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Reactions of bridging C_3 ligands in diiron complexes: Unconventional routes to new functionalized organic frames*

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Abstract: Diiron complexes containing C_3 ligands, such as vinyliminium and vinylalkylidene bridging units, display unusual reaction patterns, not observed when the same organic fragments are bound to a single metal center, or not coordinated. Bridging vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(NMe_2)CH{=}CR\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ undergo nucleophilic addition at the iminium C or at α-C position, which is uncommon since non-coordinated vinyliminium species generally undergo conjugated (Michael type) nucleophilic attack. Likewise, bridging vinyliminium ligands undergo new and unusual transformations consisting of the deprotonation and replacement of the α-CH by a variety of functional groups. These reactions, resulting in the formation of C–C and C–heteroatom single and double bonds, produce new bridging ligands of the type $[\mu\text{-}C(NMe_2)C(X)CR)$ (X = S, O, Se, SPh, CNMe, $NNCHCO_2Me$].

Removal of the vinylalkylidene ligands from the bridging coordination is achieved by a [3 + 2] cycloaddition with alkynes. The reaction leads to the formation of ferrocenes containing one polysubstituted Cp ring, which results from the cycloaddition of the bridging C_3 ligand with alkynes. This result suggests a new possible route for the synthesis of polyfunctionalized ferrocenes.

Keywords: alkynes; bridging ligands; cycloaddition; diiron complexes; functionalized ferrocenes; vinylalkylidene; vinyliminium.

INTRODUCTION

Organometallic compounds have become a fundamental and well-established synthetic tool in organic synthesis, on both industrial and laboratory scales [1]. The growing demand for more efficient, selective, and sustainable bond-forming processes has generated an impressive and ongoing effort in the design of new ligands and in the choice of the most appropriate metal–ligand combination. However, the design of new ligands is virtually limitless, whereas the choice of the metal is naturally limited, and is likely to be increasingly restricted by economical and ecological factors. Thus, only those transition metals that are nontoxic, readily available, and inexpensive are destined to fulfil the growing need for "sustainable metal catalysis".

A promising way to overcome these difficulties and expand the range of possibilities is through combinations of two (or more) metals. Indeed, the use of dinuclear (or polynuclear) transition-metal

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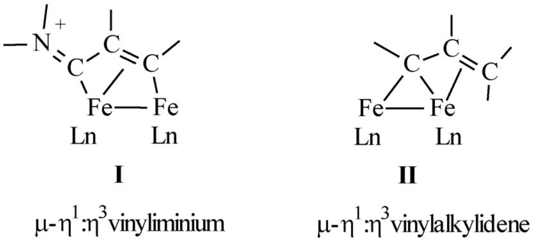
complexes offers potential for unique reactivity, as a consequence of cooperative or synergic effects associated with the presence of adjacent metal centers [2].

Moreover, dinuclear complexes, providing multisite interaction with coordinated organic fragments (e.g., bridging coordination), are expected to offer new reactivity patterns, different from those observed when the same organic molecule is bound to a single metal center [3]. These potential advantages have hitherto been under-exploited. Most relevant examples of activation modes by dinuclear species include metallo-enzymes, such as [FeFe] or [FeNi] hydrogenase, which are remarkable sources of inspiration in the design of new sustainable energy processes [4].

Our interest in the field has been focused on the chemistry of diiron complexes with bridging C_3 ligands, such as α-β-unsaturated iminium (μ-vinyliminium complexes **I**) and α-β-unsaturated alkylidenes (μ-vinylalkylidene complexes **II**), shown in Scheme 1.



Scheme 1

This report gives an overview of the synthetic strategies designed for obtaining complexes of type **I** and **II**, and focuses on the transformations performed on the bridging C_3 frame, as a consequence of multisite activation. Such new activation modes have been investigated for their possible use in metal-assisted synthesis.

DIIRON BRIDGING VINYLIMINIUM COMPLEXES

The synthetic approach

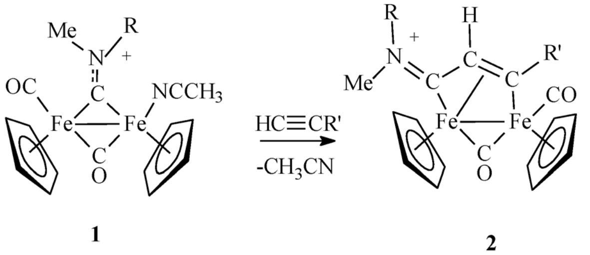
Vinyliminium ligands (otherwise indicated as azoniabutadienyl) have been known in mononuclear complexes, in a variety of coordination modes (including σ and π coordination) [5], but bridging vinyliminium complexes of type **I** (Scheme 1) were the first example of μ-η^1:η^3 coordination [6].

Bridging vinyliminium complexes might appear difficult to obtain, since their preparation implies the formation of two σ M–C bonds and one π interaction. Indeed, their synthesis is very simple and takes advantage of the activation effects due to bridging coordination. Bridging vinyliminium ligands are directly assembled on the diiron frame by alkyne insertion into metal–alkylidyne bond of μ-aminoalkylidyne complexes **1** (Scheme 2).

The reaction is general, and occurs with almost any primary alkyne, and also with a good number of internal alkynes. Furthermore, the aminocarbyne precursors **1** are easily prepared from $[Fe_2(CO)_4(Cp)_2]$ and isocyanides (CNR), both commercially available, in a two-step reaction sequence, which includes coordination of the isocyanide and alkylation at the N atom [7].

Moreover, the sequence leading to **2** can be changed, in that it is also possible to insert alkynes into the metal-bridging isocyanide bond as first step, and then produce N-alkylation [8].

The method has been used to prepare a broad range of vinyliminium complexes with different R and R' substituents, since several isocyanides (R = Me, Xyl, CH_2Ph,) and a much wider range of alkynes (R' = H, alkyl aryl, CO_2Me, $SiMe_3$) are easily available. As a consequence, we have been able to investigate the electronic and steric influence of R and R' substituents, which revealed some unexpected outcomes (see following sections).



R = Me, Xyl; R' = alkyl, aryl, CO_2Me, $SiMe_3$.

Scheme 2

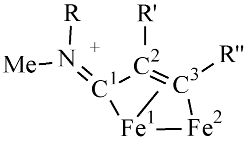
The reaction presents several interesting features: first of all, it requires the presence of a labile ligand (NCMe) as the equivalent of a coordinative unsaturation. This is presumably necessary to allow alkyne coordination in a very preliminary step of the reaction sequence, which ultimately leads to the intramolecular coupling of the coordinated ligands. Thus, the observed alkyne insertion has many analogies with other related reactions, such as the coupling of alkynes with bridging alkylidene (methylidene ligands) in dinuclear complexes [9]. These also require preliminary alkyne coordination in order to promote assembly with μ-alkylidenes, to form bridging vinylalkylidene ligands.

An other important feature is that insertion of primary alkynes is regiospecific: C–C bond formation occurs selectively between the μ-alkylidyne C and the CH moiety of the alkyne. In the case of asymmetric internal alkynes (RCCR'), the insertion reaction exhibits a lower selectivity, and mixtures of isomers are generally produced [10].

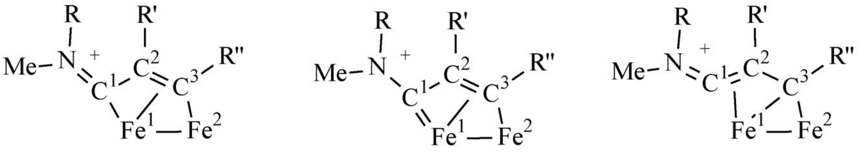
Structure and properties of the ligand

The nature of bridging vinyliminium coordination has been investigated by X-ray diffraction and spectroscopy. Some relevant structural data are listed in Table 1. Bond distances evidence a highly delocalized nature of the π interaction within the C_3 bridging chain. Therefore, a single representation form appears inadequate to accurately describe the bonding structure. As for other unsaturated C_3 bridging ligands, such as allyls [11], vinylalkylidenes [9], and allenyls [12], a better description of the bonding structure necessarily involves several resonance forms. These can be considered as extreme representations, and a full description of the bonding involves different contributions of each (Scheme 3). As an example, differences between C^1–C^2 and C^2–C^3 bond distances within the C_3 bridging chain (listed in Table 1) are almost negligible, which is appropriately represented by considering the forms **B** and **C**, in addition to the formulation **A**. As a relevant feature, the iminium C exhibits some partial amino-alkylidene character, evidenced by the resonance form **B**. Fe^1–C^1 bond distances (Table 1) are consistent with a metal–C double bond interaction.

Table 1 (Relevant bond distances); ancillary ligands Cp and CO are omitted.



R	R'	R"	C^1–C^2	C^2–C^3	Fe–C^1	Ref.
Xyl	H	$SiMe_3$	1.406(8)	1.412(8)	1.976(7)	[6]
Xyl	H	CO_2Me	1.421(8)	1.396(8)	1.843(6)	[10]
Xyl	Me	Me	1.381(8)	1.434(7)	1.819(6)	[10]
Xyl	Et	Et	1.444(5)	1.410(6)	1.853(4)	[8]



A **B** **C**

Scheme 3

The ^1H and ^{13}C resonances are in agreement with the structural data. In particular, the aminoalkylidene character of the iminium carbon (C^1) is indicated by the occurrence of a ^{13}C resonance at about 220–230 ppm, that is at higher frequencies compared to a typical iminium (in the 160–190 ppm range [13]), and closer to a typical aminocarbene resonance [14].

Likewise, ^{13}C NMR resonances due to the C^3 carbon are found at high frequencies (about 200 ppm) and are consistent with the bridging alkylidene form **C** (Scheme 3).

For simplicity, we will represent the bridging vinyliminium ligand only by the formula **A** (Scheme 3), even though this might not accurately describe its highly delocalized nature. However, this extended delocalization should be always considered, since it strongly influences the reactivity of the bridging ligand. The existence of different bonding forms suggests that bridging coordination is very versatile, and that small modifications and adjustments of the bonding mode can be easily adopted to better respond to steric and electronic changes in the bridging frame.

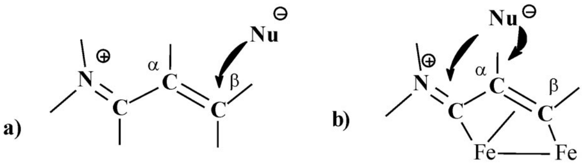
REACTIONS OF DIIRON BRIDGING VINYLIMINIUM COMPLEXES

Iminium salts, and in particular α,β-unsaturated iminiums, are very reactive species. Indeed, the reversible formation of iminium salt activates the carbonyl component toward nucleophilic attack, providing a major contribution to the rapidly expanding field or organocatalysis [15]. Activation offered by iminium ion formation is not limited to nucleophilic additions but also involves a broader range of possibilities, which include cycloaddition reactions, attack by bases (resulting in deprotonation and enamine formation), and retroaldol-type processes. The whole of these activation processes is more appropriately referred as iminium-enamine activation [16].

In light of these considerations, vinyliminium ligands are likely to be reactive species, regardless of the coordination mode they adopt. Indeed, bridging coordination is expected to provide stabilization to vinyliminium, rather than enhancing its activity toward nucleophiles. Therefore, the most relevant effect expected from bridging coordination is a change in the reaction patterns, associated with formation of metal-stabilized intermediates, not observable in noncoordinated species. Two main reaction typologies (nucleophilic addition, and α-CH deprotonation) have been investigated, and the results are thereafter briefly summarized.

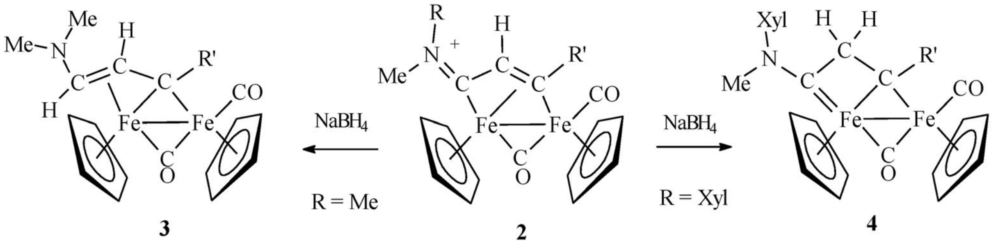
Nucleophilic additions

In general, α,β-unsaturated iminium species are activated toward nucleophilic addition, which usually takes place at the β-C, as a typical conjugate addition (Michael type). Additions rarely involve the iminium C and are never observed at the α-C (a, Scheme 4). Conversely, diiron bridging vinyliminium complexes undergo nucleophilic addition at the α-C or at the iminium C, but not at the conjugated β-C (b, Scheme 4).



Scheme 4

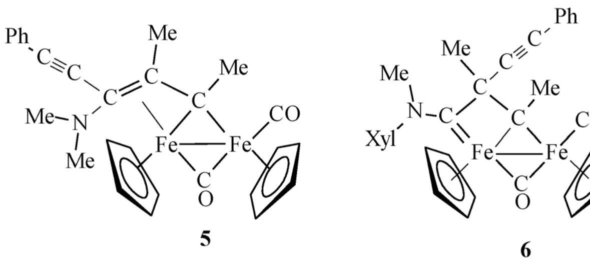
The peculiarity of nucleophilic addition at bridging vinyliminium ligand is well exemplified by hydride addition (from $NaBH_4$), shown in Scheme 5 [17]. Hydride addition occurs preferentially at the iminium C, which is consequently transformed into a stable μ-vinylalkylidene, yielding complexes of type **3** (Scheme 5). Conversely, in the presence of the sterically demanding Xyl group (Xyl = $2,6\text{-}Me_2C_6H_3$) as N substituent, H^- addition is selectively directed at the α-C, with formation of the bis-alkylidene complexes **4**. As a consequence of addition at the α-C, the ligand remains anchored to the dinuclear frame through the other two C atoms of the bridged C_3 chain, both assuming alkylidene character.



Scheme 5

It has to be outlined that hydride addition is selective, and each reaction shown in Scheme 5 affords one single product. Thus, a simple steric effect associated with the nature of the nitrogen substituents accounts for the observed selectivity, and enables the direct nucleophilic attack to the desired site (iminium C or α-C).

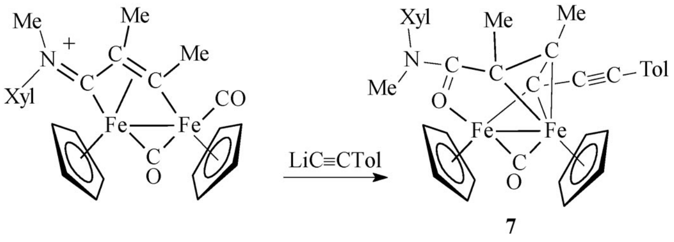
Addition of C nucleophiles, such as cyanides [18] and acetylides [19], occurs similarly. Again, the site of attack is mostly determined by steric demand of the iminium nitrogen substituents, with Xyl acting as protective group with respect to the iminium C. In Scheme 6 are shown two complexes obtained by acetylide addition: compound **5** is a vinylalkylidene complex formed by addition at the iminium C, whereas the bis-alkylidene complex **6** results from acetylide addition to the α-C.



Scheme 6

Why do bridging vinyliminium ligands display such a different reactivity compared to corresponding noncoordinated iminium functionalities? The reason is not obvious, but is presumably associated with the stability of bridging coordination modes assumed as a consequence of nucleophilic addition. The observed addition at the iminium C transforms the bridging vinyliminium into a μ-vinylalkylidene ligand (e.g., complexes of types **3** and **5**), whereas addition at the α-C produces bis-alkylidene complexes (e.g., complexes of types **4** and **6**). Both are very stable bridging coordination modes.

All the nucleophilic additions mentioned above occur at the iminium C or the α-C position, however, there are some interesting exceptions that merit being outlined. In a few cases, the ancillary ligands CO [20] and Cp [21] are also involved, as in the example shown in Scheme 7.



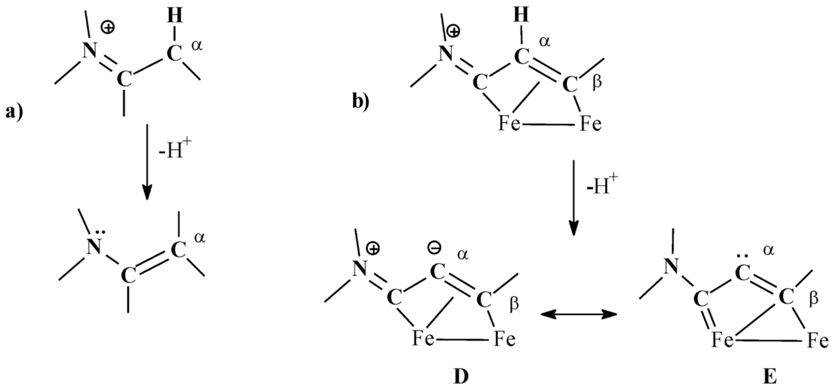
Scheme 7

Labeling experiments with ^{13}CO-enriched complexes demonstrated that acetylide attack occurs at the CO ligand, producing its cleavage [18]. Both the acyl fragment and the O atom, consequently generated, further react, and are incorporated in the bridging ligand, leading to the formation of **7**. In spite of the fact that the initial nucleophilic attack is directed to the CO, the bridging vinyliminium does not act as spectator ligand, but is involved in an intramolecular rearrangement. The overall result is a C–C bond-forming process that leads to the growth of the bridging C_3 chain, due to the inclusion of both the C atom derived from CO cleavage and the alkynyl unit.

Therefore, addition of acetylides to vinyliminium ligands provides new routes to generate C–C bonds, and obtain bridging hydrocarbyl ligands with more complex architectures, of potential synthetic interest.

Deprotonation of bridging vinyliminium complexes

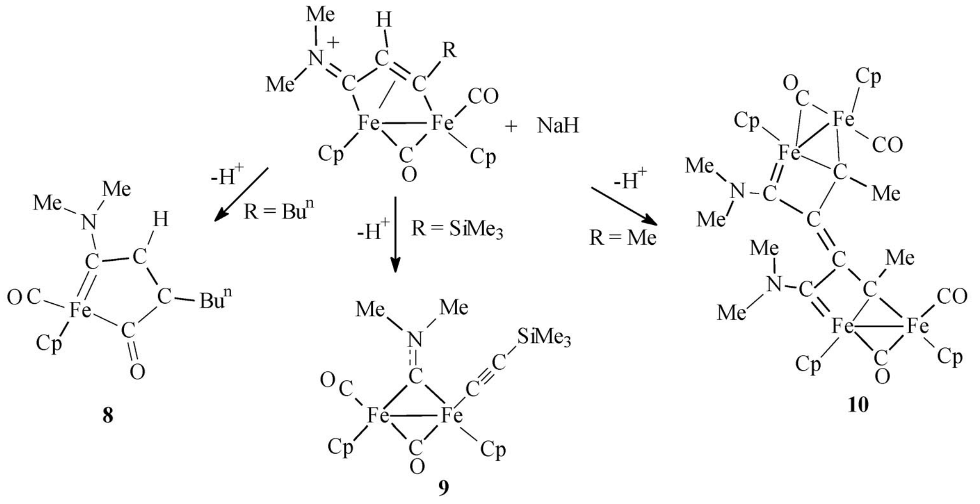
Deprotonation in the α-position of iminium compounds leads to enamines (a, Scheme 8). These are intermediates in enamine catalysis, a powerful synthetic tool for α-C substitution reactions [22]. Conjugated iminium groups (α,β-unsaturated iminium species) do not undergo α-CH deprotonation, but rather react as Michael acceptors. In theory, they can undergo γ-functionalization via dienamine intermediates, but this possibility has been, so far, scarcely investigated [23].



Scheme 8

Again, the reactivity of bridging vinyliminium ligands is different from that of noncoordinated vinyliminium species: deprotonation of α-CH can be easily achieved upon treatment with NaH (or tertiary amines), leading to the formation of unstable intermediates, which we were unable to isolate and identify. A plausible description of the deprotonated intermediates is shown in Scheme 8. Removal of α-CH proton might occur without affecting the bridging coordination, as represented by the formulation **D** (Scheme 8). In this case, the α-C would display a carbanionic character. Conversely, if proton abstraction is accompanied by a slight modification of the coordination mode, the intermediate might assume the formulation **E**, characterized by a bis-alkylidene nature. In consideration of the delocalized bond character of bridging ligand, both **D** and **E** likely contribute to represent the deprotonated intermediate.

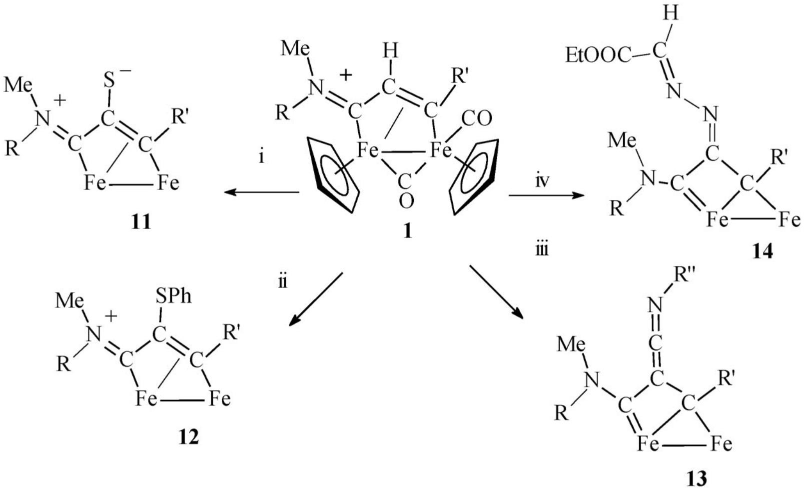
As a consequence of the instability of the species generated by α-CH proton removal, treatment of vinyliminium complexes with NaH is invariably followed by rearrangements, leading to different products [24]. Depending on the nature of the vinyliminium substituents, deprotonation can selectively yield mononuclear metallacyle complexes, such as **8**, dinuclear alkynyl complexes of type **9**, or tetranuclear compounds, like **10** (Scheme 9) [24]. These products provide support to the hypothesis formulated about the nature of the deprotonated intermediate. In particular, the rearrangement leading to **10**, which occurs via formation of a C–C double bond at the α-C position, is consistent with a type **E** representation of the intermediate (Scheme 8).



Scheme 9

Functionalization of μ-vinyliminium ligands

Reactive species generated by proton removal can be trapped by reaction with appropriate reagents, which exploit the carbene/carbanion character of the intermediate. This offers a general and very effective method for adding functional groups at the α-C position in vinyliminium ligands (Scheme 10). In particular, the carbanionic nature of the intermediate has been exploited to oxidize the α-C by group 16 elements (O, S, Se). The final result is the formation of zwitterionic complexes of type **11**, where α-CH hydrogen has been replaced by S (or O/Se) [25]. Similarly, deprotonation in the presence of PhSSPh leads to reductive cleavage of the disulfide and formation of SPh-functionalized vinyliminium complexes **12** (Scheme 10) [26].



R = Me, Xyl; R' = alkyl, aryl, COOMe.
i: NaH, S; ii: NaH, PhSSPh; iii: NaH, CNR''; iv: NaH, $N_2CH(COOEt)$.

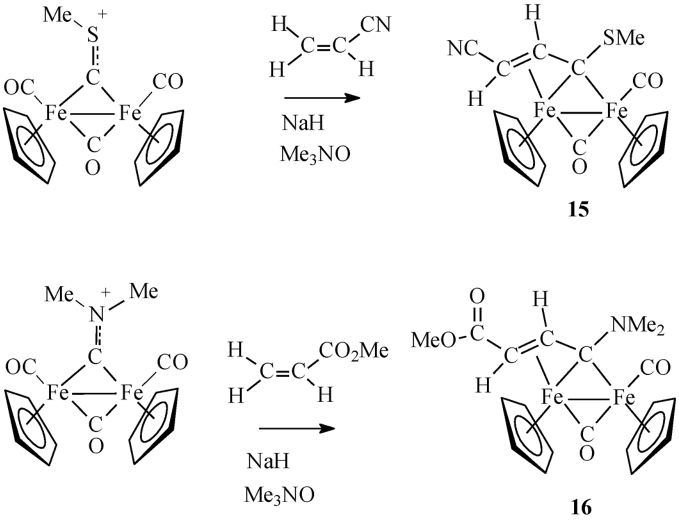
Scheme 10 Ancillary ligands CO and Cp are omitted in **11–14**, for simplicity.

On the other hand, the carbene nature of the intermediate represented by structure **E** (Scheme 8), better explains the reactions with CNR, which afford the ketenimine bis-alkylidene complexes **13** (Scheme 10) [27]. In a similar reaction, deprotonation in the presence of diazocompounds (N_2CRCO_2Me) affords the azine bis-alkylidene complexes **14** (Scheme 10) [28].

It should be remarked that in complexes **13** and **14**, α-C functionalization implies the formation of a double bond (C=C and C=N, respectively) in place of the α-CH. This transformation is accompanied and made possible by a change in the bridging coordination mode from μ-vinyliminium to bis-alkylidene. Moreover, the functionalities introduced in complexes **13** and **14** (ketenimine and azine, respectively) are uncommon and not easy to obtain.

BRIDGING VINYLALKYLIDENE DIIRON COMPLEXES

In addition to vinyliminium complexes, other unsaturated C_3 bridging ligands, such as bridging vinylalkylidenes (Scheme 11) are of interest for their potential as synthetic tools. Likewise vinyliminium, bridging vinylalkylidene complexes are conveniently prepared by assembling C_1 and C_2 ligands directly on the dinuclear precursors. In this case, the coupling involves bridging alkylidynes [μ-CN(R)(Me) or μ-CSMe] and olefins. Olefin incorporation into the bridging ligand is more difficult compared to alkyne insertion. Moreover, olefin deprotonation is required in order to form the desired



Scheme 11

vinylalkylidenes. All of these steps (olefin coordination, deprotonation, and C–C coupling) are carried out in a "one-pot reaction" and performed under relatively mild conditions, as shown in Scheme 11 [29].

The assembly of alkylidynes with olefins occurs only in the presence of Me_3NO and NaH. The former promotes CO removal to generate a coordinatively unsaturated metal center to which the olefin can coordinate, whereas the treatment with NaH accomplishes the deprotonation. A further requirement is the use of olefins activated by electron-withdrawing groups (e.g., CN, COOMe). Bridging vinylalkylidene complexes containing thio- and amino-groups formed by this method (complexes **15** and **16**, respectively) are similar to conventional α,β-unsaturated heteroatom-stabilized Fischer carbenes, except that the alkylidene C is bridging and not coordinated to a single metal center. Another point of interest is that olefin incorporation is regioselective: olefins, such as $H_2C{=}CHR$ (R = CN, CO_2Me), are incorporated in the bridging ligands as shown in Scheme 11, with the CH_2 end linked to the alkylidyne C.

RELEASE OF THE C_3 FRAME FROM THE BRIDGING COORDINATION

Transformations of bridging C_3 ligands, promoted and assisted by dinuclear coordination, provide valuable and unconventional approaches to the design of bridging organic frames of increasing complexity. Indeed, both C–C bond-forming reactions, which allow the build-up of more complex molecular architectures, and the selective introduction of a range of functional groups, result in the formation of organic frames of potential synthetic interest.

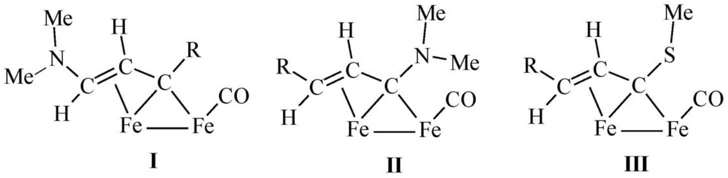
In order to become an effective synthetic tool, these transformations of bridging C_3 species must be followed by a further step consisting of the release from bridging coordination. However, vinylalkylidene, vinyliminium, and bis-alkylidene ligands are very stable in the bridging coordination, and their removal from the diiron core is difficult to achieve. Forcing conditions (prolonged thermal treatments or oxidative decomposition) are destructive and do not permit recovery of the bridging organic frame.

A possible strategy to promote the release of the bridging ligand consists of the reaction with small unsaturated molecules (i.e., alkynes), that might produce cycloaddition reactions. Metal-mediated [3 + 2] cycloadditions are well known, but these almost exclusively involve mononuclear complexes

[30]. In particular, α-β-unsaturated alkylidene complexes have been investigated as multitalent tools in organic synthesis, and one of the major applications is the formation of cyclic products [31]. Beside the classical Dötz reaction [32], cyclization of vinylalkylidenes with alkynes can afford cyclopentadienes, as well as other cycloadducts [33]. Conversely, there are a few examples of cycloadditions involving bridging vinylalkylidene ligands [34]. Nevertheless, these reactions suggest that the assembly of μ-vinylalkylidene with alkynes is feasible, providing a possible route to remove the bridging ligand. Unsaturated cycloadducts eventually formed should contain all the functionalities originally present on the μ-C_3 ligand.

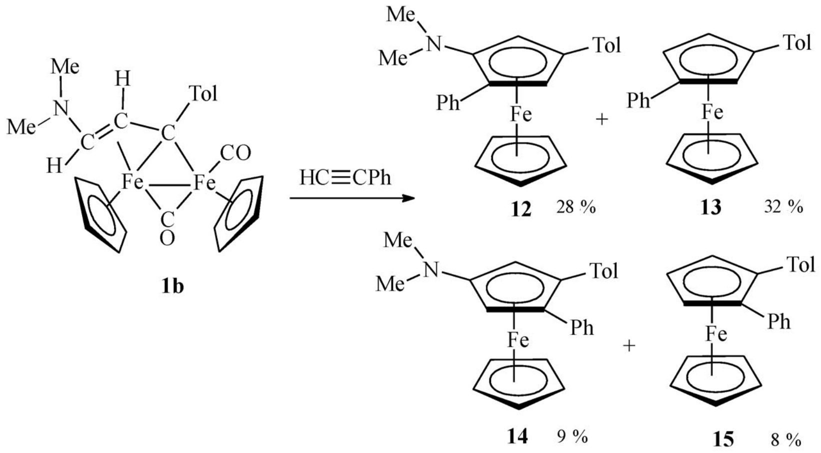
REACTIONS OF BRIDGING VINYLALKYLIDENE DIIRON WITH ALKYNES: SYNTHESIS OF FERROCENES

In light of the above considerations, we investigated the reactions of alkynes with bridging vinylalkylidene complexes (shown in Scheme 12), including the compounds **3**, **15**, and **16**, previously reported (Schemes 5 and 11). The aim was to favor the release of the bridging frame in the form of functionalized cyclopentadienes or cyclopentadienyl ligands.



Scheme 12

The result went beyond the expected transformation of bridging C_3 ligands into five-membered cycloadducts: the [3 + 2] cyclization takes place without release of any organic fragment, but it rather produces a cyclopentadienyl ring, which remains coordinated to one Fe atom (Scheme 13) [35].



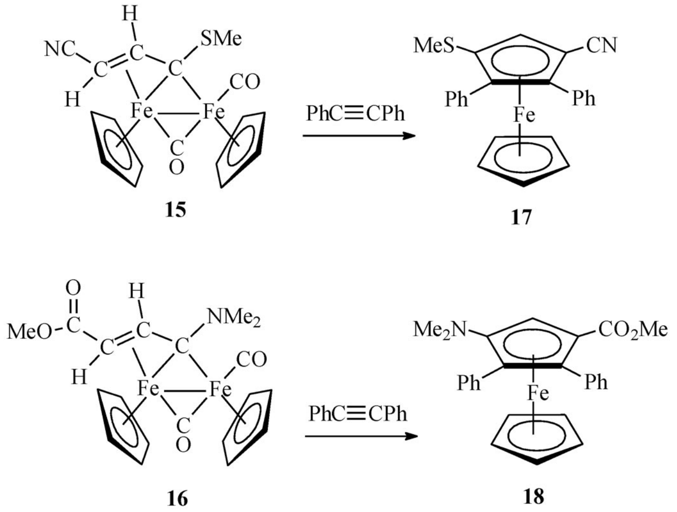
Scheme 13

The overall result is the formation of ferrocenyl products, through a rather complex reaction sequence, which leads to the fragmentation of the dinuclear compound. A polysubstituted cyclopentadienyl is produced by a [3 + 2] cycloaddition: thus, the Cp substituents are those initially present on the bridging C_3 frame and on the alkyne. In the case shown in Scheme 13, several ferrocene complexes are produced as a consequence of the fact that cyclization is neither regio- nor chemoselective. The formation of a cyclopentadienyl ligand from the vinylalkylidene requires the cleavage of one of the two vinyl substituents: H or NMe_2 generating the tri-substituted (**12**, **14**) and di-substituted ferrocenes (**13**, **15**), respectively. In the absence of chemoselectivity, both possibilities (C–H and C–N cleavage) take place, with just a slight predominance of the C–N cleavage. On the other hand, the cycloaddition is neither regiospecific, in that the incorporation of primary alkynes (HCCPh) can occur in two possible modes, affording cyclopentadienyls where the Ph group is adjacent or far from the Tol substituent (Tol = 4Me-C_6H_4) (Scheme 13).

It should be outlined that the synthesis of ferrocenes in which only one of the two Cp rings contains different substituents, or some specific functionalities (e.g., amino groups) remains a difficult synthetic task [36]. Thus, the observed [3 + 2] cycloaddition suggests that a new and more direct approach to the formation of polyfunctionalized ferrocenes is possible, as an alternative to common synthetic methods based upon repeated lithiation/substitution of the Cp ring.

However, the absence of a complete chemo- and regiocontrol and the consequent formation of a mixture of isomeric products is a serious limitation that makes the approach unsuitable for synthetic applications. Nevertheless, the reaction is general, and the appropriate choice of substituents on the C_3 ligand can improve the selectivity. Significant improvements have been obtained by using vinylalkylidene complexes of the types **II** and **III** (shown in Scheme 12), in which the NMe_2 and SMe groups are bound to the alkylidene C, rather than to the vinyl end. Moreover, the use of symmetric internal alkynes eliminates the possible formation of regioisomers and introduces a further substituent on the Cp ligand.

In the reactions shown in Scheme 14, the [3 + 2] cycloaddition involves the selective cleavage of the C–H bond in the vinyl moiety of the bridging C_3 ligand. Only one ferrocene product is consequently formed, and it contains a tetrasubstituted Cp ligand. All the functionalities originally present on the vinyl alkylidene ligand in **15** and **16** are transferred to the polysubstituted Cp in the products **17** and **18**, respectively [35].



Scheme 14

These results indicate that it is possible to gain a better control of the cyclization, providing a valuable approach to the formation of polyfunctionalized ferrocenes. Limitations due to the use of rather "sophisticated" bridging vinylalkylidene complexes as precursors would be compensated by direct formation of ferrocenes characterized by the presence of several different substituents, otherwise difficult to obtain.

CONCLUDING REMARKS

Bridging C_3 ligands such as vinyliminium and vinylalkylidenes are obtained through the assembly of bridging aminoalkylidyne ligands (e.g., μ-$CNMe_2$) with alkynes and alkenes, respectively, through simple procedures that take advantage of the activation effects due to multisite coordination.

Different bridging coordination modes are available, providing stability to the unsaturated C_3 fragments, and, at the same time, offering unconventional possibilities of transformation. These include nucleophilic additions at the α-C position, and α-CH deprotonation and functionalization of vinyliminium ligands. Transformations are favored by the flexible character of the bridging coordination, which can easily adapt to any major change occurring in the bridging organic frame, without affecting the binding properties. Even major changes, such as replacement of α-CH with a C=C or C=N double bond, do not disrupt the bridging coordination, but simply produce a rearrangement to bis-alkylidene.

The broad range of modifications and functionalizations consequently available lead to bridging organic species inaccessible to mononuclear complexes and are of potential synthetic interest. However, bridging C_3 fragments (vinyliminium and vinylalkylidene) are also difficult to remove from the diiron center, which might represent a serious limit to a possible use in metal-mediated processes. On the other hand, our investigations on the [3 + 2] cyclization involving bridging vinylalkylidene complexes and alkynes demonstrate that bridging C_3 ligands are not inert: they undergo cyclization leading to functionalized cyclopentadienyl complexes and giving direct access to polysubstituted ferrocenes.

In conclusion, diiron complexes containing bridging C_3 insasturated species combine a series of potential advantages: they undergo a variety of reactions including cyclization, and display distinctive features with respect to corresponding noncoordinated species. Moreover, these transformations are based on a cheap and environmentally safe metal, that is, iron. These potential advantages suggest that diiron complexes with bridging C_3 ligands have a promising future and should be exploited in metal-mediated synthesis.

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