

Preliminary communication

A direct and specific sonochemically assisted preparation of $\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})\text{X}$ ($\text{X} = \text{Cl}, \text{H}$)

Christophe Roger, Patrick Marseille, Christophe Salus, Jean-René Hamon and Claude Lapinte

Laboratoire de Chimie des Organométalliques, Université de Rennes I, U.A. C.N.R.S 415, Campus de Beaulieu, 35042 Rennes cédex (France)

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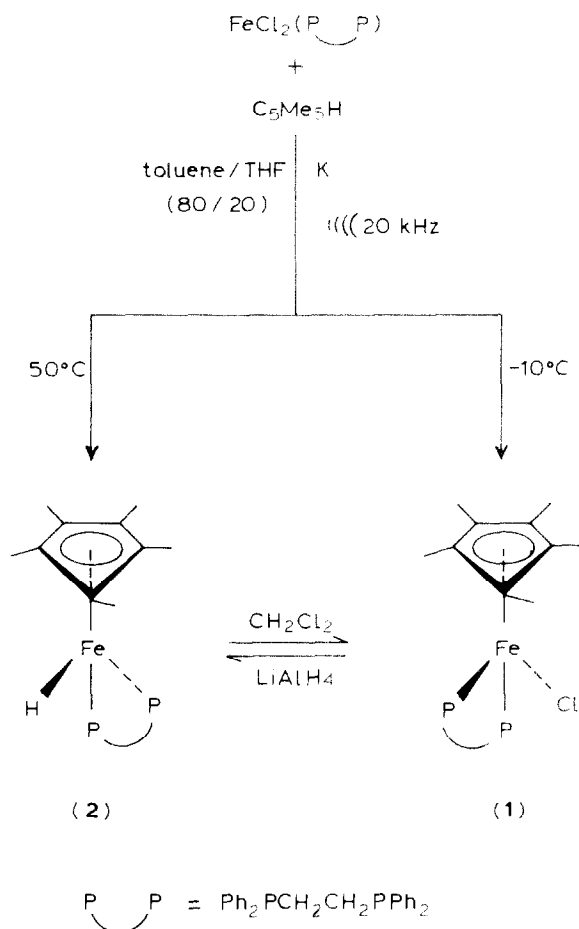
Abstract

New $\text{Fe}(\text{C}_5\text{Me}_5)\text{L}_2\text{X}$ where $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), $\text{X} = \text{Cl}, \text{H}$, have been prepared by a one-pot reaction from $\text{Fe}(\text{dppe})\text{Cl}_2$, $\text{C}_5\text{Me}_5\text{H}$, and K with activation by 20 kHz ultrasonic radiation. These electron-rich complexes were found to undergo ready one-electron oxidation to give the stable 17-electron species.

The derivatives $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$ are one of the most useful and widely studied groups of transition metal organometallic complexes [1]. Their $\text{Fe}(\text{C}_5\text{H}_5)(\text{P}_1)(\text{P}_2)\text{R}$ counterparts should provide an extensive related chemistry [2], but few studies of such complexes have been described. The compounds $\text{Fe}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{Me}, \text{SiR}'_3, \text{SnR}'_3$) and $\text{Fe}(\text{C}_5\text{H}_5)(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)\text{X}$ ($\text{R} = \text{Me}, \text{Ph}$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been prepared previously by photoinduced substitution from $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{X}$ precursors [3,4]. Very few pentamethylcyclopentadienyl $\text{Fe}(\text{C}_5\text{Me}_5)(\text{P}_1)(\text{P}_2)\text{X}$ analogues are known, although this ligand has proved useful for the organometallic chemistry of iron and many other transition metals [5]. Green and coworkers reported an elegant route to these electron-rich compounds [2a], but generation of iron atoms requires complex high technology equipment.

We report here a one-step synthesis of $\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})\text{X}$ ($\text{X} = \text{Cl}, \text{H}$) starting from $\text{C}_5\text{Me}_5\text{H}$, $(\text{dppe})\text{FeCl}_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) and K under ultrasonic activation. This synthetic strategy is connected with the recently reported method for the formation of metal carbonyls starting from metal halides [6] and with the effects of ultrasound on the generation and reactivities of some metal powders [7]. Our method shows some analogy to Green's procedure, the first step being the generation of a zerovalent iron intermediate by a two-electron reduction of the paramagnetic $\text{Fe}(\text{dppe})\text{Cl}_2$ [8].

In a typical experiment potassium (2.5 mmol, 100 mg) was exposed for 10 min in a 20 ml Schlenk tube containing a toluene/THF (80/20) mixture to the 20 kHz



Scheme 1.

ultrasonic radiation*; this caused surface erosion and pitting of the metal and produced a grey blue colloidal potassium solution. After slow cooling to -10°C , 1 mmol (525 mg) of $\text{Fe}(\text{dppe})\text{Cl}_2$ and 1 mmol (136 mg) of $\text{C}_5\text{Me}_5\text{H}$ were added, together with 5 ml of THF. Ultrasonic irradiation was continued for 30 min, and the solvent then removed under vacuum. The dark solid residue was extracted with pentane. Evaporation of the orange extract gave $\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})\text{Cl}$ (**1**) microcrystals in 50% yield. When the reaction was carried out at 50°C , the iron hydride $\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})\text{H}$ (**2**) was isolated in a 50% yield. This new, air sensitive compound shows a characteristic ^1H NMR triplet at $\delta -16.88$ ppm (C_6D_6 , TMS) with $^2J(\text{PH})$ 69 Hz. Treatment of **1** with LiAlH_4 in THF at -80°C gives a quantitative yield of **2**, which can be reconverted into **1** by reaction with methylene chloride (Scheme 1).

* Sonication is carried out with a high intensity immersion ultrasonic titanium horn in a Schlenk tube under argon. The acoustic power is 100 W.

Table 1

Cyclic voltammetry: Average of cathodic and anodic peak potentials in volts vs. saturated calomel electrode in CH_3CN with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6$ (0.1 M) as supporting electrolyte 0.1 V s^{-1}

	X	$\frac{1}{2}(E_{p,c} + E_{p,a})$	$ E_{p,c} - E_{p,a} ^a$	$I_{p,a}/I_{p,c}^b$
Fe(C ₅ Me ₅)(dppe)X	Cl	-0.470	0.069	1
	H	-0.403	0.067	1

^a Criterion for electrochemical reversibility $|E_{p,c} - E_{p,a}| < 0.059\text{V}$. ^b Criterion for chemical reversibility $i_{p,a}/i_{p,c} = 1$.

The synthesis involves use of a 10% excess of potassium as reducing agent, which shows that two electrons are needed to reduce the Fe(dppe)Cl₂. If C₅Me₅H is introduced before the iron halide, C₅Me₅K is formed and the synthesis does not work, showing that the correct order of addition of the reagents is crucial. The π -complexation of the diene may follow the reduction of the iron halide, and the temperature dependent chemoselectivity may be connected with the C-H activation process. The formation of the metal-hydride **2** does not proceed via the chloro compound **1**; thus if the reaction is carried out in two steps, involving addition of the reagents to the pre-activated potassium solution at -10°C followed by warming to 50°C , the chloro complex **1** is recovered without any trace of **2**.

The ultrasound produces a metal slurry of exceptional reactivity. Thus the reduction of the Fe(dppe)Cl₂ is complete within 10 min with a stoichiometric amount of potassium, whereas reduction of analogous compounds with an excess of sodium amalgam without sonification requires 7 days [8].

Cyclic voltammetry on **1** and **2** shows that their oxidation potentials are at least 0.3 V more negative than those of related C₅H₅ compounds. The 17-electron Fe^{III} species are stable, as indicated by their chemical electroreversibility, suggesting that the paramagnetic complexes could be readily synthesized and isolated, and an account of these will be presented soon.

Our synthesis of the new species Fe(C₅Me₅)(dppe)X is easy to carry out, and proceeds quickly to give good yields in a one-pot procedure.

The new complexes reported gave satisfactory analyses, and the mass and ¹H, ¹³C NMR spectra were as expected.

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