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Journal of Organometallic Chemistry 693 (2008) 57–67
Journal of Organometallic Chemistry
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Olefin–aminocarbyne coupling in diiron complexes: Synthesis of new bridging aminoallylidene complexes

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Received 21 September 2007; received in revised form 9 October 2007; accepted 9 October 2007
Available online 13 October 2007

Abstract

The bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; Xyl, **1b**; 4-C_6H_4OMe, **1c**; Xyl = 2,6-$Me_2C_6H_3$) react with acrylonitrile or methyl acrylate, in the presence of Me_3NO and NaH, to give the corresponding μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(N(Me)(R))C_\beta(H)C_\gamma(H)(R')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Me, R′ = CN, **3a**; R = Xyl, R′ = CN, **3b**; R = 4-C_6H_4OMe, R′ = CN, **3c**; R = Me, R′ = CO_2Me, **3d**; R = 4-C_6H_4OMe, R′ = CO_2Me, **3e**). Likewise, **1a** reacts with styrene or diethyl maleate, under the same reaction conditions, affording the complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = H, R″ = C_6H_5, **3f**; R′ = R″ = CO_2Et, **3g**). The corresponding reactions of $[Ru_2\{\mu\text{-}CN(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1d**) with acrylonitrile or methyl acrylate afford the complexes $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(N(Me)(CH_2Ph))C_\beta(H)C_\gamma(H)(R')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = CN, **3h**; CO_2Me, **3i**), respectively.

The coupling reaction of olefin with the carbyne carbon is regio- and stereospecific, leading to the formation of only one isomer. C–C bond formation occurs selectively between the less substituted alkene carbon and the aminocarbyne, and the C_β–H, C_γ–H hydrogen atoms are mutually *trans*.

The reactions with acrylonitrile, leading to **3a**–**c** and **3h** involve, as intermediate species, the nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NC\text{–}CH{=}CH_2)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Me, **4a**; M = Fe, R = Xyl, **4b**; M = Fe, R = 4-C_6H_4OMe, **4c**; M = Ru, R = $CH_2C_6H_5$, **4d**).

Compounds **3a**, **3d** and **3f** undergo methylation (by $CH_3SO_3CF_3$) and protonation (by HSO_3CF_3) at the nitrogen atom, leading to the formation of the cationic complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(N(Me)_3)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **5a**; R = CO_2Me, **5b**; R = C_6H_5, **5c**) and $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(N(H)(Me)_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **6a**; R = CO_2Me, **6b**; R = C_6H_5, **6c**), respectively.

Complex **3a**, adds the fragment $[Fe(CO)_2(THF)(Cp)]^+$, through the nitrile functionality of the bridging ligand, leading to the formation of the complex $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CNFe(CO)_2Cp)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**9**).

In an analogous reaction, **3a** and $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$, in the presence of Me_3NO, are assembled to give the tetrameric species $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CN[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2])\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Me, **10a**; R = Xyl, **10b**; R = 4-C_6H_4OMe, **10c**).

The molecular structures of **3a** and **3b** have been determined by X-ray diffraction studies.
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Keywords: Aminocarbyne; Dinuclear complexes; Allylidene; Coupling reactions; C–C bond formation

1. Introduction

Coupling reactions between bridging alkylidyne or alkylidene ligands (C_1 ligands) with small organic molecules (typically alkynes and, at a lower extent, alkenes) provide valuable routes to the C–C bond formation in dinuclear complexes [1]. These reactions, which take advantage of distinct reactivity patterns due to the bridging coordination, lead to synthesis of new multisite-bound hydrocarbyl ligands otherwise unattainable [2], and also offer helpful models for investigating the C–C bond

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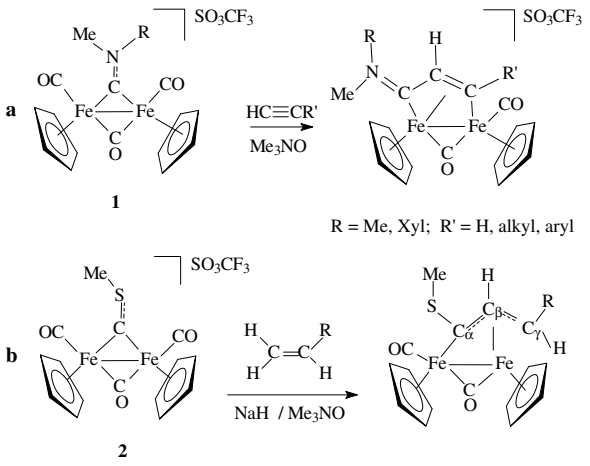
doi:10.1016/j.jorganchem.2007.10.015



Scheme 1.

formation steps relevant to the hydrocarbon chain growth in the Fischer Tropsch chemistry [3].

Our work in the field has been focused on the reactions of bridging amino- and thiocarbyne complexes with alkynes and alkenes. In particular, we have investigated the coupling between alkynes and the μ-aminocarbyne ligand in **1**, leading to the formation of μ-vinyliminium (azoniabutadienyl) complexes (Scheme 1a) [4]. Consequent studies revealed that the vinyliminium ligand can be further modified by the addition of carbon nucleophiles like acetylides [5] or cyanide [6], generating bridged fragments of increased complexity.

More recently we have described the coupling between the bridging thiocarbyne ligand in complex **2** and activated olefins, leading to the formation of new bridging thiomethylallylidene complexes (Scheme 1b) [7].

In these coupling reactions alkynes and alkenes behave differently: the reaction of **1** with alkynes simply consists of the alkyne insertion in the metal carbyne–carbon bond (Scheme 1a), whereas the coupling of the thiocarbyne ligand with olefins requires a deprotonation step (Scheme 1b).

The nature of the heteroatom (S or N) on the μ-carbyne ligand also exerts some influence on the reactivity. In general, bridging thio- and aminocarbyne ligands display similar properties, in that both contain a π donor heteroatom which provides stabilization to the adjacent carbyne carbon. However, the extent of π-interaction is different in the two ligands and this leads, in some cases, to different reaction profiles [8]. As an example, the alkyne insertion in **1** shown in Scheme 1a, does not take place on the thiocarbyne complex **2**, neither on its acetonitrile derivative. Thereby, predictions of the reactivity of **1** based upon the reactions observed for **2**, or vice versa, are often unreliable.

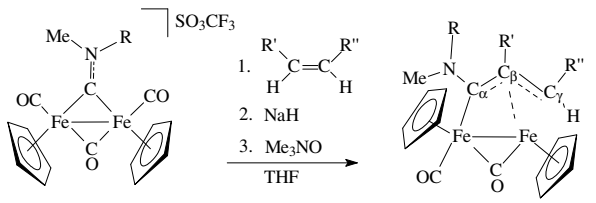
Herein we report on the successful attempt to extend the coupling reaction with olefins to the aminocarbyne complexes **1** and on further modifications of the bridging ligand consequently formed.

2. Results and discussion

The bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; Xyl, **1b**; 4-C_6H_4OMe, **1c**; Xyl = 2,6-$Me_2C_6H_3$) react with olefins (methyl acrylate, acrylonitrile, styrene, diethyl maleate), in THF solution at room temperature, in the presence of Me_3NO/NaH, to give the corresponding μ-allylidene complexes **3a**–**g** in 70–80% yields (Scheme 2).

The reaction parallels that of the thiocarbyne complex **2** with olefins: in both cases the carbyne–alkene coupling requires the displacement of a CO ligand and the presence of NaH in order to remove a proton from the olefin. However, significant differences have been evidenced in the stereochemistry of the reaction products, which concern the mutual orientation of the Cp ligands and will be discussed later.

Compounds **3a**–**g** were purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structures of **3a** and **3b** have been determined by X-ray diffraction. The ORTEP diagrams are shown in Figs. 1 and 2, while the main bond lengths and angles are reported in Table 1. The bonding parameters of the bridging ligand can be evaluated with respect to other C_3-bridging ligands present in closely related diiron complexes (Table 2). In particular, **3a**–**b** are to be compared with the μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Tol)CH{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [9] (Chart 1, **I**), and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(SMe)C(H)C(H)(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [7] (Chart 1, **II**). This analysis points out a close similarity in the bonding situation of **3a**–**b**, **I**, and **II** indicating that the μ-η^1:η^3-C(N(Me)(R))C(H)C(H)(CN) [R = Me, **3a**; Xyl, **3b**] ligand acts mainly as a bridging allylidene, as inferable also from the fact that both the C–C bonds within the ligand [C_α–C_β 1.434(4) Å, C_β–C_γ 1.432(4) Å in **3a**; C_α–C_β 1.416(3) Å, C_β–C_γ 1.435(3) Å in **3b**] and the Fe–C interactions between the ligand and the diiron frame [Fe(2)–C(13) 2.094(3), Fe(2)–C(14) 2.012(3), Fe(2)–C(15) 2.051(3) in **3a**; Fe(2)–C(13) 2.179(2), Fe(2)–C(14) 2.023(2), Fe(2)–C(15) 2.058(2) in **3b**] are very similar. It is noteworthy that in **3a**–**b** the two hydrogen atoms



	R	R'	R"	
1a	Me	H	CN	**3a**
1b	Xyl	H	CN	**3b**
1c	4-C_6H_4OMe	H	CN	**3c**
1a	Me	H	CO_2Me	**3d**
1c	4-C_6H_4OMe	H	CO_2Me	**3e**
1a	Me	H	C_6H_5	**3f**
1a	Me	CO_2Et	CO_2Et	**3g**

Scheme 2.

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