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Visible-light photolysis of [FeCp(η^6-toluene)][PF_6] as a clean, convenient and general route to iron-vinylidene and iron-acetylide complexes

Cátia Ornelas, Jaime Ruiz, Didier Astruc *

Institut des Sciences Moléculaires, UMR CNRS N° 5255, Université Bordeaux1, 33405 Talence Cedex, France

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This communication is dedicated to our friend Professor Dr. Chris Elschenbroich, an outstanding organometallic chemist, teacher and book author, at the occasion of his retirement.

Keywords:
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ABSTRACT

Visible-light photolysis of the cheap starting material [FeCp(η^6-toluene)][PF_6] (Cp=η^5-C_5H_5) using a simple 100-W globe in the presence of diphenyldiphosphinoethane (dppe) and terminal alkynes cleanly yields the vinylidene complexes [FeCp(dppe)(=C=CHR)][PF_6] and, upon further deprotonation, the iron-alkynyl complexes; the reaction is extended to ferrocenylacetylene to yield a bimetallic complex.

1. Introduction

In organoiron chemistry [1], the sandwich complexes [FeCp(η^6-arene)][PF_6] [2] occupy a large place because of their facile single-step large-scale synthesis from ferrocene and further iron-induced aromatic transformation [3]. Another application of these sandwich compounds is the visible-light photolysis, a source of the 12-electron fragment $CpFe^+$ leading, in CH_2Cl_2, to arene exchange and, in MeCN, to the synthesis of the piano–stool complexes [$CpFeL_2$(MeCN)][PF_6] [4]. We now find that, if the visible-light photolysis of [FeCp(η^6-toluene)][PF_6] using simply a 100-W globe is carried out in CH_2Cl_2 in the presence of dppe and a terminal alkyne, (i) the vinylidene complex [FeCp(dppe)(=C=CHR)][PF_6] is directly formed in high yield ; (ii) this reaction is clean and general, (iii) it is extended to 1,4-bis(ethynyl)benzene and ethynylferrocene; (iv) the mono- and bimetallic iron-vinylidene complexes are deprotonated to the neutral iron-alkynyl complexes.

Vinylidene complexes are an important class of organometallic complexes [5] that has been known for a long time and is involved in organometallic hydrocarbon transformation [6,7], catalysis [8] and molecular electronic of carbon chains [9] including mixed- and average–valence compounds [9,10]. Iron-vinylidene and alkenylidene complexes [Cp^*Fe(dppe)(=C=CHR)][PF_6] (with Cp^*=η^5-C_5Me_5), synthesized and studied by the group of Lapinte, are a very interesting organometallic family that has been used as mimics of molecular wires [10]. The parent complexes [CpFe(dppe)(=C=CHR)][PF_6] are also known but require a long, multi-step synthesis [11].

2. Results and discussion

Our first synthetic attempt was carried out using trimethylsilylacetylene. The CH_2Cl_2 solution of [FeCp(η^6-toluene)][PF_6], **1**, was irradiated with visible light overnight, and the solution changed from yellow to brown. After removal of CH_2Cl_2 and toluene *in vacuo*, [CpFe(dppe){=C=CH($SiMe_3$)}][PF_6], **2**, was the only remaining reaction product. Its ^{31}P NMR spectrum showed, besides the PF_6 peaks, only one peak at 97.0 ppm, confirming the consumption of dppe with a 1:1 stoichiometry. The brown iron-vinylidene complex **2** was deprotonated and deprotected to give the corresponding red iron-alkynyl complex **3** in THF using stoichiometric amounts of *t*-BuOK and *n*-Bu_4NF. The complex **3** was then separated from KPF_6 formed by extraction with ether or dichloromethane, and obtained in 99% yield (Scheme 1).

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* Corresponding author.
E-mail address: d.astruc@ism.u-bordeaux1.fr (D. Astruc).

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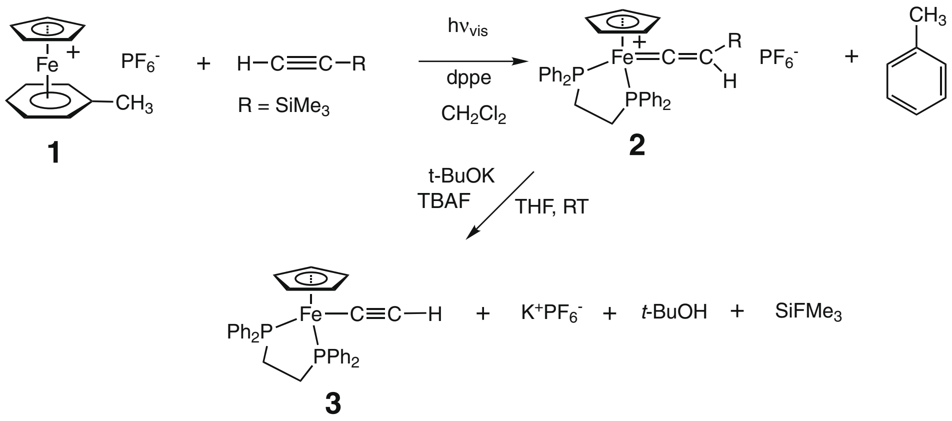


Scheme 1. Example of the visible-light generation of the 12-electron fragment $CpFe^+$ from $[FeCp(\eta^6\text{-toluene})][PF_6]$ for the clean synthesis, in the presence of a terminal alkyne, of vinylidene and alkynyl complexes.

Similarly, the brown bimetallic vinylidene complexes **4** and **6** were synthesized starting from 1,4-bis(ethynyl)benzene and ethynylferrocene, respectively. These complexes were also similarly deprotonated to quantitatively yield the corresponding brown alkynyl complexes **5** and **7** (Schemes 2 and 3). The complex **7** was characterized by standard spectroscopic and analytical techniques including the expected IR and ^{31}P NMR spectra (see Table 1 and end of this article) and mass spectrometry showing its molecular peaks at 1162.23 (Calc. for $C_{72}H_{62}P_4Fe_2$: 1162.86).

The vinylidene and alkynyl complexes were also characterized by cyclic voltammetry in dichloromethane [10,12]. The monoalkynyl complex **3** shows a reversible redox wave at 160 mV vs. $FeCp_2^*$ that corresponds to the oxidation of Fe^{II} to Fe^{III} of the iron-alkynyl complex. The symmetrical bisalkynyl complex **5** presents two reversible redox waves at 0 and 210 mV vs. $FeCp_2^*$, the difference of 210 mV between these two waves indicating a high electronic communication between the two metal centers that sharply contrasts with the lack of wave splitting observed in 1,4-bis(ferrocenylethynyl)benzene [12].

The alkynyl complex CpFe(dppe)C≡C–Fc, **7**, shows two completely reversible redox waves at 0 mV and 650 mV vs. $FeCp_2^*$. The first redox wave at 0 mV corresponds to the oxidation of the iron-alkynyl complex to the mixed-valence [13] complex $\mathbf{7}^+$ that has been reported by Sato [14], and the second wave corresponds to the oxidation of Fe^{II} to Fe^{III} of the ferrocenyl group.

In conclusion, a new, general route to iron-vinylidene and iron-alkynyl complexes has been disclosed and shown to be general and quantitative in a single-step by visible-light photolysis in dichloromethane of the cheap, easily available starting material $[FeCp(\eta^6\text{-toluene})][PF_6]$ in the presence of terminal alkynes.

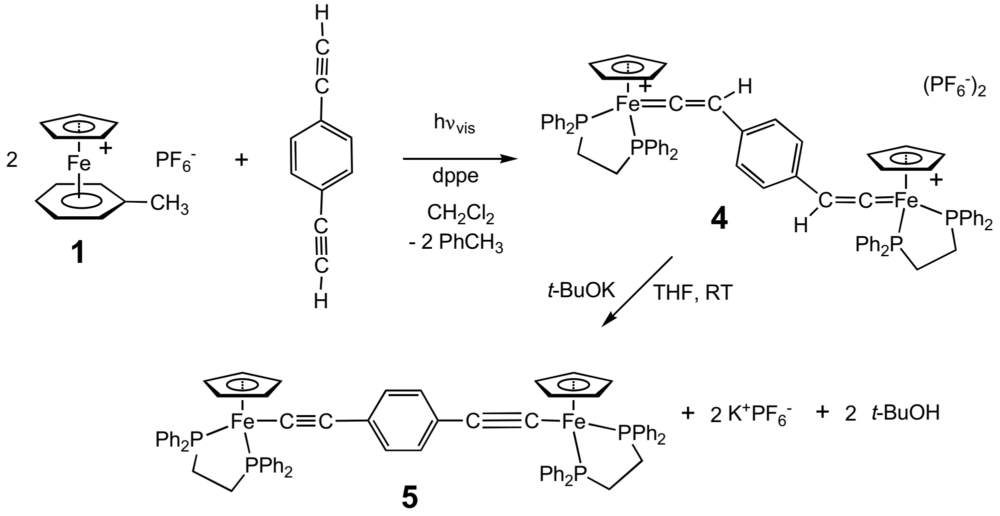
3. Spectroscopic and analytical data

*3.1. CpFe(dppe)C≡CH, **3***

^1H NMR ($CDCl_3$, 300 MHz): 7.90–7.14 (m, 20H, arom. C*H* of dppe), 4.21 (s, 5H, Cp), 2.72 and 2.26 (m, 4H, CH_2CH_2 of dppe), 1.86 (s, 1H, C≡C*H*). ^{13}C NMR ($CDCl_3$, 75.0 MHz): 142.4–127.1 (arom. of dppe), 112.1(C_β), 105.7 (C_α), 79.6 (Cp), 28.3 (CH_2 of dppe). ^{31}P NMR ($CDCl_3$, 121 MHz): 106.4 (Fe-dppe). MS (ESI *m/z*), Calc. for $C_{33}H_{30}P_2Fe$: 544.4. Found: M^+ 545.0. Anal. Calc. for $C_{33}H_{30}P_2Fe$: C, 72.81; H, 5.55. Found: C, 72.47; H, 5.41%. Infrared $\upsilon_{C\equiv C}$: 1918 cm^{-1}.

*3.2. 1,4-(CpFe(dppe)C≡C)$_2$C$_6$H$_4$, **5***

^1H NMR ($CDCl_3$, 300 MHz): 7.89–7.20 (m, 20H, arom. C*H* of dppe), 6.11 (s, 4H, C*H* of benzene bridge), 4.19 (s, 10H, Cp), 2.56 and 2.16 (m, 4H, CH_2CH_2 of dppe). ^{13}C NMR ($CDCl_3$, 75.0 MHz): 142.4–120.1 (arom.), 111.6 (C_β), 103.7 (C_α), 76.6 (Cp), 28.1 (CH_2 of dppe). ^{31}P NMR ($CDCl_3$, 121 MHz): 106.6 (Fe-dppe).



Scheme 2. Visible-light photolytic synthesis of binuclear vinylidene and alkynyl complexes from the precursor complex $[FeCp(\eta^6\text{-toluene})][PF_6]$.