Note

Assembly and incorporation of a CO₂Me group into a bridging vinyliminium ligand in a diiron complex

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ABSTRACT

The diiron complex $[Fe_2\{\mu\text{-}\kappa^1(O):\eta^1(C):\eta^3(C)\text{-}C(N(Me)(Xyl))C(H)=C(Me)C(O)OMe\}(\mu\text{-}CO)(Cp)_2]$ (**2**) has been obtained from the diiron bridging vinyliminium $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)=C(H)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1**; Xyl = 2,5-$C_6H_3Me_2$) upon treatment with NaH in the presence of $CH_2=C=CMe_2$, followed by chromatography on alumina with MeOH as eluent. The reaction consists in the incorporation of a methylcarboxylate unit, assembled from CO and MeO⁻, into the bridging vinyliminium ligand. The resulting complex **2** exhibits a C₄ fragment bridging the two iron centres through the carbonyl oxygen atom and the allylidene moiety.

The X-ray molecular structure of **2** has been determined.

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1. Introduction

Dinuclear complexes, providing multisite interactions with coordinated organic fragments can offer reactivity patterns different from those observed when the same organic fragments are bound to a single metal center [1]. This is the case of the diiron complexes **I** (Scheme 1), containing a vinyliminium ligand in allylidene type μ-coordination [2]. The bridging ligand in **I** undergoes nucleophilic attack either at the iminium carbon or at the adjacent α-C position [3], in place of the 1,4 conjugated addition normally observed in α,β unsaturated iminium species [4]. A further distinctive feature, that is consequence of the bridging coordination, is the α C–H activation, which cannot be accomplished in conjugated iminium species [5]. Removal of the α C–H proton generates very reactive intermediate, which can be trapped upon reactions with a variety of reagents, such as arylisocyanides [6], diazoacetates, [7], disulfides [8], and group 16 elements [9]. These reactions, resulting in the formation of C–C or C-heteroatom bonds, lead to the transformation of the bridging frame into more complex structures of potential synthetic interest.

In the course of these investigations concerning the α functionalization of μ-vinyliminium ligand, we found an unexpected result

consisting in the formation and incorporation of a methylcarboxylate unit into the bridging C₃ frame, that is hereafter detailed.

2. Results and discussion

Treatment of complex $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)=C(H)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1**) with NaH in the presence of $H_2C=C=CMe_2$ followed by chromatography on alumina column with CH_3OH, led to the formation of complex **2** in about 55% yield (Scheme 2).
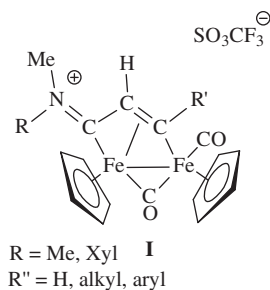
In Scheme 2, the carbon atoms of the bridging vinyliminium chain have been numbered in order to clearly distinguish them in the product **2**. The reaction, aimed to investigate the possibility of assembling allenes with μ-vinyliminium ligands, was suggested by several examples of allene incorporation into bridging hydrocarbyl ligands [10]. Conversely, in this case the allene is not involved; and the reaction consists in the incorporation of a carboxylate group, resulting, presumably, from the assembly of CO and MeO⁻ units.

Complex **2** has been characterized by IR and NMR spectroscopy, elemental analysis and X-ray diffraction. The ORTEP molecular diagram is shown in Fig. 1, whereas relevant bond lengths and angles are reported in Table 1; two independent molecules are present in the asymmetric unit. The structure can be described as being composed by a *cis*-$Fe_2(Cp)_2(\mu\text{-}CO)$ unit to which is bound a bridging allylidene ligand (C^1–C^2–C^3), containing one amino and one carboxylate substituent. The overall fragment behaves as a six-electron donor towards the metal centres, through the carbon

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Scheme 1.

atoms of the allylidene chain and the oxygen of the carbonyl function. More precisely, the bridging C_3 unit is σ-coordinated to Fe (2) [Fe(2)–C(12) 1.940(5) Å] and η^3-coordinated to Fe(1) [Fe(1)–C (12) 2.096(4) Å; Fe(1)–C(13) 2.005(4) Å; Fe(1)–C(14)-2.145(4) Å], in an allyl-like fashion; in agreement with this, the C(12)–C(13) and C (13)–C(14) interactions [1.428(6) and 1.441(6) Å, respectively], corresponding to C^1–C^2 and C^2–C^3 in Scheme 2, are very similar. The carboxylic ester group is O-coordinated to Fe(2) [Fe(2)–O(15) 2.022(3) Å] and, therefore, the C(15)–O(15) interaction [1.235(5) Å] appears slightly elongated respect to a pure double bond. The C (12)–N(1) length [1.377(6) Å] suggests the loss of the π-character of the C^1–N bond present in the parent vinyliminium species. Finally, the stereochemistry of the amino group is worthy of comment. In fact, this group is oriented such that the bulkier Xyl substituent points in the opposite side respect to the Cp ligands, close to the less cumbersome C^2–H. This situation resembles what usually found in vinyliminium complexes bearing a α C–H, even though these have a different structures compared to **2** [2].

The IR spectrum of **2** (in CH_2Cl_2 solution) shows two ν-CO bands, attributable to the bridging carbonyl (at 1726 cm^{-1}) and to the acyl fragment (at 1590 cm^{-1}), respectively. The ^{1}H NMR spectrum exhibits one single set of resonances. Major features of the ^{13}C NMR spectrum are represented by the resonances of the C^1, C^2 and C^3 carbons, which fall at δ 205.6, 74.1, 151.6 ppm, respectively.

The formation of **2** deserves a few comments. First, this seems to be the result of a non-defined sequence of steps, that include insertion of CO into the metal-vinyliminium bond and addition of MeO$^-$. This latter is most likely originated from methanol used as eluent in the alumina chromatography. According to these observations, any involvement of CH_2CCMe_2 should be excluded. However, in the absence of the allene the reaction has a different outcome: as previously reported, treatment of **1** with NaH affords selectively the metallacycle **3** (Scheme 3) [5].

Common feature in the reactions shown in Schemes 2 and 3 is the assembling of CO and vinyliminium ligands; on the other hand, a major difference consists in the fact that the dinuclear frame remains intact in the reaction leading to **2**, whereas **3** results from cleavage of the Fe–Fe bond and fragmentation of the dinuclear complex. Indeed, five-membered metallacycles, similar to **3**, have been observed in a number of cases as products of deprotonation or
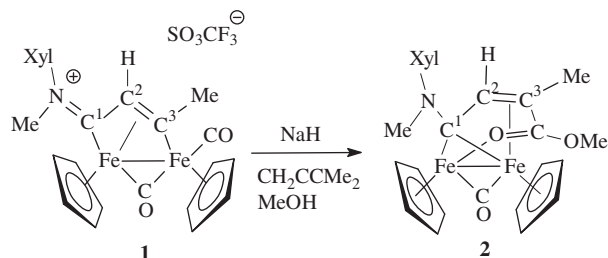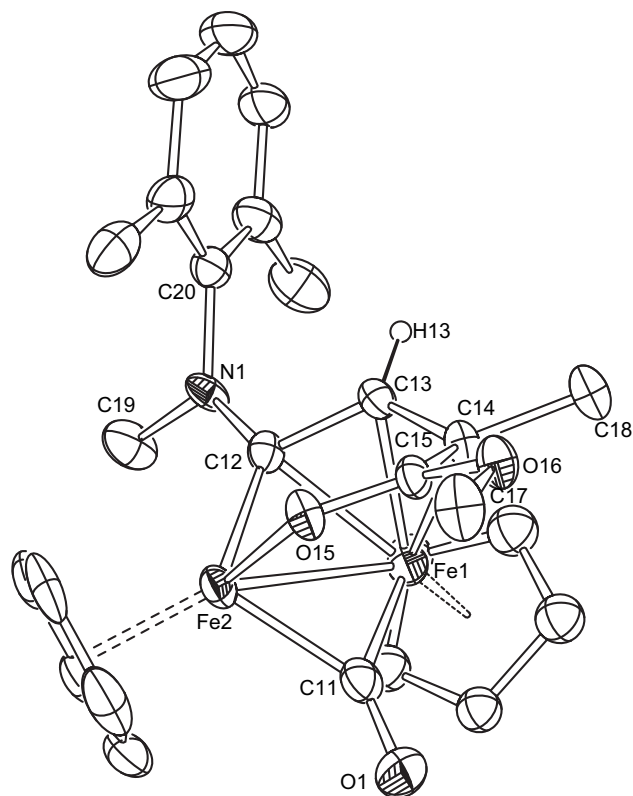

Fig. 1. Molecular structure of one of the two independent molecules of **2**, with key atoms labelled (all H atoms, except H(13), have been omitted). Thermal ellipsoids are at the 30% probability level. Only the main image of the disordered Cp bound to Fe(1) is drawn.

reduction of μ-vinyliminium species [5,9,11]. Conversely, intramolecular rearrangements involving CO and bridging C_3 ligands in diiron complexes, without affecting the dinuclear frame, are less common. Examples include the complex [Fe₂{μ-PPh₂}(μ-η^1:η^2–(H)

Table 1
Selected bond lengths (Å) and angles (°) for **2**.

Fe(1)–Fe(2)	2.5614(10)	Fe(3)–Fe(4)	2.5511(10)
Fe(1)–C(11)	1.907(5)	Fe(3)–C(41)	1.895(5)
Fe(2)–C(11)	1.899(5)	Fe(4)–C(41)	1.901(5)
Fe(1)–C(12)	2.096(4)	Fe(3)–C(42)	2.110(4)
Fe(2)–C(12)	1.940(5)	Fe(4)–C(42)	1.942(5)
Fe(1)–C(13)	2.005(4)	Fe(3)–C(43)	1.993(4)
Fe(1)–C(14)	2.145(4)	Fe(3)–C(44)	2.114(4)
Fe(2)–O(15)	2.022(3)	Fe(4)–O(45)	2.019(3)
C(11)–O(1)	1.204(6)	C(41)–O(41)	1.176(6)
C(12)–N(1)	1.377(6)	C(42)–N(2)	1.380(6)
C(12)–C(13)	1.428(6)	C(42)–C(43)	1.415(6)
C(13)–C(14)	1.441(6)	C(43)–C(44)	1.420(6)
C(14)–C(15)	1.436(6)	C(44)–C(45)	1.448(7)
C(15)–O(15)	1.235(5)	C(45)–O(45)	1.252(6)
C(15)–O(16)	1.340(5)	C(45)–O(46)	1.332(5)
O(16)–C(17)	1.453(5)	O(46)–C(47)	1.449(6)
Fe(1)–C(12)–Fe(2)	78.70(18)	Fe(3)–C(42)–Fe(4)	77.92(17)
Fe(2)–C(12)–C(13)	117.0(3)	Fe(4)–C(42)–C(43)	116.9(4)
C(12)–C(13)–C(14)	122.7(4)	C(42)–C(43)–C(44)	123.6(5)
C(13)–C(14)–C(15)	116.5(4)	C(43)–C(44)–C(45)	116.5(4)
C(14)–C(15)–O(15)	125.6(4)	C(44)–C(45)–O(45)	124.9(4)
C(14)–C(15)–O(16)	113.8(4)	C(44)–C(45)–O(46)	115.4(4)
O(15)–C(15)–O(16)	120.5(4)	O(45)–C(45)–O(46)	119.8(4)
C(15)–O(15)–Fe(2)	117.8(3)	C(45)–O(45)–Fe(4)	117.1(3)
C(12)–N(1)–C(19)	123.6(4)	C(42)–N(2)–C(49)	123.7(4)
C(12)–N(1)–C(20)	120.8(4)	C(42)–N(2)–C(50)	121.7(4)
C(19)–N(1)–C(20)	115.1(4)	C(49)–N(2)–C(50)	113.8(4)
C(13)–C(14)–C(18)	118.4(4)	C(43)–C(44)–C(48)	119.8(4)
C(15)–C(14)–C(18)	116.8(4)	C(15)–C(14)–C(18)	115.4(4)

Scheme 2.