C_\delta HMe_2)C_\beta HC_\alpha N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**5.4a**) (all H-atoms, except H(14) and H(25), have been omitted for clarity). Only the main image of the disordered Cp ligand bonded to Fe(2) is drawn. Thermal ellipsoids are at the 30% probability level.

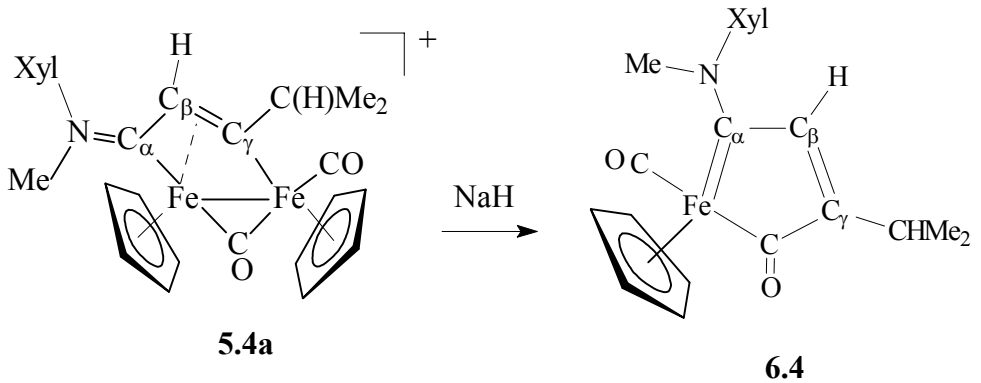
Table 4.3 Selected bond lengths (Å) and angles (°) for $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(C_\delta HMe_2)C_\beta HC_\alpha N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, **5.4a**.

Fe(1)-Fe(2)	2.5460(8)	C(11)-O(11)	1.145(6)
Fe(1)-C(12)	1.979(4)	C(12)-O(12)	1.167(5)
Fe(2)-C(12)	1.885(4)	C(13)-C(14)	1.415(6)
Fe(2)-C(11)	1.753(5)	C(14)-C(15)	1.427(6)
Fe(1)-C(13)	2.046(4)	C(15)-N(1)	1.299(5)
Fe(2)-C(13)	1.960(4)	N(1)-C(17)	1.454(6)
Fe(1)-C(14)	2.075(4)	N(1)-C(16)	1.476(6)
Fe(1)-C(15)	1.838(4)	C(13)-C(25)	1.532(6)
Fe(2)-C(13)-Fe(1)	78.89(15)	C(15)-N(1)-C(17)	123.0(4)
C(14)-C(13)-Fe(2)	121.3(3)	C(15)-N(1)-C(16)	119.8(4)
C(15)-C(14)-C(13)	118.1(4)	C(17)-N(1)-C(16)	117.1(3)

N(1)-C(15)-C(14)	132.9(4)	C(14)-C(15)-Fe(1)	77.8(2)
N(1)-C(15)-Fe(1)	147.2(3)		

The spectroscopic properties (IR and NMR spectra) of **5.4a-b** closely resemble those reported for analogous vinyliminium species. [12] The NMR spectrum of **5.4a** reveals the presence of two isomeric forms (*E* and *Z* isomers) attributable to the different orientations that the two N substituents can assume and are due to the double bond character of the C_α-N (iminium) interaction. As expected, the *E* isomer, in which the Xyl group points far from the Fe atom, and corresponds to the structure found in solid, prevails in solution (*E* and *Z* ratio 5:1). Conversely, the NMR spectrum of **5.4b,** in which the N substituents are equivalent**,** shows one single set of resonances. NOE studies carried on **5.4a-b** have outlined that the Cp substituents adopt the *cis* configuration. Taking into consideration that **3.4a** exists in solution as *cis* and *trans* isomers, and the precursor **3.4e** is present only in the *trans* form, the formation of **5.4a-b** must be accompanied by *trans-cis* isomerization. Further rearrangements involve the CO: a terminal bound CO is found on the Fe-Cγ metal centre instead of the Fe-C_α. These rearrangements of the ancillary ligand are a consequence of the 'slippage' of the bridging hydrocarbyl ligand which occurs along with the transformation into bridging vinyliminium. In fact, allyl coordination of the bridging frame shifts from one to the other metal centre and the carbon atom bridging the two metals centres changes from C_α to C_γ in **3.4a** and **5.4**. These rearrangement evidences the flexibility, and the ease by which the $Fe_2(CO)_2Cp_2$ frame accompanies the transformation of the bridging organic frame.

In order to determine whether or not the protonation reaction can be reversed upon treatment with a base, we studied the reactivity of **5.4a** with NaH. The reaction selectively afforded the metallacyclo complex **6.4**, rather than removing a proton (Scheme 4.7).



5.4a **6.4**

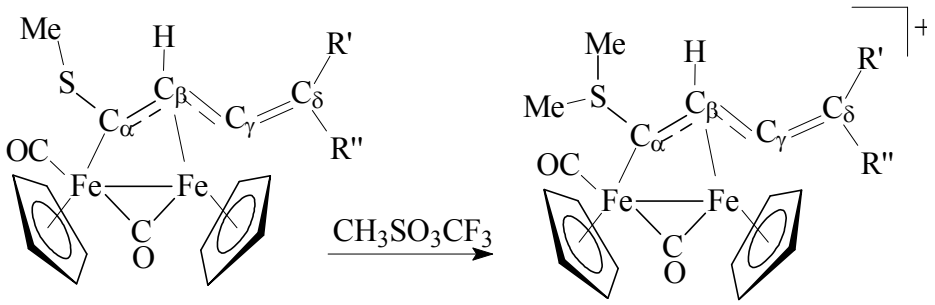
Scheme 4.7

The formation of **6.4** is consistent with the previously reported reactions of analogous vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')C_\beta HC_\alpha N(Xyl)(Me)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Me, CO_2Me, CMe_2OH) which, upon treatment with NaH, resulted in a similar fragmentation of the diiron compound and formation of the corresponding 1-metalla-2-amino-cyclopenta-1,3-dien-5-one complexes. [13]

Complex **6.4** has been characterized by IR and NMR spectroscopy, and elemental analysis. The NMR spectra evidence the presence of *E* and *Z* isomers, in about 2:1 ratio, which are due to the different orientation that the Me and Xyl groups can assume with respect to the N-C_α bond, that exhibits some double bond character. These observations are consistent with those previously reported for the metallacyclopentadienone complexes mentioned above. [13]

By contrast with the effectiveness of the protonation reaction, we found that compounds **3.4** are inert towards $CH_3SO_3CF_3$. In particular, stirring overnight a dichloromethane solution of **3.4a** with $CH_3SO_3CF_3$, gave only trace amounts of methylated product.

Compared to **3.4**, the thiomethylbutadienylidene complexes **4.4a-b** show a different behavior with respect to HSO_3CF_3 and $CH_3SO_3CF_3$. The reaction with HSO_3CF_3 does not produce any stable compound. Protonation, which presumably takes place at the S atom, is reversible, and slowly leads to the decomposition of **4.4a-b**. On the other hand, complexes **4.4a-b** undergo methylation at the S-atom, upon treatment with $CH_3SO_3CF_3$ in CH_2Cl_2 solution, affording the cationic complexes **7.4a-b**, which have been characterized by spectroscopy and elemental analysis (Scheme 4.8).



	R’	R’’	
4.4a	Me	Me	**7.4a**
4.4b	CO_2Et	H	**7.4b**

Scheme 4.8

Moreover, the X-ray molecular structure of **7.4a** has been determined (Figure 4.4 and Table 4.4).

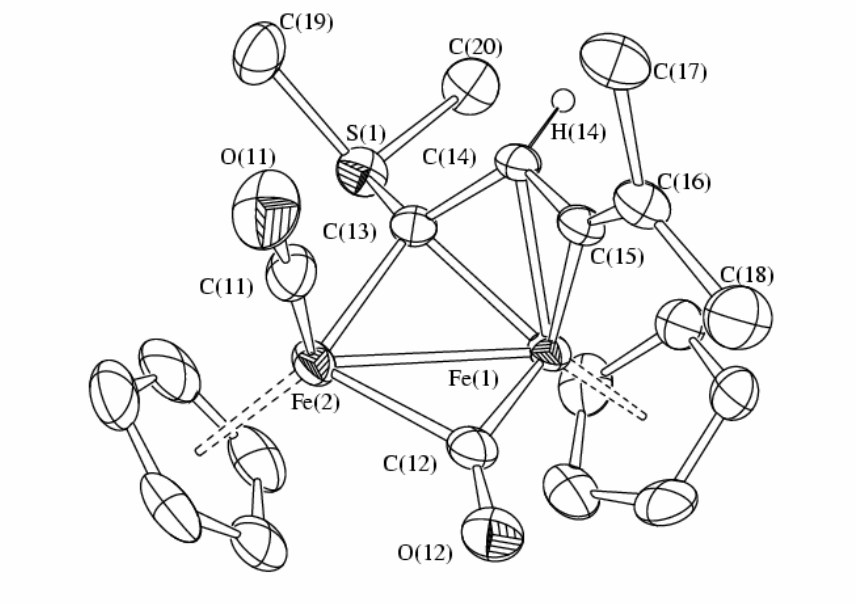


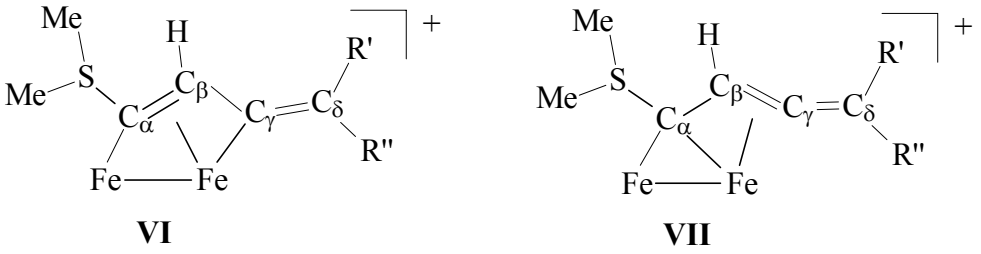
Figure 4.4 ORTEP drawing $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma C_\delta(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**7.4a**) (all H-atoms, except H(14), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

Table 4.4 Selected bond lengths (Å) and angles (°) for $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma C_\delta(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, **7.4a**.

Fe(1)-Fe(2)	2.5423(8)	C(11)-O(11)	1.141(6)
Fe(1)-C(12)	1.878(5)	C(12)-O(12)	1.171(6)
Fe(2)-C(12)	1.984(5)	C(13)-C(14)	1.417(6)
Fe(2)-C(11)	1.759(5)	C(14)-C(15)	1.398(6)
Fe(1)-C(13)	1.976(4)	C(15)-C(16)	1.323(6)
Fe(2)-C(13)	1.942(4)	C(13)-S(1)	1.773(4)
Fe(1)-C(14)	2.057(4)	S(1)-C(20)	1.791(6)
Fe(1)-C(15)	1.997(4)	S(1)-C(19)	1.798(6)
C(16)-C(17)	1.512(6)	C(16)-C(18)	1.495(7)
Fe(2)-C(13)-Fe(1)	80.91(16)	C(15)-C(16)-C(18)	122.6(4)
C(14)-C(13)-Fe(2)	123.7(3)	C(15)-C(16)-C(17)	120.0(4)
C(15)-C(14)-C(13)	116.2(4)	C(18)-C(16)-C(17)	117.3(4)

C(16)-C(15)-C(14)	143.1(4)	C(13)-S(1)-C(20)	110.1(3)
C(16)-C(15)-Fe(1)	144.6(4)	C(13)-S(1)-C(19)	101.8(3)
C(14)-C(15)-Fe(1)	72.2(2)	C(20)-S(1)-C(19)	98.8(3)

The structure of the sulphonium derivative **7.4a** closely resembles those of the parent neutral thio-1,3-butadienylidene complex *cis*-**4.4b** and the related amino compound *cis*-**3.4a**. Methylation of the S atom is remarkable in that it produces only small changes in the coordination mode of the bridging ligand, if compared to the effects generated by the protonation of **3.4a**, **3.4e**. The overall connectivity is not altered, but some bonding distances are sensibly affected. In particular Fe(1)-C(15) [1.997(4) Å] is considerably elongated compared to *cis*-**4.4b** [1.906(6) Å] whereas Fe(1)-C(13) [1.976(4) Å] results to be shortened [2.003(7) Å in *cis*-**4.4b**], suggesting that **7.4a-b** are better described as bridging sulphonium-allenylalkylidene (Scheme 4.9, **VII**), rather than sulphonium-butadienylidene complexes (Scheme 4.9, **VI**). In agreement with this, C(14)-C(15) [1.398(6) Å] displays a more pronounced π-character compared to C(13)-C(14) [1.417(6) Å].



Scheme 4.9

The spectroscopic properties of **7.4a-b** are consistent with the structural data. IR spectra (in CH_2Cl_2 solution) display the usual νCO band pattern, consisting of two absorptions, (1988 and 1809 cm^{-1} for **7.4a**), which are shifted of about 30 cm^{-1} to higher frequencies, compared to the parent complexes, as a consequence of the positive charge. The NMR spectra show single sets of resonances. NOE studies carried on both **7.4a** and **7.4b** evidence that the Cp ligands adopt the *cis* configuration also in solution. The S-methyl groups give rise to a single resonance in both ^1H and in ^{13}C NMR spectrum (δ = 3.75 and 39.6 ppm, respectively, for **7.4b**) indicating their equivalence. Major features of the ^{13}C NMR spectra are given by resonances attributable to C_α, C_β, C_γ and C_δ, which fall, in the case of **7.4a**, at 159.4, 59.6, 181.0, 114.5, respectively.

Methylation at the S atom in bridging thioalkylidene complexes of the type $[Fe_2\{\mu\text{-}C(SMe)(X)\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (X = H, CN) is well documented. [14] The formation of the

corresponding bridging sulphonium alkylidene complexes $[Fe_2\{\mu\text{-}C(SMe_2)(X)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ has been exploited to obtain a variety of bridging alkylidene complexes *via* SMe_2 displacement by nucleophiles including: amines, alcohols, thiols, phosphines and carbon nucleophiles. [15] Displacement of the SMe_2 unit from the bridging ligand has been attempted also for **7.4a-b** but without success. Indeed **7.4a-b** resulted unreactive with respect to $NaBH_4$ or NBu_4CN, in THF at room temperature, and no replacement of the SMe_2 group by hydride or cyanide was observed.

Conclusions

Allene incorporation into bridging amino and thio-alkylidyne complexes has a general character and is not affected by the nature of the heteroatom (N or S) on the bridging ligand. The coupling reaction requires proton removal from the allene and the presence of a vacant coordination site on one iron centre, in order to allow preliminary allene coordination. Allenyl-alkylidyne coupling generates a bridging C_4 frame which can be described as thio- or amino- $\eta^1\eta^3$-butadienylidene ligand or, alternatively, as bridging thio- or amino-allenylalkylidene ligands. The whole of these representations accounts for the extended π bond in the bridging frame, which supports multisite coordination and allow the addition of electrophilic reagents such as HSO_3CF_3 and $CH_3SO_3CF_3$. The reactivity of the butadienylidene ligand is influenced by the nature of the heteroatom substituents (N or S). Thus, methylation of the bridging thio-butadienylidene complexes occurs selectively at the S atom generating the corresponding sulphonium derivatives. By contrast, protonation of the amino-butadienylidene complexes takes place at the terminal carbon of the C_4 chain and transforms the bridging frame into a stable vinyliminium ligand. Once again, these reactions evidence the role of the rather flexible dinuclear frame $Fe_2(CO)_2Cp_2$ in supporting transformations of the bridging ligand, in that they are accompanied and sustained by proper changes in the coordination mode or in the configuration of the ancillary ligands (*cis-trans* isomerizations).

Experimental details

General

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^{1}H,^{13}C correlation through gs-HSQC and gs-HMBC experiments. [16] NOE measurements were recorded using the DPFGSE-NOE sequence. [17] NMR signals due to a second (minor) isomeric form (where it has been possible to detect and/or resolve them) are italicized. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds **2a-c** [18] and **1** [19] were prepared by published methods.

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha N(R)(Me)C_\beta(H)C_\gamma C_\delta(R')(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Xyl, R' = R'' = Me, 3.4a; R = Xyl, R' = Me, R'' = H, 3.4b; R = Xyl, R' = CO_2Et, R'' = H, 3.4c; R = 4-C_6H_4OMe, R' = CO_2Et, R'' = H, 3.4d; R = R' = R'' = Me, 3.4e; R' = CO_2Et, R'' = H, 3.4f). A solution of complex **2a** (205 mg, 0.330 mmol), in THF (15 mL), was treated with $H_2C{=}C{=}CMe_2$ (0.10 mL, 1.02 mmol), Et_3N (0.90 mL, 6.5 mmol) and Me_3NO (50 mg, 0.67 mmol). The mixture was stirred for 30 min, then it was filtered on alumina, and the solvent was removed under reduced pressure. Chromatography of the residue on alumina, using diethyl ether as eluent, gave a green band corresponding to **3.4a**. Yield: 132 mg, 78%. Crystals suitable for X-ray analysis were obtained by a diethyl ether solution, layered with n-pentane, at –20 °C. Anal. $C_{27}H_{29}Fe_2NO_2$ (511.22): calcd. C 63.44, H 5.72; found C 63.51, H 5.62. IR (CH_2Cl_2): ν(CO) 1946 (s), 1921 (vs), 1760 (s) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 7.76-7.10 (m, 3 H, $Me_2C_6H_3$); *5.10*, *4.70*, 4.40, 4.39 (s, 10 H, Cp); 3.91, *3.88* (s, 3 H, NMe); *3.08*, 3.02 (s, 1 H, $C_\beta H$); 2.65, *2.62*, 2.44, *2.39* (s, 6 H, $Me_2C_6H_3$); 2.18, *2.01*, *1.70*, 1.31 (s, 6 H, $C_\delta Me_2$). *trans*/*cis* ratio 3:2. ^{13}C NMR (acetone-d_6) δ 265.1, *263.7* (μ-CO); *215.6*, 214.0 (CO); *204.5*, 203.5 (C_α); 158.9, *158.4* (C_γ); 147.8 (*ipso*-$Me_2C_6H_3$); 135.1, 134.2, 129.8, *129.6*, 129.3, *128.6*, 126.7, *126.5* ($Me_2C_6H_3$); *120.2*, 118.6 (C_δ); 88.1, *86.1*, 84.6, *83.3* (Cp); 47.7, *44.4* (NMe); *47.3*, 35.2 (C_β); 26.9, *26.0*, *21.2*, 20.6 ($C_\delta Me_2$); *19.8*, 19.4, 19.0, *18.7* ($Me_2C_6H_3$).

Compounds **3.4b-c** were prepared by the same procedure described for **3.4a**, by reacting **2a** (200 mg) with Et_3N, Me_3NO and the appropriate allene.

3.4b (yield 112 mg, 70%, colour green). $C_{26}H_{27}Fe_2NO_2$ (497.19): calcd. C 62.81, H 5.47; found C 62.88, H 5.42. IR (CH_2Cl_2): ν(CO) 1950 (s), 1920 (vs), 1767 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.44-7.08 (m, 3 H, $Me_2C_6H_3$); *5.00*, *4.78*, 4.67, 4.40 (s, 10 H, Cp); 4.16, *4.08* (s, 1 H, $C_\delta H$); *3.89*, 3.80 (s, 3 H, NMe); 3.17 (s, 1 H, $C_\beta H$); 2.60, *2.57*, 2.38 (s, 6 H, $Me_2C_6H_3$); *2.17*, 2.08 (s, 3 H, $C_\delta Me$). *trans*/*cis* ratio 6:5. ^{13}C NMR ($CDCl_3$) δ 264.3, *262.1* (μ-CO); *216.0*, 214.0 (CO); *206.5*, 202.1 (C_α); 157.4, *157.2* (C_γ); 148.0 (ipso-$Me_2C_6H_3$); 134.8-126.3 ($Me_2C_6H_3$); 120.9 (C_δ); *87.0*, 86.9, 86.2, *84.9* (Cp); 47.7, *44.4* (NMe); 47.4 (C_β); 29.2, *27.9* ($C_\delta Me$); *20.8*, 19.6, 18.8, *17.9* ($Me_2C_6H_3$).

3.4c (yield 136 mg, 76%, colour green). $C_{28}H_{29}Fe_2NO_4$ (555.22): calcd. C 60.57, H 5.26; found C 60.56, H, 5.29. IR (CH_2Cl_2): ν(CO) 1964 (vs), *1922* (s), 1770 (s), 1729 (m), ν($C_\gamma C_\delta$) 1676 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.33-7.16 (m, 3 H, $Me_2C_6H_3$); *5.95*, 5.76 (d, 1 H, $C_\delta H$, $^4J_{HH}$ = 2 Hz); 5.09, 4.68, *4.48*, *4.33* (s, 10 H, Cp); 4.00 (br, 2 H, CO_2CH_2); 3.85, *3.84* (s, 3 H, NMe); *3.26*, 3.16 (d, 1 H, $C_\beta H$, $^4J_{HH}$ = 2 Hz); 2.58, 2.40 (s, 6 H, $Me_2C_6H_3$); 1.29 (br, 3 H, $CO_2CH_2CH_3$). *cis*/*trans* ratio 2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 266.3 (μ-CO); 216.3 (CO); 203.0 (C_α); 189.4, *189.2* (C_γ); 159.4 (CO_2Et); 146.0 (ipso-$Me_2C_6H_3$); 135.6-126.7 ($Me_2C_6H_3$); 111.4, *109.4* (C_δ); *88.5*, 86.0, 85.7, *84.2* (Cp); 59.2 (CO_2CH_2); 49.7, *48.8* (NMe); 47.7, *37.6* (C_β); 19.8, *19.4*, *19.0*, 18.5 ($Me_2C_6H_3$); 14.2, *13.8* ($CO_2CH_2CH_3$).

Compound **3.4d** was prepared by the same procedure described for **3.4a**, by reacting **2b** (273 mg) with Et_3N, Me_3NO and CH_2=C=CH(COOEt).

3.4d (yield 174 mg, 71%, colour green). $C_{27}H_{27}Fe_2NO_5$ (557.20): calcd. C 58.20, H 4.88; found C 58.25, H 4.76. IR (CH_2Cl_2): ν(CO) 1966 (vs), 1936 (s), 1778 (s), 1729 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.67-6.90 (m, 4 H, C_6H_4OMe); 5.98, *5.88* (d, 1 H, $C_\delta H$, $^4J_{HH}$ = 2.2 Hz); 4.72, *4.66*, *4.64*, 4.55 (s, 10 H, Cp); 4.12 (s, 3 H, OMe); 4.01 (s, 3 H, NMe); 4.00 (br, 2 H, CO_2CH_2); 3.36, *3.30* (d, 1 H, $C_\beta H$, $^4J_{HH}$ = 2.2 Hz); 1.26 (br, 3 H, $CO_2CH_2CH_3$). *cis*/*trans* ratio 3:2. ^{13}C NMR ($CDCl_3$) δ 265.7, *263.5* (μ-CO); 215.0 (CO); *202.3*, 200.7 (C_α); 189.4, *189.2* (C_γ); 156.9 (CO_2Me); 150.0, 128.6, 127.9, 125.8, 114.9, 114.2 (C_6H_4Me); *111.8*, 110.0 (C_δ); 88.7, *86.7*, 85.2, *84.5* (Cp); 59.6, *59.5* (CO_2CH_2); 55.7, *55.6* (OMe); *47.3*, 35.2 (C_β); 43.7, *43.5* (NMe); *14.5*, 14.1 ($CO_2CH_2CH_3$).

Compounds **3.4e-f** were prepared by the same procedure described for **3.4a**, by reacting **2c** (230 mg) with Et_3N, Me_3NO and the appropriate allene.

trans-**3.4e** (yield 134 mg, 72%, colour green). $C_{20}H_{23}Fe_2NO_2$ (421.09): C 57.05, H 5.51; found C 57.12, H 5.46. IR (CH_2Cl_2): ν(CO) 1919 (vs), 1764 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.50, 4.23 (s, 10 H, Cp); 3.64 (s, 6 H, NMe_2); 3.45 (s, 1 H, $C_\beta H$); 2.31, 1.79 (s, 6 H, $C_\delta Me_2$). ^{13}C NMR ($CDCl_3$) δ 267.2 (μ-CO); 214.1 (CO); 204.1 (C_α); 159.4 (C_γ); 119.0 (C_δ); 87.7, 83.5 (Cp); 46.2 (NMe_2); 35.4 (C_β); 26.8, 21.5 ($C_\delta Me_2$).

trans-**3.4f** (yield 165 mg, 80%, colour green). $C_{21}H_{23}Fe_2NO_4$ (465.10): C 54.23, H 4.98; found: C 54.29, H 4.88. IR (CH_2Cl_2): ν(CO) 1931 (vs), 1783 (s), 1730 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.04 (br, 1 H, $C_\delta H$); 4.52, 4.28 (s, 10 H, Cp); 3.65 (s, 6 H, NMe_2); 4.05 (br, 2 H, CO_2CH_2); 3.44 (br, 1 H, $C_\beta H$); 1.23 (br, 3 H, $CO_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$) δ 265.5 (μ-CO); 213.1 (CO); 202.8 (C_α); 195.5 (C_γ); 163.0 (CO_2Et); 109.2 (C_δ); 88.5, 84.8 (Cp); 59.3 (CO_2CH_2); 46.3 (NMe_2); 38.0 (C_β); 14.5 ($CO_2CH_2CH_3$).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha S(Me)C_\beta(H)C_\gamma C_\delta(R')(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R' = R'' = Me, 4.4a; R' = CO_2Et, R'' = H, 4.4b; R' = $SiMe_3$, R'' = Me, 4.4c). A solution of **1** (300 mg, 0.561 mmol), in THF (20 mL), was treated with $H_2C{=}C{=}CMe_2$ (0.10 mL, 1.02 mmol), Et_3N (1.2 mL, 8.7 mmol) and Me_3NO (84 mg, 1.12 mmol). The resulting mixture was stirred for 40 min, then it was filtered on alumina. Removal of the solvent gave a residue that was chromatographed on alumina using diethyl ether as eluent. A green band was collected affording **4.4a** as green-brown powder, upon solvent removal. Yield: 178 mg, 75%. $C_{19}H_{20}Fe_2O_2S$ (424.12): C 53.81, H 4.75; found C 53.89, H, 4.66. IR (CH_2Cl_2): ν(CO) 1959 (vs), 1936 (s), 1781 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.87, 4.54, *4.52*, *4.25* (s, 10 H, Cp); *4.16*, 4.00 (s, 1 H, $C_\beta H$); 2.90, *2.87* (s, 3 H, SMe); *2.27,* 2.11*, 1.80,* 1.65 (s, 6 H, $C_\delta Me_2$). *cis*/*trans* ratio 5:3. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 262.6, *261.3* (μ-CO); 212.7, *212.1* (CO); *188.4*, 188.1 (C_α); *158.0*, 155.4 (C_γ); 122.8*, 120.4* (C_δ); *88.2*, 87.4, *86.3*, 84.7 (Cp); *51.3,* 50.4 (C_β); 27.1, *26.7*, *21.6*, 21.1 ($C_\delta Me_2$); *20.6*, 20.4 (SMe). Compounds **4.4b-c** were prepared by the same procedure described for **4.4a**, by reacting **1** (300 mg) with Et_3N, Me_3NO and the appropriate allene $H_2C{=}C{=}C(R')(R'')$. Crystals of **4.4b** suitable for X-ray analysis were obtained by a $CDCl_3$ solution layered with n-pentane, at –20 °C.

4.4b (yield 205 mg, 78%, colour: green). $C_{20}H_{20}Fe_2O_4S$ (468.13): C 51.31, H 4.31; found: C 51.36, H, 4.30. IR (CH_2Cl_2): ν(CO) 1977 (s), 1953 (vs), 1788 (s), 1709 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.92, *5.81* (d, 1 H, $C_\delta H$, $^4J_{HH}$ = 2.20 Hz); *4.95*, 4.78, *4.57*, 4.29 (s, 10 H, Cp); 4.67, *4.56* (d, 1 H, $C_\beta H$, $^4J_{HH}$ = 2.20 Hz); 4.12, *3.98* (m, 2 H, CO_2CH_2); *2.88*, 2.87 (s, 3 H, SMe); 1.20, *1.14* (m, 3 H, $CO_2CH_2CH_3$). *trans*/*cis* ratio 3:1. ^{13}C NMR ($CDCl_3$) δ *262.1*, 259.9 (μ-CO); 210.8, *210.3* (CO); 191.5, 190.1, *189.7*, *188.5* (C_α and C_γ); 162.5, *162.4* (CO_2Et); *111.4*, 110.*2* (C_δ); 89.0*, 88.0*, 87.4, *85.9* (Cp); *59.6*, 59.5 (CO_2CH_2); 54.3, *52.5* (C_β); 20.9, *20.7* (SMe); 14.4, *14.2* ($CO_2CH_2CH_3$).

cis-**4.4c** (yield 198 mg, 73%, colour brownish green). $C_{21}H_{26}Fe_2O_2SSi$ (482.27): C 52.30, H, 5.43; found C 52.32, H 5.39. IR (CH_2Cl_2): ν(CO) 1961 (vs), 1778 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.86, 4.55 (s, 10 H, Cp); 3.87 (s, 1 H, $C_\beta H$); 2.83 (s, 3 H, SMe); 2.23 (s, 3 H, $C_\delta Me$); –0.12 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 262.9 (μ-CO); 213.2 (CO); 188.3 (C_α); 168.4 (C_γ); 125.0 (C_δ); 87.8, 85.1 (Cp); 49.4 (C_β); 20.7 (SMe); 17.9 ($C_\delta Me$); –1.9 ($SiMe_3$).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(C_\delta HMe_2)C_\beta HC_\alpha N(R)(Me)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Xyl, 5.4a; R = Me, 5.4b). Compound **3.4a** (112 mg, 0.219 mmol), was dissolved in CH_2Cl_2 (10 mL) and treated with HSO_3CF_3 (0.025 mL, 0.283 mmol). The solution was stirred for 15 min, then the solvent was removed under reduced pressure. Chromatography of the residue on an alumina column, with CH_3OH as eluent, gave a red band corresponding to **5.4a**. Yield: 123 mg, 85%. Crystals suitable for X-ray analysis were obtained by a CH_2Cl_2 solution layered with diethyl ether, at –20 °C. $C_{28}H_{30}F_3Fe_2NO_5S$ (661.29): C 50.86, H 4.57; found: C 51.00, H 4.62. IR (CH_2Cl_2): ν (CO) 2002 (vs), 1814 (s), ν(CN) 1631 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.40-6.93 (m, 3H, $Me_2C_6H_3$); 5.41, *5.23*, 5.21, *4.82* (s, 10 H, Cp); *5.08*, 4.22 (s, 1 H, $C_\beta H$); 4.69 (m, 1 H, $CHMe_2$); 4.19, *3.93* (s, 3 H, NMe); 2.24, *1.87*, 1.75 (s, 6 H, $Me_2C_6H_3$); 1.51 (dq, $^3J_{HH}$= 12 Hz, $^4J_{HH}$= 6.6 Hz, 6 H, $CHMe_2$). *E*/*Z* ratio 5:1. ^{13}C NMR ($CDCl_3$) δ 254.0 (μ-CO); 231.5 (C_α); 210.1 (CO); 208.0 (C_γ); 145.0 (ipso-$Me_2C_6H_3$); 131.4, 131.1, 129.9, 129.7, 129.5 ($Me_2C_6H_3$); *92.6*, 91.8, *91.6*, 87.6 (Cp); 58.0 (C_δ); 54.9 (C_β); 45.9 (NMe); 31.1 ($CHMe_2$); 18.0, *17.5*, 16.7 ($Me_2C_6H_3$). Complex **5.4b** was prepared by the same procedure described for **5.4a**, by reacting **3.4e** (128 mg) with HSO_3CF_3.

5.4b (yield 139 mg, 80%; colour light green). $C_{21}H_{24}F_3Fe_2NO_5S$ (571.17): C 44.16, H 4.24; found C, 44.17 %; H, 4.20. IR (CH_2Cl_2): ν(CO) 1988 (vs), 1806 (s), ν(CN) 1682 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.13, 5.08 (s, 10 H, Cp); 4.98 (s br, 1 H, $C_\beta H$); 4.92 (m, 1 H, $CHMe_2$); 3.85, 3.26 (s, 6 H, NMe); 1.90 (dq, $^3J_{HH}$= 12 Hz, $^4J_{HH}$= 7.7 Hz, 6 H, $CHMe_2$). ^{13}CNMR ($CDCl_3$) δ 255.2 (μ-CO); 224.2

(C_α); 209.3 (CO); 208.5 (C_γ); 91.2, 87.7 (Cp); 56.7 (C_β); 52.0 (C_δ); 51.7, 45.1 (NMe); 33.3 (CH*Me*$_2$).

Synthesis of [Fe(CO)(Cp){C_αN(Me)(Xyl)C_βHC_γ(C_δHMe$_2$)C(O)}] (6.4). A solution of **5.4a** (123 mg, 0.186 mmol), in THF (10 mL), was treated with NaH (44 mg, 1.91 mmol). The mixture was stirred for 30 minutes, then it was filtered through an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with THF as eluent, gave a brown band corresponding to **6.4**. Yield: 55 mg, 75%. $C_{22}H_{25}FeNO_2$ (391.28): C, 67.53, H 6.44; found: C 67.61, H, 6.39. IR (CH_2Cl_2): ν(CO) 1917 (vs), 1591 (m), ν(C_αN) 1620 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.34-7.13 (m, 3 H, $Me_2C_6H_3$); 6.43 (s, 1 H, C_βH); 4.61 (s, 5 H, Cp); 3.82 (s, 3 H, NMe); 2.70 (m, 1 H, C_δH); 2.20, 2.08 (s, 6 H, *Me*$_2$C$_6$H$_3$); 0.84 (dq, $^3J_{HH}$= 10.6 Hz, $^4J_{HH}$= 6.6 Hz, 6 H, C_δMe$_2$). *E*/*Z* ratio 2:1. ^{13}C NMR ($CDCl_3$) δ 272.6 (C=O); 264.0 (C_α); 222.5 (CO); 173.6 (C_γ); 148.6 (C_β); 145.3 (*ipso*-Me$_2$*C*$_6$H$_3$); 132.6, 132.1, 129.4, 128.9, 128.7 (Me$_2$*C*$_6$H$_3$); 84.9 (Cp); 48.7 (NMe); 37.1 (C_δ); 21.5 (C_δ*Me*$_2$); 17.3, 17.2 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe_2{μ-η^1:η^3-C_α(SMe$_2$)C_β(H)$C_\gamma$$C_\delta$(R')(R'')}(μ-CO)(CO)(Cp)$_2$][$SO_3CF_3$] (R' = R'' = Me, 7.4a; R' = CO_2Et, R'' = H, 7.4b). $CH_3SO_3CF_3$ (0.03 mL, 0.27 mmol) was added to a solution of **4.4a** (100 mg, 0.236 mmol), in CH_2Cl_2 (12 mL). The mixture was stirred for 2 h, then it was chromatographed on an alumina column. Elution with a 1:1 mixture of THF and methanol gave a green band corresponding to **7.4a**. Yield 111 mg, 80%. Crystals suitable for X-ray analysis were obtained by a dichloromethane solution layered with diethyl ether, at –20 °C. Anal. $C_{21}H_{23}F_3Fe_2O_5S_2$ (588.22): C 42.88, H 3.94; found: C 42.96, H 4.04. IR (CH_2Cl_2): ν(CO) 1988 (vs), 1809 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.86, 4.70 (s, 10 H, Cp); 4.18 (s, 1 H, C_βH); 3.35 (s, 6 H, SMe); 1.95, 1.50 (s, 6 H, C_δ*Me*$_2$). ^{13}C NMR ($CDCl_3$) δ 251.9 (μ-CO); 209.6 (CO); 155.8 (C_α); 151.2 (C_δ); 127.1 (C_γ); 86.9, 84.3 (Cp); 55.7 (C_β); 38.7 (SMe); 27.2, 20.7 (C_δ*Me*$_2$).

Complex **7.4b** was prepared by the same procedure described for **7.4a**, by reacting **4.4b** (109 mg) with $CH_3SO_3CF_3$.

7.4b (yield 107mg, 73%; colour green). $C_{22}H_{23}F_3Fe_2O_7S_2$ (632.23): C 41.79, H 3.67; found C 41.85, H, 3.59. IR (CH_2Cl_2): ν(CO) 2002 (vs), 1806 (s), 1701 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.86 (s-br, 1 H, C_δH); 5.21, 5.03 (s, 10 H, Cp); 4.88 (s-br, 1 H, C_βH); 3.93 (m, 2 H, CO_2CH_2); 3.75 (s, 6 H, SMe); 1.06 (m, 3 H, CO_2CH_2C*H*$_3$). ^{13}C NMR ($CDCl_3$) δ 252.9 (μ-CO); 207.8 (CO); 181.0 (C_γ);

159.4 (C_α); 161.9 (CO_2Et); 114.5 (C_δ); 88.2, 86.4 (Cp); 60.2 (CO_2CH_2); 59.6 (C_β); 39.6 (SMe); 14.2 ($CO_2CH_2CH_3$).

X-ray Crystallography

Crystal data for *cis*-**3.4a,** *cis*-**4.4b**, **5.4a[CF_3SO_3]·CH_2Cl_2** and **7.4a[CF_3SO_3]·0.5CH_2Cl_2**. were collected at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using Mo-Kα radiation. Intensity data were measured over full diffraction spheres using 0.3° wide ω scans, crystal-to-detector distance 5.2 cm. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART [20] was used for collecting frames of data, indexing reflections and determinations of lattice parameters. The collected frames were then processed for integration by the software SAINT and empirical absorption corrections were applied with SADABS. [21] The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2. [22] Crystal data are listed in Table 4.5. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except positions of H(14) in *cis*-**3.4a,** *cis*-**4.4b** and **7.4a[CF_3SO_3]·0.5CH_2Cl_2** and H(14) and H(25) in **5.4a[CF_3SO_3]·CH_2Cl_2** which were located in the Fourier map and refined isotropically with thermal parameter 20% greater than that of the attached carbon. One Cp ligand and the OEt group in *cis*-**4.4b**, one Cp ligand and the CH_2Cl_2 molecule in **5.4a[CF_3SO_3]·CH_2Cl_2**, and the CH_2Cl_2 molecule in **7.4a[CF_3SO_3]·0.5CH_2Cl_2** are disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group, a part from the CH_2Cl_2 molecule in **7.4a[CF_3SO_3]·0.5CH_2Cl_2** for which the two disordered images are related by an inversion centre; in this case, an occupancy factor of 0.5 was assigned to the independent image of the molecule and, then, refined anisotropically. Similar *U* restraints were applied to all C and O atoms in *cis*-**4.4b**, all C atoms in **5.4a[CF_3SO_3]·CH_2Cl_2** and all C and F atoms in **7.4a[CF_3SO_3]·0.5CH_2Cl_2**. The crystals of *cis*-**4.4b** appeared to be racemically twinned with a refined Flack parameter of 0.49(4). [23]

Table 5

Crystal data and experimental details for *cis*-**3.4a,** *cis*-**4.4b**, **5.4a[CF_3SO_3]·CH_2Cl_2** and **7.4a[CF_3SO_3]·0.5CH_2Cl_2**

Complex	*cis*-**3.4a**	*cis*-**4.4b**	**5.4a[CF_3SO_3]·CH_2Cl_2**	**7.4a[CF_3SO_3]·0.5CH_2Cl_2**
Formula	$C_{27}H_{29}Fe_2NO_2$	$C_{20}H_{20}Fe_2O_4S$	$C_{29}H_{32}Cl_2F_3Fe_2NO_5S$	$C_{21.5}H_{24}ClF_3Fe_2O_5S_2$
*F*w	511.21	468.12	746.22	630.68
T, K	296(2)	195(2)	295(2)	295(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a, Å	9.0799(4)	8.7598(6)	10.3736(6)	9.8512(6)
b, Å	29.2031(12)	12.4318(9)	18.7998(11)	26.8978(16)
c, Å	9.6739(4)	18.1162(13)	16.9447(10)	9.8626(3)
β, °	110.3590(10)	90	101.5620(10)	92.9460(10)
Cell volume, $Å^3$	2404.90(18)	1972.9(2)	3237.5(3)	2609.9(3)
Z	4	4	4	4
D_c, g cm^{-3}	1.412	1.576	1.531	1.605
μ, mm^{-1}	1.230	1.599	1.181	1.426
F(000)	1064	960	1528	1284
Crystal size, mm	0.21 × 0.17 × 0.13	0.24 × 0.18 × 0.14	0.23 × 0.19 × 0.13	0.24 × 0.20 × 0.15
θ limits, °	2.35 – 27.10	1.99 – 25.99	1.64 – 27.00	1.51 – 27.00
Reflections collected	20747	20386	35640	28837
Independent reflections	5317 [R_{int}= 0.0301]	3880 [R_{int}= 0.0419]	7061 [R_{int}= 0.0473]	5701 [R_{int}= 0.0340]
Data/restraints/parameters	5317 / 11 / 297	3880 / 117 / 245	7061 / 166 / 393	5701 / 128 / 330
Goodness on fit on F^2	1.026	1.059	1.039	1.052
R_1 ($I > 2\sigma(I)$)	0.0288	0.0549	0.0606	0.0579

wR_2 (all data)	0.0747	0.1412	0.1903	0.1935
Largest diff. peak and hole, e.Å^{-3}	0.261 / –0.187	0.933 / –0.382	0.862 / –0.736	1.352 / –0.645

References

[1] M. J. Chetcuti, P. E. Fanwick, B. E. Grant, *Organometallics* **1991**, *10*, 3003-3004.

[2] M. J.; Fildes, S. A. R. Knox, A. G. Orpen, M. L. Turner, M. I. Yates, *J. Chem. Soc., Chem. Commun.* **1989**, 1680-1682.

[3] A. Chokshi, B. D. Rowsell, S. J. Trepanier, M. J. Ferguson, M. Cowie, *Organometallics* **2004**, *23*, 4759-4770.

[4] M. H. Chisholm, K. Folting, J. A. Heppert, W. E. Streib, *J. Chem. Soc., Chem. Commun.* **1985**, 1755-1757.

[5] E. D. Jemmis, B. V. Prasad, *Polyhedron* **1988**, *7*, 871-879.

[6] D. Ristic-Petrovic; D. J. Anderson; J. R. Torkelson; M. J. Ferguson; R. McDonald; M. Cowie, *Organometallics* **2005**, *24*, 3711-3724.

[7] J. N. L. Dennett, S. A. R. Knox; J. P. H. Charmant; A. L. Gillon; A. G. Orpen, *Inorg. Chim. Acta* **2003**, *354*, 29-40.

[8] S. M. Breckenridge, S. A. MacLaughlin, N. J. Taylor, A. J. Carty*, J. Chem. Soc. Chem. Commun.* **1991**, 1718-1720.

[9] C. P. Casey, W. H. Miles, P. J. Fagan, K. J. Haller, *Organometallics* **1985**, *4*, 559-563.

[10] D. Nucciarone, N. J. Taylor, A. J. Carty, *Organometallics* **1984**, *3*, 177-179.

[11] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* **2005***, 24,* 2297-2306.

[12] a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* **2003,** *22*, 1326-1331; b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet Chem*. **2004,** *689*, 528-538.

[13] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* **2005***, 24,* 2297-2306.

[14] a) V.G. Albano, S. Bordoni, D. Braga, L. Busetto, A. Palazzi, V. Zanotti *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 847-849; b) S. Bordoni, F. Mazza, V. Zanotti *Inorg. Chim. Acta* **1994**, *223*, 31-35.

[15] L. Busetto, V. Zanotti *J. Organomet. Chem.* **2005**, *690*, 5430-5440.

[16] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem*., **1993**, *31*, 287-292.

[17] K. Stott, J. Stonehouse, J. Keeler, T.L. Hwang, AJ. Shaka, *J. Am. Chem. Soc.* **1995**, *117*, 4199-4200.

[18] Cox, G.; Dowling, C.; Manning, A. R.; McArdle, P.; Cunningham, D. *J. Organomet. Chem*. **1992**, *438*, 143-158.

[19] Quick, M.H.; Angelici, R. J. *Inorg. Chem*., **1981**, *20*, 1123-1130.

[20] *SMART & SAINT* Software Reference Manuals, Version 5.051, Bruker Analytical X-Ray Instruments Inc., Madison, Wi, **1998**.

[21] G. M. Sheldrick, *SADABS*, Program for empirical absorption correction, University of Göttingen, Germany, **1996**.

[22] G. M. Sheldrick, *SHELX97*, Program for crystal structure determination, University of Göttingen, Germany, **1997**.

[23] H. D. Flack, *Acta Crystallogr., Sect A*, **1983**, *39*, 876-881.

CHAPTER V

FUNCTIONALIZED μ-VINYLIMINIUM COMPLEXES AS ORGANOMETALLIC LIGANDS

Abstract

The –SPh functionalized vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')=C_\beta(SPh)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R' = Me, **5.5a**; R = Me, R' = Me, **5.5b**; R = Xyl, R' = CH_2OH, **5.5c**; R = Me, R' = CH_2OH, **5.5d**; Xyl = 2,6-$Me_2C_6H_3$] are generated in high yields by treatment of the corresponding vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')=C_\beta(H)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**4.5a-d**) with NaH in the presence of PhSSPh. The molecular structures of **5.5c** and **5.5d** have been determined by X-ray diffraction studies.

The –SPh functionalized vinyliminium **5.5a-d** react with $NaBH_4$, in THF solution, affording the corresponding μ-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')C_\beta(SPh)=C_\alpha(H)N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**6.5a-d**). The reaction transforms the iminium into an amine group, generating a N donor functionality. Consequently, the bridging organic frames in **6.5a-d**, containing S and N donor atoms, act as ambidentate ligands towards coordinatively unsaturated metal fragments. In particular, the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')C_\beta(SPh)=C_\alpha(H)NMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R' = Me, **6.5b**; R' = CH_2OH, **6.5d**) react with $[PdCl_2(CH_3CN)_2]$ to give $[PdCl_2(\kappa^2\text{-}N,S\text{-}\mathbf{6.5b})]$ (**7.5a**) and $[PdCl_2(\kappa^2\text{-}N,S\text{-}\mathbf{6.5d})]$ (**7.5b**), respectively. The molecular structure of **7.5b** has been determined by X ray diffraction studies.

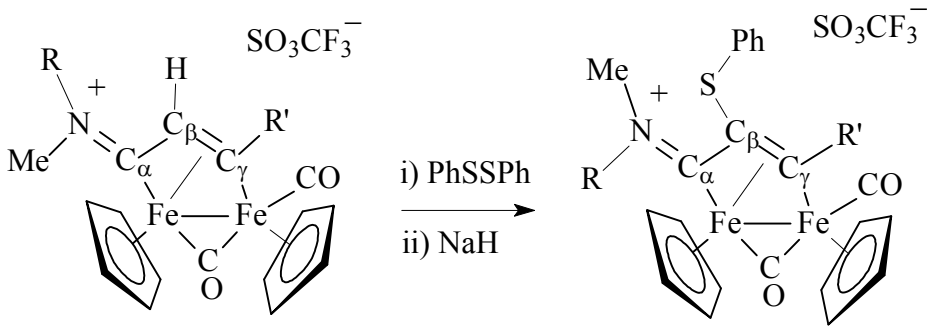
In an analogous reaction compound **6.5d** acts as 'organometallic ligand' with respect to the unsaturated rhodium fragment generated upon treatment of $[Rh(NBD)Cl]_2$ (NBD = norbornadiene), with $AgClO_4$. The reaction affords the trinuclear complex $[Rh(NBD)(\kappa^2\text{-}N,S\text{-}\mathbf{6.5d})][ClO_4]$ (**8.5**).

In the zwitterionic complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(CH_2OH)=C_\beta(S)C_\alpha=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**3.5**) the bridging ligand contains an OH group in addition to the N and S functionalities. The bridging frame can act as an O,S bidentate ligand, in that the N atom in the iminium group has no donor ability. The reaction of **3.5** with $[Ti(Cp)_2(CH_3CN)_2][SO_3CF_3]_2$ leads to the formation of the adduct $[Ti(Cp)_2(\kappa^2\text{-}O,S\text{-}\mathbf{3.5})][SO_3CF_3]_2$ (**9.5**) in which the diiron complex acts as O,S bidentate organometallic ligand.

Results and discussion

5.1. Synthesis of –SPh functionalized bridging vinyliminium diiron complexes

The vinyliminium complexes **4.5a-d** react with NaH, in THF at room temperature, in the presence of PhSSPh, affording the corresponding phenylthiolate vinyliminium complexes **5.5a-d** in about 70-80% yields (Scheme 5.1).



	R	R'	
4.5a	Xyl	Me	**5.5a**
4.5b	Me	Me	**5.5b**
4.5c	Xyl	CH_2OH	**5.5c**
4.5d	Me	CH_2OH	**5.5d**

Scheme 5.1

Complexes **5.5a-d** were purified by alumina chromatography and characterized by spectroscopy and elemental analysis. Moreover, the molecular structures of **5.5c** and **5.5d** have been ascertained by X ray diffraction studies: the ORTEP molecular diagrams are shown in figures 5.1 and 5.2, whereas the most relevant bond distances and angles are reported in Table 5.1, where they are compared with a typical C_β substituted vinyliminium complex, *i.e. cis*-[Fe_2{μ-η^1:η^3-C_γ(Me)=C_β(Me)C_α=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (**III**) [1b]. A hydrogen bond exists in both structures between the C_γ-CH_2OH hydroxo group and one oxygen atom of the $[CF_3SO_3]^-$ anion [O(1)···O(10)#1 2.833(10) Å, O(1)-H(100) 0.832(11) Å, H(100)···O(10)#1 2.07(5) Å, O(1)-H(100)-O(10)#1 153(11)° for **5.5c**; O(1)···O(10)#1 2.861(13) Å, O(1)-H(1A) 0.81(2) Å, H(1A)···O(10)#1 2.07(3) Å, O(1)-H(1A)-O(10)#1 164(8)° and O(1)···O(30')#1 2.681(16) Å, O(1)-H(1A) 0.81(2) Å, H(1A)···O(30')#1 2.01(6) Å, O(1)-H(1A)-O(30')#1 140(8)° for **5.5d**]. As it can be evinced from Table 5.1, the bonding parameters for both **5.5c** and **5.5d** are in perfect agreement with those previously reported for other vinyliminium complexes bearing a substituent on C_β, [1b, 2, 3] confirming the usual μ-η^1:η^3-coordination to the diiron frame of the unsaturated C_3 unit. Moreover, in keeping with previous findings, the N-substituents in **5.5c** adopt the *Z* configuration in order to avoid steric repulsion with the –SPh group.

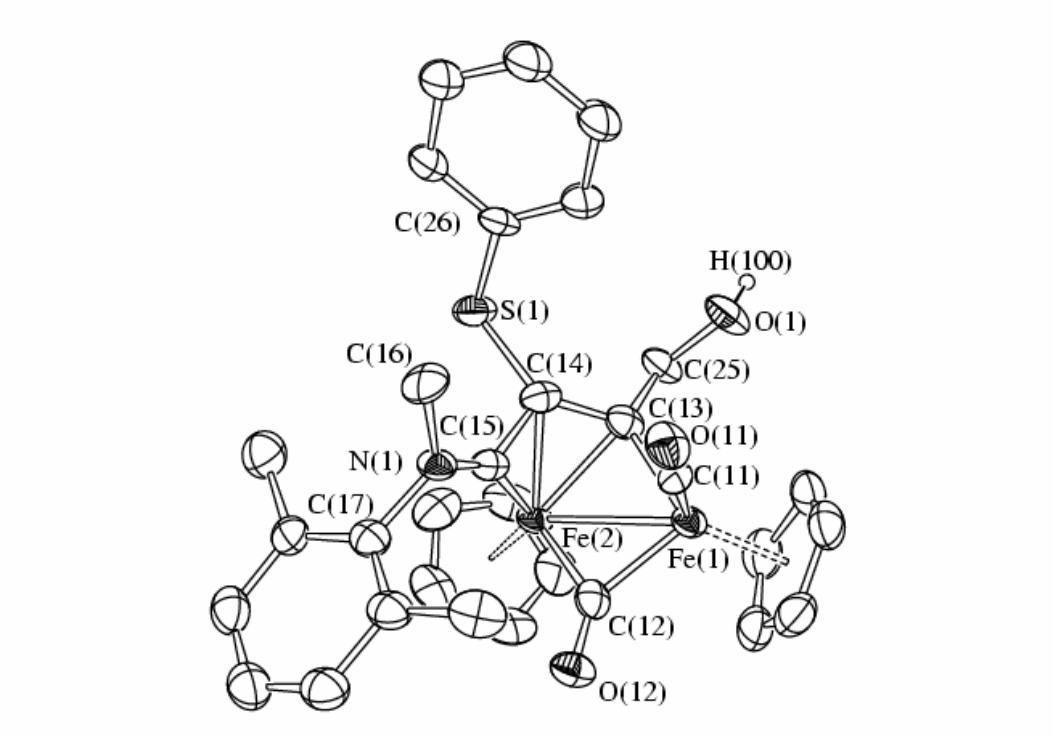


Figure 5.1 Molecular structure of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(CH_2OH)\text{=}C_\beta(SPh)C_\alpha\text{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**5.5c**), with key atoms labeled (all H-atoms, except H(100), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

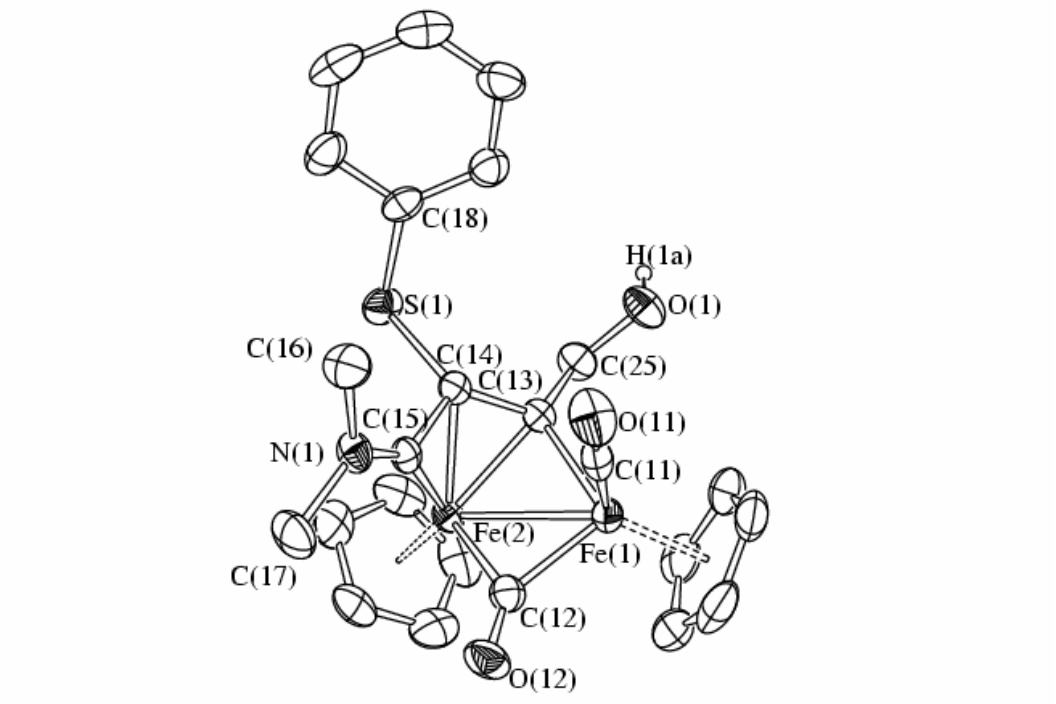
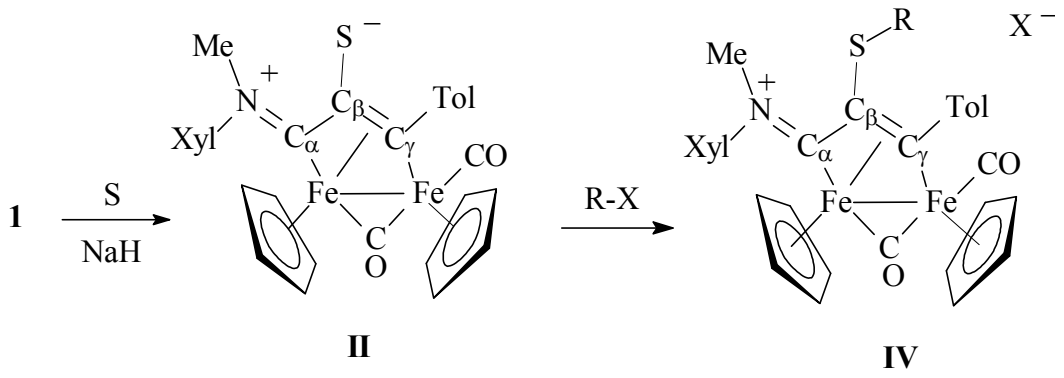


Figure 5.2 Molecular structure of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(CH_2OH)\text{=}C_\beta(SPh)C_\alpha\text{=}N(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**5.5d**) with key atoms labeled (all H-atoms, except H(1a), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

Table 5.1. Selected bond lengths (Å) and angles (°) for **5.5c** and **5.5d**. The most relevant bonding parameters of the C_β substituted vinyliminium complex *cis*-[Fe_2{μ-η^1:η^3-C_γ(Me)=C_β(Me)C_α=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (**III**) [1b] are reported as well for sake of comparison.

	5.5c	**5.5d**	**III**
Fe(1)-Fe(2)	2.558(2)	2.5460(11)	2.562(1)
Fe(1)-C(11)	1.742(12)	1.763(7)	1.750(9)
Fe(1)-C(12)	1.877(11)	1.891(6)	1.894(8)
Fe(2)-C(12)	1.961(11)	1.965(6)	1.944(8)
Fe(1)-C(13)	1.944(10)	1.959(5)	1.955(7)
Fe(2)-C(13)	2.051(10)	2.032(5)	2.035(7)
Fe(2)-C(14)	2.044(10)	2.034(5)	2.080(7)
Fe(2)-C(15)	1.868(12)	1.841(5)	1.839(7)
C(11)-O(11)	1.144(11)	1.134(8)	1.150(9)
C(12)-O(12)	1.195(10)	1.164(7)	1.181(9)
C(13)-C(14)	1.447(12)	1.428(8)	1.39(1)
C(14)-C(15)	1.454(13)	1.433(7)	1.43(1)
C(13)-C(25)	1.511(12)	1.509(7)	
C(25)-O(1)	1.399(10)	1.413(8)	
C(14)-S(1)	1.795(10)	1.800(5)	
C(15)-N(1)	1.279(11)	1.287(7)	1.314(8)
N(1)-C(16)	1.479(11)	1.450(8)	1.478(9)
N(1)-C(17)	1.452(12)	1.472(8)	1.454(8)
C(14)-C(13)-Fe(1)	119.0(8)	119.0(4)	121.8(5)
C(13)-C(14)-C(15)	117.4(10)	116.2(5)	155.5(6)
N(1)-C(15)-C(14)	133.4(10)	133.7(5)	131.3(7)
O(1)-C(25)-C(13)	107.5(8)	107.4(5)	
Sum angles at N(1)	359.3(16)	359.9(9)	360.0(9)

The overall result of the reaction shown in Scheme 5.1 consists in the replacement of the C_β-H hydrogen with the SPh group. It should be noted that an alternative route to the introduction of a thiolate functionality in the bridging ligand is provided by two distinct reaction steps: a) generation of the zwitterionic species **II**; b) alkylation of the S atom (Scheme 5.2) [3].



RX = $MeSO_3CF_3$; Me_3SiCl, CH_2CHCH_2I, $PhCH_2Br$

Scheme 5.2

Compared to the latter procedure, the reaction with PhSSPh has the advantage of being a direct, single step synthesis, although it is limited to the introduction of the SPh functionality.

Concerning the spectroscopic properties of **5.5a-d**, these are consistent with the structures found in solid and very similar to those of the complexes of type **IV,** recently reported [3]. In particular, the IR spectra of **5.5a-d** show the usual ν-CO band pattern consisting of two absorptions due to the terminal and bridging carbonyls (*e.g.* for **5.5a** at 1986 and 1826 cm^{-1}, respectively), and one additional absorption attributed to the C_α-N interaction (*e.g.* for **5.5a** at 1612 cm^{-1}). The NMR spectra, in $CDCl_3$ solution, reveal the presence of a single isomeric form. NOE studies carried on **5.5a** and **5.5c** indicate that the N-substituents adopt the *Z* configuration, with the steric demanding Xyl group pointing far from the C_β-substituent, as shown in solid (**5.5c**), and usually found in related vinyliminium complexes. It should be noted that the precursors **4.5** display the opposite *E* configuration and, therefore, the reactions must be accompanied by inversion of configuration at the iminium moiety.

Major features in the ^{13}C NMR spectra are given by the resonances due to the C_3 bridging chain, which are similar to the corresponding values of the precursors **4.5a-d**. The lowfield resonances of the C_α and C_γ are consistent with their aminocarbene and bridging alkylidene character, respectively (*e.g.* for **5.5a** at 227.4 and 214.8 ppm, respectively). Conversely, the C_β resonance is found at *ca.* 63 ppm.

The reactions with phenyldisulfide, with formation of **5.5a-d**, deserve some further comments. Most of the reactions between disulfides and metal complexes consist in the oxidative addition with S-S bond cleavage and formation of thiolate ligands. This represents a well established synthetic approach for obtaining thiolate complexes, mostly dinuclear thiolato bridged, providing an alternative and advantageous route to the use of thiolate reagents [4]. Conversely, disulfide cleavage with formation of C-S bond involving coordinated ligands is less common, in spite of the considerable interest towards metal assisted C-S bond formation [5] including, for example, the metal-catalyzed stereoselective additions of disulfides and diselenides to alkynes and olefins [6]. The formation of the complexes **5.5** indicates that cleavage of a disulfide can be exploited to generate a C-S bond and introduce a phenyl thiolate functionality into a coordinated ligand. To the best of our knowledge, there is only one related example in which the SPh functionalization of a Cp ligand in a ferrocenyl complex, was obtained upon reaction with BuLi followed by treatment with PhSSPh [7].

A further consideration concerns the reaction mechanism. Presumably, relevant steps in the reaction sequence are the proton removal from C_β and the consequent reaction with PhSSPh, leading to the reductive cleavage of the S-S bond. However, alternative mechanisms based upon the homolitic cleavage of the disulfide operated by radical intermediate species should not be excluded. Indeed, radical complexes like $[Cr(CO)_3(C_5Me_5)]^{\cdot}$ are known to react with disulfides to generate thiolate derivatives $[Cr(SR)(CO)_3(C_5Me_5)]$ [8]. Likewise, the diiron thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ was described to undergo one electron reduction generating a radical which, in turn, reacted with PhSSPh affording the thiolate complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(SPh)(CO)(Cp)_2]$ and, in minor amount, the dithiocarbene $[Fe_2\{\mu\text{-}C(SMe)(SPh)\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ [9].

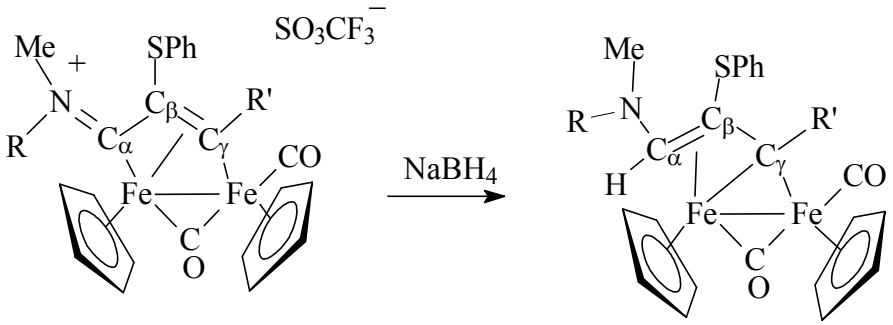
In order to investigate the point and provide possible clues in favor of a radical mechanism, compounds **4.5a-d** were treated with PhSSPh and sodium naphtalenide. The latter is a good one electron reducing agent, therefore it is expected to favor possible radical mechanisms. Unfortunately, the experiments were not conclusive: the reaction products were the same observed in the reactions with NaH, although obtained in lower yields.

The reaction between vinyliminium ligands and PhSSPh, shown in Scheme 5.1, is not general, in that the other vinyliminium complexes, namely $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')=C(H)C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R' = Tol = 4-C_6H_4Me; R = Xyl, R' = $SiMe_3$; R = Me, R' = $SiMe_3$], upon treatment with NaH in the presence of PhSSPh, failed to give the expected phenylthilolate functionalized vinyliminium complexes analogues to **5.5a-d**. Conversely, these reactions afforded the species which are known to be produced when the

corresponding vinyliminium complexes are treated with NaH in the absence of 'trapping reagents' [10]. In other words, these vinyliminium complexes react with NaH, but the deprotonated intermediate evolves without involvement of the disulfide reagent.

5.2. Transformation of –SPh functionalized vinyliminium complexes into chelating ligands

The transformation of the bridging vinyliminium ligand into a chelating frame, potentially able to coordinate further metal centres, has been pursued through the conversion of the iminium group into an effective N donor functionality. This goal has been accomplished by reacting the vinyliminium complexes **5.5a-d**, containing the SPh group, with $NaBH_4$ (Scheme 5.3). Hydride addition occurred at the iminium carbon (C_α) and transformed the vinyliminium complexes into the corresponding enamino-alkylidene complexes **6.5a-d**.



	R	R'	
5.5a	Xyl	Me	**6.5a**
5.5b	Me	Me	**6.5b**
5.5c	Xyl	CH_2OH	**6.5c**
5.5d	Me	CH_2OH	**6.5d**

Scheme 5.3

Nucleophilic addition of hydride (from $NaBH_4$) to the C_α in bridging vinyliminium complexes has been previously described. [11] Therefore, the results reported in Scheme 5.3 were reasonably predictable, although in a number of cases H^- addition has been observed to occur at the C_β instead of C_α. It was previously evidenced that steric arguments largely determine the site of attack: the steric demanding Xyl group, as N-substituent, makes the iminium carbon less accessible to the incoming nucleophile, and directs the hydride attack to the adjacent C_β. Conversely, steric demanding substituents at the C_β favour the attack at the iminium group. [11b] For this reason we

examined a few complexes with different substituents (R and R'), in order to determine which among the steric effects was predominant. Since we exclusively observed H^- addition at the iminium carbon, and complexes **6.5a-d** were obtained in good yields from the readily available type **5.5** complexes, the synthetic approach resulted very effective in producing N,S chelating organometallic ligands.

Complexes **6.5a-d** have been purified by chromatography on alumina and characterized by spectroscopy and elemental analysis.

The spectroscopic properties of **6.5a-d** closely resemble those of analogous enamino-alkylidene complexes previously reported. [11] The IR spectra exhibit the usual ν–CO band pattern consisting of two absorptions due to the terminal and bridging CO (e.g. at 1929, 1753 cm^{-1} for **6.5a**), that are shifted of about 60 cm^{-1} to lower frequencies compared to those of the parent cationic complexes.

The NMR spectra, in $CDCl_3$ solution, evidence the presence of a single isomer indicating that hydride addition is regio- and stereo-specific. The upfield shifted resonance assigned to the $C_\alpha H$ (*e.g.* at 0.98 ppm for **6.5a**) is consistent with the corresponding values in analogous enamino-alkylidene complexes previously reported. [11] These similarities indicate that **6.5a-d** adopt the same geometry with the NMe(R) group pointing far from the metal centre and the C_α-H "trans" with respect to the SPh group. In compounds **6.5b** and **6.5d** the two N bonded methyls give rise to a single signal. Their equivalence is due to fast rotation around the C_α-N bond (on the NMR timescale) at room temperature, indicating that there is not π-interaction between the two atoms and that the NMe_2 group has an amine character.

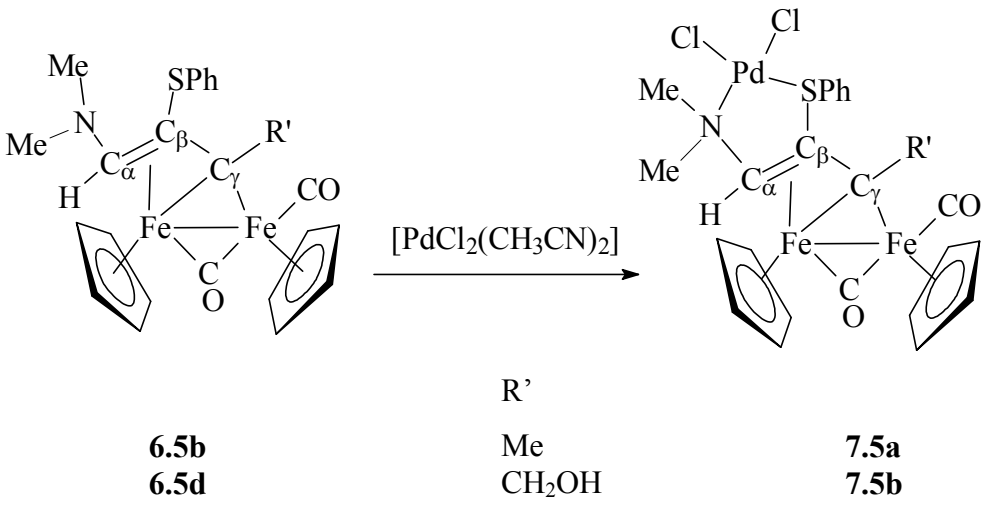
The ^{13}CNMR spectra of **6.5a-d** show resonances attributable to the C_α, C_β and C_γ carbons in the expected range (*e.g.* for **6.5a** at 107.5, 68.9 and 190.9 ppm, respectively). In particular, the C_γ resonance appears downfield shifted, in agreement with its μ-alkylidene character.

5.3. Coordination of the organometallic complexes to Pd(II), Rh(I) and Ti(IV)

The transformation of the iminium into an enamine makes the N(Me)R group available for metal coordination. The bridging frames in complexes **6.5** display N and S functionalities potentially able to act as ambidentate ligands. It should be remarked that the combination of chemically diverse donor fragments is of particular interest, in that it is expected to influence the reactivity properties of the associated metal fragment in a way different to that produced by chelating ligands with identical donor groups. [12] Among the number of different transition metal

elements which should be coordinated by the N and S atoms of the complex **6.5**, we initially investigated palladium, in consideration of the increasing interest with respect to Pd complexes displaying chelating ligands based on N,S donor atoms. [13] Indeed, Pd complexes containing heterodifunctional bidentate ligands that present hard (N) and soft (S) donors have shown interesting applications in the field of homogeneous catalysis, [14] medicinal chemistry [15] and mesomorphic materials. [16]

We have found that compounds **6.5b** and **6.5d** react with $[PdCl_2(CH_3CN)_2]$, in CH_2Cl_2 solution at room temperature, to give the trinuclear species $[PdCl_2(\kappa^2\text{-N,S-}\mathbf{6.5b})]$ (**7.5a**) and $[PdCl_2(\kappa^2\text{-N,S-}\mathbf{6.5d})]$ (**7.5b**), respectively (Scheme 5.4).



	R’	
6.5b	Me	**7.5a**
6.5d	CH_2OH	**7.5b**

Scheme 5.4

Complexes **7.5a-b** have been characterized by IR and NMR spectroscopy and elemental analysis. Moreover, the molecular structure of **7.5b·CH₃CN** has been determined by X-ray diffraction studies (Figure 5.3 and Table 5.2). The molecular structure of **7.5b** can be viewed as the result of S, N-coordination of a *cis*-$PdCl_2$ fragment to the enamino-alkylidene compound **6.5d**. For sake of comparison, the bonding parameters of **7.5b** are compared in Table 5.2 with structurally characterized enamino-alkylidene complexes such as $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Tol)CH=CHNMe}_2\}(\mu\text{-CO})(CO)(Cp)_2]$ (**I**) and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Me)C(Me)=CHN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(Cp)_2]$ (**II**). The coordination around the Pd-center is perfectly square-planar, with mean deviation from the least-squares plane of 0.0333 Å and sum angles at Pd(1) of 360.0(3)°. As the main result of Pd-coordination to the S and N functionalities of the enamino-alkylidene fragment, N(1) completely looses its planarity and becomes sp^3 hybridised [average C-N(1)-C angles are *ca* 107°] and C(15)-N(1) is considerably elongated as expected for a pure single bond [1.490(9) Å in **7.5b** to be

compared with 1.375(8) and 1.398(3) Å in **I** and **II**]. Moreover, the C(13)-C(14) [1.430(10) Å] and C(14)-C(15) [1.430(10) Å] interactions become identical within experimental errors, suggesting an allyl-like coordination to the iron centers.

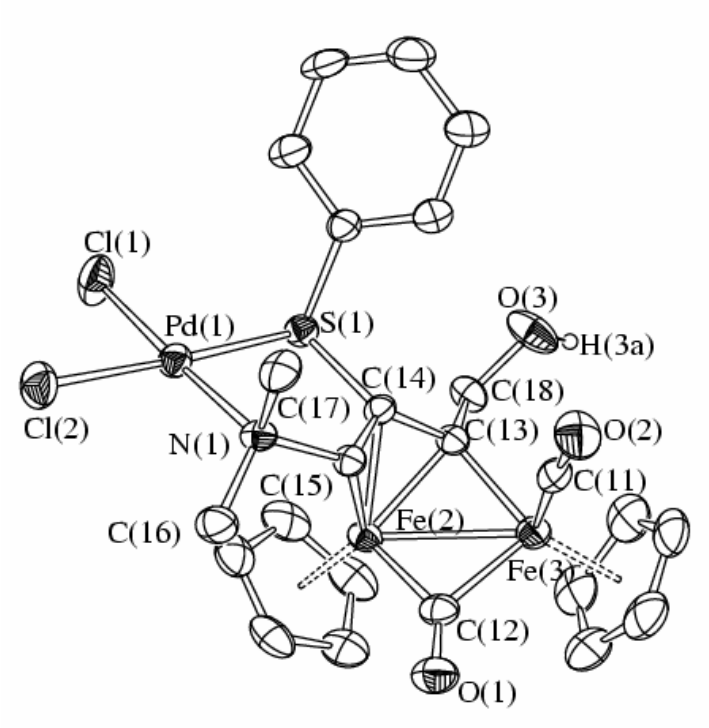


Figure 5.3 Molecular structure of **7.5b**, with key atoms labelled (all H-atoms, except H(3a), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

Table 5.2

Comparison of relevant bond lengths (Å) in **7.5b** and related enamino-alkylidene complexes.

	7.5b	**I**	**II**
Fe(2)-Fe(3)	2.5482(17)	2.555(1)	2.5260(5)
Fe(3)-C(11)	1.755(10)	1.729(6)	1.733(3)
C(11)-O(2)	1.125(11)	1.157(7)	1.149(4)
Fe(2)-C(12)	1.921(9)	1.849(7)	1.851(3)
Fe(3)-C(12)	1.941(9)	2.012(6)	1.983(3)
C(12)-O(1)	1.152(10)	1.183(7)	1.192(3)
Fe(2)-C(13)	1.981(8)	1.979(6)	1.968(3)
Fe(3)-C(13)	1.950(8)	1.977(6)	1.979(2)

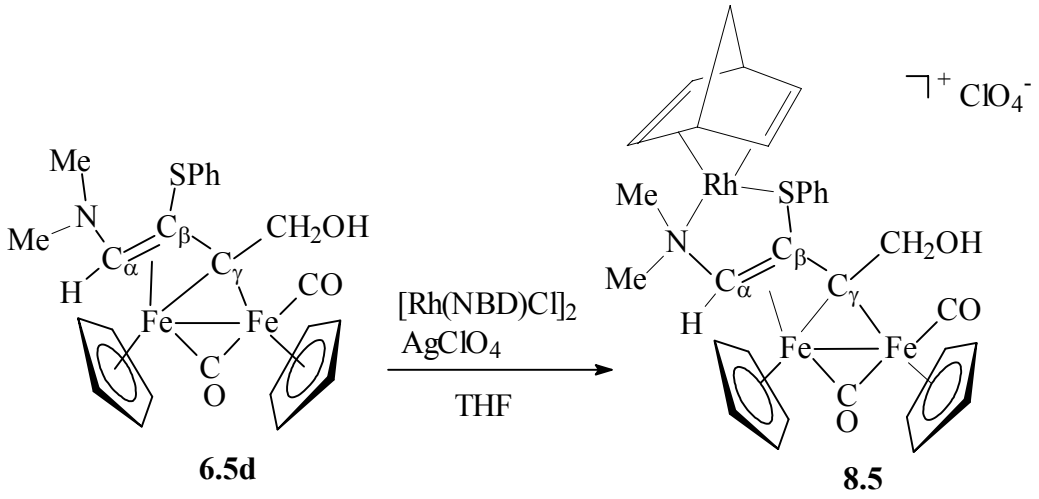
Fe(2)-C(14)	2.004(8)	2.070(6)	2.082(3)
Fe(2)-C(15)	2.062(7)	2.299(6)	2.201(3)
C(13)-C(14)	1.430(10)	1.441(8)	1.433(4)
C(14)-C(15)	1.430(10)	1.408(5)	1.413(4)
C(15)-N(1)	1.490(9)	1.375(8)	1.398(3)
C(14)-S(1)	1.795(8)	–	–
Pd(1)-N(1)	2.067(6)	–	–
Pd(1)-S(1)	2.255(2)	–	–
Pd(1)-Cl(1)	2.305(3)	–	–
Pd(1)-Cl(2)	2.306(2)	–	–

The spectroscopic data are consistent with the structure found in solid. In particular, the NMR spectra, in acetone solution, show only one set of resonances indicating the presence of a single isomer in solution which, presumably, adopts the same conformation observed in solid. The coordination of Pd(II) does not modify significantly the structure of the C_3 bridging ligand that exhibit ^{13}C NMR resonances in the usual range (*e.g.* for **7.5a** at 94.9, 85.2 and 191.8 for C_α, C_β and C_γ, respectively). Compared to the parent complexes **6.5b** and **6.5d**, the trinuclear species **7.5a-b** show, in their ^1H NMR spectra, distinct resonances for the N bound methyls. This is the consequence of Pd coordination through the NMe_2 group which does not allow rotation around the C_α-N bond.

Attempts to extend the reaction and obtain the coordination of the Pd frame with the complexes **6.5a** and **6.5c** have been unsuccessful. These latter differ from **6.5b** and **6.5d** in that they display a Xyl group (Xyl = $2,6Me_2C_6H_3$) in the place of a methyl as N-substituent. The lack of coordination properties for **6.5a** and **6.5c** are presumably the consequences of the steric hindrance of the Xyl group.

Further studies were directed to the coordination of rhodium. Likewise palladium, rhodium is one of the most used transition metal in homogeneous catalysis and the number of complexes so far investigated is huge. Nevertheless, the synthesis of new ambidentate ancillary ligands is a persistent goal, and includes the design of new N,S ligands in order to provide the most appropriate steric and electronic coordination properties. [17]

The complex $[Rh(NBD)Cl]_2$ (NBD = norbornadiene), commonly used as precursor of square planar Rh(I) complexes, has been treated with $AgClO_4$, in THF solution, in order to remove chloride ions and generate a coordinatively unsaturated species reactive towards **6.5d**. The procedure yielded the trinuclear complex $[Rh(NBD)(\kappa^2\text{-N,S-}\mathbf{6.5d})][ClO_4]$ (**8.5**) (Scheme 5.5).



6.5d **8.5**

Scheme 5.5

Compound **8.5** is stable in the solid state, but slowly decomposes in solution (acetone, CH_3CN or CH_3NO_2). This behaviour contributed to the failure of our efforts to obtain suitable crystals for X-ray diffraction.

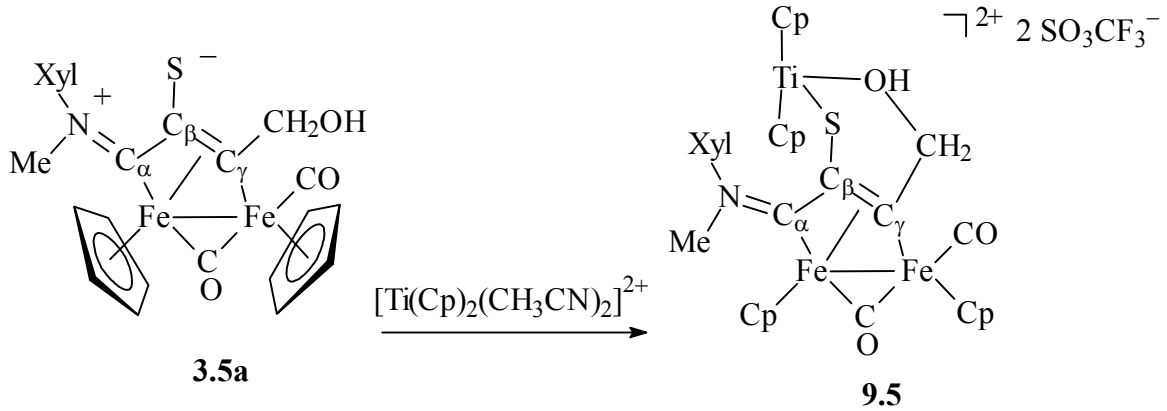
Complex **8.5** was characterized by analytical and spectroscopic techniques. NMR data show one set of signals indicating the presence of one single isomer. The coordination of the Rh(NBD) frame is evidenced by the shift of ^1H and ^{13}C NMR resonances of the norbornadiene ligand, unambiguously identified by bidimensional COSY, HSQC and HMBC experiments. As expected, all hydrogens of the NBD ligand are non-equivalent, with exception of the CH_2 geminal hydrogens. The signals due to the remaining part of the complex (the 'organometallic ligand' **6.5d**) closely resemble those observed in **7.5b**, where the same organometallic ligand is coordinate to Pd. Characteristic features are the non equivalence of the N-methyls and the high-field shifted resonance due to the C_α-H hydrogen suggesting that the coordination mode of **6.5d** is identical in the Pd and Rh complexes. IR absorptions for the terminal and bridging CO move to higher frequencies (ν-CO at 1971 and 1781 *cf.* **6.5d**: ν-CO at 1933 and 1770 cm^{-1}) due to coordination to the cationic rhodium moiety.

Noteworthy, complexes **6.5c** and **6.5d**, containing the CH_2OH group, display a further donor atom (O) in addition to S and N, potentially able to coordinate a metal atom. Therefore the organometallic species **6.5c-d** should also act as tridentate ligands, or as S,O chelating. The observed preference for the N,S chelation with Rh(I) and Pd(II) is the rather obvious consequence of the 'soft' character of the two metal ions, and of steric arguments which make tri-coordination very unlikely.

Attempts to test the coordination ability of the OH group would require a different and more oxophilic transition metal, like titanium. In particular, the species we decided to study were $[Ti(Cp)_2Cl_2]$ and $[Ti(Cp)_2(CH_3CN)_2][SO_3CF_3]_2$. Interest towards the coordination of a titanocene frame came also from the fact that titanocene dichloride and its derivatives have emerged as important new antitumoral agents, and that much attention is directed to investigate the replacement of chlorides with amino acids ligands (essentially N,O and S ligands) in order to elucidate the mechanisms for delivery of Ti to cancer cells. [18]

Unfortunately, attempts to coordinate $TiCp_2$ to the species **6.5c** and **6.5d** were unsuccessful, in that the organometallic ligands resulted unreactive with respect either $[Ti(Cp)_2Cl_2]$ or the solvate-complex $[Ti(Cp)_2(CH_3CN)_2][SO_3CF_3]_2$. However, among the 'organometallic ligands' mentioned in this paper, the zwitterionic compounds of type **3.5** appear to be better candidates, at least compared to **6.5c** and **6.5d**, to produce O,S coordination for the following reasons: i) the $C_\alpha N(Me)(R)$ group displays some aminocarbene character and, consequently, the N atom has reduced donor properties; ii) the zwitterionic nature of the ligand assigns the negative charge to the S atom, which becomes a good donor. The overall result should favour the chelating S,O *vs.* the N,S coordination.

On the light of these considerations, we studied the reaction of **3.5a** with $[Ti(Cp)_2(CH_3CN)_2]$, generated from $[Ti(Cp)_2Cl_2]$ upon treatment with $Ag(SO_3CF_3)$ in CH_3CN solution. The reaction formed the trinuclear complex **9.5** (Scheme 5.6).



3.5a **9.5**

Scheme 5.6

Complex **9.5** has been identified on the basis of elemental and spectroscopic analyses. Unfortunately, attempts to grow crystal suitable for X- ray diffraction were unsuccessful. Therefore, the molecular geometry shown in Scheme 5.6 is tentatively proposed upon the spectroscopic data and on the following considerations.

Chelation rather than mono-coordination of the $TiCp_2$ unit is likely to occur and involve the S atom: indeed dithiolate ligands [19] as well as mixed ambidentate ligands (P,S) [20] and (N,S) [21] are known to coordinate the Cp_2Ti unit. Analogies can be envisaged also with the anionic Fischer-type carbene complex $[(CO)_5Cr{=}C(R)O]^-$ (R = thiazolyl), that has been found to act as bidentate (N,O) ligand with regard to $TiCp_2$. [22] In this case, similarities include the fact that one coordination site is provided by an oxygen atom and that the ligand is an organometallic compound rather than a simple organic molecule. In complex **9.5**, the non-equivalence of the NMR signals attributable to the Cp ligands bound to Ti is consistent with the bidentate coordination, which provides an unsymmetrical environment to the $TiCp_2$ unit. On the other hand, coordination of $TiCp_2$ involving the N atom is to be excluded for the considerations reported above on the lack of coordination properties of the iminium group in the zwitterionic complex **3.5a**. The iminium group exhibits little changes in the transformation from **3.5a** to **9.5**, as evidenced by the ^{13}C NMR resonance of the C_α carbon, which is observed at 225 ppm, close to the 236 ppm value of the precursor **3.5a**.

Conclusions

The reaction of bridging vinyliminium diiron complexes with NaH, in the presence of PhSSPh, affords a simple, direct approach to the synthesis of phenyl thiolate functionalized vinyliminium complexes. Beside the SPh functionality, the bridging ligands display other functionalities containing heteroatoms: the NMe_2 group and, for some of the complexes, the OH group. Therefore, the bridging ligand should be exploited to coordinate further metal fragments.

The transformation of the bridging vinyliminium ligand into a chelating frame, potentially able to coordinate further metal centres, has been pursued through the conversion of the iminium group into an effective N donor functionality. This goal has been accomplished by reacting the SPh functionalized vinyliminium complexes with $NaBH_4$. Hydride addition occurs at the iminium carbon (C_α) and transforms the vinyliminium complexes into the corresponding enamino-alkylidene complexes. These behave as hetero-bidentate ligands and display chelating properties with respect to Pd and Rh. Moreover, the bridging ligand can also contain OH as oxygen donor functionality, in addition to S and N, making possible a S,O bidentate coordination.

Our results evidence the great versatility of these diiron organometallic species, due to the large number of transformations which can be easily operated at the bridging ligand. A further point to be remarked is the effectiveness of the complexes as bidentate S,N organometallic ligands. These contain hard and soft donors associated with the presence of the diiron backbone with peculiar electronic and steric characteristics. Their combination might provide unusual activation effects on the Pd or Rh complexes, with potential applications in homogeneous catalysis. These possibilities are currently under investigations and will be matter of future reports.

Experimental details

General

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and $^{1}H,^{13}C$ correlation through gs-HSQC and gs-HMBC experiments. [23] NOE measurements were recorded using the DPFGSE-NOE sequence. [24] All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Compounds **3.5a** [25] and **4.5a-d** [1] were prepared by published methods.

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')=C_\beta(SPh)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R' = Me, 5.5a; R = R' = Me, 5.5b; R = Xyl, R' = CH_2OH, 5.5c; R = Me, R' = CH_2OH, 5.5d]

To a solution of **4.5a** (120 mg, 0.190 mmol) in THF (10 mL) were successively added PhSSPh (205 mg, 0.939 mmol) and NaH (46 mg, 1.92 mmol). The mixture was stirred for 20 minutes and then filtered on an alumina pad. Solvent removal and chromatography of the residue on alumina, using methanol as eluent, afforded **5.5a** as a green band. Crystallization from a CH_2Cl_2 solution layered with Et_2O, at –20 °C gave **5.5a** as a green solid. Yield: 99 mg, 70%. Anal. Calc. for $C_{32}H_{30}F_3Fe_2NO_5S_2$: C, 51.84; H, 4.08; N, 1.89. Found: C, 51.96; H, 3.99; N, 1.99. IR (CH_2Cl_2) ν (CO) 1986 (vs), 1826 (s), ν(C_αN) 1612 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.45-7.13 (8 H, Ph and $Me_2C_6\mathit{H}_3$); 5.62, 4.95 (s, 10 H, Cp); 4.10 (s, 3 H, C_γMe); 3.24 (s, 3 H, NMe); 2.56, 2.01 (s, 6 H, $\mathit{Me}_2C_6H_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 250.7 (μ-CO); 227.4 (C_α); 214.8 (C_γ); 211.0 (CO); 140.7 ($C_{ipso\ Xyl}$); 135.1 ($C_{ipso\ Ph}$); 134.0-125.5 (C_{arom}); 92.3, 89.2 (Cp); 63.0 (C_β); 49.7 (NMe); 38.8 ($C_\gamma\mathit{Me}$); 17.9, 17.6 ($\mathit{Me}_2C_6H_3$).

Compounds **5.5b-d** were prepared by the same procedure described for **5.5a**, by reacting **4.5b-d** with PhSSPh/NaH. Crystals of **5.5c** and **5.5d**, suitable for X-ray analyses, were collected by CH_2Cl_2 solutions layered with diethyl ether, at –20 °C.

5.5b (yield: 80%; colour: brown). Anal. Calc. for $C_{25}H_{24}F_3Fe_2NO_5S_2$: C, 46.10; H, 3.71; N, 2.15. Found: C, 46.16; H, 3.64; N, 2.21. IR (CH_2Cl_2) ν(CO) 1988 (vs), 1818 (s), ν(C_αN) 1671 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.37-7.14 (5 H, Ph); 5.50, 4.99 (s, 10 H, Cp); 4.02 (s, 3 H, C_γMe); 3.80, 3.36 (s, 6 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 251.9 (μ-CO); 223.6 (C_α); 211.0, 209.0 (CO and C_γ); 135.1 ($C_{ipso\ Ph}$); 129.8, 127.0, 126.9 (C_{arom}); 90.0, 88.4 (Cp); 63.5 (C_β); 40.0 (C_γ*Me*); 48.1, 44.9 (NMe).

5.5c (yield: 81%; colour: brown). Anal. Calc. for $C_{32}H_{30}F_3Fe_2NO_6S_2$: C, 50.75; H, 3.99; N, 1.85. Found: C, 50.83; H, 4.06; N, 1.84. IR (CH_2Cl_2) ν(CO) 1984 (vs), 1822 (s), ν(C_αN) 1614 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.45-7.21 (8 H, Ph and $Me_2C_6H_3$); 6.72 (br, 1 H, OH); 6.21, 5.81 (dd, $^2J_{HH}$ = 14.3 Hz, $^3J_{OH}$ = 2.9 Hz, 2 H, CH_2OH); 5.61, 4.90 (s, 10 H, Cp); 3.18 (s, 3 H, NMe); 2.57, 2.02 (s, 6 H, *Me*$_2$C$_6$H$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 251.5 (μ-CO); 226.9 (C_α); 219.2 (C_γ); 211.1 (CO); 140.6 ($C_{ipso\ Xyl}$); 135.7 ($C_{ipso\ Ph}$); 134.1-126.1 (C_{arom}); 91.6, 88.5 (Cp); 73.0 (CH_2); 62.9 (C_β); 50.0 (NMe); 18.0, 17.7 (*Me*$_2$C$_6$H$_3$).

5.5d (yield: 80%; colour: green). Anal. Calc. for $C_{25}H_{24}F_3Fe_2NO_6S_2$: C, 45.00; H, 3.63; N, 2.10. Found: C, 45.06; H, 3.71; N, 2.04. IR (CH_2Cl_2) ν(CO) 1991 (vs), 1815 (s), ν(C_αN) 1670 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.37-7.14 (5 H, Ph); 5.91, 5.83 (dd, 2 H, $^2J_{HH}$ = 11 Hz, CH_2OH); 5.42, 5.04 (s, 10 H, Cp); 5.17 (br, 1 H, OH); 3.83, 3.41 (s, 6 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 253.5 (μ-CO); 222.8 (C_α); 210.5, 209.5 (CO and C_γ); 135.6 ($C_{ipso\ Ph}$); 129.6, 127.6, 127.0 (Ph); 90.8, 88.0 (Cp); 72.9 (CH_2); 63.9 (C_β); 48.8, 45.6 (NMe).

Synthesis of [Fe_2{μ-η^1-η^3-C_γ(R')C_β(SPh)=Cα(H)N(Me)(R)}(μ-CO)(CO)(Cp)$_2$] (R = Xyl, R' = Me, 6.5a; R = Me, R' = Me, 6.5b; R = Xyl, R' = CH_2OH, 6.5c; R = Me, R' = CH_2OH, 6.5d)

A THF solution (10 mL) of complex **5.5a** (120 mg, 0.162 mmol) was treated with $NaBH_4$ (60 mg, 1.58 mmol), and the resulting mixture was stirred for 30 minutes. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, gave a brown band corresponding to **6.5a**. Yield: 78 mg, 81%. Anal. $C_{31}H_{31}Fe_2NO_2S$ (593.34): calcd. C 62.75, H, 5.27; found: C 62.80, H 5.16. IR (CH_2Cl_2): ν(CO) 1929 (vs), 1753 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.98-6.99 (m, 8H, Ph and Xyl); 4.80 (s, 5H, Cp); 4.32 (s, 5H, Cp); 3.16 (s, 3H, NMe); 2.68 (s, 3H, MeC_6H_3); 2.01 (s, 3H, MeC_6H_3); 0.98 (s, 1H, C_αH). ^{13}C NMR ($CDCl_3$) δ 269.5 (μ-CO); 218.8 (CO); 190.8 (C_γ); 155.0-125.9 (C_{arom}); 107.5 (C_α); 87.9 (Cp); 83.1 (Cp); 68.9 (C_β); 40.1 (NMe); 19.1 (MeC_6H_3); 18.3 (MeC_6H_3).

Complexes **6.5b-d** were obtained by the same procedure described for **6.5a**, by reacting **5.5b** (150 mg), **5.5c** (120 mg) and **5.5d** (150 mg) with $NaBH_4$, respectively.

6.5b Yield: 96 mg, 83%. Anal. $C_{24}H_{25}Fe_2NO_2S$ (503.03): C 57.25, H, 5.01; found: C 57.30, H, 4.99. IR (CH_2Cl_2): ν(CO) 1931 (vs), 1770 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.45-7.05 (m, 5 H, Ph); 4.82 (s, 5 H, Cp); 4.58 (s, 5 H, Cp); 3.92 (s, 3 H, C_γ*Me*); 2.46 (s, 6 H, NMe); -0.10 (s, 1 H, C_α*H*). ^{13}C NMR ($CDCl_3$) δ 271.5 (μ-CO); 217.2 (CO); 185.3 (C_γ); 140.0 (ipso-Ph); 129.0, 126.0, 125.2 (Ph); 95.5 (C_α); 87.4 (Cp); 82.8 (Cp); 83.6 (C_β); 46.6 (NMe); 41.9 (C_γ*Me*).

6.5c Yield: 75 mg, 78%. Anal. $C_{31}H_{31}Fe_2NO_3S$ (609.07): C 61.10, H, 5.13; found: C, 61.04; H, 5.17. IR (CH_2Cl_2): ν(CO) 1934 (vs), 1755 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.01-7.04 (m, 8H, Ph and Xyl); 6.61, 5.49 (m, 2 H, C*H*$_2$OH); 4.85 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.21 (s, 3H, NMe); 2.73 (s, 3H, MeC_6H_3); 1.99 (s, 3H, MeC_6H_3); 1.12 (s, 1H, C_αH). *OH not observed*. ^{13}CNMR ($CDCl_3$) δ 270.1 (μ-CO); 219.0 (CO); 191.5 (C_γ); 154.4-126.2 (C_{arom}); 109.3 (C_α); 88.6 (Cp); 83.8 (Cp); 75.4 (CH_2OH); 69.2 (C_β); 41.2 (NMe); 20.0 (MeC_6H_3); 17.9 (MeC_6H_3).

6.5d Yield: 95 mg, 82%. Anal. $C_{24}H_{25}Fe_2NO_3S$ (519.03): C 55.52, H 4.85; found C 55.63, H 4.73. IR (CH_2Cl_2): ν(CO) 1933 (vs), 1770 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.31-7.07 (m, 5 H, Ph); 6.75, 5.56 (dd, 2 H, $^2J_{HH}$ = 11.1 Hz, $^3J_{OH}$ = 4.5 Hz, C*H*$_2$OH); 4.84, 4.59 (s, 10 H, Cp); 2.46 (s, 6 H, NMe); 0.29 (s, 1 H, C_αH).*OH not observed*. ^{13}C NMR ($CDCl_3$) δ 271.8 (μ-CO); 217.0 (CO); 189.4 (C_γ); 140.3 (ipso-Ph); 129.0, 126.0, 125.1 (Ph); 101.0 (C_α); 87.2, 83.0 (Cp); 85.7 (C_β); 76.6 (CH_2OH); 45.4 (NMe).

Synthesis of [$PdCl_2$(κ^2-N,S-6.5b)] (7.5a) and [$PdCl_2$(κ^2-N,S-6.5d)] (7.5b).

A solution of **6.5b** (R = CH_3) (100 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of [$PdCl_2(CH_3CN)_2$] (52 mg, 0.21 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred at room temperature for 2 h. Removal of the solvent gave a solid residue that was washed Et_2O (3 x 5 mL), and dried under reduced pressure affording **7.5a** as a brown solid**.** Yield: 125 mg, 91%. Anal. $C_{24}H_{25}Cl_2Fe_2NO_2PdS$ (678.87): C 42.42, H 3.71; found C 42.50, H 3.68. IR (CH_2Cl_2): 1964 (CO); 1796 (μ-CO) cm^{-1}.^1H NMR (acetone d_6): 7.96-7.20 (m, 5H, SPh); 5.29 (s, 5H, Cp); 5.23 (s, 5H, Cp); 4.04 (s, 3H, C_γMe); 3.01 (s, 3H, NMe); 2.51 (s, 3H, NMe); -0.52 (s, 1H, C_αH) ppm. ^{13}C NMR (acetone d_6): 264.2 (μ-CO); 214.1 (CO); 191.8 (C_γ); 130.9-127.7 (C_{arom}); 94.9 (C_α); 90.4 (Cp); 87.3 (Cp); 85.2 (C_β); 56.3 (NMe); 55.1 (NMe); 37.2 (C_γMe) ppm.

Compound **7.5b** was obtained by following the same procedure described for **7.5a**, by reacting **6.5d** (100 mg, 0.19 mmol) with $[PdCl_2(CH_3CN)_2]$. Yield: 93%. Anal. $C_{24}H_{25}Cl_2Fe_2NO_3PdS$ (694.87): C 41.45, H 3.63; found C 41.39, H 3.67. IR (CH_2Cl_2): 1966 (CO); 1799 (μ-CO) cm^{-1}. ^1H NMR (acetone d_6): 7.99-7.21 (m, 5H, SPh); 6.25 (m, 1H, C*H*$_2$OH); 5.88 (m, 1H, C*H*$_2$OH); 5.34 (s, 5H, Cp); 5.19 (s, 5H, Cp); 4.73 (br s, 1H, OH); 3.04 (s, 3H, NMe); 2.49 (s, 3H, NMe); -0.59 (s, 1H, C_αH) ppm. ^{13}C NMR (acetone d_6): 264.0 (μ-CO); 214.3 (CO); 191.3 (C_γ); 131.2-127.5 (C_{arom}); 92.4 (C_α); 89.9 (Cp); 86.1 (Cp); 85.5 (C_β); 74.5 (CH_2OH); 56.3 (NMe); 55.8 (NMe) ppm.

Synthesis of [Rh(NBD)(κ^2-N,S-6.5d)][ClO_4] (8.5).

To a THF solution (10 mL) of $[Rh(NBD)Cl]_2$ (45 mg, 0.098 mmol) at room temperature was added $AgClO_4$ (41 mg, 0.20 mmol). The mixture was stirred in the dark for 20 min, then filtered on a celite pad to remove the isoluble AgCl. The resulting yellow solution was then treated with a THF solution (10 mL) of **6.5d** (102 mg, 0.20 mmol) and stirred for 3h at room temperature. Removal of the solvent gave a orange-brown solid that was washed with Et_2O (2 x 5 mL) to give **8.5** (140 mg, 88%). Anal. Calcd for $C_{31}H_{33}ClFe_2NO_7RhS$: C, 45.76; H, 4.06; N, 1.72. Found: C, 45.80; H, 4.04; N, 1.73. IR (THF) ν(CO) 1970.53 (vs), 1780.85 (s). ^1H NMR (acetone-d_6, 400 MHz) δ 7.66-7.40 (m, 5H, SPh); 6.23 (m, 1H, C*H*$_2$OH); 5.88 (m, 1H, C*H*$_2$OH); 5.36 (s, 5H, Cp); 5.24 (s, 5H, Cp); 5.02 (br s, 1H, NBD); 4.84 (br s, 1H, NBD); 4.82 (br s, 1H, NBD); 4.50 (br s, 1H, OH); 4.32 (br s, 1H, NBD); 4.13(br s, 1H, NBD); 4.04 (br s, 1H, NBD); 2.71 (s, 3H, NMe); 2.49 (s, 3H, NMe); 1.45 (m, 2H, NBD); -0.55 (s, 1H, C_αH) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6, 400 MHz) δ 265.9 (μ-CO); 216.9 (CO); 191.6 (C_γ); 131.4-128.8 (C_{arom}); 93.6 (C_α); 90.5 (Cp); 87.7 (C_β); 87.2 (Cp); 74.3 (CH_2OH); 73.4 (CH, NBD); 64.0 (CH_2, NBD); 72.4, 62.3 (CH, 58.6, 51.9, 51.4 (CH, NBD); 51.1 (NMe).

Synthesis of [Ti(Cp)$_2$(κ^2-O,S-3.5a)][SO_3CF_3]$_2$ (9.5).

To a solution of $[Ti(Cp)_2Cl_2]$ (75 mg, 0.30 mmol) in CH_3CN (15 mL) was added $Ag(SO_3CF_3)$ (155 mg, 0.60 mmol). The reaction mixture was stirred for 30 min at room temperature in the dark, and then filtered on a celite pad. The solvent was evaporated under reduced pressure and the solid residue containing $[Ti(Cp)_2(CH_3CN)_2][SO_3CF_3]_2$ was re-dissolved in CH_2Cl_2 (10 mL). Then, a solution of **3.5a** (160 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) was added and the resulting mixture was stirred for 3h. Removal of the solvent gave a brown solid that was washed with Et_2O (3 x 5 mL) to give **9.5**. Yield 250 mg, 83%. Anal. $C_{37}H_{35}F_6Fe_2NO_9S_3Ti$ (1006.96): C 44.11, H 3.50; found: C 44.16, H, 3.45. IR (CH_2Cl_2): ν(CO) 1998 (vs), 1820 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.55-7.20 (m, 3H, $Me_2C_6H_3$); 7.01, 5.80 (d, 2H, $^2J_{HH}$ = 13.8 Hz, C*H*$_2$OH); 6.72 (br s, 1H, OH); 6.53 (s, 5H, TiCp); 6.43 (s, 5H, TiCp); 5.77 (s, 5H, FeCp); 5.12 (s, 5H, FeCp); 3.90 (s, 3H, NMe); 2.77 (s, 3H,

Me$_2$C$_6$H$_3$); 2.03 (s, 3H, *Me*$_2$C$_6$H$_3$). ^{13}CNMR ($CDCl_3$) δ 264.5 (μ-CO); 225.4 (C_α); 212.9 (CO); 193.3 (C_γ); 140.7 ($C_{ipso\ Xyl}$); 133.0 (TiCp); 132.2 (TiCp); 92.5 (FeCp); 91.3 (FeCp); 84.6 (C_β); 76.5 (CH_2OH); 49.5 (NMe); 17.9 (*Me*$_2$C$_6$H$_3$); 17.1 (*Me*$_2$C$_6$H$_3$).

X-ray crystallography

Crystal data and collection details for **5.5c** and **5.5d** are reported in Table 5.3. Crystal data for **7.5b·CH_3CN** are reported in Table 5.4. The diffraction experiments were carried out on a Bruker APEX II (for **5.5c**) and on a Bruker AXS SMART 2000 (for **5.5d** and **7.5b**) diffractometer equipped with a CCD detector using *Mo-Kα* radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [26]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [27]. Hydrogen atoms were fixed at calculated positions and refined by a riding model, except the O-bonded hydrogens in both **5.5c** and **5.5d** which were located in the Fourier map and refined isotropically using the 1.2 fold U_{iso} value of the parent *O*-atom. Restraints were applied to the O-H bonds (DFIX 0.83 0.01 line in SHELX). All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. The crystals of **5.5c** were of very low quality and the data have been cut at low angle; even though the connectivity is certain, bond distances and angles have to be considered with care. Hydrogen bonds exist in the structures of **5.5c** and **5.5d**, between the O(1)-H groups and the oxygen atoms of the triflate anion. Similar *U* restraints were applied to the C-atoms in **5.5c** (s.u. 0.01), **5.5d** (s.u. 0.02, only to the Cp ligands) and **7.5b** (s.u. 0.01). The F- and O-atoms of the $CF_3SO_3^-$ anion (located in a general position) in **5.5d** are disordered; disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group. The CH_3CN molecule in **7.5b** is disordered over two positions. Disordered atomic positions were split and refined isotropically using one occupancy parameter per disordered group. Distances in the disordered CH_3CN molecule were restrained to 1.47 Å and 1.14 Å (s.u. 0.01) for C–C and C–N, respectively.

Table 5.3

Crystal data and experimental details for **5.5c[SO_3CF_3] and 5.5d[SO_3CF_3]**.

Complex	**5.5c**	**5.5d**
Formula	$C_{32}H_{30}F_3Fe_2NO_6S_2$	$C_{25}H_{24}F_3Fe_2NO_6S_2$
*F*w	757.39	667.27
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	11.233(5)	10.302(2)
b, Å	11.463(5)	23.461(5)
c, Å	13.083(6)	11.478(2)
α, °	94.747(5)	90
β, °	98.265(6)	100.65(3)
γ, °	98.950(5)	90
Cell volume, $Å^3$	1637.3(12)	2726.3(10)
Z	2	4
D_c, g cm^{-3}	1.536	1.626
μ, mm^{-1}	1.075	1.279
F(000)	776	1360
Crystal size, mm	0.18 × 0.16 × 0.11	0.22 × 0.15 × 0.11
θ limits, °	1.58 – 23.00	1.74 – 25.55
Reflections collected	8764	25188
Independent reflections	4506 [R_{int} = 0.1602]	5102 [R_{int} = 0.0729]
Data/restraints/parameters	4506 / 163 / 421	5102 / 130 / 353
Goodness on fit on F^2	0.811	1.063
R_1 [$I > 2\sigma(I)$]	0.0577	0.0647
wR_2 (all data)	0.1237	0.1906
Largest diff. peak and hole, $e.Å^{-3}$	0.322 / –-0.353	0.877 / –0.869

Table 5.4

Crystal data and experimental details for **7.5b·CH_3CN**.

Complex	**7.5b·CH_3CN**
Formula	$C_{26}H_{28}Cl_2Fe_2N_2O_3PdS$
Fw	737.56
T, K	291(2)
λ, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	10.592(3)
b, Å	11.572(3)
c, Å	14.675(4)
α, °	68.404(3)
β, °	82.557(4)
γ, °	64.784(3)
Cell Volume, $Å^3$	1512.3(6)
Z	2
D_c, g cm^{-3}	1.620
μ, mm^{-1}	1.809
F(000)	740
Crystal size, mm	0.21×0.16×0.12
θ limits, °	2.09–26.00
Reflections collected	15295
Independent reflections	5891 [R_{int} = 0.0679]
Data / restraints /parameters	5891 / 122 / 332
Goodness on fit on F^2	1.047
R_1 ($I > 2\sigma(I)$)	0.0705
wR_2 (all data)	0.2309
Largest diff. peak and hole, e $Å^{-3}$	1.610 / –1.109

References

[1] (a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, Organometallics 22 (2003) 1326;
(b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 689 (2004) 528.

[2] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Organometallics 26 (2007) 3577.

[3] L. Busetto, M. Dionisio, F. Marchetti, R. Mazzoni, M. Salmi, S. Zacchini, V. Zanotti, J. Organomet. Chem. 693 (2008), 2383.

[4] (a) E. Becker, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 23 (2004) 2876;
(b) M. Md. Hossain, H.-M. Lin, J. Zhu, Z. Lin, S.-G. Shyu, Organometallics 25 (2006) 440;
(c) W.-F. Liaw, C.-H. Hsieh, S.-M. Peng, G.-H. Lee, Inorg. Chim. Acta 332 (2002) 153;
(d) Lee, C.-M.; G.-Y. Lin, C.-H. Hsieh, C.-H. Hu, G.-H. Lee, S.-M. Peng, W.-F. Liaw, J. Chem. Soc., Dalton Trans. (1999) 2393;
(e) W.-F. Liaw, C.-H. Chen, G.-H. Lee, S.-M. Peng, Organometallics 17 (1998) 2370;
(f) F. Y.; Petillon, P. Schollhammer, J. Talarmin, K. W. Muir, Coord. Chem. Rev. 178-180 (1998) 203;
(g) R. F. Lang, T. D. Ju, G. Kiss, C. D. Hoff, J. C. Bryan, G. J. Kubas, Inorg. Chem. 33 (1994) 3899.

[5] (a) K. Matsumoto, H. Sugiyama, J. Organomet. Chem. 689 (2004) 4564;
(b) K. Matsumoto, H. Sugiyama, Acc. Chem. Res. 35 (2002) 915.

[6] (a) I. P. Beletskaya, V. P. Ananikov, Eu. J. Org. Chem. (2007) 3431;
(b) T. Kondo, S. Uenoyama, K.Fujita, T. Mitsudo, J. Am. Chem. Soc. 121 (1999) 482.

[7] H. Seo, H. Park, B.Y. Kim, J. H. Lee, S. U. Son, Y. K. Chung, Organometallics 22 (2003) 618.

[8] T. D. Ju, K. B. Capps, R. F.; Lang, G. C. Roper, C. D. Hoff, Inorg. Chem. 36 (1997) 614.

[9] N. C. Schroeder, R. J. Angelici, J. Am. Chem.Soc. 108 (1986) 3688.

[10] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Organometallics 24 (2005) 2297.

[11] a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, Organometallics 23 (2004) 3348;
b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, J. Organomet. Chem. 690 (2005) 837.

[12] selected examples include: a) P. Braunstein, Chem. Rev. 106 (2006) 134; b) C. S. Slone, D. A. Weinberger, C. A. Mirkin, Prog. Inorg.Chem. 48 (1999) 233; c) A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.

[13] see for example: a) S. Bhattacharyya, M. Pink, J. C. Human, J.M. Zaleski, Polyhedron 25 (2006) 550; b) L. Canovese, F. Visentin, G. Chessa, P. Uguagliati, C. Santo, A. Dolmella, Organometallics 24 (2005) 3297; c) S. Perez, C. Lopez, A. Caubet, R. Bosque, X. Solans, M. Font Bardia , A. Roig, E. Molins, Organometallics 23 (2004) 224; d) R. Contreras , B. Loeb, M. Valderrama, M. Lagos, F. Burgos, P. Ramirez, J. Concepción, J. Organomet. Chem. 689 (2004) 395; e) A. Amoedo, M. Graña, J. Martinez, T. Pereira, M. López-Torres, A. Fernández, J. J. Fernández, J. M. Vila, Eur. J. Inorg. Chem. (2002) 613; f) T. Kawamoto, I. Nagasawa, H. Kuma.Y. Kushi, Inorg. Chem. 35 (1996) 2427; g) H. A. Ankersmit, N.Veldman, A. L. Spek, K. Eriksen, K. Goubitz, K. Vrieze, G. van Koten, Inorg. Chim. Acta 252 (1996) 203.

[14] a) C. Lopez, S. Perez, X. Solans, M. Font-Bardia, A. Roig, E. Molins, P. W. N. M. van Leeuwen, G. P. F. van Strijdonck, Organometallics 26 (2007) 571; b) D. Choudhary, S. Paul, R. Gupta, J. H. Clark, Green Chem. 8 (2006) 479; c) G. Chelucci., D. Muroni, A. Saba, F. Soccolini, J. Mol. Cat. A 197 (2003) 27.

[15] a) F. Shaheen, A. Badshah, M. Gielen, C. Gieck, M. Jamil, D. de Vos, J. Organomet. Chem. 693 (2008) 1117; b) K. Husain, M. Abid, A. Azam, Eur. J. Med. Chem. 42 (2007) 1300.

[16] P. Espinet, E. Garcia-Orodea, J. A. Miguel, Inorg. Chem. 39 (2000) 3645.

[17] selected examples include: a) D. Wechsler, A. Myers, R. McDonald, M. J. Ferguson, M. Stradiotto, Inorg. Chem. 45 (2006) 4562; b) S. Gladiali, G. Loriga, S. Medici, R. Taras, J. Mol. Cat. A, 196 (2003) 27; c) M. Bassetti, A. Capone, L. Mastrofrancesco, M. Salamone, Organometallics 22 (2003) 2535; d) A. J. Souers, T. D. Owens, A. G. Oliver, F. J. Hollander, J. A. Ellman, Inorg. Chem. 40 (2001) 5299; e) C. Pettinari, M. Pellei, G. Cavicchio, M. Crucianelli, W. Panzeri, M. Colapietro, A. Cassetta, Organometallics 18 (1999) 555; f) T. Sielisch, M. Cowie, Organometallics 7 (1988) 707.

[18] a) P. M. Abeysinghe, M. M. Harding, Dalton Trans. (2007) 3474; b) K. Strohfeldta, M. Tackeb, Chem. Soc. Rev. 37 (2008) 1174.

[19] a) H. A. Harris, D. R. Kanis, L.F. Dahl, J. Am. Chem. Soc. 113 (1991) 8602; b) G. Matsubayashi, M. Nakano, H. Tamura, Coord. Chem. Rev. 226 (2002) 143.

[20] K. Matsuzaki, H. Kawaguchi, P. Voth, K. Noda, S. Itoh, H. D. Takagi, K. Kashiwabara, K. Tatsumi, Inorg. Chem. 42 (2003) 5320.

[21] H. Koepf, T. Klapoetke, Chem. Ber. 119 (1986) 1986.

[22] H. G. Raubenheimer, A. du Toit, M. du Toit, J. An, L. van Niekerk, S. Cronje, C. Esterhuysen, A. M. Crouch, Dalton Trans. (2004) 1173.

[23] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, Magn. Reson. Chem. 31 (1993) 287.

[24] K. Stott, J. Stonehouse, J. Keeler, T.L. Hwang, A.J. Shaka, J. Am. Chem. Soc. 117 (1995) 4199.

[25] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Organometallics 25 (2006) 4808.

[26] G. M. Sheldrick, *SADABS*, Program for empirical absorption correction, University of Göttingen, Germany, **1996**.

[27] G. M. Sheldrick, *SHELX97*, Program for crystal structure determination, University of Göttingen, Germany, **1997**.

CHAPTER VI

FUNCTIONALISED FERROCENES FROM [3+2] CYCLOADDITIONS IN BRIDGING VINYLALKYLIDENE DIIRON COMPLEXES

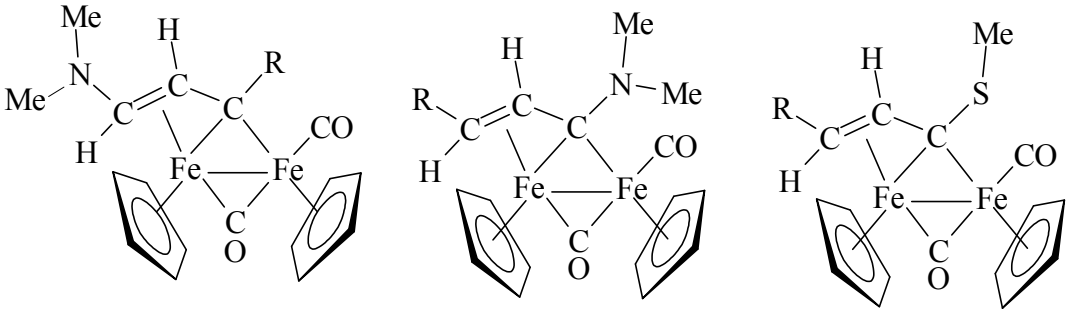
Introduction

Ferrocene containing compounds continue to attract considerable interest, largely due to applications in catalysis and material science.[1] The design of new and more efficient unsymmetrical ferrocenyl ligands or of new ferrocene-based molecular architectures requires access to ferrocene complexes with appropriate substituents, functionalities and pendant ligands on the cyclopentadienyl ring.[2] This might represent a challenge, in that common synthetic methods based upon lithiation of the Cp ring followed by appropriate substitutions, functionalizations and modifications are rather laborious and in some cases ineffective. In particular, the synthesis of ferrocenes in which only one of the two Cp rings contains different substituents,[3] or the introduction of some specific functionalities (e.g. amino groups) remains difficult, in spite of some improvements.[4]

Alternative synthetic methods remain largely unexplored despite of the fact that a number of metal mediated [3+2] cycloadditions are well known[5] which should, in theory, provide more direct routes to the formation of substituted cyclopentadienyl ligands. Few examples are reported in which [3+2] [6] or [1+2+2] [7] cycloadditions of coordinated ligands result in the direct assembling of cyclopentadienyls bearing substituents and functional groups. Even less investigated is the possibility that functionalised cyclopentadienyl complexes might be directly generated by assembling of bridging organic frames (C_2 or C_3 ligands), taking advantage of the activation effects due to multisite coordination.[8]

The assembling of small unsaturated molecules (such as alkenes or alkynes) with bridging carbyne ligands in diiron complexes provides an effective route to the formation of a variety of bridging C_3 ligands containing various functional groups distributed on the alkylidene carbon or on the vinyl end. Examples include the vinylalkylidene (allylidene) complexes **1**,[9] **2** (Chapter III)[10] and **3** (Chapter II)[11] (Scheme 6.1).

We have investigated the reactivity of such ligands with alkynes, in order to verify the possibility that our functionalised vinylalkylidene ligands might be involved in cycloaddition reactions, affording cyclopentadienes or ciclopentadienyl ligands incorporating the same functionalities. We have explored the reactivity of a range of vinylalkylidene complexes with different substituents, as well as a number of different alkynes, in order to elucidate possible factors influencing the reaction course.



	R
1.6a	$SiMe_3$
1.6b	Tol
1.6c	CO_2Me

	R
2.6a	CO_2Me
2.6b	CN

	R
3.6a	CO_2Me
3.6b	CN

Scheme 6.1

The main results can be summarized as follows: reactions of the enaminoalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}CRCHCH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = $SiMe_3$, **1.6a**; Tol, **1.6b**; CO_2Me, **1.6c**, Tol = 4-MeC_6H_4) with terminal alkynes HC≡CR' (R' = CPh_2OH, CO_2Me, Ph) lead to the formation of a mixture of 1,3 disubstituted ferrocenes [1-R-3-R'-Fc] (**5.6**, **7.6**, **9.6**, **11.6**) and 1,2,4 trisubstituted ferrocenes [1-NMe_2-2-R'-4-R-Fc] (**4.6**, **6.6**, **8.6**, **10.6**) (R = $SiMe_3$, R' = CPh_2OH, **4.6** and **5.6**; R = $SiMe_3$, R' = CO_2Me, **6.6** and **7.6**; R = $SiMe_3$, R' = Ph, **8.6** and **9.6**; R = Tol, R' = CPh_2OH, **10.6** and **11.6**). The polysubstituted Cp ring of the ferrocenyl products results from the cycloaddition of the alkyne with the bridging vinylalkylidene ligand. The reaction involves the cleavage of one of the two substituents (H or NMe_2) on the vinyl moiety, as well as of the Fe-Fe bond.

The enaminoalkylidene complex **1.6b** reacts with HC≡CPh yielding a mixture of four different ferrocenes, due to the absence of regioselectivity in the alkyne cycloaddition: [1-NMe_2-2-Ph-4-Tol-Fc] (**12.6**), [1-Tol-3-Ph-Fc] (**13.6**), [1-NMe_2-3-Ph-4-Tol-Fc] (**14.6**) and [1-Tol-2-Ph-Fc] (**15.6**). Conversely, the reactions with symmetric alkynes do not produce regioisomers: treatment of **1.6b** and **1.6c** with R'C≡CR' (R' = Et, Ph) affords a mixture of 1,2,3 trisubstituted ferrocenes [1-R-2-R'-3-R'-Fc] (**17.6**, **19.6**, **21.6**, **23.6**) and tetrasubstituted ferrocenes [1-NMe_2-2-R'-3-R'-4-R-Fc] (**16.6**, **18.6**, **20.6**, **22.6**) (R = $SiMe_3$, R' = Et, **16.6** and **17.6**; R = Tol, R' = Et, **18.6** and **19.6**; R = Tol, R' = Ph, **20.6** and **21.6**; R = CO_2Me, R' = Ph, **22.6** and **23.6**).

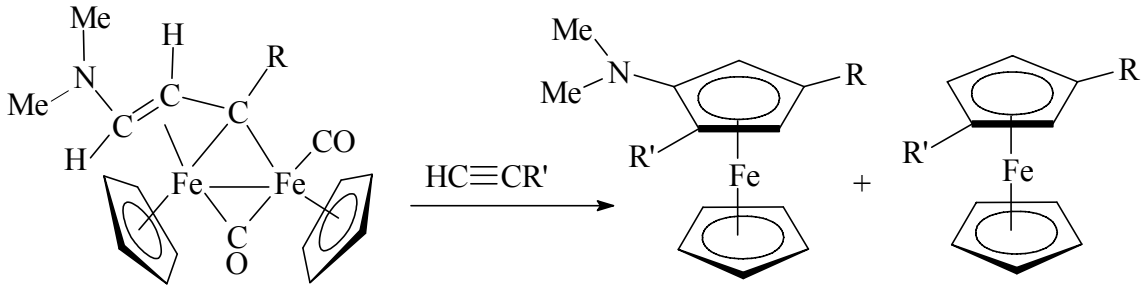
Likewise, the vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(X)CHCH(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = CO_2Me, X = NMe_2, **2.6a**, R = CN, X = NMe_2, **2.6b**, R = CO_2Me, X = SMe, **3.6a**, R = CN, X = SMe, **3.6b**) react with terminal alkynes HC≡CR' (R' = Tol, Ph) yielding a mixture of trisubstituted

ferrocenes [1-X-2-R'-4-R-Fc] (**24.6**, **26.6**, **28.6**) and [1-X-3-R'-4-R-Fc] (**25.6**, **27.6**, **29.6**) (X = NMe_2, R = CO_2Me, R' = Tol, **24.6** and **25.6**; X = NMe_2, R = CN, R' = Tol, **26.6** and **27.6**; X = SMe, R = CO_2Me, R' = Ph, **28.6** and **29.6**). Finally, the reactions of **2.6a** and **3.6b** with PhC≡CPh afford the tetrasubstituted ferrocene **22.6** and [1-SMe-2-Ph-3-Ph-4-CN-Fc] (**30.6**), respectively.

Results and discussion

Cycloaddition reactions of bridging enaminoalkylidene complexes

The bridging enaminoalkylidene complexes **1.6a** and **1.6b** react with primary alkynes (HC≡CR'; R' = CPh_2OH, CO_2Me, Ph) in toluene at refluxing temperature, leading to the formation of a mixture of substituted ferrocenes, as shown in Scheme 6.2.



	R	R'		Yield %		Yield %
1.6a	$SiMe_3$	CPh_2OH	**4.6**	*33*	**5.6**	*54*
1.6a	$SiMe_3$	CO_2Me	**6.6**	*31*	**7.6**	*47*
1.6a	$SiMe_3$	Ph	**8.6**	*28*	**9.6**	*59*
1.6b	Tol	CPh_2OH	**10.6**	*37*	**11.6**	*48*

Scheme 6.2

Separation of the ferrocene products was easily accomplished by column chromatography, and all of the ferrocenyl complexes **4.6-11.6** were characterized by spectroscopy and elemental analysis. Moreover, the molecular structure of **4.6** and **11.6** have been determined by X-ray diffraction studies. The structure of **4.6** (Figure 6.1) is that of a typical ferrocene 1,2,4 tri-substituted on one Cp ring, and with the two Cp rings in a staggered conformation (mean relative rotation 24°). An intra-molecular hydrogen bond exists between the $-NMe_2$ and the $-CPh_2(OH)$ substituents [O(1)-H(50) 0.821(10) Å, H(50)···N(1) 2.027(15) Å, O(1)···N(1) 2.793(2) Å, O(1)-H(50)-N(1) 155(3)°], and this is retained also in solution, as confirmed by the OH resonance at 8.20 ppm in the ^1H NMR spectrum, in $CDCl_3$ solution.

The structure of the ferrocene complex **11.6** (Figure 6.2) shows that the cycloaddition has produced, in this case, a 1,3 di-substituted cyclopentadienyl. Again, the two Cp rings adopt a staggered conformation, being rotated of *ca*. 23°.

Figure 6.1

*ORTEP diagram of **4.6**. All the hydrogens have been omitted except H(50). Selected bond lengths (Å): C(10)-Si(1) 1.855(2), C(7)-C(13) 1.529(3), C(13)-O(1) 1.429(2), O(1)-H(50) 0.821(10), H(50)···N(1) 2.027(15), C(8)-N(1) 1.439(3),Fe(1)-C_5H_5 (av) 2.038(7), Fe(1)-$C_5H_2R_3$ (av) 2.048(6).*

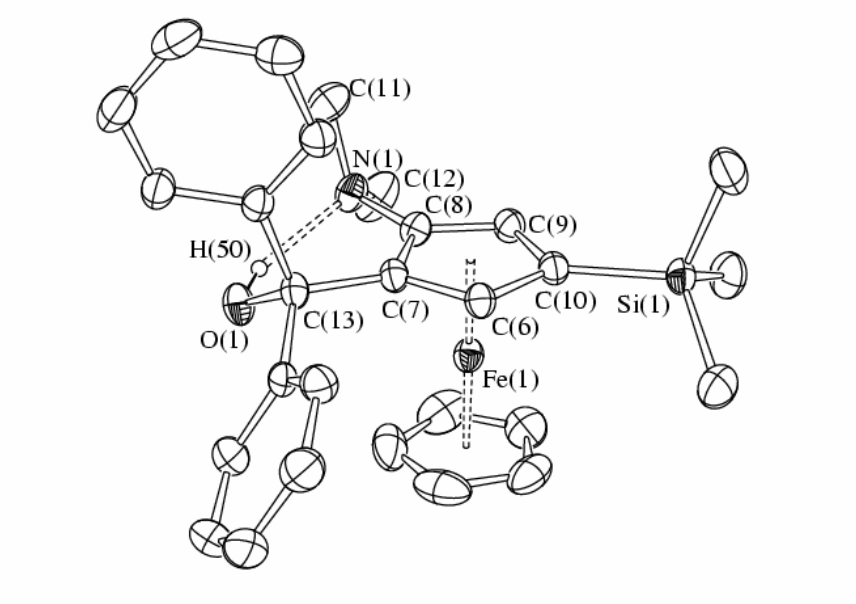
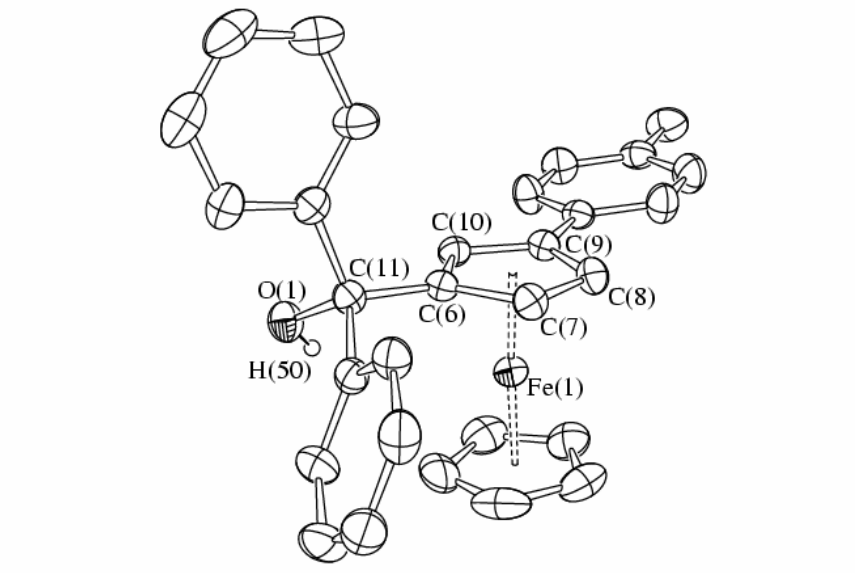


Figure 6.2

*ORTEP diagram of **11.6**. All the hydrogens have been omitted except H(50). Selected bond lengths (Å): C(6)-C(11) 1.512(3), C(11)-O(1) 1.443(2), O(1)-H(50) 0.8200, Fe(1)-C_5H_5 (av) 2.034(7), Fe(1)-$C_5H_3R_2$ (av) 2.041(7).*



The NMR spectroscopic characterization of **4.6-11.6**, based on NOE experiments and $^{1}H,^{13}C$ correlation measured through gs-HSQC and gs-HMBC experiments, is consistent with the structures found in the solid. However, in the ^{1}H NMR spectrum of **4.6**, in $CDCl_3$ solution, the two N-methyls give rise to a single resonance. Their equivalence, on the NMR time scale, is explained assuming an exchange mechanism that implies free rotation of the $Me_2N\text{-}C_{Cp}$ bond and inversion at the N atom, which is in contrast with the hydrogen bond interaction between the OH and NMe_2 observed in the solid. On the other hand, the observed low field resonace at 8.20 ppm attributable to the OH, suggests that the hydroxy group is still involved in a hydrogen bond interaction.

The ^{1}H and ^{13}C NMR spectra of **4.6-11.6** show the presence of only one set of resonances, indicating the regioselective formation of the substituted ferrocenes.

The ferrocene complexes **4.6-11.6** have been also investigated by electrochemical methods. Cyclic voltammograms showed reversible anodic peaks which, in the case of the dimethylamino ferrocenes, are at lower potentials with respect to the ferrocene/ferricinium couple, in agreement with the electron-donor character of the substituent.

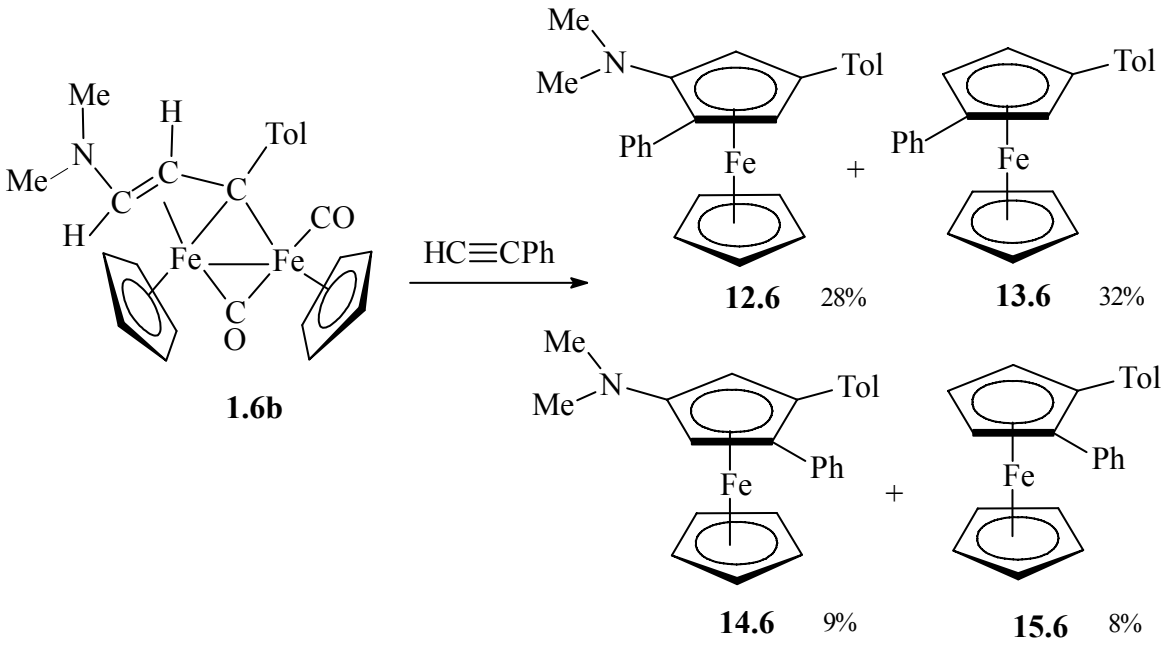
	$E_{1/2}$ (mV)
4.6	241
5.6	400
6.6	292
7.6	442
8.6	104
9.6	417
10.6	274
11.6	422

Table 6.1 Electrochemical data for **4.6-11.6** (10^{-3} M solutions in CH_3CN with $[Bu_4N][PF_6]$ 0.1M; $E_{1/2}$ in mV, referenced to the SCE, at a scan speed υ = 100 mV s^{-1}).

The results reported in Scheme 6.2 went beyond the expected release of the bridging vinylalkylidene ligand in the form of five membered cycloadducts. This latter possibility was suggested by the fact that α-β unsaturated alkylidene ligands are known to undergo cyclization with alkynes, which, beside the classical Dötz reaction, can afford cyclopentadienes as well as other cycloadducts.[12] In our case the [3+2] cyclization is not accompanied by the complete release of the

organic fragment but rather it produces its transformation into a cyclopentadienyl ring, which remains coordinated to one Fe atom.

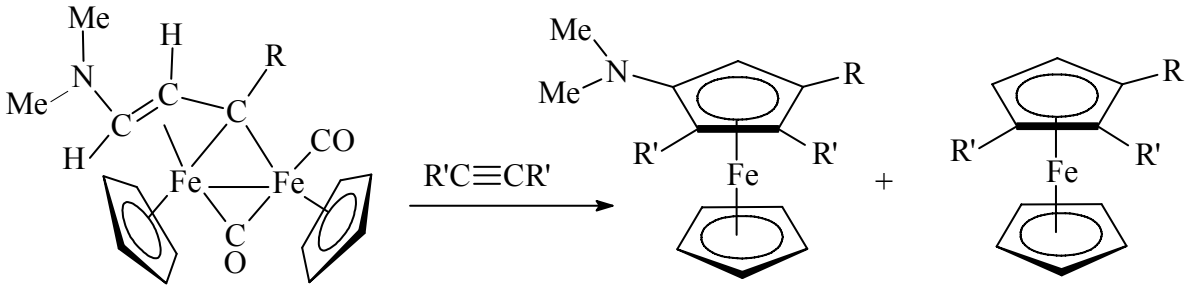
The reaction deserves further comments. First of all the observed ferrocene products are clearly the result of the assembly of the alkynes with the bridging vinylalkylidene ligands. The bridging C_3 frame can be easily recognized as constituent of the functionalised cyclopentadienyl ring, where it retains its substituents, except for those of the vinyl termination. Therefore, the enaminoalkylidene ligands of **1.6a-b** loose one of the two substituents, H or NMe_2, generating the tri-substituted (**4.6**, **6.6**, **8.6**, **10.6**) and di-substituted ferrocenes (**5.6**, **7.6**, **9.6**, **11.6**), respectively. Both possibilities (C-H and C-N cleavage) take place, as indicated by the composition of the reaction products, with a slight predominance of the C-N cleavage. On the other hand, the observed cycloaddition reactions of primary alkynes are regiospecific, in that they occur selectively in one of the two possible modes, affording cyclopentadienyls where the R' group (R' = CPh_2OH, CO_2Me, Ph) are placed far from R (R = $SiMe_3$, Tol). The regioselectivity is presumably originated by steric reasons and is due to the presence of rather hindered substituents (R and R') such as $SiMe_3$ and CPh_2OH. Indeed, the reaction shown in Scheme 6.3, in which the substituents on the C_3 bridging ligand and on the alkyne reagent are less sterically demanding, does not exhibit the same regioselectivity, leading to the formation of all four possible isomers.



Scheme 6.3

In this case the separation of the isomeric mixture by column chromatography was only partially achieved: **12.6** and **14.6** were isolated from **13.6** and **15.6** but the separation of the regioisomers was uncompleted.

An obvious approach to reduce the number of reaction products is to make use of simmetrically disubstituted alkynes, in order to avoid the formation of regioisomers. However, this would add a further substituent on the Cp ring of the ferrocene products and, consequently, might be less favorable because of steric reasons. This point has been investigated through the reactions reported in Scheme 6.4.



	R	**R'**		*Yield %*		*Yield %*
1.6a	$SiMe_3$	Et	**16.6**	*21*	**17.6**	*30*
1.6b	Tol	Et	**18.6**	*35*	**19.6**	*37*
1.6b	Tol	Ph	**20.6**	*29*	**21.6**	*36*
1.6c	CO_2Me	Ph	**22.6**	*30*	**23.6**	*32*

Scheme 6.4

As expected, increasing the number of steric demanding substituents makes the cyclization more difficult and reduces the conversion yield, in particular for R = $SiMe_3$. However, the reaction with symmetric alkynes provides a more valuable synthetic route, since no regioisomers are formed.

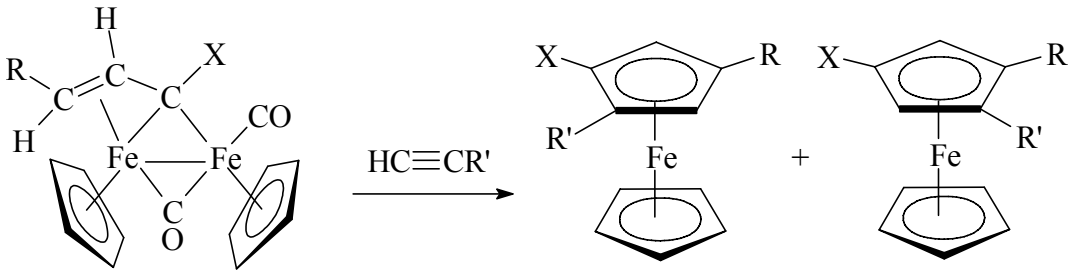
The reactions investigated and the data collected so far are too limited in order to provide a reasonable picture on the mechanism leading to the formation of the functionalized ferrocenes, neither the mechanism proposed so far for ananlogous vinylalkylidene-alkyne coupling in mononuclear complexes can provide realistic suggestions, because of the little overlap between the chemistry of bridging and terminally bonded alkylidenes. In particular, the alkyne insertion into the metal-carbene bond, which is believed to be the first step of the mechanism, appears more difficult to accomplish in the case of bridging alkylidene ligands.

The reaction presumably proceeds through several steps, including the cleavage of the Fe-Fe bond, with fragmentation of the parent dinuclear species, to ultimately yield the observed ferrocene complexes. The synthesis of the substituted ferrocenes is accompanied by the formation of $FeCp_2$,

but in very minor amounts (5-10 % yields). On the other hand, we observe the formation of $Fe_2Cp_2(CO)_4$, probably arising from the coupling of two $Fe(CO)_2Cp$ fragments. Finally, much decomposition is collected at the top of the chromatographic column.

Cycloaddition reactions of bridging vinyl-aminoalkylidene and vinyl-thioalkylidene complexes

The amino-alkylidene complexes **2.6** differ from **1.6** in that the -NMe_2 group is placed on the bridging alkylidene carbon, rather than on the vinyl moiety of the bridging C_3 chain. The same structure is also found in **3.6a**, which exhibits a -SMe group in place of -NMe_2. Beside these differences in the nature and position of the substituents, all the bridging ligands in **1.6**, **2.6** and **3.6** exhibit allylidene character and also react similarly with alkynes, affording ferrocenyl products. Therefore, complexes **2.6** and **3.6** react with alkynes, affording the ferrocene complexes **24.6-29.6** (Scheme 6.5).



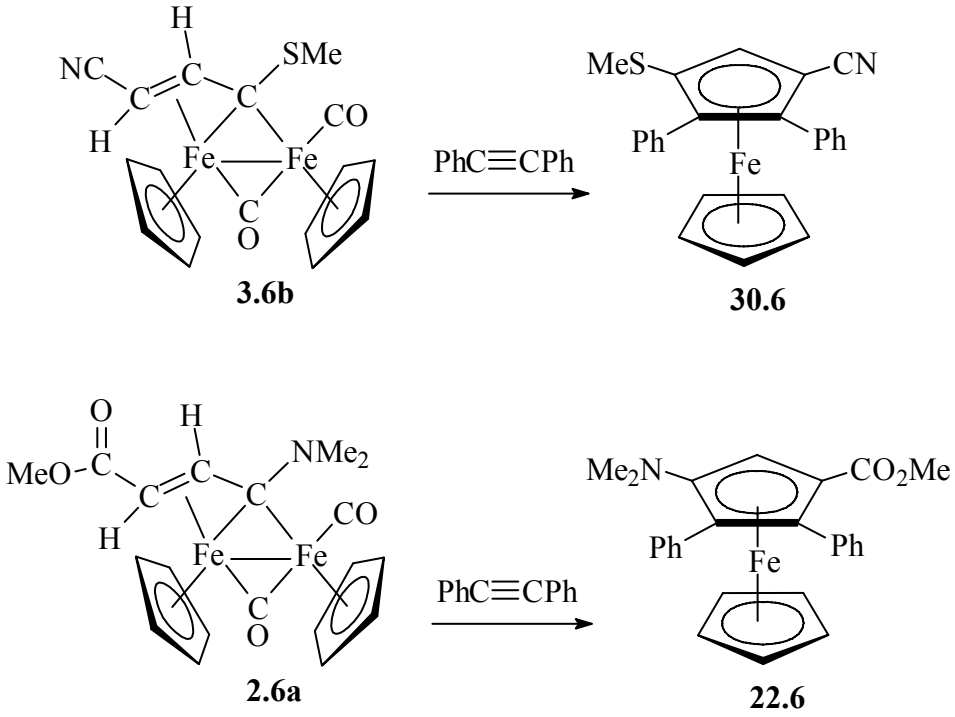
	X	R	R'		*Yield %*		*Yield %*
2.6a	NMe_2	CO_2Me	Tol	**24.6**	*30*	**25.6**	*37*
2.6b	NMe_2	CN	Tol	**26.6**	*31*	**27.6**	*40*
3.6a	SMe	CO_2Me	Ph	**28.6**	*33*	**29.6**	*36*

Scheme 6.5

Comparison with the reactions of **1.6a-b**, shown in Scheme 6.2, evidence that in this case the reaction is not regioselective, and both regioisomers are formed in comparable amounts. Conversely, the most remakable aspect of the reactions of **2.6a-b** and **3.6a** is that cycloaddition is chemoselective and only the C-H and not the C-R bond of the bridging ligands undergoes cleavage. Consequently, the ferrocene products maintain, as substituents, both functional groups that are

present on the μ-allylidene precursor: the alkylidene substituent (NMe_2 or SMe) and the CO_2Me (CN) group. As initially mentioned, this is a relevant point in consideration of the fact that the introduction of several different functionalities, including the NMe_2 group, on the same Cp ring is hard to accomplish by traditional methods starting from unsubstituted ferrocene. Indeed, none of the ferrocene complexes reported in Scheme 6.5 has been previously synthesized.

Again, the use of symmetric alkynes, as shown in Scheme 6.6, greatly simplifies the picture, leading to the formation of one single product, which is a tetrasubstituted ferrocenyl complex.



3.6b **30.6**

2.6a **22.6**

Scheme 6.6

The synthesis of **22.6**, shown in scheme 6.6, should be compared with the corresponding reaction of **1.6c** with PhC≡CPh (Scheme 6.4), that also yields **22.6,** but in mixture with the trisubstituted ferrocene **23.6**. Complexes **1.6c** and **2.6a** are isomers that could be interconverted, formally, by exchanging the position of the NMe_2 and CO_2Me substituents. Therefore, despite their similarities, their reactivity is significatively different and only **2.6a** exhibits a chemoselective character in the cyclization with alkynes. This observation indicates that a proper choice of the substituents, in terms of their nature and position on the bridging vinyl-alkylidene ligand, should provide the key to conduct selectively these cycloaddition reactions.

Conclusions

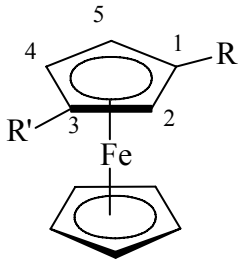
In conclusion the results presented in this chapter indicate that the [3+2] cycloaddition of α,β unsaturated carbene ligands with alkynes can be extended to bridging vinylcarbenes in diiron complexes. The reaction leads to the formation of ferrocenes and has a general character, in that it tolerates different substituents and functional groups on both bridging vinylalkylidenes and alkyne reagents. In most of the cases, the non-selective cleavage of one of the two vinyl substituents on the bridging C_3 ligand, occurring along with the cyclization, gives rise to a mixture of disubstituted and trisubstituted ferrocenyl products. Further isomers are generated, due to the lack of regiocontrol in the cycloaddition of non-simmetric alkynes. However, in other cases, where the cycloaddition reaction is chemoselective, and is associated with use symmetric alkynes, it leads to the formation of one single ferrocenyl product.

These results also suggest that a new and more direct approach to the formation of polyfunctionalised ferrocenes is possible. The limitations due to the absence of a complete chemo- and regio-control of the reaction and the use of rather 'sophisticated' bridging vinylalkylidene complexes as precursors would be compensated by the direct formation of ferrocenes characterized by the presence of 2-3 different substituents in only one of the two cyclopentadienyls. Indeed, ferrocenes of this type are difficult to obtain and, to the best of our knowledge, none of the ferrocene complexes herein reported has been previously synthesized, with the exception of an isomeric form of complex **7.6**, in which the two ring substituents are in adjacent position.[13]

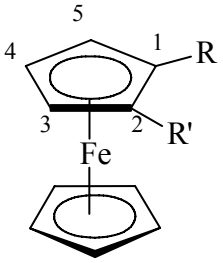
Experimental details

General

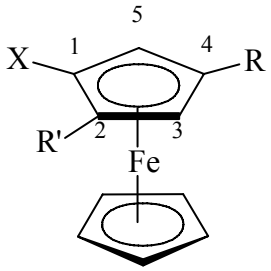
All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of silica gel. Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. ESI MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. All NMR measurements were performed on a Varian Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^1H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments.[14] Unless otherwise stated, NMR spectra were recorded at 298 K; NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. NOE measurements were recorded using the DPFGSE-NOE sequence.[15] NMR resonances are indicated according to the numbering scheme shown hereafter (Scheme 6.7). All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds **1.6a-c**,[9] **2.6a-b**,[10] and **3a-b**[11] were prepared by published methods.



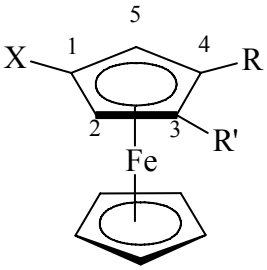
1,3 disubstituted complexes **5.6**, **7.6**, **9.6**, **11.6**, **13.6**
R = $SiMe_3$, Tol



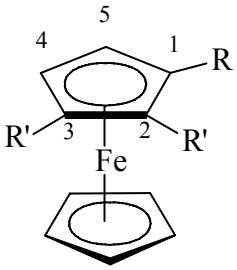
1,2 disubstituted complex **15.6**
R = Tol



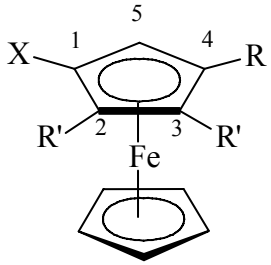
1,2,4 trisubstituted complexes **4.6**, **6.6**, **8.6**, **10.6**, **12.6**, **24.6, 26.6, 28.6**
X = NMe_2, SMe



1,3,4 trisubstituted complexes **14.6**, **25.6**, **27.6**, **29.6**, X = NMe_2, SMe



1,2,3 trisubstituted complexes **17.6**, **19.6**, **21.6**, **23.6** R' = Et, Ph



tetrasubstituted complexes **16.6**, **18.6**, **20.6**, **22.6, 30.6**
X = NMe_2, SMe

Scheme 6.7 (numbering scheme)

Synthesis of the 1,2,4-trisubstituted ferrocene 4.6 and the 1,3-disubstituted ferrocene 5.6

To a solution of **1.6a** (400 mg, 0.883 mmol) in toluene (20 mL) $HC{\equiv}CCPh_2OH$ (184 mg, 0.883 mmol) was added. The resulting solution was stirred at reflux temperature for 16 h, then it was allowed to cool to room temperature and filtered on a celite pad. Solvent removal and chromatography of the residue on a SiO_2 column with petroleum ether (b.p. 40÷60 °C) as eluent gave a first yellow/orange fraction, corresponding to **5.6**. Yield: 210 mg, 54 %. Anal. Calcd. for $C_{26}H_{28}FeOSi$: C, 70.90; H, 6.41. Found: C, 70.79; H, 6.35. ^{1}H NMR ($CDCl_3$) (see numbering scheme) δ 7.84-7.18 (m, 10H, C_6H_5), 4.16 (m, 2H, C^4H and C^5H), 4.12 (s, 5H, Cp), 3.99 (t, 1H, $^4J_{HH}$ = 1.30 Hz, C^2H), 3.40 (s, 1H, OH), 0.22 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 147.4, 147.3 ($C_{ipso\ Ph}$), 137.8-126.9 (C_{arom}), 101.9 (C^3), 77.8 (CPh_2OH), 73.3 (C^1), 73.1, 72.0 (C^4 and C^5), 72.9 (C^2), 68.9 (Cp), 1.24 ($SiMe_3$). ESI-MS (ES^+): 441 *m/z* [M^+].

A second orange/red fraction, corresponding to **4.6**, was collected by using diethyl ether as eluent. Yield: 141 mg, 33 %. Anal. Calcd. For $C_{28}H_{33}FeNOSi$: C, 69.56; H, 6.88; N, 2.90. Found: C, 69.48; H, 6.80; N, 2.92. ^{1}H NMR ($CDCl_3$) δ 8.20 (s, 1H, OH), 7.84-7.10 (m, 10H, C_6H_5), 4.06 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^5H), 4.03 (s, 5H, Cp), 3.82 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^3H), 2.35 (s, 6H, NMe_2), 0.23 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ = 146.3 ($C_{ipso\ Ph}$), 137.8-126.2 (C_{arom}), 112.5 (C^1), 94.4 (C^2), 78.4 (CPh_2OH), 70.2 (Cp), 70.0 (C^3), 67.9 (C^4), 62.0 (C^5), 46.8 (NMe_2), 0.12 ($SiMe_3$). ESI-MS (ES^+): 484 m/z [M^+].

Crystals of **4.6**, suitable for X Ray analyses, were obtained by slow evaporation of a CH_2Cl_2 solution of **4.6**.

Synthesis of the ferrocenes 6.6-30.6

The ferrocene complexes **6.6-30.6** were prepared following analogous procedures, by reacting the organometallic dinuclear precursors with the appropriate alkyne.

6.6: Anal. Calcd. for $C_{17}H_{25}FeNO_2Si$: C, 56.81; H, 7.02; N, 3.90. Found: C, 56.87; H, 6.99; N, 3.90. ^{1}H NMR ($CDCl_3$) δ 4.48 (d, 1H, $^4J_{HH}$ = 1.64 Hz, C^3H), 4.10 (s, 5H, Cp), 4.02 (d, 1H, $^4J_{HH}$ = 1.64 Hz, C^5H), 3.72 (s, 3H, CO_2Me), 2.62 (s, 6H, NMe_2), 0.13 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$) δ 171.7 (CO_2Me), 117.9 (C^1), 74.0 (C^3), 73.3 (C^2), 69.6 (Cp); 69.0 (C^4), 64.4 (C^5), 51.6 (CO_2Me), 45.1 (NMe_2), -1.01 ($SiMe_3$).

7.6: Anal. Calcd. for $C_{15}H_{20}FeO_2Si$: C, 56.95; H, 6.38. Found: C. 56.89; H, 6.41. ^{1}H NMR ($CDCl_3$) δ 4.93 (dd, 1H, $^3J_{HH}$ = 2.40 Hz, $^4J_{HH}$ = 1.24 Hz, C^{4}H), 4.74 (t, 1H, $^4J_{HH}$ = 1.24 Hz, C^{2}H), 4.31 (dd, 1H, $^3J_{HH}$ = 2.40 Hz, $^4J_{HH}$ = 1.24 Hz, C^{5}H), 4.16 (s, 5H, Cp), 3.81 (s, 3H, CO_2Me), 0.24 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$) δ 172.2 (*C*O_2Me), 76.1 (C^5), 75.3 (C^2), 73.9 (C^3), 72.8 (C^4), 70.1 (Cp), 68.9 (C^1), 51.8 (CO_2*Me*), 0.23 ($SiMe_3$).

8.6: Anal. Calcd. for $C_{21}H_{27}FeNSi$: C, 66.82; H, 7.22; N, 3.71. Found: C, 66.77; H, 7.25; N, 3.68. ^{1}H NMR ($CDCl_3$) δ 7.73-7.18 (m, 5H, C_6H_5), 4.20 (d, 1H, $^4J_{HH}$ = 1.28 Hz, C^{3}H), 4.16 (s, 5H, Cp), 4.05 (d, 1H, $^4J_{HH}$ = 1.28 Hz, C^{5}H), 2.58 (s, 6H, NMe_2), 0.28 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$) δ 139.4 (C_{ipso} Ph), 128.7, 127.1, 125.1 (Ph), 115.0 (C^1), 87.3 (C^2), 72.4 (C^3), 69.6 (Cp), 65.2 (C^4), 62.8 (C^5), 44.8 (NMe_2), 1.02 ($SiMe_3$).

9.6: Anal. Calcd. for $C_{19}H_{22}FeSi$: C, 68.25; H, 6.64. Found: C, 68.19; H, 6.66. ^{1}H NMR ($CDCl_3$) δ 7.57-7.20 (m, 5H, C_6H_5), 4.84 (dd, 1H, $^3J_{HH}$ = 2.36 Hz, $^4J_{HH}$ = 1.24 Hz, C^{4}H), 4.61 (t, 1H, $^4J_{HH}$ = 1.28 Hz, C^{2}H), 4.28 (dd, 1H, $^3J_{HH}$ = 2.36 Hz, $^4J_{HH}$ = 1.26 Hz, C^{5}H), 4.04 (s, 5H, Cp), 0.32 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$) δ 139.3 (C_{ipso} Ph), 128.6, 126.4, 126.2 (Ph), 88.5 (C^3), 74.0 (C^5), 73.6 (C^1), 71.5 (C^2), 70.1 (Cp), 69.5 (C^4), 0.05 ($SiMe_3$).

10.6: Anal. Calcd. for $C_{32}H_{31}FeNO$: C, 76.65; H, 6.23; N, 2.79. Found: C, 75.58; H, 6.30; N, 2.82. ^{1}H NMR ($CDCl_3$) δ 8.06 (s, 1H, OH), 7.64-7.24 (m, 14H, C_6H_5 and C_6H_4Me), 4.68 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^{5}H), 4.38 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^{3}H), 3.89 (s, 5H, Cp), 2.41 (s, 6H, NMe_2); 2.32 (s, 3H, C_6H_4*Me*). ^{13}CNMR ($CDCl_3$) δ 146.3 (C_{ipso}Ph), 137.8-125.9 (Ph), 110.2 (C^1), 93.0 (C^2), 81.0 (C^4), 78.4 (*C*Ph_2OH), 71.9 (Cp), 63.7 (C^3), 56.0 (C^5), 47.0 (NMe_2), 21.4 (C_6H_4*Me*). ESI-MS (ES$^+$): 502 m/z [M$^+$].

11.6: Anal. Calcd. for $C_{30}H_{26}FeO$: C, 78.61; H, 5.72. Found: C, 78.55; H, 5.70. ^{1}H NMR ($CDCl_3$) δ 7.37-7.07 (m, 14H, C_6H_5 and C_6H_4Me), 4.74 (dd, 1H, $^3J_{HH}$ = 2.56 Hz, $^4J_{HH}$ = 1.60 Hz, C^{5}H), 4.53 (t, 1H, $^4J_{HH}$ = 1.60 Hz, C^{2}H), 4.16 (dd, 1H, $^3J_{HH}$ = 2.56 Hz, $^4J_{HH}$ = 1.60 Hz, C^{4}H), 4.01 (s, 5H, Cp), 3.43 (s, 1H, OH), 2.32 (s, 3H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$) δ 146.9, 146.8 (C_{ipso}Ph), 134.9-125.9 (Ph), 100.0 (C^3), 85.8 (C^1), 77.5 (*C*Ph_2OH), 70.3 (Cp), 69.2 (C^4), 66.8 (C^2), 66.0 (C^5), 21.1 (C_6H_4*Me*). ESI-MS (ES$^+$): 459 m/z [M$^+$].

12.6: Anal. (sample containing a mixture of **12.6** and **14.6**) Calcd. for $C_{25}H_{25}FeN$: C, 75.92; H, 6.38; N, 3.54. Found: C, 75.85; H, 6.43; N, 3.60. ^{1}H NMR ($CDCl_3$) δ 7.88-7.08 (m, 9H, Ph and

C_6H_4Me), 5.19 (d, 1H, $^4J_{HH}$ = 1.24 Hz, C^3H), 4.23 (s, 5H, Cp); 4.10 (d, 1H, $^4J_{HH}$ = 1.24 Hz, C^5H), 2.64 (s, 6H, NMe_2), 2.39 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$) δ 139.1 ($C_{ipso\ Ph}$), 135.9 ($C_{ipso\ Tol}$), 130.4-126.5 (C_{arom}), 111.2 (C^1), 86.4 (C^2), 81.8 (C^4), 71.6 (C^5), 70.4 (Cp), 65.2 (C^3), 45.1 (NMe_2), 21.5 (C_6H_4Me).

13.6: Anal. (sample containing a mixture of **13.6** and **15.6**) Calcd. for $C_{23}H_{20}Fe$: C, 78.39; H, 5.72. Found: C, 78.33; H, 5.70. ^1H NMR ($CDCl_3$) δ 7.61-7.14 (m, 9H, Ph and C_6H_4Me), 5.16 (t, 1H, $^4J_{HH}$ = 1.48 Hz, C^2H), 4.81 (t, 2H, $^4J_{HH}$ = 1.48 Hz, C^4H and C^5H), 3.96 (s, 5H, Cp), 2.39 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$) δ 139.0 ($C_{ipso\ Ph}$), 135.7 ($C_{ipso\ Tol}$), 129.1-126.0 (C_{arom}), 86.9 (C^3), 86.3 (C^1), 71.4 (Cp), 67.3, 67.2 (C^4 and C^5), 65.2 (C^2), 21.4 (C_6H_4Me).

14.6: ^1H NMR ($CDCl_3$) δ 7.88-7.08 (m, 9H, Ph and C_6H_4Me), 4.84 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^2H); 4.28 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^5H), 3.99 (s, 5H, Cp), 2.72 (s, 6H, NMe_2), 2.41 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$) δ 139.4 ($C_{ipso\ Ph}$), 136.0 ($C_{ipso\ Tol}$), 131.4-126.1 (C_{arom}), 113.3 (C^1), 86.9 (C^3), 81.4 (C^4), 71.5 (Cp), 67.4 (C^2), 57.4 (C^5), 41.9 (NMe_2), 21.4 (C_6H_4Me).

15.6: ^1H NMR ($CDCl_3$) δ 7.61-7.14 (m, 9H, Ph and C_6H_4Me), 4.57 (t, 2H, $^3J_{HH}$ = 2.36 Hz, C^3H and C^5H), 4.39 (t, 1H, $^3J_{HH}$ = 2.36 Hz, C^4H),4.13 (s, 5H, Cp), 2.37 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$) δ 139.5 ($C_{ipso\ Ph}$), 135.8 ($C_{ipso\ Tol}$), 129.8-125.9 (C_{arom}), 88.7 (C^2), 86.3 (C^1); 71.2 (Cp); 70.4 (C^3 and C^5), 67.6 (C^4), 21.1 (C_6H_4Me).

16.6: Anal. Calcd. for $C_{19}H_{31}FeNSi$: C, 63.84; H, 8.75; N, 3.92. Found: C, 63.91; H, 8.69; N, 3.96. ^1H NMR ($CDCl_3$): δ = 3.99 (s, 5H, Cp); 3.68 (s, 1H, C^5H), 2.63 (s, 6H, NMe_2), 2.86-1.95 (m, 4H, CH_2CH_3), 1.26-0.86 (m, 6H, CH_2CH_3), 0.27 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ = 112.9 (C^1), 84.9, 84.0 (C^2 and C^3), 69.8 (Cp), 63.5 (C^4), 61.1 (C^5), 45.8 (NMe_2), 22.3 (CH_2CH_3), 20.4 (CH_2CH_3), 17.9 (CH_2CH_3), 15.9 (CH_2CH_3), 1.5 ($SiMe_3$).

17.6: Anal. Calcd. for $C_{17}H_{26}FeSi$: C, 64.94; H, 8.34. Found: C, 64.87; H, 8.41. ^1H NMR ($CDCl_3$): δ = 4.22 (d, 1H, $^3J_{HH}$ = 2.48 Hz, C^4H), 4.01 (s, 5H, Cp), 3.90 (d, 1H, $^3J_{HH}$ = 2.48 Hz, C^5H), 2.81-1.99 (m, 4H, CH_2CH_3), 1.25-0.92 (m, 6H, CH_2CH_3), 0.30 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ = 94.1, 92.9 (C^2 and C^3), 71.6 (C^4), 69.9 (C^5), 69.6 (Cp), 67.8 (C^1), 22.7 (CH_2CH_3), 21.3 (CH_2CH_3), 17.4 (CH_2CH_3), 15.4 (CH_2CH_3), 1.3 ($SiMe_3$).

18.6: Anal. Calcd. for $C_{23}H_{29}FeN$: C, 73.57; H, 7.79; N, 3.73. Found: C, 73.49; H, 7.85; N, 3.68. ^{1}H NMR ($CDCl_3$): δ = 7.46-7.08 (m, 4H, $C_6\mathit{H}_4Me$), 4.14 (s, 1H, C^5H), 3.98 (s, 5H, Cp), 2.67 (s, 6H, NMe_2), 2.34 (s, 3H, $C_6H_4\mathit{Me}$), 2.78-2.22 (m, 4H, $C\mathit{H}_2CH_3$), 1.19 (t, 3H, $^{3}J_{HH}$ = 7.60 Hz, $CH_2C\mathit{H}_3$), 1.01 (t, 3H, $^{3}J_{HH}$ = 7.60 Hz, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$) δ = 136.7-128.8 (C_{arom}), 111.5 (C^1), 84.5, 81.5 (C^2 and C^3), 81.0 (C^4), 71.0 (Cp), 57.4 (C^5), 45.7 (NMe_2), 21.4 ($C_6H_4\mathit{Me}$), 20.3 (CH_2CH_3), 20.1 (CH_2CH_3), 16.4 ($CH_2\mathit{CH}_3$), 15.6 ($CH_2\mathit{CH}_3$).

19.6: Anal. Calcd. for $C_{21}H_{24}Fe$: C, 75.88; H, 7.28. Found: C, 75.79; H, 7.30. ^{1}H NMR ($CDCl_3$): δ = 7.50-7.12 (m, 4H, $C_6\mathit{H}_4Me$), 4.27 (d, 1H, $^{3}J_{HH}$ = 2.50 Hz, C^4H), 4.00 (s, 5H, Cp), 3.90 (d, 1H, $^{3}J_{HH}$ = 2.50 Hz, C^5H), 2.39 (s, 3H, $C_6H_4\mathit{Me}$), 2.80-2.24 (m, 4H, $C\mathit{H}_2CH_3$), 1.31-1.00 (m, 6H, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$) δ = 136.5-129.0 (C_{arom}), 91.6, 90.4 (C^2 and C^3), 84.2 (C^1), 70.9 (Cp), 70.5 (C^4), 66.4 (C^5), 21.7 ($C_6H_4\mathit{Me}$), 21.4 (CH_2CH_3), 20.4 (CH_2CH_3), 16.4 ($CH_2\mathit{CH}_3$), 15.3 ($CH_2\mathit{CH}_3$).

20.6: Anal. Calcd. for $C_{31}H_{29}FeN$: C, 78.95; H, 6.20; N, 2.97. Found: C, 79.02; H, 6.13; N, 2.94. ^{1}H NMR ($CDCl_3$): δ = 7.80-7.09 (m, 14H, Ph and $C_6\mathit{H}_4Me$), 4.16 (s, 1H, C^5H), 4.01 (s, 5H, Cp), 2.66 (s, 6H, NMe_2), 2.34 (s, 3H, $C_6H_4\mathit{Me}$). ^{13}C NMR ($CDCl_3$) δ = 139.1-126.0 (C_{arom}), 112.5 (C^1), 87.0, 86.4 (C^2 and C^3), 80.9 (C^4), 70.6 (Cp), 58.0 (C^5), 44.9 (NMe_2), 21.7 ($C_6H_4\mathit{Me}$).

21.6: Anal. Calcd. for $C_{29}H_{24}Fe$: C, 81.29; H, 5.65. Found: C, 81.40; H, 5.61. ^{1}H NMR ($CDCl_3$): δ = 7.66-7.10 (m, 14H, Ph and $C_6\mathit{H}_4Me$), 4.40 (d, 1H, $^{3}J_{HH}$ = 2.36 Hz, C^4H), 4.15 (d, 1H, $^{3}J_{HH}$ = 2.36 Hz, C^5H), 3.99 (s, 5H, Cp), 2.36 (s, 3H, $C_6H_4\mathit{Me}$). ^{13}C NMR ($CDCl_3$) δ = 138.9-125.7 (C_{arom}), 89.8, 89.5 (C^2 and C^3), 84.5 (C^1), 71.3 (Cp), 69.9 (C^4), 66.8 (C^5), 21.0 ($C_6H_4\mathit{Me}$).

22.6: Anal. Calcd. for $C_{26}H_{25}FeNO_2$: C, 71.05; H, 5.74; N, 3.19. Found: C, 71.12; H, 5.68; N, 3.26. ^{1}H NMR ($CDCl_3$): δ = 7.70-7.02 (m, 10H, Ph), 4.84 (s, 1H, C^5H), 4.39 (s, 5H, Cp), 3.69 (s, 3H, CO_2Me), 2.47 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$) δ = 172.8 ($\mathit{C}O_2Me$), 133.5-126.4 (C_{arom}), 113.8 (C^1), 91.9, 90.4 (C^2 and C^3), 71.6 (Cp), 62.4 (C^4), 59.6 (C^5), 51.2 ($CO_2\mathit{Me}$), 44.1 (NMe_2).

23.6: Anal. Calcd. for $C_{24}H_{20}FeO_2$: C, 72.71; H, 5.09. Found: C, 72.63; H, 5.15. ^{1}H NMR ($CDCl_3$): δ = 7.56-7.20 (m, 10H, Ph), 4.89 (d, 1H, $^{3}J_{HH}$ = 2.64 Hz, C^4H), 4.77 (d, 1H, $^{3}J_{HH}$ = 2.64 Hz, C^5H), 4.31 (s, 5H, Cp), 3.60 (s, 3H, CO_2Me). ^{13}C NMR ($CDCl_3$) δ = 174.3 ($\mathit{C}O_2Me$), 133.6-126.2 (C_{arom}), 90.5, 89.9 (C^2 and C^3), 73.6 (Cp), 71.8, 71.4 (C^4 and C^5), 63.0 (C^1), 51.0 ($CO_2\mathit{Me}$).

24.6: Anal. (sample containing a mixture of **24.6** and **25.6**) Calcd. for $C_{21}H_{23}FeNO_2$: C, 66.82; H, 6.15; N, 3.71. Found: C, 66.91; H, 6.24; N, 3.74. ^{1}H NMR ($CDCl_3$): δ = 7.81-7.10 (m, 4H, C_6H_4Me), 5.03 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.83 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^3H), 4.32 (s, 5H, Cp), 3.86 (s, 3H, CO_2Me), 2.65 (s, 6H, NMe_2), 2.48 (br s, 3H, C_6H_4*Me*); ^{13}C NMR ($CDCl_3$): δ = 170.3 (*C*O_2Me), 136.2-126.8 (C_{arom}), 114.6 (C^1), 76.4 (C^2), 70.7 (Cp), 68.9 (C^3), 62.8 (C^4), 61.3 (C^5), 51.5 (CO_2*Me*), 44.3 (NMe_2), 21.3 (C_6H_4*Me*).

25.6: ^{1}H NMR ($CDCl_3$) δ 7.81-7.10 (m, 4H, C_6H_4Me), 4.61 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.37 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^2H), 4.38 (s, 5H, Cp), 3.93 (s, 3H, CO_2Me), 2.76 (s, 6H, NMe_2), 2.48 (br s, 3H, C_6H_4*Me*); ^{13}C NMR ($CDCl_3$): δ = 173.1 (*C*O_2Me), 136.2-126.8 (C_{arom}), 116.1 (C^1), 85.2 (C^3); 70.2 (Cp); 64.1 (C^2); 59.4 (C^4); 56.4 (C^5); 51.2 (CO_2*Me*); 41.8 (NMe_2); 21.1 (C_6H_4*Me*).

26.6: Anal. (sample containing a mixture of **26.6** and **27.6**) Calcd. for $C_{20}H_{20}FeN_2$: C, 69.75; H, 5.86; N, 8.14. Found: C, 69.80; H, 5.97; N, 8.14. ^{1}H NMR ($CDCl_3$) δ 7.62-6.99 (m, 4H, C_6H_4Me), 4.40 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.31 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^3H), 4.30 (s, 5H, Cp), 2.51 (s, 6H, NMe_2), 2.37 (br s, 3H, C_6H_4*Me*); ^{13}C NMR ($CDCl_3$): δ = 136.9-126.9 (C_{arom}), 120.7 (CN), 116.5 (C^1), 85.2 (C^2), 71.1 (Cp), 57.3 (C^3); 56.6 (C^5); 45.3 (C^4); 41.7 (NMe_2); 21.1 (C_6H_4*Me*).

27.6: ^{1}H NMR ($CDCl_3$) δ 7.62-6.99 (m, 4H, C_6H_4Me), 4.71 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.53 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^2H), 4.36 (s, 5H, Cp), 2.63 (s, 6H, NMe_2), 2.37 (br s, 3H, C_6H_4*Me*); ^{13}C NMR ($CDCl_3$): δ = 136.9-126.9 (C_{arom}); 121.4 (CN); 113.8 (C^1); 80.0 (C^3); 71.5 (Cp); 70.3 (C^2); 61.0 (C^5); 45.5 (C^4); 44.0 (NMe_2); 21.2 (C_6H_4*Me*).

28.6: Anal. (sample containing a mixture of **28.6** and **29.6**) Calcd. for $C_{19}H_{18}FeO_2S$: C, 62.31; H, 4.95. Found: C, 62.15; H, 4.88. ^{1}H NMR ($CDCl_3$) δ 7.78-7.11 (m, 5H, Ph), 5.05 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^3H), 4.74 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^5H), 4.23 (s, 5H, Cp), 3.76 (s, 3H, CO_2*Me*), 2.38 (s, 3H, SMe); ^{13}C NMR ($CDCl_3$) δ 170.8 (*C*O_2Me), 136.1-125.9 (C_{arom}), 90.7 (C^4), 85.7 (C^1), 85.6 (C^2), 76.8 (C^5), 73.2 (C^3), 73.1 (Cp); 51.5 (CO_2*Me*); 19.5 (SMe).

29.6: ^{1}H NMR ($CDCl_3$) δ 7.78-7.11 (m, 5H, Ph), 5.18 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^2H), 5.07 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^5H), 4.17 (s, 5H, Cp), 3.83 (s, 3H, CO_2*Me*), 2.28 (s, 3H, SMe); ^{13}C NMR ($CDCl_3$): δ = 171.4 (*C*O_2Me), 136.1-125.9 (C_{arom}), 90.6 (C^4), 86.0 (C^1), 85.6 (C^3), 73.0 (Cp), 70.8 (C^2), 70.1 (C^5), 51.7 (CO_2*Me*), 19.1 (SMe).

30.6: (yield: 48%) Anal. Calcd. for $C_{24}H_{19}FeO$: C, 78.61; H, 5.72. Found: C, 78.55; H, 5.89. ^{1}H NMR ($CDCl_3$): δ = 7.56-7.19 (m, 10H, Ph), 5.05 (s, 1H, C^5H), 4.31 (s, 5H, Cp), 2.16 (s, 3H, SMe); ^{13}C NMR ($CDCl_3$): δ = 135.1-126.5 (C_{arom} and CN); 91.1, 89.9 (C^2 and C^3), 86.9 (C^1), 73.6 (Cp), 73.2 (C^5), 51.1 (C^4), 19.1 (SMe).

X-ray Crystallography

Crystal data and collection details for **4.6** and **11.6** are reported in Table 6.2. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo–Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS). [ref: Sheldrick, G. M. *SADABS*, Program for empirical absorption correction, University of Göttingen, Germany, **1996**]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2. [ref: Sheldrick, G. M. *SHELX97*, Program for crystal structure determination, University of Göttingen, Germany, **1997**]. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(50) in **4.6**, which was located in the Fourier map and refined isotropically using the 1.5 fold U_{iso} value of the parent O(1) atom; the O(1)-H(50) distance was restrained to 0.83 Å [s.u. 0.01]. Similar *U* restraints [s.u. 0.01] were applied to all C-atoms in **11.6**.

Table 6.2

*Crystal data and experimental details for **4.6** and **11.6***

Complex	**4.6**	**11.6**
Formula	$C_{28}H_{33}FeNOSi$	$C_{30}H_{26}FeO$
Fw	483.49	458.36
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	12.1178(7)	10.3008(9)
b, Å	10.9715(7)	10.6616(9)

c, Å	19.5293(12)	11.2231(10)
α, °	90	89.3930(10)
β, °	103.5860(10)	73.7160(10)
γ, °	90	73.6680(10)
Cell Volume, Å^3	2523.8(3)	1132.25(17)
Z	4	2
D_c, g cm^{-3}	1.272	1.344
μ, mm^{-1}	0.665	0.686
F(000)	1024	480
Crystal size, mm	0.22×0.15×0.12	0.22×0.16×0.14
θ limits, °	1.73–28.00	1.90–27.00
Reflections collected	28477	12690
Independent reflections	6007 [R_{int} = 0.0367]	4902 [R_{int} = 0.0266]
Data / restraints /parameters	6007 / 1 / 297	4902 / 198 / 291
Goodness on fit on F^2	1.023	1.034
R_1 ($I > 2\sigma(I)$)	0.0368	0.0386
wR_2 (all data)	0.0996	0.0977
Largest diff. peak and hole, e Å^{-3}	0.302 / –0.179	0.256 / –0.208

References

[1] For a comprehensive overview of ferrocene and other metallocenes see: (a) *Ferrocenes: Homogeneous Catalysis - Organic Synthesis - Materials Science*; Togni, A., Hayashi, T., Eds.; Wiley –VCH: Weinheim **1995**. (b) *Metallocenes;* Togni, A. Halterman, R. L., Eds.; Wiley-VCH, Weinheim, **1998**. (c) *Ferrocenes - Ligands Materials and Biomolecules;* Štěpnička, P., Ed; John Wiley & Sons, West Sussex, **2008**.

[2] (a) Debroy, P.; Roy, S. *Coord. Chem. Rev*. **2007**, *251*, 203-221. (b) Osakada, K.; Sakano, T.; Horie, M.; Suzaki, Y. *Coord. Chem. Rev*. **2006**, *250*, 1012-1022.

[3] (a) Stoll, A. H.; Mayer, P.; Knochel, P. *Organometallics* **2007**, *26*, 6694–6697. (b) Wang, Y.; Weissensteiner, W.; Spindler, F.; Arion, V. B.; Mereiter, K. *Organometallics* **2007**, *26*, 3530-3540. (c) Christophe, P.; Odell, B.; Brown, J. M. *Chem. Commun.* **2004**, 598-599. (d) Steurer, M.; Tiedl, K.; Wang, Y.; Weissensteiner, W. *Chem. Commun.* **2005**, 4929-4931.

[4] (a) Butler, D. C. D.; Richards, C. J. *Organometallics* **2002**, *21*, 5433-5436. (b) van Leusen, D.; Hessen, B. *Organometallics* **2001**, *20*, 224-226. (c) Metallinos, C., Zaifman, J.; Dodge, L. *Org. Lett.* **2008**, *10*, 3527-3530.

[5] For reviews of transition-metal-mediated [3 + 2] cycloaddition see: (a) Li, C. L.; Liu, R. S. *Chem. Rev*. **2000**, *100*, 3127-3161. (b) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97-112. (c) Wojcicki, A.; Shuchart C. E.; *Coord. Chem. Rev.* **1990**, *105*, 35-60. (d) Rosenblum, M. *J. Organomet. Chem*. **1986**, *300*, 191-218. (e) Fruehauf, H. W. *Chem. Rev*. **1997**, *97*, 523-596.

[6] Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Yu. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349-364.

[7] (a) Carriedo, G. A.; Howard, J. A. K.; Lewis, D. B.; Lewis, G. E.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 905-912. (b) Van der Heijden, H.; Gal, A. W.; Pasman, P.; Orpen, A. G. *Organometallics* **1985**, *4*, 1847-1853. (c) Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister, C.; Prout, C. K. *Inorg. Chem*. **1986**, *25*, 1923-1925.

[8] P. Blenkiron, S. M. Breckenridge, N. J. Taylor, A. J. Carty, M. A. Pellinghelli, A. Tiripicchio, E. Sappa, *J. Organomet. Chem.* **1996**, *506*, 229-240.

[9] V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics*, **2004**, *23*, 3348-3354.

[10] L. Busetto, M. Salmi, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* **2008**, *693*, 57-67.

[11] L. Busetto, F. Marchetti, M. Salmi, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* **2007**, *692*, 2245-2252.

[12] Y.-T. Wu, B. Flynn, H. Schirmer, F. Funke, S. Müller, T. Labahn, M Nötzel, A. de Meijere. *Eur. J. Org. Chem.* **2004**, 724-748.

[13] C. Metallinos, H. Szillat, N. J. Taylor, V. Snieckus, *Adv. Synth. Catal.* **2003**, *345*, 370-382.

[14] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem*., **1993**, *31*, 287-292.

[15] K. Stott, J. Stonehouse, J. Keeler, T.L. Hwang, AJ. Shaka, *J. Am. Chem. Soc.* **1995**, *117*, 4199-4200.

CHAPTER VII

ALKYNE INSERTION INTO THE Pd-C BOND OF CYCLOPALLADATED COMPOUNDS CONTAINING [C(sp^2,ferrocene),N,S] TRIDENTATE LIGANDS

Introduction

The synthesis, characterization and study of cyclopalladated complexes [1] has attracted great interest during the past decade due to a variety of interesting applications in different areas. [2-12] Some examples showing the utility of this kind of compounds in homogeneous catalysis [2a,4], as building blocks for the synthesis of macromolecules [5], for the determination of enantiomeric excesses of chiral reagents have been described. [6,7] Beside that, it is well known that palladacycles are useful precursors in the synthesis of organic or organometallic compounds. [10-12] Most of these reactions involve the insertion of small molecules, such as CO, isonitriles, alkenes, and alkynes into the σ(Pd-C) bond. Mono, bis, and even tris insertions of alkynes into the σ[Pd-C(sp^2,aryl)] bond of cyclopalladated complexes containing organic ligands have been extensively studied over the last few years. [10-12] These studies have shown that the nature of the final product formed by the insertion of alkynes depends on a wide variety of factors including the nature of the metallated carbon, the electron-withdrawing/electron-donor nature of the substituents on the alkyne, the stoichiometry of the reaction, the remaining ligands bound to the palladium, etc. On the other hand, analogous reactions of alkynes with related derivatives containing a σ[Pd-C(sp^2,ferrocene)] bond are still largely unexplored. [13]

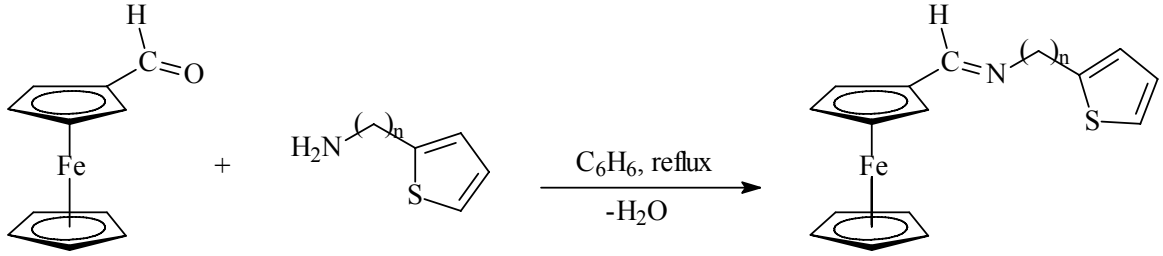
On the light of these considerations we have synthesized the novel Schiff bases [Fc-CH=N-$(CH_2)_n$-(C_4H_3S)], with n=1 (**1.7a**) or 2 (**1.7b**). Both **1.7a-b** act as [C(sp^2,ferrocene),N,S] terdentate ligands toward palladium, coordinating through the imine nitrogen, the thienyl sulphur, and the carbon atom of the Cp ring adjacent to the iminic group, while they differ in the length of the $(CH_2)_n$ chain.

Then, we have investigated the reactivity of the resulting cyclopalladated complexes [Pd{[(η^5-C_5H_3)-CH=N-$(CH_2)_n$-(C_4H_3S)]Fe(η^5-C_5H_5)}Cl] (n=1, **2.7a**; n=2, **2.7b**) toward the internal alkynes R-C≡C-R (R = Ph, Et, CO_2Me), in order to elucidate the relative influence of: (a) the substituents on the alkyne (their electron-donor/electron-withdrawing nature or sterical hindrance); (b) the length of the -$(CH_2)_n$- chain of the ligand. In all the cases we have observed the formation of the product of bis-insertion of the alkyne into the Pd-C(sp^2) ligand [Pd{[(RC=CR)$_2$(η^5-C_5H_3)-CH=N-$(CH_2)_n$-(C_4H_3S)]Fe(η^5-C_5H_5)}Cl] (n=1, R = Ph, **3.7a**; n=2, R = Ph, **3.7b**; n=1, R = Et, **3.7c**; n=2, R = Et, **3.7d**; n=1, R = CO_2Me, **3.7e**; n=2, R = CO_2Me, **3.7f**).

Results and discussion

Synthesis and characterization of the Schiff bases

The ligands [Fc-CH=N-$(CH_2)_n$-(C_4H_3S)] (n=1, **1.7a**; n=2, **1.7b**) were prepared in good yields (80% and 72%, respectively) by using the general method reported for the synthesis of related ferrocenylimines: Fc-CH=N-R_3 (with R_3 = phenyl, benzyl or naphthyl group) [14], but using H_2N-$(CH_2)_n$-(C_4H_3S) (n=1 or 2) as starting materials (Scheme 7.1). Elemental analyses and mass spectra (ESI MS) of **1.7a-b** were consistent with the proposed formulas.



n=1 **1.7a**
n=2 **1.7b**

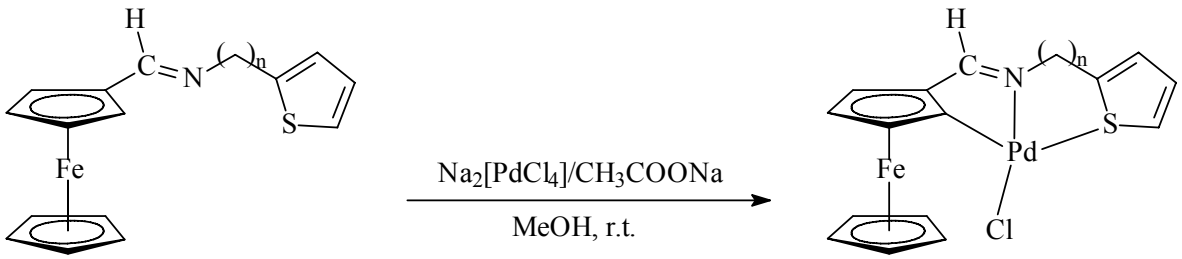
Scheme 7.1

Compounds **1.7a-b** were also characterized by mono- [^{1}H and ^{13}C{^{1}H}] and bi-dimensional [{^{1}H-^{1}H}-NOESY and {^{1}H-^{13}C}-HSQC and HMBC] NMR experiments. The ^{1}H NMR spectra show the typical pattern of monosubstituted ferrocene derivatives: a singlet and two triplets (in the range 3.90-4.60 ppm). Beside this, the singlet detected in the lowfield region 7.9-8.2 ppm (*e.g.* 8.07 ppm for **1.7b**) is ascribed to the imine proton. The similarity between the chemical shift of the imine proton in **1.7a-b** and those of related ferrocenyl Schiff bases of the type Fc-CH=N-R_3 (with R_3 = phenyl, benzyl or naphthyl group) indicates that **1.7a-b** adopt the *anti-(E)*-form in solution. [14] The existence of a cross peak between the resonance of the imine proton and the one of the -N-CH_2- unit in the {^{1}H-^{1}H}-NOESY spectra confirms this result. The resonances due to the protons of the thienyl ring fall in the range 6.5-7.2 ppm.

The main feature of the ^{13}C NMR spectra of **1.7a-b** is represented by the resonance of the imine carbon, which falls at *ca.* 160 ppm (162 ppm for **1.7b**).

Formation of the cyclopalladated complexes

The treatment of **1.7a-b** with equimolar amounts of $Na_2[PdCl_4]$ and $NaOAc{\cdot}3H_2O$ in methanol for 24 h at room temperature produced, for both **1.7a-b**, a deep red solid, corresponding to the cyclometallated complexes **2.7a-b** (Scheme 7.2).

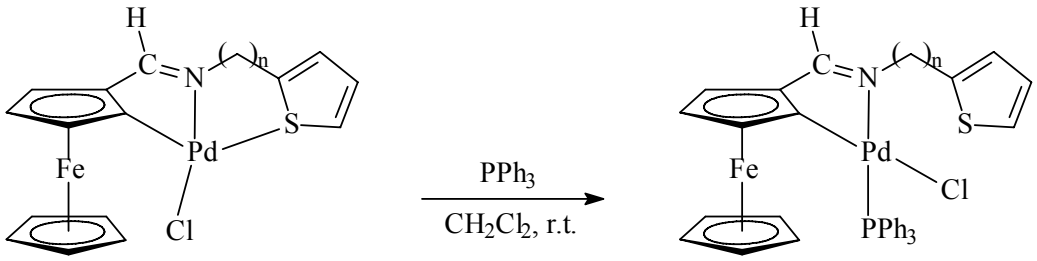


1.7a n=1 **2.7a**
1.7b n=2 **2.7b**

Scheme 7.2

Compounds **2.7a-b** were purified by chromatography on SiO_2 and fully characterized by NMR spectroscopy and elemental analysis. The characterization data are in agreement with those expected for $[Pd\{[(\eta^5\text{-}C_5H_3)\text{-}CH{=}N\text{-}(CH_2)_n\text{-}(C_4H_3S)]Fe(\eta^5\text{-}C_5H_5)\}Cl]$, in which the imine ligand acts as [C(sp^2, ferrocene),N,S] terdentate ligand. The ^1H NMR spectra of **2.7a-b** show the typical pattern of 1,2-disubstituted ferrocene derivatives: three signals of relative intensities 1:1:1 in the range 4.0-5.0 ppm, which can be assigned to the three non-equivalent hydrogens of the disubstituted Cp ring. Analogously, the ^{13}C NMR spectra of **2.7a-b** show five signals in the range 65-110 ppm, which can be ascribed to the five non-equivalent carbon atoms of the substituted Cp ring.

In order to elucidate the relative lability of the Pd-X bonds we have treated **2.7a-b** with PPh_3. When a solution of **2.7a** (or **b**) in CH_2Cl_2 is treated with the equimolar amount of PPh_3 a sudden change of colour, from dark red to bright yellow, is observed. The reaction leads to the selective formation of $[Pd\{[(\eta^5\text{-}C_5H_3)\text{-}CH{=}N\text{-}(CH_2)_n\text{-}(C_4H_3S)]Fe(\eta^5\text{-}C_5H_5)\}Cl(PPh_3)]$, where the ligand acts as [C(sp^2, ferrocene),N] group, in agreement with the higher lability of the Pd-S bond (Scheme 7.3).



Scheme 7.3

The reaction involves the cleavage of the Pd-thienyl bond and the binding of a PPh_3, which adopts a cis arrangement with respect to the metalated carbon atom, in good agreement with the *transphobia effect*. [15] The corresponding ^{31}P NMR spectra exhibit a singlet in the range 35-40 ppm. This value is consistent with data reported for related complexes with [C(sp^2, ferrocene),N] ligands in which the imine nitrogen and the phosphorous atom are in trans arrangement.

Alkyne insertion into the Pd-C bond

We have investigated the reactivity of **2.7a-b** with three different internal alkynes R-C≡C-R (R = Ph, Et, CO_2Me), which differ in the electronic and steric properties of the substituents (Table 7.1). This type of study could be useful to elucidate the relative influence of: (a) the substituents on the alkyne (their electron-donor/electron-withdrawing nature or sterical hindrance); (b) the length of the -$(CH_2)_n$- chain of the ligand.

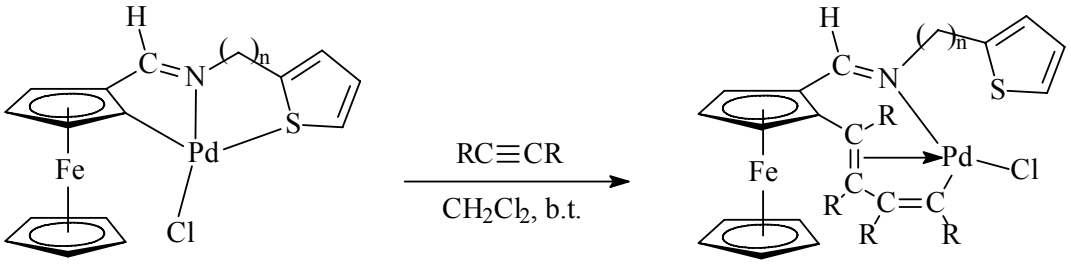
Table 7.1

Electronic and steric parameters for the substituents (R) on the alkynes[a]

R	σ_I	σ_R	Es'(CH)
Ph	0.12	0.10	3.0
Et	-0.01	-0.14	2.0
CO_2Me	0.21	0.16	4.0

[a] σ_I and σ_R are the inductive and mesomeric parameters of the substituents R. Positive σ values indicate electron-withdrawing character of the substituent, while negative values correspond to electron-donor groups. Es'(CH) values are Charton's steric parameters for R calculated according to structural data. All the values presented in this table are taken from ref. 16.

In all the cases we have observed the selective formation of the product of bis-insertion of the alkyne into the Pd-C(sp^2) ligand. When **2.7a-b** are treated with R-C≡C-R in a relative molar ratio 2:1 (alkyne/Pd) the corresponding products of bis-insertion [Pd{[$(RC=CR)_2$(η^5-C_5H_3)-CH=N-$(CH_2)_n$-(C_4H_3S)]Fe(η^5-C_5H_5)}Cl] (n=1, R = Ph, **3.7a**; n=2, R = Ph, **3.7b**; n=1, R = Et, **3.7c**; n=2, R = Et, **3.7d**; n=1, R = CO_2Me, **3.7e**; n=2, R = CO_2Me, **3.7f**) are formed in nearly quantitative yields (Scheme 7.4). We have also performed the reaction with different alkyne/Pd ratio, to examine the influence of the stoichiometry on the product distribution. Increasing the alkyne/Pd ratio up to 3:1 we have obtained the same products **3.7a-f**, with the same selectivity and with no trace of tris-insertion products. On the other hand, with a molar ratio of 1:1, we have recovered, after work up, a certain amount of unreacted starting **2.7a-b**, but we have isolated selectively **3.7a-f**, with no trace of the product of mono-insertion. All these reactions are carried out in CH_2Cl_2 at refluxing temperature (Scheme 7.4).



R		
Ph	n=1	**3.7a**
Ph	n=2	**3.7b**
Et	n=1	**3.7c**
Et	n=2	**3.7d**
CO_2Me	n=1	**3.7e**
CO_2Me	n=2	**3.7f**

Scheme 7.4

Compounds **3.7a-f** were purified by chromatography on SiO_2 and fully characterized by NMR spectroscopy and elemental analysis. The characterization data are in agreement with those reported for related palladacycles arising from the bis-insertion of alkynes into the Pd-C(sp^2,ferrocene) bond. [13] ^{1}H NMR spectra of all the compounds **3.7a-f** show a group of four signals of relative intensities 1:1:1:5 in the range 4.0-5.0 ppm, which is the typical pattern of 1,2-disubstituted ferrocenes. The resonance of the imine proton appears as a singlet in the low-field region of the spectra, and signals due to the protons of the four R groups of the inserted fragment have been identified in the spectra. However, for **3.7a-b** the signals of the phenyl groups appear as a multiplet in the range 6.50-7.50 ppm and are overlapped with the resonances due to the thienyl unit. The high-field region of the ^{1}H NMR spectra of **3.7c-d** is characterized by the presence of the resonances of the ethyl groups, and the complete assignment of these signals has been achieved by means of the two-dimensional {^{1}H-^{13}C} NMR experiments. The most relevant feature of the ^{13}C NMR spectra of all the compounds **3.7a-f** is represented by the resonance of the imine carbon, which falls in the range 160-170 ppm. The resonances due to the carbon atoms of the -Et or -OMe groups of the R substituents for **3.7c-f** have been easily identified in the high-field region of the spectra and provided additional evidence of the selective incorporation of two molecules of the alkyne into the σ-[Pd-C(sp2,ferrocene)] bond. Finally, {^{1}H-^{1}H}-NOESY investigations have allowed us to elucidate the configuration of the ligand, and in particular the relative positions of the R groups in the butadienyl chain. Characterization data are in agreement with previously reported results concerning analogous nine-membered palladacycles arising from alkyne bis-insertion. [13]

In particular, the two R groups vicinal to the Pd atom are in mutual *cis* position, while the R groups adjacent to the ferrocenyl moiety adopt a *trans* arrangement.

Conclusions

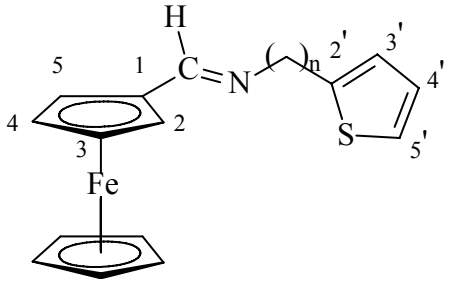
We have synthesized the new ferrocenyl Schiff bases [Fc-CH=N-$(CH_2)_n$-(C_4H_3S)] (n=1,2), which are characterized by the presence of a thienyl group. They act as terdentate ligands toward palladium, coordinating through the imine nitrogen, the thienyl sulphur and the C(sp^2) carbon atom adjacent to the imine group.

Then, we have investigated the reactivity of the resulting cyclopalladated complexes toward the internal alkynes R-C≡C-R (R = Ph, Et, CO_2Me). The reaction affords, in all the cases, the product of bis-insertion and is not affected by: (a) the nature of the substituents on the alkyne (neither their electron-donor/electron-withdrawing nature nor their sterical hindrance); (b) the length of the -$(CH_2)_n$- chain of the ligand; (c) the molar ratio between the Pd complex and the alkyne.

Experimental details

General

All the solvents were dried and distilled prior to use. Elemental analyses (C, H and N) were carried out at the Serveis de Recursos Cientifics i Tecnics (Univ. Rovira i Virgili, Tarragona). Mass spectra ESI were performed at the Servei de Espectrometria de Masses (Univ. Barcelona) with a VG-Quatro instrument. Routine ^{1}H NMR spectra and $^{13}C\{^{1}H\}$ spectra were obtained with a Gemini 200 MHz, a Bruker 250-DXR and a Mercury 400 MHz instrument. High resolution ^{1}H NMR spectra and the two dimensional [^{1}H ^{1}H NOESY and COSY and ^{1}H ^{13}C heteronuclear single quantum coherence (HSQC) and the heteronuclear multiple bond coherence (HMBC)] NMR experiments were recorded with either a Varian VRX-500 or with a Bruker Advance DMX 500 instruments at 20°C. The solvent used for the NMR studies was $CDCl_3$ (99.8%) and $SiMe_4$ was used as internal reference. $^{31}P\{^{1}H\}$ spectra were obtained with a Bruker 250-DXR instrument in $CDCl_3$ (99.9%) and using trimethylphosphite as reference [$\delta^{31}P\{P(OMe)_3\}$ = 140.17 ppm]. The numeration was referred to the following scheme:



*Synthesis of the Schiff bases [Fc-CH=N-$(CH_2)_n$-(C_4H_3S)] (n=1, **1.7a**; n=2, **1.7b**)*

Ferrocenecarboxaldehyde (1.00 g, $4.67\cdot10^{-3}$ mol) was dissolved in 20 mL of benzene. The reaction mixture was stirred at 298 K for 10 min and then filtered out. The undissolved materials were discarded, the filtrate was transferred into a flask and then equimolar amount ($4.80\cdot10^{-3}$ mol) of the corresponding amine {H_2N-$(CH_2)_n$-(C_4H_3S) (n=1 or 2)} was added. The flask was introduced in an ethyleneglycol bath and it was connected to a Dean-Stark apparatus and to a condenser. The reaction mixture was refluxed until *ca.* 10 mL had condensed on the Dean-Stark apparatus. The hot reaction mixture was filtered out and the deep-red filtrate was concentrated to dryness on a rotary evaporator. The solids formed were collected and dried. [Yield: 1.17 g (80%) and 1.08 g (72%) for

1.7a and **1.7b**, respectively]. Characterization data for **1.7a**: Anal. Calc. for $C_{16}H_{15}NFeS$: C, 62.15; H, 4.89; N, 4.53. Found: C, 62.1; H, 5.0; N, 4.6 %. MS (ESI): m/z = 309, $[M]^+$. ^{1}H NMR δ = 8.21 (s, 1H, -CH=N-), 4.20 (s, 5H, Cp), 4.46 (t, 2H, $^3J_{HH}$ = 1.5 Hz, H_3 and H_4), 4.77 (t, 2H, $^3J_{HH}$ = 1.5 Hz, H_2 and H_5), 4.83 (s, 2H, =N-CH_2-), 7.02 (br s, 2H, $H_{3'}$ and $H_{4'}$), 7.26 (d, 1H, $^3J_{HH}$ = 4.0 Hz, $H_{5'}$). ^{13}C{^{1}H} NMR δ = 163.3 (-CH=N-), 69.2 (Cp), 79.3 (C_1), 69.0 (C_2 and C_5), 71.4 (C_3 and C_4), 58.3 (=N-CH_2-), 141.2 ($C_{2'}$), 125.7 ($C_{3'}$), 127.1 ($C_{4'}$), 125.3 ($C_{5'}$). For **1.7b**: Anal. Calc. for $C_{17}H_{17}NFeS$: C, 63.17; H, 5.30; N, 4.33. Found: C, 63.3; H, 5.5; N, 4.4 %. MS (ESI): m/z = 323, $[M]^+$. ^{1}H NMR δ = 8.05 (s, 1H, -CH=N-), 4.07 (s, 5H, Cp), 4.33 (t, 2H, $^3J_{HH}$ = 1.5 Hz, H_3 and H_4), 4.58 (t, 2H, $^3J_{HH}$ = 1.5 Hz, H_2 and H_5), 3.73 (t, 2H, $^3J_{HH}$ = 6.0 Hz, =N-CH_2-), 3.18 (t, 2H, $^3J_{HH}$ = 6.0 Hz, -CH_2-), 6.84 (br s, 1H, $H_{3'}$), 6.92 (dd, 1H, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 3.0 Hz, $H_{4'}$), 7.12 (d, 1H, $^3J_{HH}$ = 5.0 Hz, $H_{5'}$). ^{13}C{^{1}H} NMR δ = 161.9 (-CH=N-), 69.1 (Cp), 80.4 (C_1), 70.6 (C_2 and C_5), 68.6 (C_3 and C_4), 63.1 (=N-CH_2-), 31.5 (-CH_2-), 142.7 ($C_{2'}$), 125.0 ($C_{3'}$), 126.8 ($C_{4'}$), 123.5 ($C_{5'}$).

*Synthesis of [Pd{[(η^5-C_5H_3)-CH=N-$(CH_2)_n$-(C_4H_3S)]Fe(η^5-C_5H_5)}Cl] (n=1, **2.7a**; n=2, **2.7b**)*

To a solution of the ferrocenylimine **1.7a** (250 mg, $1.1 \cdot 10^{-3}$ mol) in methanol (20 mL) the equimolar amounts of $Na_2[PdCl_4]$ (238 mg) and $NaOAc \cdot 3H_2O$ (110 mg) were added. The resulting solution was stirred at room temperature for 24 h. The dark red solid formed was separated from the solution by filtration and re-dissolved in the minimal amount of CH_2Cl_2. This crude product was purified by chromatography on a SiO_2 column, using CH_2Cl_2 as eluent. The product **2.7a** is eluted as a first deep red band. Yield (**2.7a**): 371 mg (70.4%). Anal. Calc. for $C_{16}H_{14}ClFeNPdS$: C, 42.77; H, 3.14; N, 3.12. Found: C, 42.8; H, 3.1; N, 3.2 %. MS (ESI): m/z = 449, $[M]^+$. ^{1}H NMR δ = 7.84 (s, 1H, -CH=N-), 7.34 (d, 1H, $^3J_{HH}$ = 5.0 Hz, $H_{5'}$), 7.23 (br s, 1H, $H_{3'}$), 7.06 (bs s, 1H, $H_{4'}$), 4.95 (dd, 1H, $^2J_{HH}$ = 15.0 Hz, $^4J_{HH}$ = 1.5 Hz, =N-CH_2-), 4.84 (br s, 1H, H_5), 4.68 (dd, 1H, $^2J_{HH}$ = 15.0 Hz, $^4J_{HH}$ = 1.5 Hz, =N-CH_2-), 4.35 (br s, 1H, H_4), 4.32 (br s, 1H, H_3), 4.27 (s, 5H, Cp). ^{13}C{^{1}H} NMR δ = 173.4 (-CH=N-), 138.2 ($C_{2'}$), 127.7 ($C_{3'}$), 127.5 ($C_{4'}$), 126.5 ($C_{5'}$), 103.1 (C_1), 86.9 (C_2), 77.4 (C_3), 71.0 (C_4), 70.2 (C_5), 69.9 (Cp), 58.8 (=N-CH_2-).

Compound **2.7b** was obtained by following the same procedure described for **2.7a**, by reacting **1.7b** with $Na_2[PdCl_4]$ and $NaOAc \cdot 3H_2O$ in methanol at room temperature.
Yield: 75.7%. Anal. Calc. for $C_{17}H_{16}ClFeNPdS$: C, 44.07; H, 3.48; N, 3.03. Found: C, 44.1; H, 3.4; N, 3.1 %. MS (ESI): m/z = 463, $[M]^+$. ^{1}H NMR δ = 7.71 (s, 1H, -CH=N-), 7.16 (d, 1H, $^3J_{HH}$ = 5.0 Hz, $H_{5'}$), 6.94 (br s, 2H, $H_{3'}$ and $H_{4'}$), 5.30 (br s, 1H, H_5), 4.84 (br s, 2H, H_3 and H_4), 4.33 (s, 5H,

Cp), 3.76 (m, 1H, =N-CH_2-), 3.70 (m, 1H, =N-CH_2-), 3.37 (m, 2H, -CH_2-). $^{13}C\{^1H\}$ NMR δ = 174.0 (-CH=N-), 140.0 ($C_{2'}$), 127.4 ($C_{4'}$), 126.3 ($C_{3'}$), 124.1 ($C_{5'}$), 109.3 (C_1), 87.0 (C_2), 74.3 (C_5), 71.2 (Cp), 68.2 (C_3), 66.3 (C_4), 61.6 (=N-CH_2-), 31.0 (-CH_2-).

Synthesis of [Pd{[(RC=CR)$_2$(η^5-C_5H_3)-CH=N-$(CH_2)_n$-(C_4H_3S)]Fe(η^5-C_5H_5)}Cl] (n=1, R = Ph, ***3.7a****; n=2, R = Ph,* ***3.7b****; n=1, R = Et,* ***3.7c****; n=2, R = Et,* ***3.7d****; n=1, R = CO_2Me,* ***3.7e****; n=2, R = CO_2Me,* ***3.7f)***

A solution of **2.7a** (150 mg, $3.3\cdot10^{-4}$ mol) in CH_2Cl_2 (20 mL) was treated with PhC≡CPh (117 mg, $6.6\cdot10^{-4}$ mol). The resulting solution was heated at refluxing temperature for 4 h. Then, the solvent was removed under reduced pressure. This crude product was purified by chromatography on a SiO_2 column, using CH_2Cl_2 as eluent. The product **3.7a** is eluted as a first orange band. Yield (**3.7a**): 250 mg (94%). Anal. Calc. for $C_{44}H_{34}ClFeNPdS$: C, 65.59; H, 4.26; N, 1.74. Found: C, 65.6; H, 4.2; N, 1.8 %. MS (ESI): m/z = 806, $[M]^+$. ^1H NMR δ = 7.68 (s, 1H, -CH=N-), 7.60-6.60 (m, 23H, Ph and C_4H_3S), 5.56 (d, 1H, $^2J_{HH}$ = 14 Hz, =N-CH_2-), 4.89 (d, 1H, $^2J_{HH}$ = 14 Hz, =N-CH_2-), 4.65 (br s, 1H, H_3), 4.60 (br s, 1H, H_4), 4.37 (br s, 1H, H_5), 4.13 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR δ = 164.8 (-CH=N-), 154.5 (C_{olef}), 145.5 (C_{olef}), 140.7 ($C_{2'}$), 134.6 (C_{olef}), 139.8-126.0 (C_{Ph}), 127.7 ($C_{3'}$), 127.5 ($C_{4'}$), 126.2 ($C_{5'}$), 110.2 (C_{olef}), 89.1 (C_2), 75.8 (C_3), 73.2 (C_5), 72.4 (C_4), 72.2 (C_1), 72.1 (Cp), 58.3 (=N-CH_2-).

Compounds **3.7b-f** were prepared by following the same procedure described for **3.7a**, by reacting **2.7a-b** with the appropriate alkyne (molar ratio alkyne/Pd 2:1).

3.7b: Yield: 93%. Anal. Calc. for $C_{45}H_{36}ClFeNPdS$: C, 65.93; H, 4.43; N, 1.71. Found: C, 66.1; H, 4.2; N, 1.8 %. MS (ESI): m/z = 820 $[M]^+$. ^1H NMR δ = 7.62 (s, 1H, -CH=N-), 7.55-6.60 (m, 23H, Ph and C_4H_3S), 4.68 (br s, 1H, H_5), 4.65 (m, 1H, =N-CH_2-), 4.62 (br s, 1H, H_4), 4.38 (br s, 1H, H_3), 4.12 (s, 5H, Cp), 3.66 (m, 1H, -CH_2-), 3.46 (m, 1H, =N-CH_2-), 2.77 (m, 1H, -CH_2-). $^{13}C\{^1H\}$ NMR δ = 164.6 (-CH=N-), 155.0 (C_{olef}), 145.1 (C_{olef}), 142.2 ($C_{2'}$), 133.9 (C_{olef}), 140.0-125.9 (C_{Ph}), 127.4 ($C_{4'}$), 126.2 ($C_{3'}$), 123.8 ($C_{5'}$), 109.7 (C_{olef}), 88.5 (C_2), 75.1 (C_5), 72.6 (C_3), 72.1 (C_1), 71.8 (C_4), 71.7 (Cp), 63.9 (=N-CH_2-), 32.1 (-CH_2-).

3.7c: Yield: 91%. Anal. Calc. for $C_{28}H_{34}ClFeNPdS$: C, 54.81; H, 5.59; N, 2.28. Found: C, 55.0; H, 5.5; N, 2.3 %. MS (ESI): m/z = 614 $[M]^+$. ^1H NMR δ = 7.95 (s, 1H, -CH=N-), 7.25 (dd, 1H, $^3J_{HH}$ =

5.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, $H_{5'}$), 7.19 (dd, 1H, $^{3}J_{HH}$ = 3.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, $H_{3'}$), 6.98 (dd, 1H, $^{3}J_{HH}$ = 5.0 Hz, $^{3}J_{HH}$ = 3.5 Hz, $H_{4'}$), 5.62 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, =N-CH_2-), 4.97 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, =N-CH_2-), 4.53 (t, 1H, $^{3}J_{HH}$ = 2.5 Hz, H_4), 4.50 (dd, 1H, $^{3}J_{HH}$ = 2.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, H_5), 4.42 (dd, 1H, $^{3}J_{HH}$ = 2.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, H_3), 4.17 (s, 5H, Cp), 2.80-2.72 (m, 2H, C$H_2$$CH_3$), 2.68-2.60 (m, 2H, C$H_2$$CH_3$), 2.56-2.48 (m, 2H, C$H_2$$CH_3$), 2.30-2.22 (m, 2H, C$H_2$$CH_3$), 2.18-2.10 (m, 2H, C$H_2$$CH_3$), 2.10-2.01 (m, 2H, C$H_2$$CH_3$), 1.52 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.49-1.41 (m, 2H, C$H_2$$CH_3$), 1.33-1.25 (m, 2H, C$H_2$$CH_3$), 1.22 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3), 0.96 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3), 0.92 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3). $^{13}C\{^{1}H\}$ NMR δ = 165.8 (-CH=N-), 144.8 (C_{olef}), 140.7 ($C_{2'}$), 136.7 (C_{olef}), 127.1 ($C_{3'}$), 126.9 ($C_{4'}$), 125.7 ($C_{5'}$), 107.9 (C_{olef}), 99.8 (C_{olef}), 89.7 (C_2), 76.1 (C_1), 73.5 (C_3), 71.6 (C_5), 70.7 (C_4), 70.6 (Cp), 57.8 (=N-CH_2-), 35.0 (CH_2CH_3), 25.1 (CH_2CH_3), 24.5 (CH_2CH_3), 21.9 (CH_2CH_3), 17.7 (CH_2CH_3), 14.8 (CH_2CH_3), 13.9 (CH_2CH_3), 12.7 (CH_2CH_3).

3.7d: Yield: 89%. Anal. Calc. for $C_{29}H_{36}ClFeNPdS$: C, 55.50; H, 5.79; N, 2.23. Found: C, 55.5; H, 5.6; N, 2.3 %. MS (ESI): m/z = 628 $[M]^+$. ^{1}H NMR δ = 7.69 (s, 1H, -CH=N-), 7.09 (dd, 1H, $^{3}J_{HH}$ = 5.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, $H_{5'}$), 6.89 (dd, 1H, $^{3}J_{HH}$ = 5.0 Hz, $^{3}J_{HH}$ = 3.5 Hz, $H_{4'}$), 6.86 (dd, 1H, $^{3}J_{HH}$ = 3.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, $H_{3'}$), 4.49 (t, 1H, $^{3}J_{HH}$ = 2.5 Hz, H_4), 4.41 (dd, 1H, $^{3}J_{HH}$ = 2.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, H_5), 4.36 (dd, 1H, $^{3}J_{HH}$ = 2.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, H_3), 4.31 (m, 1H, =N-CH_2-), 4.20 (s, 5H, Cp), 3.87 (m, 1H, =N-CH_2-), 3.36 (m, 1H, -CH_2-), 3.23 (m, 1H, -CH_2-), 2.76-2.68 (m, 2H, C$H_2$$CH_3$), 2.67-2.58 (m, 2H, C$H_2$$CH_3$), 2.52-2.44 (m, 2H, C$H_2$$CH_3$), 2.25-2.16 (m, 2H, C$H_2$$CH_3$), 2.11-2.03 (m, 2H, C$H_2$$CH_3$), 2.06-1.98 (m, 2H, C$H_2$$CH_3$), 1.55 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.43-1.34 (m, 2H, C$H_2$$CH_3$), 1.30-1.22 (m, 2H, C$H_2$$CH_3$), 1.18 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.06 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3), 0.91 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, CH_2CH_3). $^{13}C\{^{1}H\}$ NMR δ = 165.1 (-CH=N-), 145.0 (C_{olef}), 142.2 ($C_{2'}$), 135.9 (C_{olef}), 126.8 ($C_{4'}$), 126.1 ($C_{3'}$), 125.6 ($C_{5'}$), 108.0 (C_{olef}), 99.1 (C_{olef}), 89.3 (C_2), 75.1 (C_1), 73.1 (C_3), 71.2 (C_5), 70.5 (Cp), 70.1 (C_4), 64.0 (=N-CH_2-), 35.2 (CH_2CH_3), 31.8 (-CH_2-), 25.1 (CH_2CH_3), 24.2 (CH_2CH_3), 21.9 (CH_2CH_3), 17.4 (CH_2CH_3), 14.7 (CH_2CH_3), 14.0 (CH_2CH_3), 12.5 (CH_2CH_3).

3.7e: Yield: 90%. Anal. Calc. for $C_{28}H_{26}ClFeNO_8PdS$: C, 45.84; H, 3.58; N, 1.91. Found: C, 45.8; H, 3.6; N, 1.8 %. MS (ESI): m/z = 733 $[M]^+$. ^{1}H NMR δ = 8.01 (s, 1H, -CH=N-), 7.30 (dd, 1H, $^{3}J_{HH}$ = 5.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, $H_{5'}$), 7.15 (dd, 1H, $^{3}J_{HH}$ = 3.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, $H_{3'}$), 7.02 (dd, 1H, $^{3}J_{HH}$ = 5.0 Hz, $^{3}J_{HH}$ = 3.5 Hz, $H_{4'}$), 5.80 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, =N-CH_2-), 5.03 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, =N-CH_2-), 4.70 (t, 1H, $^{3}J_{HH}$ = 2.5 Hz, H_4), 4.44 (dd, 1H, $^{3}J_{HH}$ = 2.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, H_5), 4.37 (dd, 1H, $^{3}J_{HH}$ = 2.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, H_3), 4.20 (s, 5H, Cp), 3.90 (s, 3H, CO_2CH_3), 3.85 (s, 3H,

CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3). $^{13}C\{^1H\}$ NMR δ = 177.0 (CO_2CH_3), 175.9 (CO_2CH_3), 175.0 (CO_2CH_3), 174.3 (CO_2CH_3), 167.4 (-CH=N-), 145.3 (C_{olef}), 141.2 ($C_{2'}$), 137.1 (C_{olef}), 128.7 ($C_{3'}$), 127.6 ($C_{4'}$), 126.3 ($C_{5'}$), 108.8 (C_{olef}), 100.1 (C_{olef}), 91.2 (C_2), 75.3 (C_1), 72.9 (C_3), 70.9 (C_5), 70.4 (C_4), 70.1 (Cp), 59.9 (=N-CH_2-), 55.6 (CO_2CH_3), 52.1 (CO_2CH_3), 51.8 (CO_2CH_3), 50.6 (CO_2CH_3).

3.7f: Yield: 92%. Anal. Calc. for $C_{29}H_{28}ClFeNO_8PdS$: C, 46.59; H, 3.78; N, 1.87. Found: C, 46.4; H, 3.8; N, 1.9 %. MS (ESI): m/z = 747 $[M]^+$. ^1H NMR δ = 8.02 (s, 1H, -CH=N-), 7.26 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.0 Hz, $H_{5'}$), 7.13 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 3.5 Hz, $H_{4'}$), 6.91 (dd, 1H, $^3J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 1.0 Hz, $H_{3'}$), 5.11 (m, 1H, =N-CH_2-), 4.80 (dd, 1H, $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 1.5 Hz, H_5), 4.70 (dd, 1H, $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 1.5 Hz, H_3), 4.46 (t, 1H, $^3J_{HH}$ = 2.5 Hz, H_4), 4.01 (s, 5H, Cp), 3.91 (s, 3H, CO_2CH_3), 3.80 (m, 1H, =N-CH_2-), 3.75 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 3.59 (s, 3H, CO_2CH_3), 3.51 (m, 1H, -CH_2-), 3.24 (m, 1H, -CH_2-). $^{13}C\{^1H\}$ NMR δ = 178.1 (CO_2CH_3), 176.3 (CO_2CH_3), 175.2 (CO_2CH_3), 174.9 (CO_2CH_3), 168.1 (-CH=N-), 146.1 (C_{olef}), 141.2 ($C_{2'}$), 136.0 (C_{olef}), 127.4 ($C_{4'}$), 127.2 ($C_{3'}$), 124.1 ($C_{5'}$), 108.2 (C_{olef}), 99.4 (C_{olef}), 88.1 (C_2), 75.4 (C_1), 72.6 (C_3), 72.4 (C_5), 70.3 (Cp), 70.0 (C_4), 66.5 (=N-CH_2-), 55.9 (CO_2CH_3), 53.7 (CO_2CH_3), 52.2 (CO_2CH_3), 51.0 (CO_2CH_3), 29.9 (-CH_2-).

References

[1] (a) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917; (b) R.G. Newkome, G.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451, and references therein; (c) V.V. Dunina, O.A. Zalevskaya, V.M. Potatov, Russ. Chem. Rev. (Engl. Transl.) 57 (1998) 250, and references therein; (d) A.D. Ryabov, Chem. Rev. 90 (1990) 403, and references therein; (e) I. Omae, Coord. Chem. Rev. 83 (1998) 137, and references therein.

[2] (a) I. Omae, Applications of Organometallic Compounds, Wiley, Chichester, UK, 1988 (Chapter 20, p. 423); (b) A.K. Klaus, in: A.E. Peters, H.S. Freeman (Eds.), Modern Colorants: Synthesis and Structure, vol. 3, Blackie Academic, London, UK, 1995, p. 1.

[3] (a) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215, and references therein; (b) N.J. Thompson, J.L. Serrano, M.J. Baena, P. Espinet, Chem. Eur. J. 2 (1996) 214, and references therein.

[4] (a) Y. Wu, J. Hou, X. Cui, R. Yuan, J. Organomet. Chem. 637-639 (2001) 793; (b) A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, J. Dupont, J. Org. Lett. 2 (2000) 2187; (c) A. Bose, C.R. Saha, J. Mol. Catal. 49 (1989) 271; (d) P.K. Santra, C.R. Saha, J. Mol. Catal. 39 (1987) 279.

[5] M. Torres-Lopez, A. Fernandez, J.J. Fernandez, A. Suarez, S. Castro-Juiz, J.M. Vila, M.T. Pereira, Organometallics 20 (2001) 1350.

[6] S.B. Wild, Coord. Chem. Rev. 166 (1997) 291, and references therein.

[7] J. Albert, J.M. Cadena, J.R. Granell, X. Solans, M. Font-Bardia, Tetrahedron: Asymmetry 11 (2000) 1943.

[8] C. Lopez, R. Bosque, D. Sainz, X. Solans, M. Font-Bardia, Organometallics 16 (1997) 3261.

[9] M. Ghedini, A. Crispini, Comments Inorg. Chem. 21 (1999) 53.

[10] (a) J. Spencer, M. Pfeffer, Adv. Met-Org. Chem. 6 (1998) 103, and references therein; (b) M. Pfeffer, Recl. Trav. Chim. Pays-Bas 109 (1990) 567, and references therein; (c) A.D. Ryabov, Synthesis (1985) 233, and references therein.

[11] (a) A.E. Kellyu, I.A. McGregor, A.C. Willis, J.H. Nelson, E. Werger, Inorg. Chim. Acta 352 (2003) 79; (b) N. Gul, J.H. Nelson, A.C. Willis, A.D. Ross, Organometallics 21 (2002) 2041; (c) J. Vicente, I. Saura-Llamas, M.C. Ramirez de Arellano, J. Chem. Soc., Dalton Trans. 2529 (1995); (d) J. Vicente, J.A. Abad, J. Gil-Rubio, I. Jones, M.C. Ramirez de Arellano, J. Chem. Soc., Dalton Trans. (1995) 2529; (e) J. Vicente, I. Saura-Llamas, M.G. Palin, J. Chem. Soc., Dalton Trans. (1995) 2535; (f) J. Albert, J. Granell, J. Sales, X. Solans, J. Organomet. Chem. 379 (1989) 177; (g) A. Bohn, K. Polborn, K. Sunkel, W. Beck, Z. Naturforsch. B 53 (1999) 448; (h) J.P. Sutter, M. Pfeffer, A. de Cian, J. Fischer, Organometallics 11 (1992) 386; (i) A.D. Ryabov, R. van Eldik, G.

Le Borgne, M. Pfeffer, Organometallics 12 (1993) 1386; (k) M. Pfeffer, J.P. Sutter, A. de Cian, J. Fischer, Organometallics 12 (1993) 1167; (l) M. Pfeffer, J.P. Sutter, M.A. Rotteveel, A. de Cian, J. Fischer, Tetrahedron 48 (1992) 2427.

[12] (a) M. Pfeffer, J.P. Sutter, A. de Cian, J. Fischer, Organometallics 12 (1993) 1167; (b) M. Pfeffer, M.A. Rotteveel, J.P. Sutter, A. de Cian, J. Fischer, J. Organomet. Chem. 371 (1989) C21; (c) G. Zhao, Q.G. Wang, T.C.W. Mak, J. Organomet. Chem. 574 (1999) 311; (d) C. Lopez, D. Tramuns, X. Solans, J. Organomet. Chem. 471 (1994) 265; (e) M. Benito, C. Lopez, X. Morvan, X. Solans, M. Font-Bardia, J. Chem. Soc., Dalton Trans. (2000) 4470; (f) R. Bosque, M. Benito, C. Lopez, New J. Chem. 25 (2001) 827; (g) M. Benito, C. Lopez, X. Solans, M. Font-Bardia, Tetrahedron: Asymmetry 25 (1998) 827; (h) W. Tao, L.J. Silverberg, A.L. Reingold, R.F. Heck, Organometallics 8 (1989) 2550; (i) G. Zhao, Q.G. Wang, T.C.W. Mak, J. Organomet. Chem. 574 (1999) 311; (j) C. Lopez, A. Caubet, X. Solans, M. Font-Bardia, J. Organomet. Chem. 598 (2000) 87; (k) G. Zhao, Q.G. Wang, T.C.W. Mak, Tetrahedron: Asymmetry 9 (1998) 2253.

[13] S. Perez, C. Lopez, A. Caubet, A. Pawelczyc, X. Solans, M. Font-Bardia, Organometallics 22 (2003) 2396.

[14] (a) C. Lopez, J. Sales, X. Solans, R. Zquiak, J. Chem. Soc., Dalton Trans. (1992) 2321–2328; (b) R. Bosque, C. Lopez, J. Sales, X. Solans, M. Font-Bardia, J. Chem. Soc., Dalton Trans. (1994) 735–746.

[15] J. Vicente, A. Arcas, D. Bautista, P.G. Jones, Organometallics 16 (1997) 2127.

[16] C. Hansch, A. Leo, D. Koekman, Exploring QSAR: Hydrophobic, Electronic and Steric Constants; American Chemical Society: Washington, DC, 1995.

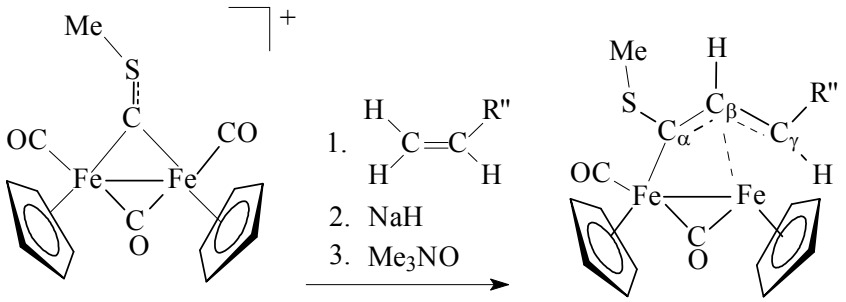
CHAPTER VIII

CONCLUSIONS

Conclusions

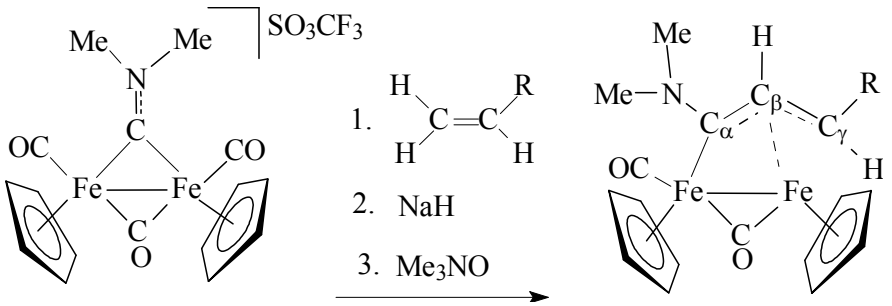
The results achieved during the Ph.D. can be summarized in the following points:

- We have extended the assembling between small unsaturated molecules and bridging carbyne ligands in diiron complexes to other species. In particular, we have investigated the coupling between olefins and thiocarbyne (Chapter II), leading to the synthesis of thioallylidene bridging diiron complexes. This reaction is regio- and stereospecific and represents a rare example of olefin incorporation into a bridging ligand producing a C_1 to C_3 chain growth.



Moreover, we have evidenced the possibility that the bridging C_3 frame, obtained by alkene-carbyne coupling, can be further modified by methylation of the S atom and displacement of the SMe_2 group. This approach provides a route for replacing the μ–C-S bond with a μ–C-C or μ–C-H bond.

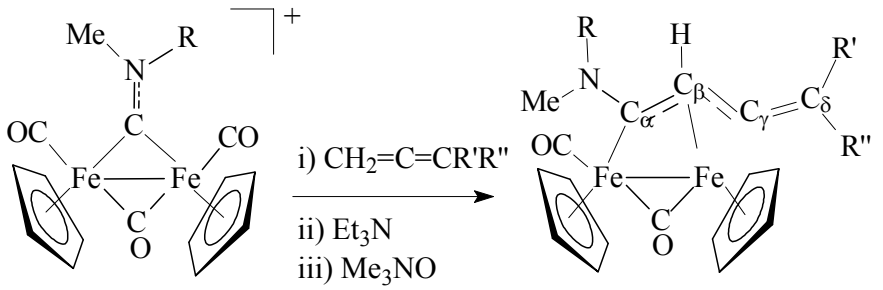
Then, we have extended the study to the coupling between olefins and aminocarbyne (Chapter III).



This result shows that the coupling between activated olefins and heteroatom substituted μ-carbynes has a general character and is not trivial. Indeed, bridging

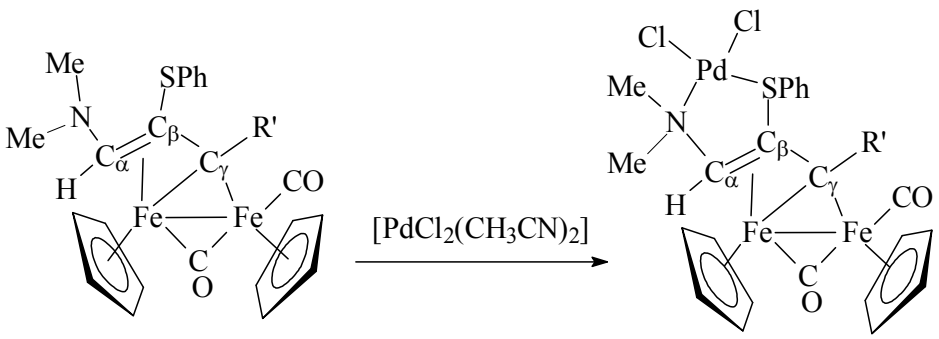
thio- and aminocarbyne ligands display similar properties, in that both contain a π donor heteroatom which provides stabilization to the adjacent carbyne carbon. However, the extent of π-interaction is different in the two ligands and this leads, in some cases, to different reaction profiles, so that predictions of the reactivity of aminocarbyne based upon the reactions observed for thiocarbyne, or vice versa, are often unreliable.

- As we have shown, the coupling of bridging alkylidyne ligands with alkynes and alkenes provides excellent routes to the synthesis of bridging C_3 hydrocarbyl ligands. As a possible extension of these results we have examined the synthesis of C_4 bridging frames through the combination of μ-C_1 alkylidynes with allenes (Chapter IV).



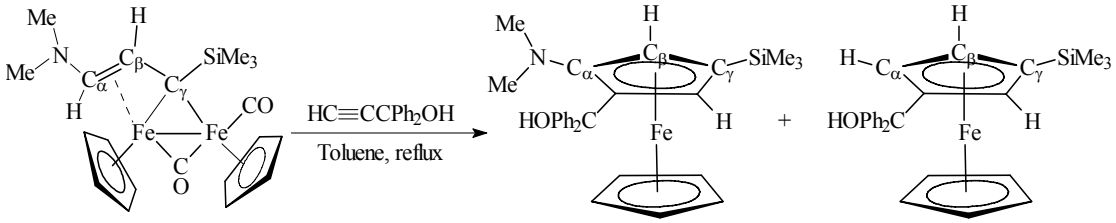
The reaction has a general character and leads to the formation of novel thio- and aminobutadienylidene complexes. It should be remarked that examples of incorporation of allenes into bridging hydrocarbyl ligands are relatively limited, in spite of the fact that cumulenes are generally more reactive than alkenes.

- Diiron complexes bearing bridging functionalized C_3 organic frames display the presence of donor atoms, such as N and S, potentially able to coordinate unsaturated metal fragments and act as 'organometallic ligands' (Chapter V).



Their coordination ability can be properly tuned through appropriate transformations. Thus, systems containing both -NMe_2 and -SPh groups behave as hetero bidentate ligand and display chelating properties with respect to Pd and Rh. Moreover, the bridging ligand can also contain OH as oxygen donor functionality, in addition to S and N, making possible a S, O bidentate coordination.

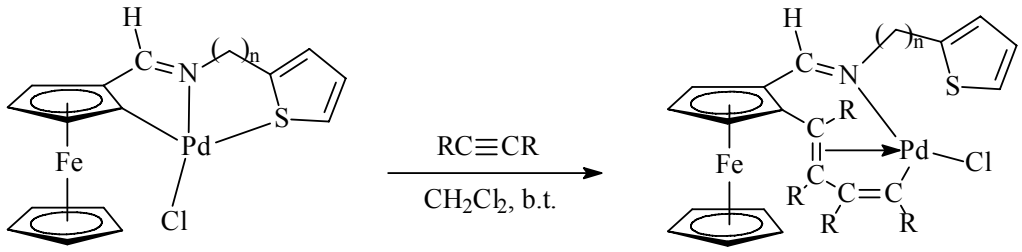
- As shown before, the assembling of small organic molecules and bridging carbyne ligands in diiron complexes leads to the formation of variously functionalized C_3 organic frames. In this assembling process the activation/stabilization effects induced by the dimetal frame on the organic ligand play a key role. On the other hand, the possibility of releasing the organic frame from the bridging coordination appears particularly appealing in the direction of a metal-assisted organic synthesis. Within this field, we have investigated the possibility of involving the C_3 bridging ligand in cycloaddition reactions with alkynes, with the aim of generating variously functionalized five-membered cycles (Chapter VI). Almost unexpectedly, the [3+2] cyclization does not lead to the complete release of the organic fragment but rather it produces its transformation into a cyclopentadienyl ring, which remains coordinated to one Fe atom.



This result introduces a new approach to the formation of polyfunctionalised ferrocenes. The limitations due to the absence of a complete chemo- and regio-control of the reaction and the use of rather 'sophisticated' bridging vinylalkylidene complexes as precursors would be compensated by the direct formation of ferrocenes characterized by the presence of 2-3 different substituents in only one of the two cyclopentadienyls. Indeed, ferrocenes of this type are difficult to obtain.

- Furthermore, I have spent a research period of about six months at the Department of Inorganic Chemistry of the Barcelona University, under the supervision of Prof. Concepción López, with the aim of studying the chemistry of polydentate ferrocenyl ligands and their use in organometallic synthesis (Chapter VII). More in specific, we have prepared the new ferrocenyl Schiff bases [Fc-CH=N-$(CH_2)_n$-(C_4H_3S)] (n=1,2),

which are characterized by the presence of a thienyl group. They act as terdentate ligands toward palladium, coordinating through the imine nitrogen, the thienyl sulphur and the C(sp^2) carbon atom adjacent to the imine group. Then, we have investigated the reactivity of the resulting cyclopalladated complexes toward the internal alkynes R-C≡C-R (R = Ph, Et, CO_2Me).



The reaction affords, in all the cases, the product of bis-insertion and is not affected by: (a) the nature of the substituents on the alkyne (neither their electron-donor/electron-withdrawing nature nor their sterical hindrance); (b) the length of the -$(CH_2)_n$- chain of the ligand; (c) the molar ratio between the Pd complex and the alkyne.

List of publications

Busetto, L.; Marchetti, F.; Mazzoni, R.; Salmi, M.; Zacchini, S.; Zanotti, V.
"**Bridging Vinyliminium and Enaminoalkylidene diiron Complexes as Organometallic Ligands"**
Eur. J. Inorg. Chem. **2009**, *9*, 1268-1274. DOI: 10.1002/ejic.200801198

Busetto, L.; Marchetti, F.; Mazzoni, R.; Salmi, M.; Zacchini, S.; Zanotti, V.
"SPh functionalized bridging vinyliminium diiron and diruthenium complexes"
J. Organomet. Chem. **2008**, *693*, 3191-3196. DOI: 10.1016/j.jorganchem.2008.07.009

Busetto, L.; Dionisio, M.; Marchetti, F.; Mazzoni, R.; Salmi, M.; Zacchini, S.; Zanotti, V.
"Zwitterionic diiron vinyliminium complexes: alkylation, metalation and oxidative coupling at the S and Se functionalities"
J. Organomet. Chem. **2008**, *693*, 2383-2391. DOI: 10.1016/j.jorganchem.2008.04.010

Busetto, L.; Marchetti, F.; Salmi, M.; Zacchini, S.; Zanotti, V.
"Coupling of allenes with μ-alkylidyne ligands in diiron complexes: synthesis of novel bridging thio- and aminobutadienylidene complexes"
Eur. J. Inorg. Chem. **2008**, *15*, 2437-2447. DOI: 10.1002/ejic.200800048

Busetto, L.; Salmi, M.; Zacchini, S.; Zanotti, V.
"Olefin-aminocarbyne coupling in diiron complexes: synthesis of new bridging aminoallylidene complexes"
J. Organomet. Chem. **2008**, *693*, 57-67. DOI: 10.1016/j.jorganchem.2007.10.015

Busetto, L.; Marchetti, F.; Salmi, M.; Zacchini, S.; Zanotti, V.
"C-C bond formation through olefin-thiocarbyne coupling in diiron complexes"
J. Organomet. Chem. **2007**, *692*, 2245-52. DOI: 10.1016/j.jorganchem.2007.01.052