



Visible-light photolysis of $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$ as a clean, convenient and general route to iron-vinylidene and iron-acetylide complexes

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ARTICLE INFO

Article history:

Received 28 August 2008

Received in revised form 29 September 2008

Accepted 30 September 2008

Available online 8 October 2008

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:

Vinylidene

Carbene

Acetylide

Photolysis

Iron

Sandwich complex

ABSTRACT

Visible-light photolysis of the cheap starting material $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$ ($\text{Cp}=\eta^5\text{-C}_5\text{H}_5$) using a simple 100-W globe in the presence of diphenyldiphosphinoethane (dppe) and terminal alkynes cleanly yields the vinylidene complexes $[\text{FeCp}(\text{dppe})(=\text{C}=\text{CHR})][\text{PF}_6]$ and, upon further deprotonation, the iron-alkynyl complexes; the reaction is extended to ferrocenylacetylene to yield a bimetallic complex.

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1. Introduction

In organoiron chemistry [1], the sandwich complexes $[\text{FeCp}(\eta^6\text{-arene})][\text{PF}_6]$ [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 $[\text{CpFeL}_2(\text{MeCN})][\text{PF}_6]$ [4]. We now find that, if the visible-light photolysis of $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$ 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 $[\text{FeCp}(\text{dppe})(=\text{C}=\text{CHR})][\text{PF}_6]$ 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-

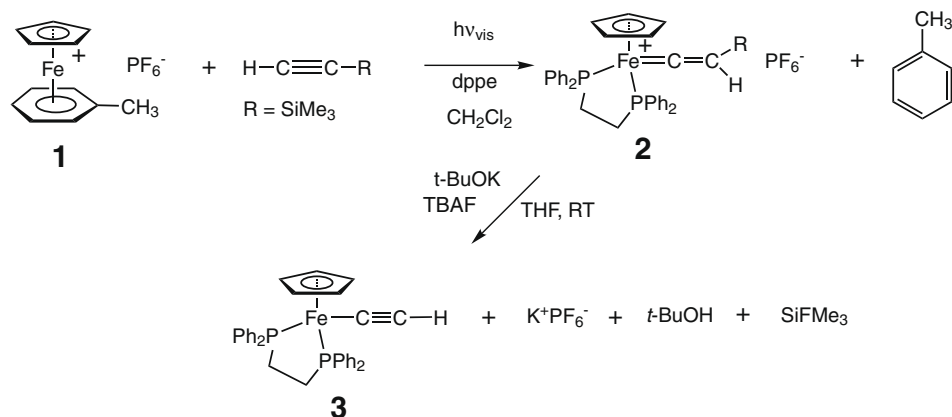
and average-valence compounds [9,10]. Iron-vinylidene and alkenylidene complexes $[\text{Cp}^+\text{Fe}(\text{dppe})(=\text{C}=\text{CHR})][\text{PF}_6]$ (with $\text{Cp}^+=\eta^5\text{-C}_5\text{Me}_5$), synthesized and studied by the group of Lapinte, are a very interesting organometallic family that has been used as mimics of molecular wires [10]. The parent complexes $[\text{CpFe}(\text{dppe})(=\text{C}=\text{CHR})][\text{PF}_6]$ 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 $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$, **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*, $[\text{CpFe}(\text{dppe})(=\text{C}=\text{CH}(\text{SiMe}_3))][\text{PF}_6]$, **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*-Bu₄NF. 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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Scheme 1. Example of the visible-light generation of the 12-electron fragment CpFe^+ from $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$ 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 $\text{C}_{72}\text{H}_{62}\text{P}_4\text{Fe}_2$: 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 $\text{CpFe}(\text{dppe})\text{C}\equiv\text{C}-\text{Fc}$, **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 **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 $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$ in the presence of terminal alkynes.

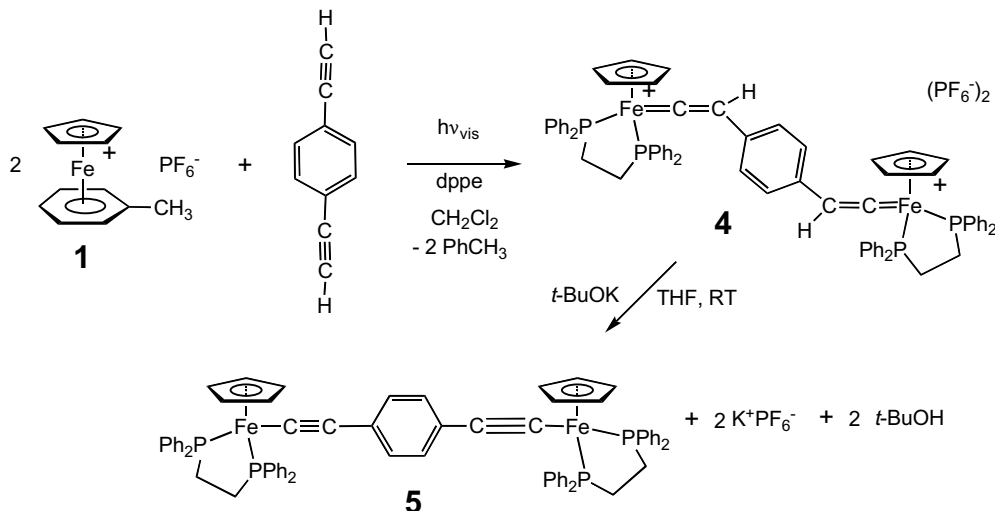
3. Spectroscopic and analytical data

3.1. $\text{CpFe}(\text{dppe})\text{C}\equiv\text{CH}$, **3**

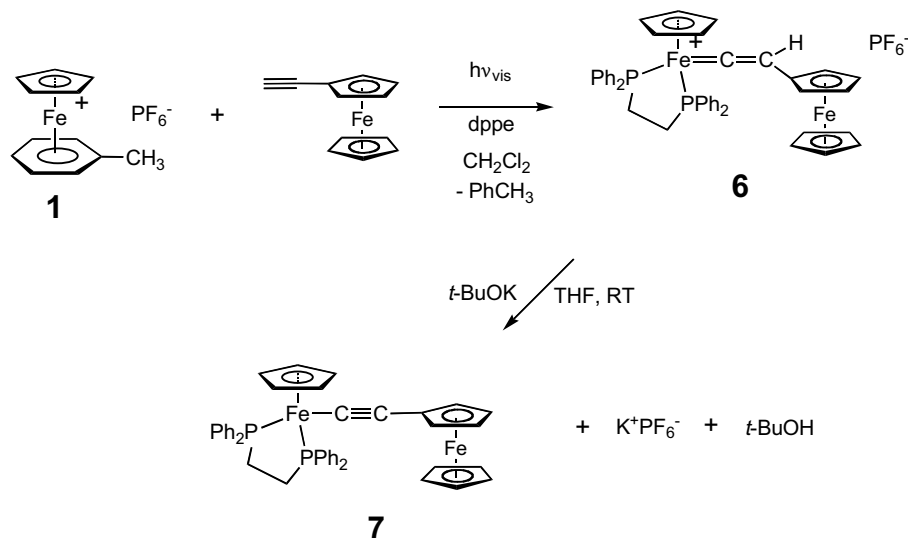
^1H NMR (CDCl_3 , 300 MHz): 7.90–7.14 (m, 20H, arom. CH of dppe), 4.21 (s, 5H, Cp), 2.72 and 2.26 (m, 4H, CH_2CH_2 of dppe), 1.86 (s, 1H, $\text{C}\equiv\text{CH}$). ^{13}C NMR (CDCl_3 , 75.0 MHz): 142.4–127.1 (arom. of dppe), 112.1 (C_β), 105.7 (C_α), 79.6 (Cp), 28.3 (CH_2 of dppe). ^{31}P NMR (CDCl_3 , 121 MHz): 106.4 (Fe-dppe). MS (ESI m/z), Calc. for $\text{C}_{33}\text{H}_{30}\text{P}_2\text{Fe}$: 544.4. Found: M^+ 545.0. Anal. Calc. for $\text{C}_{33}\text{H}_{30}\text{P}_2\text{Fe}$: C, 72.81; H, 5.55. Found: C, 72.47; H, 5.41%. Infrared $\nu_{\text{C}\equiv\text{C}}$: 1918 cm^{-1} .

3.2. 1,4-($\text{CpFe}(\text{dppe})\text{C}\equiv\text{C}$) $_2\text{C}_6\text{H}_4$, **5**

^1H NMR (CDCl_3 , 300 MHz): 7.89–7.20 (m, 20H, arom. CH of dppe), 6.11 (s, 4H, CH 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 $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$.



Scheme 3. Visible-light photolytic synthesis of ferrocenylvinylidene and alkynyl complexes from the precursor complex $[\text{FeCp}(\eta^6\text{-toluene})][\text{PF}_6]$.

Table 1
Electrochemical, I.R. and P NMR data of the complexes 2–7.

Complex	Cyclic voltammetry ^a		I.R.		³¹ P NMR		
	1st $E_{1/2}$ (mV)	2nd $E_{1/2}$ (mV)	ν_{CC}	ν_{PF_6}	δ_{ppm} (dppe)	δ_{ppm} (PF ₆)	
Vinylidene complexes	2	825	1025	1642	839	97.0	-144.1
	4	800	1020	1632	839	92.4	-144.1
	6	510	690	1967	839	93.5	-144.1
Alkynyl complexes	3	160	–	1918	–	106.4	–
	5	0	210	2060	–	106.6	–
	7	0	650	2066	–	106.4	–

^a $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ vs. FeCp_2^+ (in V). Electrolyte: $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp_2^+ ; scan rate: 0.200 Vs^{-1} ; 20 °C.

(MALDI-TOF; m/z). Calc. for $\text{C}_{72}\text{H}_{62}\text{P}_4\text{Fe}_2$: 1162.85. Found: M^+ 1162.23. Anal. Calc. for $\text{C}_{72}\text{H}_{62}\text{P}_4\text{Fe}_2$: C, 74.37; H, 5.37. Found: C, 73.93; H, 5.32%. Infrared $\nu_{\text{C}=\text{C}}$: 2060 cm^{-1} .

3.3. $\text{CpFe}(\text{dppe})\text{C}\equiv\text{C-Fc}$, **7** (Fc = ferrocenyl)

¹H NMR (CDCl_3 , 300 MHz): 7.74–7.20 (m, 20H, arom. CH of dppe), 4.21 (s, 5H, Cp), 3.77–3.65 (m, 9H, Cp of Fc), 2.75 and 2.38 (m, 4H, CH_2CH_2 of dppe). ¹³C NMR (CDCl_3 , 75.0 MHz): 142.4–127.4 (arom.), 79.0 (Cp), 73.4–65.8 (Cp of Fc), 25.6 (CH_2 of dppe). ³¹P NMR (CDCl_3 , 121 MHz): 106.4 (Fe-dppe). Anal. Calc. for $\text{C}_{43}\text{H}_{38}\text{P}_2\text{Fe}_2$: C, 70.90; H, 5.26. Found: C, 70.56; H, 5.21%. Infrared $\nu_{\text{C}=\text{C}}$: 2066 cm^{-1} .

Acknowledgments

We are grateful to Fundação para a Ciência e a Tecnologia (FCT), Portugal (Ph.D. grant to CO), the Institut Universitaire de France (IUF, DA), the CNRS and the Université Bordeaux I for financial support.

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