

Synthesis, Structure, and Properties of 1,1'-Diamino- and 1,1'-Diazidoferrocene

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We report an improved synthesis of 1,1'-diaminoferrocene, employing the reduction of 1,1'-diazidoferrocene with H_2 -Pd/C, along with extensive characterization data for both compounds. Diaminoferrocene undergoes a reversible $1e^-$ oxidation in CH_3CN at a potential of -602 mV vs $Fc^{0/+}$, one of the most negative redox potentials for a ferrocene derivative. The chemical reversibility of this process was confirmed by isolation of the stable, 17-electron $[Fc(NH_2)_2]^+$ cation as PF_6^- , OTf^- , and $TCNE^-$ salts. In the solid state, diaminoferrocene exists in two conformations: one with the NH_2 groups eclipsed, and the other with the NH_2 groups offset by one-fifth turn around the Cp-Fe-Cp axis. Diazidoferrocene, on the other hand, exhibits only the fully eclipsed conformation in the solid state. The Fe-Cp(centroid) vectors in the diazidoferrocene molecules are roughly aligned with the crystallographic c -axis, and the molecules form layers perpendicular to this axis. The compound is thermally unstable at elevated temperatures, and rapid heating above its melting point results in explosion.

Introduction

Diamines are widely used in coordination chemistry as chelating ligands and as precursors to a variety of other ligand systems.¹ The unique structural properties and presence of a redox-active Fe(II) center in 1,1'-diaminoferrocene set it apart from common organic diamines, rendering it of interest to us as an electrochemically active ligand. Related ferrocene diphosphine ligands^{2–10} are widely used in catalysis, and substituted ferrocenylamines have also been extensively studied.^{11–16} As a result, it was surprising to find little mention of 1,1'-diaminoferrocene in the literature.¹⁷ Perhaps one of the reasons its chemistry has not been examined in more detail is that simple routes to the compound do

not appear to be viable. For example, an obvious precursor to diaminoferrocene, 1,1'-dinitroferrocene, cannot be obtained by conventional means, such as nitration of ferrocene with HNO_3 .^{18,19} In addition, nitrocyclopentadienides fail to produce the desired product when reacted with $FeCl_2$.¹⁸ Nitroferrocene has been obtained in low yields by reacting lithioferrocene with n -propyl nitrate¹⁸ or N_2O_4 ,¹⁹ but no such method is reported for preparing the disubstituted analogue.

Despite these drawbacks, diaminoferrocene was prepared in-situ by Knox and Pauson in 1961 via reduction of 1,1'-diphenylazoferrocene and was characterized as a urethane derivative.²⁰ Two years later, Nesmeyanov et al. reported the synthesis of diaminoferrocene using diazidoferrocene as a precursor.²¹ Despite these early pioneering efforts, however, little is known about the chemical and physical properties of diaminoferrocene.

Here we describe (i) an improved high-yield synthesis of diaminoferrocene from diazidoferrocene (a modified Nesmeyanov procedure), (ii) characterization studies, including electrochemical data and solid-state structures, and (iii) chemical oxidation of diaminoferrocene to the isolable ferrocenium cation. In addition, the thermal properties of diazidoferrocene are described.

Results and Discussion

Improved Syntheses of Diazido- and Diaminoferrocene. As shown in Scheme 1, 1,1'-dibromoferrocene was employed as the immediate precursor to

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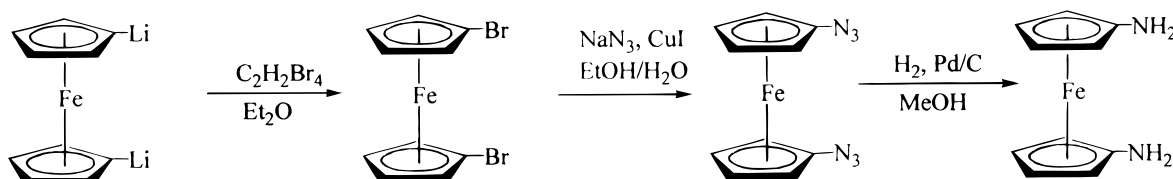
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Scheme 1



diazidoferrocene. The literature procedure for producing significant quantities of the dibromide calls for reaction of readily accessible 1,1'-dilithioferrocene²² with 1,2-dibromotetrafluoroethane.^{23,24} Due to federal restrictions on obtaining this haloalkane,²⁵ we investigated the use of easily available 1,1,2,2-tetrabromoethane as a replacement and found it to be an excellent alternative.

Subsequent halide displacement using NaN_3/CuI in $\text{EtOH}/\text{H}_2\text{O}$ afforded diazidoferrocene in good yield. Although Nesmeyanov et al. effected this transformation by heating the reagents under reflux for a brief period of time, we found that the best results are obtained by stirring the reactants at ambient temperature for ca. 48 h. Monitoring the reaction by TLC shows the initial formation of the intermediate 1-bromo-1'-azidoferrocene, which is then slowly converted to the final product. This reaction and subsequent workup were performed under subdued lighting due to the light-sensitivity of 1,1'-diazidoferrocene.

The product was crystallized from Et_2O to give golden flakes that melt at 56 °C. We caution that extreme care should be exercised when handling solid diazidoferrocene, as it is prone to explosion if heated rapidly above this temperature (see below). Nonetheless, in our hands, the compound appears to be quite stable at room temperature and has been stored for several months in the dark at 5 °C without detectable decomposition. We also note that the material appears to be stable in solution, at least for several hours at room temperature. This being the case, when prepared solely as a precursor to diaminoferrocene, the ether extract can be used directly in the next step, thus minimizing potential hazards associated with isolating the solid. Aside from reduction to the diamine described below, the compound undergoes typical azide-type reactivity with reagents such as phosphines and low-valent transition metal complexes.²⁶ The compound is sensitive to prolonged exposure to light, either as a solid or in solution; a complex mixture appears to be formed in either case, from which we have been unable to characterize a pure product.

Diaminoferrocene was prepared from diazide by reduction with H_2 -Pd/C in MeOH. Removal of the Pd/C catalyst and crystallization at -30 °C afforded diaminoferrocene as a yellow crystalline solid in 77% yield. This contrasts with the original procedure,²¹ which calls for reduction using LiAlH_4 followed by an aqueous

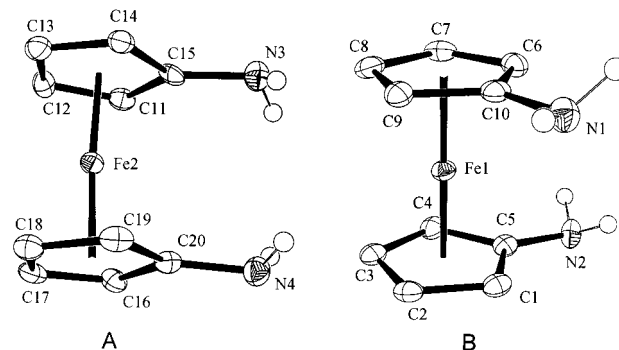


Figure 1. ORTEP diagram of the two independent $\text{Fc}(\text{NH}_2)_2$ molecules shown with 50% thermal ellipsoids.

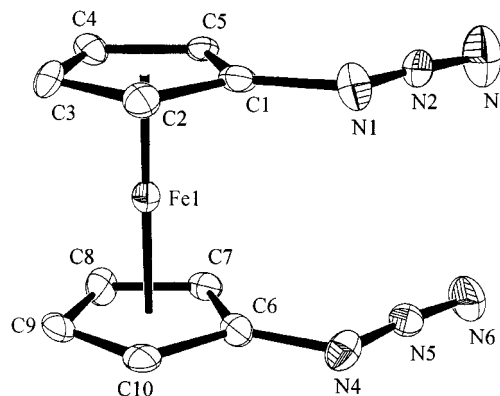


Figure 2. ORTEP diagram of $\text{Fc}(\text{N}_3)_3$ shown with 50% thermal ellipsoids. Only one of two molecules in the asymmetric unit is shown.

workup. In our hands the latter was much more time-consuming and always gave lower yields.

Exposing solutions of diaminoferrocene to air results in rapid oxidation, as evidenced by the appearance of a characteristic dark-green color; workup is therefore best carried out under nitrogen. Despite its sensitivity in solution, the product is stable as a solid in air for several months at room temperature. Diaminoferrocene melts at 183–186 °C and can be sublimed at 90 °C/0.001 mmHg. Chemically, the compound shows reactivity remarkably similar to simple organic diamines. It undergoes quaternization, substitution, and condensation reactions, yielding a range of new chelating ligands, details of which will be reported in due course.²⁶

Electrochemistry. Cyclic voltammetry of diaminoferrocene in CH_3CN shows a reversible oxidation wave with $E_{1/2} = -0.602 \text{ V}$ vs $\text{Fc}^{0/+}$ couple (Figure 3), one of the most negative shifts in redox potential observed for a ferrocene derivative.¹⁷ This large cathodic shift is due to the high degree of electron donation from the amino groups and is comparable to the redox potentials in bis-(dimethylamino)ferrocene ($E_{1/2} = -0.23 \text{ V}$ vs SCE, ca. -0.63 V vs Fc/Fc^+)¹¹ and decamethylferrocene ($E_{1/2} = -0.510 \text{ V}$ vs Fc/Fc^+).²⁷ Effectively, the donating ability

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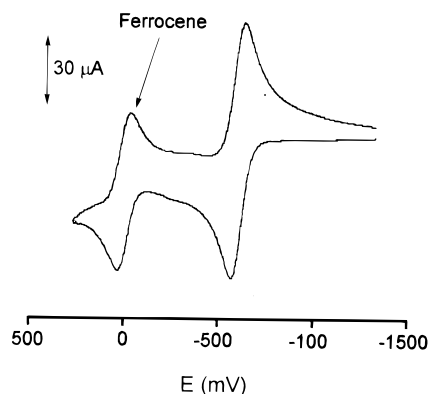


Figure 3. Cyclic voltammogram of $\text{Fc}(\text{NH}_2)_2$ with ferrocene as internal reference: 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ in CH_3CN ; 80 mV/s; glassy carbon working electrode; relative to $E_{1/2}$ for $\text{Fc}^{0/+}$ at 0 mV.

of each amino functionality is therefore roughly equal to that of five methyl groups. This correlates roughly with Hammett's σ_p values of -0.66 and -0.17 for an amino and methyl group, respectively.²⁸

The redox potential of diaminoferrocene readily explains why solutions of the compound are air-sensitive, a tendency mirrored also in bis(dimethylamino)ferrocene and decamethylferrocene. Diaminoferrocene can be chemically oxidized using AgOTf or milder oxidants such as $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ or TCNE, resulting in the stable green $[\text{Fc}(\text{NH}_2)_2]^+$ radical cation isolated as OTf^- , PF_6^- , and TCNE^- salts, respectively. The cation is paramagnetic with a room-temperature μ_{eff} of $2.1 \mu_B$. The ^1H NMR spectrum of the cation shows three broad, paramagnetically shifted resonances with relative integrations of 1:1:1, corresponding to the three different types of hydrogen atoms present. The $E_{1/2}$ for the $[\text{Fc}(\text{NH}_2)_2]^{+/0}$ couple is identical to that seen for the $E_{1/2}$ for the $\text{Fc}(\text{NH}_2)_2^{0/+}$ couple, indicating that the species generated chemically is identical to that observed electrochemically.

Cyclic voltammetry measurements of diazidoferrocene at scan speeds > 80 mV/s show a quasi-reversible oxidation process with $E_{1/2} = +40$ mV vs Fc/Fc^+ . At slower scan rates, however, the $i_{\text{pa}}/i_{\text{pc}}$ ratio drops below 1, indicating that the process is not truly reversible. Consistent with this behavior on the electrochemical time scale, chemical oxidation of diazidoferrocene under a variety of conditions failed to yield an isolable radical cation.

Thermal Decomposition of Diazidoferrocene.

First, it is very important to note that rapid heating of diazidoferrocene above its melting point leads to explosive decomposition. However, when the compound is heated slowly ($< 3^\circ/\text{min}$), diazidoferrocene melts very cleanly at $56\text{--}58^\circ\text{C}$ with concomitant gas evolution. Monitoring this process by TGA shows a reproducible loss of weight (19–21%) (Figure 4), consistent with elimination of 2 equiv of N_2 . The black/purple residue remaining was completely insoluble in all solvents examined, and its identity remains unknown at this stage. Interestingly, when the thermolysis was termi-

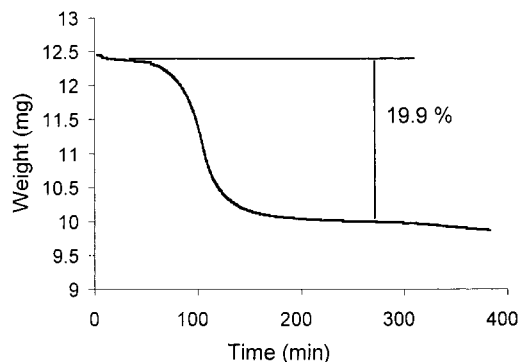


Figure 4. TGA plot for thermal decomposition of $\text{Fc}(\text{N}_3)_2$. Temperature profile: ramp $22.00\text{--}55.00^\circ\text{C}$ @ $5^\circ/\text{min}$; hold for 40.00 min; ramp $55.00\text{--}70.00^\circ\text{C}$ @ $0.20^\circ/\text{min}$; hold for 200.00 min; ramp $70.00\text{--}130.00^\circ\text{C}$ @ $0.5^\circ/\text{min}$.

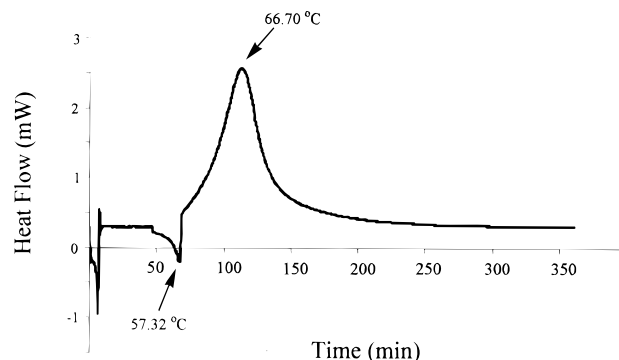


Figure 5. DSC plot for thermal decomposition of $\text{Fc}(\text{N}_3)_2$. Temperature profile is the same as for the TGA plot in Figure 4.

nated early (13–17% weight loss), extraction of the residue into chloroform resulted in a dark-purple solution, from which a mixture of compounds could be identified using EI-MS. The major component (also observable by ^1H NMR spectroscopy) was unreacted diazidoferrocene ($m/z = 268$); a minor component is a compound with a molecular ion at $m/z = 424$ that we tentatively ascribe to bis-azoferrocene $[\text{Fc}(\text{N}_2)]_2$. Unfortunately, low yields and irreproducibility of these reactions so far preclude further characterization, although the possibility that the insoluble black/purple material contains oligoazoferrocenes²⁹ is presently being investigated in more detail.

The controlled decomposition of diazidoferrocene was also monitored by DSC (see Figure 5). Two main features are of note: (i) an endotherm corresponding to melting, and (ii) a large exotherm corresponding to decomposition. From the exotherm, the ΔH of decomposition is calculated to be -64 kcal/mol.

X-ray Crystallographic Studies. Diaminoferrocene crystallizes in the space group $P\bar{1}$ with two unique molecules in the asymmetric unit (Figure 1, Table 1). The C–N bond lengths and metrical parameters associated with the Cp rings are unremarkable. The Cp's in both molecules are eclipsed, but while in molecule A the NH_2 groups are also eclipsed (1,1'-rotamer), in molecule B they are offset by one-fifth of a turn around the Cp–

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Table 1. Selected Bond Distances and Angles for 1,1'-Diaminoferrocene

Fe(1)–C(1)	2.042(3)	Fe(2)–C(11)	2.042(3)
Fe(1)–C(3)	2.047(4)	Fe(2)–C(13)	2.060(3)
Fe(1)–C(5)	2.073(3)	Fe(2)–C(15)	2.052(3)
Fe(1)–C(7)	2.027(3)	Fe(2)–C(17)	2.043(3)
Fe(1)–C(9)	2.059(3)	Fe(2)–C(19)	2.050(3)
Fe(1)–C(2)	2.029(3)	Fe(2)–C(12)	2.046(3)
Fe(1)–C(4)	2.055(3)	Fe(2)–C(14)	2.057(3)
Fe(1)–C(6)	2.043(3)	Fe(2)–C(16)	2.051(3)
Fe(1)–C(8)	2.035(3)	Fe(2)–C(18)	2.042(4)
Fe(1)–C(10)	2.095(3)	Fe(2)–C(20)	2.076(3)
N(1)–C(5)	1.410(4)	N(3)–C(15)	1.415(5)
N(2)–C(10)	1.409(5)	N(4)–C(20)	1.412(5)
N(1)–C(5)–C(1)	126.9(3)		
N(1)–C(5)–C(4)	125.2(3)		
N(2)–C(10)–C(6)	125.7(3)		
N(2)–C(10)–C(9)	127.2(3)		
N(3)–C(15)–C(11)	126.5(3)		
N(3)–C(15)–C(14)	125.6(3)		
N(4)–C(20)–C(16)	126.1(3)		
N(4)–C(20)–C(19)	126.1(3)		

Table 2. Selected Bond Distances and Angles for 1,1'-Diazoferrocene

Fe(1)–C(1)	2.039(7)	Fe(1)–C(2)	2.062(7)
Fe(1)–C(3)	2.037(7)	Fe(1)–C(4)	2.055(6)
Fe(1)–C(5)	2.065(6)	Fe(1)–C(6)	2.070(6)
Fe(1)–C(7)	2.044(7)	Fe(1)–C(8)	2.054(7)
Fe(1)–C(9)	2.034(6)	Fe(1)–C(10)	2.055(6)
N(1)–N(2)	1.232(8)	N(1)–C(1)	1.442(9)
N(2)–N(3)	1.142(8)	N(4)–N(5)	1.248(8)
N(4)–C(6)	1.435(9)	N(5)–N(6)	1.137(8)
N(2)–N(1)–C(1)	115.1(6)	N(1)–N(2)–N(3)	171.4(7)
N(5)–N(4)–C(6)	113.6(6)	N(4)–N(5)–N(6)	172.4(7)

Fe–Cp axis (1,2'-rotamer). The presence of two distinct rotamers in the same crystal suggests that the rotation around the Cp–Fe–Cp bond is relatively uninhibited and that the solid-state structure is governed mainly by hydrogen bonding and crystal packing forces.

Diazoferrocene crystallizes in the space group *Pbca* with two molecules in the asymmetric unit (Figure 2, Table 2). Both molecules are in the fully eclipsed conformation (1,1'-rotomers). The geometry of all four independent azide groups is essentially the same. These groups are not linear, but slightly bent, with an average N'–N''–N''' angle of 172° and average N'–N'' and N''–N''' distances of 1.24 and 1.13 Å, respectively. This geometry is consistent with that reported for other aromatic azides.³⁰ The azide groups in molecule A are in the plane of the Cp rings and are aligned with each other. Molecule B has a similar configuration but with the azide groups tilted slightly out of plane from the Cp rings. The packing of the unit cell consists of eight layers of diazoferrocene molecules stacked to form a 50.3 Å long *c*-axis.

Experimental Section

General Considerations. Standard Schlenk-line and glove-box techniques were used unless otherwise indicated. CH₃CN was distilled over CaH₂ under a nitrogen atmosphere. All other solvents were passed through a column of activated alumina and degassed with argon prior to use. FcLi₂(TMEDA) was prepared according to the literature procedure.²² [Bu₄N][PF₆] was purchased from Aldrich, recrystallized from EtOH, and dried under vacuum for 18 h at room temperature. *N,N,N,N*-

Tetramethylethylenediamine was purchased from Aldrich and distilled from Na metal. All other chemicals were purchased from Aldrich (Ferrocene, NaN₃, AgOTf, [Cp₂Fe][PF₆]), Kodak (Br₂HCCCHBr₂), Alfa (ⁿBuLi), and Fisher (CuCl) and used as received. Tetracyanoethylene was sublimed prior to use. C₆D₆ was vacuum transferred from sodium/benzophenone. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. ¹H and ¹³C{¹H} NMR spectra were recorded at ambient temperature on a Bruker AM-300 or DRX-500 spectrometer. ¹H NMR chemical shifts are given relative to C₆D₅H (7.16 ppm) and CHCl₃ (7.26 ppm). ¹³C{¹H} NMR spectra are relative to C₆D₆ (128.3 ppm). Thermogravimetric analyses were performed using a TA Instruments TGA 2950 analyzer. Electrochemical measurements were performed using a BAS-100b electrochemical analyzer with a BAS C3 cell stand mounted inside an inert atmosphere glovebox. Magnetic susceptibilities were determined using Evans NMR method with CD₃CN as solvent.³¹ IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

1,1'-Dibromoferrocene. A 2 L flask equipped with a mechanical stirrer and an addition funnel was charged with FcLi₂(TMEDA) (43.0 g, 138 mmol). Et₂O (500 mL) was added, and the resulting suspension was cooled to –60 °C. The addition funnel was charged with C₂H₂Br₄ (35.0 mL, 303 mmol) and 200 mL of Et₂O, and the resulting solution was slowly added to the FcLi₂ suspension with vigorous stirring over a period of 6 h. The solution was allowed to warm to ambient temperature and stirred for an additional 10 h, and the resulting dark-red solution was hydrolyzed with 50 mL of H₂O. From this point, the workup was done in air. The mixture was stirred for an additional 10 min, during which time a layer of black oil formed at the bottom. The top red layer was decanted off the oil and pumped down, first by rotary evaporation, then at 10^{–3} mmHg, to give a red, sticky solid. The solid was extracted with Et₂O and filtered, resulting in a dark-red solution. The solvent was again removed to yield a red oil, which was redissolved in hot MeOH and crystallized at –30 °C, resulting in 33.5 g (97 mmol, 71%) of yellow crystalline solid. ¹H NMR (C₆D₆): δ 4.16 (t, 4H); 3.71 (t, 4H) ppm. ¹H NMR (CDCl₃): δ 4.42 (t, 4H); 4.17 (t, 4H) ppm. Lit. ¹H NMR (CDCl₃): τ 5.51 (t, 4H); 5.77 (t, 4H).²³

1,1'-Diazoferrocene. *Caution: Although we have carried out the procedure described below without incident, we strongly advise against isolation of solid diazoferrocene on this scale due to its thermal instability (see Results and Discussion) The following can be scaled down considerably without significant diminution in yield.* The following procedure was carried out in air behind a safety shield. A 2 L flask was charged with FcBr₂ (45.0 g, 130 mmol), CuCl (28.0 g, 280 mmol), and 1 L of 95% EtOH. A solution of NaN₃ (34.0 g, 520 mmol) in 100 mL of H₂O was added, resulting in the formation of a dark-brown suspension. The reaction flask was wrapped in foil and the solution stirred for 48 h. The mixture was then poured into H₂O (1.5 L) and extracted with Et₂O (5 × 200 mL). The Et₂O fraction was dried over MgSO₄, concentrated to 250 mL, and cooled to –30 °C, yielding 15.8 g of golden crystals, which were isolated by filtration. Further concentration and cooling of the filtrate resulted in an additional 4.9 g of product. Total yield: 20.7 g (59%). ¹H NMR (CDCl₃): δ 4.36 (t, *J* = 1.9 Hz, 4H); 4.16 (t, *J* = 1.9 Hz, 4H), ppm. ¹³C NMR (CDCl₃): δ 100.5, 66.6, 61.7 ppm. Mp: 56–58 °C (dec) (lit. 58.5–59 °C).²¹ Anal. Calcd for C₁₀H₈N₆Fe: C, 44.81; H, 3.01; N, 31.35. Found: C, 44.89; H, 3.36; N, 31.25.

1,1'-Diaminoferrocene from Diazoferrocene. A solution of diazoferrocene (7.55 g, 28.2 mmol) in 250 mL of MeOH

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was degassed by bubbling N₂ through it using a stainless steel cannula for 5 min. To this solution was added 0.1 g of Pd/C (5% Pd) powder, and H₂ gas was bubbled through the solution at a moderate rate for 6 h. The mixture was then filtered, concentrated to 50 mL, and cooled to −30 °C to give 4.7 g of yellow crystals (21.7 mmol, 77%). ¹H NMR (C₆D₆): δ 3.74 (t, 4H), 3.65 (t, 4H), 1.87 (s, br, 4H). Mp: 183–186 °C. IR (Nujol): ν 3344 s, 3266 m, 3171 m, 3098 w, 3081 w, 2954 s, 2924 s, 2854 s, 1608 m, 1485 s, 1463 s, 1377 m, 1242 m, 1039 m, 1027 m cm^{−1}. Anal. Calcd for C₁₀H₁₂N₂Fe: C, 55.59; H, 5.60; N, 12.97. Found: C, 55.75; H, 5.76; N, 12.95.

1,1'-Diaminoferrocene Directly from Dibromoferrocene. To a solution of FeBr₂ (6.88 g, 20.0 mmol) in 200 mL of absolute ethanol was added CuCl (4.4 g, 45 mmol), followed by a solution of NaN₃ (6.5 g, 100 mmol) in 20 mL of H₂O. The reaction flask was wrapped in foil and the mixture stirred for 42 h. The brown mixture was then filtered, and the filtrate was partitioned between H₂O and Et₂O. The organic fractions were combined and washed with additional portions of H₂O until washings were colorless. The red solution was then dried over MgSO₄, filtered, concentrated to 60 mL, and diluted with 100 mL of MeOH. The solution was then transferred to Schlenk flask and degassed with N₂. The solution was treated as air-sensitive from this point on. To the solution was added 0.1 g of Pd/C (5% Pd), and a gentle stream of H₂ gas was blown over the solution with stirring for 4 h. At this point the mixture was filtered through a pad of Celite, concentrated to approximately 30 mL, and cooled to −40 °C. After 24 h yellow needlelike crystals were collected. Yield: 1.30 g, 30%.

[Fc(NH₂)₂][PF₆]. A flask was charged with diaminoferrocene (150 mg, 0.690 mmol) and FcPF₆ (229 mg, 0.690 mmol), and 30 mL of CHCl₃ was added. The green mixture was allowed to stir for 1 h. The solvent was removed under reduced pressure, and the remaining dark solid was washed with Et₂O (2 × 20 mL). The remaining green solid was dried under vacuum to give 210 mg of dark-green powder (84%). The product can be recrystallized from CH₂Cl₂/Et₂O. μ_{eff} : 2.1 μ_{B} . Anal. Calcd for C₁₀H₁₂N₂F₆FeP: C, 33.27; H, 3.35; N, 7.76. Found: C, 33.43; H, 3.12; N, 7.70.

[Fc(NH₂)₂][OTf]. A flask was charged with diaminoferrocene (350 mg, 1.62 mmol) and AgOTf (385 mg, 1.50 mmol). CH₃CN was added, and the resulting green solution was allowed to stir for 1 h. The solvent was removed under reduced pressure, and the green residue was washed with 20 mL of Et₂O. The residue was extracted with CH₃CN and filtered, leaving behind silver nuggets. The solvent was removed under reduced pressure, affording 450 mg of green product (82% based on AgOTf). The product was recrystallized from CH₂Cl₂/Et₂O as green needles. μ_{eff} : 2.1 μ_{B} . ¹H NMR (CD₃CN): δ 40.6 (s, br, 4H), 22.7 (s, br, 4H), −38.6 (s, br, 4H). Anal. Calcd for C₁₁H₁₂N₂FeO₃S: C, 36.18; H, 3.31; N, 7.67. Found: C, 36.32; H, 3.45; N, 7.55.

[Fc(NH₂)₂][TCNE]. A solution of tetracyanoethylene (247 mg, 1.92 mmol) in 15 mL of CH₃CN was added to a solution of diaminoferrocene in 20 mL of CH₃CN. The mixture turned dark-green immediately, followed by the formation of dark-green microcrystalline precipitate. The mixture was allowed to stir for 10 min, then stored at −30 °C for 8 h. Dark-bronze crystals (150 mg, 0.43 mmol, 22%) were isolated by filtration. IR (solid, ATR): ν 3419 m, 3389 s, 3319 m, 3216 m, 2200 m, 2180 sh, 2170 s, 1639 m, 1540 m, 1516 m, 1365 m cm^{−1}. Anal. Calcd for C₁₆H₁₂N₆Fe: C, 55.84; H, 3.51; N, 24.42. Found: C, 56.15; H, 3.87; N, 24.07.

General Procedures X-ray Crystallography. Pertinent details for the individual compounds can be found in Table 3. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂ (diaminoferrocene) or Et₂O (diazidoferrocene). A crystal of

Table 3. Crystallographic Data for 1,1'-Diaminoferrocene and 1,1'-Diazidoferrocene

	1,1'-diaminoferrocene	1,1'-diazidoferrocene
molecular formula	C ₁₀ H ₁₂ N ₂ Fe	C ₁₀ H ₈ N ₆ Fe
fw	216.07	268.06
cryst color, habit	red, block	red, plate
cryst size (mm)	0.25 × 0.18 × 0.18	0.11 × 0.28 × 0.18
cryst syst	triclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	7.3909(6)	9.0408(7)
<i>a</i> (Å)	10.3570(8)	9.0390(6)
<i>c</i> (Å)	11.6657(4)	50.187(5)
α , deg	88.130(1)	90.000
β , deg	77.995(1)	90.000
γ , deg	88.089(1)	90.000
<i>V</i> (Å ³)	872.66(9)	4101.21(3)
<i>Z</i>	4	16
<i>D_c</i> (g cm ^{−3})	1.644	1.730
temp, °C	−148	−134
radiation (λ)	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
μ , cm ^{−1}	16.72	12.65
<i>T</i> _{max} , <i>T</i> _{min}	0.869, 0.659	0.920, 0.771
<i>R</i> _{merge}	0.036	0.057
<i>R</i> , <i>R</i> _w	0.033, 0.039	0.036, 0.045
GOF	1.85	1.03
largest shift/error	0.00	0.00
max, min, e [−] Å ^{−3}	0.45/−0.37	0.35/−0.24

appropriate size was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,³² centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.³³ Cell dimensions reported in Table 1 were calculated from all reflections with *I* > 10σ. Data analysis and absorption correction were performed using Siemens XPREP.³⁴ The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structures were solved and refined with the teXsan software package.³⁵ All non-hydrogen atoms were refined anisotropically. The N–H hydrogen atoms in Fc(NH₂)₂ were refined isotropically, and the rest were included as fixed contributions. ORTEP diagrams were created using the ORTEP-3 software package.³⁶

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Supporting Information Available: Table of positional and thermal parameters and bond distances and angles for crystal structures of diaminoferrocene and diazidoferrocene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(32) SMART Area-Detector Software package, Madison, WI, 1995.

(33) SAINT: SAX Area Detector Integration Program; Madison, WI, 1995.

(34) XPREP: Part of SHELXTL Crystal Structure Determination Package, Madison, WI, 1995.

(35) TeXsan, Crystal Structure Analysis Software Package; Molecular Structure Corporation: The Woodlands, TX, 1992.

(36) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.