$C_i$ symmetry, contains two parallel, distorted square planar $[NiS_3P]$ units linked together by the arms of the ligands. Each nickel is coordinated by two sulfurs and a phosphorus from one ligand and a sulfur from the other ligand to form a distorted square planar $[NiS_3P]$ array with the trans S1–Ni–S3 and P1–Ni1–S2 angles being 156.0 (2)° and 171.8 (2)°, respectively. The two $[NiS_3P]$ units are aligned on top of one another in an eclipsed configuration in which the nickel atoms are separated by a Ni1–Ni1′ distance of 3.035 (4) Å.[8]

Electrochemical studies[9] indicate that $[Pr_4N]_2[Ni_2\{P(o\text{-}C_6H_4S)_3\}_2]$ (**1**) is oxidized by one electron to a [Ni(II)Ni(III)] species at −0.57 V and then to a [Ni(III)Ni(III)] species at −0.05 V (vs SCE) (Figure 2). Controlled potential electrolysis studies show both the [Ni(II)Ni(III)] and [Ni(III)Ni(III)] dimers to be thermally stable. $[Ni_2\{P(o\text{-}C_6H_4S)_3\}_2]^{2-}$ can be oxidized in situ or from isolated **1** by the addition of $[Cp_2Fe]BF_4$ to yield the mixed-valence [Ni(II)Ni(III)] complex, $[Pr_4N][Ni_2\{P(o\text{-}C_6H_4S)_3\}_2]$ (**2**), in good yield.

The X-ray structure determination[10] of **2** (Figure 3) illustrates that the [Ni(II)Ni(II)] dimer has undergone a substantial structural change upon oxidation to the [Ni(III)Ni(II)] species. The $[Ni_2\{P(o\text{-}C_6H_4S)_3\}_2]^-$ anion has a crystallographically imposed $C_2$ axis centered between the two $[NiS_4P]$ square pyramidal units which are bridged by the S1 and S1′ sulfur atoms. The structural transformation from **1** to **2** is accomplished by a twisting motion about the Ni–Ni axis with the two unique thiolates in **1** (S2 and S2′) moving into the $\mu_2$ bridging positions. Associated with this structural change is a 0.53 Å shortening in the Ni–Ni distance to a value of 2.501 (2) Å, which could be indicative of a substantial Ni–Ni interaction.[8b] The structural change must be rapid on the time scale of the electrochemical measurements; the cyclic voltammogram of isolated **2** in DMF is completely analogous to that of **1**.[9,11] The crystallographic symmetry that relates the two nickel centers in **2** rules out a type I (trapped-valence) electron configuration.[12]

In addition to the crystallographic evidence, the electronic spectrum of compound **2** suggests a delocalized mixed-valence state. Compound **2** absorbs more strongly in the visible region than does **1**, and it also exhibits two bands (lacking in **1**) of medium intensity in the near-IR region at 920 and 1325 nm.[13] If the 920 and 1325 nm bands are assigned as intervalence transitions (IT), their broad band widths of the order 50 000–30 000 cm$^{-1}$ along with their solvent dependence[14] are suggestive of a class II mixed-valence species.[12,15] Compound **2** gives a rhombic EPR spectrum ($DMF/CH_2Cl_2$ glass at 100 K) with $g_x = 2.12$, $g_y = 2.09$, and $g_z = 2.03$.

The results described above are consistent with the observation that thiolates can stabilize the Ni(III) oxidation level at biologically relevant redox potentials.[1a] Moreover, it is apparent that the chelating ability of the ligand has a marked effect upon the stability of the Ni(III)–thiolate center. We have synthesized and characterized a molecule that represents half the $[Ni_2\{P(o\text{-}C_6H_4S)_3\}_2]^{2-}$ dimer. That molecule which contains the $[Ni^{II}S_3P]$ core, $[Et_4N][(2\text{-}PhC_6H_4S)Ni\{P(o\text{-}C_6H_4S)_2(Ph)\}]$ (**3**),[16] cannot be oxidized to a stable Ni(III)–thiolate species and in fact shows an irreversible CV wave at a potential of about −0.25 V (vs SCE), a result that is consistent with the work reported by others.[17] These results can be extrapolated to indicate that the chelating nature of the hydrogenase proteins may be significant in stabilizing its $[Ni^{III}$-S-Cys] center.

Compound **2** is unique because it is a crystallographically characterized mixed-valence nickel thiolate compound, as well as a robust Ni(III)–thiolate system.[18] Also, further work has shown that the properties of the $[P(o\text{-}C_6H_4S)_3]^{3-}$ ligand can be exploited to prepare other mixed-valence complexes of the type described above, including $[M_2\{P(o\text{-}C_6H_4S)_3\}_2]^-$ (M = Co and Fe).[19]

**Acknowledgment.** This research was supported by a grant from the National Institutes of Health (GM 36308). We thank S. A. Koch for assistance with the X-ray structures and J. Lauher for use of his molecular graphics programs.

**Supplementary Material Available:** Tables of crystallographic parameters, atomic coordinates, thermal parameters, bond distances and angles, and ORTEP diagrams for **1–3** (35 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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[9] Electrochemical studies: Solutions were 0.001 M in DMF with 0.1 M supporting electrolyte $[Bu_4N][BF_4]$; scan rate was 200 mV/s, referenced to the saturated calomel electrode (SCE). Compound **1** (Pt electrode) shows two one-electron oxidations $(E_{pc} + E_{pa})/2 = E_{1/2}$ $(\Delta E_p, i_{pa}/i_{pc})$ at −0.57 V (100 mV, 1.02) and −0.05 V (60 mV, 0.98). Compound **2** (glassy carbon electrode) shows a one-electron reduction at −0.50 V (130 mV, 0.92) and a one-electron oxidation at 0.05 V (90 mV, 0.94).

[10] Crystal data for $\mathbf{2}\cdot 2CH_3OH$: $Ni_2S_6P_2O_2NC_{50}H_{60}$, monoclinic, $C2/c$; $a = 13.843$ (1) Å, $b = 17.487$ (2) Å, $c = 21.224$ (3) Å, $\beta = 94.26$ (1)°, $V = 5124$ (2) Å$^3$, $Z = 4$. A total of 2549 unique reflections with $I > 3\sigma(I)$ were refined to $R = 0.052$ and $R_w = 0.069$. The cation is disordered.

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[13] UV–vis (DMF) $\lambda_{max}$ nm ($\epsilon$ M$^{-1}$ cm$^{-1}$): compound **1** 453 (2275), 605 (1010); compound **2** 395 (7010), 450 (5000), 680 (2025), 920 (1265), 1325 (1225).

[14] Near-IR peaks shift when the spectrum is taken in DMSO.

[15] Bellitto, C.; Dessy, G.; Fares, V. *Inorg. Chem.* **1985**, *24*, 2815.

[16] Crystal data for $\mathbf{3}\cdot CH_3OH$: $NiS_3PNC_{39}OH_{46}$, monoclinic, $P2_1$; $a = 9.701$ (4) Å, $b = 20.247$ (6) Å, $c = 10.424$ (4) Å, $\beta = 114.52$ (3)°, $V = 1863$ (2) Å$^3$, $Z = 2$. A total of 2616 reflections with $I > 3\sigma(I)$ were refined to $R$ $(R_w) = 0.044$ (0.058). The methylene groups of the cation are disordered. Selected bond distances (Å) and angles (deg): Ni–S1 2.177 (2), Ni–S2 2.180 (2), Ni–S3 2.215 (2), Ni–P1 2.115 (2); S1–Ni–S2 166.1 (9), S1–Ni–S3 98.48 (9), S1–Ni–P1 87.65 (8), S2–Ni–S3 86.91 (9), S2–Ni–P1 87.65 (9), P1–Ni–S4 173.4 (1).

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# Vesicle of a Hybrid Bolaamphiphile: Flip-Flop Behavior of Spin Labels

Kangning Liang and Yongzheng Hui*

*Shanghai Institute of Organic Chemistry*
*Chinese Academy of Sciences, Shanghai 200032, China*

*Received March 26, 1992*

Vesicle monolayers formed by hydrocarbon bolaamphiphiles, single hydrophobic chains with two polar groups, one at each end, provide a lot more intriguing properties than the usual bilayer membranes.[1-4] Fluorocarbon amphiphiles possess many peculiar characteristics, such as limited miscibility with hydrocarbon amphiphiles.[5-10] In this communication, we report the synthesis of a single-chain hybrid bolaamphiphile with nearly equal lengths

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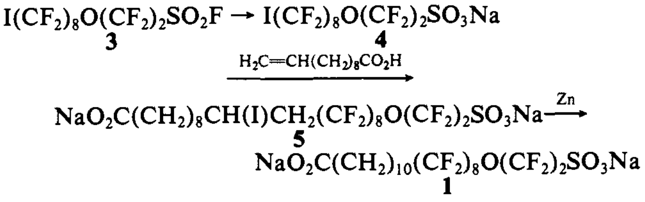
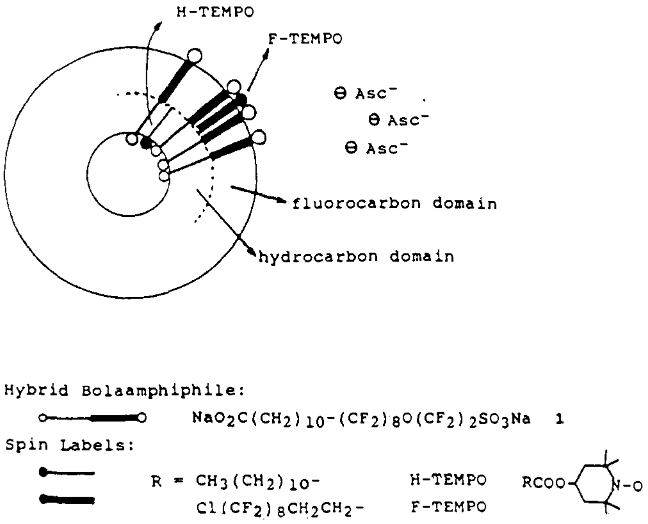
**Scheme I**



$$\underset{\mathbf{3}}{\mathrm{I(CF_2)_8O(CF_2)_2SO_2F}} \rightarrow \underset{\mathbf{4}}{\mathrm{I(CF_2)_8O(CF_2)_2SO_3Na}} \xrightarrow{\mathrm{H_2C{=}CH(CH_2)_8CO_2H}} \underset{\mathbf{5}}{\mathrm{NaO_2C(CH_2)_8CH(I)CH_2(CF_2)_8O(CF_2)_2SO_3Na}} \xrightarrow{\mathrm{Zn}} \underset{\mathbf{1}}{\mathrm{NaO_2C(CH_2)_{10}(CF_2)_8O(CF_2)_2SO_3Na}}$$

**Scheme II.** Schematic Illustration of Vesicle Monolayer of **1** and Distribution of Spin Labels in Hydrocarbon and Fluorocarbon Domains



of a hydro- and a fluorocarbon segment, synthesized from the addition of $\omega$-iodo fluorocarbon sulfonate to 10-undecenoic acid (cf. Scheme I). Product from the adduct was obtained by refluxing in the presence of zinc.[11]

Sonication dispersed **1** initially to a turbid and ultimately to an optically transparent solution. Electron micrographs confirmed the presence of vesicles whose diameter ranged between 2000 and 5000 Å with a thickness of 30 Å, which accords with the length of a single bolaamphiphile. Vesicles exhibit a metachromatic effect[12] on the absorption of dye, neutral red, at both pH 4 ($\lambda_{max}$ from 550 to 520 nm) and pH 6.86 ($\lambda_{max}$ from 535 to 520 nm). These observations suggest that the sulfonate group of **1** is located on the outer surface of the vesicle monolayer. Since the thicker fluorocarbon segment is attached to the larger sulfonate group, outward orientation of the sulfonate group is favored.

For hydrocarbon vesicle monolayers the average distance between bolaamphiphiles in curved vesicle monolayers is larger than those in bilayers and therefore causes weaker interaction. As a result, a favorable rotation along a single bond in the methylene chain occurs. No sign of liquid crystal formation has, so far, been observed in any monolayer vesicle membrane of hydrocarbon bolaamphiphiles.[13] Nevertheless, the strong hydrophobic interaction between fluorocarbon segments and edge-shaped amphiphile **1** enables a tight packing in the vesicle monolayer; thereby the "gel" state can take shape in the curved vesicle monolayer, and the vesicle of **1** displays a clear phase-transition temperature $T_m$ (32.5 °C by DSC; 28.0 °C by turbidity measurement).

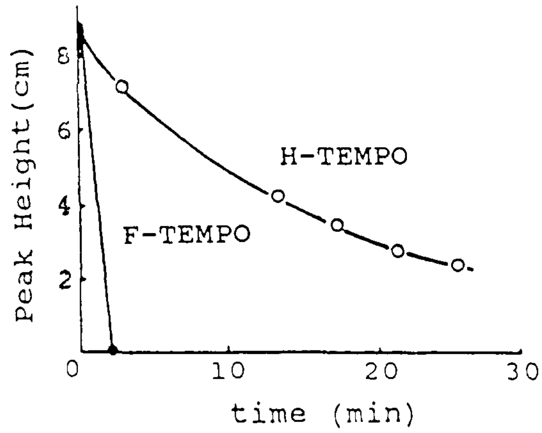


**Figure 1.** Time course of paramagnetic resonance signal of spin labels on vesicle monolayer after the addition of sodium ascorbate at 26 °C. The concentrations of F-Tempo, H-Tempo, sodium ascorbate, and **1** are $4.22 \times 10^{-5}$, $1.04 \times 10^{-4}$, $1.12 \times 10^{-3}$, and 0.028 M, respectively.

Vesicles of **1** entrapped and retained either a hydrocarbon spin label, H-Tempo,[14] or a fluorocarbon spin label, F-Tempo,[15] because both hydro- and fluorocarbon domains coexist in vesicle monolayer (Scheme II). The H-Tempo or F-Tempo was cosonicated with dispersion of **1**; non-entrapped probe was removed by gel filtration on Sephadex G-50. The line shapes of the paramagnetic resonance of trapped probes indicate that those molecules are bound to the vesicle membrane, and the peaks at high field are broadened as the free rotation of molecules is hindered. Ascorbate existing in aqueous solution reduces the nitroxide spin labels to the nonparamagnetic hydroxylamine derivatives. Mutual phobicity between hydro- and fluorocarbon species causes the H- and F-Tempo to be located in their own domain in the vesicle monolayer of **1**. Since sodium ascorbate could contact nitroxide species on the outer surface of vescile monolayer,[15] the signals of paramagnetic label F-Tempo would disappear within 2 min. These results imply that the F-Tempo is indeed located on the outer semi-monolayer, which provides further evidence that the outer semi-monolayer of the vesicle monolayer of **1** is of the fluorocarbon domain. The paramagnetic resonance of probe at the inner vesicle surface is not affected by the addition of sodium ascorbate until the label molecules cross to the outer semi-monolayer through flip-flop. In fact, the signals of H-Tempo decrease steadily after addition of sodium ascorbate (cf. Figure 1). The rate of change of the spin-labei magnetism in the internal semi-monolayer of vesicle depends on the exchange of molecules between semi-monolayers through kinetic properties of both inward and outward translocation processes. According to the time course of ESR signals shown in Figure 1, the rate constant of outward flip-flop of H-Tempo, $k_o$, can be calculated to be 0.047 min$^{-1}$ at 26 °C and 0.014 min$^{-1}$ at 5.0 °C,[16] corresponding to a half-time of 14.7 min at 26

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[11] Synthesis of **1**: To a 50-mL round-bottomed flask were added 10 g (13.8 mmol) of $\omega$-iodo fluorocarbon sulfonyl fluoride **3** and 10 mL of water; then 0.8 g (20 mmol) of sodium hydroxide was added. The mixture was stirred at room temperature for 8 h. It was then filtered, and the solid was washed several times with water. The solid **4** was dried under high vacuum and used without further purification. To a round-bottomed flask were added all the solid **4** prepared above, 2.42 g (13.0 mmol) of 10-undecenoic acid, 1.2 g (14.3 mmol) of sodium bicarbonate, 20 mL of acetonitrile, and 15 mL of water. A mixture of 2.6 g (14.9 mmol) of sodium dithionite and 1.4 g (16.7 mmol) of sodium bicarbonate was slowly added to the reaction mixture, and then the reaction mixture was stirred at room temperature for 3 h. After being filtered, the solid was then placed in a Soxhlet extractor and extracted with ethanol. Removal of the solvent gave solid **5**. XPS showed the solid to contain the elements C, O, F, Na, S, and I. Half the amount of **5** was dissolved in absolute ethanol, and 6.5 g (100 mmol) of zinc powder was added. The mixture was refluxed for 10 h and then was filtered. After cooling off, the filtrate gave a white solid of **1**. It was twice recrystallized from absolute ethanol, and 0.44 g (total yield 8%) was obtained: mp >200 °C; IR $\nu_{max}$ 1050, 1200, 1465, 1550, 2850, 2920 cm$^{-1}$. Anal. Calcd for $C_{21}H_{20}O_6F_{20}SNa_2$: C, 30.52; H, 2.44; S, 3.88. Found: C, 31.58; H, 2.63; S, 3.43.

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[13] (a) It is reported by Fuhrhop et al. that both the carboxylate group and the sulfonate group exhibit a metachromatic effect[12] on the absorption spectra of methylene blue and acridine orange at pH 7, but only the sulfonate headgroup shows a metachromatic effect at pH 4.[13b] (b) Fuhrhop, J.-H.; David, H.-H.; Mathieu, J.; Liman, U.; Winter, H.-J.; Boekema, E. *J. Am. Chem. Soc.* **1986**, *108*, 1785.

[14] H-Tempo was synthesized by the procedures reported elsewhere:[15] IR $\nu_{max}$ 1734 cm$^{-1}$. Anal. Calcd for $C_{21}H_{40}O_3N$: C, 71.14; H, 11.5; N, 3.9. Found: C, 71.28; H, 11.6; N, 4.11.

[15] Liang, K.; Hui, Y. To be published.

°C, almost 5 orders slower than that of fatty acids in hydrocarbon vesicles.[17] The limited miscibility between hydrocarbon and fluorocarbon compounds results in an unfavorable solubilization of hydrocarbon spin label, H-Tempo, in the fluorocarbon phase, which causes a slow flip-flop rate of H-Tempo in the vesicle monolayer of **1**.

This study established the vesicle monolayer of **1** as the simplest system with well-defined hydro- and fluorocarbon domains. Consequently, it can be used in the study of interactions such as charge and energy transfer between hydro- and fluorocarbon molecules. Such a study is the object of our current attention.

**Registry No.** **1**, 142319-50-4; **3**, 68136-90-3; **4**, 142319-51-5; **5**, 142319-52-6; 10-undecenoic acid, 112-38-9.

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(16) If every inward or outward translocation of a paramagnetic molecule is an independent event, then the time rate of change of the internal spin label paramagnetism is given by

$$dN_i/dt = k_iN_o - k_oN_i \qquad (1)$$

Since the reduction of spin label by sodium ascorbate is much faster than the inward translocation process of spin-label molecules on outer semi-monolayer, then

$$dN_i/dt = -k_oN_i \qquad (2)$$

and

$$\ln N_i = -k_ot + C \qquad (3)$$

where $C$ is a constant and $k_o$ is the rate constant of the outward translocation process.

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# Synthesis and Crystallographic Characterization of $[CsHN(SiMe_3)]_4$, a Cesium-Based Heterocubane

Kris F. Tesh,[†] Brian D. Jones,[†] Timothy P. Hanusa,*[,†] and John C. Huffman[‡]

*Department of Chemistry, Vanderbilt University*
*Nashville, Tennessee 37235*
*Molecular Structure Center, Department of Chemistry, Indiana University*
*Bloomington, Indiana 47405*

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The unsolvated bis(trimethylsilyl)amido complexes of the alkali metals display a remarkable progression of structures as the metallic radii increase. In the solid state, the lithium compound is a cyclic trimer,[1] whereas the sodium salt exists as chains of $[NaN(SiMe_3)_2]_n$ units.[2] Rather than forming an analogous nonmolecular substance, the potassium amide crystallizes as a discrete dimer with a nearly square $K–N(SiMe_3)_2–K'–N(SiMe_3)_2'$ ring.[3,4] The factors that induce the sodium complex to form a polymeric material when the lithium and potassium counterparts do not are unknown. We are interested in the ability of the (trimethylsilyl)amido group to support low coordination numbers in compounds of the heavy s-block metals,[5-7] and we report here the unusual result obtained from attempts to generate [bis(trimethylsilyl)amido]cesium.[8]

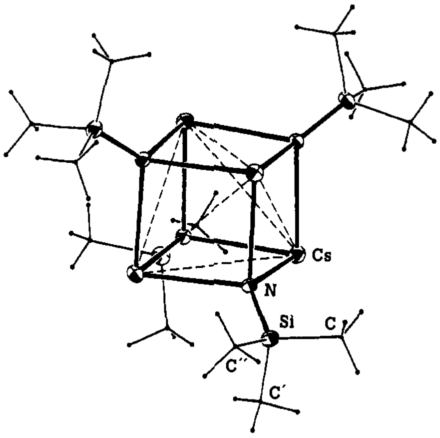

**Figure 1.** ORTEP view of $[CsHN(SiMe_3)]_4$, with thermal ellipsoids drawn at the 50% probability level. The dashed lines between the cesium atoms illustrate the alternate description of the compound as a $Cs_4$ tetrahedron capped on each face with $\mu_3$-amido groups. For clarity, the methyl groups of the $SiMe_3$ units are rendered as lines.

Addition of a few crystals of iron(III) nitrate to a deep blue solution of cesium in liquid ammonia followed by a slight molar excess of hexamethyldisilazane in hexane causes a slow discharge of the blue color. Upon evaporation of the ammonia, a tan residue is left that has modest solubility in aromatics; cubes of a cream-colored solid can be grown from hexane.[9] Its EI mass spectrum contains a weak signal for the parent ion at $m/z$ 884, consistent with the $C_{12}H_{40}Cs_4N_4Si_4^+$ ion. The base peak ($m/z$ 797) represents the loss of a single $N(SiMe_3)$ group from the parent ion, i.e., $\{Cs_4H[HN(SiMe_3)]_3\}^+$. Strong signals corresponding to the $Cs^+$, $Cs_2^+$, and $Cs_3^+$ ions are also observed. The IR spectrum of the material (KBr pellet) reveals a broad $\nu$(NH) centered at 3150 $cm^{-1}$.[10] These results suggest that the compound should be formulated as the mono(trimethylsilyl)amido species, $[CsHN(SiMe_3)]_4$.[11] The fragmentation pattern in the mass spectrum is reminiscent of the behavior of various alkyllithium tetramers $[LiR]_4$ (R = Et, $CH_2SiMe_2$, $t$-Bu), whose parent ions are weak or nonexistent but which display strong signals for $[Li_4R_3]^+$ fragments.[12-14]

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[‡] Indiana University.

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(4) After our publication of the structure of unsolvated $[KN(SiMe_3)_2]_2$, we became aware of an earlier report of $[KN(SiMe_3)_2]_2$·(toluene), in which the toluene is present as lattice solvent (Williard, P. G. *Acta. Crystallogr.* **1988**, *C44*, 270–272). The geometry of the potassium amide itself appears to be essentially identical in the two structures.

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(8) The synthesis of $CsN(SiMe_3)_2$ from $CsNH_2$ or Cs metal and $HN(SiMe_3)_2$ in liquid ammonia has been reported without details (Wannagat, U. *Pure Appl. Chem.* **1969**, *19*, 329–342). It is not certain in what respects that synthesis differs from the present one.

(9) In a typical preparation, Cs metal (0.80 g, 6.0 mmol) was loaded in a flask and transferred to an argon-equipped Schlenk line. Ammonia was condensed into the flask at −78 °C (ca. 200 mL), followed by countercurrent addition of $Fe(NO_3)_3·9H_2O$. Hexamethyldisilazane (1.15 g, 7.1 mmol) in hexane (15 mL) was dripped into the mixture, and the reaction was allowed to come to room temperature. Evaporation of the residual hexane left the crude product in quantitative yield. Although it has only trace solubility in alkanes, addition of hexane to the crude material, followed by slow evaporation and periodic replacement of the lost hexane, will generate crystalline material; this process requires more than 30 days.

(10) The $^1H$ NMR spectrum at 20 °C contains the singlet expected for the $SiMe_3$ groups at $\delta$ 0.21 ($C_6D_6$). The resonance for the amido hydrogens was not observed.

(11) An N–Si bond of the hexamethyldisilazane must be cleaved in the synthesis; although the mechanism is unknown, the presence of ammonia appears to be important. If elemental Cs and $HN(SiMe_3)_2$ are allowed to react in refluxing hexane (3 days), an unidentified brown precipitate forms, and only a small amount of the monosilylamide can be isolated.

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