Addition of protic nucleophiles to alkynyl(methoxy)carbene ligands in diiron complexes

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Abstract

Different protic nucleophiles (*i.e.* Ph_2C=NH, PhSH, $MeCO_2H$, PhOH) can be added to the C≡C bond of $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C(OMe)C{\equiv}CTol\}(Cp)_2][SO_3CF_3]$ (**1**), affording new diiron alkenyl methoxy carbene complexes. The additions of Ph_2C=NH and $MeCO_2H$ are completely regio and stereoselctive, resulting in the formation of the 5-aza-1-metalla-1,3,5-hexatriene $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)(N{=}CPh_2)\}(Cp)_2][CF_3SO_3]$, (**2**) and the 2-(acyloxy)alkenyl methoxy carbene complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)OC(O)Me\}(Cp)_2][CF_3SO_3]$ (**5**); the *E* isomer of the former and the *Z* of the latter are formed exclusively. Conversely, the addition of PhSH is regio but not stereoselective; thus, both the *E* and *Z* isomers of $Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)(SPh)\}(Cp)_2][CF_3SO_3]$ (**3**), are formed in comparable amounts. The cationic species **3** and **5** are demethylated after chromatography through Al_2O_3, resulting in the formation of the acyl complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(O)C_\beta H{=}C_\gamma(Tol)(SPh)\}(Cp)_2]$ (**4**), and $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(O)C_\beta H{=}C_\gamma(Tol)OC(O)Me\}(Cp)_2]$ (**6**), respectively, both with a *Z* configured C=C bond. Finally, the reaction of **1** with PhOH proceeds only in the presence of an excess of Et_3N affording the 2-(alkoxy)alkenyl acyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(O)C_\beta H{=}C_\gamma(Tol)(OPh)\}(Cp)_2]$ (**7**). The crystal structures of **4·CH_2Cl_2** and **7·0.5CH_2Cl_2** have been determined by X-ray diffraction experiments.

1. Introduction

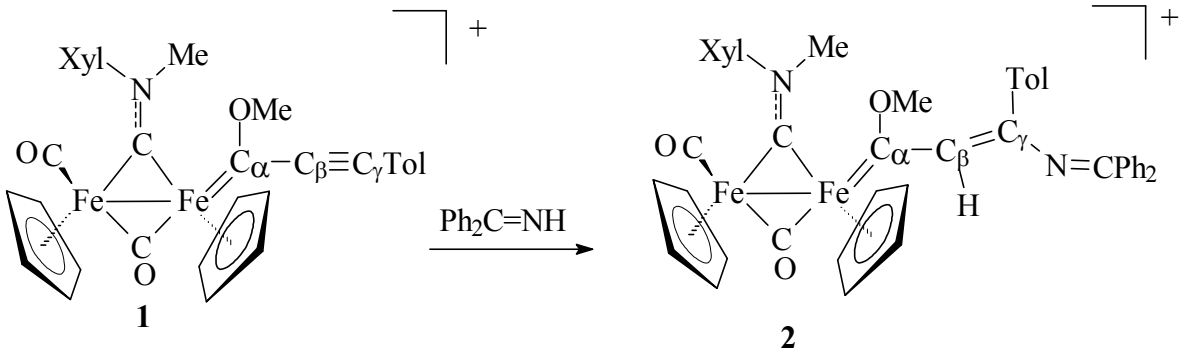
Mononuclear alkynyl(alkoxy)carbene complexes have been extensively investigated and successfully applied as versatile tools in organic synthesis [1]. Particularly interesting are nucleophilic addition to the triple of the alkynyl moiety, since they provide an easy and direct way to form new C-X bonds (X = N, O, P, S) and generate alkenylcarbene complexes which, in turn, promote cycloaddition reactions [2]. Extension of these investigations to di- and polynuclear transition metal complexes have been, so far, more limited, in spite of the awareness that two or more metals can cooperate in catalytic transformations have the possibility to promote new processes unknown for the metals alone [3].

We have previously described the synthesis and chemistry of diiron complexes containing alkynyl methoxy carbene ligands: $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C(OMe)C{\equiv}CR'\}(Cp)_2][SO_3CF_3]$. Their reactivity towards primary and secondary amines, as well as carbon nucleophiles, has been described in details [4, 5]. Herein, we report on the extension of these studies to other protic nucleophiles (*i.e.* imines, thiols, carboxylic acids and alcohols).

2. Results and Discussion

The reaction of the alkynyl methoxy carbene complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta{\equiv}C_\gamma Tol\}(Cp)_2][SO_3CF_3]$ (**1**), with $Ph_2C{=}NH$, in CH_2Cl_2 solution, results in the formation of the 5-aza-1-metalla-1,3,5-hexatriene $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)(N{=}CPh_2)\}(Cp)_2][CF_3SO_3]$ (**2**), in high yields (89 %) (Scheme 1).

Scheme 1

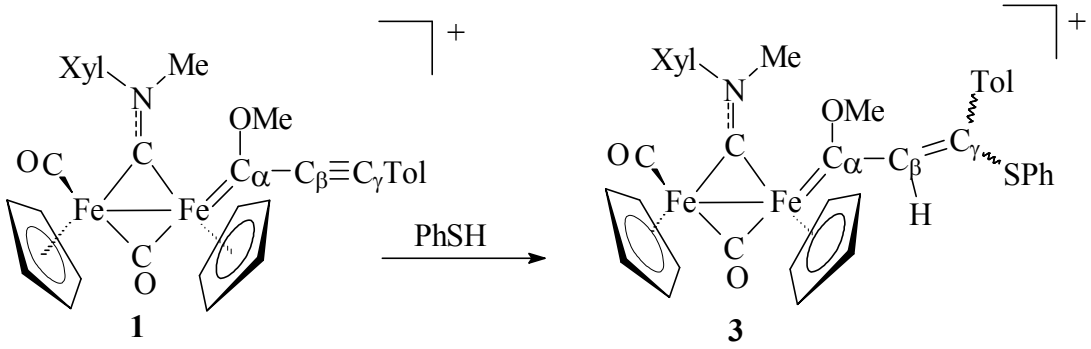


The IR spectrum of **2** shows a terminal and a bridging ν(CO) at values typical for a cationic complex (*i.e.* 1987 and 1811 cm^{-1}), whereas two bands at 1603 and 1570 cm^{-1} are attributable to the C=N stretching of the imine and the bridging aminocarbyne, respectively. The NMR data indicate

the presence in solution of a single species; thus, the addition of $Ph_2C{=}NH$ to the C≡C bond in **1** is completely regio and stereoselective. It has been reported that imine addition to mononuclear alkynylcarbene usually affords the *Z* isomer [6]. Conversely, our previous studies on the addition of primary and secondary amines to **1** indicate that the *E* isomers are prevailing [4]. The similarities between of the C_β-*H* resonance of **2** (at δ 6.40 ppm) with those of the products obtained by amine addition, suggests that also **2** adopts the *E* configuration. The ^{13}C NMR spectrum of **2** shows resonances typical for the bridging aminocarbyne (δ 334.0 ppm), and for the bridging and terminal carbonyls (δ 260.3 and 213.8 ppm, respectively). The carbene carbon C_α resonates at 312.0 ppm, whereas the resonances of C_β and C_γ fall within the typical range for olefinic carbons (δ 121.6 and 147.5 ppm, respectively); finally, the imine carbon resonates at δ 167.9 ppm.

In a similar way, PhSH adds regioselectively to the C≡C bond in **1** affording the 2-(phenylthio)alkenyl methoxy carbene complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)(SPh)\}(Cp)_2]$ $[CF_3SO_3]$ (**3**), (Scheme 2) in good yields (80 %).

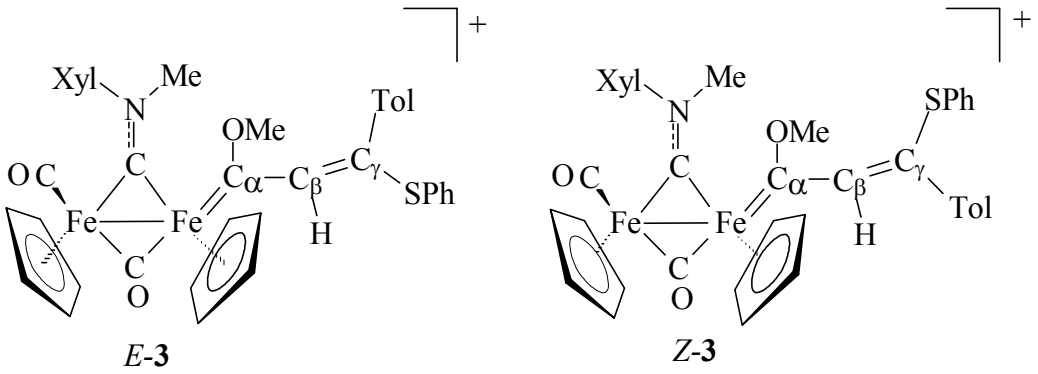
Scheme 2



1 **3**

The IR spectrum of **3** presents ν(CO) at 1989 and 1813 cm^{-1}, which are consistent with its cationic nature. The NMR spectra indicate that two isomers are present in solution in similar concentration (isomers ratio = 1.2 : 1). Addition of thiols to alkynyl alkoxy carbenes is, generally, not stereoselective, but results in a mixture of *E* and *Z* isomers [7]. Considering the fact that the major isomer of **9** shows δ(C_β-*H*) at 6.29 ppm, whereas it resonates at δ *ca*. 6.99-7.64 ppm in the minor isomer, it is reasonable to assign an *E* configuration to the former and *Z* to the latter (Scheme 3). The ^{13}C NMR spectrum of **3** shows two sets of four resonances at low fields (δ 332.5, 317.0, 260.5, 211.9 *E*-**3**; δ 332.2, 310.2, 259.6, 211.6 *Z*-**3**) due to the bridging aminocarbyne, the terminal alkenyl methoxy carbene and the bridging and terminal CO, respectively.

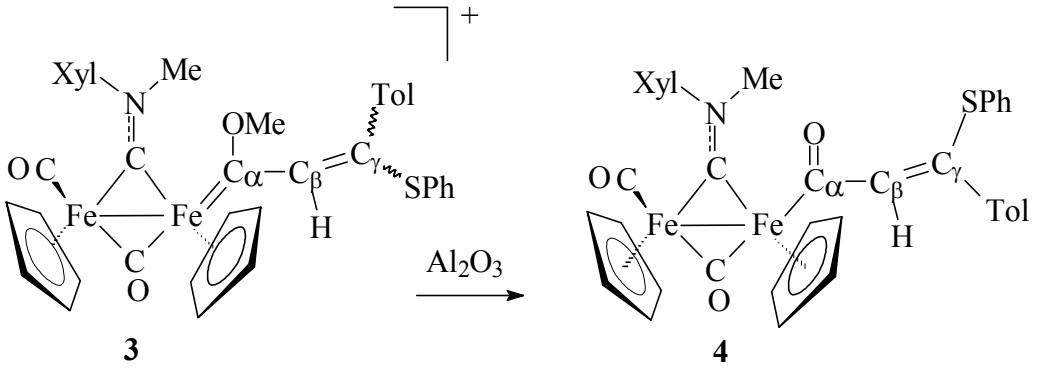
Scheme 3



E-**3** *Z*-**3**

Attempts to separate the two isomers of **3** by column chromatography on alumina resulted, instead, on its demethylation (Scheme 4) and the neutral 2-(phenylthio)alkenyl acyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(O)C_\beta H{=}C_\gamma(Tol)(SPh)\}(Cp)_2]$ (**4**), was isolated in satisfactory yields (75 %).

Scheme 4



3 **4**

The molecular structure of **4** has been determined by X-ray diffraction (Figure 1 and Table 1). The structure of **4** can be discussed in terms of two moieties, *i.e.* the diiron fragment $Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$ and the terminal 2-(phenylthio)alkenyl acyl ligand $C_\alpha(O)C_\beta H{=}C_\gamma(Tol)(SPh)$. The former is essentially unchanged respect to the parent compound **1** [4], and its stereochemistry is similar to the one found in analogous diiron and diruthenium aminocarbyne complexes [8, 9]. The Fe(1)-Fe(2) interaction [2.4896(12) Å] is typical for a single bond, and the Cp ligands assume a *cis* arrangement respect to the $Fe_2(\mu\text{-}C)_2$ core. The C(13)-N(1) interaction [1.314(6) Å] shows some double bond character and, thus, the bridging aminocarbyne ligand can be alternatively described as a μ-iminium. The Xyl substituent on μ-CN(Me)(Xyl) is on the same side of the terminal CO, as found in **1**. The μ-CO ligand displays a marked asymmetry

[Fe(1)-C(12) 1.827(6) Å; Fe(2)-C(12) 1.982(6) Å] as a consequence of the different electron density on the two Fe atoms; in particular, it shows a shorter contact to Fe(1), which brings the less π-acidic ligand. Also the bridging aminocarbyne ligand presents some asymmetry [Fe(1)-C(13) 1.815(5) Å; Fe(2)-C(13) 1.890(5) Å], even if less marked. The Fe(1)-C(23) interaction [1.944(5) Å] has mainly the character of a pure σ Fe-C(sp^2) bond, whereas both C(23)-O(1) [1.218(6) Å] and C(24)-C(25) [1.337(7) Å] are double bonds, as expected for an acyl and an olefin, respectively. The (2-phenylthio)alkenyl acyl ligand assumes a *Z* configuration respect to the C(24)=C(25) double bond. Finally, the C(23)-C(24) [1.480(7) Å] is typical for a single C(sp^2)-C(sp^2) single bond and it suggests lack of conjugation between the acyl and vinyl thioether, as confirmed by the non-coplanarity between their π-systems [dihedral angle Fe(1)-C(23)-C(24)-C(25) 119.4(5)°].

Figure 1

Molecular structure of the cation **4**, with key atoms labelled (all H atoms, except H(24), have been omitted). Displacement ellipsoids are at 30% probability level.

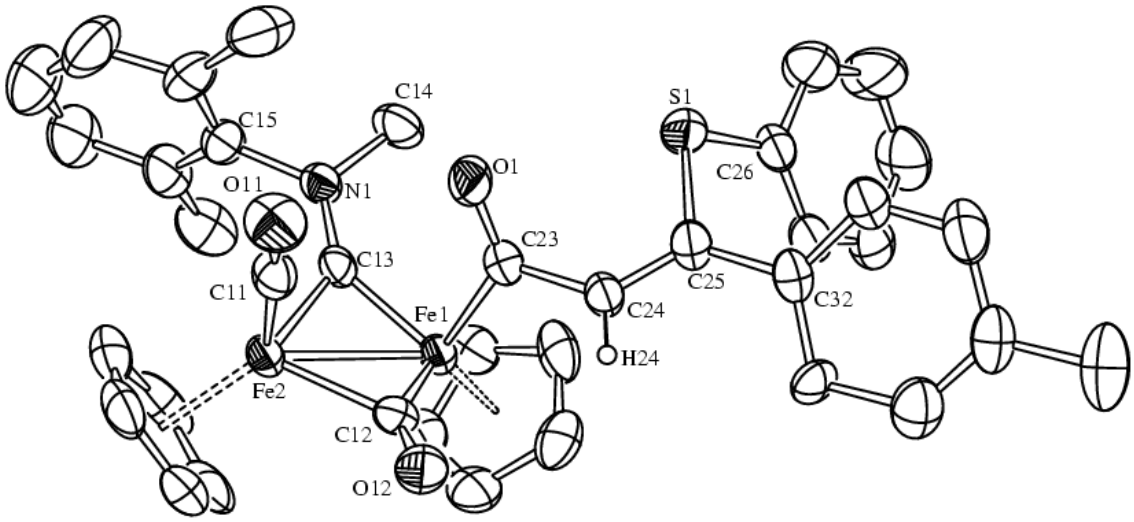


Table 1

Selected bond lengths (Å) and angles (°) for complex **4**.

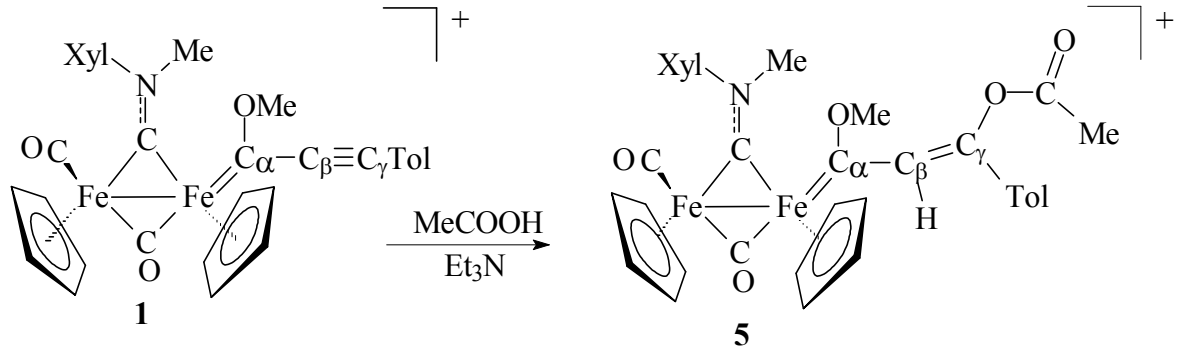
Fe(1)-Fe(2)	2.4896(12)	C(12)-O(12)	1.194(6)
Fe(2)-C(11)	1.735(6)	C(13)-N(1)	1.314(6)
Fe(2)-C(12)	1.982(6)	C(23)-O(1)	1.218(6)
Fe(1)-C(12)	1.827(6)	C(23)-C(24)	1.480(7)
Fe(2)-C(13)	1.890(5)	C(24)-C(25)	1.333(7)
Fe(1)-C(13)	1.815(5)	C(25)-S(1)	1.802(6)
Fe(1)-C(23)	1.944(5)	S(1)-C(26)	1.744(6)

C(11)-O(11)	1.157(6)	C(25)-C(32)	1.470(7)
Fe(1)-C(23)-O(1)	126.0(4)	C(24)-C(25)-S(1)	117.7(4)
Fe(1)-C(23)-C(24)	116.8(4)	C(24)-C(25)-C(32)	124.0(5)
O(1)-C(23)-C(24)	117.2(4)	S(1)-C(25)-C(32)	118.2(4)
C(23)-C(24)-C(25)	124.7(5)	C(25)-S(1)-C(26)	103.7(3)

The IR spectrum of **4** shows ν(CO) at 1968, 1775 and 1572 cm^{-1}, in agreement with the presence of a terminal and a bridging CO ligands, and the acyl group. The NMR data indicate that only one species is present in solution, to which is possible to assign a *Z* configuration on the basis of the solid state structure. Since the parent complex **3** was a mixture of the *E* and the *Z* isomers in almost the same amounts; the demethylation of **3** must be accompanied, consequently, by partial isomerisation of the C=C double bond. The principal features of the ^{1}H NMR spectrum of **4** are the resonance at δ 4.62 due to C_β-*H* and the two resonances at δ 4.91 and 4.28 ppm due to the inequivalent Cp ligands. The ^{13}C NMR spectrum shows four resonances at low fields [δ 335.4, 268.7, 263.6, 213.6 ppm] attributable to the bridging aminocarbyne, the μ-CO, the acyl carbon and terminal CO ligand, respectively. The carbon atoms of the vinyl thioether resonate at higher fields, *i.e.* δ 132-137 ppm (C_γ) and δ 140.8 ppm (C_β).

The addition of $MeCO_2H$ to **1** takes place in the presence of Et_3N (Scheme 5), as expected, since the presence of a base is usually required for obtaining the addition of carboxylic acids to alkynylcarbene complexes [10]. The 2-(acyloxy)alkenyl methoxy carbene complex $[Fe_2\{\mu$-$CN(Me)(Xyl)\}(\mu$-$CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)OC(O)Me\}(Cp)_2][CF_3SO_3]$ (**5**), is, therefore, obtained in high yields (95 %) after removal of all the volatiles under reduced pressure.

Scheme 5

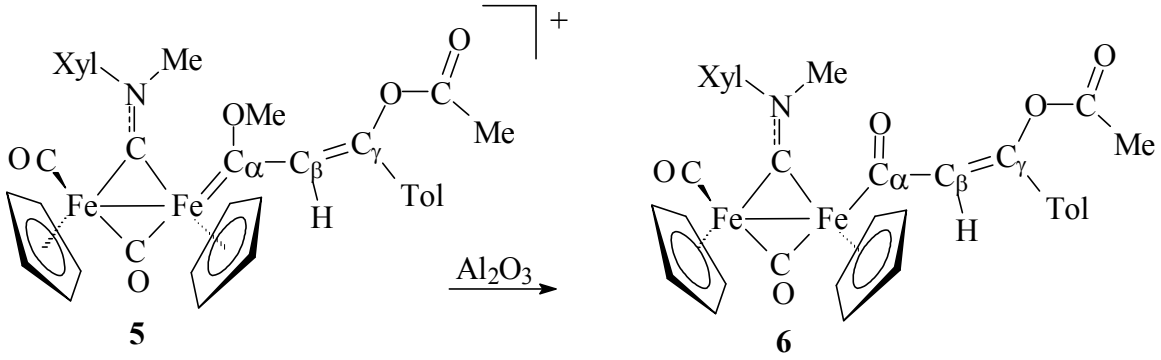


1 **5**

The IR spectrum of **5** indicates that it maintains a cationic nature (ν(CO) 1993 and 1820 cm^{-1}) and addition of $MeCO_2H$ is indicated by the strong ν(OCOMe) band at 1759 cm^{-1}. The NMR data shows that a single species is present in solution and, thus, the addition is regio and stereoselective. The δ(C_β-*H*) resonance at 7.05-7.48 ppm suggests a *Z* configuration for the double bond, and this is also the stereochemistry usually observed for this class of reactions [1, 10]. The new 2-(acyloxy)alkenyl methoxy carbene ligand displays typical resonances in the ^{13}C NMR spectrum, *i.e.* δ 314.5 (C_α), 130.5-125.7 (C_β and C_γ), 169.0 (O*C*OMe) and 21.4 ppm (OCO*Me*).

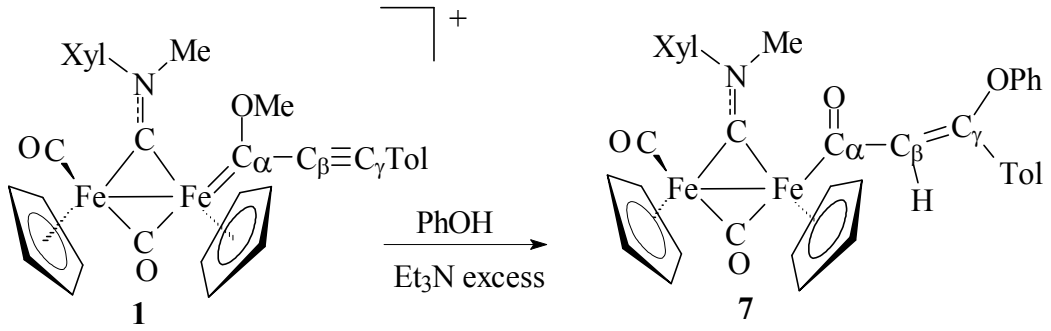
As observed for **3**, also **5** is converted into the 2-(acyloxy)alkenyl acyl complex [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(O)C_βH=C_γ(Tol)OC(O)Me}($Cp)_2$] (**6**), (Scheme 6). The loss of cationic character in **6** is consistent with the lowering of ν(CO) (1967 and 1771 cm^{-1}) compared to **5**. The NMR spectra indicate that no isomerisation of the C=C double bond has occurred and, thus, only the *Z* isomer is present in solution (the configuration of the double bond has been assigned on the basis of comparison with NMR data of analogous species and NOE studies).

Scheme 6



Finally, addition of PhOH to the C≡C bond of **1** can be obtained only in the presence of a large excess of Et_3N; no reaction was, in fact, observed, in the absence of base as a consequence of the minor reactivity of PhOH compared to the other nucleophiles considered. The reaction is accompanied by demethylation and, thus, the 2-(alkoxy)alkenyl acyl complex [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(O)C_βH=C_γ(Tol)(OPh)}($Cp)_2$] (**7**) is formed (Scheme 7).

Scheme 7



Compound **7** has been characterised both in solution by spectroscopic methods and in the solid state by X-ray diffraction studies (Figure 2 and Table2).

Figure 2

Molecular structure of the cation **7**, with key atoms labelled (all H atoms, except H(24), have been omitted). Only one of the two independent molecules is represented. Displacement ellipsoids are at 30% probability level.

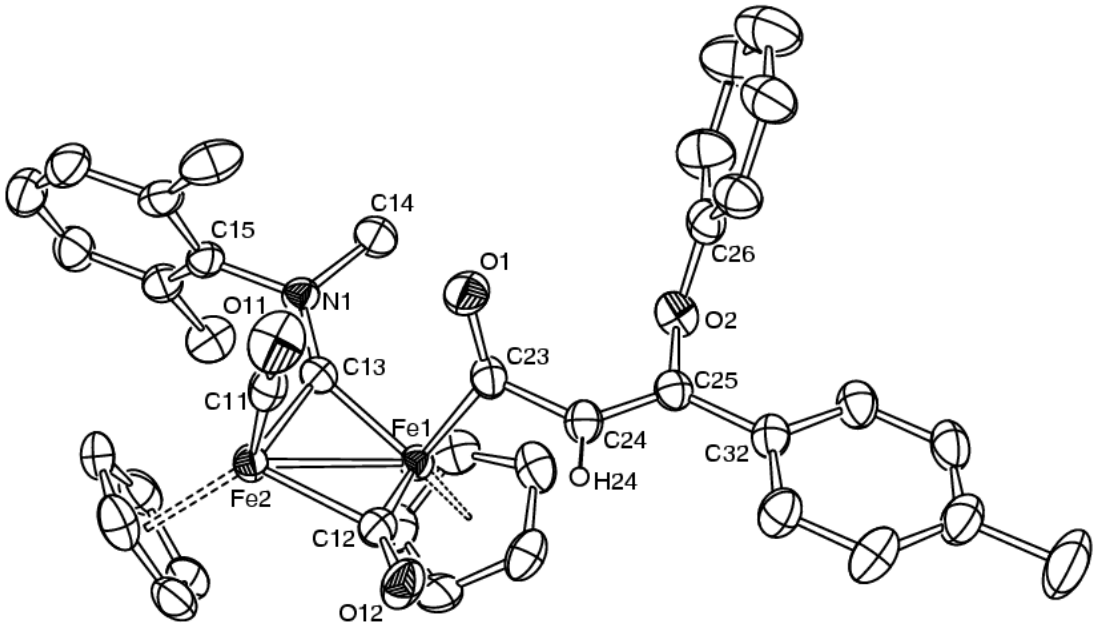


Table 2

Selected bond lengths (Å) and angles (°) for complex **7**.

Fe(1)-Fe(2)	2.4922(9)	Fe(3)-Fe(4)	2.4935(9)
Fe(2)-C(11)	1.749(4)	Fe(4)-C(51)	1.739(4)
Fe(2)-C(12)	1.991(3)	Fe(4)-C(52)	2.003(4)
Fe(1)-C(12)	1.845(3)	Fe(3)-C(52)	1.840(4)
Fe(2)-C(13)	1.883(3)	Fe(4)-C(53)	1.873(3)

Fe(1)-C(13)	1.829(3)	Fe(3)-C(53)	1.824(3)
Fe(1)-C(23)	1.944(3)	Fe(3)-C(63)	1.947(4)
C(11)-O(11)	1.149(4)	C(51)-O(51)	1.154(4)
C(12)-O(12)	1.182(4)	C(52)-O(52)	1.175(4)
C(13)-N(1)	1.311(4)	C(53)-N(2)	1.308(4)
C(23)-O(1)	1.219(4)	C(63)-O(3)	1.218(4)
C(23)-C(24)	1.500(5)	C(63)-C(64)	1.502(5)
C(24)-C(25)	1.332(4)	C(64)-C(65)	1.335(5)
C(25)-O(2)	1.394(4)	C(65)-O(4)	1.406(4)
O(2)-C(26)	1.382(4)	O(4)-C(66)	1.381(4)
C(25)-C(32)	1.474(5)	C(65)-C(72)	1.463(5)
Fe(1)-C(23)-O(1)	127.5(3)	Fe(3)-C(63)-O(3)	127.3(3)
Fe(1)-C(23)-C(24)	113.9(2)	Fe(3)-C(63)-C(64)	115.4(3)
O(1)-C(23)-C(24)	118.6(3)	O(3)-C(63)-C(64)	117.3(3)
C(23)-C(24)-C(25)	124.5(3)	C(63)-C(64)-C(65)	125.2(3)
C(24)-C(25)-O(2)	117.1(3)	C(64)-C(65)-O(4)	116.8(3)
C(24)-C(25)-C(32)	126.6(3)	C(64)-C(65)-C(72)	126.9(3)
O(2)-C(25)-C(32)	115.9(3)	O(4)-C(65)-C(72)	115.8(3)
C(25)-O(2)-C(26)	118.7(3)	C(65)-O(4)-C(66)	119.1(3)

The molecular structure of **7** strongly resembles that of **4**, concerning both bond lengths and bond angles. The only difference is related to the conformation of the C(25)-XPh (X = O, S) group, which points on different sides of the plane determined by the olefin carbons C(24)=C(25) in the two species; this is probably due to the different bond angles assumed by the heteroatoms in **4** and **7** [C(25)-O(2)-C(26) 103.7(3)° for **4**; C(25)-O(2)-C(26) 118.7(3)°, C(65)-O(4)-C(66) 119.1(3)° for **7**)

The *Z* configuration of the double bond is maintained in solution as confirmed by NOE experiments. Thus, irradiation of the Tol doublet at 7.44 ppm generates a strong enhancement of the C_β-*H* resonance (δ 6.84 ppm). The 2-(alkoxy)alkenyl acyl ligand shows typical signals in the ^{13}C NMR spectrum at δ 262.2 (C_α), 126.2 (C_β) and 138.6 ppm (C_γ).

Finally, it has to be outlined the easy by which the compounds obtained from addition of O-H and S-H nucleophiles undergo loss of methyl group, upon cromatography on Al_2O_3 or in the presence of a large excess of base, affording **4**, **6** and **7**. This behaviour is in contrast with that of the related 2-(amino)alkenyl carbene complexes [Fe_2{μ-CN(Me)(R)}(μ-

CO)(CO){C_α(OMe)C_βH=C_γ(R')(NMe_2)}($Cp)_2$][CF_3SO_3], obtained by addition of Me_2NH to **1**, which are recovered unchanged after chromatography on Al_2O_3 [4]. The comparison indicates that the nature of the substituent in the γ position of the alkenyl carbene ligand strongly influences the stability of the alcoxycarbene group. Conjugation with the more basic NMe_2 group presumably reduces the positive charge on the alkoxycarbene carbon and, consequently, its reactivity. Comparisons can be done also with the species [Fe_2(μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(OMe)C_βH=C_γ(Tol)(NHR)}($Cp)_2$][CF_3SO_3], obtained by addition of primary amines to **1**. In a similar manner, these complexes, when treated with NaH or Al_2O_3, undergo deprotonation of the NH group instead of demethylation of the carbene functionality. [4]

3. Conclusions

The results above described, toghether with those previously reported on the reactions with amines and carbon nucleophiles well demonstrate that coordination at the diiron cationic frame enhances the electrophilic character of the alkynyl(methoxy)carbene ligand. Addition of N-H, O-H and S-H protic nucleophiles occur selectively at the triple bond of the alkynyl group affording alkenyl carbene complexes bearing the heteroatom in the γ position. All the reactions reported are completely regioselective and, in the case of N-H and O-H nucleophiles, also stereoselective. The reactions provide a general entry to alkenyl(alkoxy)carbene complexes containing a variety of different functionalities on the alkenyl moiety. A further possibility to modify the ligands is given by the observed demethylation of the alkoxycarbene group, with transformation into the corresponding acyl ligands.

4. Experimental

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Infrared spectra were recorded 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 Varian Gemini 300 and Varian Mercury 400 instruments. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via ^1H,^{13}C correlation measured using gs-HSQC and gs-HMBC experiments [11]. Monodimensional NOE measurements were recorded using the DPFGSE-NOE sequence [12]. All chemicals were used as received from Aldrich Co., except [Fe_2(μ-CN(Me)(Xyl)}(μ-CO)(CO){C(OMe)C≡CTol}($Cp)_2$][SO_3CF_3] (**1**) [4] which was prepared by published methods.

*4.1 Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(OMe)C_βH=C_γ(Tol)(N=CPh_2)}$(Cp)_2$] [CF_3SO_3] (**2**)*

HN=CPh_2 (0.140 mL, 0.820 mmol) was added to a solution of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(OMe)C≡CTol}$(Cp)_2$][SO_3CF_3] (200 mg, 0.266 mmol) in CH_2Cl_2 (15 mL) and the mixture stirred at room temperature for 20 minutes; during this time, the complete conversion of **1** into **2** was monitored *via* IR. Thus, the solvent was removed under reduced pressure and the residue washed with Et_2O (2×5 mL) and petroleum ether (2×5 mL). The final product was further purified by filtration through celite using CH_2Cl_2 as solvent. Yield 220.8 mg (89 %). Anal. Calcd. For $C_{47}H_{43}F_3Fe_2N_2O_6S$: C, 60.53; H, 4.65; N, 3.00. Found: C, 60.89; H, 4.24; N, 3.35. IR (CH_2Cl_2, 293 K): ν(CO) 1987 (vs), 1811 (s); ν(C=N) 1603 (ms). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.81-7.22 (m, 17H, arom), 6.40 (s, 1H, $C_\beta H$), 5.17, 4.41 (s, 10H, Cp), 4.18 (s, 3H, N*Me*), 3.03 (s, 3H, O*Me*), 2.52, 2.23 (s, 6H, $C_6H_3Me_2$), 2.40 (s, 3H, p-C_6H_4Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 334.0 (μ-*C*), 312.0 (Fe-C_α), 260.3 (μ-*C*O), 213.8 (*C*O), 167.9 (N=*C*), 148.4 (*C*ipso Xyl), 147.5 (C_γ), 140.2, 136.9, 133.9, 133.1, 132.9, 132.3 (*C*-Me Xyl + *C*-Me Tol + *C*ipso Tol + *C*ipso Ph), 130.4-126.4 (*C*-H arom), 121.6 (C_βH), 92.6, 88.1 (Cp), 62.7 (O*Me*), 54.3 (N-*Me*), 21.4 (p-C_6H_4Me), 18.6, 17.0 ($C_6H_3Me_2$).

Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(OMe)C_βH=C_γ(Tol)(SPh)}$(Cp)_2$] [CF_3SO_3], 3. PhSH (0.060 mL, 0.60 mmol) was added to a solution of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(OMe)C≡CTol}$(Cp)_2$][SO_3CF_3] (290 mg, 0.386 mmol) in CH_2Cl_2 (15 mL) and the mixture stirred at room temperature for 30 minutes; during this time, the complete conversion of **1** into **3** was monitored *via* IR. Thus, the solvent was removed under reduced pressure and the residue washed with Et_2O (2×5 mL) and petroleum ether (2×5 mL). The final product was further purified by filtration through celite using CH_2Cl_2 as solvent. Yield 266.0 mg (80 %). Anal. Calcd. For $C_{40}H_{38}F_3Fe_2NO_6S_2$: C, 55.76; H, 4.45; N, 1.63. Found: C, 55.68; H, 4.68; N, 1.75. IR (CH_2Cl_2, 293 K): ν(CO) 1989 (vs), 1813 (s). ^{1}H NMR ($CDCl_3$, 293 K) Isomer E: δ 7.64-6.99 (m, 12H, arom), 6.29 (s, 1H, $C_\beta H$), 5.02, 4.47 (s, 10H, Cp), 4.32 (s, 3H, N*Me*), 3.11 (s, 3H, O*Me*), 2.55, 2.34, 2.15 (s, 9H, $C_6H_3Me_2$ + p-C_6H_4Me); Isomer *Z*: δ 7.64-6.99 (m, 13H, arom + $C_\beta H$), 5.25, 4.54 (s, 10H, Cp), 4.15 (s, 3H, N*Me*), 3.96 (s, 3H, O*Me*), 2.60, 2.28, 2.08 (s, 9H, $C_6H_3Me_2$ + p-C_6H_4Me). Isomer ratio E : Z = 1.2 :1. ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) Isomer E: δ 332.5 (μ-*C*), 317.0 (Fe-C_α), 260.5 (μ-*C*O), 211.9 (*C*O), 147.3 (*C*ipso Xyl), 142.0-130.8 (C_γ + *C*-Me Xyl + *C*-Me Tol + *C*ipso Tol + *C*ipso Ph), 134.9-126.9 (C_βH +*C*-H arom), 92.4, 88.4 (Cp), 64.3 (O*Me*), 54.2 (N-*Me*), 21.4 (p-C_6H_4Me), 18.6, 17.1($C_6H_3Me_2$); Isomer Z: δ 332.2 (μ-*C*), 310.2 (Fe-C_α), 259.6 (μ-*C*O), 211.6 (*C*O), 147.0 (*C*ipso Xyl), 142.0-130.8 (C_γ + *C*-Me Xyl + *C*-Me Tol + *C*ipso Tol + *C*ipso Ph), 134.9-126.9

(C_βH +*C*-H arom), 92.4, 88.6 (Cp), 63.8 (O*Me*), 54.2 (N-*Me*), 21.3 (p-C_6H_4*Me*), 18.6, 17.1(C_6H_3*Me*$_2$).

Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(O)C_βH=C_γ(Tol)(SPh)}(Cp)$_2$], 4. Complex **3** (266.0 mg, 0.309 mmol) was dissolved in CH_2Cl_2 (5 mL) and transferred on top of a Al_2O_3 column. Product **4** was obtained as a green fraction using THF as eluent. Yield 161.6 mg (75 %). Anal. Calcd. For $C_{38}H_{35}Fe_2NO_3S$: C, 65.44; H, 5.06; N, 2.01. Found: C, 65.11; H, 5.28; N, 1.78. IR (CH_2Cl_2, 293 K): ν(CO) 1968 (vs), 1775 (s); ν(C=O) 1572 (w). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.38-6.93 (m, 12H, arom), 4.91, 4.28 (s, 10H, Cp), 4.62 (s, 1H, C_β*H*), 4.44 (s, 3H, N*Me*), 2.60, 2.44, 2.22 (s, 9H, C_6H_3*Me*$_2$ + p-C_6H_4*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 335.4 (μ-*C*), 268.7, 263.6 (Fe-C_α + μ-*C*O), 213.6 (*C*O), 148.6 (*C*ipso Xyl), 142.6 (*C*ipso Tol), 140.8 (C_βH), 137.1, 136.0, 135.1, 132.9, 131.7 (C_γ + *C*-Me Xyl + *C*-Me Tol + *C*ipso Ph), 130.8-125.6 (*C*-H arom), 89.1, 86.1 (Cp), 51.6 (N-*Me*), 21.1 (p-C_6H_4*Me*), 18.5, 17.8 (C_6H_3*Me*$_2$).

Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(OMe)C_βH=C_γ(Tol)OC(O)Me}(Cp)$_2$][CF_3SO_3], 5. $MeCO_2H$ (0.15 mL, 2.62 mmol) and Et_3N (0.10 ml, 0.717 mmol) were added to a solution of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(OMe)C≡CTol}(Cp_2)][TfO] (238.0 mg, 0.317 mmol) in CH_2Cl_2 (10 mL), and the solution stirred at room temperature for 2 hours. The solvent was, then, removed *in vacuo* and the residue washed with Et_2O (2x10 ml) and petroleum ether (2x10 ml). Yield 244.4 mg (95 %). Anal. Calcd. For $C_{36}H_{36}F_3Fe_2NO_8S$: C, 53.29; H, 4.47; N, 1.73. Found: C, 53.58; H, 4.11; N, 1.92. IR (CH_2Cl_2, 293 K): ν(CO) 1993 (vs), 1820 (s); ν(OCOMe) 1759 (s). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.48-7.05 (m, 8H, arom + C_β*H*), 5.22, 4.48 (s, 10H, Cp), 4.14 (s, 3H, N*Me*), 3.78 (s, 3H, O*Me*), 2.48, 2.23 (s, 6H, C_6H_3*Me*$_2$), 2.28 (s, 3H, p-C_6H_4*Me*), 2.06 (s, 3H, CO*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 333.3 (μ-*C*), 314.5 (Fe-C_α), 260.0 (μ-*C*O), 212.5 (*C*O), 169.0 (*C*OMe), 147.5 (*C*ipso Xyl), 140.6 (*C*ipso Tol), 133.3, 133.0 (*C*-Me Xyl), 130.5-125.7 (*C*-Me Tol + C_γ + C_βH + *C*-H arom), 93.1, 88.7 (Cp), 63.7 (O*Me*), 54.8 (N-*Me*), 21.5 (p-C_6H_4*Me*), 21.4 (CO*Me*), 18.6, 17.1 (C_6H_3*Me*$_2$).

Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(O)C_βH=C_γ(Tol)OC(O)Me}(Cp)$_2$], 6. Complex **5** (244.4 mg, 0.301 mmol) was dissolved in CH_2Cl_2 (5 mL) and transferred on top of a Al_2O_3 column. Product **6** was obtained as a green fraction using THF as eluent. Yield 166.2 mg (81 %). Anal. Calcd. For $C_{34}H_{33}Fe_2NO_5$: C, 63.08; H, 5.14; N, 2.16. Found: C, 63.44; H, 5.29; N, 1.94. IR (CH_2Cl_2, 293 K): ν(CO) 1967 (vs), 1771 (vs). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.44-7.13 (m, 7H, arom), 5.45 (s, 1H, C_β*H*), 4.91, 4.25 (s, 10H, Cp), 4.27 (s, 3H, N*Me*), 2.56, 2.50 (s, 6H, C_6H_3*Me*$_2$),

2.33 (s, 3H, p-C_6H_4*Me*), 2.10 (s, 3H, CO*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 336.8 (μ-*C*), 268.9 (μ-*C*O), 262.0 (Fe-C_α), 213.9 (*C*O), 169.3 (*C*OMe), 148.5 (*C*ipso Xyl), 139.2 (*C*ipso Tol), 135.2 (*C*-Me Tol), 133.4, 132.2 (*C*-Me Xyl), 130.3-123.4 (*C*-H arom + C_γ), 101.4 (C_βH), 89.4, 86.3 (Cp), 51.9 (N-*Me*), 21.5 (p-C_6H_4*Me*), 21.3 (CO*Me*), 18.6, 17.7 ($C_6H_3Me_2$).

Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(O)C_βH=C_γ(Tol)(OPh)}(Cp)$_2$], 7. PhOH (130.1 mg, 1.38 mmol) and Et_3N (0.60 mL, 4.30 mmol) were added to a solution of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(OMe)C≡CTol}(Cp_2)][TfO] (122.5 mg, 0.163 mmol) in CH_2Cl_2 (10 mL), an the mixture stirred for 1 hour at room temperature. Then, the solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (3 ml) and chromatographed through Al_2O_3. The final product was obtained as a green fraction using CH_2Cl_2/THF (1:1) as eluent. Yield 62.2 mg (56 %). Anal. Calcd. For $C_{38}H_{35}Fe_2NO_4$: C, 66.99; H, 5.18; N, 2.06. Found: C, 67.15; H, 5.07; N, 1.85. IR (CH_2Cl_2, 293 K): ν(CO) 1965 (vs), 1773 (s). ^1H NMR ($CDCl_3$, 293 K): δ 7.44, 7.09 (d AB, 4H, $^3J_{HH}$ = 7.5 Hz, p-C_6H_4Me), 7.24 (m, 3H, $C_6H_3Me_2$), 7.14 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-OC_6H_5), 6.91 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *o*-OC_6H_5), 6.86 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-OC_6H_5), 6.84 (s, 1H, $C_\beta H$), 4.84, 4.27 (s, 10H, Cp), 4.13 (s, 3H, N*Me*), 2.55, 2.37 (s, 6H, $C_6H_3Me_2$), 2.31 (s, 3H, p-C_6H_4*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 336.2 (μ-*C*), 268.9 (μ-*C*O), 262.2 (Fe-C_α), 214.4 (*C*O), 158.0 (*C*ipso OPh), 148.6 (*C*ipso Xyl), 138.6 (C_γ), 138.5 (*C*ipso Tol), 135.4 (*C*-Me Tol), 133.3, 132.7 (*C*-Me Xyl), 130.3, 128.1, 128.0 (*C*-H Xyl), 129.4, 126.8 (*C*H Tol), 129.2 (*m*-OC_6H_5), 126.2 (C_βH), 121.4 (*p*-OC_6H_5), 116.9 (*o*-OC_6H_5), 89.5, 86.2 (Cp), 51.5 (N-*Me*), 21.5 (p-C_6H_4*Me*), 18.7, 17.8 ($C_6H_3Me_2$).

X-ray structural determinations. Crystal data and collection details for **4·CH_2Cl_2** and **7·0.5CH_2Cl_2** are reported in Table 3. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [13]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [14]. Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. The CH_2Cl_2 molecule in **4·CH_2Cl_2** is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group.

Table 3

Crystal data and experimental details for **4·CH_2Cl_2** and **7·0.5CH_2Cl_2.**

Complex	**4·CH_2Cl_2**	**7·0.5CH_2Cl_2**
Formula	$C_{39}H_{37}Cl_2Fe_2NO_3S$	$C_{38.5}H_{36}ClFe_2NO_4$
F*w*	782.36	723.83
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	17.008(3)	21.415(4)
b, Å	9.758(2)	15.696(3)
c, Å	22.955(5)	21.716(4)
β, °	102.71(3)	109.87(3)
Cell volume, Å^3	3716.4(13)	6864(2)
Z	4	8
D_c, g cm^{-3}	1.398	1.401
μ, mm^{-1}	1.018	0.964
F(000)	1616	3000
Crystal size, mm	0.36×0.25×0.16	0.25×0.21×0.15
θ limits, °	1.36-25.03	1.15-26.37
Reflections collected	32010	67038
Independent reflections	6571 (R_{int} = 0.0841)	14039 (R_{int} = 0.0693)
Data/restraints/parameters	6571 / 52 / 435	14039 / 408 / 846
Goodness on fit on F^2	0.968	0.974
*R*1 [$I > 2\sigma(I)$]	0.0579	0.0477
*wR*2 (all data)	0.1795	0.1414
Largest diff. peak and hole, e.Å^{-3}	0.724 / -0.441	0.604 / -0.574

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