

Preliminary communication

Synthesis of η^1 -butadienyl iron complex upon coupling of two organometallic η^1 -vinyl units and selective decomplexation at one end

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Abstract

The symmetric binuclear iron μ -bis(ethylidene) complex $[\text{Cp}^*(\text{dppe})\text{Fe}(=\text{CHCH}_2\text{CH}_2\text{CH}=\text{)}\text{Fe}(\text{dppe})\text{Cp}^*][\text{PF}_6]_2$ (**2**) reacts with the equivalent of two KO^tBu in THF to provide the mononuclear η^1 -butadienyl complex $\text{Cp}^*(\text{dppe})\text{Fe}(\text{CH}=\text{CH}-\text{CH}=\text{CH}_2)$ (**4**) isolated in 76% yield. © 1998 Elsevier Science S.A. All rights reserved.

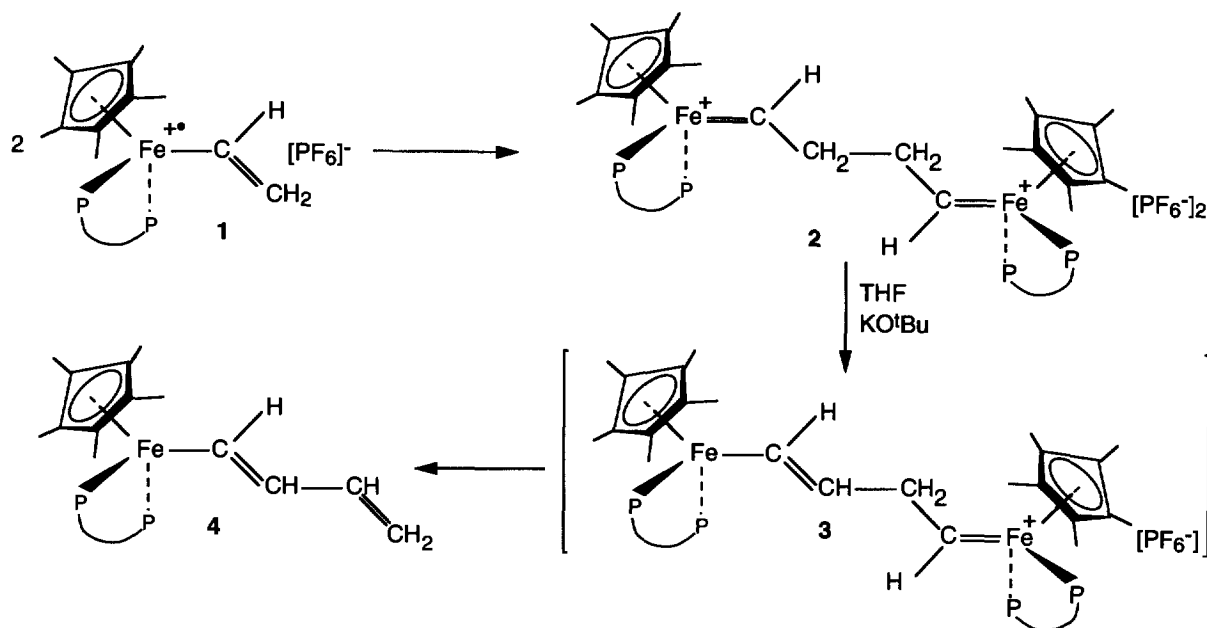
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The formation of new carbon–carbon bonds is one of the most important objectives in organo-transition metal chemistry. The dimerization by ligand–ligand coupling via 17-electron transition metal radicals constitutes one of the possible reactions to reach this goal [1,2]. This behavior is fairly broad and the coupling through the ligand can be achieved with complex possessing of unsaturated hydrocarbon ligands such as *inter alia* cyclopentadienyl [3], cyclooctatetraene [4,5], vinylidene [6], alkynyl [7] or dienyl [8]. However, the products formed in this way are symmetric by nature, and this constitutes the principal limitation of this type of C–C bond formation.

Recently, we found that the 17-electron iron(III) vinyl radical cation $[\text{Cp}^*\text{Fe}(\text{dppe})(\text{CH}=\text{CH}_2)]^+$ (**1**) duplicates in solid state to give the stable bis(carbene) complex $[\text{Cp}^*(\text{dppe})\text{Fe}(=\text{CHCH}_2\text{CH}_2\text{CH}=\text{)}\text{Fe}(\text{dppe})\text{Cp}^*][\text{PF}_6]_2$ (**2**) isolated with quite a good yield [9]. The high thermal stability of the μ -bis(ethylidene) **2** is very

unique among the non-heteroatom stabilized carbene derivatives of the first row transition metals [10–12] and even in comparison with isostructural analog of the third row transition metals [13]. This chemical inertness is obviously associated with a loss of the electrophilic reactivity usually observed with these types of carbene derivatives [11]. Thus, the binuclear carbene complex **2** and its mononuclear analog $[\text{Cp}^*(\text{dppe})\text{Fe}(=\text{CHCH}_3)] [\text{PF}_6]_2$ do not react with alkene or phosphane to yield cyclopropane or phosphonium derivatives respectively. This unusual chemical behavior offered us a unique opportunity to find a route towards a mononuclear derivative with a four carbon ligand by selective removal of one of the σ -bound terminal $\text{Cp}^*\text{Fe}(\text{dppe})$ units. This chemistry constitutes an independent and complementary work to our project on the formation of new carbon–carbon bonds by ligand–ligand coupling of 17-electron radicals. Indeed, despite the high yield of the coupling reactions, the interest of this synthetic approach may remain limited without chemical routes to selectively remove the capping groups in the symmetric binuclear compounds. In this communication we report the first step toward this goal.

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Scheme 1.

The bis(ethylidene) complex **2** prepared as previously described was reacted with two equivalent potassium *tert*-butoxides in THF at -80°C . Upon warming to 20°C , the initially brown solution turned progressively yellow over 1 h. After removal of the solvent and pentane extraction, a red–orange powder corresponding to the iron η^1 -butadienyl complex $\text{Cp}^*(\text{dppe})\text{Fe}(\text{CH}=\text{CH}-\text{CH}=\text{CH}_2)$ (**4**) was obtained in 76% yield (Scheme 1). Further recrystallization from pentane at -20°C provided an analytically pure compound. Under the above-mentioned conditions, the use of one equivalent of potassium *tert*-butoxide resulted in incomplete conversion of **2**. Complex **4** was characterized by mass spectrometry, multinuclear magnetic resonance spectroscopy and cyclic voltammetry.

The formation of **4** should proceed through a one-proton abstraction reaction with KO^tBu providing the vinyl-carbene **3** as a putative intermediate. A subsequent 1,2-hydride migration at the carbene side yields the butadienyl ligand. Similar migrations in monomeric alkylidene complexes are well known [14,15]. It has also been established that this process is accelerated by the presence of an electron releasing substituent at the C_β position [16–19] and it is anticipated that the first deprotonation should increase the electron density on the C_β atom of the remaining alkylidene fragment. As a consequence, the intramolecular hydride shift occurs faster than the intermolecular second deprotonation, even if the reaction is carried out with 5-fold excess of the base. After the hydride migration step, the decoordination of the iron building block from the $\text{C}=\text{C}$ double bond should be a favored process. Indeed, the

bulky $\text{Cp}^*\text{Fe}(\text{dppe})$ unit has never been observed to be coordinated in the η^2 -mode with any unsaturated C_2 ligands. In particular, it was observed that the stable 16-electron species $[\text{Cp}^*\text{Fe}(\text{dppe})][\text{PF}_6]$ does not react in THF with ethylene [20]. Moreover, under the experimental conditions, the in situ generated $[\text{Cp}^*\text{Fe}(\text{dppe})]^+$ fragment reacts with the second equivalent of KO^tBu to decompose. The first step of the proposed mechanism is supported by the easy deprotonation of the Fischer-type bis(carbene) compound $[\text{Cp}^*(\text{dppe})\text{Fe}\{\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{OCH}_3)=\}\text{Fe}(\text{dppe})\text{Cp}^*][\text{PF}_6]_2$ (**5**) with two equivalents of KO^tBu in similar conditions. In this case, the vinyl-heterocarbene intermediate resulting from the first deprotonation is stable enough to undergo a second proton abstraction and the expected symmetric dimer $[\text{Cp}^*(\text{dppe})\text{Fe}\{\text{C}(\text{OCH}_3)-\text{CH}=\text{CH}-\text{C}(\text{OCH}_3)=\}\text{Fe}(\text{dppe})\text{Cp}^*]$ with the dimethoxybutadiendiyl bridge is isolated almost quantitatively [21].

The new air-sensitive complex **4** shows the characteristic ^1H NMR resonances for the C_4 η^1 -coordinated ligand: a broad doublet at δ 7.96 (C_6D_6 , TMS) with $^3J(\text{HH})$ of 16.4 Hz, a doublet of doublets at δ 5.63 with $^3J(\text{HH})$ of 16.2 and 16.4 Hz, a double triplet at δ 6.71 with $^3J(\text{HH})$ of 16.2 and 10 Hz, and doublet at δ 4.49 with $^3J(\text{HH})$ of 10 Hz corresponding to the proton bound to the α - δ carbon atoms respectively. In the ^{13}C NMR spectrum, the α - δ carbon resonances of the butadienyl ligand are observed at δ 180.6, 146.5, 144.2 and 99.8 respectively. The high resolution FAB mass spectral analysis of a sample of **4** dissolved in *meta*-nitrobenzyl alcohol (*m*-NBA) shows the expected

molecular pic for this mononuclear complex ($M_{\text{calc}} = 642.2267$; $M_{\text{found}} = 642.2253$). The initial scan in the cyclic voltammogram of **4** from -1 to $+0.7$ V (versus SCE) at a platinum electrode (CH_2Cl_2 , 0.1 M tetrabutylammonium hexafluorophosphate, 20°C , 0.100 V s^{-1}) is characterized by an anodic wave with a well-defined current maximum and a cathodic wave almost reversible ($E_p^a = -0.32$ V, $E_p^c = -0.39$ V, $i^c/i^a = 0.6$). Comparison with the CV data of the vinyl iron complex **1** indicates that the electron density at the metal centers are very similar for both the vinyl and the butadienyl complexes. Moreover, the stabilities of the two 17-electron iron(III) radical cations $[\mathbf{1}]^+$ and $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{CH}=\text{CH}-\text{CH}=\text{CH}_2)]^+$ ($[\mathbf{4}]^+$) are not significantly different [9].

To our knowledge, it is the first time that an organometallic complex with a butadienyl ligand has been obtained by a C_2 ligand–ligand coupling and subsequent cleavage of one organometallic terminal fragment [22]. This synthesis of the new electron-rich complex **4** is easy to carry out and proceeds quickly. From its redox properties access to the μ -octatetrenediyl-bridged binuclear complex $[\text{Cp}^*(\text{dppe})\text{Fe}(\text{=CH}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}=\text{Fe}(\text{dppe})\text{Cp}^*)][\text{PF}_6]_2$ could be an accessible synthetic target upon an oxidative coupling and will be the subject of future research in our group.

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