

First Homoleptic Complexes of Isocyanoferrocene

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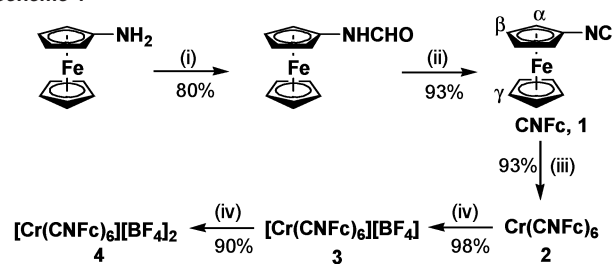
Isocyanide complexes of transition metals are of fundamental and practical interest, particularly because of their valuable role in organic and organometallic synthesis, catalysis, and radiological medicine.¹ The chemistry of isocyanoferrocene, CNFc (**1**), an intriguing potentially redox-active ligand, has remained practically undeveloped since the discovery of the compound in the late 1980s.² This is, undoubtedly, due to the tedious synthesis of FeNH₂ coupled with irreproducibility^{2a} of its conversion into CNFc. The isolated complexes of **1** are limited to (OC)₅Cr(CNFc) and (OC)₄Fe-(CNFc).^{2,3} Notably, the electronic properties of isocyanoferrocene as a ligand have been suggested to be comparable to those of methyl isocyanide.^{2b,c}

It has long been accepted that ferrocenyl (Fc) is a slightly stronger electron-donating substituent than methyl.⁴ Despite many parallels in the chemistries of ferrocene and arenes, consideration of ferrocenyl's π system as a potential electron acceptor has not been addressed experimentally. This is not surprising given that the five-membered rings of Cp₂Fe already possess an effective negative charge of ca. 0.35.⁴ Herein, we describe the first binary complexes of **1**, [Cr(CNFc)₆]^{0,1+,2+}. Their properties indicate that the π -accepting potential of the ferrocenyl fragment, customarily compared to an alkyl group, is similar to that of aryl substituents.

An efficient synthesis of peach-colored **1** was accomplished by treating solid FeNH₂⁵ with a 65/35 mol % mixture of phenyl formate/phenol,⁶ followed by dehydration of the resulting ferrocenylformamide with *strictly* 1.0 equiv of POCl₃ in the presence of ⁱPr₂NH in CH₂Cl₂ (Scheme 1). The superior formylating potency of PhOCHO as compared to other commonly used reagents, such as EtOCHO or acetic-formic anhydride, permitted us to conduct the formylation step at ambient temperature. This prevented previously encountered^{2a} extensive thermal decomposition of FeNHCHO. Combining 6 equiv of **1** with Cr(η^6 -naphthalene)₂ in THF afforded crystalline, orange-red Cr(CNFc)₆ (**2**). Oxidation of **2** with 1.0 equiv of AgBF₄ in CH₂Cl₂ gave [Cr(CNFc)₆][BF₄] (**3**), which was separated from the Ag metal by filtering the reaction mixture through a bed of Celite and isolated as saddle-brown microcrystals. Subsequent treatment of **3** with 1.0 equiv of AgBF₄ in CH₂Cl₂ provided [Cr(CNFc)₆][BF₄]₂ (**4**) as a sparkling, forest-green solid.

Spectroscopic and magnetic properties of **2**, **3**, and **4** are fully consistent with their formulations as low-spin, octahedral complexes of Cr(0), Cr(I), and Cr(II), respectively. The energy of the "T_{1u}"-like ν (CN) band increases upon going from **2** (1971 cm⁻¹) to **3** (2053 cm⁻¹) to **4** (2131 cm⁻¹). This indicates sequential oxidation of the chromium rather than the iron atoms. The above ν (CN) energies compare well with the corresponding ν (CN) data reported

Scheme 1^a



^a (i) ex. PhOCHO/PhOH, 20 °C; (ii) POCl₃, ex. ⁱPr₂NH, 0 °C; (iii) ¹/₆ Cr(η^6 -naphthalene)₂, 20 °C; (iv) AgBF₄, 20 °C.

for [Cr(CNAryl)₆]^{0,1+,2+}.⁸ Also, the CN stretching frequencies of **2** and **3** are significantly depressed with respect to that of free CNFc (**4**) (2122 cm⁻¹), reflecting substantial back-bonding within these complexes. Compounds **3** and **4** are paramagnetic with μ_{eff} (24.5 °C) = 1.78 and 2.76 μ_{B} , respectively.

The complexes **2**, **3**, and **4** are unique due to the incorporation of seven potentially electroactive metal centers within a relatively compact ML₆ motif.⁹ The X-ray structure of **2**·CH₂Cl₂ is shown in Figure 1.¹⁰ The metric parameters of the nearly perfectly octahedral Cr(CN)₆ core are in accord with those observed for other binary isocyanides of chromium(0).¹¹ The average C–N–C(Fc) angle in **2** is 162°. Such a degree of bending at the N atom is also typical for zerovalent, octahedral complexes of bulky aryl isocyanides (aryl = 2,6-Me₂C₆H₄, 2,6-ⁱPr₂C₆H₄).^{11b,12} Notably, the average C–N–C(^tBu) angle in Cr(CN^tBu)₆ is 153°.^{11a} The less pronounced bending of aryl-substituted isocyanide ligands in their low-valent complexes has been attributed to partial delocalization of the back-donated electron density into the aromatic rings, which can be described by the linear resonance structures M=C=N⁺=Aryl⁻.^{1a,b} The shortest Fe···Fe distance within **2** is 6.29 Å, which is only 0.93 Å greater than that in zwitterionic Fc₄B.¹³

The remarkable air, light, and thermal stabilities of **2**, **3**, and **4** constitute compelling evidence that the ferrocenyl substituent in **1** is much closer to an aryl rather than an alkyl group in terms of its electronic influence. Indeed, species [Cr(CNAryl)₆]^{0,1+,2+} are generally air- and thermally robust in the solid state.⁸ On the contrary, the only two binary alkyl isocyanides of Cr(0) known, Cr(CN^tBu)₆ and Cr(CNC₆H₁₁)₆, are very air- and light-sensitive.^{7b,11a} Furthermore, elusive [Cr(CNAlkyl)₆]⁺ species¹⁴ are too thermally unstable to be isolated. Similar to [Cr(CNAryl)₆]²⁺, **4** is reluctant to add another ligand, while seven-coordinate [Cr(CNAlkyl)₇]²⁺ (Alkyl = ^tBu, C₆H₁₁) is well documented.¹⁴

Our DFT calculations on an optimized model of **1** suggest that partial delocalization of back-donated electron density into the nonbenzoid π^* system of the CNFc ligands is, indeed, feasible. From Figure 2 it is apparent that CNFc's LUMO+2 is especially

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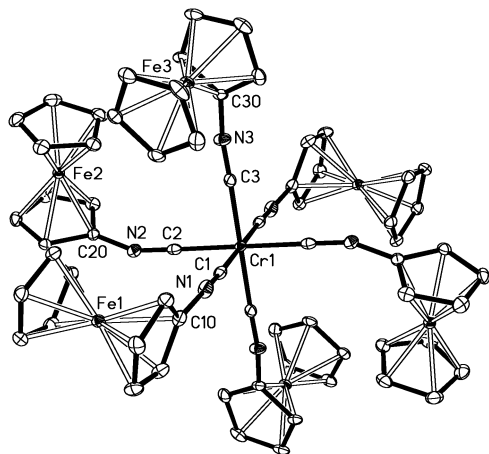


Figure 1. ORTEP diagram of **2**·CH₂Cl₂. Hydrogen atoms and a CH₂Cl₂ molecule of crystallization are omitted for clarity.

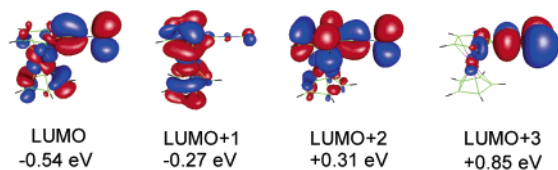


Figure 2. Four closely spaced lowest unoccupied molecular orbitals of **1** and their corresponding energies calculated at the 6-31 G (D, F) level.

Table 1. ¹H, ¹³C, and ¹⁴N NMR Chemical Shifts^a in ppm for **1–4**

	H ^α	H ^β	H ^γ	C ^α	C ^β	C ^γ	N
1	4.566	4.134	4.315	67.2	67.2	71.0	172.1
2	4.273	4.182	4.336	67.6	67.6	70.8	310.4
3	1.316	5.729	3.984	109.2	77.5	71.7	863.5
4	-1.039	7.751	3.832	158.5	97.3	72.6	1044.4

^a In CD₂Cl₂ at 25.0 °C versus Me₄Si (¹H and ¹³C) and liquid NH₃ (¹⁴N); see Scheme 1 for atom labeling legend.

suitable for such an interaction to occur. One may also notice striking analogies of CNFc's LUMO+1, LUMO+2, and LUMO+3 to CNPh's LUMO+1, LUMO, and LUMO+2,^{1a,15} respectively.

The paramagnetic complexes **3** and **4** give relatively narrow ¹H, ¹³C, and ¹⁴N NMR signals (Table 1). This fact is consistent with their ²T and ³T ground states, respectively, characterized by very short electron spin relaxation times, T_{1e}.¹⁶ The ¹H paramagnetic shifts for **3** and **4**, determined relative to the chemical shifts of the corresponding nuclei in diamagnetic **2**, exhibit approximately Curie behavior at 200 K < T < 300 K (i.e., Δδ ∝ 1/T and Δδ{T = ∞} ≈ 0) and are practically contact in origin because of the high symmetry of the complexes.¹⁷ The ¹H paramagnetic shifts for the substituted five-membered rings of **3** and **4** are large and occur in both directions, thus confirming the presence of unpaired spin in their π systems.^{12,16}

Finally, cyclic voltammograms of **2** in THF exhibit two one-electron successive quasi-reversible anodic waves at E_{1/2} = -0.916 V and -0.402 V versus Cp₂Fe⁺/Cp₂Fe. Undoubtedly, these correspond to the Cr-centered oxidations generating the cations of **3** and **4**, respectively. The above E_{1/2} values are comparable to those observed for the [Cr(CNArlyl)₆]^{0/1+} and ^{1+/2+} (Arlyl = 2,6-Me₂C₆H₄, 2,6-*i*-Pr₂C₆H₄) couples,⁸ but are much less negative than those obtained for the [Cr(CNAlkyl)₆]^{0/1+} and ^{1+/2+} couples.^{14a} Application of higher potentials to a solution of **2** produced a broad, structured anodic wave at E_{1/2} ≈ +0.3 V. This is likely due to iron-centered oxidations of multiple Fc substituents. The latter assignment is supported by the fact that the first wave in the electrochemical

oxidation of Cr(CO)₅(CNFc) describes a quasi-reversible Fe(II)/Fe(III) process with E_{1/2} = +0.305 V.^{2b,c}

In summary, we have reported herein on the first binary complexes of isocyanoferrrocene and demonstrated that the donor/acceptor ratio^{1b} of the CNFc ligand is similar to those of aryl isocyanides but quite different from those of alkyl isocyanides. We hope that this communication will open a new intriguing chapter in the multifaceted chemistry¹ of metal isocyanides. Our current efforts are focused on the exploration of the unique series of mixed-valence species [Cr(CNFc)₆]ⁿ⁺ (n > 2).

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for **1–4**, X-ray crystallographic information for **2**, variable temperature ¹H NMR data for **3** and **4**, and details of the DFT calculations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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