

Review

Carbene ligands in diiron complexes [☆]

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Abstract

The diiron frame $\text{Fe}_2\text{Cp}_2\text{CO}_2$ allows the coordination of a variety of carbene ligands, including heteroatom substituted (Fischer type) and alkylidenes, in both bridging and terminal coordination modes. Synthetic strategies have been devised for obtaining aminocarbenes and thiocarbenes, by nucleophilic addition on the corresponding bridging amino- and thio-carbyne cationic complexes $[\text{Fe}_2(\mu\text{-CX})(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ ($\text{X} = \text{SMe}$, NMe_2 , $\text{N}(\text{Me})\text{Xyl}$), respectively. A more general approach to the synthesis of diiron complexes bridged by carbenes, exploits the electrophilic character of the sulphonium complex $[\text{Fe}_2\{\mu\text{-C}(\text{CN})\text{-}(\text{SMe}_2)\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ and the *facile* displacement of the SMe_2 moiety by nucleophiles. These methods afford a large variety of heteroatom (N, P, O, S) substituted carbene complexes and also μ -alkylidenes.

Terminally bonded alkynyl methoxy carbene complexes have been obtained by the classical Fischer method, consisting in nucleophilic addition at a terminal CO, to generate an acyl intermediate, followed by oxygen atom methylation. The coordination to diiron cationic complexes makes the alkynylmethoxy carbene ligands very reactive towards the addition of nucleophiles, like amines and carbanions. These additions are regio- and stereoselective, occurring exclusively at the alkynyl moiety.

Finally, new multidentate and functionalized bridging ligands are described. They are anchored to the diiron frame through an aminocarbene, or an alkylidene binding end, or both. These ligands result from intramolecular couplings and rearrangements which involve the μ -aminocarbyne, the terminally bonded nitrile ligands and acetylides.

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Keywords: Carbene; Carbyne; Diiron complexes; Bridging ligands

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1. Introduction

Since the first tungsten(0) carbene complex reported by Fischer and Maasböl in [1], transition metal carbene complexes have experienced a rapid and enormous development which has been paralleled by applications in organic synthesis [2] and catalysis [3]. Both heteroatom stabilized carbenes (Fischer) and electrophilic (Schrock) [4] carbenes are considered among the most versatile organometallic reagents.

The overwhelming majority of carbene complexes are mononuclear and investigations concerning di- and polynuclear carbene complexes have been considerably more limited [5]. However, they represent an area of growing interest in the development of new reagents and catalysts because of the potential advantage of cooperative effects due to the presence of two, or more, metal atoms [6]. An additional reason which makes attractive the studies on dinuclear complexes derives from the possibility of favouring further coordination modes for the carbene ligands, which in turn, are expected to produce a considerable extension and modification of their reactivity. As an example, Sierra has recently reviewed [5] on the different mode, for a heteroatom substituted metal carbene (Fischer type carbenes) to join a second metal atom. As shown in Chart 1, the bond, which can be direct or mediated by a hydrocarbon chain, may occur through: (i) the carbene carbon (I); (ii) the heteroatom (II); (iii) the metal atom (III). In addition, carbenes can 'bridge' two metal atoms (IV), and Fischer carbenes may assume a further coordination mode (V) due to the heteroatom–metal interaction, which is believed to contribute significantly to their stability [7].

Bridging carbenes are usually more stable, and less reactive compared to the corresponding terminally coordinated species. Notwithstanding this, they have been intensively investigated, and in particular complexes bearing the bridging methylene (μ -CH₂) have provided valuable organometallic models for investigating Fischer–Tropsch processes [8].

Herein we will briefly review our contribution in the field of the dinuclear complexes containing

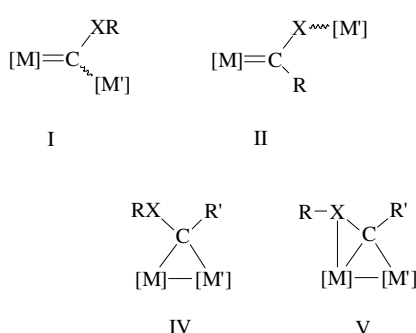


Chart 1.

carbene ligands, both bridging and terminally coordinated.

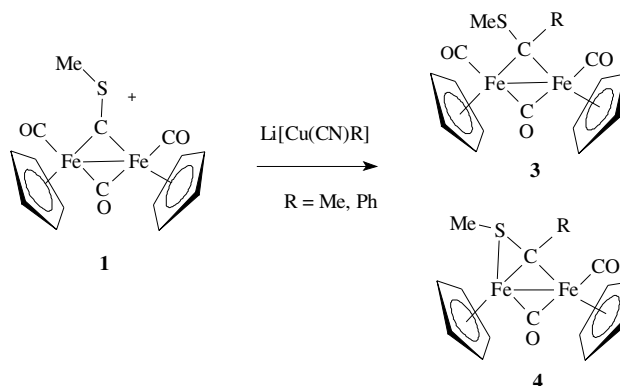
2. Dinuclear complexes with bridging Fischer carbene ligands

2.1. Synthesis from bridging carbyne complexes

Several methods have been devised for the synthesis of bridging carbenes; among them, the outstanding contributions of F.G.A. Stone have to be recognized [9] for his modular approach to the construction of clusters with bridging carbenes and carbynes, and the fruitful use of isolobal analogy concepts [10]. The reaction of mononuclear carbynes with appropriate metal containing nucleophiles or metal hydrides is still a useful route for synthesis of bridging carbene complexes [11]. Bridging carbynes are also good source of μ -carbenes: a significant example concern the bridging methyldiene complex $[\text{Fe}_2(\mu\text{-CH})(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]^+$, which has been studied in details over more than a decade by Casey et al. [12]. The relevant electrophilic character of the μ -CH ligand allows a large variety of nucleophilic additions at the bridging carbon, including the remarkable 'hydrocarbation' [13] and provide access to a variety of bridging carbene complexes.

Several years ago our attention was directed to related diiron complexes characterized by the presence of heteroatom substituted bridging carbyne ligands: the thiocarbyne $[\text{Fe}_2(\mu\text{-CSMe})(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (**1**) [14] and aminocarbyne $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (R = Me, CH₂Ph, Xyl) (**2**) [15]. Our aim was to find methods for generating Fischer type bridging thio- and amino-carbene complexes and to study their chemistry.

The thiocarbyne complex **1** undergoes addition at the bridging carbyne carbon by a variety of nucleophilic reagents, including: NaBH₄ [16], cyanide [17], and several organocopper reagents [18] (Scheme 1). In all the cases,

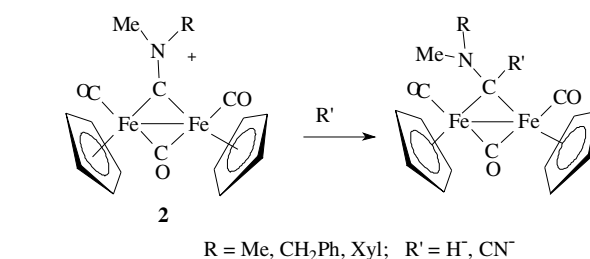


Scheme 1.

the reaction products are the expected bridging thiocarbene complexes, which frequently exhibit S–Fe interaction (e.g., **4**). This latter coordination mode is promoted by loss of CO, easily achieved under photolytic conditions.

It should be noted that not all the nucleophilic reagents attack exclusively the bridging carbon; thus, the reaction pathway shown in Scheme 1 lacks of general character. Indeed, other organometallic reagents (e.g., Grignard reagents or lithium acetylides) give selective additions at the Cp or at the CO, rather than reacting with the carbyne ligand [18]. However, even in these cases, the bridging thiocarbene does not act as a simple spectator ligand, but is involved in intramolecular rearrangements, which ultimately afford stable bridging thiocarbene complexes. As an example, the addition of Grignard reagents (RMgCl; R = allyl, Ph, CH₂Ph, Prⁱ) to the Cp ligands of **1** leads to the formation of the cyclopentadiene compounds [Fe₂(μ-C(SMe)(μ-CO)(CO)₂(C₅H₅R)(Cp)] (**5**) which, in turn, undergo hydride migration from cyclopentadiene to the μ-carbyne carbon, affording the μ-thiocarbene **6** (Scheme 2) [18,19]. Likewise, nucleophilic attacks at the terminally coordinated CO are followed by acyl migration to generate the μ-thiocarbene complexes [Fe₂{μ-C(SMe)COR}(μ-CO)(CO)(Cp)₂] (**7**) (Scheme 2) [18].

The aminocarbene complex [Fe₂{μ-CN(R)Me}(μ-CO)(CO)₂(Cp)₂][SO₃CF₃] (**2**) (R = Me, CH₂Ph, Xyl) exhibits a chemistry which parallels that of **1**. However, additions of nucleophiles (R') to the carbyne carbon, to generate bridging aminocarbene complexes [Fe₂{μ-C(R')N(R)Me}(μ-CO)(CO)₂(Cp)₂] were limited to the reactions with NaBH₄ (H⁻ addition) and NBu₄CN (CN⁻ addition) (Scheme 3) [20]. Carbon nucleophiles, like organo-lithium and Grignard reagents, have been shown to attack regioselectively the Cp, whereas organocopper reagents selectively react at the CO [21]. Moreover, the compounds thus formed: the cyclopentadiene complexes [Fe₂{μ-CN(R)Me}(μ-CO)(CO)₂(C₅H₅R)(Cp)] and acyl complexes [Fe₂{μ-CN(R)Me}(μ-CO)(CO)(COR)(Cp)₂], respectively, have been proved very stable, and did not undergo any of the rearrangements observed in the case of the thiocarbene analogues.



Scheme 3.

A possible explanation of the lower reactivity of the aminocarbene ligand is the strong π -interaction between the N atom and the carbyne carbon, which contains a significant amount of double bond character, as shown by diffraction studies on a variety of complexes [21,22]. Therefore, aminocarbynes **2** do not provide a general entry to the synthesis of the corresponding bridging aminocarbene complexes.

The synthetic approach depicted in Scheme 3, although limited to the cyanide and hydride addition, has been successfully employed to introduce a second bridging aminocarbene ligand. Thus, compound **8** (Chart 2) has been obtained by using a stepwise

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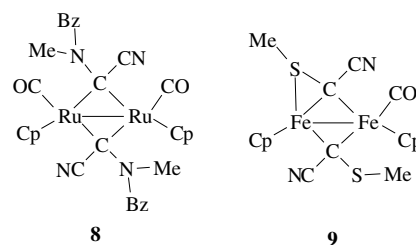
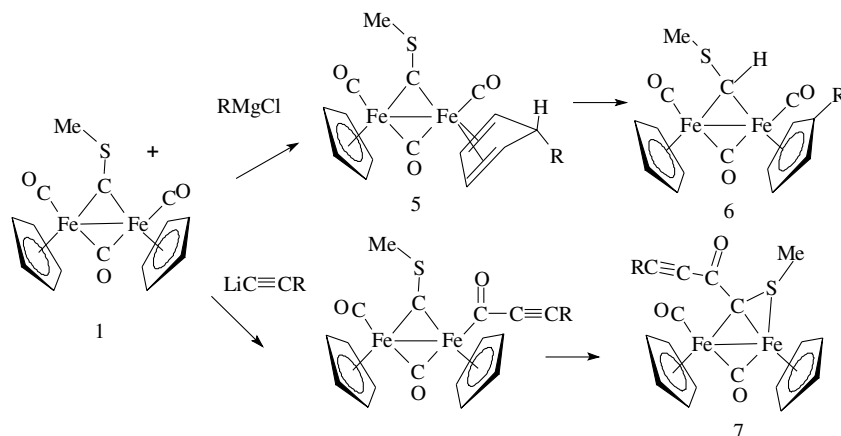


Chart 2.



Scheme 2.

sequence consisting in alkylation of an isocyanide ligand, to generate an aminocarbyne, followed by CN^- addition [23].

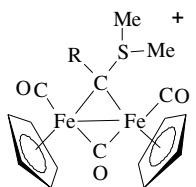
A similar approach has been also applied to the synthesis of a double bridging thiocarbene complex **9** (Chart 2), starting from the bis- μ -thiocarbonyl complex $[\text{Fe}_2(\mu\text{-CS})_2(\text{CO})_2(\text{Cp})_2]$ [24].

2.2. Syntheses from μ -sulphonium alkylidene

A more effective approach to the synthesis of bridging aminocarbene complexes has been provided by the sulphonium carbenes $[\text{Fe}_2\{\mu\text{-C(R)(SMe}_2)\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ ($\text{R} = \text{H}$ (**10a**), $\text{R} = \text{CN}$ (**10b**)), (Chart 3), which in turn, have been generated from the S-methylation of the thiocarbene parent complexes $[\text{Fe}_2\{\mu\text{-C(R)(SMe)}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]$ [25].

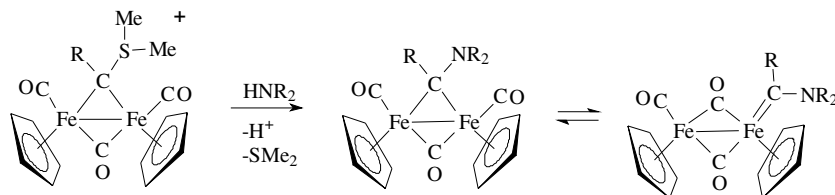
Complexes **10a–b** have been shown to act as a precursors of a large variety of aminocarbene complexes via the *facile* displacement of SMe_2 by secondary amines [20,25a] (Scheme 4).

This successful synthesis led to the observation that aminocarbene ligands can easily switch their coordination mode from bridging to terminal. This is possible because, within the $\text{Fe}_2(\text{CO})_2\text{Cp}_2$ frame, CO and carbene ligands are fluxional and can easily exchange their coordination positions (Scheme 4). Thus, the amino carbene ligands preferentially adopt the terminal coordination in the presence of rather hindered nitrogen substituents (steric factors). Conversely, electron withdrawing substituents on the carbene carbon (e.g., cyanide) provide stabilization to the bridging coordination. Indeed, cyano-aminocarbene complexes have been found predominantly bridging.



R = H, **10a**; CN, **10b**

Chart 3.



10a-b

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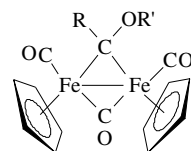
Scheme 4.

The sulphonium derivatives **10a–b** also provide access to μ -alkoxy carbenes, since the SMe_2 fragment is easily displaced by alcohols. A variety of bridging alkoxy carbene diiron complexes have been prepared by this route (Chart 4, **12**) [26]; the carbene ligand steadily occupy the bridging coordination and do not show any tendency to exchange with the terminal CO.

Bridging phosphino carbene complexes have been analogously obtained by reaction of **10a–b** with phosphanes ($\text{HPR}'\text{R}''$) in the presence of NEt_3 (Scheme 5) [27]. The reactions generate phosphonium intermediates **13**, which are deprotonated by NEt_3 to form the bridging phosphino carbene complexes **14**. This is a remarkable result in view of the fact that Fischer type carbene ligands containing P as heteroatom are still rather uncommon, particularly in the bridging coordination [28]. In spite of recent results in the synthesis of stable free phosphino carbenes and in their direct complexation [29], these species show some reluctance to act as ligands [30]. Therefore, any possible approach to the synthesis of phosphino carbene complexes is of interest.

Heteroatoms provide stabilization to the electrophilic carbene carbon by π -donation. As expected, P is a less efficient π -donor respect to O or N. The consequence is that phosphino carbenes are easily alkylated or protonated at the P atom generating stable phosphonium complexes. It is also to be mentioned that the phosphino carbene complexes **14** adopt a bridging coordination without any exchange with terminal CO.

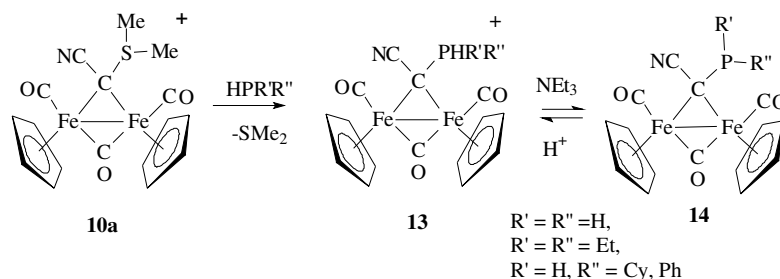
Finally, **10a–b** are also precursors of bridging alkylidene complexes **15** and **16**, arising from displacement of



12

R = H, CN;
R' = Me, Et, Prⁱ, Ph, CH₂Ph,
Ar, C(O)CH₃;

Chart 4.



Scheme 5.

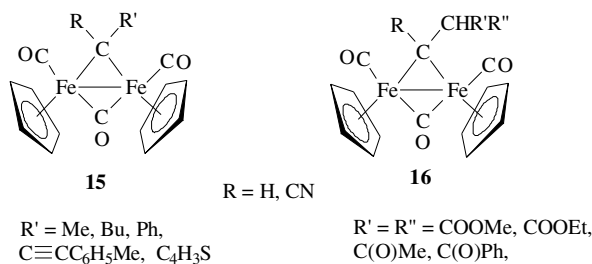


Chart 5.

SMe_2 by carbon nucleophiles (Chart 5). These latter include: organocopper reagents $\text{LiCu}(\text{CN})\text{R}'_2$ ($\text{R}' = \text{Me, Bu, Ph, C}\equiv\text{CC}_6\text{H}_5\text{Me, C}_4\text{H}_3\text{S}$) and carbanions derived from methyl or ethyl malonate, ethylacetoacetate, 2,4-pentanedione, dibenzoylmethane and benzylcyanide [31].

3. Dinuclear complexes with terminal Fischer carbene ligands

The synthesis of diiron complexes containing terminally bonded alkoxy carbene ligands has been accomplished following the classical Fischer procedure, consisting in a nucleophilic attack at a CO ligand to form an acyl intermediate, which is subsequently methylated at the oxygen atom. In particular our attention has been attracted by alkynyl alkoxy carbene ligands, because they exhibit a versatile chemistry, with interesting application in organic synthesis [2f,32]. In particular, alkynylcarbenes easily participate in a number of cycloaddition reactions [33] and also undergo Michael addi-

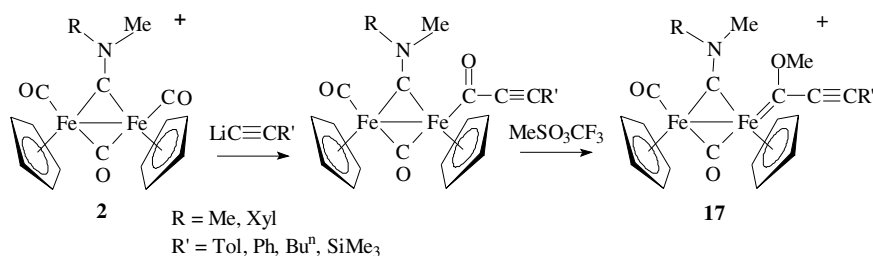
tion with a variety of protic nucleophiles [32]. Diiron alkynyl methoxy carbenes **17** have been obtained starting from the aminocarbene complexes **2**, taking advantage of the demonstrated regioselective addition of acetylides to the CO ligand (Scheme 6).

Reactions of **17** with primary and secondary amines have been described [34]: by contrast with the corresponding reactions of mononuclear chromium and tungsten alkynyl alkoxy carbene complexes $(\text{CO})_5\text{-M}=\text{C}(\text{OEt})\text{C}\equiv\text{CR}$, which undergo ‘aminolysis’ and generate aminocarbene compounds [35], amines give selective addition at the alkynyl moiety of **17**. The coordination of the alkynyl carbene to a cationic diiron frame result in a enhanced electrophilic character and explains the observed regioselective additions. Moreover, the reactions are stereoselective and exclusively produce *cis*-addition at the multiple bond, as found in the reactions with HNMe_2 affording the alkoxy carbene complexes **18** (Scheme 7).

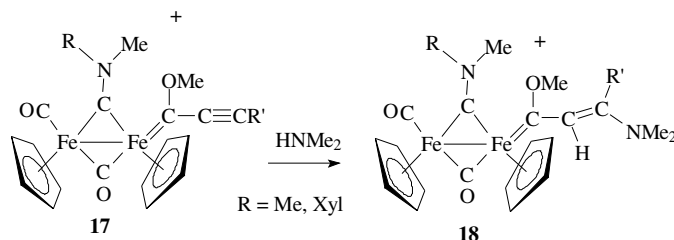
Primary amines ($\text{H}_2\text{NR}'$), both aliphatic and aromatic, react analogously leading to the formation of 4-(NH-amino)-1-metalla-1,3-diene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{R})(\text{NHR}')\}-(\text{Cp})_2]$ (**19**).

Attempts to promote intramolecular couplings between the carbene and the carbyne ligands, aimed at further increasing the complexity of the coordinated organic fragment, have been proved unsuccessful. However, deprotonation of **19** was found to occur at the nitrogen atom to generate the unusual vinyl complexes **20**, (Scheme 8) [34].

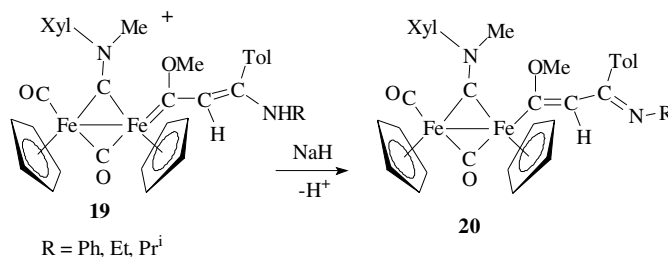
The reactions of **17** with carbon nucleophiles (carbanions of the type CHR'_2^- , $\text{R} = \text{CN, COOMe}$) have been



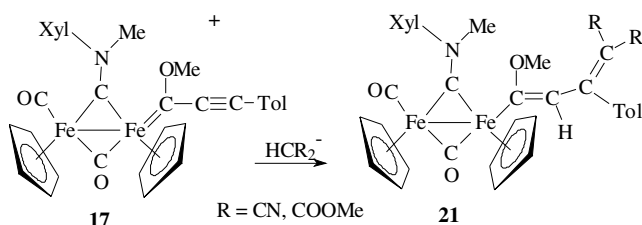
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

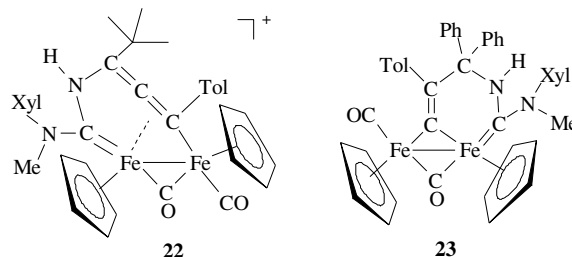


Chart 6.

also investigated. Similarly to the reactions with amines, these reagents attack the alkyne moiety yielding the diynyl complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{O-Me})\text{C}(\text{H})\text{C}(\text{Tol})(\text{CR}_2)\}(\text{Cp})_2]$ (**21**) (Scheme 9).

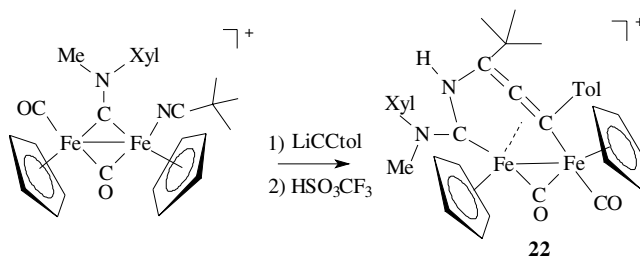
4. Dinuclear complexes bearing multidentate aminocarbene ligands

Recently, we have described the synthesis of diiron complexes with bridging multidentate ligands in which one of the biting ends show diaminocarbene character (Chart 6, compounds **22** [36] and **23** [37]).

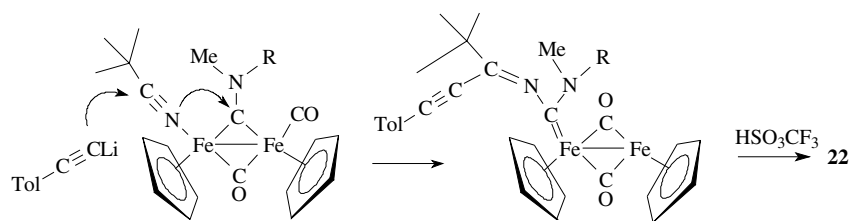
The complex **22** contains a bridging allenyl-diaminocarbene ligand: the allenyl moiety bridges the Fe atoms in a $\mu\text{-}\eta^1, \eta^3$ fashion, whereas the diaminocarbene is terminally bonded, which corresponds, as above discussed, to the favourite coordination mode for this type of ligand. Likewise, the complex $[\text{Fe}_2\{\mu\text{-}\eta^1, \eta^2\text{-C}=\text{C}(\text{Tol})\text{-C}(\text{Ph})_2\text{N}(\text{H})\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**23**), contains a ligand which is anchored to a single Fe atom through a diaminocarbene moiety, whereas is bridging throughout a vinylidene.

Compound **22** is the result of a rather unusual rearrangement and intramolecular coupling which involve the bridging aminocarbyne, the terminal trimethyl acetonitrile ligand and an acetylide $\text{LiC}\equiv\text{CR}$ reagent (Scheme 10).

The reaction sequence is still not established, although plausible hypothesis has been presented [36]. These indicate that the diamino carbene is formed by coupling between the bridging aminocarbyne and a terminally coordinated azavinylidene intermediate, generated from acetylide attack at the trimethylacetonitrile



Scheme 10.



Scheme 11.

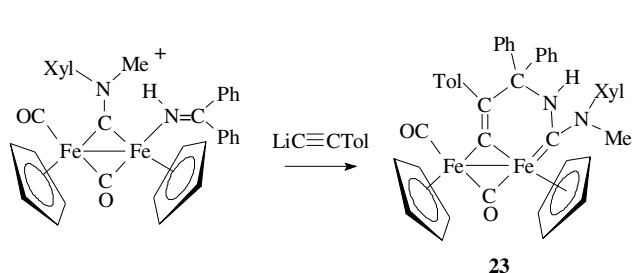
ligand (Scheme 11). The diaminocarbene thus formed, shifts from the bridging to the terminal position. At the end, coordination of the alkynyl group to the unsaturated Fe atom and protonation of the iminic nitrogen lead to **22**.

The reaction which yields **23**, containing a μ -vinylidene-diaminocarbene ligand, presents many analogies to that above described: it occurs between the imine complex $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}(\mu\text{-CO})(\text{CO})(\text{HN}=\text{CPh}_2)(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ and *p*-tolylacetylide (Scheme 12).

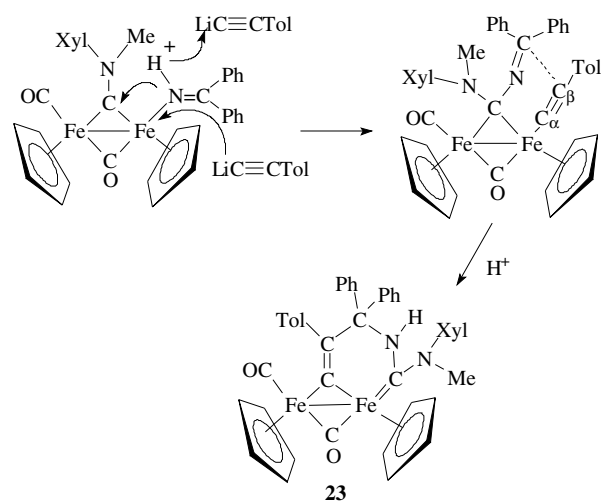
Again, an azavinylidene intermediate ligand is presumably generated, in this case via deprotonation of the coordinated imine $\text{HNC}=\text{CPh}_2$. The azavinylidene intermediate migrates to the μ -aminocarbene, affording the diaminocarbene moiety. Subsequent coordination of the acetylide and intramolecular coupling explain the formation of **23** as summarized in Scheme 13.

The multidentate bridging ligands in **22** and **23** contain a terminally coordinated diaminocarbene moiety, originated from a bridging aminocarbene. The σ -donor properties of the diaminocarbene moiety is expected to be similar to those of related NHC (*N*-heterocyclic carbene ligands) [38] and, therefore, strongly contributing to the overall stability of the complexes **22** and **23**.

Unfortunately, the reactions leading to **22** and **23** are not of general character: different results have been observed changing the nature of the acetylide reagent or the coordinated nitrile. Nevertheless, the overall sequences described in Schemes 11 and 13 indicate that intramolecular coupling between the μ -carbyne and terminally coordinated ligands represent an efficient route to promote additions at the bridging carbyne carbon, otherwise difficult to obtain by direct nucleophilic attack.

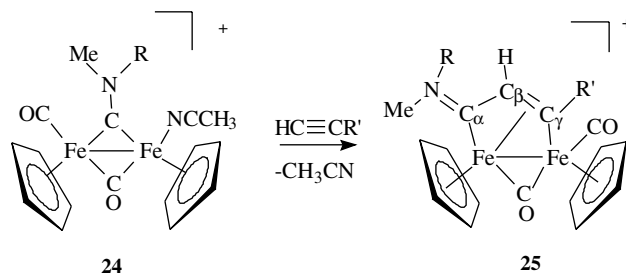


Scheme 12.

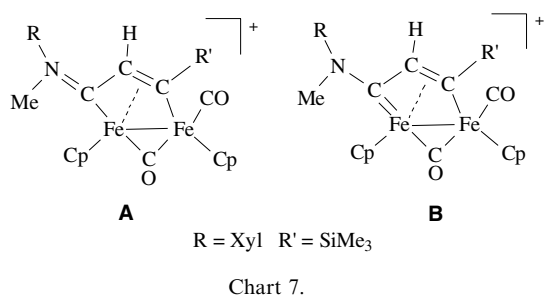


Scheme 13.

This point is well exemplified by the reactions of the amino carbyne with alkynes: the amino carbyne complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{Xyl}$) (**2**) do not react with alkynes, whereas their acetonitrile derivatives $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}(\mu\text{-CO})(\text{CO})(\text{NCMe})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (**24**) promptly undergo alkyne insertion ($\text{HC}\equiv\text{CR}'$) ($\text{R}' = \text{SiMe}_3, \text{Me}, \text{Bu}^n, p\text{-Tol}, \text{Ph}, \text{H}$) into one of the metal carbyne carbon, affording bridging vinyliminium compounds $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{R}')=\text{CHC}=\text{N}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})-(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (**25**) (Scheme 14) [39]. The presence of a labile MeCN ligand in **24** allows alkyne coordination. Thus the insertion is very likely, the result of an intramolecular coupling between the μ -carbyne and the activated alkyne ligand. The reaction is of general applicability: both primary alkynes and disubstituted



Scheme 14.



acetylenes ($R'C\equiv CR'$; $R' = R'' = COOMe, Ph, Me, Et$; $R'C\equiv CR''$, $R' = Me, R'' = Pr^i$) insert in the metal carbyne bond affording the corresponding vinyliminium complexes $[Fe_2\{\mu-\eta^1:\eta^3-C(R')=C(R'')C=N(Me)(R)\}-(\mu-CO)(CO)(Cp)_2][SO_3CF_3]$ in high yield [39]. Moreover, the insertion of primary alkynes is regioselective: the C–C bond formation selectively occurs between the carbyne carbon and the CH moiety of the alkyne (Scheme 14).

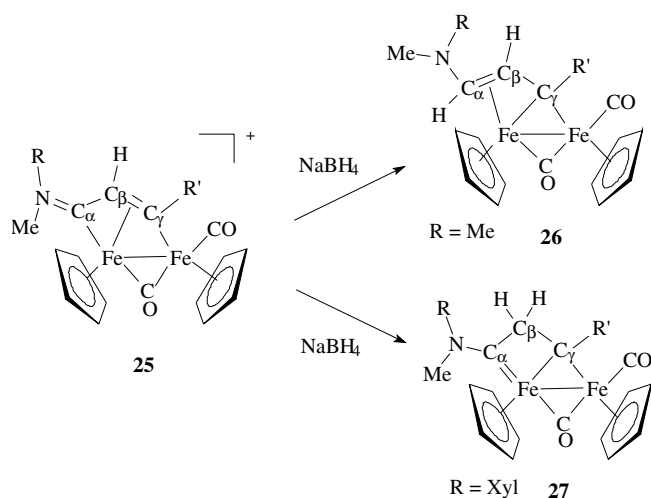
The bridging ligand resulting from alkyne insertion has been considered a $\mu-\eta^1:\eta^3$ -vinyliminium. However, alternative descriptions are possible and structural and spectroscopic data have evidenced that iminium moiety display some aminocarbene character [39] (Chart 7B). In other words, the bonding mode assumed by the bridging vinyliminium shows some analogies with those described for the complexes **22** and **23**, since it consists of an unsaturated hydrocarbonyl moiety bridging the two Fe atoms and an aminocarbene part, terminally coordinated.

The aminocarbene character of the vinyliminium ligand becomes more evident upon modification due to nucleophilic addition, which is described in the following paragraph.

5. Bridging bis-carbene complexes

The bridging vinyliminium ligand in **25** has been shown to react with $NaBH_4$ to give hydride addition [40]. The latter occurs selectively at the iminium carbon, or at the adjacent C_β , depending on the substituents at the iminium nitrogen (Scheme 15). When $R = Me$, hydride attack occurs at the iminium, affording the vinylalkylidene complexes $[Fe_2\{\mu-\eta^1:\eta^3-C(R')CH=CHNMe_2\}(\mu-CO)(CO)(Cp)_2]$ (**26**). By contrast, when the iminium carbon (C_α) is sterically protected by the more hindering Xyl substituent, addition is directed to C_β , yielding the bis-alkylidene complexes $[Fe_2\{\mu-\eta^1:\eta^2-C(R')CH_2CN(Me)(Xyl)\}(\mu-CO)(CO)(Cp)_2]$ (**27**) [40].

In both cases, hydride addition changes the nature and coordination mode of the bridging ligand and induces the C_γ carbon to assume a bridging carbene char-



acter. Conversely, changes in the nature of the C_α and C_β depend upon the site of hydride attack. Addition at the C_α carbon generate type **26** complexes which can be appropriately described as bridging vinylcarbenes. The resulting $\mu-\eta^1,\eta^3$ coordination mode is quite common among dinuclear complexes [41], including diiron compounds [42]. On the other hand, the addition on the C_β carbon gives the complex **27** with loss of interaction between the Fe atoms and C_β . The bridging ligand remains anchored to the Fe–Fe through the C_α and C_γ , which assume the nature of aminocarbene and bridging alkylidene, respectively. Again, the multidentate ligand adopts the more stable coordination mode with the aminocarbene moiety terminally coordinated and the alkylidene bridging.

Moreover, it has been shown that the C_β -H in **25** is acidic and can be removed upon treatment with NaH [43]. This observation is in agreement with the aminocarbene character of the ligand, since C–H hydrogen, adjacent to Fischer carbenes, are known to be acidic [44]. C_β -H proton removal generates unstable and reactive intermediate species whose nature has not been demonstrated. One possibility is that the deprotonated species assumes the bis-carbene coordination as in **27**. This is suggested by the observation that one of the products of the deprotonation is the tetranuclear complex **28** (Chart 8), clearly derived from the dimerization of two deprotonated vinyliminium ligands. Interestingly, the organic fragment $[C_\alpha N(Me)(R)C_\beta C_\gamma(R')]_2$ is coordinated to two $[Fe_2Cp_2(CO)_2]$ units through four ‘biting ends’ exclusively made of terminal and bridging carbene ligands.

Analogous dimerizations, consequent to deprotonation, have been reported for some alkoxy- and aminocarbene complexes, which undergo oxidative coupling to give bridging bis-carbene complexes in an overall reaction described as “dehydrodimerization” [45].

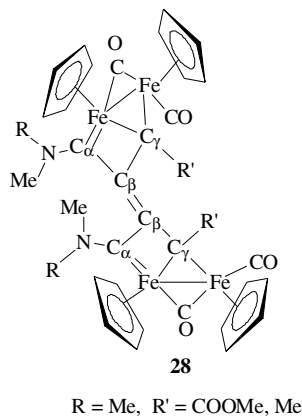


Chart 8.

6. Conclusions

Diiron complexes characterized by the $\text{Fe}_2\text{Cp}_2(\text{CO})_2$ frame represent an efficient support for the coordination a variety of carbene ligands, both bridging and terminal. Synthetic methods have been developed for obtaining Fischer type carbenes based on the electrophilic character of the carbyne ligands ($\mu\text{-CNR}_2$ and $\mu\text{-CSMe}$) or sulphonium methylidene [$\mu\text{-C}(\text{CN})(\text{SMe}_2)$]. Their stability and the preferential site mode of coordination (terminal or bridging) depend on the nature of the heteroatom (N, P, O, S); indeed the aminocarbenes appear to be the more stable and preferentially adopt a terminal coordination.

Alternatively, the classical Fischer method, consisting in nucleophilic addition at a terminal CO to generate an acyl intermediate followed by oxygen atom methylation, provides access to terminally bonded alkoxy carbene ligands.

In addition, carbenes can be generated by intramolecular couplings and rearrangements of ligands coordinated to the diiron frame. In particular, bridging aminocarbyne complexes containing nitrile or imine ligands react with alkynes or acetylides affording new and unusual organic molecules, exhibiting an aminocarbene and/or an alkylidene biting end.

Noteworthy, diiron complexes display an important role in metal assisted synthesis of highly functionalized organic molecules, by promoting nucleophilic addition and intramolecular couplings of coordinated ligands. Moreover, metal coordination offer regio and stereo control on most of these reactions. The bimetallic frame also provide stabilization to the organic species thus generated, by means of a variety of coordination modes in which carbene ligands are dominant.

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