

Lutetium Alkyls Supported by a Dearomatized and Functionalized Terpyridine Ligand: Preparation of Fluorinated Anilide Complexes

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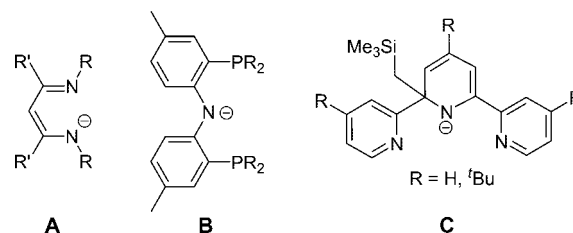
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Summary: Lutetium alkyl complexes supported by a mono-anionic, tridentate ligand system formed by the dearomatization and functionalization of a 2,2':6',2''-terpyridine have been reacted with 2,4,6-triphenylaniline or the fluorinated anilines 4-F-C₆H₄NH₂ and C₆F₅NH₂ to give both terminal mono(amide) and bis(amide) lutetium(III) complexes, which have been fully characterized. Both [tBu₃(2'-Me₃SiCH₂)tpy]Lu[NH(2,4,6-Ph₃-C₆H₂)]₂ (**3**) and [tBu₃(2'-Me₃SiCH₂)tpy](C₅Me₅)Lu(NHC₆F₅) (**7**) have been structurally characterized. The fluorinated anilide complexes [tBu₃(2'-Me₃SiCH₂)tpy](C₅Me₅)Lu(NHAr_F) (Ar_F = 4-F-C₆H₄ (**6**), C₆F₅ (**7**)) provide rare examples of lutetium organofluorine complexes, with **7** featuring an intramolecular F...H–C interaction that is present in both solid state and solution.

Introduction

Since the discovery of ferrocene,¹ cyclopentadienyl-based ligand sets have dominated the landscape of organometallic chemistry. However, in recent years there has been a shift toward using non-Cp, monoanionic, multidentate ligand sets to stabilize highly reactive metal centers, in particular for the group 3 and lanthanide metals.² For example, the flexible bidentate “NacNac” ligand framework (**A**) has been used extensively over the past decade, but it tends to be susceptible to unwanted reactivity at the imine functional groups.^{3,4} The rigid tridentate PNP ligand



set (**B**)⁵ is less prone to adverse side reactions, and this stability has been exploited to stabilize extremely reactive systems such as Ti alkylidenes,^{5d,f,j} alkylidynes,^{5b,c} and phosphinidines,^{5f} Ta^{5a} alkylidenes, and Nb^{5e} dinitrogen complexes. Our recent discovery of the dearomatization and functionalization of 2,2':6',2''-terpyridines by lutetium(III) alkyls to form the monoanionic, tridentate NNN' ligand systems (**C**)⁶ prompted us to investigate the ability of this unusual ligand framework to support f-element complexes containing multiply bonded functional groups.⁷ Toward this goal, we now report the reactivity of one of these systems, [tBu₃(2'-Me₃SiCH₂)tpy]Lu(CH₂SiMe₃)₂ (**1**), with anilines.

Results and Discussion

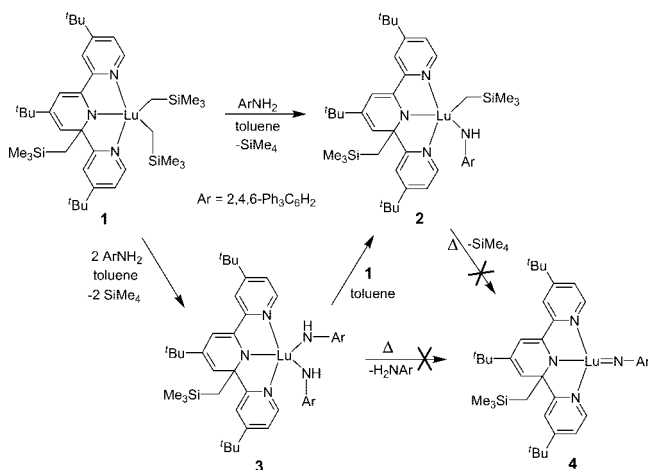
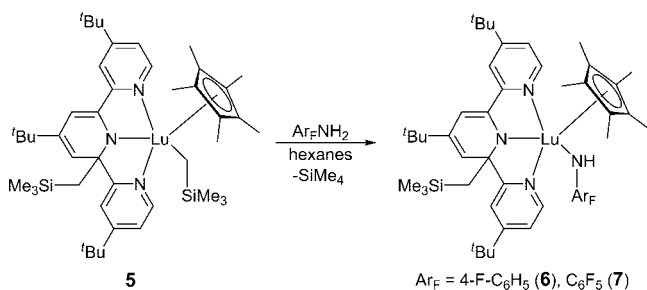
Reaction of [tBu₃(2'-Me₃SiCH₂)tpy]Lu(CH₂SiMe₃)₂ (**1**) with 1 or 2 equiv of 2,4,6-triphenylaniline at ambient temperature resulted in the formation of the mono(amide) and bis(amide) complexes **2** (43% isolated yield) and **3** (73% isolated yield), respectively, along with elimination of tetramethylsilane. For **3**, the diastereotopic doublets attributed to the terpyridyl-based methylene protons at δ 0.94 and 2.04 ppm ($^2J_{H-H}$ = 14.0 Hz) are shifted from those of **1** (1.18 and 2.31 ppm; $^2J_{H-H}$ = 14.5 Hz),⁶ while the two anilide N–H signals appear at δ 4.82 and 5.62 ppm. For **2**, the terpyridyl-based methylene protons appear at approximately δ 1.1 and 2.25 ppm (upfield signal obscured by a tBu peak; $^2J_{H-H}$ = 14.5 Hz), while the anilide N–H peak is located at δ 5.68 ppm. The asymmetric nature of **2** is revealed by the diastereotopic doublets for the methylene protons of the sole –CH₂SiMe₃ ligand at δ –0.35 and –0.45 ppm ($^2J_{H-H}$ = 11.3 Hz). Alternatively, complex **2** can be prepared by the conproportionation of **1** and **3** (78% isolated yield). Heating either complex **2** (benzene-*d*₆, 60 °C, 20 days) or **3** (toluene-*d*₈, 75 °C, 1 day) did not result in the formation of the lutetium-

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Scheme 1. Synthesis of the Lutetium Anilide Complexes 2 and 3**Scheme 2. Synthesis of the Fluorinated Anilide Complexes 6 and 7**

imido species **4** as monitored by ^1H NMR spectroscopy; higher temperatures afforded intractable materials.

Single crystals of **3** suitable for X-ray diffraction analysis were obtained from a concentrated hexanes solution at -35°C . In addition to the modified terpyridyl ligand, two anilide ligands are coordinated to the lutetium(III) center in a distorted square-pyramidal geometry with one of the anilide ligands residing in the apical position and the remaining nitrogen atoms completing the base of the pyramid. The two terminal $\text{Lu}-\text{N}_{\text{anilide}}$ bonds have distances of 2.177(7) and 2.207(6) Å and are slightly shorter than those reported for other structurally characterized lutetium anilide complexes. For example, $(\text{C}_5\text{Me}_5)_3\text{Lu}[\text{N}(\text{H})\text{Dipp}](\text{CH}_2\text{SiMe}_3)(\text{bpy})$ and $(\text{C}_5\text{Me}_5)_2\text{Lu}[\text{N}(\text{H})\text{Dipp}]_2(\text{bpy})$ [Dipp = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$, bpy = 2,2'-bipyridine] have $\text{Lu}-\text{N}_{\text{anilide}}$ distances ranging between 2.208(7) and 2.22(1) Å,⁸ and a $\text{Lu}-\text{N}_{\text{anilide}}$ bond distance of 2.238(4) Å was observed in the derivatized bipyridine complex $(\text{C}_5\text{Me}_5)_3\text{Lu}[2,2'\text{-bipy-6-CH}(\text{O})\text{CH}_2\text{SiMe}_3][\text{N}(\text{H})\text{Dipp}]$.⁹ Lastly, the anionic amide moiety within the terpyridyl ligand binds to the lutetium metal with a distance of 2.226(7) Å and compares well to the structurally analogous systems [$\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}$] $\text{Lu}(\text{CH}_2\text{SiMe}_3)_2$ (**1**) ($\text{Lu}-\text{N}_{\text{amide}} = 2.217(7)$ Å) and [$\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}$](C_5Me_5) $\text{Lu}(\text{CH}_2\text{SiMe}_3)$ (**5**) ($\text{Lu}-\text{N}_{\text{amide}} = 2.253(4)$ Å).⁶

Reaction of the pentamethylcyclopentadienyl lutetium alkyl **5** with equimolar amounts of 4-fluoroaniline or pentafluoroaniline at ambient temperature resulted in the formation of the monoanilide complexes **6** (72% isolated yield) and **7** (60% isolated yield), respectively. The diastereotopic methylene protons of the

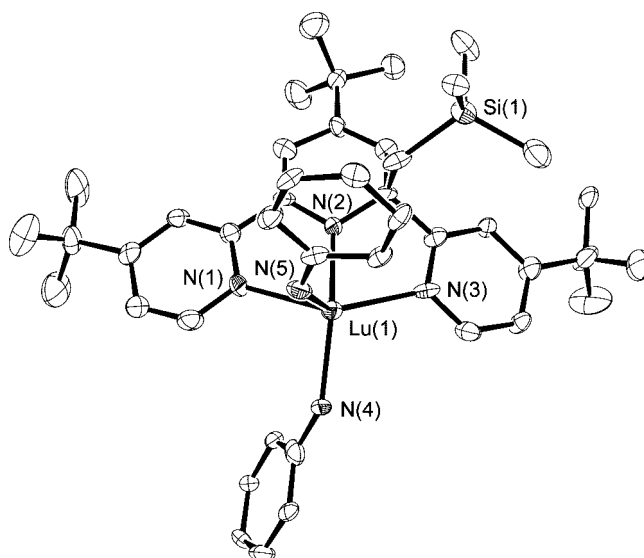


Figure 1. Thermal ellipsoid plot of **3** with ellipsoids projected at the 50% probability level. The 2,4,6-Ph substituents on the two anilide ligands have been omitted for clarity. Selected bond distances (Å) and angles (deg): $\text{Lu}(1)-\text{N}(1)$ 2.317(7), $\text{Lu}(1)-\text{N}(2)$ 2.226(7), $\text{Lu}(1)-\text{N}(3)$ 2.338(7), $\text{Lu}(1)-\text{N}(4)$ 2.207(6), $\text{Lu}(1)-\text{N}(5)$ 2.177(7), $\text{Lu}(1)-\text{N}(4)-\text{C}(46)$ 147.6(6), $\text{Lu}(1)-\text{N}(5)-\text{C}(28)$ 141.2(6), $\text{N}(1)-\text{Lu}(1)-\text{N}(3)$ 134.8(2).

$-\text{CH}_2\text{SiMe}_3$ group on the terpyridyl ligand shift slightly in the ^1H NMR spectrum from δ 1.23 and 2.17 ppm ($^2J_{\text{H-H}} = 14.4$ Hz) for **5** to δ 1.18 and 2.19 ppm ($^2J_{\text{H-H}} = 14.5$ Hz) for the 4-fluoro derivative **6**. However, in the case of the pentafluorophenyl derivative **7** there is a major shift in the signals to δ 1.58 and 1.77 ppm ($^2J_{\text{H-H}} = 14.3$ Hz). This significant deviation is attributed to the interaction between an *ortho* fluorine atom on the C_6F_5 group interacting with the methylene protons on terpyridyl ligand (*vide infra*). The anilide N–H resonances are observed at δ 4.60 and 4.52 ppm for complexes **6** and **7**, respectively. The ^{19}F NMR spectrum of **6** displays the expected multiplet centered at δ -133.82 ppm for the single aromatic fluorine. Evidence for the fluorine–methylene interaction is also present in the ^{19}F NMR spectrum of **7** with the *ortho* fluorines appearing as a multiplet (instead of a doublet of doublets) shifted slightly downfield to δ -162.66 ppm, rather than upfield as expected, relative to $\text{C}_6\text{F}_5\text{NH}_2$ (δ -163.94 (dd), -166.55 (t), -175.26 (m) ppm in C_6D_6). The *meta* and *para* fluorine resonances all shift upfield relative to $\text{C}_6\text{F}_5\text{NH}_2$, showing up at δ -167.88 ppm (triplet) and -184.53 ppm (multiplet), respectively.

Single-crystal X-ray diffraction confirmed the existence of the $\text{F}\cdots\text{H}-\text{C}_{\text{methylene}}$ interaction in complex **7** (Figure 2). Specifically, the structure reveals a fluorine–hydrogen interaction between the *ortho* fluorine F(1) and one of the hydrogen atoms attached to C(28). The $\text{F}(1)\cdots\text{C}(28)$ separation of 3.316(8) Å with a $\text{F}(1)-\text{H}(28a)-\text{C}(28)$ angle of approximately 151° is consistent with intramolecular hydrogen bonding.¹⁰ The $\text{F}(1)\cdots\text{H}(28a)-\text{C}(28)$ interaction has a distance of 2.434 Å, which is shorter than the $\text{H}\cdots\text{F}$ van der Waals contact separation of 2.55 Å.¹¹ Thus, this interaction is maintained in both the solid state and solution, as evidenced by the ^1H and ^{19}F NMR data obtained for complex **7**.

The terpyridyl amide–lutetium linkage, $\text{Lu}(1)-\text{N}(1) = 2.239(5)$ Å, compares well with the analogous bond distances

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in complexes **1**, **3**, and **5**. The terminal Lu–N_{anilide} bond has a distance of 2.244(5) Å, which is slightly longer than those reported for other lutetium anilide complexes^{8,9} and is likely a consequence of the electron-withdrawing pentafluorophenyl group on the amide ligand. There are only a handful^{12–14} of structurally characterized lanthanide complexes supported by fluorinated amide ligands: (η -C₆H₅Me)Nd[N(C₆F₅)₂]₃,¹² Sm[N(H)C₆F₅]₃(THF)₃,¹² and Sm[N(SiMe₃)(C₆F₅)]₃.¹³ However, unlike these Sm and Nd complexes, which all exhibit metal–fluorine interactions, the closest Lu–F distance in **7** is 2.943(4) Å, which is longer than the sum of the ionic radii of both lutetium (0.861 Å) and fluorine (1.285 Å).¹⁵ The lack of any Lu···F interactions in **7** is most likely the manifestation of steric saturation at the lutetium metal center provided by both the pentamethylcyclopentadienyl and alkylated terpyridyl ligands.

In summary, although the modified terpyridyl framework **C** is not able to support lutetium complexes containing multiply bonded functional groups, we have demonstrated that both alkyl complexes **1** and **5** react with anilines to give new lutetium anilide complexes. Importantly, **6** and **7** provide rare examples of lutetium complexes supported by fluorinated amide ligands, with **7** featuring an intramolecular F···H–C interaction that is maintained in both solid state and solution.

Experimental Section

General Procedures. All reactions and manipulations were carried out using either a MBraun 150 B-G or a Vacuum Atmospheres (MO 40-2 Dri-train) recirculating nitrogen atmosphere drybox, or using standard Schlenk and high-vacuum-line techniques. Glassware was dried at 150 °C before use. ¹H, ¹³C{¹H}, ¹⁹F, DEPT-135, and two-dimensional ¹³C{¹H}–¹H NMR spectra were collected using a Bruker Avance 300 MHz spectrometer. Chemical shifts were referenced to the protio solvent impurity in benzene-*d*₆ at δ 7.16 ppm (¹H) and δ 128.39 ppm (¹³C{¹H}). For ¹⁹F NMR spectra, CFCl₃ was used as an external reference at δ 0.00 ppm. ¹H and ¹³C{¹H} NMR assignments were confirmed through the use of DEPT-135 and HMQC NMR experiments.

Melting points were determined with a Mel-Temp II capillary melting point apparatus equipped with a Fluke 51 II K/J thermocouple using capillary tubes flame-sealed under nitrogen; values are uncorrected. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facility, using a VG ProSpec mass spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer Series II 2400 CHNS analyzer.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), 4 Å molecular sieves (Aldrich), and alumina (Brockman I, Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich) and hexanes (Aldrich) were passed through a column of activated alumina under nitrogen and stored over activated 4 Å molecular sieves prior to use. Benzene-*d*₆ (Aldrich) was dried over activated 4 Å molecular sieves prior to use. 4-Fluoroaniline (Aldrich) was passed through a column of activated alumina and stored over activated 4 Å molecular sieves prior to use. 4,4',4''-Tri-*tert*-butyl-2,2':6',2''-terpyridine (Aldrich),

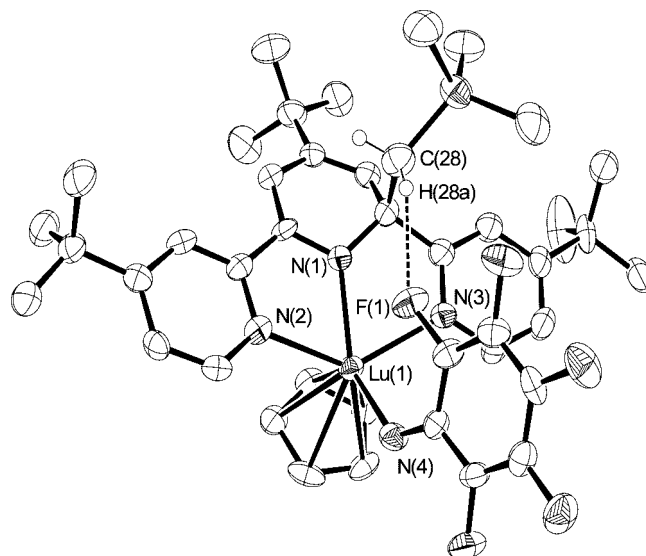


Figure 2. Thermal ellipsoid plot of **7** with ellipsoids projected at the 50% probability level. The methyl groups on the C₅Me₅ ligand have been omitted for clarity. Dashed line highlights the interaction between F(1) and the methylene proton H(28a) on the functionalized terpyridine ligand. Selected bond distances (Å) and angles (deg): Lu(1)–N(1) 2.239(5), Lu(1)–N(2) 2.367(5), Lu(1)–N(3) 2.382(5), Lu(1)–N(4) 2.244(5), Lu(1)–N(4)–C(37) 131.7(4), N(2)–Lu(1)–N(3) 133.53(19).

2,4,6-triphenylaniline (Aldrich), and pentafluoroaniline (Aldrich) were purified by recrystallization from toluene at –35 °C. [Bu₃(2'-Me₃SiCH₂)tpy]Lu(CH₂SiMe₃)₂ (**1**) and [Bu₃(2'-Me₃SiCH₂)tpy]-(C₅Me₅)Lu(CH₂SiMe₃) (**5**) were prepared according to literature procedures.⁶

Synthesis of [Bu₃(2'-Me₃SiCH₂)tpy]Lu[NH(2,4,6-Ph₃-C₆H₂)]-(CH₂SiMe₃) (2**).** *Method A.* A 125-mL side-arm flask equipped with a stir bar was charged with [Bu₃(2'-Me₃SiCH₂)tpy]Lu-(CH₂SiMe₃)₂ (**1**) (0.109 g, 0.13 mmol) and toluene (30 mL). To the resulting dark green solution was added dropwise a 10 mL toluene solution of 2,4,6-triphenylaniline (0.042 g, 0.13 mmol) with stirring. The reaction mixture immediately turned a dark red color, and stirring was continued for 90 min. The volatiles were removed under reduced pressure to give **2** as an analytically pure dark red powder (0.060 g, 0.06 mmol, 43%). *Method B.* A 20-mL scintillation vial equipped with a stir bar was charged with **3** (0.130 g, 0.10 mmol) and toluene (10 mL). To the resulting room-temperature dark red solution was added portionwise a 10 mL toluene solution of **1** (0.076 g, 0.091 mmol). The resultant reaction mixture was stirred at room temperature for 20 min. The volatiles were removed under reduced pressure to give **2** as an analytically pure dark red powder (0.152 g, 0.071 mmol, 78%). ¹H NMR (benzene-*d*₆, 301 K): δ 8.31 (d, 1H, 5.8 Hz, Ar-*H*), 8.17 (d, 1H, 5.8 Hz, Ar-*H*), 7.87 (d, 1H, 1.4 Hz, Ar-*H*), 7.65 (d, 1H, 1.4 Hz, Ar-*H*), 7.56–7.53 (m, 10H, Ar-*H*), 7.12–7.00 (m, 7H, Ar-*H*), 6.58 (m, 2H, Ar-*H*), 5.92 (s, 1H, Ar-*H*), 5.68 (s, 1H, NH), 5.32 (s, 1H, Ar-*H*), 2.25 (d, 1H, 14.0 Hz, CH₂SiMe₃), 1.42 (s, 9H, CMe₃), 1.06 (s, 9H, CMe₃), 0.98 (s, 9H, CMe₃), 0.07 (s, 9H, CH₂SiMe₃), 0.01 (s, 9H, CH₂SiMe₃), –0.35 (d, 1H, 11.3 Hz, CH₂SiMe₃), –0.45 (d, 1H, 11.3 Hz, CH₂SiMe₃). The remaining CH₂SiMe₃ resonance is obscured by the resonance at δ 1.06. ¹³C{¹H} NMR (benzene-*d*₆, 301 K): δ 174.45 (s, C_{Ar}), 164.49 (s, C_{Ar}), 162.76 (s, C_{Ar}), 162.50 (s, C_{Ar}), 155.70 (s, C_{Ar}), 150.04 (s, C_{Ar}), 148.20 (s, C_{Ar}), 146.39 (s, C_{Ar}), 146.06 (s, C_{Ar}), 144.59 (s, C_{Ar}), 142.66 (s, C_{Ar}), 130.73 (s, C_{Ar}), 130.08 (s, C_{Ar}), 129.51 (s, C_{Ar}), 129.30 (s, C_{Ar}), 129.22 (s, C_{Ar}), 127.52 (s, C_{Ar}), 126.58 (s, C_{Ar}), 126.02 (s, C_{Ar}), 125.82 (s, C_{Ar}), 119.77 (s, C_{Ar}), 119.69 (s, C_{Ar}), 118.48 (s, C_{Ar}), 117.51 (s, C_{Ar}), 108.76 (s, C_{Ar}), 92.62 (s, C_{Ar}), 69.33 (s, CCH₂SiMe₃), 39.87 (s,

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CH_2SiMe_3), 38.77 (s, CH_2SiMe_3), 35.70 (s, CMe_3), 35.36 (s, CMe_3), 34.51 (s, CMe_3), 30.50 (s, CMe_3), 30.47 (s, CMe_3), 30.39 (s, CMe_3), 4.62 (s, CH_2SiMe_3), 1.35 (s, CH_2SiMe_3). Anal. Calcd for $\text{C}_{89}\text{H}_{75}\text{N}_4\text{LuSi}_2$ (1071.39 g/mol): C, 66.14; H, 7.06; N, 5.23. Found: C, 65.86; H, 6.95; N, 5.15. Mp = 183–184 °C (dec).

Synthesis of $[\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}]\text{Lu}[\text{NH}(2,4,6\text{-Ph}_3\text{-C}_6\text{H}_2)]_2$ (3). A 125-mL side-arm flask equipped with a stir bar was charged with $[\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}]\text{Lu}(\text{CH}_2\text{SiMe}_3)_2$ (**1**) (0.239 g, 0.29 mmol) and toluene (40 mL). To the dark green solution was added portionwise a 10 mL toluene solution of 2,4,6-triphenylaniline (0.147 g, 0.46 mmol) with stirring. The reaction mixture immediately turned a dark red color, and stirring was continued for 30 min. The volatiles were removed under reduced pressure to give **3** as an analytically pure dark red powder (0.270 g, 0.21 mmol, 73%). ^1H NMR (benzene- d_6 , 298 K): δ 7.76 (d, 1H, 1.6 Hz, Ar-H), 7.70 (d, 1H, 5.8 Hz, Ar-H), 7.57–7.55 (m, 6H, Ar-H), 7.51 (d, 1H, 1.6 Hz, Ar-H), 7.49–7.46 (m, 5H, Ar-H), 7.40–7.37 (m, 6H, Ar-H), 7.26–7.16 (m, 2H, Ar-H), 7.13–6.81 (m, 16H, Ar-H), 6.59 (dd, 1H, 5.8 Hz, 1.9 Hz, Ar-H), 6.25 (dd, 1H, 5.8 Hz, 1.9 Hz, Ar-H), 5.73 (s, 1H, Ar-H), 5.62 (s, 1H, NH), 5.24 (s, 1H, Ar-H), 4.82 (s, 1H, NH), 2.04 (d, 1H, 14.0 Hz, CH_2SiMe_3), 1.37 (s, 9H, CMe_3), 1.08 (s, 9H, CMe_3), 1.07 (s, 9H, CMe_3), 0.94 (d, 1H, 14.0 Hz, CH_2SiMe_3), -0.62 (s, 9H, CH_2SiMe_3). $^{13}\text{C}\{\text{H}\}$ NMR (benzene- d_6 , 298 K): δ 174.84 (s, C_{Ar}), 164.23 (s, C_{Ar}), 161.68 (s, C_{Ar}), 161.27 (s, C_{Ar}), 154.90 (s, C_{Ar}), 153.55 (s, C_{Ar}), 149.50 (s, C_{Ar}), 148.55 (s, C_{Ar}), 147.01 (s, C_{Ar}), 145.93 (s, C_{Ar}), 144.32 (s, C_{Ar}), 144.10 (s, C_{Ar}), 142.75 (s, C_{Ar}), 142.53 (s, C_{Ar}), 130.53 (s, C_{Ar}), 130.12 (s, C_{Ar}), 129.85 (s, C_{Ar}), 129.66 (s, C_{Ar}), 129.61 (s, C_{Ar}), 129.22 (s, C_{Ar}), 129.19 (s, C_{Ar}), 129.10 (s, C_{Ar}), 130.53 (s, C_{Ar}), 130.12 (s, C_{Ar}), 129.93 (s, C_{Ar}), 129.85 (s, C_{Ar}), 129.66 (s, C_{Ar}), 129.61 (s, C_{Ar}), 129.22 (s, C_{Ar}), 129.19 (s, C_{Ar}), 129.10 (s, C_{Ar}), 128.89 (s, C_{Ar}), 128.48 (s, C_{Ar}), 128.24 (s, C_{Ar}), 128.17 (s, C_{Ar}), 127.76 (s, C_{Ar}), 127.19 (s, C_{Ar}), 126.67 (s, C_{Ar}), 126.54 (s, C_{Ar}), 126.51 (s, C_{Ar}), 126.03 (s, C_{Ar}), 125.83 (s, C_{Ar}), 119.75 (s, C_{Ar}), 119.28 (s, C_{Ar}), 117.45 (s, C_{Ar}), 116.86 (s, C_{Ar}), 108.04 (s, C_{Ar}), 90.80 (s, C_{Ar}), 68.52 (s, $\text{CCH}_2\text{SiMe}_3$), 39.00 (s, CH_2SiMe_3), 35.66 (s, CMe_3), 35.27 (s, CMe_3), 34.49 (s, CMe_3), 30.54 (s, CMe_3), 30.49 (s, CMe_3), 30.36 (s, CMe_3), 1.16 (s, CH_2SiMe_3). Anal. Calcd for $\text{C}_{79}\text{H}_{82}\text{N}_5\text{LuSi}$ (1304.58 g/mol): C, 72.73; H, 6.34; N, 5.37. Found: C, 72.46; H, 6.63; N, 5.00. Mp = 141–142 °C (dec).

Synthesis of $[\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}](\text{C}_5\text{Me}_5)\text{Lu}(\text{NH-4-F-C}_6\text{H}_4)$ (6). A 125-mL side-arm flask equipped with a stir bar was charged with $[\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}](\text{C}_5\text{Me}_5)\text{Lu}(\text{CH}_2\text{SiMe}_3)$ (**5**) (0.298 g, 0.34 mmol) and hexanes (30 mL). To the dark green solution was added 4-fluoroaniline (0.032 mL, 0.34 mmol) with stirring. The reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure to give **6** as an analytically pure dark green powder (0.220 g, 0.24 mmol, 72%). ^1H NMR (benzene- d_6 , 298 K): δ 8.25 (d, 1H, 5.8 Hz, Ar-H), 8.15 (d, 1H, 5.8 Hz, Ar-H), 7.87 (d, 1H, 1.4 Hz, Ar-H), 7.57 (d, 1H, 1.4 Hz, Ar-H), 6.85 (t, 2H, 8.8 Hz, Ar-H), 6.70 (dd, 1H, 5.8 Hz, 1.9 Hz, Ar-H), 6.60 (m, 3H, Ar-H), 6.28 (d, 1H, 1.4 Hz, Ar-H), 5.31 (d, 1H, 1.4 Hz, Ar-H), 4.60 (s, 1H, NH), 2.19 (d, 1H, 14.5 Hz, CH_2SiMe_3), 1.88 (s, 15H, C_5Me_5), 1.38 (s, 9H, CMe_3), 1.18 (d, 1H, 14.5 Hz, CH_2SiMe_3), 1.00 (s, 9H, CMe_3), 0.97 (s, 9H, CMe_3), -0.36 (s, 9H, CH_2SiMe_3). $^{13}\text{C}\{\text{H}\}$ NMR (benzene- d_6 , 298 K): δ

173.79 (s, C_{Ar}), 163.97 (s, C_{Ar}), 163.10 (s, C_{Ar}), 162.86 (s, C_{Ar}), 155.87 (s, C_{Ar}), 155.86 (s, C_{Ar}), 149.83 (s, C_{Ar}), 148.38 (s, aryl C_{Ar}), 147.87 (s, aryl C_{Ar}), 146.39 (s, C_{Ar}), 119.96 (s, C_{Ar}), 119.61 (s, C_{Ar}), 119.53 (s, C_{Ar}), 117.34 (d, 6.9 Hz, *o*- $\text{C}_6\text{H}_4\text{F}$), 116.68 (s, C_{Ar}), 116.34 (s, C_5Me_5), 115.82 (d, 21.5 Hz, *m*- $\text{C}_6\text{H}_4\text{F}$), 111.79 (s, C_{Ar}), 96.97 (s, C_{Ar}), 68.73 (s, $\text{CCH}_2\text{SiMe}_3$), 35.40 (s, CMe_3), 35.31 (s, CMe_3), 35.19 (s, CMe_3), 32.28 (s, CH_2SiMe_3), 30.72 (s, CMe_3), 30.48 (s, CMe_3), 30.43 (s, CMe_3), 11.47 (s, C_5Me_5), 0.37 (CH_2SiMe_3). ^{19}F NMR (benzene- d_6 , 298 K): δ -133.82 (m, 1F). Anal. Calcd for $\text{C}_{47}\text{H}_{66}\text{N}_4\text{FLuSi}$ (909.10 g/mol): C, 62.09; H, 7.32; N, 6.16. Found: C, 61.85; H, 7.53; N, 5.90. MS(EI, 70 eV): m/z 909 (M^+), 820 ($\text{M}^+ - \text{SiMe}_4$), 798 ($\text{M}^+ - \text{NH}(\text{C}_6\text{H}_4\text{F})$). Mp = 147–148 °C.

Synthesis of $[\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}](\text{C}_5\text{Me}_5)\text{Lu}(\text{NHC}_6\text{F}_5)$ (7). A 125-mL side-arm flask equipped with a stir bar was charged with $[\text{Bu}_3(2'\text{-Me}_3\text{SiCH}_2)\text{tpy}](\text{C}_5\text{Me}_5)\text{Lu}(\text{CH}_2\text{SiMe}_3)$ (**5**) (0.370 g, 0.42 mmol) and hexanes (40 mL). To the dark green solution was added a 10 mL hexanes solution of pentafluoroaniline (0.076 g, 0.42 mmol) with stirring. The resultant reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure to give **7** as an analytically pure dark green powder (0.247 g, 0.25 mmol, 60%). ^1H NMR (benzene- d_6 , 298 K): δ 8.27 (d, 1H, 5.8 Hz, Ar-H), 8.12 (d, 1H, 5.8 Hz, Ar-H), 7.89 (s, 1H, 1.4 Hz, Ar-H), 7.65 (s, 1H, 1.4 Hz, Ar-H), 6.79 (dd, 1H, 5.8 Hz, 1.6 Hz, Ar-H), 6.69 (dd, 1H, 5.8 Hz, 1.6 Hz, Ar-H), 6.32 (s, 1H, 1.4 Hz, Ar-H), 5.33 (s, 1H, 1.4 Hz, Ar-H), 4.52 (s, 1H, NH), 1.83 (s, 15H, C_5Me_5), 1.77 (d, 1H, 14.3 Hz, CH_2SiMe_3), 1.58 (d, 1H, 14.3 Hz, CH_2SiMe_3), 1.39 (s, 9H, CMe_3), 1.03 (s, 9H, CMe_3), 0.97 (s, 9H, CMe_3), -0.26 (s, 9H, CH_2SiMe_3). $^{13}\text{C}\{\text{H}\}$ NMR (benzene- d_6 , 298 K): δ 173.70 (s, C_{Ar}), 164.15 (s, C_{Ar}), 162.94 (s, C_{Ar}), 162.86 (s, C_{Ar}), 149.76 (s, C_{Ar}), 147.70 (s, C_{Ar}), 147.52 (s, C_{Ar}), 146.47 (s, C_{Ar}), 119.95 (s, C_{Ar}), 119.80 (s, C_{Ar}), 119.58 (s, C_{Ar}), 117.55 (s, C_{Ar}), 117.37 (s, C_{Ar}), 117.01 (s, C_{Ar}), 116.97 (s, C_5Me_5), 115.70 (s, C_{Ar}), 115.24 (s, C_{Ar}), 110.98 (s, C_{Ar}), 97.27 (s, C_{Ar}), 68.89 (s, $\text{CCH}_2\text{SiMe}_3$), 35.50 (s, CMe_3), 35.29 (s, CMe_3), 34.39 (s, CMe_3), 31.43 (s, CH_2SiMe_3), 30.72 (s, CMe_3), 30.46 (s, CMe_3), 30.36 (s, CMe_3), 11.41 (s, C_5Me_5), 0.48 (s, CH_2SiMe_3). ^{19}F NMR (benzene- d_6 , 298 K): δ -162.66 (m, 2F, ortho), -167.88 (t, 2F, meta), -184.53 (m, 1F, para). Anal. Calcd for $\text{C}_{47}\text{H}_{62}\text{N}_4\text{F}_5\text{LuSi}$ (981.08 g/mol): C, 57.54; H, 6.37; N, 5.71. Found: C, 57.88; H, 6.73; N, 5.48. MS (EI, 70 eV): m/z 981 (M^+), 893 ($\text{M}^+ - \text{SiMe}_4$), 799 ($\text{M}^+ - \text{NH}(\text{C}_6\text{F}_5)$). Mp = 195–196 °C.

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Supporting Information Available: X-ray crystallographic data for **3** and **7** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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