Journal of Organometallic Chemistry 693 (2008) 3191–3196

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

SPh functionalized bridging-vinyliminium diiron and diruthenium complexes

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ARTICLE INFO

Article history:
Received 23 June 2008
Received in revised form 14 July 2008
Accepted 14 July 2008
Available online 19 July 2008

Keywords:
Vinyliminium
Zwitterionic complexes
Disulfides
Diiron complexes

ABSTRACT

The SPh functionalized vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')=C_\beta(SPh)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R′ = Me, **2a**; R = Me, R′ = Me, **2b**; R = 4-C_6H_4OMe, R′ = Me, **2c**; R = Xyl, R′ = CH_2OH, **2d**; R = Me, R′ = CH_2OH, **2e**; Xyl = 2,6-$Me_2C_6H_3$] are generated in high yields by treatment of the corresponding vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')=C_\beta(H)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1a**–**e**) with NaH in the presence of PhSSPh. Likewise, the diruthenium complex $[Ru_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Me)=C_\beta(SPh)C_\alpha=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**2f**) was obtained from the corresponding vinyliminium complex $[Ru_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Me)=C_\beta(H)C_\alpha=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**1f**). The synthesis of **2c** is accompanied by the formation, in comparable amounts, of the aminocarbyne complex $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4OMe)\}(SPh)(\mu\text{-}CO)(CO)(Cp)_2]$ (**3**).
The molecular structures of **2d**, **2e** and **3** have been determined by X-ray diffraction studies.

1. Introduction

Bridging vinyliminium complexes **1** [1] (Scheme 1) exhibit a remarkable reactivity, which results from the combination of two distinct features: the presence of an iminium group and the bridging coordination of the organic frame. Indeed, both iminium activation [2] and transformation of multiside bound organic frames [3] represent topics of current interest, for their effectiveness in providing new reactions and improved synthetic strategies. We exploited these activation effects to transform bridging vinyliminium ligands into new multifunctional coordinated species through new and unconventional reaction routes. These include proton removal from the C_β-H in the presence of 'trapping' reagents, such as diazocompounds or group 16 elements. The reactions led to the formation of diazine-bis alkylidenes **I** [4], and zwitterionic complexes **II** [5], respectively (Scheme 1).

Herein we report an extension of these studies, aimed at investigating the deprotonation of vinyliminium complexes in the presence of PhSSPh.

In order to study the influence that the substituents R and R′ exert on the reactivity of the complexes **1**, a number of different vinyliminium complexes have been investigated. Moreover, the study includes a diruthenium vinyliminium complex, in order to evidence possible effects due to the nature of the metal atom.

2. Results and discussion

The vinyliminium complexes **1a**–**f** react with NaH, in THF at room temperature, in the presence of PhSSPh, affording the corresponding phenylthiolate derivatives **2a**–**f** in about 70–80% yields (Scheme 2).

Complexes **2a**–**f**, were purified by alumina chromatography and characterized by spectroscopy and elemental analysis. Moreover, the molecular structures of **2d** and **2e** have been ascertained by X-ray diffraction studies: the ORTEP molecular diagrams are shown in Figs. 1 and 2, whereas the most relevant bond distances and angles are reported in Table 1, where they are compared with a typical C_β substituted vinyliminium complex, i.e. *cis*-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Me)=C_\beta(Me)C_\alpha=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**III**) [1b]. A hydrogen bond exists in both structures between the C_γ-CH_2OH hydroxo group and one oxygen atom of the $[CF_3SO_3]^-$ anion [O(1)···O(10)#1 2.833(10) Å, O(1)–H(100) 0.832(11) Å, H(100)···O(10)#1 2.07(5) Å, O(1)–H(100)–O(10)#1 153(11)° for **2d**; O(1)···O(10)#1 2.861(13) Å, O(1)–H(1A) 0.81(2) Å, H(1A)···O(10)#1 2.07(3) Å, O(1)–H(1A)–O(10)#1 164(8)° and O(1)···O(30′)#1 2.681(16) Å, O(1)–H(1A) 0.81(2) Å, H(1A)···O(30′)#1 2.01(6) Å, O(1)–H(1A)–O(30′)#1 140(8)° for **2e**]. As it can be evinced from Table 1, the bonding parameters for both **2d** and **2e** are in perfect agreement with those previously reported for other vinyliminium complexes bearing a substituent on C_β, [1b,5,6] confirming the usual $\mu\text{-}\eta^1:\eta^3$-coordination to the diiron frame of the unsaturated C_3 unit. In particular the Fe(2)–C(15) [1.868(12) and 1.841(5) Å for **2d** and **2e**, respectively] and C(15)–N(1) [1.279(11) and 1.287(7) Å for **2d** and **2e**, respectively]

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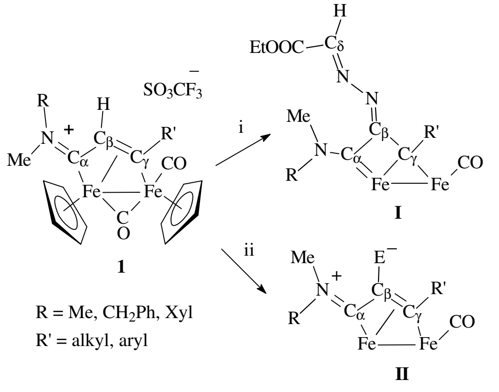
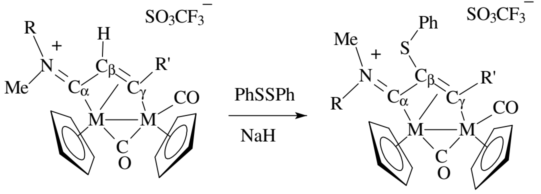
0022-328X/$ - see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2008.07.009



R = Me, CH_2Ph, Xyl
R' = alkyl, aryl

i: NaH, $N_2CH(COOEt)$; ii: NaH, E (E = O, S, Se).

Scheme 1. Ancillary μ-CO and Cp ligands in I and II have been omitted for clarity.



	M	R	R'	
1a	Fe	Xyl	Me	**2a**
1b	Fe	Me	Me	**2b**
1c	Fe	4-C_6H_4OMe	Me	**2c**
1d	Fe	Xyl	CH_2OH	**2d**
1e	Fe	Me	CH_2OH	**2e**
1f	Ru	Xyl	Me	**2f**

Scheme 2.

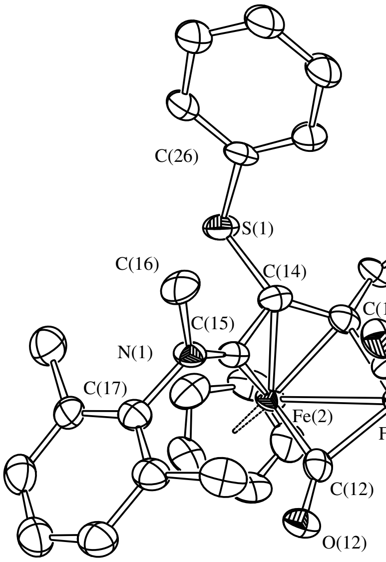


Fig. 1. Molecular structure of $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(CH_2OH){=}C_\beta(SPh)\text{-}C_\alpha{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**2d**), with key atoms labeled (all H-atoms, except H(100), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

interactions display some π-charater in agreement with the partial aminocarbene nature of the ligand. Moreover, in keeping with previous findings, the *N*-substituents in **2d** adopt the *Z*-configuration in order to avoid steric repulsion with the –SPh group.

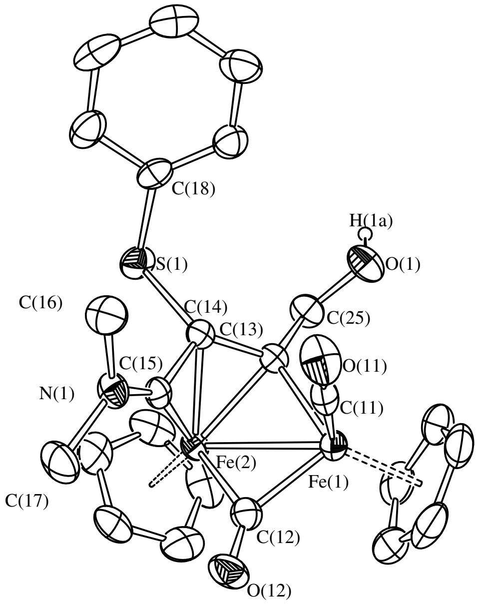


Fig. 2. Molecular structure of $[Fe_2\{\mu\text{-}\ \eta^1:\eta^3\text{-}C_\gamma(CH_2OH){=}C_\beta(SPh)C_\alpha{=}N(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**2e**) with key atoms labeled (all H-atoms, except H(1a), have been omitted for clarity). Thermal ellipsoids are at the 30% probability level.

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

	2d	**2e**	**III**
Fe(1)–Fe(2)	2.558(2)	2.5460(11)	2.562(1)
Fe(1)–C(11)	1.742(12)	1.763(7)	1.750(9)
Fe(1)–C(12)	1.877(11)	1.891(6)	1.894(8)
Fe(2)–C(12)	1.961(11)	1.965(6)	1.944(8)
Fe(1)–C(13)	1.944(10)	1.959(5)	1.955(7)
Fe(2)–C(13)	2.051(10)	2.032(5)	2.035(7)
Fe(2)–C(14)	2.044(10)	2.034(5)	2.080(7)
Fe(2)–C(15)	1.868(12)	1.841(5)	1.839(7)
C(11)–O(11)	1.144(11)	1.134(8)	1.150(9)
C(12)–O(12)	1.195(10)	1.164(7)	1.181(9)
C(13)–C(14)	1.447(12)	1.428(8)	1.39(1)
C(14)–C(15)	1.454(13)	1.433(7)	1.43(1)
C(13)–C(25)	1.511(12)	1.509(7)	
C(25)–O(1)	1.399(10)	1.413(8)	
C(14)–S(1)	1.795(10)	1.800(5)	
C(15)–N(1)	1.279(11)	1.287(7)	1.314(8)
N(1)–C(16)	1.479(11)	1.450(8)	1.478(9)
N(1)–C(17)	1.452(12)	1.472(8)	1.454(8)
C(14)–C(13)–Fe(1)	119.0(8)	119.0(4)	121.8(5)
C(13)–C(14)–C(15)	117.4(10)	116.2(5)	155.5(6)
N(1)–C(15)–C(14)	133.4(10)	133.7(5)	131.3(7)
O(1)–C(25)–C(13)	107.5(8)	107.4(5)	
Sum angles at N(1)	359.3(16)	359.9(9)	360.0(9)

The most relevant bonding parameters of the C_β substituted vinyliminium complex *cis*-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Me){=}C_\beta(Me)C_\alpha{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**III**) [1b] are reported as well for sake of comparison.

The overall result of the reaction shown in Scheme 1 consists in the replacement of the C_β-H hydrogen with the SPh group. It should be noted that an alternative route to the introduction of a thiolate functionality in the bridging ligand is provided by two distinct reaction steps: (a) generation of the zwitterionic species **II**; (b) alkylation of the S atom (Scheme 3) [6].

Compared to the latter procedure, the reaction with PhSSPh has the advantage of being a direct, single step synthesis.

Concerning the spectroscopic properties of **2a**–**f**, these are consistent with the structures found in solid and very similar to those of the complexes of type **IV**, recently reported [6]. In particular, the IR spectra of **2a**–**f** show the usual ν-CO band pattern consisting of