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Note

The synthesis and cyclic voltammetry of select ferrocene piano-stool isocyanide complexes

Brian D. Humphrey [a,*], Raidiri E. Castilo [b], Amy H. Vega [b], Argelia Feliciano [b], Marjorie E. Squires [b]

[a] Department of Chemistry and Biochemistry, Montclair State University, Upper Montclair, NJ 07043, USA
[b] Department of Natural Sciences, Felician College, Lodi, NJ 07644, USA

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ABSTRACT

Ferrocene piano-stool isocyanide complexes ($[CpFeL_3]^+$, Cp = η^5-C_5H_5, L = tert-butyl isocyanide (**1**), cyclohexyl isocyanide (**2**), and 2,6-dimethylphenyl isocyanide (**3**)) are formed by chemical oxidation of ferrocene in the presence of a stoichiometric amount of isocyanide ligand (1:3). The complexes are characterized by elemental analysis, routine spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR, and UV–Vis), and cyclic voltammetry.

1. Introduction

Ferrocene based piano-stool complexes are of current interest for several reasons including possible anticancer/antitumor activity [1–3], unique non-linear optics capabilities [4–8], and as electron transfer agents [9]. In addition, isocyanide ligands have been identified with enhanced catalytic activity in organometallic complexes [10–12]. Furthermore, such complexes have been of interest because of many synthesis applications in organometallic chemistry, which were recently reviewed [13].

The synthesis of ferrocene piano-stool isocyanide complexes $[CpFe(CNR)_3]^+$ has been accomplished previously through a variety of synthetic routes [13–23]. These methods include ligand displacement by isonitriles on a preexisting piano-stool complex [14–18], synthesis from ferrocene-isonitrile dimers [18], and synthesis from catalytic electrochemical oxidation [20] or photochemical reaction of ferrocene half-sandwich complexes ($[CpFe(arene)]^+$, arene = η^6 arene) [13,21–23]. Here we report, for the first time, a simple one step synthesis of these complexes directly from ferrocene.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from commercial vendors and used as received with the exception of solvents which were purified prior to use. Infrared spectra were obtained on a Nicolet 4700 (or 20DXC) FT-IR spectrometer utilizing a Spectra Tech diffuse reflectance insert and UV–Vis spectra were obtained on a Hewlett–Packard 8452A diode array spectrophotometer. ^{1}H and ^{13}C NMR experiments were performed on a Bruker Avance 300 MHz spectrometer. Elemental analysis was carried out by Galbraith Laboratories, Inc. in Knoxville, TN.

2.1.1. Preparation of Tris–tert-butyl isocyanide cyclopentadiene iron(II) hexafluorophosphate, $[FeCp(tert\text{-}butyl\ isocyanide)_3][PF_6]$ (1)

To a stirring solution of ferrocene (497.5 mg, 2.674 mmol) in 60 mL reagent grade ethanol was added cerric ammonium nitrate (1469 mg, 2.680 mmol). After stirring for 10 min the solution turned from clear orange to clear blue. To this clear blue solution was added tert-butyl isocyanide (0.91 mL, 669 mg, 8.046 mmol). After stirring for overnight the resulting amber/brown solution had solvent removed *in vacuo*. The product was washed with hexane (3 × 5 mL). The dried residue was dissolved in 25 mL acetone to this stirred solution was added tetra-methyl ammonium hexafluorophosphate (591.1 mg, 2.698 mmol). After stirring overnight the resulting brown solution was filtered through celite. The solvent was removed *in vacuo* and the resulting residue washed with methylene chloride (3 × 5 mL) affording amber/brown crystals after recrystallization from ethanol. Yield: 47.2%.

^{1}H NMR (δ, $CDCl_3$): 4.69 (s, 5H), 1.50 (br s, 27H).

^{13}C NMR (δ, $CDCl_3$): 157.0, 82.1, 59.4, 30.6.

UV–Vis (CH_3CN) λ_{max} (ε) = sh 209 (12 900), 222 (13 600), 364 nm (719).

IR (KBr): 3128, 3106, 2982, 2938, 2877, 2170, 2137, 2059, 1462, 1424, 1400, 1371, 1234, 1201, 875, 844, 830, 741, 560 cm^{-1}.

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* Corresponding author. Tel.: +1 973 655 5138; fax: +1 973 655 7772.
E-mail address: humphreyb@mail.montclair.edu (B.D. Humphrey).

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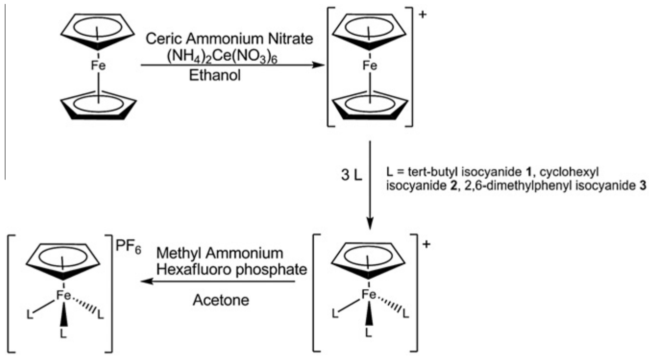

Scheme 1.

Elemental *Anal.* Calc. for $C_{20}H_{32}N_3FePF_6$ – 515.304: C, 46.62; H, 6.26; N, 8.15. Found: C, 46.41; H, 6.16; N, 8.08%.

2.1.2. Preparation of Tris–cyclohexyl isocyanide cyclopentadiene iron(II) hexafluorophosphate, [FeCp(cyclohexyl isocyanide)$_3$][PF$_6$] (**2**)

To a stirring solution of ferrocene (1095.2 mg, 5.888 mmol) in 100 mL reagent grade ethanol was added cerric ammonium nitrate (3225.5 mg, 5.883 mmol). After stirring for 10 min solution turned from clear orange to clear blue. To this blue solution was added cyclohexyl isocyanide (2.2 mL, 1931.6 mg, 17.69 mmol). After stirring overnight the resulting light brown solution had solvent removed *in vacuo*. The residue was washed with hexane (3 × 10 mL). The dried residue was dissolved in 30 mL acetone to this stirred solution was added tetra-methyl ammonium hexafluorophosphate (1302.8 mg, 5.946 mmol). After stirring overnight the resulting brown solution was filtered through celite. The solvent was removed *in vacuo* and the resulting residue was washed with methylene chloride (3 × 5 mL). The residue was purified by column chromatography on silica gel (acetone) then recrystallized from ethanol. Yield: 38.7%.

^{1}H NMR (δ, $CDCl_3$): 4.73 (s, 5H), 3.98 (br m, 3H), 1.89 (br m, 6H), 1.67 (br m, 12H), 1.46 (br m, 12H).

^{13}C NMR (δ, $CDCl_3$): 81.9, 55.5, 32.7, 24.9, 22.7.

UV–Vis (CH_3CN) λ_{max} (ε) = 222 (14 900), 364 nm (682).

IR (KBr): 3118, 2936, 2869, 2183, 2140, 2048, 1449, 1364, 1323, 1270, 1235, 1152, 1129, 1020, 931, 842, 660, 557 cm^{-1}.

Elemental *Anal.* Calc. for $C_{26}H_{38}N_3FePF_6$ – 593.418: C, 52.63; H, 6.45; N, 7.08. Found: C, 52.47; H, 6.41; N, 7.07%.

2.1.3. Preparation of Tris–2,6-dimethylphenyl isocyanide cyclopentadiene iron(II) hexafluorophosphate, [FeCp(2,6-dimethylphenyl isocyanide)$_3$][PF$_6$] (**3**)

To a stirring solution of ferrocene (1006.59 mg, 5.410 mmol) in 75 mL reagent grade ethanol was added cerric ammonium nitrate (3037.7 mg, 5.541 mmol). After stirring for 10 min the solution turned from clear orange to clear blue. To this clear blue solution was added 2,6-dimethylphenyl isocyanide (1970 mg, 15.02 mmol). After stirring overnight the resulting red/brown solution had solvent removed *in vacuo*. The residue was washed with hexane (3 × 5 mL). The dried residue was dissolved in 25 mL acetone. To this stirred solution was added tetra-methyl ammonium hexafluorophosphate (1198.5 mg, 5.470 mmol). After stirring overnight the resulting brown solution was filtered through celite. The solvent was removed *in vacuo* and the resulting residue washed with methylene chloride (3 × 5 mL) affording yellow/golden crystals after recrystallization from ethanol. Yield: 49.2%.

^{1}H NMR (δ, $CDCl_3$): 7.18 (br m, 9H), 5.28 (s, 5H), 2.44 (s, 18H).

^{13}C NMR (δ, $CDCl_3$): 136.0, 130.3, 129.1, 86.1, 19.2.

UV–Vis (CH_3CN) λ_{max} (ε) = sh 209 (13 500), 230 (15 800), 272 (13 900), 366 nm (790).

Table 1
UV–Vis spectral data summary for compounds **1**, **2**, and **3** (acetonitrile as solvent).

Compound	λ_{max}, nm (ε, L mol^{-1} cm^{-1})			
1	sh 209 (12 900)	222 (13 600)		364 (719)
2		222 (14 900)		364 (682)
3	sh 209 (13 500)	230 (15 800)	272 (13 900)	366 (790)

sh: shoulder.

IR (KBr): 3117, 3070, 3041, 2980, 2920, 2862, 2166, 2140, 2115, 2000, 1962, 1735, 1591, 1475, 1382, 864, 842, 671 cm^{-1}.

Elemental *Anal.* Calc. for $C_{32}H_{32}N_3FePF_6$ – 659.436: C, 58.29; H, 4.89; N, 6.37. Found: C, 58.16; H, 5.09; N, 6.38%.

2.2. Electrochemistry

Cyclic voltammetry was performed using a BAS 100 A electrochemical analyzer and a standard three electrode electrochemical cell configuration with a platinum working electrode (BAS 3.0 mm diameter), platinum wire counter electrode, and a Ag/AgCl reference electrode. The experiments were carried out under inert atmosphere (N_2 or Ar) at room temperature in dry acetonitrile containing 0.10 M tetra-butyl ammonium perchlorate (TBAP) as supporting electrolyte. A scan rate of 0.2 V/s was used for all experiments and ferrocene was added as an internal potential reference.

3. Results and discussion

3.1. Synthesis

The synthetic route leading to the formation of the ferrocene piano-stool complexes is shown in Scheme 1.

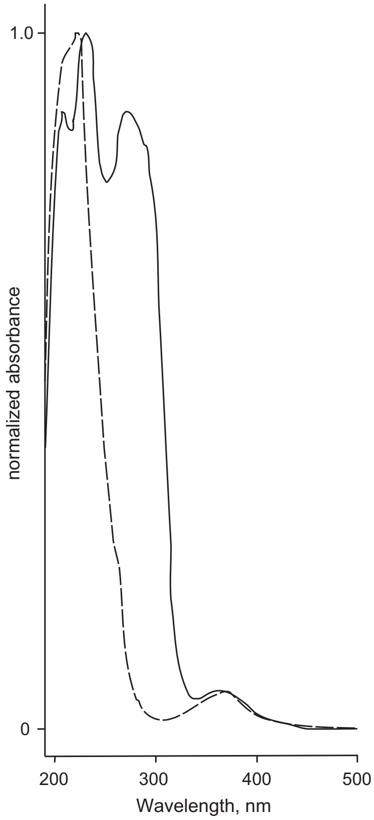

Fig. 1. Normalized UV–Vis absorption spectra of compounds **1** (dashed line) and **3** (solid line).

There are three distinct steps in the synthesis: (1) oxidation of ferrocene to ferrocenium ion, (2) addition of a stoichiometric amount of isocyanide ligand, and (3) formation of the piano-stool complex (accompanied by displacement of a cyclopentadienyl ring along with reduction of the iron center). The resulting cationic complex is isolated and purified as the hexafluorophosphate salt.

3.2. UV–Vis spectra

Absorption data for compounds **1**, **2**, and **3** are summarized in Table 1.

Compounds **1** and **2** have remarkably similar UV–Vis spectra (λ_{max} = 222 and 364 nm) which is expected since only the alkyl group of the isocyanide ligand is structurally different (only a shoulder at 209 nm exhibited by compound **1** distinguishes the two spectra).

The normalized spectra of compounds **1** and **3** are shown in Fig. 1 (normalized for direct comparison of spectral features).

The aromatic ring functionality of the ligand in compound **3** gives rise to the distinct absorption at 272 nm, the rest of the spectral features are similar to **1** showing little shift in peak maxima.

Table 2
Primary infrared peaks for compounds **1**, **2**, and **3**.

1	2	3	Peak assignment
3128w	3118w	3117w	metal bound cyclopentadienyl
3106w			
		3070w	
		3041w	
2982m		2980m	
2938m	2936s	2920m	
2877m	2869s	2862w	
2170s	2184s	2166s	Metal bound isocyanide
2137s	2139s		
		2115s	
2059w	2048w		
		2000w	
		1962w	
		1735w	
		1591w	
1462w	1449m	1475m	
1424w			
1400w			
1371m	1364m	1382m	
	1323m		
	1270w	1277w	
1234m	1239w		
1201m		1186w	
	1152m	1167w	
	1128m	1090w	
	1020m	1036w	
	931m		
844s	842s	842s	Hexafluorophosphate anion

s: strong; m: medium; w: weak.

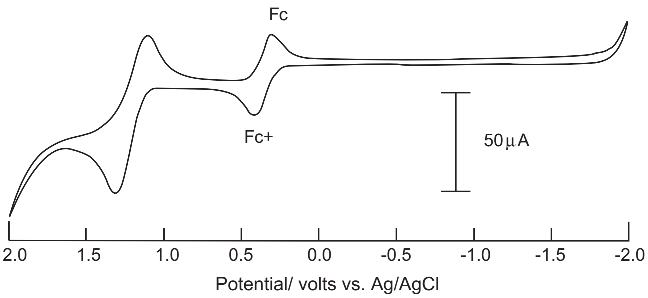

Fig. 2. Cyclic voltammetry of compound **1** in 0.10 M TBAP in acetonitrile with ferrocene (Fc) as an internal standard: scan rate 0.2 V/s.

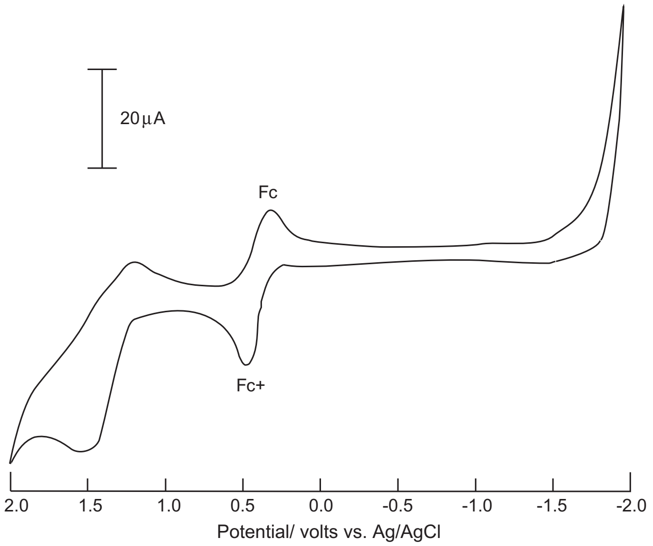

Fig. 3. Cyclic voltammetry of compound **2** in 0.10 M TBAP in acetonitrile with ferrocene (Fc) as an internal standard: scan rate 0.2 V/s.

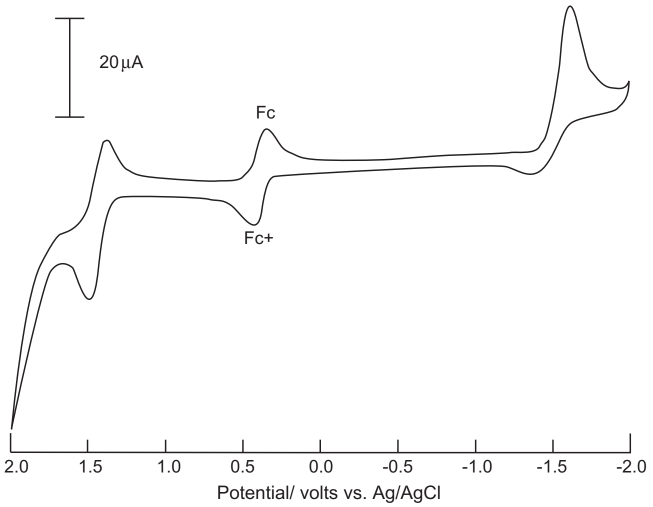

Fig. 4. Cyclic voltammetry of compound **3** in 0.10 M TBAP in acetonitrile with ferrocene (Fc) as an internal standard: scan rate 0.2 V/s.

Table 3
Cyclic voltammetry data summary for compounds **1**, **2**, and **3** (V vs. Fc/Fc$^+$).

Compound	$E_{1/2}$ (V)	E_{pc} (V)
1	0.86	
2	0.98	
3	1.05	−2.05

3.3. Infrared spectra

The primary infrared absorption bands for compounds **1**, **2**, and **3** are summarized in Table 2.

In each case the spectral features are dominated by the isocyanide ligand absorption features. The assignment of these bands corresponds to the same assignment for the ligand and has been omitted in Table 2. Significant absorption bands which are unique are assigned in Table 2.

These unique bands include a metal cyclopentadienyl ring CH stretch [24], and a Fe(II) bound isocyanide stretch [25]. In addition, there is a PF_6^- vibration. It should be noted that the metal isocyanide absorption for compounds **1** and **3** are in agreement with previously reported results for the cation with different anions [14–19].

3.4. Electrochemistry

Cyclic voltammetry (CV) was used to determine the electrochemical characteristics of compounds **1**, **2**, and **3**. Ferrocene (Fc) was added as an internal potential reference. The results are shown in Figs. 2–4.

All three compounds exhibit iron center redox waves significantly anodic of ferrocene as summarized in Table 3.

The iron center response is ideally reversible for compounds **1** and **3**, while quasi reversible for compound **2**. Compound **3** (CV shown in Fig. 4) has an additional irreversible reduction process due to the aromatic rings.

4. Conclusions

A novel, inexpensive synthetic method was used to produce three ferrocene piano-stool isocyanide complexes. The complexes were characterized by elemental analysis, NMR, IR, UV–Vis, and cyclic voltammetry. We are planning to extend this synthetic method to prepare ferrocene piano-stool isocyanide polymers and supramolecular species.

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