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New and Selective Routes to Functionalized Biferrocenes and Terferrocenes by [3 + 2] Cycloadditions of Alkynes with Bridging C_3 Ligands in Diiron Complexes

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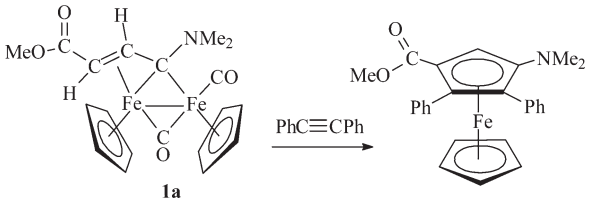
The diiron bridging enaminoalkylidene complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Fc)CHCH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2**), containing a ferrocenyl group on the bridging ligand, reacts with HC≡CR, affording the corresponding 3-R-substituted 1,1′′-biferrocene (R = CPh_2OH, **4a**; R = Tol, **4b**; R = CO_2Me, **4c**; R = CH_2OH, **4d**). In a related reaction, the μ-vinylaminoalkylidene complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(NMe_2)CHCH(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**1a**), upon treatment with ethynylferrocene, leads to the formation of 2-NMe_2-4-CO_2Me-1,1′′-biferrocene (**4f**). Conversely, the μ-enaminoalkylidene complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Tol)CHCH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**1b**) reacts with ethynylferrocene, affording a mixture of monosubstituted biferrocene **4b** and disubstituted 2-NMe_2-4-Tol-1,1′′-biferrocene (**4e**), in comparable yields. Reaction of **2** with ethynylferrocene (HC≡CFc) leads to the formation of a mixture of 1,3-terferrocene (**5a**) and the 5-NMe_2-substituted 1,3-terferrocene (**5b**). Investigation of the reactivity of the vinyliminium complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Fc)CHCNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**3**) with HC≡CCPh_2OH is also reported: the reaction affords selectively the 3-NMe_2-4-R-disubstituted 1,1′′-biferrocene (**6**). The molecular structure of **5a** has been determined by X-ray diffraction studies.

Introduction

Ferrocenes are exceptionally valuable organometallic scaffolds for the construction of functional molecules with potential application in catalysis, materials science, and biomedicinal chemistry.[1] In order to connect different ferrocene units and/or to confer the desired properties, ferrocene cyclopentadienyl (Cp) rings must be provided with appropriate substituents and functionalities (polysubstituted ferrocenes). Functionalization of the Cp ring can be challenging from a synthetic point of view, particularly in the case of ferrocenes, in which only one Cp ring contains different substituents.[2] These difficulties might limit the design of molecular architectures based on ferrocenes.[3] A possible alternative approach consists in the assembling of cyclopentadienyls, by metal-mediated [3 + 2] cycloaddition of molecular fragments properly constructed in order to contain the desired substituents and functionalities.[4] We have recently shown that [3 + 2] cycloaddition involving bridging C_3 ligands in diiron complexes and alkynes (C_2) leads to the formation of polysubstituted Cp ligands, directly affording ferrocenes.[5] An example, shown in Scheme 1, illustrates the reaction of the bridging vinylaminoalkylidene complex **1a** with PhC≡CPh. All the functionalities present on the parent C_3 and C_2 fragments are maintained in the resulting functionalized Cp ring of the ferrocene product. Conversely, the dinuclear

Scheme 1



1a

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

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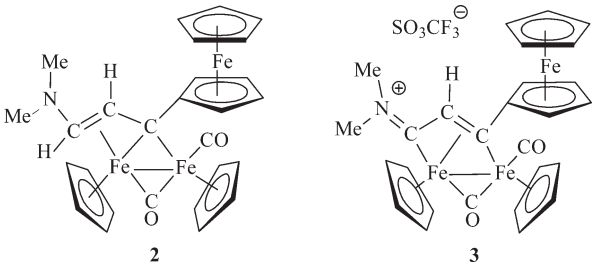
Scheme 2



2 **3**

parent compound undergoes fragmentation, with elimination of one Fe unit, formally corresponding to $[Fe(H)(CO)_2Cp]$.

The direct formation of polysubstituted ferrocenes, occurring in a "one pot reaction", compensates the synthetic effort for the construction of a bridging C_3 ligand containing the appropriate functionalities, as well as the loss of an Fe-containing fragment. Indeed, a variety of diiron complexes bearing different bridging C_3 ligands (such as vinylalkylidenes and vinyliminiums) are readily available by simple synthetic procedures, and C_3 substituents comprise a range of groups, including NMe_2, SMe, CO_2R, CN, and $SiMe_3$.[6] Also, ferrocenyls (Fc) are among the possible substituents, as shown in Scheme 2, since **2** and **3** display ferrocenyl−vinylalkylidene and ferrocenyl−vinyliminium ligands, respectively.[7]

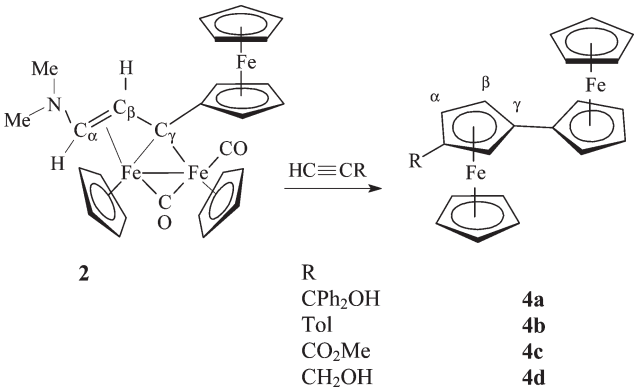
In light of these results, we became interested in extending studies on the [3 + 2] cyclization reactions to C_3 ligands containing ferrocenyl substituents (e.g., **2** and **3**). The aim was to exploit the one-pot synthesis of functionalized ferrocenes for obtaining biferrocenes (including polysubstituted biferrocenes). Indeed, biferrocenes are species of great interest, due to the nature of interactions between metal centers, and they have been extensively investigated; nevertheless, synthetic methods for obtaining these types of complexes are somewhat limited.[8] The present report concerns a possible alternative synthetic approach.

Results and Discussion

Reactions of the Enaminoalkylidene Complex 2 with Alkynes. The bridging enaminoalkylidene complex **2** reacts with HC≡CR (R = CPh_2OH, Tol, CO_2Me, CH_2OH; Tol = 4-C_6H_4Me), in refluxing toluene, affording the 3-R-substituted 1,1″-biferrocenes (R = CPh_2OH, **4a**; R = Tol, **4b**; R = CO_2Me, **4c**; R = CH_2OH, **4d**) in 40−60% yields (Scheme 3).

In Scheme 3, carbon atoms of the bridging chain of **2** have been labeled to better identify them as constituents of the cyclopentadienyl ring in the products **4a**−**d**. Compounds **4a**−**d** were purified by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. The prolonged heating required to perform the reaction produces a considerable amount of decomposition, resulting in modest yields; nevertheless, the reaction is selective, leading to the formation of a single product in a single isomeric form, as indicated by NMR spectra. In theory, several products might be produced, in that the formation of a Cp ring by [3 + 2] cycloaddition requires the loss of one of the two substituents (H or NMe_2) from the vinyl end of the bridging C_3 ligand. In similar reactions, previously reported,

Scheme 3



2

R	
CPh_2OH	**4a**
Tol	**4b**
CO_2Me	**4c**
CH_2OH	**4d**

both possibilities (C−H and C−N cleavage) take place, producing di- and trisubstituted ferrocenes.[5] Conversely, the reactions shown in Scheme 3 are chemoselective, but unfortunately the C−N bond is selectively cleaved, depriving the diferrocene products of a valuable NMe_2 substituent. Furthermore, the observed cycloaddition reactions are regiospecific, since the incorporation of primary alkynes occurs selectively in one of the two possible modes, affording a Cp ring where R and Fc substituents are in 1,3-positions. In other words, the reactions selectively yield 3-substituted 1,1″-diferrocenes. This point is evidenced in the NMR spectra by the absence of any significant NOE effect between the ferrocenyl substituent and the carbon atom bearing the R group. The regioselectivity is presumably originated by steric reasons, in that the formation of the observed isomer involves minor repulsion between the substituents.

The most relevant aspect of the reaction is that it provides a possible alternative approach to the synthesis of biferrocenes. Traditional methods are based on the Ullmann coupling of haloferrocenes by copper, discovered by Rausch.[9] Other similar methods, subsequently developed, require the coupling with lithioferrocene or ferrocenyl Grignards.[10] These strategies mainly produce 1′,1‴-disubstituted biferrocene compounds (Scheme 4, **B**), or similar centrosymmetric compounds which are, by far, the most investigated biferrocene compounds.[8,11] Conversely, **4a**−**d** are 3-substituted 1,1″-biferrocenes (Scheme 4 **A**). This is a rather uncommon substitution pattern, which is available selectively neither by coupling of ferrocenes nor by functionalization of diferrocenes.

Reaction of Enaminoalkylidene Complexes 1a,b with Ethynylferrocene. The aforementioned cycloaddition reactions result in the formation of biferrocenes for the reason that a ferrocenyl group (Fc) is a substituent on the C_3 fragment. Thus, when the [3 + 2] cycloaddition generates the substituted Cp ring of a ferrocene unit, a ferrocenyl results bound to it. In theory, the same result should be obtained by placing Fc as a substituent on the alkyne C_2 unit instead of the C_3 ligand. In order to verify this possibility, the bridging enaminoalkylidene complex **1b** has been treated with HC≡CFc in

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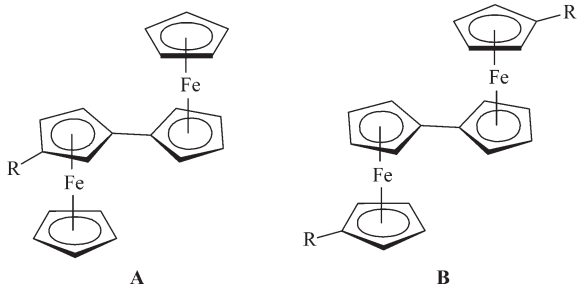
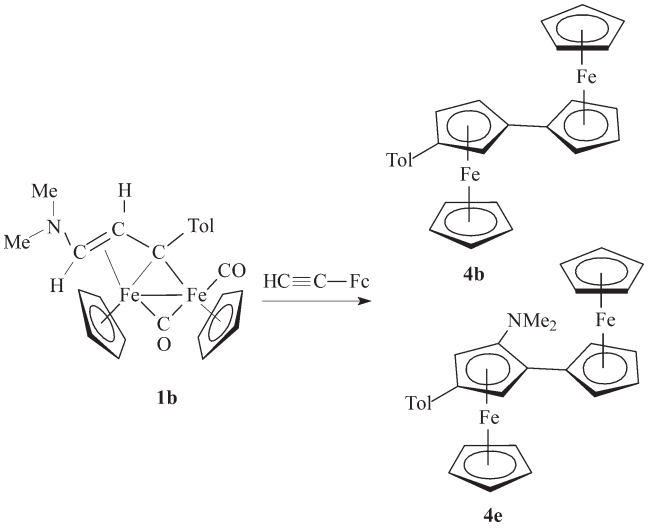
Scheme 4



Scheme 5

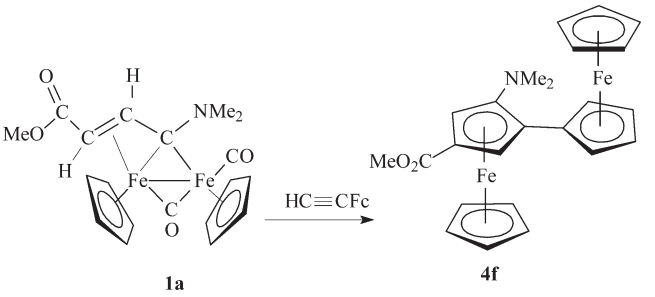


refluxing toluene (Scheme 5). The reaction can be compared to that of **2** with HC≡CTol shown in Scheme 3: the difference is that the Fc and Tol have been inverted as substituents at the C_2 and C_3 fragments, respectively. The reaction affords a mixture of the monosubstituted biferrocene **4b** and the 2,4-disubstituted-1,1′′-biferrocene **4e**, in comparable yields (ca. 30% for both **4b** and **4e**) (Scheme 5).

Thus, the reaction of **1b** with ethynylferrocene exhibits a very similar outcome compared to that of **2** with HC≡CTol, except for the lack of chemoselectivity. Both C−H and C−N bonds at the vinyl end of the bridging C_3 frame can undergo cleavage, leading to the expected formation of **4b**, and also of the disubstituted biferrocene **4e**, in comparable amounts. Compounds **4b**,**e** were separated by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. In particular, the NMR data for **4e** show a significant NOE effect between the methyls of the amino group and the ferrocenyl substituent, thus indicating the substitution pattern of **4e**, which corresponds to a 2,4-disubstituted biferrocene.

The presence of a NMe_2 substituent on a cyclopentadienyl ring should be advantageously used to further modify or to connect the biferrocene unit to other species. However, the lack of selectivity, resulting in the formation of a product mixture, is a limit for possible synthetic applications. We have previously found that more selective [3 + 2] cycloaddition reactions take place between alkynes and bridging vinylalkylidenes in which the NMe_2 group is connected to the alkylidene carbon, instead of the vinyl end.[5] This is the case shown in Scheme 1, in which all the functionalities

Scheme 6



present on the C_3 fragment, including the NMe_2 group, are transferred to the resulting Cp ring of the ferrocene product. Therefore, we also investigated the reaction of the vinylaminoalkylidene **1a**[12] with ethynylferrocene. As expected, the reaction leads to the formation of a single product: namely, the 2,4-disubstituted 1,1′′-biferrocene **4f** (Scheme 6).

In this case, the reaction is both chemo- and regioselective, since alkyne incorporation occurs selectively, with alkyne CH termination exclusively bound to the C−CO_2Me moiety of the μ-C_3 frame (Scheme 6).

Compound **4f** was purified by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. Also in this case, the geometry of the molecule and the substitution pattern at the cyclopentadienyl ring were determined by NMR and NOE investigations.

Reaction of Enaminoalkylidene Complex 2 with Ethynylferrocene. The synthetic approach described above can be further extended to the preparation of terferrocenes. Indeed, if both the C_3 bridging ligand and C_2 reagent (alkyne) contain a ferrocenyl substituent, their assembly, through a [3 + 2] cyclization, is expected to produce species with three connected ferrocene units. Indeed, we have found that the reaction of **2** with ethynylferrocene, in refluxing toluene, affords a mixture of the terferrocenes **5a**,**b**, in about 50% and 20% yields, respectively (Scheme 7).

Compounds **5a**,**b** were separated by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. Moreover, the molecular structure of **5a** has been determined by X-ray diffraction. The ORTEP diagram is shown in Figure 1, and the main bond lengths and angles are reported in Table 1. The molecular structure of **5a**, as determined by X-ray diffraction, is composed of a 1,-3-terferrocene molecule, where the central $FeCp_2$ unit is 1,-3-substituted at the same Cp ligand by two further ferrocene moieties. Bonding parameters within the six Cp ligands are as expected. The inter-Cp contact (C(10)−C(11) = 1.462(3) Å) is essentially a single bond.

It has to be noted that **5a**,**b** are 1,3-terferrocenes, which corresponds to one of the possible constitutionally isomeric forms of terferrocenes, that also include 1,2-terferrocenes and 1,1′-terferrocenes (Scheme 8). Isomeric mixtures of these compounds, together with polyferrocenyls and other products, are usually obtained by random combination of ferrocenyl radicals[13] or by using related synthetic methods.[14] More specific methods have been developed for the selective

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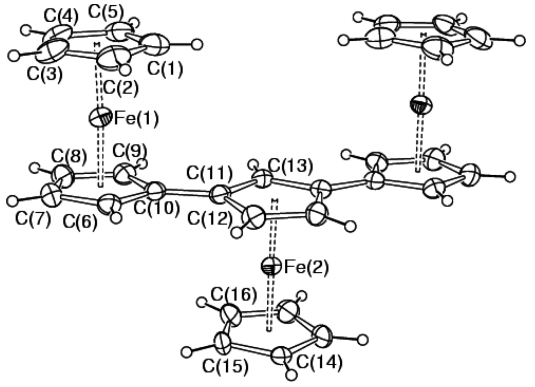
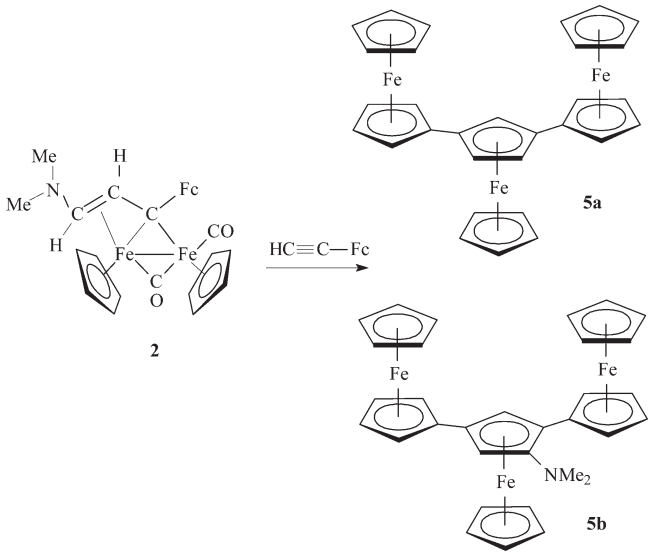


Figure 1. ORTEP drawing of **3a**. Only the main images of the Cp ligands bonded to Fe(1) and Fe(2) have been represented. Thermal ellipsoids are at the 30% probability level. Only independent atoms have been labeled.

Scheme 7



preparation of 1,1′-terferrocenes,[15] 1,2-terferrocenes,[16] and also 1,3-terferrocenes.[17] In particular, access to this latter isomer requires a laborious multistep procedure, which involves the formation of 1,4-diferrocenylcyclopentadiene as intermediate species.[17]

In other words, synthetic routes based on the assembly of ferrocenyl units are simple but unselective and are mostly directed to the formation of 1,1′-terferrocenes. This is also consistent with the fact that ferrocene oligomers and polymers usually assume fulvene-based architectures.[18] In the absence of convenient and selective access to 1,3-terferrocenes, our reaction might represent an interesting and valuable synthetic approach.

NMR data of **5a** are in agreement with the solid-state structure and with published data.[17] In particular, the ^{1}H NMR spectrum (in $CDCl_3$) confirms the symmetry of the molecule. Indeed, a single resonance is observed for the two nonsubstituted external Cp rings (at 4.09 ppm) and one resonance accounts for the central nonsubstituted Cp ring (at 3.88 ppm). Analogously, the ^{13}C NMR spectrum shows only one resonance for the two external Cp rings (at 69.5 ppm) and one resonance for the central Cp group (at 70.6 ppm).

In the case of **5b**, the presence of the amino group causes a loss of symmetry of the molecule and subsequently increases the complexity of the NMR spectra. In particular, the ^{1}H NMR spectrum shows resonances due to the Cp rings in the typical range 4−5 ppm and a single resonance due to the methyls of the amino group at 2.62 ppm.

Finally, the reaction is accompanied by the formation, as byproducts, of small amounts of $FeCp_2$ and $[Fe_2Cp_2(CO)_4]$.

Reaction of the Vinyliminium Complex 3 with Propargyl Alcohols. Cycloaddition reactions involving alkynes and bridging C_3 ligands in diiron complexes are not restricted to bridging vinylalkylidenes: it has been shown that also bridging vinyliminium ligands undergo [3 + 2] cycloaddition, affording polysubstituted ferrocenes, although the reaction is limited to propargyl alcohols.[19] Interestingly, these reactions also generate products derived from a [3 + 2 + 1] cycloaddition that involve CO and are reminiscent of the classical Dotz benzannulation. In consideration of these previous results, we investigated the reactivity of the vinyliminium complex **3** with $HC{\equiv}CCPh_2OH$. The reaction, performed in refluxing toluene, leads to the formation of [3-NMe_2-4-CPh_2OH-1,1″-biferrocene] (**6**) in about 40% yield (Scheme 9).

Compound **6** was purified by chromatography on alumina and characterized by NMR spectroscopy and elemental analysis. In particular, the NMR spectra (in $CDCl_3$) show a significant NOE effect between the *N*-methyls and the protons of the CPh_2OH, indicating that NMe_2 and CPh_2OH substituents are in adjacent positions. Moreover, the observed low-field resonance at 6.84 ppm, attributable to the hydroxy group, suggests that the −OH is involved in a hydrogen-bonding interaction with the nitrogen atom of the amino group.

In spite of the relatively low yield, the reaction is selective, in that it generates only **6** and not other isomeric forms. Noteworthy, compound **6** is a 3,4-disubstituted 1,1″-biferrocene, corresponding to a substitution pattern different from that observed in **4e**,**f**, which are 2,4-disubstituted 1,1″-biferrocenes. This is simply the consequence of a different distribution of the Fc, NMe_2, and R substituents (R = CPh_2OH, Tol, CO_2Me) on the C_2 (alkyne) and bridging C_3 fragments involved in the cycloaddition. This observation implies that substitution patterns of the biferrocene products can be predetermined, to a certain extent, by an appropriate choice of bridging functionalized ligands and alkyne reagents.

Electrochemical Investigation. Electrochemical data concerning our biferrocene and triferrocene complexes are of interest in that biferrocenes, or in general conjugated ferrocenyl units, can find application in many fields, thanks to their remarkable electrical, redox, and magnetic properties.[20] In general, complexes containing conjugated ferrocenyls exhibit some degree of electronic communication between the Fc units, which can be evaluated by cyclic

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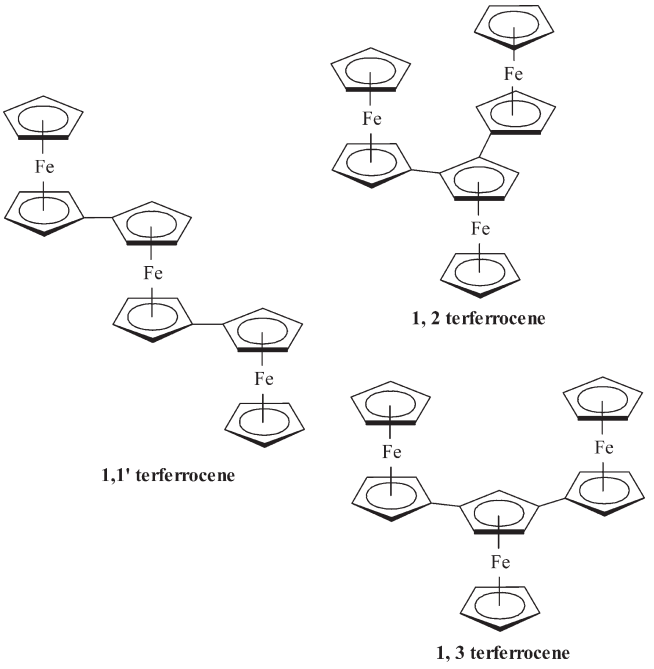
(20) See for example: (a) Nijhuis, C. A.; Dolatowska, K. A.; Ravoo, B. J.; Huskens, J.; Reinhoudt, D. N. *Chem. Eur. J.* **2007**, *13*, 69–80. (b) Diallo, A. K.; Menuel, S.; Monflier, E.; Ruiz, J.; Astruc, D. *Tetrahedron Lett.* **2010**, *51*, 4617–4619.

Table 1. Selected Bond Lengths (Å) for 5a

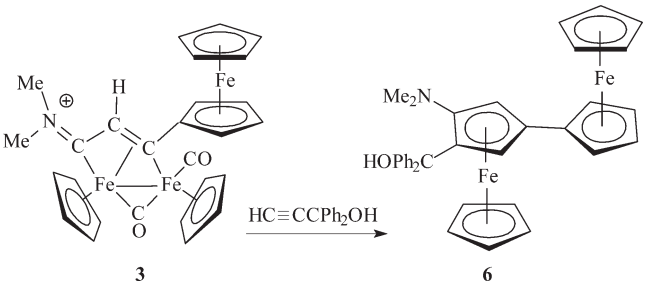
Fe(1)−Cp(1)[a]	2.024(5)−2.053(5), av 2.037(15)	C−C Cp(1)[a]	1.405(7)−1.416(8), av 1.409(16)
Fe(1)−Cp(2)[b]	2.029(2)−2.040(2), av 2.034(5)	C−C Cp(2)[b]	1.416(3)−1.427(3), av 1.421(7)
Fe(2)−Cp(3)[c]	2.033(3)−2.055(2), av 2.047(5)	C−C Cp(3)[c]	1.414(4)−1.427(3), av 1.424(7)
Fe(2)−Cp(4)[d]	1.971(7)−2.052(7), av 2.019(13)	C−C Cp(4)[d]	1.361(14)−1.413(12), av 1.40(2)
C(10)−C(11)	1.462(3)		

[a] Cp(1) is defined by atoms C(1), C(2), C(3), C(4), and C(5). [b] Cp(2) is defined by atoms C(6), C(7), C(8), C(9), and C(10). [c] Cp(3) is defined by atoms C(11), C(12), and C(13) and their symmetrical images. [d] Cp(4) is defined by atoms C(14), C(15), and C(16) and their symmetrical images.

Scheme 8



Scheme 9



voltammograms.[21] For example, biferrocene displays strongly interacting metal centers and correspondingly undergoes two reversible one-electron oxidations at separated potential values (at about +0.31 and +0.65 V, respectively).[22] On the other hand, complexes **4a**−**f** and **6** (see the Experimental Section) exhibit a rather broad variety of cyclic voltammetric responses, which virtually cover all classes (according to the so-called Robin−Day classification) used to evaluate the degree of electronic communication.[23] Complex **6** exhibits two apparently reversible oxidations with a difference in redox potential of about 240 mV. Likewise, compounds **4e**,**f** give rise to separate oxidations (ΔE_p of about 290 mV), but these do not seem reversible. The separation of the two redox processes is much smaller in **4a**, whereas the voltammograms of **4b**,**c**,**d** exhibit a single oxidation potential (typical for class I). These results reflect the presence of several different factors influencing the redox processes: (i) the two ferrocenyl units are nonequivalent for the presence of one or two substituents in only one Fc unit; (ii) the substituents display markedly different inductive effects (there are both electron-donating and electron-withdrawing substituents, in different combinations) with consequent effects on the oxidation potential (i.e., electron-donating substituents render the oxidation easier); (iii) the substitution patterns include a number of different situations (i.e., 2,4-disubstituted 1,1′′-biferrocene etc.) with possible consequences on the steric hindrance and, therefore, on the coplanarity of the fulvene system. This, in turn, can influence the electronic communication between the ferrocenyl units.

Concerning the terferrocene complexes, three distinct redox processes are observed for **5a**, which are consistent with the data reported in the literature for the 1,1′-terferrocene,[22] whereas only two are found in the case of **5b**.

A better understanding of the redox processes taking place in our complexes certainly requires more extended and accurate electrochemical as well as structural investigations, but this goes well beyond the scope of this work, dealing with synthetic aspects, and will be the focus of upcoming studies.

Conclusions

[3 + 2] cycloaddition of alkynes with bridging C_3 ligands in diiron complexes can be exploited to form functionalized biferrocenes, provided that the C_3 or the C_2 fragments contain a ferrocenyl substituent, as well as other functional groups. Bridging C_3 ligands include vinylalkylidenes and vinyliminium, which can be easily constructed so that they contain the most appropriate substituents. As a consequence of the cyclization and subsequent rearrangement, these functions are transferred to one of the fulvene rings of the biferrocene products. Thus, the reaction provides access to biferrocenes with unusual substitution patterns: 3-substituted, 2,4-disubstituted, and 3,4-disubstituted 1,1′′-biferrocenes, which can be hardly obtained otherwise. It should be remarked that these reactions are selective and that through the appropriate design of the bridging C_3 frame, and the choice of most suitable alkyne reagents, it is possible to control the type of functional groups and substitution pattern of the biferrocene products. The same strategy can be applied to the synthesis of terferrocenes, provided that both C_3 and C_2 fragments contain a ferrocenyl substituent. Their assembly occurs selectively, affording 1,3-terferrocenes, which are less common among the possible terferrocene isomeric forms.

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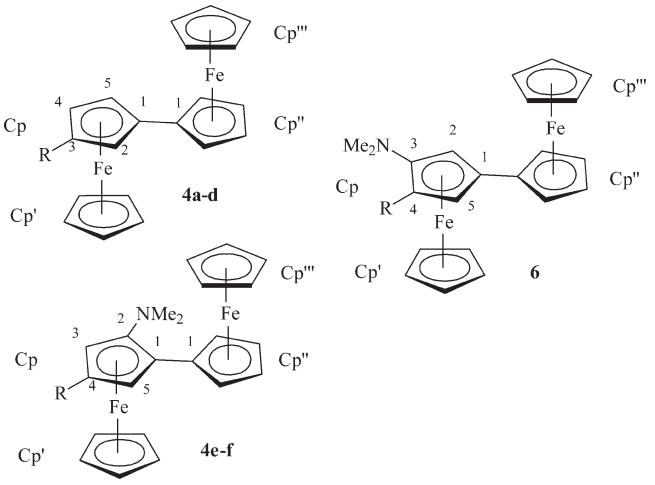
Scheme 10



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. Chromatographic separations were carried out on columns of alumina. 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. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and ^{1}H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments.[24] All NMR spectra were recorded at 298 K. NOE measurements were recorded using the DPFGSE-NOE sequence.[25] NMR resonances are indicated according to the numbering scheme shown above in Scheme 10. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Compounds **1a**,[12] **1b**,[26] and **2** and **3**[7] were prepared by published methods.

Synthesis of 3-CPh$_2$OH-1,1′′-biferrocene (4a). To a solution of **2** (300 mg, 0.531 mmol) in toluene (25 mL) was added HC≡CCPh$_2$OH (230 mg, 1.10 mmol). The resulting solution was stirred at reflux overnight and then was cooled to room temperature and filtered on a Celite pad. Solvent removal and chromatography of the residue on an alumina column with petroleum ether (bp 40−60 °C) as eluent gave a first yellow fraction, corresponding to nonsubstituted ferrocene (FeCp$_2$). A second orange fraction, corresponding to **4a**, was collected by using diethyl ether as eluent. Yield: 123 mg, 42%. Anal. Calcd for $C_{33}H_{28}Fe_2O$: C, 71.77; H, 5.11. Found: C, 71.79; H, 5.23. ^{1}H NMR ($CDCl_3$): δ 7.62−7.12 (m, 10H, C_6H_5), 4.46 (dd, 1H, $^3J_{HH}$ = 2.48 Hz, $^4J_{HH}$ = 1.44 Hz, H^5, Cp), 4.42 (m, 1H, Cp′′), 4.33 (t, 1H, $^4J_{HH}$ = 1.44 Hz, H^2, Cp), 4.31 (m, 1H, Cp′′), 4.21 (m, 2H, Cp′′), 4.03, 4.00 (s, 11H, Cp′, Cp′′′ and H^4, Cp), 3.48 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$): δ 147.5, 147.0 (C_{ipso} Ph), 129.8−127.0 (C_{arom}), 99.5 (C^3, Cp), 85.3 (C^1, Cp), 82.6 (C^1, Cp′′), 77.7 (*C*−OH), 70.2, 69.6 (Cp′ and Cp′′′), 69.7 (C^4, Cp), 68.5, 68.3, 66.6, 66.5 (Cp′′), 66.5 (C^2, Cp), 65.6 (C^5, Cp).

Synthesis of 3-Tol-1,1′′-biferrocene (4b). Complex **4b** was prepared following the same procedure described for **4a**, by reacting **2** with HC≡CTol. Yield: 51%. Anal. Calcd for $C_{27}H_{24}Fe_2$: C, 70.47; H, 5.26. Found: C, 70.69; H, 5.16. ^{1}H NMR ($CDCl_3$): δ 7.44−7.03 (m, 4H, C_6H_4Me), 4.83 (t, 1H, $^4J_{HH}$ = 1.4 Hz, H^2, Cp), 4.64 (m, 1H, Cp′′), 4.49 (m, 1H, Cp′′), 4.44 (m, 1H, Cp′′), 4.37 (m, 1H, Cp′′), 4.20 (m, 2H, H^4 and H^5, Cp), 4.03, 3.87 (s, 10H, Cp′ and Cp′′′), 2.34 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): δ 135.8 (C_{ipso} Tol), 129.8, 128.8, 126.6, 125.9 (*C*H, Tol), 85.1 (C^3, Cp), 84.5 (C^1, Cp′′), 83.5 (C^1, Cp), 71.2, 69.5 (Cp′ and Cp′′′), 68.0 (C^4 and C^5, Cp), 67.2 (Cp′′), 66.8 (Cp′′), 66.6 (Cp′′ and C^2, Cp), 65.2 (Cp′′), 21.0 (C_6H_4Me).

Synthesis of 3-CO$_2$Me-1,1′′-biferrocene (4c). Complex **4c** was prepared following the same procedure described for **4a**, by reacting **2** with HC≡CCO$_2$Me. Yield: 58%. Anal. Calcd for $C_{22}H_{20}Fe_2O_2$: C, 61.73; H, 4.71. Found: C, 61.59; H, 4.83. ^{1}H NMR ($CDCl_3$): δ 4.88 (dd, 1H, $^3J_{HH}$ = 2.44 Hz, $^4J_{HH}$ = 1.32 Hz, H^4, Cp), 4.65 (m, 2H, Cp′′ and H^2, Cp), 4.50 (m, 1H, Cp′′), 4.34 (m, 2H, Cp′′), 4.21 (dd, 1H, $^3J_{HH}$ = 2.44 Hz, $^4J_{HH}$ = 1.32 Hz, H^5, Cp), 4.04, 3.98 (s, 10H, Cp′ and Cp′′′), 3.69 (s, 3H, CO_2Me). ^{13}C NMR ($CDCl_3$): δ 174.4 (*C*O$_2$Me), 85.5 (C^1, Cp), 81.4 (C^1, Cp′′), 73.0 (C^5, Cp), 72.1 (C^2, Cp), 71.5 (C^4, Cp), 70.8 (C^3, Cp), 70.1, 68.7 (Cp′ and Cp′′′), 68.0, 67.3, 66.1, 64.9 (Cp′′), 50.9 (CO_2*Me*).

Synthesis of 3-CH$_2$OH-1,1′′-biferrocene (4d). Complex **4d** was prepared following the same procedure described for **4a**, by reacting **2** with HC≡CCH$_2$OH. Yield: 37%. Anal. Calcd for $C_{21}H_{20}Fe_2O$: C, 63.04; H, 5.04. Found: C, 62.95; H, 5.13. ^{1}H NMR ($CDCl_3$): δ 4.70 (m, 1H, Cp′′), 4.55 (m, 1H, H^5, Cp), 4.46 (m, 2H, Cp′′), 4.35 (m, 3H, H^4, Cp and C*H*$_2$OH), 4.19 (t, 1H, $^4J_{HH}$ = 1.4 Hz, H^2, Cp), 4.08 (m, 1H, Cp′′), 4.04, 4.00 (s, 10H, Cp′ and Cp′′′), 1.60 (br s, 1H, CH$_2$O*H*). ^{13}C NMR ($CDCl_3$): δ 90.1 (C^3, Cp), 86.1 (C^1, Cp′′), 83.2 (C^1, Cp), 71.4 (C^5, Cp), 70.8 (C^4, Cp), 70.0 (C^2, Cp), 69.5, 69.0 (Cp′ and Cp′′′), 68.2, 67.7, 67.0, 65.8 (Cp′′), 60.9 (*C*H$_2$OH).

Synthesis of 4b and 2-NMe$_2$-4-Tol-1,1′′-biferrocene (4e). To a solution of **1b** (250 mg, 0.531 mmol) in toluene (25 mL) was added HC≡CFc (200 mg, 0.95 mmol). The resulting solution was stirred at reflux overnight and then was cooled to room temperature and filtered on a Celite pad. Solvent removal and chromatography of the residue on an alumina column with petroleum ether (bp 40−60 °C) as eluent gave first a yellow fraction, corresponding to nonsubstituted ferrocene (FeCp$_2$). A second orange fraction, corresponding to **4b**, was collected by using diethyl ether as eluent. Yield of **4b**: 68 mg, 28%.

Then, a third red-orange fraction was collected using a 1/1 (v/v) diethyl ether/CH_2Cl_2 mixture, corresponding to **4e**. Yield of **4e**: 85 mg, 32%. Anal. Calcd for $C_{29}H_{29}Fe_2N$: C, 69.21; H, 5.81. Found: C, 69.38; H, 5.76. ^{1}H NMR ($CDCl_3$): δ 7.65−7.10 (m, 4H, C_6H_4Me), 5.01 (d, 1H, $^4J_{HH}$ = 1.2 Hz, H^3, Cp), 4.80 (d, 1H, $^4J_{HH}$ = 1.2 Hz, H^5, Cp), 4.66−4.59 (m, 3H, Cp′′), 4.26 (m, 1H, Cp′′), 4.10, 4.03 (s, 10H, Cp′ and Cp′′′), 2.62 (s, 6H, NMe$_2$), 2.34 (s, 3H, C_6H_4Me). ^{13}C NMR ($CDCl_3$): δ 135.2 ($C_{ipso\ Tol}$), 130.5−125.9 (C_{arom}), 112.5 (C^2, Cp), 87.3 (C^1, Cp′′), 84.6 (C^1, Cp), 82.0 (C^4, Cp), 71.2 (C^5, Cp), 70.0, 69.2 (Cp′ and Cp′′′), 68.1, 67.0, 65.5 (Cp′′), 66.4 (C^3, Cp and Cp′′), 45.7 (NMe$_2$), 21.0 (C_6H_4Me).

Synthesis of 2-NMe$_2$-4-CO$_2$Me-1,1′′-biferrocene (4f). Complex **4f** was prepared following the same procedure described for **4a**, by reacting **1a** with HC≡CFc. Yield: 52%. Anal. Calcd for $C_{24}H_{25}Fe_2NO_2$: C, 61.18; H, 5.35. Found: C, 61.25; H, 5.23. ^{1}H NMR ($CDCl_3$): δ 4.50 (d, 1H, $^4J_{HH}$ = 1.32 Hz, H^3, Cp), 4.35 (m, 1H, H^5, Cp), 4.35, 4.16, 4.04 (m, 4H, Cp′′), 4.09, 3.94 (s, 10H, Cp′ and Cp′′′), 3.65 (s, 3H, CO_2Me), 2.59 (s, 6H, NMe$_2$). ^{13}C NMR ($CDCl_3$): δ 175.1 (*C*O$_2$Me), 114.0 (C^2, Cp), 88.0 (C^1, Cp), 84.6 (C^1, Cp′′), 74.0 (C^3, Cp), 72.8 (C^5, Cp), 69.6 (Cp′′), 69.6, 69.0 (Cp′ and Cp′′′), 66.9, 65.1 (Cp′′), 64.4 (C^4, Cp and Cp′′), 51.1 (CO_2*Me*), 45.0 (NMe$_2$).

Synthesis of 5a,b. Complexes **5a**,**b** were prepared following the same procedure described for **4a**, by reacting **2** with HC≡CFc.

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Table 2. Crystal Data and Collection Details for 5a·$CHCl_3$

formula	$C_{31}H_{27}Cl_3Fe_3$
fw	673.43
T, K	296(2)
λ, Å	0.710 73
cryst syst	orthorhombic
space group	$Cmc2_1$
a, Å	18.391(2)
b, Å	20.224(3)
c, Å	7.7205(10)
cell vol, Å^3	2871.5(6)
Z	4
D_c, g cm^{-3}	1.558
μ, mm^{-1}	1.794
F(000)	1368
cryst size, mm	0.26 × 0.23 × 0.18
θ limits, deg	1.50−25.98
index ranges	$-22 \le h \le 22$ $-24 \le k \le 24$ $-9 \le l \le 9$
no. of rflns collected	14 125
no. of indep rflns	2924 (R_{int} = 0.0240)
completeness to θ_{max} %	100.0
no. of data/restraints/params	2924/303/286
goodness on fit on F^2	1.062
R1 ($I > 2\sigma(I)$)	0.0186
wR2 (all data)	0.0481
abs struct param	0.050(16)
largest diff peak/hole, e Å^{-3}	0.171/−0.195

In this case the two products **5a**,**b** have been separated by chromatography on alumina. **5a** was collected using diethyl ether as eluent, while **5b** was collected with CH_2Cl_2.

Yield of **5a**: 49%. Anal. Calcd for $C_{30}H_{26}Fe_3$: C, 65.03; H, 4.73. Found: C, 64.95; H, 4.82. ^{1}H NMR ($CDCl_3$): δ 4.09 (s, 10H, Cp_{free}), 3.88 (s, 5H, Cp_{free}), 4.61−4.10 (m, 11H, Cp). ^{13}C NMR ($CDCl_3$): δ 82.0 (C_{ipso} Cp), 70.6 (Cp_{free}), 69.5 (Cp_{free}), 71.9−65.0 (Cp). Crystals of **5a**, suitable for X-ray analysis, were obtained by slow evaporation of a $CDCl_3$ solution.

Yield of **5b**: 21%. Anal. Calcd for $C_{32}H_{31}Fe_3N$: C, 64.36; H, 5.23. Found: C, 64.55; H, 5.08. ^{1}H NMR ($CDCl_3$): δ 4.14 (s, 5H, Cp_{free}), 4.05 (s, 5H, Cp_{free}), 3.98 (s, 5H, Cp_{free}), 2.62 (s, 6H, NMe_2); the presence of the amino group causes the loss of symmetry of the molecule and subsequently increases the complexity of the NMR spectra. In particular, the signals due to the protons of the Cp rings appear as a multiplet between 4.42 and 3.84 ppm. ^{13}C NMR ($CDCl_3$): δ 112.0 (*C*-NMe_2), 84.0−82.6 (C_{ipso} Cp), 72.3−66.3 (CH), 45.3 (NMe_2).

Synthesis of 3-NMe_2-4-CPh_2OH-1,1″-biferrocene (6). Complex **6** was prepared following the same procedure described for **4a**, by reacting **3** with HC≡$CCPh_2$OH. Yield: 40%. Anal. Calcd for $C_{35}H_{33}Fe_2NO$: C, 70.61; H, 5.59. Found: C, 70.75; H, 5.52. ^{1}H NMR ($CDCl_3$) δ 7.47−7.00 (m, 10H, C_6H_5), 6.84 (s, 1H, OH), 4.55 (m, 1H, Cp″), 4.37 (m, 1H, Cp″), 4.24 (m, 1H, Cp″), 4.17 (m, 1H, Cp″), 4.08, 3.83 (s, 10H, Cp′ and Cp‴), 3.96 (br s, 1H, H^5, Cp), 3.90 (br s, 1H, H^2, Cp), 2.55 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 147.6 (C_{ipso} Ph), 132.3−125.9 (C_{arom}), 114.6 (C^3, Cp), 87.5 (C^1, Cp″), 87.0 (C^4, Cp), 86.3 (C^1, Cp), 77.4 (*C*Ph_2OH), 69.3, 69.1 (Cp′ and Cp‴), 69.2 (C^2, Cp), 69.0 (C^5, Cp), 68.1, 68.1, 66.9, 66.8 (Cp″), 43.4 (NMe_2).

Electrochemical Measurements. Electrochemical data were obtained from 10^{-3} M solutions in CH_2Cl_2 with 0.1 M [Bu_4N][PF_6]. $E_{1/2}$ (in mV, referenced to the SCE, at scan speed v = 100 mV s^{-1}): **4a**, 388, 430; **4e**, 225, 520; **4f**, 170, 460; **6**, 192, 435; **5a**, 290, 479, 880; **5b**, 161, 680 mV.

X-ray Crystallography. Crystal data and collection details for **5a**·$CHCl_3$ 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).[27] Structures were solved by direct methods and refined by full-matrix least squares on the basis of all data using F^2.[28] All hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The asymmetric unit contains half of the complex **5a** and half of the $CHCl_3$ molecule (both on *m*). Similar *U* restraints were applied to the C and Cl atoms (standard deviation 0.005). The nonsubstituted Cp ligands bonded to Fe(1) and Fe(2) are disordered over two positions. Disordered atomic positions were split and refined using one occupancy parameter per disordered group. The $CHCl_3$ molecule is disordered over four positions, two by two related by *m* symmetry. The two independent atomic positions were split and refined using one occupancy parameter per disordered group. The C−Cl distances in $CHCl_3$ were restrained to 1.75 Å (standard deviation 0.01).

Supporting Information Available: A CIF file giving crystallographic data for **5a**·$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Determination*; University of Göttingen, Göttingen, Germany, 1997.