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Ferrocene-Substituted Amidinate Derivatives: Syntheses and Crystal Structures of Lithium, Iron(II), and Cobalt(II) Complexes

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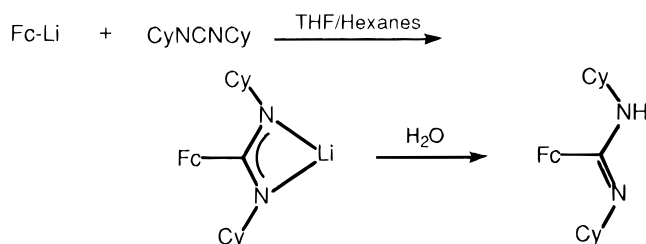
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Amidinate ligands have proven to be extremely versatile ligands for the preparation of a wide range of transition metal, main group, and f-block derivatives.^{1–3} Among the classes of compounds reported to date are olefin polymerization catalysts,^{4–6} dinitrogen complexes,^{7,8} metal–metal-bonded species,^{7,9} and coordination complexes.¹⁰ We recently described some early transition metal derivatives supported by the *N,N'*-bis(trimethylsilyl)benzamidinate ligand, whose chemistry had earlier been developed extensively by Edlmann¹ and others. In particular, we reported some Sc, Ti, and Zr derivatives that undergo interesting reduction chemistry and function as olefin polymerization and alkyne dimerization catalysts.^{8,11,12}

Here we describe the synthesis and characterization of a new class of amidinate derivatives containing redox-active centers that have the potential for use in a wide range of applications such as the preparation of metal-containing polymers, polymetallic complexes, and electrochemically controlled (“redox switched”) catalysts.¹³ For our initial studies, we chose to examine incorporation of the ferrocenyl (Fc) group because of its well-established chemistry, its high stability, and the ease with which simple derivatives can be prepared. In our first account on the subject, we focus on synthetic aspects, describing the preparation of an amidinate precursor ligand and its use in the synthesis of some transition metal derivatives; future papers will describe electrochemical and reactivity studies on these and related compounds.

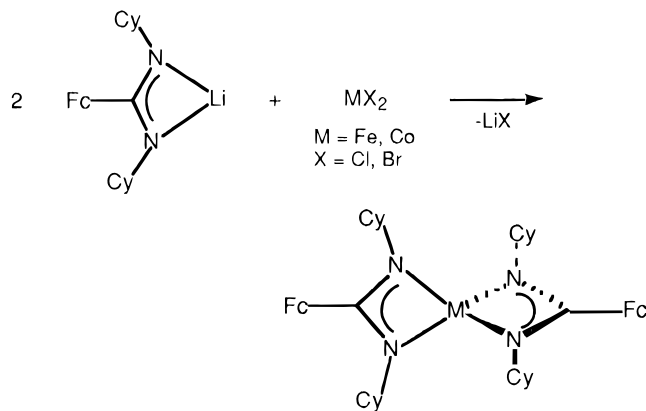
Ferrocenyllithium (FcLi) reacted cleanly with CyNCNCy in THF/hexanes at room temperature to generate the lithium amidinate $\text{FcC}(\text{NCy})_2\text{Li}$. It is noteworthy that an attempt to prepare the *N,N'*-bis(trimethylsilyl) analogue by similar methodology has been reported¹ to give no reaction, apparently due to the lower electrophilicity of the carbodiimide in this case. When FcLi was generated by the direct lithiation of Cp_2Fe by *t*-BuLi, the lithium amidinate could not be isolated directly due to contamination by appreciable amounts of FcLi_2 and Cp_2Fe .¹⁴ Accordingly, the mixture was hydrolyzed with excess water, and the solvent was stripped, affording an orange mixture consisting of $\text{FcC}(\text{NCy})\text{NHCy}$, $\text{Fc}[\text{C}(\text{NCy})\text{NHCy}]_2$, and Cp_2Fe .



Fe. Sublimation of the mixture at 65 °C/10^{−2} mmHg overnight removed Cp_2Fe and carbodiimide; pure $\text{FcC}(\text{NCy})\text{NHCy}$ was then obtained in 50% yield by crystallization of the residue from boiling hexanes.

The free-base compound was converted to a synthetically useful lithium salt by deprotonation with $\text{LiN}(\text{SiMe}_3)_2$ in toluene (the sodium derivative was prepared similarly using $\text{NaN}(\text{SiMe}_3)_2$). Concentration of the solution followed by the addition of Et_2O resulted in the crystallization of the etherate, $[\text{FcC}(\text{NCy})_2\text{Li}(\text{Et}_2\text{O})]_2$, in 90% yield. X-ray crystallography revealed a dimeric structure in common with related alkali metal bis(trimethylsilyl)benzamidinates. As shown in Figure 1, the dimer rests on a crystallographic inversion center. Thus, the central Li_2N_2 core is planar in contrast to the puckered core of the related $[\text{MeC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2\text{Li}(\text{THF})]_2$.¹⁵ Li–N bond lengths range from 2.010 to 2.158 Å and are comparable to related parameters (1.993–2.387 Å) in $[\text{MeC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2\text{Li}(\text{THF})]_2$. Remaining parameters are unexceptional.

The lithium ferrocenyl amidinate functions as a useful reagent in salt metathesis reactions with metal halides. For example, treatment of FeCl_2 with 2 equiv of $\text{FcC}(\text{NCy})\text{Li}(\text{Et}_2\text{O})$ in THF, followed by crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, afforded orange crystals of the trimetallic $[\text{FcC}(\text{NCy})_2]_2\text{Fe}$ in good yield.



A similar reaction with CoBr_2 in Et_2O gave $[\text{FcC}(\text{NCy})_2]_2\text{Co}$, also in good yield. We note that these compounds are the first examples of monomeric amidinates of Fe(II) and Co(II),² results that can be attributed to the relatively high degree of steric protection provided by the cyclohexyl groups.

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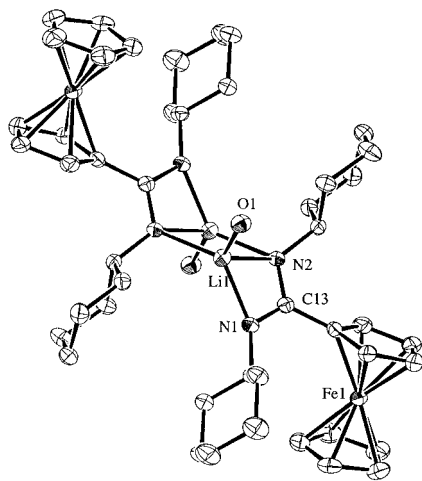


Figure 1. Crystal structure of $[\text{FcC}(\text{NCy})_2\text{Li}(\text{Et}_2\text{O})]_2$. Ethyl groups are omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Li}(1)-\text{N}(1)$ 2.010(6), $\text{Li}(1)-\text{N}(2)$ 2.158(6), $\text{Li}(1)-\text{N}(2)^*$ 2.111(6), $\text{Li}(1)-\text{O}(1)$ 1.951(6), $\text{Li}(1)-\text{N}(2)-\text{Li}(1)^*$ 70.4(2), $\text{N}(2)-\text{Li}(1)-\text{N}(2)$ 109.6(2), $\text{N}(1)-\text{Li}(1)-\text{N}(2)$ 65.8(2).

Magnetic susceptibility measurements (by Evans' solution NMR method^{16,17}) gave μ_{eff} values typical for tetrahedral Fe(II) and Co(II) (5.02 and 4.62 μ_{B} , respectively).¹⁸ Single-crystal X-ray diffraction studies on both complexes revealed many similarities, and some subtle differences. First, although both crystals were grown from Et_2O at -40°C , they cocrystallized with varying amounts of noncoordinated solvent and in different space groups. The iron derivative crystallized in the tetragonal space group $P4/n$ with $1/4$ equiv of ether (disordered on a 4-fold axis). Conversely, the cobalt derivative crystallized with 1 equiv of solvent in the acentric orthorhombic space group $P2_12_12_1$. As shown in Figures 2 and 3, coordination about the central metal is roughly tetrahedral in each case, with dihedral angles between the two N–M–N planes of 84.80 and 89.07° for iron and cobalt, respectively. The crystal structure of a related Cr(II) derivative, $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Cr}$,¹⁹ revealed distorted square planar geometry with a torsion angle between the two four-membered CrNCN rings of 22.8° . In this case, the deviation from planarity was attributed to the bulk of the $-\text{SiMe}_3$ groups. Fe–N bond distances are virtually identical with an average of 2.037 Å. As expected, Co–N bonds are a little shorter, averaging 2.011 Å. In both derivatives, the ferrocenyl groups are not expected to have significant $\pi-\pi$ interactions with the NCN heteroallylic fragments because of dihedral angles of $\sim 45^\circ$ for the Cp planes with the NCN planes.

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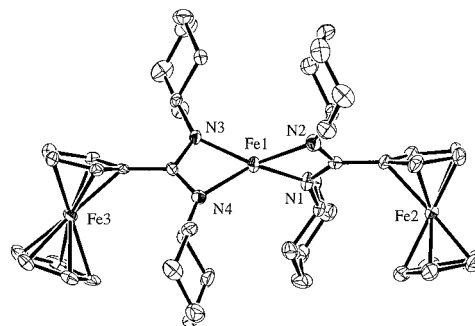


Figure 2. Crystal structure of $[\text{FcC}(\text{NCy})_2\text{Fe}]_2 \cdot 0.25\text{Et}_2\text{O}$. Ether is omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Fe}(1)-\text{N}(1)$ 2.027(4), $\text{Fe}(1)-\text{N}(2)$ 2.052(4), $\text{Fe}(1)-\text{N}(3)$ 2.027(4), $\text{Fe}(1)-\text{N}(4)$ 2.043(4), $\text{N}(1)-\text{Fe}(1)-\text{N}(2)$ 65.1(2), $\text{N}(3)-\text{Fe}(1)-\text{N}(4)$ 65.4(1).

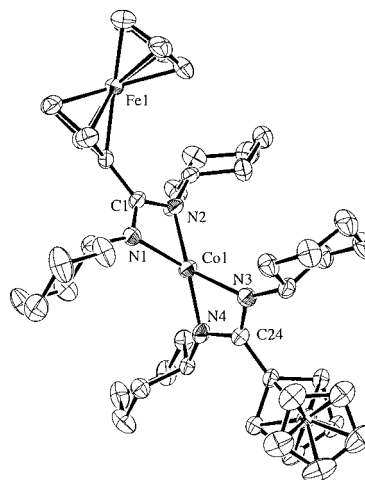


Figure 3. Crystal structure of $[\text{FcC}(\text{NCy})_2\text{Co}]_2 \cdot \text{Et}_2\text{O}$. Ether is omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Co}(1)-\text{N}(1)$ 2.020(4), $\text{Co}(1)-\text{N}(2)$ 2.006(4), $\text{Co}(1)-\text{N}(3)$ 2.009(4), $\text{Co}(1)-\text{N}(4)$ 2.010(4), $\text{N}(1)-\text{Co}(1)-\text{N}(2)$ 65.8(2), $\text{N}(3)-\text{Co}(1)-\text{N}(4)$ 66.0(1).

In summary, a new class of ferrocene-containing amidinates has been isolated and preliminary work on transition metal derivatives has been reported. Further studies into the potential uses of these and related redox-active amidinates are in progress.

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Supporting Information Available: Text giving full characterization data for all new compounds and details of the structure determinations, tables of crystal data, data collection parameters, temperature factors, and positional parameters, and ORTEP representations (42 pages). Ordering information is given on any current masthead page.

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