Functionalized Ferrocenes from [3+2] Cycloadditions in Bridging Vinylalkylidene Diiron Complexes

Luigi Busetto,[†] Fabio Marchetti,[‡,§] Rita Mazzoni,[†] Mauro Salmi,[†] Stefano Zacchini,[†] and Valerio Zanotti*[,†]

Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy, and Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

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Reactions of the vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}CRCHCH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = $SiMe_3$, **1a**; Tol, **1b**; CO_2Me, **1c**, Tol = 4-MeC_6H_4) with HC≡CR′ (R′ = CPh_2OH, CO_2Me, Ph) lead to the formation of a mixture of 1,3-disubstituted ferrocenes [1-R-3-R′-Fc] (**5**, **7**, **9**, **11**) and 1,2,4-trisubstituted ferrocenes [1-NMe_2-2-R′-4-R-Fc] (**4**, **6**, **8**, **10**) (R = $SiMe_3$, R′ = CPh_2OH, **4** and **5**; R = $SiMe_3$, R′ = CO_2Me, **6** and **7**; R = $SiMe_3$, R′ = Ph, **8** and **9**; R = Tol, R′ = CPh_2OH, **10** and **11**). The polysubstituted Cp ring of the ferrocenyl products results from the cycloaddition of the alkyne with the bridging vinylalkylidene ligand and involves the cleavage of one of the two substituents (H or NMe_2) on the vinyl moiety, as well as of the Fe−Fe bond. The cycloaddition reaction has been extended to a variety of bridging vinylalkylidene diiron complexes with different substituents and functionalities on the C_3 bridging ligand, and to different alkynes. Thus, the vinylalkylidene complex **1b** reacts with HC≡CPh, yielding a mixture of four different ferrocenes, due to the absence of regioselectivity in the alkyne cycloaddition: [1-NMe_2-2-Ph-4-Tol-Fc] (**12**), [1-Tol-3-Ph-Fc] (**13**), [1-NMe_2-3-Ph-4-Tol-Fc] (**14**), and [1-Tol-2-Ph-Fc] (**15**). Conversely, the reactions with symmetric alkynes do not produce regioisomers: treatment of **1b** and **1c** with R′C≡CR′ (R′ = Et, Ph) affords a mixture of 1,2,3-trisubstituted ferrocenes [1-R-2-R′-3-R′-Fc] (**17**, **19**, **21**, **23**) and tetrasubstituted ferrocenes [1-NMe_2-2-R′-3-R′-4-R-Fc] (**16**, **18**, **20**, **22**) (R = $SiMe_3$, R′ = Et, **16** and **17**; R = Tol, R′ = Et, **18** and **19**; R = Tol, R′ = Ph, **20** and **21**; R = CO_2Me, R′ = Ph, **22** and **23**).

Likewise, the vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(X)CHCH(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = CO_2Me, X = NMe_2, **2a**; R = CN, X = NMe_2, **2b**; R = CO_2Me, X = SMe, **3a**; R = CN, X = SMe, **3b**) react with alkynes HC≡CR′ (R′ = Tol, Ph), yielding a mixture of trisubstituted ferrocenes [1-X-2-R′-4-R-Fc] (**24**, **26**, **28**) and [1-X-3-R′-4-R-Fc] (**25**, **27**, **29**) (X = NMe_2, R = CO_2Me, R′ =Tol, **24** and **25**; X = NMe_2, R = CN, R′ =Tol, **26** and **27**; X = SMe, R = CO_2Me, R′ = Ph, **28** and **29**). Finally, the reactions of **2a** and **3b** with PhC≡CPh afford the tetrasubstituted ferrocenes **22** and [1-SMe-2-Ph-3-Ph-4-CN-Fc] (**30**), respectively. The crystal structures of **4** and **11** have been determined by X-ray diffraction studies.

Introduction

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

Alternative synthetic methods remain largely unexplored despite the fact that a number of metal-mediated [3+2] cycloadditions are well known[5] which should, in theory, provide more direct routes to the formation of substituted cyclopenta-

* To whom correspondence should be addressed. E-mail: valerio.zanotti@unibo.it.

† Università di Bologna.

‡ Università di Pisa.

§ Fabio Marchetti, born in 1974 in Bologna, Italy.

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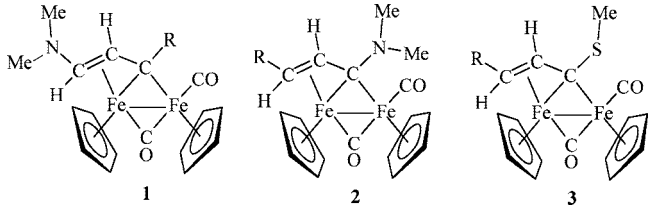
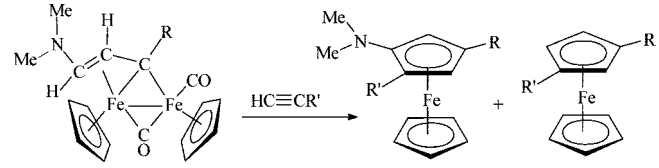
Scheme 1



Scheme 2



	R	R'		Yield %		Yield %
1a	$SiMe_3$	CPh_2OH	**4**	*33*	**5**	*54*
1a	$SiMe_3$	CO_2Me	**6**	*31*	**7**	*47*
1a	$SiMe_3$	Ph	**8**	*28*	**9**	*59*
1b	Tol	CPh_2OH	**10**	*37*	**11**	*48*

dienyl ligands. Few examples are reported in which [3+2][6] or [1+2+2][7] cycloadditions of coordinated ligands result in the direct assembling of cyclopentadienyls bearing substituents and functional groups. Even less investigated is the possibility that functionalized cyclopentadienyl complexes might be directly generated by assembling of bridging organic frames (C_2 or C_3 ligands), taking advantage of the activation effects due to multisite coordination.[8]

We have been exploring the chemistry of bridging vinylalkylidene (allylidene) diiron complexes and have described synthetic methods for obtaining a variety of bridging C_3 ligands containing various functional groups distributed on the alkylidene carbon or on the vinyl end. Examples include the complexes **1**,[9] **2**,[10] and **3**[11] (Scheme 1).

We were intrigued by the possibility that our functionalized vinylalkylidene ligands might be involved in cycloaddition reactions with alkynes, affording cyclopentadienes or cyclopentadienyl ligands, incorporating the same functionalities.

Herein we report on these investigations that involved a range of vinylalkylidene complexes with different substituents, as well as a number of different alkynes, in order to elucidate possible factors influencing the reaction course.

Results and Discussion

Cycloaddition Reactions of Bridging Enaminoalkylidene Complexes. The bridging enaminoalkylidene complexes **1a** and **1b** react with primary alkynes HC≡CR′ (R′ = CPh_2OH, CO_2Me, Ph) in toluene at reflux temperature, leading to the formation of a mixture of substituted ferrocenes, as shown in Scheme 2.

Separation of the ferrocene products was easily accomplished by column chromatography, and all of the ferrocenyl complexes **4**−**11** were characterized by spectroscopy and elemental analysis. Moreover, the molecular structures of **4** and **11** have been determined by X-ray diffraction. The structures of **4** (Figure 1 and Table 1) and **11** (Figure 2 and Table 2) are those of typical ferrocenes 1,2,4-trisubstituted and 1,3-disubstituted on one Cp ring, respectively. The two Cp rings are almost parallel [angles between the least-squares mean planes of the five-membered rings are 3.5° and 3.3° for **4** and **11**, respectively] and adopt a staggered conformation [mean relative rotations 24° and 23° for **4** and **11**, respectively].

The Fe−C interactions with the substituted C_5 ring [average 2.048(6) and 2.041(7) Å for **4** and **11**, respectively] are sensibly longer than those with the unsubstituted Cp rings [average 2.038(7) and 2.034(7) Å for **4** and **11**, respectively] and also the C−C distances are elongated in the substituted rings [average 1.429(7) and 1.423(7) Å for **4** and **11**, respectively] compared to the nonsubstituted cyclopentadienyl rings [average 1.380(10) and 1.391(10) Å for **4** and **11**, respectively].

The N(1) atom in **4** is essentially sp^3 hybridized, displaying a strong pyramidalization [sum angles 335.1(3)°], and the C(8)−N(1) interaction [1.439(3) 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(11) 1.461(3) Å; N(1)−C(12) 1.461(3) Å]. The lone pair on N(1) is, therefore,

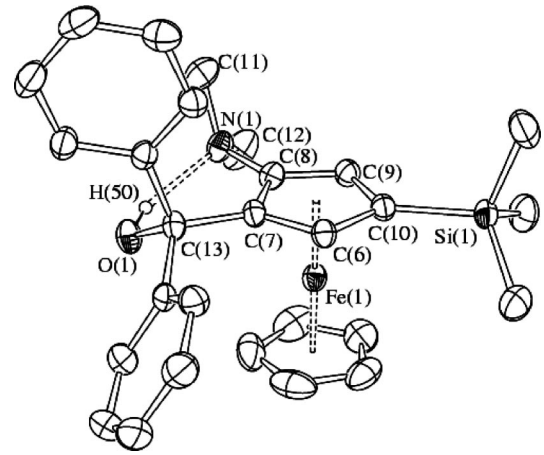


Figure 1. ORTEP diagram of **4**. All the hydrogens have been omitted except H(50). Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 4

Fe(1)−$C_5H_2R_3$(av)	2.048(6)	Fe(1)−C_5H_5(av)	2.038(7)
C(6)−C(7)	1.423(3)	O(1)−H(50)	0.821(10)
C(7)−C(8)	1.428(3)	H(50)···N(1)	2.027(15)
C(8)−C(9)	1.423(3)	O(1)···N(1)	2.793(2)
C(9)−C(10)	1.430(3)	C(8)−N(1)	1.439(3)
C(10)−C(6)	1.440(3)	C(11)−N(1)	1.461(3)
C−C(av) in C_5H_5	1.380(10)	C(12)−N(1)	1.461(3)
C(7)−C(13)	1.529(3)	C(10)−Si(1)	1.855(2)
C(13)−O(1)	1.429(2)		
C(7)−C(6)−C(10)	109.87(17)	N(1)−C(8)−C(9)	128.52(18)
C(6)−C(7)−C(8)	107.00(16)	C(6)−C(10)−Si(1)	128.62(15)
C(7)−C(8)−C(9)	108.06(17)	C(9)−C(10)−Si(1)	125.77(15)
C(8)−C(9)−C(10)	109.49(17)	C(8)−N(1)−C(11)	111.41(18)
C(9)−C(10)−C(6)	105.57(16)	C(8)−N(1)−C(12)	113.87(18)
C(6)−C(7)−C(13)	128.36(17)	C(11)−N(1)−C(12)	109.8(2)
C(8)−C(7)−C(13)	124.52(17)	C(7)−C(13)−O(1)	109.38(15)
C(7)−C(8)−N(1)	123.36(18)	O(1)−H(50)···N(1)	155(3)

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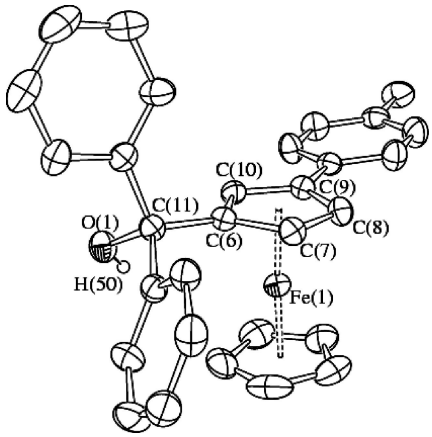


Figure 2. ORTEP diagram of **11**. All the hydrogens have been omitted except H(50). Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 11

Fe(1)−$C_5H_3R_2$(av)	2.041(7)	Fe(1)−C_5H_5(av)	2.034(7)
C(6)−C(7)	1.422(3)	C(6)−C(11)	1.512(3)
C(7)−C(8)	1.417(3)	C(11)−O(1)	1.443(2)
C(8)−C(9)	1.429(3)	O(1)−H(50)	0.8200
C(9)−C(10)	1.422(3)	C−C(av) in C_5H_5	1.391(10)
C(10)−C(6)	1.423(3)		
C(7)−C(6)−C(10)	106.90(18)	C(7)−C(6)−C(11)	128.23(18)
C(6)−C(7)−C(8)	108.65(18)	C(10)−C(6)−C(11)	124.75(18)
C(7)−C(8)−C(9)	108.33(19)	C(6)−C(11)−O(1)	109.85(16)
C(8)−C(9)−C(10)	106.75(18)	C(9)−C(10)−C(6)	109.36(18)

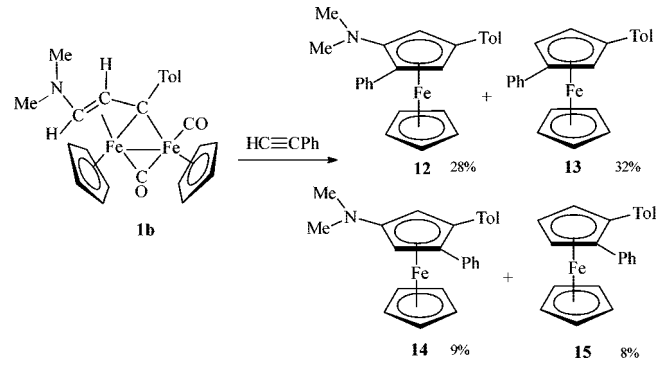
available for instance for the formation of hydrogen bonds. Thus, a weak intramolecular hydrogen bond exists in **4** between the −NMe_2 and the −CPh_2(OH) substituents [O(1)−H(50) 0.821(10) Å, H(50)···N(1) 2.027(15) Å, O(1)···N(1) 2.793(2) Å, O(1)−H(50)−N(1) 155(3)°].

In the case of **4**, all the C(10)−Si(1) [1.855(2) Å], C(7)−C(13) [1.529(3) Å], and C(13)−O(1) [1.429(2) Å] are essentially single bonds, as well as C(6)−C(11) [1.512(3) Å] and C(11)−O(1) [1.443(2) Å] in **11**.

The NMR spectroscopic characterization of **4**−**11**, based on DEPT and NOE experiments and ^{1}H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments, is consistent with the structures found in the solid. The ^{1}H NMR spectra show the typical pattern of di- and trisubstituted ferrocene derivatives, whereas the nonsubstituted Cp rings give rise to a singlet in the range 4.20−3.90 ppm. Noteworthy, in the ^{1}H NMR spectra of **4**, in $CDCl_3$ solution, the two N-methyls give rise to a single resonance. Their equivalence, on the NMR time scale, is explained assuming an exchange mechanism that implies free rotation around the Me_2N−C_{Cp} bond and inversion at the N atom. The exchange process takes place in spite of the hydrogen bond interaction between the OH and NMe_2, clearly evidenced in the solid but also present in solution, as suggested by the low-field resonance at 8.20 ppm attributable to the OH group. Variable-temperature ^{1}H NMR experiments suggested a low activation barrier for this exchange process: complete coalescence of the signals due to the NMe_2 occurred only at about −75 °C, whereas two distinct resonances were observed at −90 °C (see Experimental Section).

The ferrocene complexes **4**−**11** have been also investigated by electrochemical methods (see Experimental Section). Cyclic voltammograms show reversible anodic peaks, which, in the case of the dimethylamino ferrocenes, are at lower potentials with respect to the ferrocene/ferricinium couple, in agreement with the electron-donor character of the substituent.

Scheme 3



The results reported in Scheme 2 went beyond the expected release of the bridging vinylalkylidene ligand in the form of five-membered cycloadducts. This latter possibility was suggested by the fact that α,β-unsaturated alkylidene ligands are known to undergo cyclization with alkynes, which, beside the classical Dötz reaction, can afford cyclopentadienes as well as other cycloadducts.[12] In our case the [3+2] cyclization does not lead to the release of the organic fragment, but rather it produces its transformation into a cyclopentadienyl ring, which remains coordinated to one Fe atom.

The reaction deserves further comments. First of all, the observed ferrocene products are clearly the result of the assembly of alkynes with the bridging vinylalkylidene ligands. The bridging C_3 frame can be easily recognized as a constituent of the functionalized cyclopentadienyl ring, where it retains its substituents except for those of the vinyl moiety. Therefore, the bridging C_3 ligands in **1a**,**b** lose one of the two substituents: H or NMe_2, generating the trisubstituted (**4**, **6**, **8**, **10**) and disubstituted ferrocenes (**5**, **7**, **9**, **11**), respectively. Both possibilities (C−H and C−N cleavage) take place, as indicated by the composition of the reaction products, with a slight predominance of the C−N cleavage. Furthermore, the observed cycloaddition reactions are regiospecific, in that the incorporation of primary alkynes occurs selectively in one of the two possible modes, affording cyclopentadienyls where the R′ group (R′ = CPh_2OH, CO_2Me, Ph) is exclusively placed far from R (R = $SiMe_3$, Tol). The regioselectivity is presumably originated by steric reasons and is due to the presence of rather hindered substituents (R and R′) such as $SiMe_3$ and CPh_2OH. Indeed, the reaction shown in Scheme 3, in which substituents on the C_3 bridging ligand and on the alkyne reagent are less sterically demanding, does not exhibit the same regioselectivity, leading to the formation of all four different isomers.

In this case separation of the isomeric mixture by column chromatography was only partially achieved: **12** and **14** were isolated from **13** and **15**, but separation of the regioisomers was incomplete.

An obvious strategy to reduce the number of reaction products is to make use of symmetrically disubstituted alkynes, in order to avoid the formation of regioisomers. However, this approach led to the addition of a further substituent on the Cp ring of the metallocene products and, consequently, might be less favorable by steric reasons. This point has been investigated through the reactions reported in Scheme 4.

As expected, increasing the number of sterically demanding substituents makes the cyclization more difficult and reduces the conversion yield, in particular when R = $SiMe_3$.

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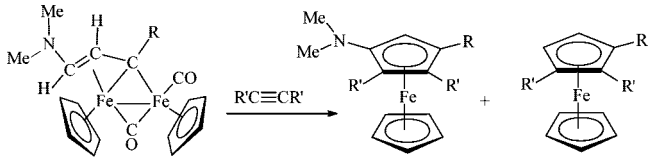
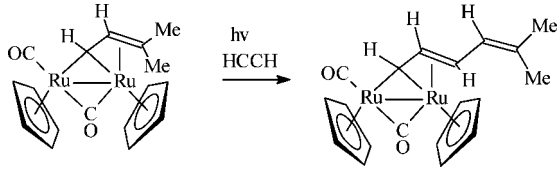
Scheme 4



	R	R'		Yield %		Yield %
1a	$SiMe_3$	Et	**16**	*21*	**17**	*30*
1b	Tol	Et	**18**	*35*	**19**	*37*
1b	Tol	Ph	**20**	*29*	**21**	*36*
1c	CO_2Me	Ph	**22**	*30*	**23**	*32*

Scheme 5

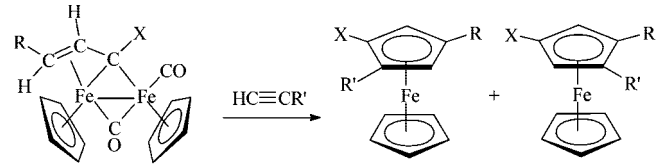


The data so far collected are too limited to provide a realistic picture of the reaction sequence that leads to the functionalized ferrocenes. The mechanisms so far proposed for analogous vinylalkylidene−alkyne−CO cyclization in mononuclear complexes (e.g., the classical Dötz benzannulation) provide reasonable suggestions, although there is only a limited overlap between the chemistry of bridging and terminally bonded alkylidenes. In particular, the benzannulation is supposed to proceed via decarbonylation of the carbene complex precursor, which is the rate-determining step. This allows alkyne coordination, immediately followed by insertion in the metal−carbene bond.[13] By analogy, the cyclization involving **1a**−**c** might proceed through the displacement of the vinyl coordination, affording an unsaturated μ-η^1:η^1-vinylalkylidene intermediate, which allows alkyne coordination and subsequent insertion.

Examples of alkyne insertion and coupling with bridging vinylalkylidene ligands are known.[14] They generally produce the elongation of the bridging hydrocarbyl chain, which maintains the bridging alkylidene character (Scheme 5).[15] Multiple alkyne insertion (oligomerization) is possible, but the formation of cyclization products is unusual.[16]

In the light of these considerations, the observed cyclization leading to the substituted ferrocenes appears very unique in that, to the best of our knowledge, it is the first example of cyclization involving a bridging vinylalkylidene ligand, which affords a polysubstituted cyclopentadienyl. A further unusual result is the cleavage of the Fe−Fe bond with fragmentation of the parent dinuclear species. The dinuclear $Fe_2CO_2Cp_2$ frame is generally very robust and remains intact, even supporting quite remarkable transformations of bridging ligands. Exceptions are rare and mostly involve the formation of metallacycles.[17] The fragmentation produces a Fe and a C_5H_5 ring, which give rise to the observed ferrocenes, whereas the residual part of the molecule, which formally corresponds to $XFe(CO)_2Cp$ (X = NMe_2, H),

Scheme 6



	X	R	R'		Yield %		Yield %
2a	NMe_2	CO_2Me	Tol	**24**	*30*	**25**	*37*
2b	NMe_2	CN	Tol	**26**	*31*	**27**	*40*
3a	SMe	CO_2Me	Ph	**28**	*33*	**29**	*36*

leads to the formation of significant amounts of $[Fe_2(CO)_4(Cp)_2]$. This has been ascertained by carrying out the reaction of **1a** with HC≡CPh in a NMR tube, in toluene d_8 at 105 °C, and by monitoring the reaction during a 15 h period of time. Noteworthy, in this experiment we did not observe any intermediate species: the progressive disappearance of the resonances of the precursor was simply paralleled by the rising of signals due to the ferrocene products. This evidence supports the hypothesis that the rate-determining step consists in the creation of a vacant coordination site by displacement of the vinyl coordination in the first step of the reaction sequence.

Cycloaddition Reactions of Bridging Vinyl-Aminoalkylidene and Vinyl-Thioalkylidene Complexes. Further investigations concerned the complexes **2** and **3**. The amino- alkylidene complexes **2** differ from **1** in that the NMe_2 group is placed on the bridging alkylidene carbon, rather than on the vinyl moiety of the bridging C_3 chain. The structure of **3a** is the same as **2a**, except for containing a SMe group in place of NMe_2. Beside these differences concerning the nature and position of the substituents, all of the bridging ligands in **1**, **2**, and **3** exhibit vinylalkylidene character and also react similarly with alkynes, affording ferrocenyl products. Therefore, complexes **2** and **3** reacted with alkynes affording the ferrocene complexes **24**−**29** (Scheme 6).

Comparison with the reactions of **1a**,**b** shown in Scheme 2 evidences that in this case the reaction is not regioselective, and both regioisomers are formed in comparable amounts. Conversely, the most remarkable aspect of the reactions of **2a**,**b** and **3a** is that cycloaddition is chemoselective, and only the C−H and not the C−R bond of the bridging ligands undergoes cleavage. Consequently, the ferrocene products maintain, as substituents, both functional groups that are present on the bridging C_3 ligand in the precursor complexes: the alkylidene substituent (NMe_2 or SMe) and the CO_2Me or CN group. As initially mentioned, this is a relevant point in consideration of the fact that the introduction of several different functionalities, including the NMe_2 group, on the same Cp ring is hard to accomplish by traditional methods, starting from unsubstituted ferrocene. Indeed, none of the ferrocene complexes reported in Scheme 6 have been previously synthesized.

Again, the use of symmetric alkynes, as shown in Scheme 7, greatly simplifies the picture, leading to the formation of one single product, which is a tetrasubstituted ferrocenyl complex.

The synthesis of **22** from **2a**, shown in Scheme 7, should be compared with the corresponding reaction of **1c** with PhCCPh (Scheme 4), which also yields **22**, but in mixture with the trisubstituted ferrocene **23**. Noteworthy, complexes **1c** and **2a** are isomers: in theory, their interconversion should be achieved by exchanging the position of the NMe_2 and CO_2Me substituents. In spite of the similarities, their reactivity is significantly different, and only **2a** exhibits a chemoselective character in the cyclization with alkynes. This observation indicates that a proper choice of the substituents,

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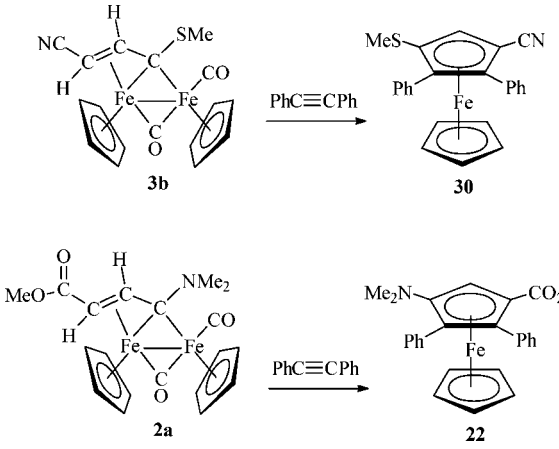
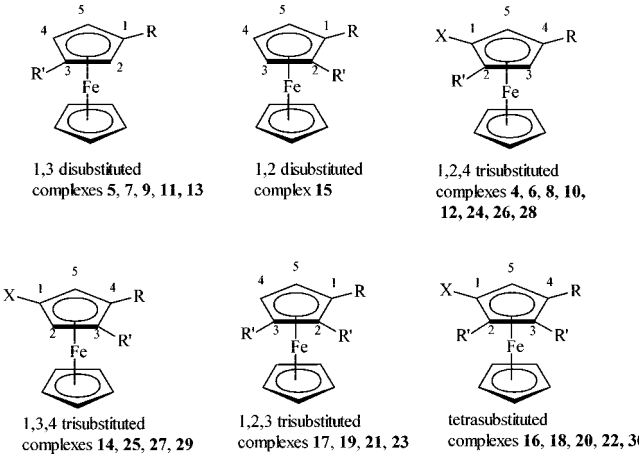
Scheme 7



Scheme 8



in terms of their nature and position on the bridging vinylalkylidene ligand, should provide the key to selectively conduct these cycloaddition reactions.

Conclusions

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

These results also suggest that a new and more direct approach to the formation of polyfunctionalized ferrocenes is possible. The limitations due to the absence of a complete chemo- and regiocontrol of the reaction and the use of rather "sophisticated" bridging vinylalkylidene complexes as precursors would be compensated by the direct formation of ferrocenes characterized by the presence of two or three different substituents in only one of the two cyclopentadienyls. Indeed, ferrocenes of this type are difficult to obtain, and to the best of our knowledge, none of the ferrocene complexes herein reported have been previously synthesized, with the exception of an isomeric form of complex **7**, in which the two ring substituents are in adjacent position.[18]

Experimental Section

General Data. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of SiO_2. Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer, and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. ESI-MS spectra were recorded on a Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. All NMR measurements were performed on a Varian Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and ^1H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments.[19] Unless otherwise stated, NMR spectra were recorded at 298 K. For the isomers **12**−**14**, **24**−**25**, **26**−**27**, and **28**−**29**, not fully separated by chromatography, yields have been determined by integration of the NMR signals. NOE measurements were recorded using the DPFGSE-NOE sequence.[20] NMR resonances are indicated according to the numbering scheme shown hereafter (Scheme 8). All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds **1a**−**c**,[9] **2a**,**b**,[10] and **3a**,**b**[11] were prepared by published methods.

Synthesis of [1-SiMe$_3$-3-CPh$_2$OH-Fc] (5) and [1-NMe$_2$-2-CPh$_2$OH-4-SiMe$_3$-Fc] (4). To a solution of **1a** (400 mg, 0.883 mmol), in toluene (20 mL), was added HC≡CCPh$_2$OH (184 mg, 0.883 mmol). The resulting solution was stirred at reflux temperature for 16 h, then was allowed to cool to room temperature and filtered on a Celite pad. Solvent removal and chromatography of the residue on a SiO_2 column with petroleum ether (bp 40−60 °C) as eluent gave first a yellow-orange fraction, corresponding to **5**. Yield: 210 mg, 54%. Anal. Calcd for $C_{26}H_{28}FeOSi$: C, 70.90; H, 6.41. Found: C, 70.79; H, 6.35. ^1H NMR ($CDCl_3$) (see numbering scheme): 7.84−7.18 (m, 10H, C_6H_5), 4.16 (m, 2H, C^4H and C^5H), 4.12 (s, 5H, Cp), 3.99 (t, 1H, $^4J_{HH}$ = 1.30 Hz, C^2H), 3.40 (s, 1H, OH), 0.22 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): 147.4, 147.3 ($C_{ipso\ Ph}$), 137.8−126.9 (C_{arom}), 101.9 (C^3), 77.8 (CPh_2OH), 73.3 (C^1), 73.1, 72.0 (C^4 and C^5), 72.9 (C^2), 68.9 (Cp), 1.24 ($SiMe_3$). ESI-MS (ES^+): 441 *m*/*z* [M^+].

A second orange-red fraction, corresponding to **4**, was collected by using diethyl ether as eluent. Yield: 141 mg, 33%. Anal. Calcd for $C_{28}H_{33}FeNOSi$: C, 69.56; H, 6.88; N, 2.90. Found: C, 69.48; H, 6.80; N, 2.92. ^1H NMR ($CDCl_3$): 8.20 (s, 1H, OH), 7.84−7.10 (m, 10H, C_6H_5), 4.06 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^5H), 4.03 (s, 5H, Cp), 3.82 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^3H), 2.35 (s, 6H, NMe_2), 0.23 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): 146.3 ($C_{ipso\ Ph}$), 137.8−126.2 (C_{arom}), 112.5 (C^1), 94.4 (C^2), 78.4 (CPh_2OH), 70.2 (Cp), 70.0 (C^3), 67.9 (C^4), 62.0 (C^5), 46.8 (NMe_2), 0.12 ($SiMe_3$). ESI-MS (ES^+): 484 *m*/*z* [M^+]. ^1H NMR (CD_2Cl_2, 183 K): 9.27 (s, 1H, OH), 7.70−7.02 (m, 10H, C_6H_5), 4.05 (br s, 1H, C^5H), 3.85 (s, 5H, Cp),

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3.72 (br s, 1H, C^3H), 2.51 (s, 3H, NMe), 1.59 (s, 3H, NMe), 0.13 (s, 9H, $SiMe_3$). Crystals of **4**, suitable for X-ray analysis, were obtained by slow evaporation of a CH_2Cl_2 solution.

Complexes **6** and **7** were prepared following the same procedure described for **4** and **5**, by reacting **1a** with HC≡CCO_2Me.

[1-NMe$_2$-2-CO$_2$Me-4-SiMe$_3$-Fc] (6). Yield: 31%. Anal. Calcd for $C_{17}H_{25}FeNO_2Si$: C, 56.81; H, 7.02; N, 3.90. Found: C, 56.87; H, 6.99; N, 3.90. ^{1}H NMR ($CDCl_3$): 4.48 (d, 1H, $^4J_{HH}$ = 1.64 Hz, C^3H), 4.10 (s, 5H, Cp), 4.02 (d, 1H, $^4J_{HH}$ = 1.64 Hz, C^5H), 3.72 (s, 3H, CO_2Me), 2.62 (s, 6H, NMe_2), 0.13 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$): 171.7 (*C*O_2Me), 117.9 (C^1), 74.0 (C^3), 73.3 (C^2), 69.6 (Cp), 69.0 (C^4), 64.4 (C^5), 51.6 (CO_2*Me*), 45.1 (NMe_2), −1.01 ($SiMe_3$).

[1-SiMe$_3$-3-CO$_2$Me-Fc] (7). Yield: 47%. Anal. Calcd for $C_{15}H_{20}FeO_2Si$: C, 56.95; H, 6.38. Found: C, 56.89; H, 6.41. ^{1}H NMR ($CDCl_3$): 4.93 (dd, 1H, $^3J_{HH}$ = 2.40 Hz, $^4J_{HH}$ = 1.24 Hz, C^4H), 4.74 (t, 1H, $^4J_{HH}$ = 1.24 Hz, C^2H), 4.31 (dd, 1H, $^3J_{HH}$ = 2.40 Hz, $^4J_{HH}$ = 1.24 Hz, C^5H), 4.16 (s, 5H, Cp), 3.81 (s, 3H, CO_2Me), 0.24 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$): 172.2 (*C*O_2Me), 76.1 (C^5), 75.3 (C^2), 73.9 (C^3), 72.8 (C^4), 70.1 (Cp), 68.9 (C^1), 51.8 (CO_2*Me*), 0.23 ($SiMe_3$).

Complexes **8** and **9** were prepared following the same procedure described for **4**−**5**, by reacting **1a** with HC≡CPh.

[1-NMe$_2$-2-Ph-4-SiMe$_3$-Fc] (8). Yield: 28%. Anal. Calcd for $C_{21}H_{27}FeNSi$: C, 66.82; H, 7.22; N, 3.71. Found: C, 66.77; H, 7.25; N, 3.68. ^{1}H NMR ($CDCl_3$): 7.73−7.18 (m, 5H, C_6H_5), 4.20 (d, 1H, $^4J_{HH}$ = 1.28 Hz, C^3H), 4.16 (s, 5H, Cp), 4.05 (d, 1H, $^4J_{HH}$ = 1.28 Hz, C^5H), 2.58 (s, 6H, NMe_2), 0.28 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$): 139.4 ($C_{ipso\ Ph}$), 128.7, 127.1, 125.1 (Ph), 115.0 (C^1), 87.3 (C^2), 72.4 (C^3), 69.6 (Cp), 65.2 (C^4), 62.8 (C^5), 44.8 (NMe_2), 1.02 ($SiMe_3$).

[1-SiMe$_3$-3-Ph-Fc] (9). Yield: 59%. Anal. Calcd for $C_{19}H_{22}FeSi$: C, 68.25; H, 6.64. Found: C, 68.19; H, 6.66. ^{1}H NMR ($CDCl_3$): 7.57−7.20 (m, 5H, C_6H_5), 4.84 (dd, 1H, $^3J_{HH}$ = 2.36 Hz, $^4J_{HH}$ = 1.24 Hz, C^4H), 4.61 (t, 1H, $^4J_{HH}$ = 1.28 Hz, C^2H), 4.28 (dd, 1H, $^3J_{HH}$ = 2.36 Hz, $^4J_{HH}$ = 1.26 Hz, C^5H), 4.04 (s, 5H, Cp), 0.32 (s, 9H, $SiMe_3$). ^{13}CNMR ($CDCl_3$): 139.3 ($C_{ipso\ Ph}$), 128.6, 126.4, 126.2 (Ph), 88.5 (C^3), 74.0 (C^5), 73.6 (C^1), 71.5 (C^2), 70.1 (Cp), 69.5 (C^4), 0.05 ($SiMe_3$).

Complexes **10** and **11** were prepared following the same procedure described for **4** and **5**, by reacting **1b** with HC≡$CCPh_2OH$.

[1-NMe$_2$-2-CO$_2$Me-4-Tol-Fc] (10). Yield: 37%. Anal. Calcd for $C_{32}H_{31}FeNO$: C, 76.65; H, 6.23; N, 2.79. Found: C, 75.58; H, 6.30; N, 2.82. ^{1}H NMR ($CDCl_3$): 8.06 (s, 1H, OH), 7.64−7.24 (m, 14H, C_6H_5 and C_6H_4Me), 4.68 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^5H), 4.38 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^3H), 3.89 (s, 5H, Cp), 2.41 (s, 6H, NMe_2); 2.32 (s, 3H, C_6H_4*Me*). ^{13}CNMR ($CDCl_3$): 146.3 ($C_{ipso\ Ph}$), 137.8−125.9 (Ph), 110.2 (C^1), 93.0 (C^2), 81.0 (C^4), 78.4 (*C*Ph_2OH), 71.9 (Cp), 63.7 (C^3), 56.0 (C^5), 47.0 (NMe_2), 21.4 (C_6H_4*Me*). ESI-MS (ES^+): 502 *m*/*z* [M^+].

[1-SiMe$_3$-3-CO$_2$Me-Fc] (11). Yield: 48%. Anal. Calcd for $C_{30}H_{26}FeO$: C, 78.61; H, 5.72. Found: C, 78.55; H, 5.70. ^{1}H NMR ($CDCl_3$): 7.37−7.07 (m, 14H, C_6H_5 and C_6H_4Me), 4.74 (dd, 1H, $^3J_{HH}$ = 2.56 Hz, $^4J_{HH}$ = 1.60 Hz, C^5H), 4.53 (t, 1H, $^4J_{HH}$ = 1.60 Hz, C^2H), 4.16 (dd, 1H, $^3J_{HH}$ = 2.56 Hz, $^4J_{HH}$ = 1.60 Hz, C^4H), 4.01 (s, 5H, Cp), 3.43 (s, 1H, OH), 2.32 (s, 3H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$): 146.9, 146.8 ($C_{ipso\ Ph}$), 134.9−125.9 (Ph), 100.0 (C^3), 85.8 (C^1), 77.5 (*C*Ph_2OH), 70.3 (Cp), 69.2 (C^4), 66.8 (C^2), 66.0 (C^5), 21.1 (C_6H_4*Me*). ESI-MS (ES^+): 459 *m*/*z* [M^+].

Complexes **12**−**15** were prepared following the same procedure described for **4** and **5**, by reacting **1b** with HC≡CPh.

[1-NMe$_2$-2-Ph-4-Tol-Fc] (12). Yield: 28%. Anal. (sample containing a mixture of the isomers **12** and **14**) Calcd for $C_{25}H_{25}FeN$: C, 75.92; H, 6.38; N, 3.54. Found: C, 75.85; H, 6.43; N, 3.60. ^{1}H NMR ($CDCl_3$): 7.88−7.08 (m, 9H, Ph and C_6H_4Me), 5.19 (d, 1H, $^4J_{HH}$ = 1.24 Hz, C^3H), 4.23 (s, 5H, Cp); 4.10 (d, 1H, $^4J_{HH}$ = 1.24 Hz, C^5H), 2.64 (s, 6H, NMe_2), 2.39 (s, 3H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$) 139.1 ($C_{ipso\ Ph}$), 135.9 ($C_{ipso\ Tol}$), 130.4−126.5 (C_{arom}), 111.2 (C^1), 86.4 (C^2), 81.8 (C^4), 71.6 (C^5), 70.4 (Cp), 65.2 (C^3), 45.1 (NMe_2), 21.5 (C_6H_4*Me*).

[1-Tol-3-Ph-Fc] (13). Yield: 32%. Anal. (sample containing a mixture of the isomers **13** and **15**) Calcd for $C_{23}H_{20}Fe$: C, 78.39; H, 5.72. Found: C, 78.33; H, 5.70. ^{1}H NMR ($CDCl_3$): 7.61−7.14 (m, 9H, Ph and C_6H_4Me), 5.16 (t, 1H, $^4J_{HH}$ = 1.48 Hz, C^2H), 4.81 (t, 2H, $^4J_{HH}$ = 1.48 Hz, C^4H and C^5H), 3.96 (s, 5H, Cp), 2.39 (s, 3H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$): 139.0 ($C_{ipso\ Ph}$), 135.7 ($C_{ipso\ Tol}$), 129.1−126.0 (C_{arom}), 86.9 (C^3), 86.3 (C^1), 71.4 (Cp), 67.3, 67.2 (C^4 and C^5), 65.2 (C^2), 21.4 (C_6H_4*Me*).

[1-NMe$_2$-3-Ph-4-Tol-Fc] (14). Yield: 9%. ^{1}H NMR ($CDCl_3$): 7.88−7.08 (m, 9H, Ph and C_6H_4Me), 4.84 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^2H); 4.28 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^5H), 3.99 (s, 5H, Cp), 2.72 (s, 6H, NMe_2), 2.41 (s, 3H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$): 139.4 ($C_{ipso\ Ph}$), 136.0 ($C_{ipso\ Tol}$), 131.4−126.1 (C_{arom}), 113.3 (C^1), 86.9 (C^3), 81.4 (C^4), 71.5 (Cp), 67.4 (C^2), 57.4 (C^5), 41.9 (NMe_2), 21.4 (C_6H_4*Me*).

[1-Tol-2-Ph-Fc] (15). Yield: 8%. ^{1}H NMR ($CDCl_3$): 7.61−7.14 (m, 9H, Ph and C_6H_4Me), 4.57 (t, 2H, $^3J_{HH}$ = 2.36 Hz, C^3H and C^5H), 4.39 (t, 1H, $^3J_{HH}$ = 2.36 Hz, C^4H),4.13 (s, 5H, Cp), 2.37 (s, 3H, C_6H_4*Me*). ^{13}C NMR ($CDCl_3$) 139.5 ($C_{ipso\ Ph}$), 135.8 ($C_{ipso\ Tol}$), 129.8−125.9 (C_{arom}), 88.7 (C^2), 86.3 (C^1); 71.2 (Cp); 70.4 (C^3 and C^5), 67.6 (C^4), 21.1 (C_6H_4*Me*).

Complexes **16** and **17** were prepared following the same procedure described for **4** and **5**, by reacting **1a** with EtC≡CEt.

[1-NMe$_2$-2-Et-3-Et-4-SiMe$_3$-Fc] (16). Yield: 21%. Anal. Calcd for $C_{19}H_{31}FeNSi$: C, 63.84; H, 8.75; N, 3.92. Found: C, 63.91; H, 8.69; N, 3.96. ^{1}H NMR ($CDCl_3$): 3.99 (s, 5H, Cp), 3.68 (s, 1H, C^5H), 2.63 (s, 6H, NMe_2), 2.86−1.95 (m, 4H, CH_2CH$_3$), 1.26−0.86 (m, 6H, CH$_2$CH_3), 0.27 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): 112.9 (C^1), 84.9, 84.0 (C^2 and C^3), 69.8 (Cp), 63.5 (C^4), 61.1 (C^5), 45.8 (NMe_2), 22.3 (*C*H_2CH$_3$), 20.4 (*C*H_2CH$_3$), 17.9 (CH$_2$*C*H_3), 15.9 (CH$_2$*C*H_3), 1.5 ($SiMe_3$).

[1-SiMe$_3$-2-Et-3-Et-Fc] (17). Yield: 30%. Anal. Calcd for $C_{17}H_{26}FeSi$: C, 64.94; H, 8.34. Found: C, 64.87; H, 8.41. ^{1}H NMR ($CDCl_3$): 4.22 (d, 1H, $^3J_{HH}$ = 2.48 Hz, C^4H), 4.01 (s, 5H, Cp), 3.90 (d, 1H, $^3J_{HH}$ = 2.48 Hz, C^5H), 2.81−1.99 (m, 4H, CH_2CH$_3$), 1.25−0.92 (m, 6H, CH$_2$CH_3), 0.30 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): 94.1, 92.9 (C^2 and C^3), 71.6 (C^4), 69.9 (C^5), 69.6 (Cp), 67.8 (C^1), 22.7 (*C*H_2CH$_3$), 21.3 (*C*H_2CH$_3$), 17.4 (CH$_2$*C*H_3), 15.4 (CH$_2$*C*H_3), 1.3 ($SiMe_3$).

Complexes **18** and **19** were prepared following the same procedure described for **4** and **5**, by reacting **1b** with EtC≡CEt.

[1-NMe$_2$-2-Et-3-Et-4-Tol-Fc] (18). Yield: 35%. Anal. Calcd for $C_{23}H_{29}FeN$: C, 73.57; H, 7.79; N, 3.73. Found: C, 73.49; H, 7.85; N, 3.68. ^{1}H NMR ($CDCl_3$): 7.46−7.08 (m, 4H, C_6H_4Me), 4.14 (s, 1H, C^5H), 3.98 (s, 5H, Cp), 2.67 (s, 6H, NMe_2), 2.34 (s, 3H, C_6H_4*Me*), 2.78−2.22 (m, 4H, CH_2CH$_3$), 1.19 (t, 3H, $^3J_{HH}$ = 7.60 Hz, CH$_2$CH_3), 1.01 (t, 3H, $^3J_{HH}$ = 7.60 Hz, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): 136.7−128.8 (C_{arom}), 111.5 (C^1), 84.5, 81.5 (C^2 and C^3), 81.0 (C^4), 71.0 (Cp), 57.4 (C^5), 45.7 (NMe_2), 21.4 (C_6H_4*Me*), 20.3 (*C*H_2CH$_3$), 20.1 (*C*H_2CH$_3$), 16.4 (CH$_2$*C*H_3), 15.6 (CH$_2$*C*H_3).

[1-Tol-2-Et-3-Et-Fc] (19). Yield: 37%. Anal. Calcd for $C_{21}H_{24}Fe$: C, 75.88; H, 7.28. Found: C, 75.79; H, 7.30. ^{1}H NMR ($CDCl_3$): 7.50−7.12 (m, 4H, C_6H_4Me), 4.27 (d, 1H, $^3J_{HH}$ = 2.50 Hz, C^4H), 4.00 (s, 5H, Cp), 3.90 (d, 1H, $^3J_{HH}$ = 2.50 Hz, C^5H), 2.39 (s, 3H, C_6H_4*Me*), 2.80−2.24 (m, 4H, CH_2CH$_3$), 1.31−1.00 (m, 6H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): 136.5−129.0 (C_{arom}), 91.6, 90.4 (C^2 and C^3), 84.2 (C^1), 70.9 (Cp), 70.5 (C^4), 66.4 (C^5), 21.7 (C_6H_4*Me*), 21.4 (*C*H_2CH$_3$), 20.4 (*C*H_2CH$_3$), 16.4 (CH$_2$*C*H_3), 15.3 (CH$_2$*C*H_3).

Complexes **20** and **21** were prepared following the same procedure described for **4** and **5**, by reacting **1b** with PhC≡CPh.

[1-NMe$_2$-2-Ph-3-Ph-4-Tol-Fc] (20). Yield: 29%. Anal. Calcd for $C_{31}H_{29}FeN$: C, 78.95; H, 6.20; N, 2.97. Found: C, 79.02; H, 6.13;

N, 2.94. ^{1}H NMR ($CDCl_3$): 7.80−7.09 (m, 14H, Ph and C_6H_4Me), 4.16 (s, 1H, C^5H), 4.01 (s, 5H, Cp), 2.66 (s, 6H, NMe_2), 2.34 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): 139.1−126.0 (C_{arom}), 112.5 (C^1), 87.0, 86.4 (C^2 and C^3), 80.9 (C^4), 70.6 (Cp), 58.0 (C^5), 44.9 (NMe_2), 21.7 (C_6H_4Me).

[1-Tol-2-Ph-3-Ph-Fc] (21). Yield: 36%. Anal. Calcd for $C_{29}H_{24}Fe$: C, 81.29; H, 5.65. Found: C, 81.40; H, 5.61. ^{1}H NMR ($CDCl_3$): 7.66−7.10 (m, 14H, Ph and C_6H_4Me), 4.40 (d, 1H, $^3J_{HH}$ = 2.36 Hz, C^4H), 4.15 (d, 1H, $^3J_{HH}$ = 2.36 Hz, C^5H), 3.99 (s, 5H, Cp), 2.36 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): 138.9−125.7 (C_{arom}), 89.8, 89.5 (C^2 and C^3), 84.5 (C^1), 71.3 (Cp), 69.9 (C^4), 66.8 (C^5), 21.0 (C_6H_4Me).

Complexes **22** and **23** were prepared following the same procedure described for **4** and **5**, by reacting **1c** with PhC≡CPh.

[1-NMe$_2$-2-Ph-3-Ph-4-CO$_2$Me-Fc] (22). Yield: 30%. Anal. Calcd for $C_{26}H_{25}FeNO_2$: C, 71.05; H, 5.74; N, 3.19. Found: C, 71.12; H, 5.68; N, 3.26. ^{1}H NMR ($CDCl_3$): 7.70−7.02 (m, 10H, Ph), 4.84 (s, 1H, C^5H), 4.39 (s, 5H, Cp), 3.69 (s, 3H, CO_2Me), 2.47 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): 172.8 (CO_2Me), 133.5−126.4 (C_{arom}), 113.8 (C^1), 91.9, 90.4 (C^2 and C^3), 71.6 (Cp), 62.4 (C^4), 59.6 (C^5), 51.2 (CO_2Me), 44.1 (NMe_2).

[1-CO$_2$Me-2-Ph-3-Ph-Fc] (23). Yield: 32%. Anal. Calcd for $C_{24}H_{20}FeO_2$: C, 72.71; H, 5.09. Found: C, 72.63; H, 5.15. ^{1}H NMR ($CDCl_3$): 7.56−7.20 (m, 10H, Ph), 4.89 (d, 1H, $^3J_{HH}$ = 2.64 Hz, C^4H), 4.77 (d, 1H, $^3J_{HH}$ = 2.64 Hz, C^5H), 4.31 (s, 5H, Cp), 3.60 (s, 3H, CO_2Me). ^{13}C NMR ($CDCl_3$): 174.3 (CO_2Me), 133.6−126.2 (C_{arom}), 90.5, 89.9 (C^2 and C^3), 73.6 (Cp), 71.8, 71.4 (C^4 and C^5), 63.0 (C^1), 51.0 (CO_2Me).

Complexes **24** and **25** were prepared following the same procedure described for **4** and **5**, by reacting **2a** with HC≡CTol.

[1-NMe$_2$-2-Tol-4-CO$_2$Me-Fc] (24). Yield: 30%. Anal. (sample containing a mixture of the isomers **24** and **25**) Calcd for $C_{21}H_{23}FeNO_2$: C, 66.82; H, 6.15; N, 3.71. Found: C, 66.91; H, 6.24; N, 3.74. ^{1}H NMR ($CDCl_3$): 7.81−7.10 (m, 4H, C_6H_4Me), 5.03 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.83 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^3H), 4.32 (s, 5H, Cp), 3.86 (s, 3H, CO_2Me), 2.65 (s, 6H, NMe_2), 2.48 (br s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): 170.3 (CO_2Me), 136.2−126.8 (C_{arom}), 114.6 (C^1), 76.4 (C^2), 70.7 (Cp), 68.9 (C^3), 62.8 (C^4), 61.3 (C^5), 51.5 (CO_2Me), 44.3 (NMe_2), 21.3 (C_6H_4Me).

[1-NMe$_2$-3-Tol-4-CO$_2$Me-Fc] (25). Yield: 37%. ^{1}H NMR ($CDCl_3$): 7.81−7.10 (m, 4H, C_6H_4Me), 4.61 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.37 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^2H), 4.38 (s, 5H, Cp), 3.93 (s, 3H, CO_2Me), 2.76 (s, 6H, NMe_2), 2.48 (br s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): 173.1 (CO_2Me), 136.2−126.8 (C_{arom}), 116.1 (C^1), 85.2 (C^3), 70.2 (Cp), 64.1 (C^2), 59.4 (C^4), 56.4 (C^5), 51.2 (CO_2Me), 41.8 (NMe_2), 21.1 (C_6H_4Me).

Complexes **26** and **27** were prepared following the same procedure described for **4** and **5**, by reacting **2b** with HC≡CTol.

[1-NMe$_2$-2-Tol-4-CN-Fc] (26). Yield: 31%. Anal. (sample containing a mixture of the isomers **26** and **27**) Calcd for $C_{20}H_{20}FeN_2$: C, 69.75; H, 5.86; N, 8.14. Found: C, 69.80; H, 5.97; N, 8.14. ^{1}H NMR ($CDCl_3$): 7.62−6.99 (m, 4H, C_6H_4Me), 4.40 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.31 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^3H), 4.30 (s, 5H, Cp), 2.51 (s, 6H, NMe_2), 2.37 (br s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): 136.9−126.9 (C_{arom}), 120.7 (CN), 116.5 (C^1), 85.2 (C^2), 71.1 (Cp), 57.3 (C^3), 56.6 (C^5), 45.3 (C^4), 41.7 (NMe_2), 21.1 (C_6H_4Me).

[1-NMe$_2$-3-Tol-4-CN-Fc] (27). Yield: 40%. ^{1}H NMR ($CDCl_3$): 7.62−6.99 (m, 4H, C_6H_4Me), 4.71 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^5H), 4.53 (d, 1H, $^4J_{HH}$ = 1.40 Hz, C^2H), 4.36 (s, 5H, Cp), 2.63 (s, 6H, NMe_2), 2.37 (br s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): 136.9−126.9 (C_{arom}); 121.4 (CN), 113.8 (C^1), 80.0 (C^3), 71.5 (Cp), 70.3 (C^2), 61.0 (C^5), 45.5 (C^4), 44.0 (NMe_2), 21.2 (C_6H_4Me).

Complexes **28** and **29** were prepared following the same procedure described for **4** and **5**, by reacting **3a** with HC≡CPh.

[1-SMe-2-Ph-4-CO$_2$Me-Fc] (28). Yield: 33%. Anal. (sample containing a mixture of the isomers **28** and **29**) Calcd for $C_{19}H_{18}FeO_2S$: C, 62.31; H, 4.95. Found: C, 62.15; H, 4.88. ^{1}H NMR ($CDCl_3$): 7.78−7.11 (m, 5H, Ph), 5.05 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^3H), 4.74 (d, 1H, $^4J_{HH}$ = 1.60 Hz, C^5H), 4.23 (s, 5H, Cp), 3.76 (s, 3H, CO_2Me), 2.38 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$): 170.8 (CO_2Me), 136.1−125.9 (C_{arom}), 90.7 (C^4), 85.7 (C^1), 85.6 (C^2), 76.8 (C^5), 73.2 (C^3), 73.1 (Cp), 51.5 (CO_2Me), 19.5 (SMe).

[1-SMe-3-Ph-4-CO$_2$Me-Fc] (29). Yield: 36%. ^{1}H NMR ($CDCl_3$): 7.78−7.11 (m, 5H, Ph), 5.18 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^2H), 5.07 (d, 1H, $^4J_{HH}$ = 1.30 Hz, C^5H), 4.17 (s, 5H, Cp), 3.83 (s, 3H, CO_2Me), 2.28 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$): 171.4 (CO_2Me), 136.1−125.9 (C_{arom}), 90.6 (C^4), 86.0 (C^1), 85.6 (C^3), 73.0 (Cp), 70.8 (C^2), 70.1 (C^5), 51.7 (CO_2Me), 19.1 (SMe).

Complex **30** was prepared following the same procedure described for **4** and **5**, by reacting **3b** with PhC≡CPh.

[1-SMe-2-Ph-3-Ph-4-CN-Fc] (30). Yield: 48%. Anal. Calcd for $C_{24}H_{19}FeO$: C, 78.61; H, 5.72. Found: C, 78.55; H, 5.89. ^{1}H NMR ($CDCl_3$): 7.56−7.19 (m, 10H, Ph), 5.05 (s, 1H, C^5H), 4.31 (s, 5H, Cp), 2.16 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$): 135.1−126.5 (C_{arom} and CN); 91.1, 89.9 (C^2 and C^3), 86.9 (C^1), 73.6 (Cp), 73.2 (C^5), 51.1 (C^4), 19.1 (SMe).

Electrochemical Measurements. Electrochemical data for **4**−**11** were obtained form 10^{-3} M solutions in CH_3CN with 0.1 M $[Bu_4N][PF_6]$ ($E_{1/2}$ in mV, referenced to the SCE, at a scan speed v = 100 mV s^{-1}): **4**, 241; **5**, 400; **6**, 292; **7**, 442, **8**, 104; **9**, 417; **10**, 274; **11**, 422 mV.

X-ray Crystallography. Crystal data and collection details for **4** and **11** are reported in Table 3. 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(50) in **4**, which was located in the

Table 3. Crystal Data and Experimental Details for 4 and 11

	4	**11**
formula	$C_{28}H_{33}FeNOSi$	$C_{30}H_{26}FeO$
fw	483.49	458.36
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	12.1178(7)	10.3008(9)
b, Å	10.9715(7)	10.6616(9)
c, Å	19.5293(12)	11.2231(10)
α, deg	90	89.3930(10)
β, deg	103.5860(10)	73.7160(10)
γ, deg	90	73.6680(10)
cell volume, Å^3	2523.8(3)	1132.25(17)
Z	4	2
D_c, g cm^{-3}	1.272	1.344
μ, mm^{-1}	0.665	0.686
F(000)	1024	480
cryst size, mm	0.22 × 0.15 × 0.12	0.22 × 0.16 × 0.14
θ limits, deg	1.73−28.00	1.90−27.00
reflns collected	28 477	12 690
indep reflns	6007 [R_{int} = 0.0367]	4902 [R_{int} = 0.0266]
data/restraints /params	6007/1/297	4902/198/291
goodness on fit on F^2	1.023	1.034
R_1 ($I > 2\sigma(I)$)	0.0368	0.0386
wR_2 (all data)	0.0996	0.0977
largest diff peak and hole, e Å^{-3}	0.302/−0.179	0.256/−0.208

(21) Sheldrick, G. M. *SADABS, Program for empirical absorption correction*; University of Göttingen: Germany, 1996.

(22) Sheldrick, G. M. *SHELX97, Program for crystal structure determination*; University of Göttingen: Germany, 1997.

Fourier map and refined isotropically using the 1.5-fold U_{iso} value of the parent O(1) atom; the O(1)−H(50) distance was restrained to 0.83 Å [s.u. 0.01]. Similar *U* restraints [s.u. 0.01] were applied to all C atoms in **11**.

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Supporting Information Available: Crystallographic data for compounds of **4** and **11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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