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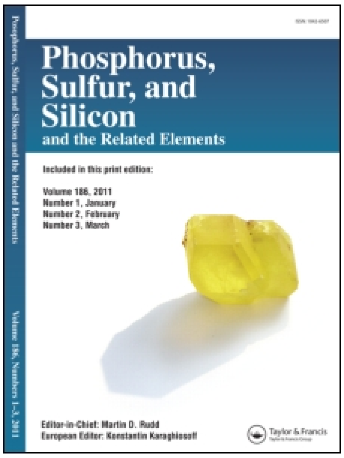

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Syntheses and Characterization of 1,1'-Bis(3-Pyridylethynyl)Ferrocene and 1,1'-Bis(4-Pyridylethynyl)Ferrocene

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Two novel disubstituted ferrocene, 1,1'-bis(3-pyridylethynyl)ferrocene **1** and 1,1'-bis(4-pyridylethynyl)ferrocene **2**, were synthesized and fully characterized by elemental analysis, ^1H NMR, ^{13}C NMR, IR, and X-ray crystallography. Compound **1**crystallizes in monoclinic, space group Cc, a=17.26Å, b=9.77Å, c=10.85Å, β=105.45; R_1 =0.0399, wR_2=0.1077, GooF=1.023. The two arms of the ferrocene are parallel, which will play an important role both in the coordination chemistry and electronic communication of the ferrocene.

Keywords: disubsitituted; ferrocene; ethynyl; pyridine

INTRODUCTION

Electronic communication has received much attention and is a field with great potential of development. Intramolecular electronic communication between two or more metal centers, one of which is ferrocene subunit, is a more active field in this regard. The extent of intramolecular electronic communication mainly depends on the nature of the metals [1], the bridges between the metal centers [2-3], and the chelating sites [1]. Ferrocene has become a choice due to its well-known redox activity and the ease of synthesis. Carbon-rich bridges such as -C≡C-, $-C\equiv C-C_6H_4-C\equiv C-$ and the combinations of the two and chelating sites like pyridine and polypyridine have been a study point. However, most published work concerns "body" ferrocenes with either the carbon-rich "arms" or pyridine and polypyridine "hands". Only a few monosubstituted ferrocenes with one such arm and hand have been studied [4]. This defect prompted us to design and construct ferrocenes with two arms and two hands. Our research interest is to synthesize disubstituted ferrocenes with linear, up to nanoscale, all conjugated, carbon-rich, rigid bridges and polypyridine hands, and to investigate intramolecular long-range, two-way electronic communications. In this paper, we present our preliminary study on the model precursors, 1,1'-bis(3-pyridylethynyl)ferrocene **1** and 1,1'-bis(4-pyridylethynyl)ferrocene **2**.

RESULTS AND DISCUSSION

Compounds **1** and **2** were synthesized by palladium-promoted coupling reactions of 1,1'-diiodoferrocene and 3-pyridylethyne or 4-pyridylethyne respectively in satisfying yield. Standard palladium-promoted coupling reactions were also applied in the preparation of 3-[2-(trimethylsilyl)-1-ethynyl]pyridine and 4-[2-(trimethylsilyl)-1-ethynyl]pyridine, which were converted to the terminal alkynes by potassium fluoride in methanol. The deprotonation of the commercial reagent, 4-bromopyridine hydrochloride described in literature [5] was proved to be not easy and not necessary. Instead of 4-bromopyridine, 4-bromopyridine hydrochloride was used without further treatment and the coupling reaction of it with trimethylsilylacetylene in diethylamine was found to be quantitative (based on ^{1}H NMR analysis). The 4-ethynylpyridine was purified by sublimination under vacuum. Compounds **1** and **2** were purified by chromatography. Slow diffusion of n-hexane into the solution of **1** in dichloromethane gave red needle crystals. The X-ray crystallographic data are listed in **TABLE 1.**

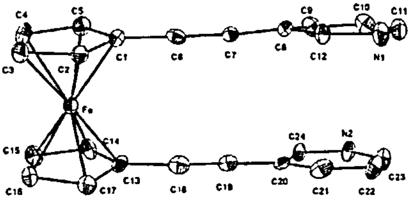

FIGURE 1. Crystal structure of **1**, drawn at 20% thermal ellipsoids. Hydrogen atoms omitted for clarity. Distances (Å) and torsion angles (deg): C3-C16: 3.2154, C1-C13: 3.3634, C6-C18: 3.4670, C7-C19: 3.4815, C8-C20: 3.6130, C11-C23: 3.7673, C1-C13-C20-C8: 0.78; C8-C11-C23-C20: 11.39

TABLE 1. Crystal Data and Structure Refinement for 1

empirical formula	$C_{24}H_{16}FeN_2$
formula weight	388.24
temperature	-100°C
crystal system	monoclinic
space group	Cc
unit cell dimensions	a= 17.26Å
	b=9.77Å
	c=10.85Å
	β=105.45°
	V=1764.56
	Z=4
density (calcd.)	1.461
no.of reflns collected	8054
unique reflns	4057 (3491 $I \geq 2\sigma(I)$)
refinement	Full-matrix least-squares on F^2
data/restraints/params	4057 / 3 / 338
goodness of fit on F^2	1.023
final R indices (obsd. data)	R_1= 0.0399, wR_2=0.1077
R indices (all data)	R_1= 0.0474, wR_2=0.1141
largest diff. peak and hole	0.25 and -0.35

The two arms of the ferrocene are parallel as shown in **FIGURE 1**, suggesting that π-π stacking is preferred. Racemic isomers are found in the crystals of **1**. Both **1** and **2** give us clean ^{13}C NMR spectra as shown in **FIGURE 2**. The broadened ^{13}C NMR of **1** in solution may imply free rotation of the two side chains along the bridging axes, which might be important for its complexation with other metal.

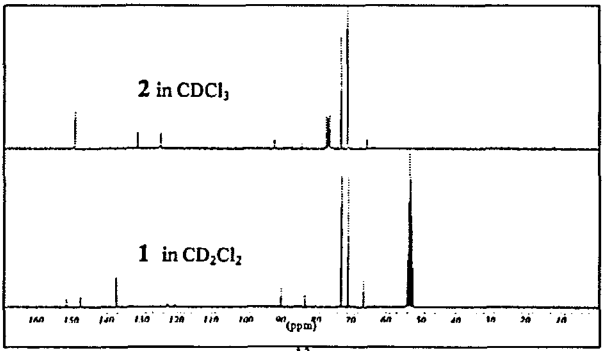

FIGURE 2. ^{13}C NMR of 1 and 2

EXPERIMENTAL

Schlenk technique under argon was applied to all the coupling reactions. Common methods were used to dry the solvents. All chemicals were purchased from ARCOS and Fluka and were used as received.

Synthesis of 4-ethynylpyridine. To the well degased 4-bromopyridine hydrochloride diethylamine solution, trimethylsilylacetylene and $Pd(PPh_3)_2Cl_2$ / CuI were added successively. The mixture was stirred overnight, and the solvent was removed. The residue was dissolved in methanol and KF was added. Some hours later, methanol was removed, followed by sublimination.

3-Ethynylpyridine. Similar method was used.

1,1'-Bis(3-pyridylethynyl)ferrocene 1. To a well degased solution of 1,1'-diiodoferrocene in diisopropylamine were added 3-pyridylethylene, $Pd(PPh_3)_2Cl_2$ / CuI. After reluxing overnight, the solvent was removed and some water was added. The product was extracted with dichloromethane, dried over $MgSO_4$. Chromatography gave compound **1** as red power. Yield 30%. EI-MS, 388.0 (M^+),165.7 ($Cp\text{-}C_2\text{-}Py^+$); IR (KBr), 2206cm-1 (s, $\nu_{C\equiv C}$); ^1H NMR (CD_2Cl_2), 8.60 (s, 2H), 8.45 (s, 2H), 7.61 (d, J=7.69Hz, 2H), 7.14 (m, 2H), 4.58 (s, 4H), 4.37 (s, 4H); ^{13}C NMR (CD_2Cl_2), 152.33, 148.38,138.27, 123.50, 121.40, 90.77, 84.02, 73.59, 71.60, 67.16.

1,1'-Bis(4-pyridylethynyl)ferrocene 2. Red solid, Yield 33%.EI-MS, 387.9 (M^+), 165.9 ($Cp\text{-}C_2\text{-}Py^+$); IR (KBr), 2205cm-1(s, $\nu_{C\equiv C}$);^1H NMR ($CDCl_3$), 8.48 (d, J=5.34Hz, 4H), 7.23 (d, J=5.34Hz, 4H), 4.60 (t, J=1.88Hz, 4H), 4.40 (t, J=1.88Hz, 4H); ^{13}C NMR ($CDCl_3$), 149.75, 131.96, 125.43, 92.53, 84.73, 73.50, 71.56, 66.09; Anal. Calcd (Found) for $C_{24}H_{16}FeN_2$ C, 74.25 (73.12); H, 4.15 (3.90); N, 7.22 (6.98).

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