

New pyridyl-functionalized organoiron alkynyl complexes. Easy access to polymetallic architectures featuring an electroactive site by simple co-ordination reactions

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Abstract

The functionalized complexes **3a–d** [(dppe)Cp*Fe(C≡C–L)] (L = 4-Py, 3-Py, 2-Py) were isolated with good yields from the alkynyl complex **1** [(dppe)Cp*Fe(C≡CH)] (dppe = 1,2-bis(diphenylphosphino)ethane) from the corresponding bromopyridines using a Sonogashira-coupling reaction. These redox active compounds are stable under two redox states and react as usual pyridyl ligands towards methyl iodide or (THF)W(CO)₅. They allow easy access to the corresponding pyridinium salt **4a** or to the dimetallic iron–tungsten complex **5a**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organoiron(II); Organoiron(III); Iron acetylide; Sonogashira-coupling; Substituted pyridine; Pyridinium salt; Dinuclear complex

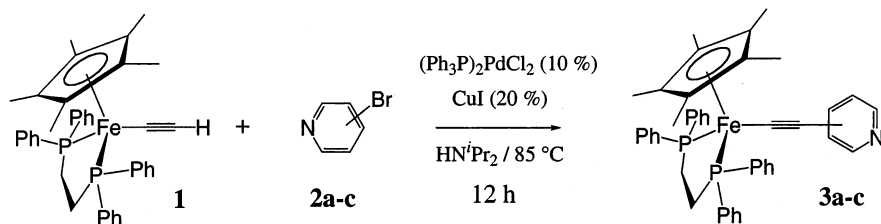
1. Introduction

Disposition in space of organic or organometallic molecular units possessing a pyridyl moiety by use of different metal centers acting as templates is a convenient access to supramolecular assemblies, well-defined in size and shape [1–3]. For instance, the complexation of such a unit to Pd(II) or Pt(II) complexes proved to be sufficiently strong and specific regarding geometric isomers to allow successful prediction of the structures obtained [4,5]. We are strongly involved in the synthesis of organometallic architectures possessing several electroactive '(dppe)Cp*Fe' units and in the study of their potential as new nanoscopic devices for molecular electronics [6–11]. Regarding its very promising electronic and magnetic properties, they are currently developing synthetic means to allow the incorporation of this fragment into various molecular assemblies [12]. Thus,

the availability of similar organoiron building blocks presenting a remote pyridyl co-ordination group appeared very appealing [13]. Recently, the authors reported on the use of the Sonogashira-coupling to covalently graft the '(dppe)Cp*Fe–C≡C' moiety on various haloaromatic units [12]. In this communication, we now report on the easy access to new pyridyl-functionalized organoiron alkynyl complexes and the ability of the new coupling products to behave as redox ligands toward a metal center.

Whereas the coupling of organic -ynes with nitrogen heterocycles using the Sonogashira- or derived-coupling reactions has been known for a long time [14–21], the coupling of transition metal σ -co-ordinated -ynes is much more rare, and quite new for transition metal alkynyls [22,23]. As depicted in Scheme 1, the Sonogashira-coupling reaction between the (dppe)Cp*FeC≡CH complex (**1**) [24] and several bromopyridyl substrates allows the straightforward isolation of the corresponding organoiron-functionalized pyridines **3a–c** with fair yields [25].

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(2-3a: 4-Py; 2-3b: 3-Py; 2-3c: 2-Py)

Scheme 1.

These complexes were fully characterized by means of usual spectrometric and elemental analyses. The presence of the triple bond was clearly evidenced by the resonances of its quaternary carbon atoms and by a characteristic IR frequency. The α carbon resonance, being coupled with the two phosphorus atoms of the dppe, appears as a triplet with a constant of ca. 38 Hz (Table 1). The multiplicity of the triple bond stretching mode may arise from Fermi coupling with other vibrational modes as already stated for this family of molecules [26], since the purity of the isolated molecules was assessed by the spectroscopic data, only one signal being observed for the dppe phosphorus atoms, and by the correct elemental analysis. As for their non-heterocyclic analogs previously reported, these complexes possess a second stable redox state (**3a-c**⁺) in an accessible potential range as evidenced by reversible cyclic voltammograms. The mono-oxidized state can be successfully isolated and characterized after chemical oxidation using ferrocinium hexafluorophosphate (Table 1) [27]. In accordance with the data gathered for similar compounds, the paramagnetic oxidized complexes present a low spin iron(III) center with a single unpaired electron [24].

These complexes appear to behave as typical pyridines. Thus, **3a** reacts with methyl iodide to afford the corresponding pyridinium salt **4a** with good yields [28]. The ¹³C resonance of the acetylenic C_α carbon at low field and FTIR spectroscopy (Table 1) suggest an intermediate electronic structure between a pure alkynyl form with the positive charge located on nitrogen and an allenylidene form derived from a dihydropyridine ring with the positive charge located on iron. However, Mössbauer spectra at 80 K (IS = 0.245 mm s⁻¹, QS = 2.020 mm s⁻¹) is typical for an iron(II) site with a σ -iron-carbon bond. A significantly weaker QS is expected for compounds of this series with a iron-carbon double bond, therefore, the alkynyl structure is assumed to be preserved in **4a** [29]. The large shift stated for the oxidation potential of the iron-centered process in **4a** relative to **3a** is noticeable and indicates a good

electronic interaction between the nitrogen atom of the heterocycle and the iron nucleus.

In order to assess the potential of these molecules as ligands, we attempted co-ordination of one of these complexes to a metal center. Tungsten hexacarbonyl seemed to be well-suited for this purpose [13,18,21,22], thus, the W(CO)₆ complex was reacted with **3a** under UV-irradiation. Photochemical displacement of one carbonyl from tungsten center occurred and the desired complex **5a** was isolated in good yields [30]. The presence of the tungsten pentacarbonyl center was evidenced by apparition of carbonyl stretching modes (2069, 1924 and 1883 cm⁻¹) in FTIR and by carbonyl resonances at 217 and 216 ppm (relative intensities 1:4) in ¹³C-NMR, as well as by a change in the redox potential of **5a** relative to complex **3a**. The shift towards more positive values indicates that the iron-centered redox process is influenced by the electropositive tungsten center and suggests the occurrence of an electronic interaction between the metals. Additionally, as indicated by the observation of a single reversible redox system, we established that the pyridine ligand remained co-ordinated to the tungsten center in the oxidized state of complex **5a**. Moreover, the complex **5a** + prepared following the procedure described for oxidation of **3** displays the same cyclic voltammogram as that of **5a** and a $\nu_{\text{C}\equiv\text{C}}$ bond stretching at lower energy (Table 1). The CO stretching frequencies of **5a** + are very close to those of **5a** (2070, 1927 and 1892 cm⁻¹). See Scheme 2 for corresponding reactions.

In conclusion, the new organoiron-functionalized pyridyl compounds are good ligands, even in their oxidized states. Thus, the premise that **3/3**⁺ compounds might be disposed in space using templating metal centers seems to be valid. Several other metal centers giving rise to stable complexes with pyridine are currently being tested in our group in order to establish the potential of such an approach and to investigate a possible co-operative electronic or magnetic behavior between remote electrons [31]. Additionally, regarding the NLO properties of very similar complexes

Table 1
Yields and selected spectroscopic data for complexes^a

Compound	Yield(%)	FTIR: $\nu_{\text{C}=\text{C}}$ in CH_2Cl_2 (cm^{-1})	Cyclic voltammetry ^b	$^{31}\text{P}\{^1\text{H}\}$ -NMR ^c : dppe	$^{13}\text{C}\{^1\text{H}\}$ -NMR ^d : C_α and C_β
3a	73	2059, 2024	−0.032	100.9	155.0 (38 Hz)
3a +	87	1990	−0.032	—	—
3b	79	2057, 2031	−0.105	101.1	147.5 (39 Hz)
3b +	87	1991 ^d	−0.105	—	—
3c	80	2053, 2028	−0.083	101.7	145.7 (38 Hz)
3c +	87	2006 ^d	−0.083	—	—
4a ^e	90	1991	0.221	98.3	204.4 (38 Hz)
5a	73	2016	0.055	100.3	172.3 (37 Hz)
5a +	68	1976	0.055	—	—

^a NMR data from ^{31}P , ^1H and ^{13}C spectra recorded at 81, 200 and 50 MHz respectively.

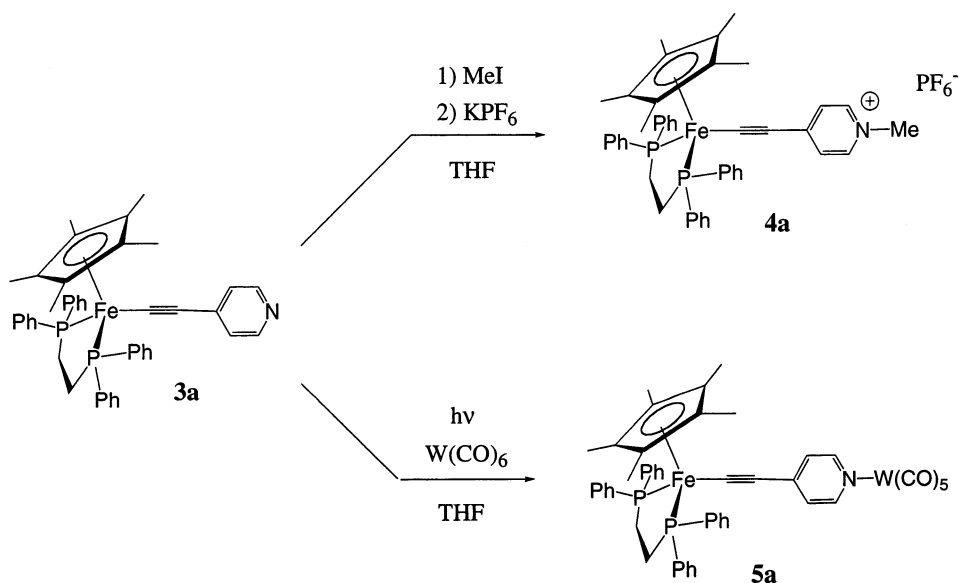
^b E° in V vs. SCE (ferrocene–ferrocenium couple was used as an internal calibrant for the potential measurements, $E^\circ = 0.460$ V vs. SCE), Pt electrode, 25°C, 0.1 M NBu_4PF_6 .

^c In C_6D_6 .

^d Very weak absorption.

^e NMR in acetone- d_6 for this complex.

^f Proposed assignment.



Scheme 2.

[21,32,33], compounds as **3a–d**, **5a** and analogs possessing a stable oxidized state appear as interesting models of redox-switchable NLO devices [25,31].

Acknowledgements

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- [25] In a typical coupling reaction, 200 mg of complex **1** (0.325 mmol), 23 mg of bis(triphenylphosphine) dichloropalladium complex (0.032 mmol) and 13 mg of copper iodide (0.065 mmol) were introduced under argon in a Schlenk tube. Subsequently, the halogenoaromatic substrate was introduced in 10 ml of di-*iso*-propylamine and the mixture was refluxed for 12 h. The solvent was then cryogenically trapped and the brown residue was extracted with toluene and filtered through a celite pad. Evaporation of the toluene and washing with small portions of *n*-pentane (2 × 5 ml) at –40°C and acetonitrile (5 ml) yielded the corresponding desired complex **3**. The pure compound can be isolated as bright orange powder by recrystallization from a toluene–pentane mixture.
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- [27] Synthesis of the oxidized salts. 0.92 equivalents of [Fe(η^5 -C₅H₅)₂][PF₆] were added to a solution of the corresponding compound **3a–c** in 15 ml dichloromethane. Stirring was maintained for 1 h at r.t. and the solution was concentrated in vacuo to ca. 5 ml. Addition of 50 ml of *n*-pentane allowed precipitation of a solid. Decantation and subsequent washing with 3 × 3 ml portions of toluene followed by 3 × 3 ml diethyl ether, drying under vacuum yielded the pure **3a–c** + salt as a dark purple product (87%).
- [28] To a stirred solution of **3a** in THF, three equivalents of MeI and one equivalent of KPF₆ were added after 5 h. The reaction mixture is stirred overnight and the solution was concentrated in vacuo. Extraction with dichloromethane and addition of *n*-pentane allowed precipitation of a dark purple solid. Decantation and subsequent washing with small portions of *n*-pentane and drying under vacuum yielded the pure **4a** salt as a dark purple product (90%).
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- [30] A solution of **3a** and 1.1 equivalents of W(CO)₆ in 200 ml of THF were photolyzed over a period of 10 min with a mercury vapor 250 W lamp under permanent argon bubbling at r.t. After evaporation of the solvent, the unreacted W(CO)₆ was sublimed out of the solid residue and the remaining solid was extracted with toluene before being washed several times with small fractions of pentane (–40°C). Drying in vacuo yielded the complex as a deep orange product **5a**.
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