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Polysubstituted ferrocenes from [3 + 2] cycloaddition of alkynes with diiron bridging C_3 ligands: Vinyliminium, bis-alkylidene and enimine

Rita Mazzoni, Mauro Salmi, Stefano Zacchini, Luigi Busetto, Valerio Zanotti*

Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

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ABSTRACT

The vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')=C(R)C=NMe_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = H, R′ = Tol, **6a**; R = H, R′ = Me, **6b**; R = R′ = Me, **6c**; R = H, R′ = CO_2Me, **6d**; R = R′ = Et, **6e**; R = H, R′ = *n*Bu **6f**; Tol = *p*-MeC_6H_4) react with $HC{\equiv}CCPh_2OH$ affording the corresponding polysubstituted ferrocenes [1-NMe_2-2-CPh_2OH-4-R′-5-R-Fc] (**7a**–**f**). The polysubstituted Cp ring results from [3 + 2] cycloaddition of the bridging ligand with the alkyne, and formation of ferrocenyl products implies fragmentation of the diiron parent complexes. The reaction of **6a** yields also the oxo-η^5-cyclohexadienyl complex $[Fe\{\eta^5\text{-}C_6H_2O(NMe_2)(Tol)(CPh_2OH)\}(Cp)]$ (**8**), which results from a [3 + 2 + 1] cycloaddition involving the bridging vinyliminium, the alkynol and CO.

The bis-alkylidene complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(R')CH_2C = N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**9**) (Xyl = 2,6-$Me_2C_6H_3$) reacts similarly with alkynes ($HC{\equiv}CR$, R = Ph, CPh_2OH, CO_2Me) affording polysubstituted ferrocenes as a mixture of the two isomeric forms: [1-N(Me)(Xyl)-3-R-4-Tol-Fc] (R = Ph, **10a**; R = CPh_2OH, **11a**, R = CO_2Me **12a**) and [1-N(Me)(Xyl)-2-R-4-Tol-Fc] (**10b**, **11b**, **12b**), respectively. Likewise, the μ-enimine complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et) = C(Et)C{=}NMe\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**13**) undergoes [3 + 2] cycloaddition with alkynes ($HC{\equiv}CR$, R = Tol, CH_2OH) leading to the formation of the corresponding polysubstituted ferrocenes [1-NH(Me)-2-R-4-Et-5-Et-Fc] (R = Tol, **14**; R = CH_2OH, **15**). The X-ray molecular structure of **7c** has been determined.

1. Introduction

Metal promoted cycloaddition reactions involving alkynes are among the most valuable synthetic routes for the construction of cyclic molecules, including heterocycles [1]. Developments in this field are impressive and include a broad variety of reactions: from the classic cobalt-catalyzed Pauson–Khand [2] to the numerous protocols based on Fischer carbene complexes [3] and the Copper-catalyzed azide–alkyne cycloaddition (CuAAC) [4].

Our recent work in the area has been focused on the [3 + 2] cycloaddition reactions of alkynes with bridging C_3 ligands (vinyl-alkylidenes) in diiron complexes, resulting in the formation of ferrocenes [5]. One example is shown in Scheme 1 [5a]. The [3 + 2] cycloaddition affords a poly-substituted cyclopentadienyl ligand, which remains coordinated to one Fe atom and generates a ferrocenyl complex. The reaction implies fragmentation of the parent dinuclear complex, with cleavage of the Fe–Fe bond and release of an iron containing fragment. This synthetic approach can be advantageously used for the direct synthesis of ferrocenes in which only one cyclopentadienyl ligand contains different substituents, provided that the parent C_3 and C_2 fragments have been properly constructed in order to contain the desired functionalities [6].

We have found that other diiron bridging C_3 ligands can afford similar cycloadditions. Indeed, also bridging vinyliminium ligands diiron undergo [3 + 2] cycloaddition with alkynes, but the reaction is restricted to propargyls and to a limited number of diiron vinyliminium complexes [7]. Moreover, these reactions also afford oxo-η^5-cyclohexadienyl complexes and phenols (Scheme 2, compounds **3** and **4** respectively). The observed formation of six membered rings implies [3 + 2 + 1] cycloaddition involving the μ-vinyliminium, the alkyne and CO, somewhat resembling the classic Dötz benzannulation [8]. Conversely, reactions of vinyliminium diiron complexes (including **1**) with propargyl alcohol ($HOCH_2C{\equiv}CH$) give selectively [3 + 2] cycloaddition without CO incorporation. However, in this case two alkynol units are involved: one gives rise to the expected cyclopentadienyl ring, whereas the second unit generates an alkynyl pending chain by dehydrative etherification. (Scheme 2, complexes **5a** and **5b**) [9].

Therefore, the reactivity of bridging vinyliminium complexes is, by far, less predictable and more intriguing compared to that of

* Corresponding author. Tel.: +39 (0)512093695.
E-mail address: valerio.zanotti@unibo.it (V. Zanotti).

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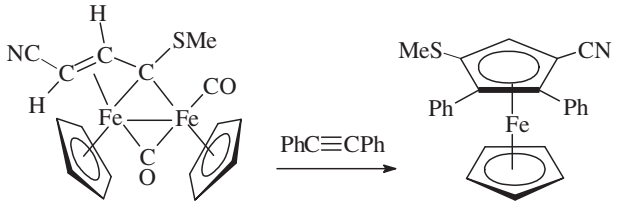


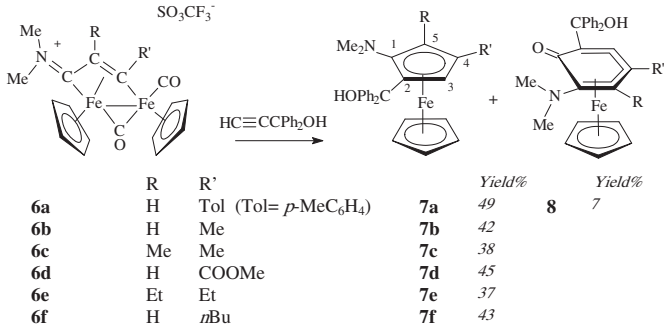
Scheme 1.

μ-vinylalkylidenes. In the light of the above considerations, we extended our studies on vinyliminium complexes in order to evidence new possible reaction profiles associated to the presence of different substituents and functions on the bridging C_3 ligand. Here we also report on cycloaddition reactions that involve other bridging C_3 ligands, such as bis-alkylidenes and enimines (aza-butadienyl).

2. Results and discussion

Since previously reported [3 + 2 + 1] cycloadditions with tertiary propargyl alcohols have been limited to the complex **1**, containing the $SiMe_3$ group, we extended our investigations to other vinyliminium complexes bearing different substituents. Results are shown in Scheme 3. The carbon atoms of the substituted Cp ring have been numbered in Scheme 3, in order to make clearer data assignments reported in the Experimental section.

Only in one case, namely the reaction of **6a** with $HC{\equiv}CCPh_2OH$, we observed the formation of the oxo-η^5-cyclohexadienyl complex **8**, which was obtained in low yield. We have also performed the reaction of **6a** with $HCCCPh_2OH$ under CO atmosphere in order to favor the formation of **8**, but we did not observe any relevant effect on products composition. In the other cases, [3 + 2] cycloaddition takes place without incorporation of CO, affording selectively the ferrocenyl products **7**. Reactions were carried out in refluxing toluene and products were purified by alumina chromatography and characterized by NMR spectroscopy and elemental analysis. Reported yields refer to isolated crystalline products. In agreement with previous findings, fragmentation of the dinuclear parent complex give rise to the functionalized ferrocenes **7**, whereas the residual part of the molecule, which formally correspond to $[Fe(CO)_2Cp]^+$, is either lost during separation on alumina column, or leads to decomposition products [7]. Moreover, the molecular



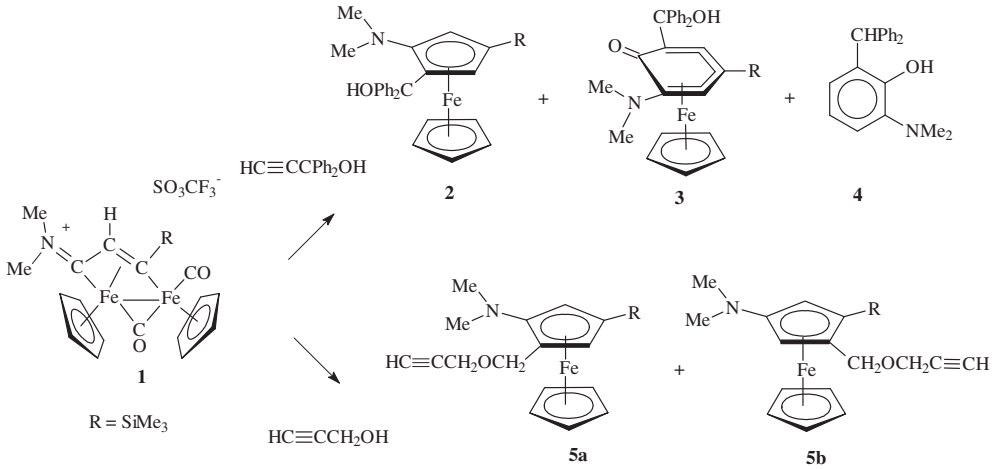
	R	R'		Yield%		Yield%
6a	H	Tol (Tol= *p*-MeC_6H_4)	**7a**	49	**8**	7
6b	H	Me	**7b**	42		
6c	Me	Me	**7c**	38		
6d	H	COOMe	**7d**	45		
6e	Et	Et	**7e**	37		
6f	H	*n*Bu	**7f**	43		

Scheme 3.

structure of **7c** has been determined by X-ray diffraction (Fig. 1 and Table 1).

The structure of **7c** is that of a typical ferrocene tetra-substituted on one Cp ring. The two Cp rings are almost parallel [angle between the least squares mean planes of the five-membered rings is 5.6°]. The N(1)-atom is essentially sp^3 hybridized displaying a strong pyrimidalisation [sum angles 339.7(8)°], and the C(8)–N(1) interaction [1.441(6) Å] is essentially a single bond. In fact, this bonding distance is very similar to the N–Me interactions within the same molecule [N(1)–C(13) 1.484(7) Å; N(1)–C(14) 1.453(7) Å]. The lone pair on N(1) is, therefore, available for instance for the formation of hydrogen bonds. Thus, a weak intra-molecular hydrogen bond exists in **7c** between the $-NMe_2$ and the $-CPh_2(OH)$ substituents [O(1) H(1a) 0.833(19) Å, H(1a)···N(1) 1.96(3) Å, O(1)···N(1) 2.743(5) Å, O(1)–H(1a)–N(1) 155(6)°]. A similar situation was previously found in the closely related tri-substituted ferrocene [1-NMe_2-2-CPh_2OH-4-$SiMe_3$-Fc] (**2**) (Scheme 2) [5a].

Results shown in Scheme 3 evidence some interesting features. One aspect is the specific character of the [3 + 2 + 1] cycloaddition which, unfortunately, remains almost restricted to the vinyliminium complex **1**. A second observation is that formation of the propargylic side chain by incorporation of a second alkynol, previously observed in complexes **5** (Scheme 2), does not occur in **7**. Therefore, dehydrative etherification to form the pending alkynyl function, is restricted to reactions with $HC{\equiv}CCH_2OH$, and does not occur with the tertiary propargyl alcohol $HC{\equiv}CCPh_2OH$. Steric arguments should explain the different behavior; the hindrance due to the phenyl groups might be unfavorable to the addition of a second alkynol unit. A further peculiar aspect is the regioselectivity



Scheme 2.

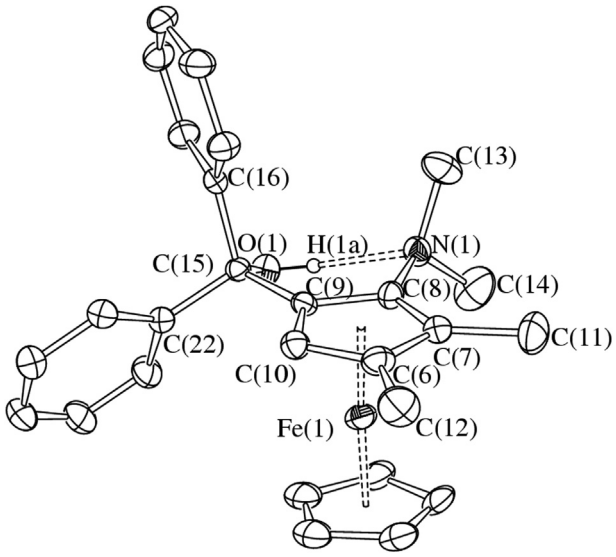


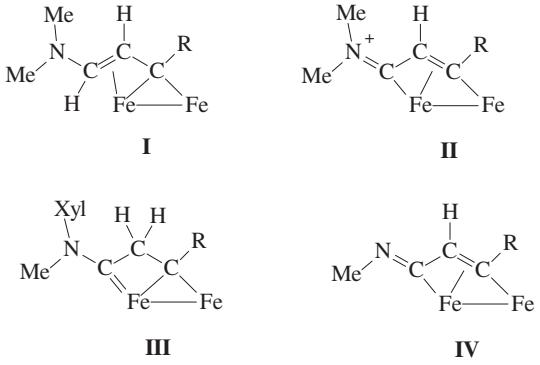
Fig. 1. ORTEP diagram of **7c**. All the hydrogen atoms have been omitted except H(1a). Thermal ellipsoids are drawn at 30% probability level.

of the [3 + 2] cycloaddition, in that incorporation of the primary alkyne to form the five membered ring takes place in just one of the two possible modes, and generates one single isomeric form. In complexes **7a**–**f** the NMe_2 and the CPh_2OH substituents are close so that hydrogen bond can be formed between the OH and NMe_2 groups, as evidenced in the crystal structure of **7c** discussed above. Remarkably, the reactions of bridging vinyliminium ligands above discussed do not find any counterpart in the corresponding uncoordinated α,β-unsaturated iminiums. Indeed, conjugated iminium compounds are reactive species, which mostly act as Michael acceptors and provide a key activation mode for α,β-unsaturated carbonyls (iminium catalysis) [10]. Iminiums can also undergo cyclization reactions, but these are different from the [3 + 2] cycloadditions shown in Scheme 3 [11]. In other words, our results further evidence the unique role of dinuclear complexes in promoting reactions at bridging ligands which are otherwise unattainable, or are not observed when the same organic fragment is uncoordinated, or is bound to a single metal center [12].

Beside vinylalkylidene and vinyliminium diiron complexes (Scheme 4, **I** and **II**, respectively), other readily accessible diiron

Table 1
Selected bond distances (Å) and angles (deg) of **7c**.

Fe(1)–$C_5H_2R_3$(av)	2.0412(12)	Fe(1)–C_5H_5(av)	2.047(4)
C(6)–C(7)	1.416(7)	O(1)–H(1a)	0.833(19)
C(7)–C(8)	1.426(7)	H(1a)···N(1)	1.96(3)
C(8)–C(9)	1.443(6)	O(1)···N(1)	2.743(5)
C(9)–C(10)	1.412(7)	C(8)–N(1)	1.441(6)
C(10)–C(6)	1.413(7)	C(13)–N(1)	1.484(7)
C–C(av) in C_5H_5	1.41(3)	C(14)–N(1)	1.453(7)
C(6)–C(12)	1.525(7)	C(7)–C(11)	1.513(7)
C(9)–C(15)	1.534(6)	C(15)–O(1)	1.428(6)
C(15)–C(16)	1.545(7)	C(15)–C22)	1.527(6)
C(7)–C(6)–C(10)	108.4(5)	N(1)–C(8)–C(9)	120.9(4)
C(6)–C(7)–C(8)	107.4(5)	C(7)–C(8)–N(1)	130.4(5)
C(7)–C(8)–C(9)	108.3(5)	C(8)–C(9)–C(15)	124.9(4)
C(8)–C(9)–C(10)	106.6(4)	C(10)–C(9)–C(15)	128.3(4)
C(9)–C(10)–C(6)	109.3(5)	C(8)–N(1)–C(13)	111.0(4)
C(7)–C(6)–C(12)	126.8(5)	C(8)–N(1)–C(14)	117.6(4)
C(10)–C(6)–C(12)	124.8(5)	C(13)–N(1)–C(14)	111.1(5)
C(6)–C(7)–C(11)	124.0(5)	C(9)–C(15)–O(1)	110.1(4)
C(8)–C(7)–C(11)	128.5(5)	O(1)–H(1a)···N(1)	155(6)



Scheme 4.

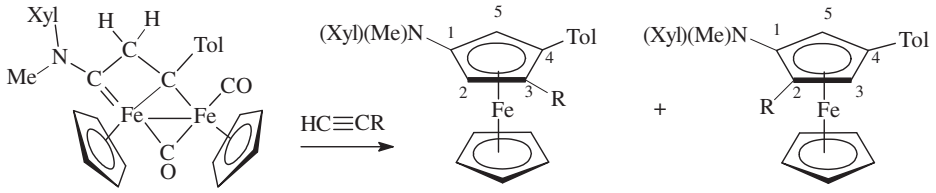
complexes with bridging C_3 ligands are possible candidates to undergo cycloaddition with alkynes [13]. In particular, bis-alkylidene complexes **III** [14] and bridging conjugated imines **IV** [15] (Scheme 4) are related to the above mentioned species **I** and **III**. Bis-alkylidenes **III** and vinylalkylidenes **I** can exhibit the same composition and be considered isomeric forms, except for the fact that the N-substituents are generally different in the two cases: a Xyl group (Xyl = 2,6-$Me_2C_6H_3$) is usually present in complexes **III**, whereas complexes **I** generally display the NMe_2 moiety. Indeed, both **I** and **III**, are generated by hydride addition to the corresponding vinyliminium complexes. When the addition occurs at the iminium carbon the corresponding products are the vinylalkylidenes **I**; conversely, hydride addition at the adjacent α-position affords the bis-alkylidenes **III** [14].

Likewise, complexes **II** and **IV** are strictly related in that **IV** can be easily transformed into **II** upon alkylation at the N atom [15].

We have examined the reactivity of type **III** complexes with alkynes. In particular, we have found that the diiron complex **9** reacts with alkynes (HC≡CR′, R′ = Ph; CPh_2OH; CO_2Me) affording the 1,3,4 tri-substituted ferrocenyl products (e.g. **10a**, **11a** and **12a**), together with the corresponding 1,2,4 tri-substituted isomers (**10b**, **11b** and **12b**) (Scheme 5).

All the reactions shown in Scheme 5 were carried out in toluene at reflux temperature. Products were purified by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. A mixture of two isomers is formed due to the absence of regioselectivity. The 1,3,4 tri-substituted ferrocenes (**10a**, **11a**, **12a**) are the major isomeric forms, probably favored by lower steric hindrance associated to the mutual position of the Xyl and R groups. This result is in contrast with the regioselectivity observed in formation of **7** (Scheme 3), above discussed and ascribed to the $CH_2OH\cdots NMe_2$ interaction. The absence of regioseolectivity in **11** might be due to steric hindrance associated to the Xyl group, which should make unfavorable an analogous $CH_2OH\cdots N(Xyl)Me$ interaction. Separation of the isomeric mixture by column chromatography was only partially achieved. Nevertheless, it was possible to evaluate yields for each isomer by integration of the NMR resonances of corresponding signals.

As mentioned in the introduction, carbene complexes are well known and useful tools in the synthesis of cyclic molecules [3a]. Bis- and multicarbene [16], as well as multimetal carbene complexes [17], have also a great potential in organic synthesis, derived from the presence of two metal-carbene fragments in the same molecule and by multisite coordination. Most common bis-carbene complexes display two identical metal carbene units, in which the metal centers are bound through a molecular fragment acting as linker, or directly bound, but there are many more possible combinations. In spite of these multifold possibilities, the coordination



	R	*yield%*		*yield%*	
9	Ph	*52*	**10a**	*10*	**10b**
9	CPh_2OH	*41*	**11a**	*5*	**11b**
9	CO_2Me	*44*	**12a**	*8*	**12b**

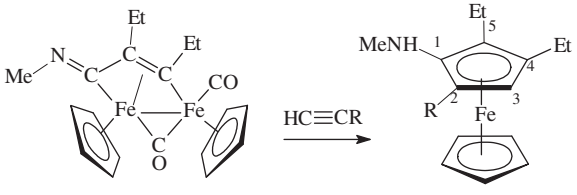
Scheme 5.

mode shown by the bis-carbene complex **9** is unique, in that it consists of a bridging alkylidene and a terminally bound amino-carbene (Fischer type carbene) coordinated to two adjacent Fe atoms. Due to its unusual character, the observed reactivity can be hardly compared to that of common bis-carbenes [18]. A more significant comparison can be made with other bridging C_3 ligands in complexes with same diiron frame. For example, formation of ferrocenes **10**, **11** and **12** is very similar to the result obtained by [3 + 2] cycloadditions involving bridging vinylalkylidenes (Scheme 1) [5]. Formation of the ferrocenyl product **10**, **11** and **12** implies the cleavage of a C–H bond in the sp^3 carbon of the bridging ligand. An analogous C–H cleavage takes place in the transformation of bridging diiron vinylalkylidenes into functionalized ferrocenes (Scheme 1), but it involves the vinyl unit (a sp^2 carbon) and should be easier to accomplish. In spite of these differences, both type of bridging C_3 ligands lead to similar results, suggesting that the formation of stable ferrocenes is the driving force which controls the reaction outcome.

Finally, we have investigated the reactions of the bridging enimine (azabutadienyl) diiron complex **13** with alkynes. Complex **13** reacts with alkynes HC≡CR (R = Tol, CH_2OH) in refluxing toluene affording the corresponding polysubstituted ferrocenes: [1-NH(Me)-2-R-4-Et-5-Et-Fc] (R = Tol, **14**; R = CH_2OH, **15**), respectively (Scheme 6).

The ferrocenes **14** and **15** were purified by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. Yields were moderate and a few other byproducts and decomposition products were formed, which we were unable to identify.

Complex **13** exhibits close analogies with the corresponding vinyliminium complexes, but also some important differences, in that **13** is a neutral complex rather than positively charged. This is consequence of the imine nature of the bridging frame, in place of an iminium group. Again, the difference does not alter the reaction



	R		*yield%*
13	Tol	**14**	*24*
13	CH_2OH	**15**	*20*

Scheme 6.

outcome, and [3 + 2] cycloaddition with alkynes is observed resulting in Fe–Fe cleavage and formation of ferrocenes. An interesting feature in this reaction is hydrogen addition at the N atom in order to form the observed –NHMe substituent at the Cp ring. By contrast with the reaction shown in Scheme 5, where a C–H bond was cleaved in order to form the substituted Cp ring, in this case a N–H bond has to be formed, although it is not obvious what is the hydrogen source. If adventitious water, contained in the solvent or in the alumina used in the chromatographic separation step, is the source, this would imply protonation to form N–H. Protonation of the N atom in **13** to form the corresponding vinyliminium as initial reaction step seems unlikely, in that this reaction is known but requires strong protic acids (e.g. HBF_4) [15]. An alternative hypothesis is that [3 + 2] cycloaddition occurs at the μ-enimine ligand, generating cyclobutadienylimine intermediate species, and producing the Fe–Fe cleavage. Hydrogen addition at the N atom of the cyclobutadienylimine is known and does not require very acidic conditions [19]. However, these are just hypotheses and, in the absence of relevant clues, other possibilities cannot be excluded. A further observation is that dehydrative etherification of ferrocenyl methanol product **15** does not occur, unlike the reaction shown in Scheme 2 and yielding **5**. The reason is that etherification of ferrocenyl methanol requires the presence of $[Fe(CO)_2Cp][SO_3CF_3]$ (usually indicated as [Fp][OTf]) acting as catalyst. We have previously shown that [Fp][OTf] is released upon fragmentation of the cationic vinyliminium complexes [9]. Conversely, reactions involving neutral diiron complexes, such as the species containing μ-vinylalkylidenes, μ-bisalkylidenes and μ-enimine are not expected to release any cationic iron fragment such as [Fp][OTf].

3. Conclusion

Our results indicate that the [3 + 2] cycloaddition of bridging C_3 ligands in diiron complexes with alkynes to form polysubstituted ferrocenes has a general character. Indeed, beside bridging vinylalkylidene and vinyliminium ligands, also bis-alkylidenes and enimines undergo [3 + 2] cycloaddition with alkynes. Formation of the observed ferrocenyl products implies rearrangements which depend on the nature of the parent C_3 fragment (e.g. C–H bond cleavage or N–H bond formation, in addition to Fe–Fe cleavage and C–C bond formation). These transformations are not common, neither easy to obtain under different conditions and evidence the unique properties associated to bridging coordination and multisite interaction. The stability of ferrocenyl products is presumably the driving force which accounts for the observed transformations, regardless possible differences in the nature of the bridging C_3 fragments. Finally, the reactions here reported further demonstrate that diiron complexes with bridging C_3 ligands can provide a valuable synthetic route for obtaining polysubstituted ferrocenes.

4. Experimental details

4.1. General

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 on a Varian Mercury Plus 400 instrument and recorded at 298 K. Chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. Spectra were fully assigned *via* DEPT experiments and ^{1}H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments. NOE measurements were recorded using the DPFGSE-NOE sequence. For isomeric mixtures, not fully separated by chromatography, yields have been determined by integration of the NMR signals. NMR resonances in the functionalized Cp rings have been indicated according to the numbering system shown in Schemes 3, 5 and 6. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Complexes **6a**–**f** [20], **9** [14], and **13** [15] were prepared as described in the literature.

4.2. Synthesis of [1-NMe_2-2-CPh_2OH-4-Tol-Fc] (**7a**) and [Fe{η^5-$C_6H_2O(NMe_2)(Tol)(CPh_2OH)$}(Cp)] (**8**)

A solution of **6a** (620 mg, 1.0 mmol), in toluene (20 mL), was treated with HC≡$CCPh_2OH$ (416 mg, 2.0 mmol), and the resulting mixture was heated at reflux temperature for 16 h. Removal of the solvent and chromatography of the residue on alumina column, with petroleum ether (b.p. 40–60 °C) as eluent, gave a first yellow/orange fraction containing **7a**. Elution with Et_2O gave a second orange fraction containing **8**.

7a Yield: 244 mg, 49%. Anal. Calcd. for $C_{32}H_{31}FeNO$: C, 76.65; H, 6.23. Found: C, 76.57; H, 6.14. ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1H, OH); 7.64–7.24 (m, 14H, Ph and Tol); 4.68 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^3H); 4.38 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^5H); 3.85 (s, 5H, Cp); 2.41 (s, 6H, NMe_2); 2.32 (s, 3H, C_6H_4Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 146.3 ($C_{ipso\text{-}Ph}$); 137.8–125.9 (C_{arom}); 110.2 (C^1); 93.0 (C^2); 81.0 (C^4); 78.4 (CPh_2OH); 71.9 (Cp_{free}); 63.7 (C^3); 56.0 (C^5); 46.9 (NMe_2); 21.4 (C_6H_4Me).

8 Yield: 37 mg, 7%. Anal. Calcd. for $C_{33}H_{31}FeNO_2$: C, 74.86; H, 5.90. Found: C, 74.79; H, 6.01. ^{1}H NMR ($CDCl_3$) δ 9.51 (s, 1H, O*H*); 7.88–7.09 (m, 14H, Ph and Tol); 5.51 (d, 1H, $^{4}J_{HH} = 1.2$ Hz, C^3H); 5.03 (d, 1H, $^{4}J_{HH} = 1.2$ Hz, C^5H); 4.43 (s, 5H, Cp); 2.80 (s, 6H, NMe_2); 2.35 (s, 3H, C_6H_4Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 148.4 (C^1); 145.4, 143.8 ($C_{ipso\text{-}Ph}$); 137.2–126.5 (C_{arom}); 113.5 (C^2); 92.4 (C^6); 85.5 (C^5); 80.9 (C-CPh_2OH); 74.1 (Cp_{free}); 67.7, 67.6 (C^3 and C^4); 40.7 (NMe_2); 21.2 (C_6H_4Me).

4.3. Synthesis of [1-NMe_2-2-CPh_2OH-4-R′-5-R-Fc] (R = H, R′ = Me, **7b**; R = R′ = Me, **7c**; R = H, R′ = CO_2Me, **7d**; R = R′ = Et, **7e**; R = H, R′ = nBu, **7f**)

Complexes **7b**–**f** were prepared by the same procedure described for **7a**, by reacting **6b**–**f** with HC≡$CCPh_2OH$. Crystals of **7c** suitable for X-ray analysis were obtained by slow evaporation from a CH_2Cl_2 solution.

7b Yield: 178 mg, 42%. Anal. Calcd. for $C_{26}H_{27}FeNO$: C, 73.42; H, 6.40. Found: C, 73.27; H, 6.54. ^{1}H NMR ($CDCl_3$) 8.07 (s, 1H, OH); 7.84–7.07 (m, 10H, Ph); 4.12 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^3H); 3.97 (s, 5H, Cp); 3.83 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^5H); 2.33 (s, 6H, NMe_2); 1.96 (s, 3H, Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 146.5 ($C_{ipso\text{-}Ph}$); 132.6–126.2 (C_{arom}); 108.9 (C^1); 91.4 (C^2); 80.1 (C^4); 78.3 (CPh_2OH); 70.9 (Cp_{free}); 67.1 (C^3); 59.1 (C^5); 47.0 (NMe_2); 15.2 (*Me*).

7c Yield: 167 mg, 38%. Anal. Calcd. for $C_{27}H_{29}FeNO$: C, 73.81; H, 6.65. Found: C, 73.75; H, 6.73. ^{1}H NMR ($CDCl_3$) 8.26 (s, 1H, OH); 7.55–7.11 (m, 10H, Ph); 4.16 (s, 1H, C^3H); 3.89 (s, 5H, Cp); 2.61 (s, 6H, NMe_2); 2.06 (s, 3H, Me); 1.91 (s, 3H, Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 146.5 ($C_{ipso\text{-}Ph}$); 135.4–126.8 (C_{arom}); 110.9 (C^1); 90.7 (C^2); 80.4, 80.2 (C^4 and C^5); 77.9 (CPh_2OH); 70.5 (Cp_{free}); 67.5 (C^3); 46.1 (NMe_2); 13.4 (Me); 11.8 (Me).

7d Yield: 210 mg, 45%. Anal. Calcd. for $C_{27}H_{27}FeNO_3$: C, 69.09; H, 5.80. Found: C, 68.98; H, 5.92. ^{1}H NMR ($CDCl_3$) 8.44 (s, 1H, OH); 7.48–7.01 (m, 10H, Ph); 4.36 (d, 1H, $^{4}J_{HH} = 1.6$ Hz, C^3H); 4.04 (s, 5H, Cp); 3.99 (d, 1H, $^{4}J_{HH} = 1.6$ Hz, C^5H); 3.70 (s, 3H, CO_2Me); 2.56 (s, 6H, NMe_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 170.5 (CO_2Me); 146.3 ($C_{ipso\text{-}Ph}$); 136.8–126.4 (C_{arom}); 112.3 (C^1); 92.0 (C^2); 77.8 (CPh_2OH); 71.2, 70.8 (C^3 and C^5); 69.7 (Cp_{free}); 68.8 (C^4); 51.4 (CO_2Me); 46.8 (NMe_2).

7e Yield: 173 mg, 37%. Anal. Calcd. for $C_{29}H_{33}FeNO$: C, 74.52; H, 7.12. Found: C, 74.61; H, 7.20. ^{1}H NMR ($CDCl_3$) 8.30 (s, 1H, OH); 7.52–7.06 (m, 10H, Ph); 4.22 (s, 1H, C^3H); 3.98 (s, 5H, Cp); 2.60 (s, 6H, NMe_2); 2.80–2.24 (m, 4H, CH_2CH_3); 1.28–0.94 (m, 6H, CH_2CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 145.9 ($C_{ipso\text{-}Ph}$); 136.7–128.8 (C_{arom}); 111.8 (C^1); 90.7 (C^2); 81.2, 80.8 (C^4 and C^5); 78.1 (CPh_2OH); 70.8 (Cp_{free}); 67.3 (C^3); 46.1 (NMe_2); 20.4, 20.1 (CH_2CH_3); 15.6, 14.8 (CH_2CH_3).

7f Yield: 201 mg, 43%. Anal. Calcd. for $C_{29}H_{33}FeNO$: C, 74.52; H, 7.12. Found: C, 74.43; H, 7.06. ^{1}H NMR ($CDCl_3$) 8.29 (s, 1H, OH); 7.54–7.00 (m, 10H, Ph); 4.31 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^3H); 3.97 (s, 5H, Cp); 3.86 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^5H); 2.45 (s, 6H, NMe_2); 2.04 (m, 2H, CH_2); 1.81 (m, 2H, CH_2); 1.59 (m, 2H, CH_2); 1.15 (m, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 146.1 ($C_{ipso\text{-}Ph}$); 136.0–127.9 (C_{arom}); 112.0 (C^1); 91.6 (C^2); 80.6 (C^4); 79.2 (CPh_2OH); 69.9 (Cp_{free}); 67.4 (C^3); 59.5 (C^5); 44.8 (NMe_2); 33.2, 28.4, 22.1, 14.5 (Bu^n).

4.4. Synthesis of [1-N(Me)(Xyl)-3-R-4-Tol-Fc] (R = Ph, **10a**; R = CPh_2OH, **11a**, R = CO_2Me **12a**) and [1-N(Me)(Xyl)-2-R-4-Tol-Fc] (**10b**, **11b**, **12b**)

The ferrocene complexes **10**–**12** were prepared by the same procedure described for **7a**, by reacting **9** with HC≡CPh, HC≡$CCPh_2OH$ and HC≡CCO_2Me, respectively.

10 Yield (overall yield **10a** + **10b**): 298 mg, 62%. Yield (**10a**): 52%; yield (**10b**): 10%. Anal. Calcd. for (isomeric mixture of **10a** and **10b**) $C_{32}H_{31}FeN$: C, 79.17; H, 6.44. Found: C, 79.23; H, 6.37.

10a ^{1}H NMR ($CDCl_3$) 7.34–6.86 (m, 12H, $C_6H_3Me_2$, C_6H_4Me and C_6H_5); 4.34 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^2H); 4.06 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^5H); 3.99 (s, 5H, Cp); 3.55 (s, 3H, NMe); 2.35 (s, 3H, C_6H_4Me); 2.12 (s, 3H, $C_6H_3Me_2$); 2.08 (s, 3H, $C_6H_3Me_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 148.4 ($C_{ipso\text{-}Xyl}$); 134.0–125.4 (C_{arom}); 102.5 (C^1); 82.3, 81.5 (C^3 and C^4); 72.0 (Cp_{free}); 71.0, 70.4 (C^2 and C^5); 46.1 (NMe); 23.4 (C_6H_4Me); 18.2, 17.8 ($C_6H_3Me_2$).

10b ^{1}H NMR ($CDCl_3$) δ 7.34–6.86 (m, 12H, $C_6H_3Me_2$, C_6H_4Me and C_6H_5); 4.19 (d, 1H, $^{4}J_{H,H} = 1.4$ Hz, C^5H); 4.02 (m, 6H, Cp_{free} and C^3H); 3.64 (s, 3H, NMe); 2.28 (s, 3H, C_6H_4Me); 2.16 (s, 3H, $C_6H_3Me_2$); 2.04 (s, 3H, $C_6H_3Me_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 148.1 ($C_{ipso\ Xyl}$); 134.0–125.4 (C_{arom}); 104.0 (C^1); 84.1, 80.7 (C^2 and C^4); 72.3, 69.9 (C^3 and C^5); 69.4 (Cp_{free}); 48.3 (NMe); 21.8 (C_6H_4Me); 17.5, 17.2 ($C_6H_3Me_2$).

11 Yield (overall yield **11a** + **11b**): 272 mg, 46%. Yield (**11a**): 41%; yield (**11b**): 5%. Anal. Calcd. for (isomeric mixture of **11a** and **11b**) $C_{39}H_{37}FeNO$: C, 79.18; H, 6.30. Found: C, 79.09; H, 6.41.

11a ^{1}H NMR ($CDCl_3$) δ 7.43–6.95 (m, 17H, $C_6H_3Me_2$, C_6H_4Me and C_6H_5); 4.17 (m, 2H, C^2H and C^5H); 4.04 (s, 5H, Cp); 3.60 (s, 3H, NMe); 2.34 (s, 3H, C_6H_4Me); 2.02 (s, 3H, $C_6H_3Me_2$); 1.98 (s, 3H, $C_6H_3Me_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 147.6, 147.0 ($C_{ipso\ Xyl}$ and C_{ipso} Ph); 137.0–125.8 (C_{arom}); 105.1 (C^1); 82.2, 80.3 (C^3 and C^4); 71.1 (Cp_{free}); 70.2 (C^2 and C^5); 46.7 (NMe); 22.9 (C_6H_4Me); 19.9, 18.4 ($C_6H_3Me_2$); O*H* not observed.

11b ^{1}H NMR ($CDCl_3$) δ 7.43–6.95 (m, 17H, $C_6H_3Me_2$, C_6H_4Me and C_6H_5); 3.99–3.96 (m, 7H, C^3H, C^5H and Cp_{free}); 3.49 (s, 3H, NMe); 2.21 (s, 3H, C_6H_4Me); 1.96 (s, 3H, $C_6H_3Me_2$); 1.90 (s, 3H, $C_6H_3Me_2$); O*H* not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 148.4, 146.6 ($C_{ipso\ Xyl}$ and C_{ipso} Ph); 137.0–125.8 (C_{arom}); 104.0 (C^1); 81.0 (C^2 and C^4); 73.2, 72.6 (C^3 and C^5); 70.8 (Cp_{free}); 45.5 (NMe); 24.0 (C_6H_4Me); 17.9, 17.5 ($C_6H_3Me_2$).

12 Yield (overall yield **12a** + **12b**): 243 mg, 52%. Yield (**12a**): 44%; yield (**12b**): 8%. Anal. Calcd. for (mixture of **12a** and **12b**) $C_{28}H_{29}FeNO_2$: C, 71.95; H, 6.25. Found: C, 72.03; H, 6.21.

12a ^{1}H NMR ($CDCl_3$) δ 7.31–6.99 (m, 7H, $C_6H_3Me_2$ and C_6H_4Me); 4.44 (d, 1H, $^4J_{H,H} = 1.4$ Hz, C^2H); 4.18 (d, 1H, $^4J_{H,H} = 1.4$ Hz, C^5H); 4.07 (s, 5H, Cp); 3.52 (br s, 6H, NMe and CO_2Me); 2.30 (s, 3H, C_6H_4Me); 2.11 (s, 3H, $C_6H_3Me_2$); 2.02 (s, 3H, $C_6H_3Me_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.1 (CO_2Me); 136.1–126.3 (C_{arom}); 103.3 (C^1); 80.0, 78.9 (C^3 and C^4); 71.5, 68.0 (C^2 and C^5); 70.4 (Cp_{free}); 51.0 (CO_2Me); 44.8 (NMe); 22.8 (C_6H_4Me); 19.9, 18.5 ($C_6H_3Me_2$).

12b ^{1}H NMR ($CDCl_3$) δ 7.31–6.99 (m, 7H, $C_6H_3Me_2$ and C_6H_4Me); 4.29 (d, 1H, $^4J_{H,H} = 1.4$ Hz, C^5H); 3.96 (m, 6H, Cp_{free} and C^3H); 3.60 (s, 3H, NMe); 3.48 (s, 3H, CO_2Me); 2.31 (s, 3H, C_6H_4Me); 2.06 (s, 3H, $C_6H_3Me_2$); 1.99 (s, 3H, $C_6H_3Me_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.4 (CO_2Me); 136.1–126.3 (C_{arom}); 104.9 (C^1); 83.6, 82.0 (C^2 and C^4); 74.0, 71.9 (C^3 and C^5); 70.1 (Cp_{free}); 52.1 (CO_2Me); 46.7 (NMe); 23.9 (C_6H_4Me); 21.1, 20.3 ($C_6H_3Me_2$).

4.5. Synthesis of [1-N(Me)-2-R-3-Et-5-Et-Fc] (R = Tol, **14**; R = CH_2OH, **15**)

The ferrocene complexes **13**–**14** were prepared by the same procedure described for **7a**, by reacting **13** with HC≡CTol, and HC≡CCH_2OH, respectively.

14 Yield: 163 mg, 45%. Anal. Calcd. for $C_{22}H_{27}FeN$: C, 73.13; H, 7.53. Found: C, 73.05; H, 7.62. ^{1}H NMR ($CDCl_3$) δ 7.58–7.05 (m, 4H, C_6H_4Me); 4.14 (s, 1H, C^3H); 4.00 (s, 5H, Cp); 2.68 (s, 3H, NMe); 2.50–2.25 (m, 7H, CH_2CH_3 and C_6H_4Me); 1.29–1.12 (m, 6H, CH_2CH_3); N*H* not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 135.7–125.8 (C_{arom}); 106.1 (C^1); 84.8 (C^2); 80.8, 80.2 (C^4 and C^5); 71.3 (C^3); 70.6 (Cp_{free}); 37.6 (NMe); 21.3 (C_6H_4Me); 20.8, 19.5 (CH_2CH_3); 15.4, 14.8 (CH_2CH_3).

15 Yield: 141 mg, 47%. Anal. Calcd. for $C_{16}H_{23}FeNO$: C, 63.80; H, 7.70. Found: C, 63.91; H, 7.63. ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 1H, OH); 4.80–4.66 (m, 2H, CH_2OH); 4.27 (s, 1H, C^3H); 4.04 (s, 5H, Cp); 2.84 (s, 3H, NMe); 2.51–2.23 (m, 4H, CH_2CH_3); 1.18–0.96 (m, 6H, CH_2CH_3); N*H* not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 104.3 (C^1); 98.9 (C^2); 84.5 (C^4 and C^5); 72.1 (C^3); 70.2 (Cp_{free}); 57.3 (CH_2OH); 43.0 (NMe); 20.7, 19.2 (CH_2CH_3); 15.3, 15.0 (CH_2CH_3).

Table 2
Crystal data and experimental details for **7c**.

Formula	$C_{27}H_{29}FeNO$
Fw	439.36
T, K	296(2)
λ, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.646(2)
b, Å	12.337(2)
c, Å	15.607(3)
β, °	111.795(2)
Cell volume, Å^3	2260.9(6)
Z	4
D_c, g cm^{-3}	1.291
μ, mm^{-1}	0.685
F(000)	928
Crystal size, mm	0.16 × 0.12 × 0.10
θ limits, °	1.73–25.09
Reflections collected	21161
Independent reflections	4026 [$R_{int} = 0.1512$]
Data/restraints/parameters	4026/279/320
Goodness on fit on F^2	1.019
R_1 ($I > 2\sigma(I)$)	0.0605
wR_2 (all data)	0.1629
Largest diff. peak and hole, e Å^{-3}	0.351/−0.371

4.5.1. X-ray crystallography

Crystal data and collection details for **7c** are reported in Table 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) [21]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [22]. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(1a), 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(1a) distance was restrained to 0.83 Å [s.u. 0.02]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Similar *U* restraints [s.u. 0.01] were applied to all C-atoms. The unsubstituted Cp-ring bonded to Fe(1) is disordered over two positions; disordered atomic positions were split and refined using one occupancy parameter per disordered group and restrained to have similar geometries (SAME line in SHELXTL).

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Appendix A. Supplementary material

CCDC 926883 for **7c**, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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