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SYNTHESIS OF NOVEL SYMMETRICAL AND NONSYMMETRICAL 6-MEMBERED HETEROCYCLES WITH PENDANT ELECTRON-RICH ORGANOIRON SUBSTITUENTS*

The functionalized complexes [(dppe)Cp*Fe(C≡C)]$_2$—(Py) (Py = 2,6-C_5H_3N and 3,5-C_5H_3N (dppe = 1,2-bis(diphenylphosphino)ethane) were isolated in good yields from reaction of the chloro complex (dppe)Cp*FeCl with the protected bis-acetylenic heterocyclic precursor. These electron-rich pyridyl ligands constitute interesting examples of organometallic heterocycles bearing redox-active substituents. The attempts to find an alternative route starting from the alkynyl complex [(dppe)Cp*Fe(C≡CH)] and the corresponding dibromopyridines using a Sonogashira cross-coupling reaction are also described. By this route, the mono-functionalized products [(dppe)Cp*Fe(C≡C)]-2,6-Py-Br and [(dppe)Cp*Fe(C≡C)]-3,5-Py-Br could be cleanly isolated. These compounds open the way to the generation of heteroaromatics featuring nonequivalent alkyne substituents as [(dppe)Cp*Fe(C≡C)]-2,6-Py-[(C≡C)SiMe$_3$] or [(dppe)Cp*Fe(C≡C)]-3,5-Py-[(C≡C)SiMe$_3$] by further coupling.

INTRODUCTION

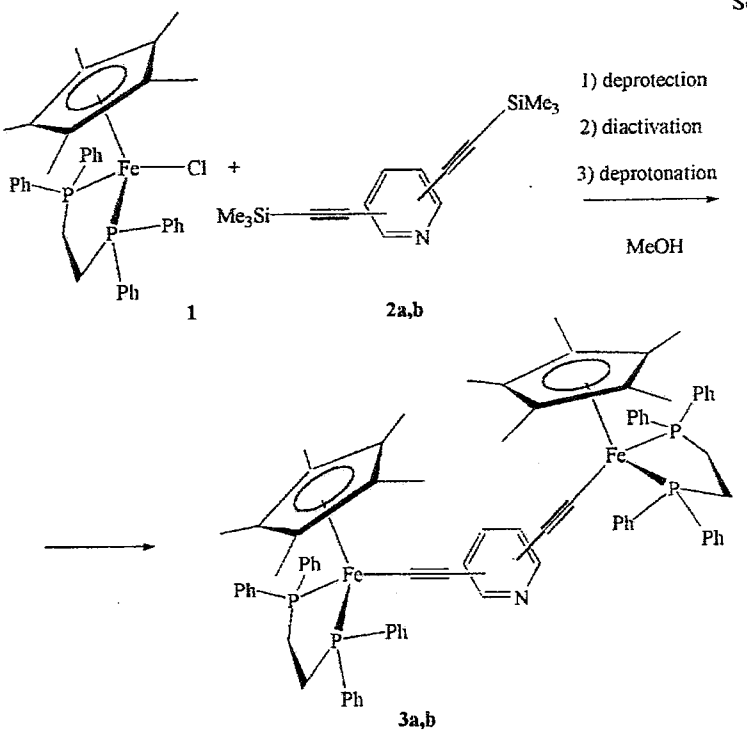
Used in conjunction with templating metal centres, heterocyclic ligands like the pyridyl groups have ever played a central role in the realisation of supra- or supermolecular assemblies [1—9]. Based on such approaches, many molecular architectures exhibiting remarkable optic [10, 11], electronic, photonic or magnetic [12—21] properties could be realised these last years. One of the keys feature underlying these achievements was the great synthetic background allowing to functionalize at will the pyridyl core. When needed, fine-tuning of the properties of this heterocycle was often possible by appropriate substitution [22—24]. Organic substituents were traditionally used for this purpose. Yet, with the advent of organometallic chemistry, introduction of metal complexes as substituents appears as another interesting possibility. Several organometallic examples of pyridyl ligand bearing a σ-ligated transition metal complex [25—32] or polymetallic cluster [33] have been reported. The electron-rich metal center has usually a profound influence on the properties of the ring, and the introduction of pendant σ-ligated transition metal complexes in such heterocycles may constitute a logical further step toward conception of more acute molecular or supramolecular devices. In that respect, we have recently communicated the synthesis of pyridyl units bearing one electron-rich and electroactive "(dppe)Cp*FeC≡C-" unit [34]. This fragment is one among the most electron donating organometallic substituents available to date [35]. The alkyne linker, while reducing the steric strain in these compounds, proved to convey efficiently the metal electronic influence onto the pyridyl ring [36]. In the present paper, we now report the synthesis of pyridyl groups bearing two "(dppe)Cp*FeC≡C-" fragments symmetrically positioned as well as their characterisation. We also report the synthesis of difunctional pyridyl units bearing one such organoiron substituent and a bromine substituent.

Synthesis of the symmetrical difunctional pyridines. The pentamethylcyclopentadienyliron complex **1** and bis(trimethylsilylethynyl)-pyridines **2a,b** were used as starting compounds. Pyridines bearing two

* In commemoration of centenary of academician A. N. Nesmeyanov.

(dppe)Cp*Fe substituents in 2,6- (3a) and 3,5-positions (3b) were conveniently synthesised by classic one-pot dimetallation of the corresponding organic pyridyl precursor **2a** or **2b** bearing silyl-protected alkyne functionalities (see Scheme 1) [37]. For 2a, the deprotection was achieved by potassium fluoride in methanol. Once deprotected, each alkynyl group was trapped by the reactive 16-electron $[(dppe)Cp^*Fe]^+$ intermediate simultaneously generated *in situ* from **1** by anion metathesis using potassium hexafluorophosphate to give the corresponding 2,6-pyridylvinylidene. With **2b**, the deprotection was effected using potassium carbonate and the complexation to the 3,5-pyridylvinylidene was realised in a subsequent step by addition of sodium tetraphenylborate. Isolation or further characterisation of the vinylidene complexes was however not attempted. They were cleanly deprotonated by potassium *tert*-butylate and give quantitatively the desired compounds **3a,b** bearing iron-alkynyl functionalities. The later can be isolated by extraction from crude polar medium obtained after evacuation of methanol as moderately air-sensitive bright orange solids. The postulated divinylidene intermediate may appear as speculative, however such species are usually invoqued in similar reactions [38, 39]. Moreover, we could observe the presence of a vinylidene-alkynyl species in the medium by infrared spectroscopy before addition of the base*.

Scheme 1



2,3a: 2,6-Py; **2,3b**: 3,5-Py

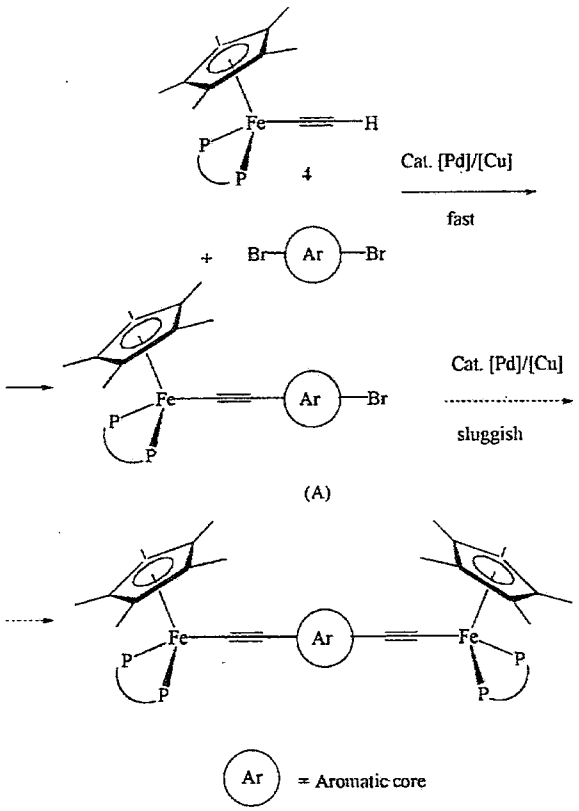
The dinuclear complexes were fully characterised by means of usual spectrometric methods and high resolution LSIMS, which allowed the precise observation (5 ppm range) of the molecular ions at 1304.4039 amu and 1303.3985 amu for **3a** and **3b** respectively. In addition, correct elemental analyses could be obtained for **3a**. Infrared and NMR data clearly indicated the presence of a symmetrically substituted pyridyl group in the complexes, while the presence of the triple bond was evidenced each time by the characteristic IR frequency of the unsymmetrical stretching mode at 2048 cm^{-1} for 3a and 2060

* The characteristic vibration of the iron vinylidene group appears at 1555 cm^{-1}, while the alkynyl stretching mode is observed at 1992 cm^{-1}.

cm^{-1} for **3b**. Preservation of the triple bond was also obvious from the resonances of its quaternary carbon atoms. The α-carbon nuclei being coupled with the two phosphorus atoms of the dppe on the iron center, appears as a triplet with a characteristic coupling constant of *ca.* 39 Hz [40]. The coupling of the β-carbon is often too weak to be resolved. The infrared and NMR data gathered for these complexes are reminiscent of the data previously published for the monofunctional alkynylironpyridines [36] but no fine structure due to Fermi coupling is observede.

Attempted catalytic access to 3a,b. Palladium-catalysed cross-coupling reactions of organic alkynes with nitrogen heterocycles are known for a long time and constitute an easy access to alkynyl-functionalized pyridines like **2a,b** [41, 42]. Yet, the possible extension of this catalytic coupling to transition metal σ-coordinated ynes was demonstrated only recently [43] and has allowed us to access to the monofunctionalized aromatics bearing the electron rich "(dppe)Cp*FeC≡ C" substituent starting from cpmlex **4** [40]. This catalytic coupling could also be extended to bromopyridines [34]. While such a coupling reaction works well with monobrominated substrates, we have recently established that the use of dibromo aromatics in corresponding coupling reactions does not allow the isolation of the dimetallated compound [44]. Presumably, the very electron-rich iron alkynyl centre deactivates the aromatic cycle in the monofunctionalized bromo intermediate (A) toward further catalytic activation of the second halogen (Scheme 2).

Scheme 2



Halogen substituents at heteroaromatic rings are known to undergo easier oxidative addition in cross-coupling reactions than at their corresponding aromatic homologues. This is especially true when they are alpha-positioned relative to the heteroatom [45]. Thus, it was of interest to test the direct coupling of **1** with the corresponding dibrominated pyridines **5a** and **5b**. The crude reaction products isolated using the usual work-up were analysed by means of ^{1}H and ^{31}P NMR or LSIMS and proved to be mixtures of complexes (see Table 1). In each case, by comparison with data gathered on the authentic samples of **3a,b** previously made, these complexes could be firmly identified admixed with

Table 1

Conversion and selectivity for mono- and di-coupled complexes in the catalytic procedure depending on the dibromo substrate used

Br_2Ar substrate used	Br_2Ar/4 ratio	Reaction time (h)	Conversion[a] of 4 (%)	Selectivity[a] (Yield[b], %)	
				for mono-coupled pdct	for di-coupled pdct
m-Br_2Ph[c]	5,0	15	100	100 (75)	0
m-Br_2Ph[c]	0,5	15	30	70[d]	0[d]
3,5-Br_2Py	2,0	14	100	100 (80)	0
3,5-Br_2Py	0,5	14	91	20[d]	37[d]
2,6-Br_2Py	2,0	14	100	91 (54)	9
2,6-Br_2Py	0,5	14	100	54	46

[a] Estimated by ^1H and ^{31}P NMR by considering the relative (dppe)Cp*Fe signal areas in the toluene extract. For the dicoupled products, this percentage has been halved to give the relative yield.
[b] Yield on starting dibromo substrate of pure isolated product after work up.
[c] See ref. [44].
[d] Not determined; other unidentified complexes are present.

another (dppe)Cp*Fe-containing complex (**6a,b**) which corresponds to the mono-activation product (A; Scheme 2).

With the most favourable **5a** substrate, after reacting slightly more than two equivalents of iron-alkynyl complex **4**, under more forcing conditions than the usual work-up, roughly 50% of the di-coupled product are formed after the end of the reaction. Longer reaction times result in darkening of the reaction medium and accumulation of new products, presumably originating from slow decomposition of the primary products of the reaction. Renewal of catalyst after 14 hours and pursuing the heating of the reaction medium 15 additional hours does also not result in complete conversions to the desired difunctional product **3a**. Moreover the presence of starting complex **4** in excess at the end of the reaction complicates the purification of **3a**. Without surprise, similar di-coupling reaction attempted with **5b** resulted in a lower amount of dicoupled product along with **6b** (see Table 2). This can be traced back to a lower activating effect exerted on the bromine atoms due to their more remote position relative to **5a**.

In conclusion, these catalytic approaches present no advantage over the conventional synthesis previously described, since the separation of the dimetallated products from other products in a quantitative fashion appears very difficult.

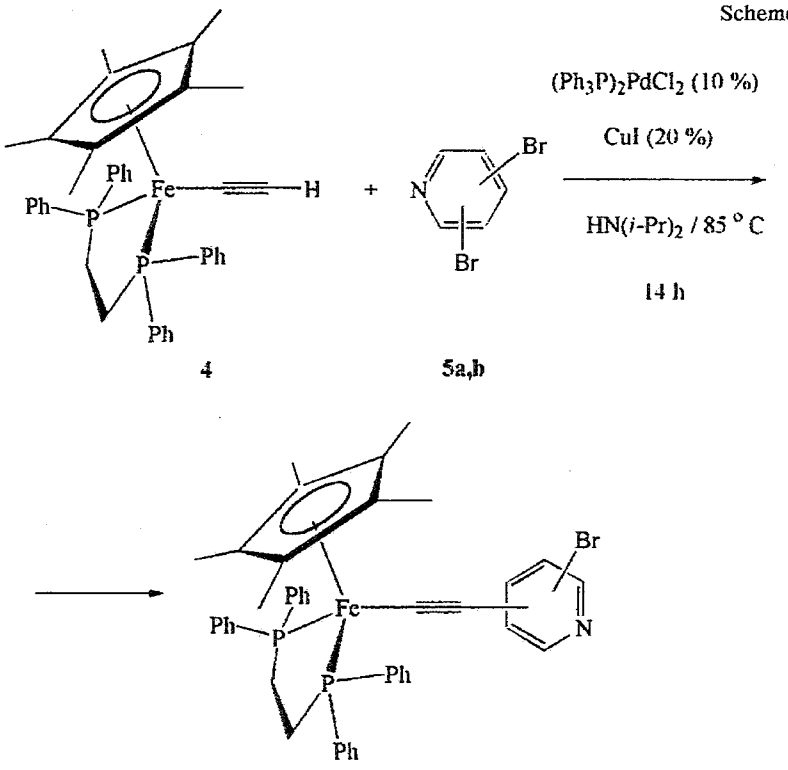
Table 2

The first oxidation redox potential for various mono- and di-functional 2- or 3-pyridyl complexes in CH_2Cl_2[a]

Compound	E_0 (ΔE_p, i_{pa}/i_{pc}) in volts	Compound	E_0 (ΔE_p, i_{pa}/i_{pc}) in volts
(dppe)Cp*Fe—C≡C-2-Py[b]	−0.08 (0.09, 1)	**6a**	−0.03 (0.07, 1)
(dppe)Cp*Fe—C≡C-3-Py[b]	−0.11 (0.09, 1)	**6b**	−0.04 (0.07, 1)
3a	−0.18 (0.08, 1)	**8a**	−0.07 (0.08, 1)
3b	−0.13 (0.07, 1)	**8b**	−0.06 (0.08, 1)

[a] Conditions: [^{n}Bu$_4$N] [PF_6], 0.1 M, 20 °C relative to SCE calibrated with ferrocene at 0.460 V, Pt electrode, sweep rate 0.100 V.s^{-1}.
[b] See ref. [36].

Scheme 3



5,6a: 2,6-Py; 5,6b: 3,4-Py

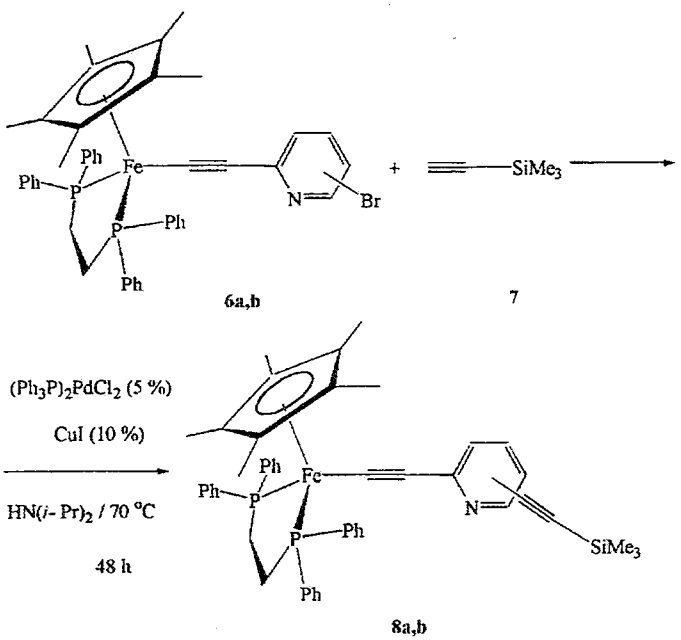
Nonsymmetrical functionalization of the pyridyl core. We were able to take advantage of the detrimental effect exerted by the iron alkynyl substituent for isolation of the mono-coupled products **6a,b** mentioned above. Indeed, by the reacting a slight excess of the dibromosubstrate **5a** or **5b**, the product resulting from the monofunctionalization of the pyridyl ring **6a** or **6b** could be isolated in a clean fashion (see Table 1 and Scheme 3). This product which appears to be the dominant product of the catalysed coupling in each case results from sequential activation of one of the bromo substituents. Traces of di-coupled product **3a** also invariably formed during the reaction and which are present after extraction can be purified by oxidation using a slight amount of ferricinium hexafluorophosphate. Indeed, the dinuclear complex is oxidized more easily than **6a** (see Table 2), which is then conveniently separated from mono-oxidized products by selective extraction and isolated in 52%. The similar reaction attempted with **5b** gave also the corresponding *meta*-substituted **6b** bromocomplex (quantitative by NMR). The latter can then be cleanly isolated using the usual work-up in 80% yield.

The new nonsymmetrical products **6a** and **6b** were characterised by usual spectroscopic means and by LSIMS spectrometry for **6a**. ^{1}H NMR is indicative of an non symmetrical substitution of the pyridyl ring bearing 3 protons. Infrared and ^{13}C NMR show the presence of a triple bond in the compounds by a characteristic stretching vibrational mode* 3 at 2032 cm^{-1} (**6a**) or 2036 cm^{-1} (**6b**) and two resonance signals typical of the triply bonded quaternary alkyne carbon atoms at 154.0 and 121.7 ppm (**6a**) or 154.3 and 115.5 ppm (**6b**) with the characteristic coupling of *ca.* 38 Hz for the former one (Cα).

* A second very weak absorption around resp. 2090 cm^{-1} for **6a** and 2089 cm^{-1} for **6b** can also be detected in the triple bond region. This could be a combination mode or overtone from less energetic vibrational modes, but might also arise from Fermi coupling of such modes with the triple bond stretch [26].

Attempted further coupling of isolated **6a** with an equivalent of **4** did not give better results than the one-pot reaction. The coupling with an organic alkyne like trimethylsilylacetylene (7) works however far better, since 7 can be introduced in large excess without being detrimental to the isolation of the coupled product. Thus the nonsymmetrical bis-acetylenic 2,6-pyridine complex **8a** or 3,5-pyridine complex **8b** could be obtained in good yield (66% and 49% resp.). In the latter case, the reaction is more sluggish. Approx. 13% of non reacted **6b** remains after 14 h and therefore **8b** was not isolated pure. This illustrates that the activating effect of the heteroatom in the cycle is more effective for *ortho*- than for *meta*-bromine substituents.

Scheme 4



The new bis-alkynyl mononuclear complexes were also fully characterised by means of usual spectroscopy. Infrared spectrometry does not allow plain observation of a new acetylenic streching mode corresponding to silylated alkyne group in addition to the iron alkynyl strech at *ca.* 2035 cm^{-1}, however a very weak absorption can be located at 2161 (**8a**) or 2158 cm^{-1} (**8b**). More conclusively, ^{1}H NMR indicated the presence of a trimethylsilyl group in the new compounds and a pattern similar to the one observed for **6a,b**, but slightly shifted regarding the other signals, while ^{13}C NMR allowed the observation of two new extra quaternary carbon atoms at 107.2 ppm and 91.7 ppm for **8a** or at 102.7 ppm and 96.5 ppm for **8b**. A primary carbon signal at *ca.* 0.1 ppm was also observed in both cases for the trimethylsilyl group in addition to a set of signals reminiscent of these observed for the corresponding **6a,b** complexes. The resonance signals of the triple bond carbon atoms are located at 149.1 ppm (Cα; $^{1}J_{CP}$ = 38 Hz) and 122.1 ppm (Cβ) for **8a** and 150.9 ppm (Cα; $^{1}J_{CP}$ = 41 Hz) and 115.6 ppm (Cβ) for **8b**.

DISCUSSION

The dinuclear compounds **3a,b** constitute new examples of substituted pyridyl ligands bearing symmetrically appended strong electron releasing groups. To our knowledge such dinuclear transition metal complexes are quite rare, the only compounds bearing some similarity with **3a,b** having been reported recently. with ruthenium- and osmium- [39] or platinum- [46] alkynyl substituents

grafted on a central 2,4-pyridyl ring. Regarding the (dppe)Cp*Fe-C≡C-fragment, the spectroscopic data resemble much to these previously reported by us for the analogous dinuclear complexes featuring a *meta*-substituted phenyl ring in place of the pyridyl cycle. Indeed the infrared stretching frequency for the antisymmetric mode of the triple bond appeared at 2054 cm^{-1} and indicates a similar bond-order than that presently observed in the disubstituted pyridyl series. The ^{1}H, ^{31}P and ^{13}C NMR spectra were also very close to the ones observed here* **4** [37]. On the whole, this indicate that replacement of a carbon atom by a nitrogen atom in the aromatic ring produces only minor changes in the electronic distribution of the iron termini in the neutral complex.

Next, we have tried to get some insight in the modifications brought to the pyridyl ligand by introduction of a second iron alkynyl substituent from the infrared spectra. Several medium to intense stretching modes attributable to the pyridyl ring were observed each time in the aromatic region for all compounds. As was done previously for monosubstituted pyridyl ligands [36] the two most intense of them between 1600 and 1530 cm^{-1} may be identified as respectively the ring-stretches ν_{8a} and ν_{8b}, according to the classification of Kline and Turkewich [47]. However attempting to extract information from their intensity and frequency shifts using trends established for 2- or 3-substituted pyridines is not very rewarding [48, 49]. For **3a,b** the changes in these vibrational modes are reminiscent of those reported for 2- or 3-chloropyridines and thus may be diagnostic of π-electron-releasing substituents conjugated with the ring. Relative to their corresponding monosubstituted counterparts, the magnitude of the shifts would indicate a stronger interaction in the case of **3a** and a weaker one in the case of **3b****. These results have however to be taken cautiously since use of the correlations established for monosubstituted pyridines in the case of disubstituted pyridines like **3a,b** is perhaps not appropriate***.

The strong electron donating power of the (dppe)Cp*Fe substituent is more clearly illustrated by the sluggishness of the second bromine activation using a Sonogashira catalysed coupling procedure which renders this approach uninteresting from a purely synthetic point of view, when **3a,b** are desired.

Interestingly, comparison of these results with those obtained with the *meta*-dibromobenzene indicate that the heterocyclic nitrogen atom in *ortho*-position exerts effectively a beneficial influence on the second bromine activation step in the catalysis. Indeed, no di-coupled product could be detected in the later case by means of NMR spectroscopy, and only by FAB-MS were traces of this complex in the crude reaction mixture evidenced.

Yet, we were able to use the deactivating effect of such an electron-rich alkynyl substituent to our profit and the complexes **6a,b** and **8a,b**, much more appealing from a synthetic point of view, were isolated. Notably, **8a,b** should allow nonsymmetrical difunctionalization of the corresponding dibromopyridyl ligand after deprotection of the trimethylsilyl group and metallation with a different metal complex. Non symmetrically bridged dialkynyl complexes of transition metal featuring a central aromatic ring are rare and, to our knowledge, unknown with an heteroaromatic ring [51, 52] although synthons equivalent to **8** have been reported recently with a 2,5-thienyl unit [53].

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* The ^{31}P shift previously reported for the *meta*-phenyl analogue has been re-checked in C_6D_6. The right value is 101.9 ppm i. e. very close to the one observed for **3a,b**.

** For **3a**, the first mode (ν8a) is twice less intense (1558 cm^{-1}) than the second one (ν8b; 1538 cm^{-1}) and both appear at lower wavenumbers than in unsubstituted pyridine (resp. 1600 and 1582 cm^{-1}), and notably also lower than in the 2- and 4-monosubstituted pyridine (resp. 1577 and 1545 cm^{-1}; 1582 and 1563 cm^{-1}) [36]. In the case of **3b**, the second mode (1559 cm^{-1}) is more intense than the first one (1585 cm^{-1}) and both come out at higher wavenumber than for the 3-monosubstituted pyridine (resp. 1569 and 1548 cm^{-1}) [36].

*** For instance, the charge disturbance induced by the symmetrically positioned substituents in **3a,b** may resemble more to that found in a 4-substituted ring [50].

Finally, compounds **3a,b** can also be considered for their electronic intramolecular interactions between the iron nuclei, especially in their oxidized states. Like for their 1,4-phenylethynyl analogues [54] these difunctional ligands present stable mono- and dioxidized congeners. Studies are currently underway in order to have more information regarding the influence of the nitrogen heteroatom on the electron delocalization in the monooxidized state, and on the spin exchange processes in the dioxidized state [*55*]. The first oxidation potentials recorded by cyclic voltammetry for all these complexes indicate a slight electronic interaction between the two electron-rich iron alkynyl substituents since the first oxidation for the dinuclear (dppe)Cp*Fe complexes is easier of *ca.* 100 mV relative to the corresponding mononuclear 2-pyridyl in 2,6-complexes and *ca.* 30 mV in 3,5-complexes relative to the 3-pyridyl complex previously reported (see Table 2) [36]. Interestingly, the interaction is stronger in case 2,6-isomer, when the shorter path between the substituents goes through the nitrogen atom, than when it is goes through a carbon atom as in the 3,5-isomer. Expectedly, the oxidation of mononuclear complexes bearing the electron-withdrawing silylated alkyne substituent is slightly more difficult (10 mV) relative to its unsubstituted 2-pyridyl counterpart. Similarly, these data suggests that the bromine substituent behave as an electron-attracting group in **6a,b**, rendering their oxidation more difficult of *ca.* 50...30 mV, thus that the inductive influence dominates over the π-electron donating character.

In conclusion, new organoiron-difunctionalized pyridyl compounds **3a,b** with (dppe)Cp*Fe electron-rich substituents could be isolated and were characterised. By means of a Pd-catalysed coupling reaction, we also report the easy isolation of very interesting monometallated and monobrominated synthons like **6a,b** which open the way to nonsymmetrical dimetallation of the pyridyl core, starting from the corresponding commercial symmetrical dibromopyridine. We plane now to access to more complex molecular assemblies featuring such symmetrically or nonsymmetrically dimetallated redox-switchable building blocks and have already begun to explore their coordination chemistry then remains to be investigated.

EXPERIMENTAL

1. General data

Reagent grade toluene, tetrahydrofuran (THF), diethyl ether and *n*-pentane were dried and distilled from sodium benzophenone ketyl prior to use. The protected bis-ethynyl pyridines ($Me_3Si—C\equiv C)_2$-2,6-Py (**2a**), [56] ($Me_3Si—C\equiv C)_2$-3,5-Py (**2b**)* the iron complexes (dppe)Cp*FeCl (**1**) [57] and (dppe)Cp*Fe(C≡CH) (**4**) [58] were prepared according to the published procedures while other chemicals were used as received. All the manipulations were carried out under argon atmosphere using Schlenk techniques or in a Jacomex 532 dry box under nitrogen. Transmitance-FTIR spectra were recorded using a Bruker IFS28 spectrometer. NMR spectra were registered on a multinuclear Bruker 300 MHz or 200 MHz instruments (AM300WB and 200DPX). Chemical shifts are given in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra, to H_3PO_4 for ^{31}P NMR spectra. Cyclic voltammograms were recorded using a PAR 263 instrument. LSIMS analyses were effected at the "Centre Regional de Mesures Physiques de l'Ouest" (C. R. M. P. O. Rennes-France) on a high resolution MS/MS ZabSpec TOF Micromass spectrometer (8 kV). Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Solaise, France.

* The synthesis of **2b** was adapted from the one reported for **2a** [56].

2. Synthesis of the organoiron complexes

[(η^2-dppe)(η^5-C_5Me_5)Fe—C≡C]$_2$-2,6-(C_5H_3N) (3a). In a Schlenk tube, 0.395 g of 2,6-bis(trimethylsilylethynyl)pyridine (**2a**; 1.45 mmol), 2.2 equivalents of [(η^5-C_5Me_5)(η^2-dppe)FeCl] (2.000 g, 3.2 mmol), 2.2 equivalents of KPF_6 (0.586 g, 3.2 mmol), 2.2 equivalents of potassium fluoride (0.189 g, 3.2 mmol) were introduced in 50 mL of methanol. This suspension was stirred overnight at room temperature to yield a blue solution and 0.376 g of KO-*t*-Bu (3.2 mmol) was subsequently added under vigorous stirring. The mixture became immediately orange after *ca.* 15 min and the solvent was evacuated. The residue was then extracted with toluene (3×20 mL) and the extract concentrated to dryness. Subsequent washing by 10 mL of *n*-pentane and drying in vacuo yielded the desired complex **3a** as an orange slightly air-sensitive powder (98%, 1.850 g), $C_{81}H_{81}Fe_2N_1P_4 \cdot 0.5CH_2Cl_2$: Calcd., %: C, 72.69; H, 6.14; N, 1.04. Found, %: C, 72.68; H, 6.32; N, 1.20. FTIR (Nujol, cm^{-1}) ν 2048 (s, C≡C); 1558 (m, Py); 1548 (w, Py); 1538 (m, Py). FTIR (CH_2Cl_2, cm^{-1}) ν 2043 (s, C≡C); 1559 (m, Py); 1551 (m, Py); 1539 (m, Py). $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6) δ_P 102.1 (s, 2P, dppe). ^1H NMR (200 MHz, C_6D_6) δ_H 8.20-7.00 (m, 41H, 8 C_6H_5 + C_5H_3N/H_{para}); 6.79 (d, 2H, $^3J_{HH}$ = 7.6 Hz, C_5H_3N/H_{meta}); 2.97 (m, 4H, CH_{2dppe}); 1.90 (m, 4H, CH_{2dppe}); 1.54 (s, 30H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δC 147.7 (s, $^2J_{CH}$ = 6 Hz, C_5H_4N/C_{ipso}); 140.4-127.4 (m, Ph_{dppe}); 139.3 (t, $^2J_{CP}$ = 40 Hz, Fe—C≡C); 128.4 (s, $^1J_{CH}$ = 158 Hz, C_5H_4N/C_{metaN}); 123.1 (m, Fe—C≡C); 119.5 (s, $^1J_{CH}$ = 163 Hz, $^2J_{CH}$ = 6 Hz, C_5H_4N/C_{paraN}); 88.1 (s, $C_5(CH_3)_5$); 31.5 (m, CH_{2dppe}); 10.6 (s, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_5$). MS (FAB$^+$, *m*-NBA) *m/z* 1304 (M, 100%); 906 (M+H-dppe, 85%); 589 (M-"(CC)-Py-(CC)-(pppe)Cp*Fe", 50%).

[(η^2-dppe)(η^5-C_5Me_5)Fe—C≡C]$_2$-3,5-(C_5H_3N) (3b). In a Schlenk flask, 0.181 g of 3,5-bis-(trimethylsilylethynyl)pyridine (**2b**; 0.66 mmol) in 40 mL of methanol were stirred overnight in the presence of 0.221 g of sodium carbonate (1.60 mmol). Then, 1.000 g of [Fe(η^5-C_5Me_5)(η^2-dppe)Cl] (1.60 mmol) and 0.549 g of $NaBPh_4$ (1.60 mmol) were added and the mixture was refluxed for 8 hours. After cooling to room temperature 0.180 g of KO-*t*-Bu (1.60 mmol) was introduced in the orange suspension. The stirring was maintained for 15 mn and the solvent was removed under a vacuum. The residue was subsequently extracted with dichloromethane (3×10 mL). Evaporation of the dichloromethane, washing with *n*-pentane (4×10 mL) and drying *in vacuo* yielded the complex **3b** as a slightly air-sensitive orange powder (0,760 g, 88%). FTIR (Nujol, cm^{-1}) ν 2060 (s, C≡C); 1585 (vw, Py); 1559 (m, Py). FTIR (CH_2Cl_2, cm^{-1}) ν 2044 (s, C≡C); 1586 (vw, Py); 1557 (m, Py). $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6) δP 101.6 (s, 2P, dppe). ^1H NMR (200 MHz, C_6D_6) δH 8.43 (d, 2H, $^3J_{HH}$ = 1.7 Hz, C_5H_3N/H_{ortho}); 8.03-7.06 (m, 21H, 4C_6H_5 + C_5H_3N/H_{para}); 2.60 (m, 2H, CH_{2dppe}); 1.83 (m, 2H, CH_{2dppe}); 1.52 (s, 15H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δC 146.9 (s, $^1J_{CH}$ = 177 Hz, C_5H_4N/C_{ortho}); 140.9 (t, $^2J_{CP}$ = 39 Hz, Fe—C≡C); 140.2-129.2 (m, Ph_{dppe}); 136.9 (s, $^1J_{CH}$ = 165 Hz, C_5H_4N/C_{paraN}); 126.9 (s, $^2J_{CH}$ = 7.6 Hz, C_5H_4N/C_{ipso}); 117.4 (m, Fe—C≡C); 88.0 (s, $C_5(CH_3)_5$); 31.3 (m, CH_{2dppe}); 10.6 (s, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_5$). MS (FAB$^+$, *m*-NBA) *m/z* 1304 (M+H, 50%); 905 (M-dppe, 85%); 589 (M-"(CC)-Py-(CC)-(dppe)Cp*Fe", 100%).

General procedure for the catalytic coupling reactions of the iron-alkynyl compound 4 with 0.5 equivalents of dibromoarene substrate. In a Schlenk tube, 0.200 g of complex (η^2-dppe)(η^5-C_5Me_5)Fe—C≡CH (**4**; 0.320 mmol), 0.024 g of bis(triphenylphosphine)dichloropalladium complex (10%, 0.032 mmol) and 0.032 g of copper iodide (20%, 0.064 mmol) are introduced under argon. Subsequently, the dibromopyridine substrate **4a,b** (38 mg; 0.155 mmol) is added in 10 mL of diisopropylamine and the mixture is refluxed for 14 h. The solvent is then cryogenically trapped, the brown residue is extracted with toluene and the extract filtered on a celite pad. Evaporation of the toluene yields a brownish solid which proves to be a mixture of products (see text). Its relative content in unreacted **4**, mono- and di-coupled products is established by ^{31}P, ^1H NMR.

[(η^2-dppe)(η^5-C_5Me_5)Fe—C≡C-2-C_5H_3N-6-Br] (6a). In a Schlenk tube, 0.615 g of complex [(η^5-C_5Me_5)(η^2-dppe)Fe—C≡C—H] (**4**; 1.00 mmol), 0.070 g of bis(triphenylphosphine)-dichloropalladium (0.10 mmol), 0.038 g of copper iodide (0.20 mmol) and 0.484 g of 2,6-dibromopyridine (2.00 mmol) were introduced. Subsequently 20 mL of diisopropylamine were added and the mixture was refluxed for 14 h. The solvent was then trapped cryogenically and the brown residue was extracted with a toluene/*n*-pentane mixture and filtered on a celite pad. After removal of the solvents, subsequent washings with 3×10 mL of cold *n*-pentane and 10 mL of acetonitrile allowed the isolation of a mixture of **6a** and **3a**. Further purification was undertaken by selective oxidation of **3a** using one equivalent of ferricinium hexafluorophosphate in CH_2Cl_2. After *ca.* 15 min of stirring the orange solution was concentrated and the oxidized compound was precipitated by addition of 50 mL of *n*-pentane. The solution was then filtered and the solvent was removed under vacuum. Further washings with portions of cold

n-pentane (4×10 mL) and drying under a vacuum yielded the pure **6a** as a slightly air-sensitive orange powder (400 mg, 54%). FTIR (Nujol, cm^{-1}) ν 2032 (s, C≡C); 1567 (s, Py); 1552 (m, Py); 1527 (m, Py). ^{31}P {^1H} NMR (81 MHz, C_6D_6) δP 101.1 (s, 2P, dppe). ^1H NMR (200 MHz, C_6D_6) δH 8.13-6.85 (m, 20H, 4 C_6H_5); 6.83 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, C_5H_3N/H_{meta}); 6.75 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, C_5H_3N/H_{meta}); 6.62 (m, 1H, $^3J_{HH}$ = 7.8 Hz, C_5H_3N/H_{para}); 2.68 (m, 2H, CH_{2dppe}); 2.11 (m, 2H, CH_{2dppe}); 1.50 (s, 15H, $C_5(CH_3)_5$). ^{13}C {^1H} NMR (50 MHz, C_6D_6) δC 154.0 (t, $^2J_{CP}$ = 38 Hz, Fe—C≡C); 147.8 (m, $C_5H_3N/C_{ortho}N$); 142.0 (s, $^2J_{CH}$ = 12 Hz, $C_5H_3N/C_{ortho}N$); 139.8-127.6 (m, Ph_{dppe}); 137.4 (s, $^1J_{CH}$ = 162 Hz, $C_5H_4N/C_{para}N$); 123.4 (s, $^1J_{CH}$ = 166 Hz, $^2J_{CH}$ = 6 Hz, $C_5H_4N/C_{meta}N$); 121.7 (s, Fe—C≡ C) ; 121.6 (s, $^1J_{CH}$ = 173 Hz, $^2J_{CH}$ = 7 Hz, $C_5H_4N/C_{meta}N$); 88.6 (s, $C_5(CH_3)_5$); 31.1 (m, CH_{2dppe}); 10.5 (s, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_5$). MS (FAB$^+$, *m*-NBA) *m/z* 771 (M+1, 55%); 636 (M+1-Cp*, 3%); 589 (M-"CC-Py-Br", 100%).

[(η^2-dppe)(η^5-C_5Me_5)Fe—C≡C-3-C_5H_3N-5-Br] (6b). In a Schlenk flask, 530 mg of complex [(η^5-C_5Me_5)(η^2-dppe)Fe—C≡ C—H] (**4**, 0.86 mmol), 61 mg of bis(triphenylphosphine)-dichloropalladium (0.09 mmol), 33 mg of copper iodide (0.17 mmol) and 417 mg of 3,5-dibromopyridine (1.72 mmol) were introduced. Subsequently 30 mL of diisopropylamine were added and this mixture was refluxed for 14 h. The solvent was then trapped cryogenically and the brown residue was extracted with a toluene/*n*-pentane mixture and filtered on a celite pad. After removal of the solvents, subsequent washings with 3×10 mL of cold *n*-pentane and 10 mL of acetonitrile yielded the pure **6b** as an orange powder after drying under vaccum (530 mg, 80%). FTIR (Nujol, cm^{-1}) ν 2089 (w, C≡C); 2036 (s, C≡C); 1558 (s, Py); 1540 (m, Py); 1533 (m, Py). FTIR (CH_2Cl_2, cm^{-1}) ν 2089 (w, C≡C); 2038 (s, C≡C); 1558 (m, Py); 1534 (w, Py); 1518 (w, Py). ^{31}P NMR {^1H} (81 MHz, C_6D_6) δP 100.5 (s, 2P, dppe). ^1H NMR (300 MHz, $CDCl_3$) δH 7.79-7.27 (m, 22H, 4 C_6H_5 + C_5H_3N/H_{ortho}); 7.04 (s, 1H, C_5H_3N/H_{para}); 2.60 (m, 2H, CH_{2dppe}); 1.97 (m, 2H, CH_{2dppe}); 1.41 (s, 15H, $C_5(CH_3)_5$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δC 154.3 (t, $^2J_{CP}$ = 38 Hz, Fe—C≡C); 149.7 (s, $^1J_{CH}$ = 179 Hz, $C_5H_3N/C_{ortho}N$); 144.0-127.4 (m, Ph_{dppe}); 143.6 (s, $^1J_{CH}$ = 190 Hz, $C_5H_3N/C_{ortho}N$); 138.7 (s, $^1J_{CH}$ = 170 Hz, $C_5H_4N/C_{para}N$); 128.5 (s, $C_5H_4N/C_{meta}N$); 120.2 (s, $C_5H_4N/C_{meta}N$); 115.5 (s, Fe—C≡C); 88.1 (s, $C_5(CH_3)_5$); 30.5 (m, CH_{2dppe}); 10.1 (s, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_5$).

[(η^2-dppe)(η^5-C_5Me_5)Fe—C≡C-2-C_5H_3N-6-C≡C—SiMe3] (8a). In a Schlenk flask, 180 mg of complex [(η^5-C_5Me_5)(η^2-dppe)Fe—C≡ C-2-C_5H_3N-6-Br)] (**6a**) (0.23 mmol), 16 mg of bis(triphenylphosphine)dichloropalladium (0.02 mmol), 9 mg of copper iodide (0.05 mmol) and 20 mL of diisopropylamine were introduced under argon. Subsequently, a large excess of trimethylsilylacetylene (0.34 ml, 2.3 mmol) was syringed in the medium and the orange mixture was stirred for 48 h at 70 °C. The solvent was then evacuated and the remaining residue was extracted with toluene (4×10 mL). The extract was filterred on a celite pad. Evaporation of the solvent and washings with small portions of *n*-pentane (2×10 mL) yielded then coupled product **8a** as an orange-yellow slightly air-sensitive solid (66%, 120 mg). FTIR (Nujol, cm^{-1}) ν 2161 (vw, C≡C); 2035 (s, C≡C); 1566 (m, Py); 1560 (w); 1539 (m, Py). FTIR (CH_2Cl_2, cm^{-1}) ν 2163 (vw, C≡C); 2040 (s, C≡C); 1571 (s, Py); 1549 (s, Py). ^{31}P {^1H} NMR (81 MHz, C_6D_6) δP 101.3 (s, 2P, dppe). ^1H NMR (200 MHz, C_6D_6) δH 8.17-6.86 (m, 23H, 4 C_6H_5 + C_5H_3N); 2.71 (m, 2H, CH_{2dppe}); 1.78 (m, 2H, CH_{2dppe}); 1.51 (s, 15H, $C_5(CH_3)_5$); 0.19 (s, 9H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (50 MHz, C_6D_6) δC 149.1 (t, $^2J_{CP}$ = 38 Hz, Fe—C≡C); 148.2 (s, $^2J_{CH}$ = 6 Hz, C_5H_3N/C_{ipso}); 143.4 (s, $^2J_{CH}$ = 6 Hz, C_5H_4N/C_{ipso}); 139.9-127.5 (m, Ph_{dppe} + $C_5H_4N/C_{para}N$); 124.8 (s, $^1J_{CH}$ = 166 Hz, $^2J_{CH}$ = 7 Hz, $C_5H_4N/C_{meta}N$); 122.1 (m, Fe—C≡C); 121.7 (s, $^1J_{CH}$ = 157 Hz, $^2J_{CH}$ = 6 Hz, $C_5H_4N/C_{meta}N$); 107.2 (s, C≡C—Si); 91.7 (s, C≡C—Si); 88.4 (s, $C_5(CH_3)_5$); 31.2 (m, CH_{2dppe}); 10.6 (s, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_5$); 0.1 (s, $^1J_{CH}$ = 120 Hz, $Si(CH_3)_3$).

[(η^2-dppe)(η^5-C_5Me_5)Fe—C≡C-3-C_5H_3N-5-C≡C—SiMe3] (8b). In a Schlenk flask, 300 mg of complex [(η^5-C_5Me_5)(η^2-dppe)Fe—C≡ C-3-C_5H_3N-5-Br] (**6b**) (0.39 mmol), 27 mg of bis(triphenylphosphine)dichloropalladium (0.04 mmol), 15 mg of copper iodide (0.08 mmol) and 30 mL of diisopropylamine were introduced under argon. Subsequently, a large excess of trimethylsilylacetylene (0.56 ml, 3.9 mmol) was syringed in the medium and the orange mixture was stirred for 48 h at 70 °C. The solvent was then cryogenically trapped and the brown residue was extracted with toluene (4×10 mL) and filtered on a celite pad. After removal of the solvents, subsequent washings with 2×10 mL of cold *n*-pentane allowed the isolation of a brown powdered mixture (190 mg) of **8b** and **6b** (ratio 78/22). Only characterisation of **8b** (49%) is given in the following. FTIR (Nujol, cm^{-1}) ν 2158 (w, C≡C); 2034 (s, C≡C); 1564 (m, Py). ^{31}P {^1H} NMR (81 MHz, C_6D_6) δP 100.9 (s, 2P, dppe). ^1H NMR (200 MHz, C_6D_6) δH 8.72 (d, 1H, $^3J_{HH}$ = 2.1 Hz, C_5H_3N); 8.57 (d, 1H, $^3J_{HH}$ = 2.1 Hz, C_5H_3N); 7.91-6.96 (m, 21H, 4 C_6H_5 + C_5H_3N); 2.45 (m, 2H, CH_{2dppe}); 1.74 (m, 2H, CH_{2dppe}); 1.45 (s, 15H, $C_5(CH_3)_5$); 0.20 (s, 9H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δC 150.9 (t, $^2J_{CP}$ = 41 Hz, Fe—C≡C); 150.7 (s, $^1J_{CH}$ =

183 Hz, $C_5H_4N/C_{ortho N}$); 145.3 (s, $^1J_{CH}$ = 182 Hz, $C_5H_4N/C_{ortho N}$); 139.1 (s, $^1J_{CH}$ = 166 Hz, C_5H_4N/C_{para}); 138.7-127.3 (m, Ph_{dppe}); 126.5 (s, $C_5H_4N/C_{meta N}$); 119.0 (s, $^2J_{CH}$ = 8 Hz, $C_5H_4N/C_{meta N}$); 115.6 (s, Fe—C≡C); 102.7 (s, C≡C—Si); 96.5 (s, C≡C—Si); 88.0 (s, $C_5(CH_3)_5$); 30.5 (m, CH_{2dppe}); 10.1 (s, $^1J_{CH}$ = 126 Hz, $C_5(CH_3)_5$); 0.0 (s, $^1J_{CH}$ = 120 Hz, $Si(CH_3)_3$).

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