



## Synthesis and chemical oxidation of 3-ferrocenylpyrrole and ferrocenyl-substituted triazoles: Iron versus ligand based oxidation

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### ABSTRACT

Copper catalyzed [3+2] cycloaddition reactions between ethynylferrocene and benzylazides yields 1-benzyl-4-ferrocenyl-1,2,3-triazoles (**2–5**). Reaction between phenylacetylene and azidoferrrocene yields 1-ferrocenyl-4-phenyl-1,2,3-triazole (**6**). Anodic electrochemistry of **2–6** suggests reversible oxidation at potentials more positive than ferrocene. Chemical oxidation of **2** and 3-ferrocenylpyrrole (**1**) with dichlorodicyanoquinone (DDQ) yields the salts  $[2^+][DDQ^-]$  and  $[1^+][DDQ^-]$ , respectively. <sup>57</sup>Fe Mössbauer spectroscopy reveals the presence of low-spin Fe<sup>II</sup> in  $[1^+][DDQ^-]$  while Fe<sup>II</sup> is oxidized to low-spin Fe<sup>III</sup> in  $[2^+][DDQ^-]$ . Magnetization measurements indicate that  $[1^+][DDQ^-]$  is paramagnetic and cannot be viewed as a simple neutral charge transfer complex reminiscent of the mixed stack diamagnetic  $[ferrocene]^0[TCNE]^0$ .

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### 1. Introduction

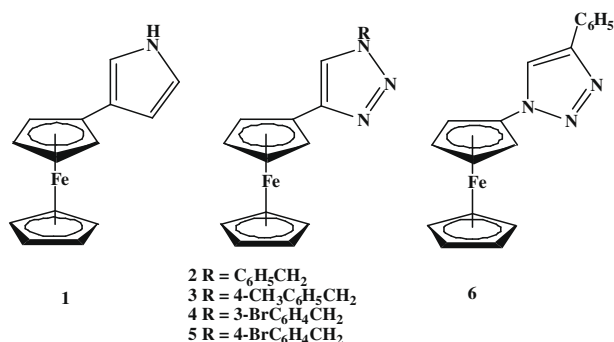
Copper catalyzed [3+2] cycloaddition (“click”) reactions have been used to functionalize dendrimers [1], modify graphite surfaces [2] and self-assembled monolayers at electrodes [3] with 4-ferrocenyl-1,2,3-triazoles. The functionalized electrodes allow for studies of electron transfer rates in a variety of redox processes. A fundamental assumption in the latter studies has been that oxidation occurs at the Fe<sup>II</sup> of the ferrocene moiety. Evidence supporting this assumption is found in the spectroelectrochemistry of 1,1'-bis(4-pyridyl) ferrocene where oxidation leads to a UV spectrum consistent with formation of a ferrocenium ion [4]. On the other hand, the nitrogen containing ferrocene derivative 3-ferrocenylpyrrole (**1**) undergoes a reversible, electrochemical oxidation at 0.25 V versus SCE in acetonitrile solution, however, electrochemistry alone could not distinguish between oxidation at the Fe<sup>II</sup> center and oxidation of the pyrrole substituent [5].

In related work, the premise that oxidation of ferrocenes with phosphorus-containing substituents occurs at iron has recently been explored by several groups [6–9]. Studies of the chemical and electrochemical oxidation of ferrocenyl phosphines indicate that oxidation and/or intramolecular electron transfer results in the apparent loss of electrons from the phosphorus rather than

the iron(II) center. For example, electrochemical oxidation of 1,1'-bis(diphenylphosphino) ferrocene (dppf) and 1,1'-bis(diisopropylphosphino) ferrocene (dippf) leads to the dimerization of phosphorus-centered radicals [7]. Similarly, the anodic electrochemistry of  $[CpFe(C_5H_4)]_3P$ ,  $[CpFe(C_5H_4)]_2PPh$ ,  $[CpFe(C_5H_4)]_2P=O(Ph)$  and  $[CpFe(C_5H_4)]_3P=Se$ , is consistent with loss of an electron from a largely ferrocenyl-based HOMO with significant phosphine- or phosphine chalcogenide character [8]. In these ferrocenylphosphines, electrochemical oxidation also appears to lead to products derived from dimerization of phosphorus-centered radicals [9]. Anodic oxidation of 1,1'-bis(di-*tert*-butylpropylphosphino)ferrocene (dtbpf), however, is reversible and does not lead to dimerization, reflecting the larger substituents on phosphorus [10].

Chemical oxidation of  $[CpFe(C_5H_4)]_3P$  and  $[CpFe(C_5H_4)]_2PPh$  with DDQ yields products containing the  $DDQ^-$  anion and low-spin Fe<sup>II</sup> [11]. The possibility that oxidation of ferrocenylpyrrole and related ferrocene-substituted nitrogen heterocycles might lead to loss of an electron from a HOMO with significant nitrogen character rather than iron, led to the present study of the chemical oxidation of **1** and 1-benzyl-4-ferrocenyl-1,2,3-triazole (**2**). In this paper, we report on the synthesis and characterization of five ferrocene-substituted triazoles, 1-benzyl-4-ferrocenyl-1,2,3-triazole (**2**), 1-(*p*-methylbenzyl)-4-ferrocenyl-1,2,3-triazole (**3**), 1-(*m*-bromobenzyl)-4-ferrocenyl-1,2,3-triazole (**4**), 1-(*p*-bromobenzyl)-4-ferrocenyl-1,2,3-triazole (**5**) and 1-ferrocenyl-4-phenyl-1,2,3-triazole (**6**). We also describe the differences in the chemical oxidation products of **1** and **2**.

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## 2. Experimental

All compounds described in this work were handled using Schlenk techniques or in a M.I. Braun glove-box under purified argon or nitrogen atmospheres. Ethynylferrocene [12], 3-ferrocenylpyrrole (**1**) [5] and benzyl azides [13] were prepared by literature methods. Solvents were purified by refluxing over Na/benzophenone (petroleum ether) or P<sub>2</sub>O<sub>5</sub> (dichloromethane) and distilled prior to use. Elemental analyses (C, H, N) were performed by Columbia Analytical Services, Inc.

NMR spectra were recorded at 300 MHz for <sup>1</sup>H, and 75.4 MHz for <sup>13</sup>C{<sup>1</sup>H} on a Varian Mercury VX300 spectrometer. Proton chemical shifts are reported relative to residual protons in the solvent (CHCl<sub>3</sub> at δ 7.24 ppm) referenced to TMS at 0.00 ppm. Carbon chemical shifts are reported relative to solvent (CHCl<sub>3</sub> t at δ 77.0 ppm) referenced to TMS at 0.00 ppm.

Electrochemical measurements were made under nitrogen on a BAS 100 B/W electrochemical workstation at 22 °C using 1 × 10<sup>-3</sup> M solutions in dry CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte at a scan rate of 100 mV/s. The working electrode was a 3-mm Pt disk with a Pt wire as auxiliary electrode. A silver wire was used as a pseudo-reference electrode with ferrocene added as an internal standard with all potentials referenced to ferrocene (*E*<sub>1/2</sub> = 0.00 V).

Variable temperature Mössbauer spectra were recorded on a standard constant acceleration apparatus [14] operated in the mode using a γ-ray source of 25 mCi <sup>57</sup>Co in a rhodium metal matrix. Temperature control was achieved using an uncalibrated silicon diode coupled to a Lake Shore Cryotronics Model DT-500 set point controller. Temperature measurements were made using a calibrated silicon diode driven by a 10 μA constant current source in conjunction with a digital voltmeter. Mössbauer spectra were fitted using a least-squares-Lorentzian program [15]. Magnetization measurements were performed on a Lakeshore AC susceptometer and a Quantum Design MPMS SQUID device.

### 2.1. Preparation of 1-benzyl-4-ferrocenyl-1,2,3-triazole (**2**)

Two-hundred fifty milligram (1.2 mmol) ethynylferrocene was added to a solution of 236 mg (1.8 mmol) benzylazide in 25 mL 50% aqueous <sup>t</sup>butanol (v/v) containing 30 mg (0.12 mmol) CuSO<sub>4</sub>·5H<sub>2</sub>O and 60 mg (0.30 mmol) sodium ascorbate. Heating the mixture at 60 °C for 48 h yielded a yellow-orange slurry. The reaction mixture was poured into 25 mL of water and extracted 3 × 25 mL dichloromethane. The organic layers were combined, dried over magnesium sulfate and filtered. Evaporation of solvent from the filtrate yielded an orange solid that was chromatographed on alumina using dichloromethane as the eluent. A single orange fraction was eluted and evaporated to dryness yielding 120 mg (29% yield) of 1-benzyl-4-ferrocenyl-1,2,3-triazole (**2**) as a bright orange powder. Re-crystallization from dichloromethane/petroleum ether was used to obtain analytically pure samples. Brown

residues that remain at the top of the column could not be successfully eluted with more polar solvents such as chloroform or methanol. A slightly improved yield (34%) was obtained from reactions at ambient temperature for 3 days. m.p. 157–158 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.09 s (5H, C<sub>5</sub>H<sub>5</sub>), 4.33 m (2H, C<sub>5</sub>H<sub>4</sub>), 4.74 m (2H, C<sub>5</sub>H<sub>4</sub>), 5.52 s (2H, CH<sub>2</sub>), 7.25–7.39 m (6H, C<sub>6</sub>H<sub>5</sub>, CH).

(C<sub>6</sub>D<sub>6</sub>): δ 3.99 s (5H, C<sub>5</sub>H<sub>5</sub>), 4.10 m (2H, C<sub>5</sub>H<sub>4</sub>), 4.74 m (2H, C<sub>5</sub>H<sub>4</sub>), 4.85 s (2H, CH<sub>2</sub>), 6.72–7.3 m (6H, C<sub>6</sub>H<sub>5</sub>, CH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): singlets at δ 54.01, 66.83, 68.94, 69.92, 75.99, 118.77, 127.83, 128.63, 129.06, 134.87, 147.22.

Anal. Calc. for C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>Fe: C, 66.50; H, 4.99, N, 12.24. Found: C, 66.30; H, 4.92; N, 12.01%.

### 2.2. Ruthenium-catalyzed reaction of ethynylferrocene with benzyl azide

A 5-mm screw capped NMR tube was charged with a solution of 26 mg (0.12 mmol), 19 mg (0.14 mmol) benzyl azide and 3 mg Cp\*<sup>n</sup>Ru(PPh<sub>3</sub>)<sub>2</sub>Cl in 0.5 mL C<sub>6</sub>D<sub>6</sub>. The tube was heated to 80 °C for 2 h and the composition of the mixture evaluated by <sup>1</sup>H NMR. Resonances assigned to the starting materials disappeared and were replaced by resonances assigned to 1-benzyl-5-ferrocenyl-1,2,3-triazole.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.01 s (5H, C<sub>5</sub>H<sub>5</sub>), 3.84 m (2H, C<sub>5</sub>H<sub>4</sub>), 4.34 m (2H, C<sub>5</sub>H<sub>4</sub>), 5.27 s (2H, CH<sub>2</sub>), 6.85–7.80 m (6H, C<sub>6</sub>H<sub>5</sub>, CH).

### 2.3. Preparation of 1-(*p*-methylbenzyl)-4-ferrocenyl-1,2,3-triazole (**3**)

Following the procedure described above for **2**, reaction of 250 mg (1.2 mmol) ethynylferrocene, 263 mg (1.8 mmol) *p*-methylbenzylazide, 30 mg (0.12 mmol) CuSO<sub>4</sub>·5H<sub>2</sub>O and 60 mg (0.30 mmol) sodium ascorbate at 60 °C for 4 days yielded 139 mg (33% yield) 1-(*p*-methylbenzyl)-4-ferrocenyl-1,2,3-triazole (**3**) as a yellow-orange solid after chromatography and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether. m.p. 157–159 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.35 s (3H, CH<sub>3</sub>), 4.21 s (5H, C<sub>5</sub>H<sub>5</sub>), 4.48 m (2H, C<sub>5</sub>H<sub>4</sub>), 4.88 m (2H, C<sub>5</sub>H<sub>4</sub>), 5.44 s (2H, CH<sub>2</sub>), 7.00–7.39 m (5H, C<sub>6</sub>H<sub>4</sub>, CH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): singlets at δ 21.13, 53.81, 66.67, 68.72, 69.83, 75.72, 118.62, 127.90, 129.71, 131.81, 138.55, 147.10.

Anal. Calc. for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>Fe: C, 67.24; H, 5.36; N, 11.76. Found: C, 67.14; H, 5.04; N, 11.75%.

### 2.4. Preparation of 1-(*m*-bromobenzyl)-4-ferrocenyl-1,2,3-triazole (**4**)

Following the procedure described above for **2**, reaction of 250 mg (1.2 mmol) ethynylferrocene, 378 mg (1.8 mmol) *m*-bromobenzylazide, 30 mg (0.12 mmol) CuSO<sub>4</sub>·5H<sub>2</sub>O and 60 mg (0.30 mmol) sodium ascorbate for 4 days at 60 °C yielded 185 mg (36% yield) 1-(*m*-methylbenzyl)-4-ferrocenyl-1,2,3-triazole (**4**) as a yellow-orange solid after chromatography and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether. m.p. 158–160 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.07 s (5H, C<sub>5</sub>H<sub>5</sub>), 4.31 m (2H, C<sub>5</sub>H<sub>4</sub>), 4.72 m (2H, C<sub>5</sub>H<sub>4</sub>), 5.48 s (2H, CH<sub>2</sub>), 7.15–7.50 m (5H, C<sub>6</sub>H<sub>4</sub>, CH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): singlets at δ 53.16, 66.56, 68.66, 69.50, 75.04, 118.69, 123.03, 126.26, 130.62, 130.68, 131.75, 137.10, 147.50.

Anal. Calc. for C<sub>19</sub>H<sub>16</sub>BrN<sub>3</sub>Fe: C, 54.07; H, 3.82; N, 9.95. Found: C, 54.03; H, 3.46; N, 9.82%.

### 2.5. Preparation of 1-(*p*-bromobenzyl)-4-ferrocenyl-1,2,3-triazole (**5**)

Following the procedure described above for **2**, reaction of 157 mg (0.76 mmol) ethynylferrocene, 297 mg (1.4 mmol) *p*-bromobenzylazide, 32 mg (0.13 mmol) CuSO<sub>4</sub>·5H<sub>2</sub>O and 44 mg (0.23 mmol) sodium ascorbate for 4 days at ambient temperature yielded 79 mg (25% yield) 1-(*p*-bromobenzyl)-4-ferrocenyl-1,2,3-

triazole (**5**) as a yellow-orange solid after chromatography and crystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether. m.p. 185–186 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.04 s (5H,  $\text{C}_5\text{H}_5$ ), 4.27 m (2H,  $\text{C}_5\text{H}_4$ ), 4.67 m (2H,  $\text{C}_5\text{H}_4$ ), 5.48 s (2H,  $\text{CH}_2$ ), 7.14 d ( $J = 8.1$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 7.35 s (1H, CH), 7.51 d ( $J = 8.1$  Hz, 2H,  $\text{C}_6\text{H}_4$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): singlets at  $\delta$  53.31, 66.57, 68.66, 69.58, 72.34, 118.57, 122.79, 129.45, 132.24, 133.86, 147.46.

Anal. Calc. for  $\text{C}_{19}\text{H}_{16}\text{BrN}_3\text{Fe}$ : C, 54.07; H, 3.82; N, 9.95. Found: C, 54.32; H, 3.63; N, 9.85%.

### 2.6. Preparation of 1-(ferrocenyl)-4-phenyl-1,2,3-triazole (**6**)

A solution of ferrocenylazide [16] was prepared in situ by stirring 114 mg (1.8 mmol)  $\text{NaN}_3$  and 466 mg (1.8 mmol) bromoferrocene in 25 mL 50% aqueous  $t$ -butanol (v/v) at ambient temperature for 2 days. Subsequently, 400  $\mu\text{L}$  (3.4 mmol) phenylacetylene, 30 mg (0.12 mmol)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 60 mg (0.30 mmol) sodium ascorbate were added and the reaction mixture stirred at ambient temperature for 4 days. Following the workup described for **2**, 60 mg (10% yield) of 1-ferrocenyl-4-phenyl-1,2,3-triazole (**6**) was isolated as a yellow-orange solid after chromatography and crystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether. Compound **6** decomposes above 215 °C without melting.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 4.26 s (5H,  $\text{C}_5\text{H}_5$ ), 4.32 m (2H,  $\text{C}_5\text{H}_4$ ), 4.91 m (2H,  $\text{C}_5\text{H}_4$ ), 7.36 d ( $J = 7.5$  Hz, 1H, phenyl), 7.45 t ( $J = 7.5$  Hz, 2H, phenyl), 7.88 d ( $J = 7.5$  Hz, 2H, phenyl), 7.96 s (1H, CH).

Anal. Calc. for  $\text{C}_{18}\text{H}_{15}\text{N}_3\text{Fe}$ : C, 65.68; H, 4.59; N, 12.77. Found: C, 65.74; H, 4.25, N, 12.28%.

### 2.7. Reaction of 3-ferrocenylpyrrole (**1**) with DDQ

An orange solution of 90 mg (0.40 mmol) DDQ in 12 mL THF was added dropwise to an orange solution of 100 mg (0.40 mmol) **1** in 30 mL THF at ambient temperature where **1**, as prepared in Ref. [5], had the expected elemental Analysis: calculated, C, 66.96; H, 5.22; N, 5.58. Found: C, 67.225; H, 5.14; N, 5.63%. The resulting deep purple solution was evaporated to dryness, yielding 170 mg (90% yield)  $[\mathbf{1}^+][\text{DDQ}^-]$  as a purple solid. The compound does not melt and its dark color prevents the observation of an accurate decomposition temperature. No visible color changes were observed upon exposure of  $[\mathbf{1}^+][\text{DDQ}^-]$  to air. The effects of prolonged exposure to atmospheric oxygen and water on the Mössbauer spectra of the compound were not investigated.

Anal. Calc. for  $\text{C}_{22}\text{H}_{12}\text{Cl}_2\text{FeN}_3\text{O}_2$ : C, 55.27; H, 2.74; N, 8.79. Found: C, 55.68; H, 3.31; N, 8.11%.

In a separate experiment, an orange solution of 180 mg (0.80 mmol) DDQ in 10 mL THF was added dropwise to an orange solution of 100 mg (0.40 mmol) **1** in 20 mL THF at ambient temperature. The purple solution was stirred for 66 h, precipitating a dark solid. The Mössbauer spectrum was essentially identical to that of the preceding 1:1 preparation save that there was no evidence of  $\text{Fe}^{\text{III}}$  impurity (see arrow in Fig. 2 for the 1:1 preparation).

### 2.8. Reaction of 1-benzyl-4-ferrocenyl-1,2,3-triazole (**2**) with DDQ

An orange solution of 34 mg (0.15 mmol) DDQ in 20 mL  $\text{CH}_2\text{Cl}_2$  was added dropwise to an orange solution of 50 mg (0.15 mmol) **2** in 10 mL  $\text{CH}_2\text{Cl}_2$  at ambient temperature over one hour. A dark precipitate forms rapidly upon mixing. After an additional 30 min of reaction, the nearly colorless supernatant was decanted and the dark product dried under vacuum, yielding 56 mg (67% yield)  $[\mathbf{2}^+][\text{DDQ}^-]$  as a bright purple solid. No visible color changes were observed upon exposure of  $[\mathbf{2}^+][\text{DDQ}^-]$  to air for periods <15 min. The effect of prolonged exposure to atmospheric oxygen and water were not investigated. Once again, the compound does not melt

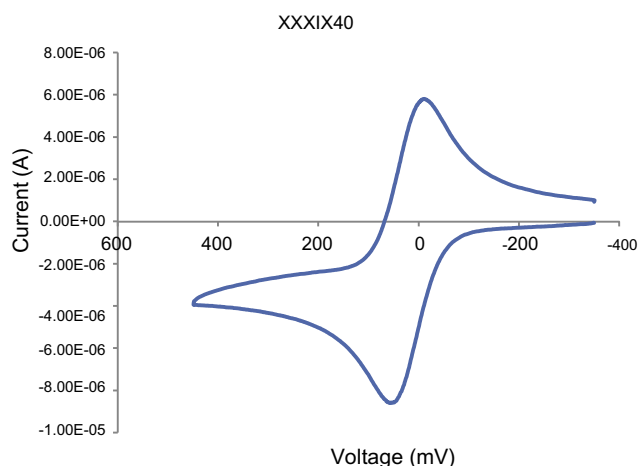


Fig. 1. Cyclic voltammogram of **2** at 22 °C ( $1 \times 10^{-3}$  M solutions in dry  $\text{CH}_2\text{Cl}_2$ ,  $0.1$  M  $^t\text{Bu}_4\text{NPF}_6$ ) at a scan rate of 100 mV/s. The working electrode was a 3 mm Pt disk with a Pt wire as auxiliary electrode. A silver wire was used as a pseudo-reference electrode with ferrocene added as an internal standard with all potentials referenced to ferrocene ( $E_{1/2} = 0.00$  V).

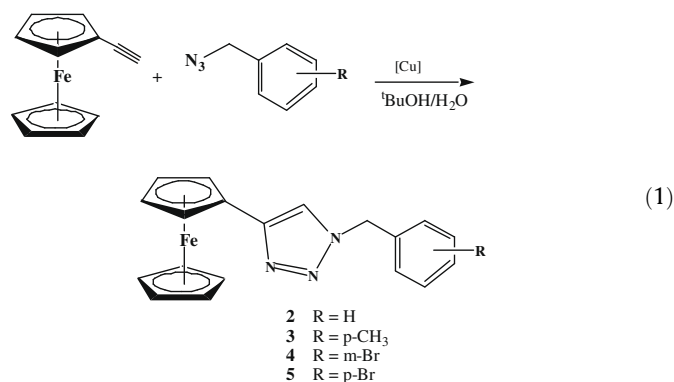
and its dark color prevents the observation of an accurate decomposition temperature.

Anal. Calc. for  $\text{C}_{27}\text{H}_{17}\text{Cl}_2\text{FeN}_5\text{O}_2$ : C, 56.87; H, 3.00; N, 12.28. Found: C, 56.02; H, 3.08; N, 11.99%.

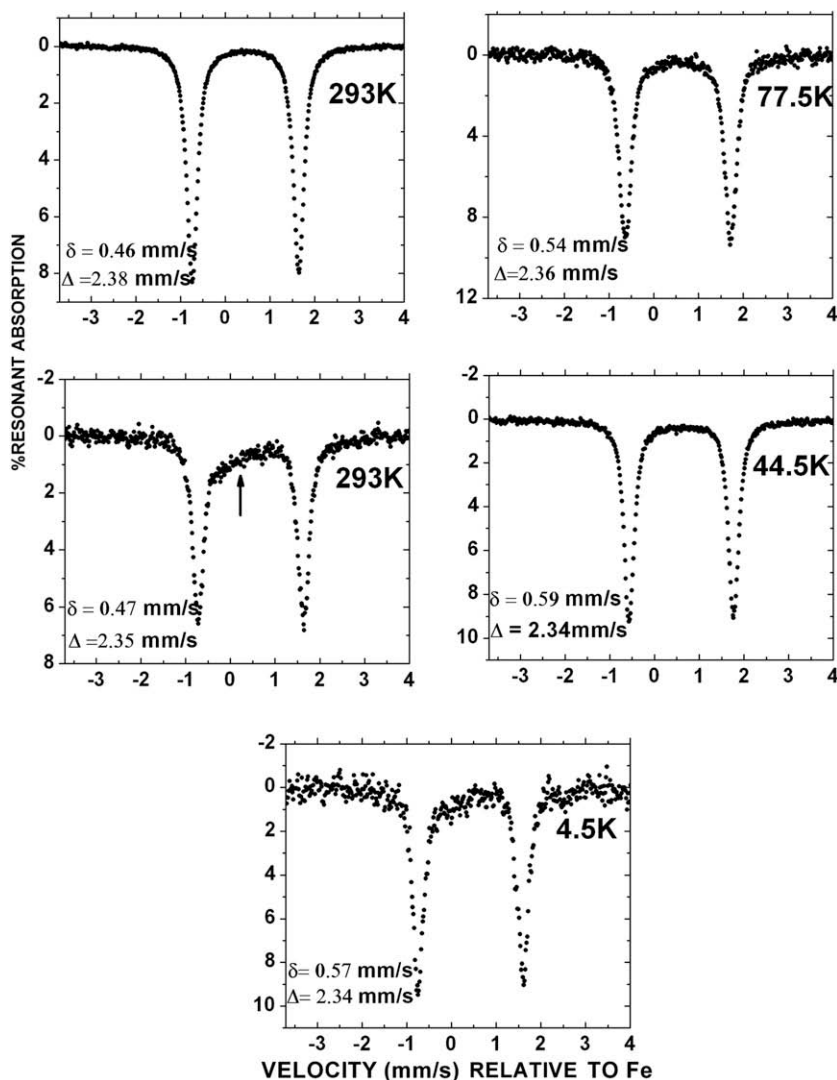
## 3. Results

### 3.1. Synthesis of 1,4-triazoles **2–5**

Copper catalyzed [3+2] cycloaddition of azides to alkynes [17] provides a versatile route for the synthesis of 1,2,3-triazoles. Thus reaction between ethynylferrocene and a series of benzyl azides yields 1,4-triazoles (**2–5**) as shown in Eq. (1). Compounds **2–5**



are isolated as orange, air and thermally stable solids soluble in dichloromethane, THF, acetonitrile and acetone, sparingly soluble in aromatic hydrocarbons with minimal solubility in saturated hydrocarbon solvents. The yields obtained from reactions in aqueous  $t$ -BuOH (50% v/v) at ambient temperature and at 60 °C are moderate, falling in a range from 29% to 36%. Little effort was spent on optimizing yields but yields seem to be somewhat independent of temperature. A high yield synthesis of **2** by Eq. (1) in ionic liquids was reported [18] however the spectra and other characterization data were not provided. The yields from 1,3-dipolar addition of ethynylferrocene to surface bound azidothiols appear to be quantitative as well. During the course of our work, additional ferrocenyl-1,2,3-triazoles were reported, including 1-*p*- $\text{CH}_3$ - $\text{OC}_6\text{H}_4\text{CH}_2$ -4-ferrocenyl-1,2,3-triazole in 68% yield [19]. Finally,



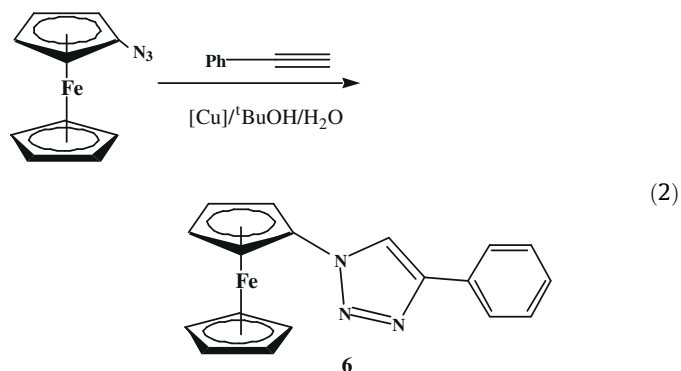
**Fig. 2.**  $^{57}\text{Fe}$  Mössbauer spectrum of **1** at 293 K, top left,  $[\mathbf{1}^+][\text{DDQ}^-]$  at 293, 77.5, 44.5 and 4.2 K. The arrow in the 293 K spectrum (bottom left) indicates the presence of a  $\text{Fe}^{\text{III}}$  impurity in the sample. Spectra at 293 and 4.5 K were obtained on different samples of  $[\mathbf{1}^+][\text{DDQ}^-]$  than spectra at 77.5 and 44.5 K.

1-pentyl-4-ferrocenyl-1,2,3-triazole was isolated from the copper catalyzed reaction of ethynyl ferrocene with azidopentane in aqueous THF in an unspecified yield [1] suggesting that further modifications in reaction conditions (solvent, temperature and catalyst concentration) should increase the yields of **2–5**.

In principle, the reaction in Eq. (1) can lead to two isomers of the triazole: a 1,4- and a 1,5-isomer. The literature on copper catalyzed [3+2] cycloaddition reactions between alkynes and azides suggests a selectivity for the 1,4-isomer while the 1,5-isomer is observed when  $\text{Cp}^*\text{Ru}(\text{PPh}_3)_3\text{Cl}$  is used as the catalyst [20]. Comparing the  $^1\text{H}$  NMR spectra of 1-benzyl-4-phenyl-1,2,3-triazole with 1-benzyl-5-phenyl-1,2,3-triazole in benzene, the chemical shift of the methylene proton of the former is  $\approx 0.4$  ppm upfield of the corresponding resonance for the 1,5-isomer. A similar difference is observed when comparing the  $\text{CH}_2$  resonance in **2** ( $\delta$  4.85) with the product of the  $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$  catalyzed reaction between ethynylferrocene and benzyl azide ( $\delta$  5.27) suggesting that **2–5** are indeed the 1,4-isomers of 1,2,3-triazoles in Eq. (1).

One additional compound, 1-ferrocenyl-4-phenyl-1,2,3-triazole (**6**), was prepared by reaction of azidoferrocene with phenylacetylene as shown in Eq. (2). Compound **6** is also an air-stable, diamagnetic, orange compound that differs from **2** to **5** in having the ferrocene bonded to one of the nitrogens in the triazole ring. All

five new compounds analyzed correctly for carbon, hydrogen and nitrogen.



### 3.2. Electrochemistry of **2–6**

The anodic electrochemistry of **2–6** was investigated by cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$  solution with  $[\text{nBu}_4\text{N}][\text{PF}_6]$  as the supporting electrolyte. The results are summarized in Table 1 and a representative cyclic voltammetric scan (CV) for **2** shown in Fig. 1.

**Table 1**  
Electrochemical data for 3-ferrocenylpyrrole (**1**) and ferrocenyltriazoles **2–6**.<sup>a</sup>

Compound	$E_{1/2}^{0/+}$	$\Delta E^c$	$i_p^a/i_p^c$
<b>1</b> <sup>b</sup>	–150	160	1.04
<b>2</b>	37	60	0.93
<b>3</b>	31	68	0.93
<b>4</b>	32	68	0.97
<b>5</b>	22	64	1.04
<b>6</b>	193	59	1.01
Ferrocene	0	76	1.00

<sup>a</sup> Experimental conditions: 1 mM solution in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  as the supporting electrolyte. Potentials in mV relative to  $\text{FcH}/\text{FcH}^+$  at a scan rate 100 mV/s.

<sup>b</sup> In  $\text{CH}_3\text{CN}$  with  $\text{LiClO}_4$  as supporting electrolyte relative to  $\text{FcH}/\text{FcH}^+$ . See Ref. [5].

<sup>c</sup>  $\Delta E = E_{pa} - E_{pc}$ .

Reversible waves ( $\Delta E = 60\text{--}68$  mV,  $i_{pc}/i_{pa} = 0.93\text{--}1.04$ ) are observed for **2–5** at slightly more positive potentials relative to ferrocene (22–37 mV versus  $\text{FcH}/\text{FcH}^+$ ). These values are similar to those reported for 1-pentyl-4-ferrocenyl-1,2,3-triazole ( $E_{1/2} = 8$  mV in  $\text{CH}_2\text{Cl}_2$ ,  $\Delta E = 60$  mV,  $i_{pc}/i_{pa} = 1.0$ ) [1]. Ferrocenyl substituted pyridines and pyrimidines [4] are oxidized at potentials ranging from 620 to 790 mV in THF versus SCE. When referenced to SCE, the oxidation potentials of **2–5** ranged from 422 to 437 mV, making them slightly easier to oxidize than ferrocenylpyridines and pyrimidines [21]. Relatively small electronic effects of the substituents on the benzyl group on  $E_{1/2}$  are observed. An electron donating methyl group in **3** only shifts the potential closer to that of ferrocene by 6 mV. Curiously, the electron withdrawing bromide substituents in **4** and **5** actually decreases the oxidation potential between 5 (**4**) and 15 mV (**5**). The triazoles, however, are more difficult to oxidize than ferrocenylpyrrole (**1**) by 170–200 mV. Even after accounting for the differences in solvent and supporting electrolyte for the electrochemical measurements, the oxidation potential for **1** appears to be significantly lower than for **2–5** [5].

The oxidation of N-bonded ferrocene in **6** is also reversible but occurs at much more positive potentials than **2–5**. Comparisons of the electrochemistry of **6** with other N-substituted ferrocenyl heterocycles is hampered by differences in solvent and supporting electrolyte both of which can effect the oxidation potential. Nevertheless, the oxidation potential of **6** (193 mV versus  $\text{FcH}$ ) is about  $\approx 150$  mV more positive than the potential for N-ferrocenylpyrrole (50 mV) [22]. The  $E_{1/2}$  for **6** is also considerably more positive than  $E_{1/2}$  for 1,1'-diaminoferrocenes [23]. For example,  $E_{1/2}$  for 1,1'-bis(diphenylamino)ferrocene in acetonitrile is  $-400$  mV relative to  $\text{FcH}/\text{FcH}^+$ , close to 600 mV easier to oxidize than **6**.

### 3.3. Chemical oxidation of **1** and **2**

The electrochemical potentials for **1–6** suggest that only a strong oxidant like dichlorodicyanoquinone (DDQ) will oxidize these compounds. Reaction of **1** with one equivalent of DDQ in THF produces a purple salt,  $[\mathbf{1}^+][\text{DDQ}^-]$ , in high yield.  $^{57}\text{Fe}$  Mössbauer spectra of  $[\mathbf{1}^+][\text{DDQ}^-]$  were recorded over the temper-

**Table 2**  
 $^{57}\text{Fe}$  Mössbauer spectral parameters<sup>a</sup> for **1**,  $[\mathbf{1}^+][\text{DDQ}^-]$  and  $[\mathbf{2}^+][\text{DDQ}^-]$ .

Compound	Temperature (K)	Isomer shift <sup>b</sup> ( $\delta$ )	Quadrupole splitting ( $\Delta$ )
<b>1</b>	293	0.46	2.38
$[\mathbf{1}^+][\text{DDQ}^-]$	293	0.47	2.35
	77.5	0.54	2.36
	44.5	0.59	2.34
	4.5	0.57	2.34
<b>2</b>	77.5	0.57	2.35
	293	0.48	0.25
$[\mathbf{2}^+][\text{DDQ}^-]$	293	0.48	0.25
	77.5	0.59	0.24

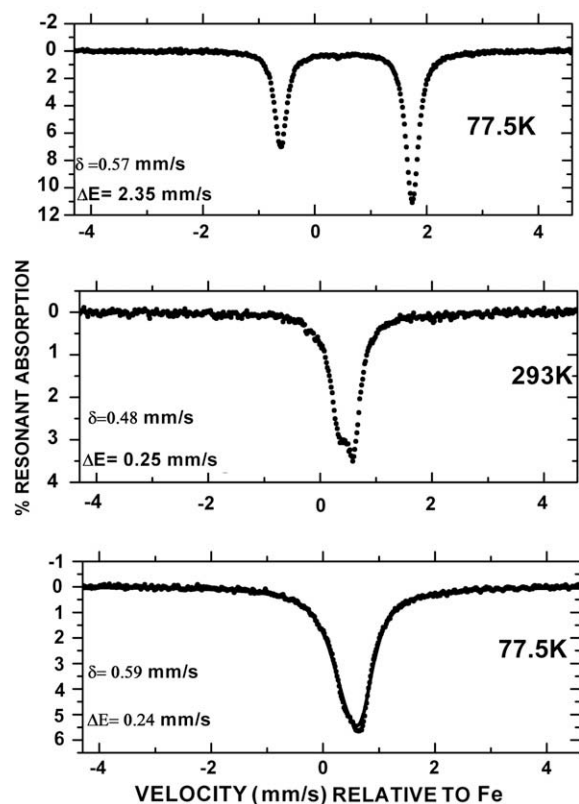
<sup>a</sup> mm/s.

<sup>b</sup> Relative natural iron foil (6.4  $\mu\text{m}$ ).

ature range 293–4.2 K. These spectra, shown in Fig. 2, are virtually indistinguishable from that of the neutral **1** and are fully consistent with oxidation at the pyrrole ring as opposed to the iron(II) centers. The isomer shift and the quadrupole splittings (Table 2 and Fig. 2) are characteristic of low-spin  $\text{Fe}^{\text{II}}$  in ferrocenes i.e.  $\delta$  (with respect to iron metal)  $\sim 0.4\text{--}0.6$  mm/s,  $\delta = 2.20\text{--}2.40$  mm/s [24].

Given the similarities in the cyclic voltammetry of **2–6**, only compound **2** was selected for chemical oxidation with DDQ [25a]. Reaction between **2** (Fig. 3, top) and one equivalent of DDQ also yields a dark purple solid,  $[\mathbf{2}^+][\text{DDQ}^-]$ . The  $^{57}\text{Fe}$  Mössbauer spectra (Fig. 3, middle and bottom) of  $[\mathbf{2}^+][\text{DDQ}^-]$  at both ambient (293 K) and (77.5 K) are characteristic of the low-spin  $\text{Fe}^{\text{III}}$  of typical ferrocenium ions, i.e. the isomer shift is little if at all changed on oxidation from low-spin  $\text{Fe}^{\text{II}}$  to low-spin  $\text{Fe}^{\text{III}}$  while the electric field gradient tensor largely collapses resulting in a decrease in quadrupole splittings from generally  $>2$  mm/s for the low-spin  $\text{Fe}^{\text{II}}$  to  $<0.5$  mm/s for the low-spin  $\text{Fe}^{\text{III}}$  ferrocenium centers. The latter feature has been studied in the work of Collins and Travis [25b] and molecular orbital studies in references therein.

The zero field cooled isothermal magnetization of  $[\mathbf{2}^+][\text{DDQ}^-]$  at 2 K is shown in Fig. 4 wherein it is apparent that  $M$  at 5 T ( $\sim 9300$  emu/mol) is significantly below the saturation value (11,165 emu/mol) expected for spin only behavior of an  $S = 1$  per mole species (i.e. two unpaired electrons). This is consistent with measurable antiferromagnetic interactions between the components of  $[\mathbf{1}^+][\text{DDQ}^-]$  (presumably the pyrrol radical cation and the  $\text{DDQ}^-$  radical anion and for  $[\mathbf{2}^+][\text{DDQ}^-]$  between the ferrocenium center and the  $\text{DDQ}^-$  radical anion).



**Fig. 3.**  $^{57}\text{Fe}$  Mössbauer spectra of **2** at 77.5 K (top). The asymmetry of the spectrum is likely primarily the result of texture in the context of the direction of the principal component of the electric field gradient tensor relative to the direction of  $E_\gamma$  (the high nitrogen content of **2** suggests that grinding of the crystals to minimize texture may be hazardous and was not done),  $[\mathbf{2}^+][\text{DDQ}^-]$  at 293 K (middle), and  $[\mathbf{2}^+][\text{DDQ}^-]$  at 77.5 K (bottom).

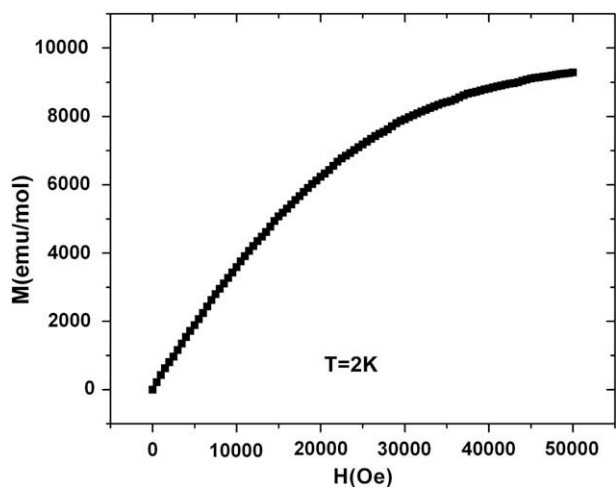


Fig. 4. DC magnetization of  $[2^+][DDQ^-]$  vs.  $H$  at 2 K.

Magnetization measurements via SQUID magnetometry lead to the effective moment temperature dependencies (2–300 K) for  $[1^+][DDQ^-]$  and  $[2^+][DDQ^-]$  shown in Figs. 5 and 6, respectively, and that are qualitatively remarkably similar. At ambient temperature the average moments are  $\sim 2.1$ – $2.2$  Bohr magnetons/spin carrying unit superficially approximating ferrocene donor–acceptor complex salts containing two unpaired electrons that do not interact strongly [26]. Recall that the average spin-only  $\mu$ /spin unit for non-interacting spins (neglecting orbital contributions) is  $\sim 1.73$  BM i.e.  $\langle \mu \rangle = [(\sum_i \mu_i^2)^{1/2}]/(N)^{1/2}$  where  $N$  is the number of independent metals or radicals or metals and radicals. However, with decreasing temperature magnetic exchange interaction generally becomes stronger relative to  $k_B T$  and for the present complexes leads to a gradual decrease of the effective moments to limiting values of  $\sim 0.15$  BM for  $[1^+][DDQ^-]$  and  $1.5$  BM for  $[2^+][DDQ^-]$  at 2 K. This gradual decrease is clearly attests to primarily antiferromagnetic interactions as opposed to single ion zero field splitting effects. In event, the larger overall decrease of  $\mu_{\text{eff}}$  for the former suggests stronger antiferromagnetic exchange in this material than the latter. However, any further comment on the detailed magnetism of these systems is clearly speculative in the absence of definitive structure determinations save to say that there is no evidence of cooperative long-range order at the lowest temperatures that we can conveniently reach. See for example the low field susceptibility of  $[2^+][DDQ^-]$  (bottom of Fig. 6) in this context.

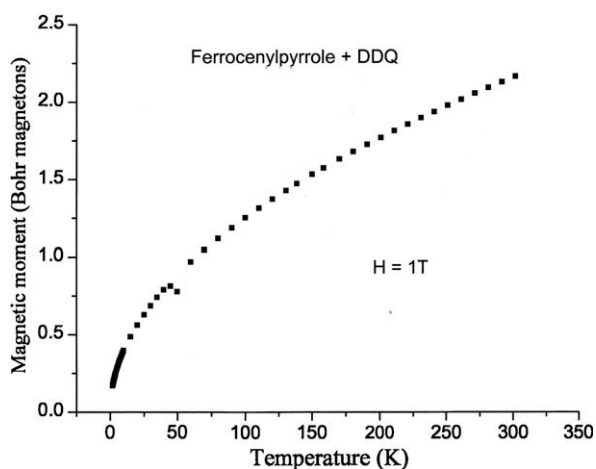


Fig. 5. Effective moment per mol of  $[1^+][DDQ^-]$  vs.  $T$  at 1 T.

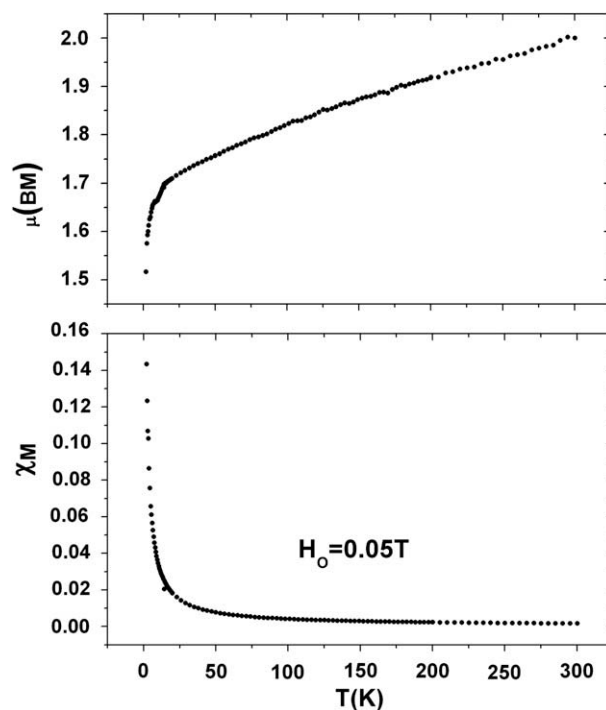
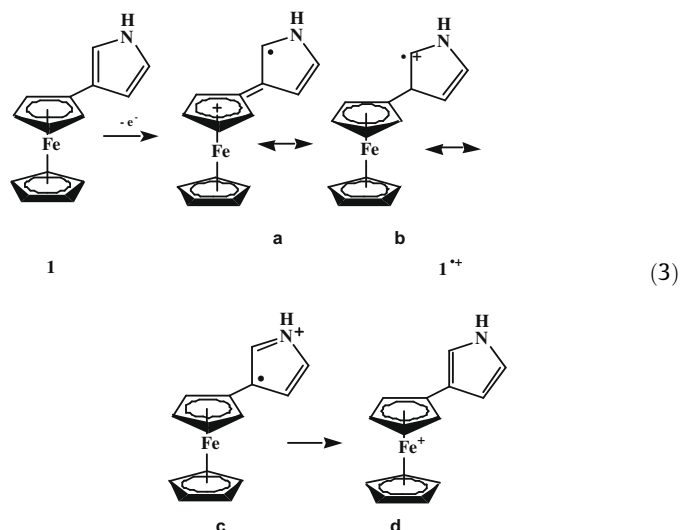


Fig. 6. Effective moment per mol of  $[2^+][DDQ^-]$  vs.  $T$  at 0.05 T (top) and the corresponding molar susceptibility (bottom).

#### 4. Discussion

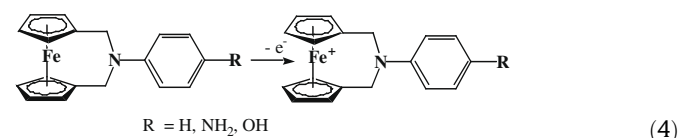
The anodic electrochemistry of **1–6** reveals similar cyclic voltammograms but distinctly different oxidation potentials. The electrochemistry of 3-ferrocenylpyrrole (**1**) reveals a single oxidation at  $E_p^a = -150$  mV versus SCE in  $CH_3CN$  ( $LiClO_4$  as the supporting electrolyte), a potential more negative than ferrocene itself [5]. The separation between the anodic and cathodic peaks in the cyclic voltammogram,  $\Delta E_p = E_p^a - E_p^c = 160$  mV and  $E_p^a - E_{p/2} = 90$  mV suggests that the oxidation is not entirely reversible. The ratio  $i_p^a/i_p^c = 1.04$ , however, suggests a reversible process. These data were interpreted using the scheme in Eq. (3) [5] where initial oxidation occurs at the pyrrole ligand and is followed by intramolecular electron transfer from iron yielding a ferricenium ion. However, the Mössbauer spectroscopy study of the present investigation of  $[1^+][DDQ^-]$  clearly demonstrates that in the solid state, the product of chemical oxidation of **1** contains low-spin iron(II) not iron(III).



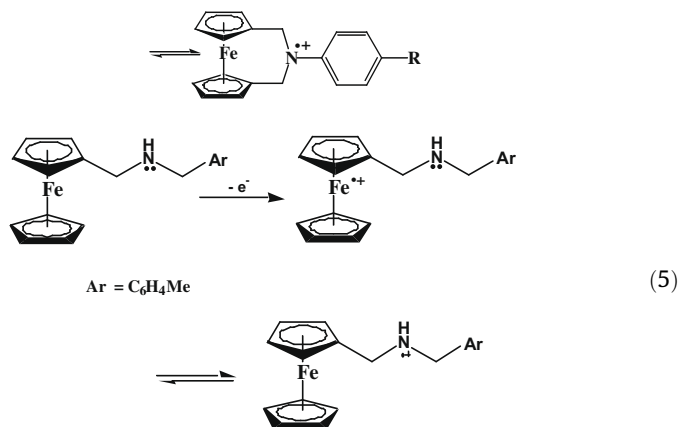
The susceptibility data (both  $\mu_{\text{eff}}$  versus  $T$  and  $M$  versus  $H$ ) confirm that electron transfer has indeed occurred and that the product of the reaction between **1** and DDQ is not a (diamagnetic) neutral charge transfer complex similar to the mixed stack tetracyanoethylene complex of ferrocene [27], or the iodine adduct of  $\text{FcCH}=\text{NC}_6\text{H}_4=\text{NCHFc}$ ,  $[\text{FcCH}=\text{NC}_6\text{H}_4=\text{NCHFc}][\text{I}_{4.5}]$  [28]. The temperature dependence of the Mössbauer spectra of  $[\text{FcCH}=\text{NC}_6\text{H}_4=\text{NCHFc}][\text{I}_{4.5}]$ , a mixed iron(II) and iron(III) complex at ambient  $T$  reveals [28] an increase in the fraction of low-spin  $\text{Fe}^{\text{II}}$  relative to  $\text{Fe}^{\text{III}}$  at lower temperatures concurrent with a decrease in the effective moment. These results are consistent with a unique retro-electron transfer process from the poly-iodide anion to  $\text{Fe}^{\text{III}}$  and that is fully reversible. No such behavior is observed for either of  $[\mathbf{1}^{\cdot+}][\text{DDQ}^-]$  or  $[\mathbf{2}^{\cdot+}][\text{DDQ}^-]$ .

The electrochemistry of **2** alone provides few clues to the nature of the oxidized product. Like the electrochemistry of **1**, the anodic electrochemistry of **2** suggests a single-electron, reversible process in solution. The oxidation potential of **2** is only slightly more positive than that of ferrocene but **2** is, apparently, considerably more difficult to oxidize than **1**. Again, electron transfer from an electron donor, **2**, to the electron acceptor (DDQ) is confirmed by the magnetic susceptibility measurements. In the solid state, dramatically different behavior is observed in the Mössbauer spectra of  $[\mathbf{2}^{\cdot+}][\text{DDQ}^-]$ . The chemical oxidation of **2** clearly favors a product where iron has been oxidized from  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$ . Compound  $[\mathbf{2}^{\cdot+}][\text{DDQ}^-]$  contains essentially all low-spin  $\text{Fe}^{\text{III}}$  at 293 and 77.5 K. This is the exact opposite of the observations for  $[\mathbf{1}^{\cdot+}][\text{DDQ}^-]$ .

The limited number of chemically oxidized ferrocenyl-substituted nitrogen heterocycles studied to date makes it difficult to fully explain the origin of the differences between  $[\mathbf{1}^{\cdot+}][\text{DDQ}^-]$  and  $[\mathbf{2}^{\cdot+}][\text{DDQ}^-]$ . The observation that the oxidation potential for **1** is lower than pyrrole itself suggests that oxidation occurs initially at iron followed by intramolecular electron transfer as proposed in Eq. (3) [5]. A similar explanation has been proposed for the anodic electrochemistry of nitrogen containing ferrocenophanes (Eq. (4)) and aminomethylferrocenes (Eq. (5)) where equilibria between nitrogen-centered cation radicals and ferrocenium radical cations are established [29].



(4)



(5)

One interpretation of the apparent oxidation of the pyrrole ligand in  $[\mathbf{1}^{\cdot+}][\text{DDQ}^-]$  and the observation of  $\text{Fe}^{3+}$  in  $[\mathbf{2}^{\cdot+}][\text{DDQ}^-]$  is in terms of Eqs. (4) and (5). For  $[\mathbf{1}^{\cdot+}][\text{DDQ}^-]$ , the equilibrium may favor a ligand centered radical cation while in  $[\mathbf{2}^{\cdot+}][\text{DDQ}^-]$ , the equilibrium likely lies on the side of the ferricenium ion.

## 5. Conclusions

While the anodic electrochemistry of **1** and **2** appears to be consistent with oxidation of ferrocene  $\text{Fe}^{\text{II}}$  to ferrocenium  $\text{Fe}^{\text{III}}$ , the products of chemical oxidation with the single-electron oxidant DDQ lead to surprisingly different results. The product of chemical oxidation of **1** suggests loss of an electron from the ligand, delocalization of the odd electron into the  $\pi$ -system of the pyrrole ligand or initial oxidation at iron followed by intramolecular electron transfer from the ligand to iron. The structure of  $[\mathbf{1}^{\cdot+}]$  is mostly likely to be either **a**, **b**, **c**, or a hybrid thereof, in Eq. (3) rather than **d**. The strongest evidence for this conclusion comes from the Mössbauer spectra, a technique that has proven to be accurate in distinguishing low-spin  $\text{Fe}^{\text{II}}$  from  $\text{Fe}^{\text{III}}$  in the solid state. Low-spin  $\text{Fe}^{\text{III}}$ , however, is clearly seen in the Mössbauer spectrum of the product of chemical oxidation of **2**. The contrasting behavior of two seemingly similar ferrocene-substituted nitrogen heterocycles suggests that further studies of the chemical oxidation of a wider range of compounds are warranted. Finally, the present results may in part ultimately reflect the fundamental differences between solution species as obtained via classical electrochemical oxidations versus direct chemical reactions accompanied in some cases by rapid crystallization of the solid and for which imponderable lattice effects can be important in the context of the species that is actually stabilized.

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