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

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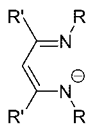
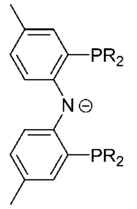
*Summary: Lutetium alkyl complexes supported by a monoanionic, tridentate ligand system formed by the dearomatization and functionalization of a 2,2′:6′,2″-terpyridine have been reacted with 2,4,6-triphenylaniline or the fluorinated anilines 4-F-$C_6H_4NH_2$ and $C_6F_5NH_2$ to give both terminal mono(amide) and bis(amide) lutetium(III) complexes, which have been fully characterized. Both [^{t}Bu$_3$(2′-Me_3SiCH_2)tpy]Lu[NH(2,4,6-Ph_3-C_6H_2)]$_2$ (**3**) and [^{t}Bu$_3$(2′-Me_3SiCH_2)tpy](C_5Me_5)Lu(NHC_6F_5) (**7**) have been structurally characterized. The fluorinated anilide complexes [^{t}Bu$_3$(2′-Me_3SiCH_2)tpy](C_5Me_5)Lu(NHAr$_F$) (Ar$_F$ = 4-F-C_6H_4 (**6**), C_6F_5 (**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, [^{t}Bu$_3$(2′-Me_3SiCH_2)tpy]Lu(CH_2SiMe_3)$_2$ (**1**), with anilines.



A



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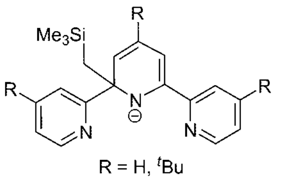

C

Results and Discussion

Reaction of [^{t}Bu$_3$(2′-Me_3SiCH_2)tpy]Lu(CH_2SiMe_3)$_2$ (**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 ($^2J_{\text{H-H}} = 14.0$ Hz) are shifted from those of **1** (1.18 and 2.31 ppm; $^2J_{\text{H-H}} = 14.5$ 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 ^{t}Bu peak; $^2J_{\text{H-H}} = 14.5$ 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 $-CH_2SiMe_3$ ligand at δ −0.35 and −0.45 ppm ($^2J_{\text{H-H}} =$ 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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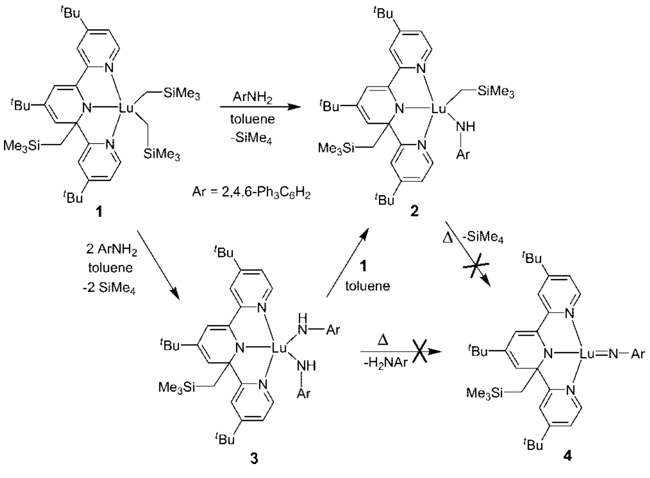
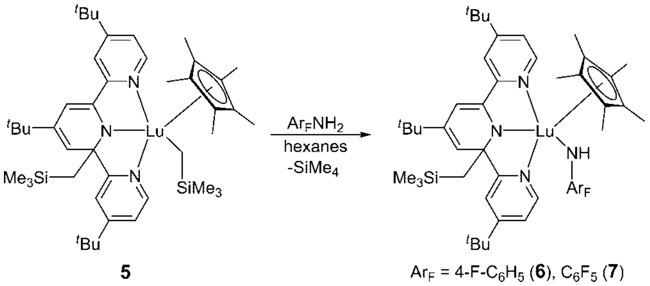
Scheme 1. Synthesis of the Lutetium Anilide Complexes 2 and 3



Scheme 2. Synthesis of the Fluorinated Anilide Complexes 6 and 7



imido species **4** as monitored by ^{1}H 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 Lu−N$_{anilide}$ 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, $(C_5Me_5)Lu[N(H)Dipp](CH_2SiMe_3)(bpy)$ and $(C_5Me_5)Lu[N(H)Dipp]_2(bpy)]$ (Dipp = 2,6-$^{i}Pr_2C_6H_3$, bpy = 2,2′-bipyridine) have Lu−N$_{anilide}$ distances ranging between 2.208(7) and 2.22(1) Å,[8] and a Lu−N$_{anilide}$ bond distance of 2.238(4) Å was observed in the derivatized bipyridine complex $(C_5Me_5)Lu[2,2'\text{-bipy-}6\text{-}CH(O)CH_2SiMe_3][N(H)Dipp]$.[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 $[^{t}Bu_3(2'\text{-}Me_3SiCH_2)tpy]Lu(CH_2SiMe_3)_2$ (**1**) (Lu−N$_{amide}$ = 2.217(7) Å) and $[^{t}Bu_3(2'\text{-}Me_3SiCH_2)tpy](C_5Me_5)Lu(CH_2SiMe_3)$ (**5**) (Lu−N$_{amide}$ = 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 −CH_2SiMe_3 group on the terpyridyl ligand shift slightly in the ^{1}H NMR spectrum from δ 1.23 and 2.17 ppm ($^{2}J_{H\text{-}H}$ = 14.4 Hz) for **5** to δ 1.18 and 2.19 ppm ($^{2}J_{H\text{-}H}$ = 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 ($^{2}J_{H\text{-}H}$ = 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 $C_6F_5NH_2$ (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 $C_6F_5NH_2$, showing up at δ −167.88 ppm (triplet) and −184.53 ppm (multiplet), respectively.

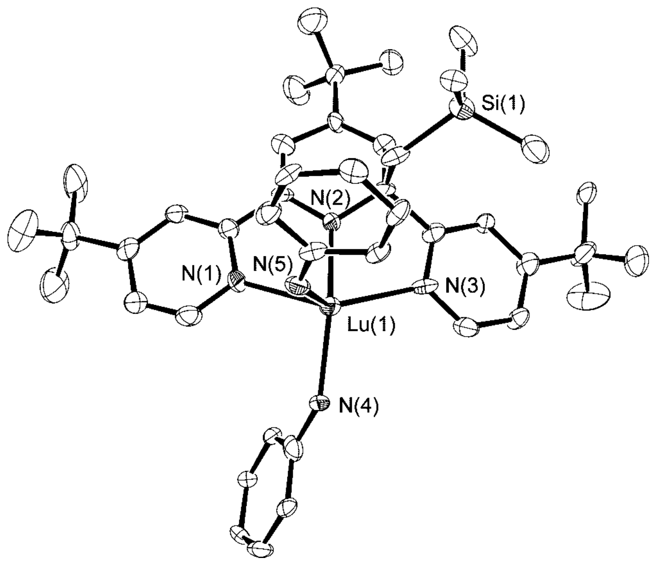


Figure 1. Thermal ellipsoid plot of **3** with ellipsoids projected at the 50% probability level. The 2,4,6-Ph substituents on the two anilide ligands have been omitted for clarity. Selected bond distances (Å) and angles (deg): Lu(1)−N(1) 2.317(7), Lu(1)−N(2) 2.226(7), Lu(1)−N(3) 2.338(7), Lu(1)−N(4)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

Single-crystal X-ray diffraction confirmed the existence of the F···H−C$_{methylene}$ 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 F(1)···C(28) separation of 3.316(8) Å with a F(1)−H(28a)−C(28) angle of approximately 151° is consistent with intramolecular hydrogen bonding.[10] The F(1)···H(28a)−C(28) interaction has a distance of 2.434 Å, which is shorter than the H···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 ^{1}H and ^{19}F NMR data obtained for complex **7**.

The terpyridyl amide−lutetium linkage, Lu(1)−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$_{\text{anilide}}$ 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-C_6H_5Me)Nd[N(C_6F_5)$_2$]$_3$,[12] Sm[N(H)C_6F_5]$_3$(THF)$_3$,[12] and Sm[N(SiMe$_3$)(C_6F_5)]$_3$.[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$\cdots$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$\cdots$H$-$C interaction that is maintained in both solid state and solution.

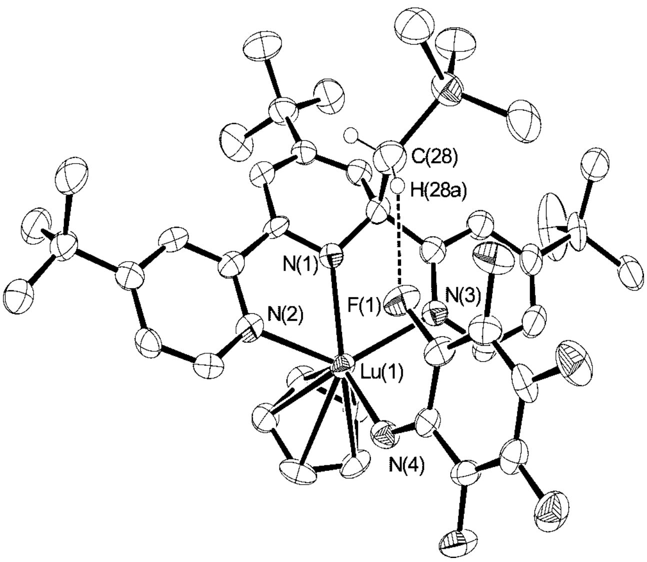

Figure 2. Thermal ellipsoid plot of **7** with ellipsoids projected at the 50% probability level. The methyl groups on the C_5Me_5 ligand have been omitted for clarity. Dashed line highlights the interaction between F(1) and the methylene proton H(28a) on the functionalized terpyridine ligand. Selected 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).

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. ^{1}H, ^{13}C{^{1}H}, ^{19}F, DEPT-135, and two-dimensional ^{13}C{^{1}H}$-^1$H 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 (^{1}H) and δ 128.39 ppm (^{13}C{^{1}H}). For ^{19}F NMR spectra, $CFCl_3$ was used as an external reference at δ 0.00 ppm. ^{1}H and ^{13}C{^{1}H} 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), 2,4,6-triphenylaniline (Aldrich), and pentafluoroaniline (Aldrich) were purified by recrystallization from toluene at $-$35 °C. [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy]Lu(CH$_2$SiMe$_3$)$_2$ (**1**) and [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy]-(C_5Me_5)Lu(CH$_2$SiMe$_3$) (**5**) were prepared according to literature procedures.[6]

Synthesis of [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy]Lu[NH(2,4,6-Ph$_3$-C$_6$H$_2$)]-(CH$_2$SiMe$_3$) (2). *Method A.* A 125-mL side-arm flask equipped with a stir bar was charged with [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy]Lu-(CH$_2$SiMe$_3$)$_2$ (**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%). ^{1}H 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, N*H*), 5.32 (s, 1H, Ar-*H*), 2.25 (d, 1H, 14.0 Hz, C*H*$_2$SiMe$_3$), 1.42 (s, 9H, C*Me*$_3$), 1.06 (s, 9H, C*Me*$_3$), 0.98 (s, 9H, C*Me*$_3$), 0.07 (s, 9H, CH$_2$Si*Me*$_3$), 0.01 (s, 9H, CH$_2$Si*Me*$_3$), $-$0.35 (d, 1H, 11.3 Hz, C*H*$_2$SiMe$_3$), $-$0.45 (d, 1H, 11.3 Hz, C*H*$_2$SiMe$_3$). The remaining C*H*$_2$SiMe$_3$ resonance is obscured by the resonance at δ 1.06. ^{13}C{H} NMR (benzene-*d*$_6$, 301 K): δ 174.45 (s, C$_{\text{Ar}}$), 164.49 (s, C$_{\text{Ar}}$), 162.76 (s, C$_{\text{Ar}}$), 162.50 (s, C$_{\text{Ar}}$), 155.70 (s, C$_{\text{Ar}}$), 150.04 (s, C$_{\text{Ar}}$), 148 20 (s, C$_{\text{Ar}}$), 146.39 (s, C$_{\text{Ar}}$), 146.06 (s, C$_{\text{Ar}}$), 144.59 (s, C$_{\text{Ar}}$), 142.66 (s, C$_{\text{Ar}}$), 130.73 (s, C$_{\text{Ar}}$), 130.08 (s, C$_{\text{Ar}}$), 129.51 (s, C$_{\text{Ar}}$), 129.30 (s, C$_{\text{Ar}}$), 129.22 (s, C$_{\text{Ar}}$), 127.52 (s, C$_{\text{Ar}}$), 126.58 (s, C$_{\text{Ar}}$), 126.02 (s, C$_{\text{Ar}}$), 125.82 (s, C$_{\text{Ar}}$), 119.77 (s, C$_{\text{Ar}}$), 119.69 (s, C$_{\text{Ar}}$), 118.48 (s, C$_{\text{Ar}}$), 117.51 (s, C$_{\text{Ar}}$), 108.76 (s, C$_{\text{Ar}}$), 92.62 (s, C$_{\text{Ar}}$), 69.33 (s, *C*CH$_2$SiMe$_3$), 39.87 (s,

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$\mathit{C}\mathrm{H_2SiMe_3}$), 38.77 (s, $\mathit{C}\mathrm{H_2SiMe_3}$), 35.70 (s $\mathit{C}\mathrm{Me_3}$), 35.36 (s $\mathit{C}\mathrm{Me_3}$), 34.51 (s $\mathit{C}\mathrm{Me_3}$), 30.50 (s, $\mathrm{C}\mathit{Me}_3$), 30.47 (s, $\mathrm{C}\mathit{Me}_3$), 30.39 (s, $\mathrm{C}\mathit{Me}_3$), 4.62 (s, $\mathrm{CH_2Si}\mathit{Me}_3$), 1.35 (s, $\mathrm{CH_2Si}\mathit{Me}_3$). Anal. Calcd for $\mathrm{C_{89}H_{75}N_4LuSi_2}$ (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 [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy]Lu[NH(2,4,6-Ph$_3$-C$_6$H$_2$)]$_2$ (3). A 125-mL side-arm flask equipped with a stir bar was charged with [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy]Lu(CH$_2$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%). ^{1}H 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, N*H*), 5.24 (s, 1H, Ar-*H*), 4.82 (s, 1H, N*H*), 2.04 (d, 1H, 14.0 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 1.37 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 1.08 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 1.07 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 0.94 (d, 1H, 14.0 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), −0.62 (s, 9H, $\mathrm{CH_2Si}\mathit{Me}_3$). ^{13}C{H} NMR (benzene-d_6, 298 K): δ 174.84 (s, $\mathrm{C_{Ar}}$), 164.23 (s, $\mathrm{C_{Ar}}$), 161.68 (s, $\mathrm{C_{Ar}}$), 161.27 (s, $\mathrm{C_{Ar}}$), 154.90 (s, $\mathrm{C_{Ar}}$), 153.55 (s, $\mathrm{C_{Ar}}$), 149.50 (s, $\mathrm{C_{Ar}}$), 148.55 (s, $\mathrm{C_{Ar}}$), 147.01 (s, $\mathrm{C_{Ar}}$), 145.93 (s, $\mathrm{C_{Ar}}$), 144.32 (s, $\mathrm{C_{Ar}}$), 144.10 (s, $\mathrm{C_{Ar}}$), 142.75 (s, $\mathrm{C_{Ar}}$), 142.53 (s, $\mathrm{C_{Ar}}$), 130.53 (s, $\mathrm{C_{Ar}}$), 130.12 (s, $\mathrm{C_{Ar}}$), 129.85 (s, $\mathrm{C_{Ar}}$), 129.66 (s, $\mathrm{C_{Ar}}$), 129.61 (s, $\mathrm{C_{Ar}}$), 129.22 (s, $\mathrm{C_{Ar}}$), 129.19 (s, $\mathrm{C_{Ar}}$), 129.10 (s, $\mathrm{C_{Ar}}$), 130.53 (s, $\mathrm{C_{Ar}}$), 130.12 (s, $\mathrm{C_{Ar}}$), 129.93 (s, $\mathrm{C_{Ar}}$), 129.85 (s, $\mathrm{C_{Ar}}$), 129.66 (s, $\mathrm{C_{Ar}}$), 129.61 (s, $\mathrm{C_{Ar}}$), 129.22 (s, $\mathrm{C_{Ar}}$), 129.19 (s, $\mathrm{C_{Ar}}$), 129.10 (s, $\mathrm{C_{Ar}}$), 128.89 (s, $\mathrm{C_{Ar}}$), 128.48 (s, $\mathrm{C_{Ar}}$), 128.24 (s, $\mathrm{C_{Ar}}$), 128.17 (s, $\mathrm{C_{Ar}}$), 127.76 (s, $\mathrm{C_{Ar}}$), 127.19 (s, $\mathrm{C_{Ar}}$), 126.67 (s, $\mathrm{C_{Ar}}$), 126.54 (s, $\mathrm{C_{Ar}}$), 126.51 (s, $\mathrm{C_{Ar}}$), 126.03 (s, $\mathrm{C_{Ar}}$), 125.83 (s, $\mathrm{C_{Ar}}$), 119.75 (s, $\mathrm{C_{Ar}}$), 119.28 (s, $\mathrm{C_{Ar}}$), 117.45 (s, $\mathrm{C_{Ar}}$), 116.86 (s, $\mathrm{C_{Ar}}$), 108.04 (s, $\mathrm{C_{Ar}}$), 90.80 (s, $\mathrm{C_{Ar}}$), 68.52 (s, $\mathit{C}\mathrm{CH_2SiMe_3}$), 39.00 (s, $\mathit{C}\mathrm{H_2SiMe_3}$), 35.66 (s, $\mathit{C}\mathrm{Me_3}$), 35.27 (s, $\mathit{C}\mathrm{Me_3}$), 34.49 (s, $\mathit{C}\mathrm{Me_3}$), 30.54, (s, $\mathrm{C}\mathit{Me}_3$), 30.49 (s, $\mathrm{C}\mathit{Me}_3$), 30.36 (s, $\mathrm{C}\mathit{Me}_3$), 1.16 (s, $\mathrm{CH_2Si}\mathit{Me}_3$). Anal. Calcd for $\mathrm{C_{79}H_{82}N_5LuSi}$ (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 [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy](C$_5$Me$_5$)Lu(NH-4-F-C$_6$H$_4$) (6). A 125-mL side-arm flask equipped with a stir bar was charged with [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy](C$_5$Me$_5$)Lu(CH$_2$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%). ^{1}H 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, N*H*), 2.19 (d, 1H, 14.5 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 1.88 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 1.38 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 1.18 (d, 1H, 14.5 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 1.00 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 0.97 (s, 9H, $\mathrm{C}\mathit{Me}_3$), −0.36 (s, 9H, $\mathrm{CH_2Si}\mathit{Me}_3$). ^{13}C{H} NMR (benzene-d_6, 298 K): δ 173.79 (s, $\mathrm{C_{Ar}}$), 163.97 (s, $\mathrm{C_{Ar}}$), 163.10 (s, $\mathrm{C_{Ar}}$), 162.86 (s, $\mathrm{C_{Ar}}$), 155.87 (s, $\mathrm{C_{Ar}}$), 155.86 (s, $\mathrm{C_{Ar}}$), 149.83 (s, $\mathrm{C_{Ar}}$), 148.38 (s, aryl $\mathrm{C_{Ar}}$), 147.87 (s, aryl $\mathrm{C_{Ar}}$), 146.39 (s, $\mathrm{C_{Ar}}$), 119.96 (s, $\mathrm{C_{Ar}}$), 119.61 (s, $\mathrm{C_{Ar}}$), 119.53 (s, $\mathrm{C_{Ar}}$), 117.34 (d, 6.9 Hz, o-$\mathit{C}_6\mathrm{H_4F}$), 116.68 (s, $\mathrm{C_{Ar}}$), 116.34 (s, $\mathit{C}_5\mathrm{Me_5}$), 115.82 (d, 21.5 Hz, m-$\mathit{C}_6\mathrm{H_4F}$), 111.79 (s, $\mathrm{C_{Ar}}$), 96.97 (s, $\mathrm{C_{Ar}}$), 68.73 (s, $\mathit{C}\mathrm{CH_2SiMe_3}$), 35.40 (s, $\mathit{C}\mathrm{Me_3}$), 35.31 (s, $\mathit{C}\mathrm{Me_3}$), 35.19 (s, $\mathit{C}\mathrm{Me_3}$), 32.28 (s, $\mathit{C}\mathrm{H_2SiMe_3}$), 30.72 (s, $\mathrm{C}\mathit{Me}_3$), 30.48 (s, $\mathrm{C}\mathit{Me}_3$), 30.43 (s, $\mathrm{C}\mathit{Me}_3$), 11.47 (s, $\mathrm{C_5}\mathit{Me}_5$), 0.37 ($\mathrm{CH_2Si}\mathit{Me}_3$). ^{19}F NMR (benzene-$d_6$, 298 K): δ −133.82 (m, 1F). Anal. Calcd for $\mathrm{C_{47}H_{66}N_4FLuSi}$ (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 ($\mathrm{M^+}$), 820 ($\mathrm{M^+ - SiMe_4}$), 798 ($\mathrm{M^+ - NH(C_6H_4F)}$). Mp = 147–148 °C.

Synthesis of [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy](C$_5$Me$_5$)Lu(NHC$_6$F$_5$) (7). A 125-mL side-arm flask equipped with a stir bar was charged with [^{t}Bu$_3$(2′-Me$_3$SiCH$_2$)tpy](C$_5$Me$_5$)Lu(CH$_2$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%). ^{1}H 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, N*H*), 1.83 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$), 1.77 (d, 1H, 14.3 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 1.58 (d, 1H, 14.3 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 1.39 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 1.03 (s, 9H, $\mathrm{C}\mathit{Me}_3$), 0.97 (s, 9H, $\mathrm{C}\mathit{Me}_3$), −0.26 (s, 9H, $\mathrm{CH_2Si}\mathit{Me}_3$). ^{13}C{H} NMR (benzene-d_6, 298 K): δ 173.70 (s, $\mathrm{C_{Ar}}$), 164.15 (s, $\mathrm{C_{Ar}}$), 162.94 (s, $\mathrm{C_{Ar}}$), 162.86 (s, $\mathrm{C_{Ar}}$), 149.76 (s, $\mathrm{C_{Ar}}$), 147.70 (s, $\mathrm{C_{Ar}}$), 147.52 (s, $\mathrm{C_{Ar}}$), 146.47 (s, $\mathrm{C_{Ar}}$), 119.95 (s, $\mathrm{C_{Ar}}$), 119.80 (s, $\mathrm{C_{Ar}}$), 119.58 (s, $\mathrm{C_{Ar}}$), 117.55 (s, $\mathrm{C_{Ar}}$), 117.37 (s, $\mathrm{C_{Ar}}$), 117.01 (s, $\mathrm{C_{Ar}}$), 116.97 (s, $\mathit{C}_5\mathrm{Me_5}$), 115.70 (s, $\mathrm{C_{Ar}}$), 115.24 (s, $\mathrm{C_{Ar}}$), 110.98 (s, $\mathrm{C_{Ar}}$), 97.27 (s, $\mathrm{C_{Ar}}$), 68.89 (s, $\mathit{C}\mathrm{CH_2SiMe_3}$), 35.50 (s, $\mathit{C}\mathrm{Me_3}$), 35.29 (s, $\mathit{C}\mathrm{Me_3}$), 34.39 (s, $\mathit{C}\mathrm{Me_3}$), 31.43 (s, $\mathit{C}\mathrm{H_2SiMe_3}$), 30.72 (s, $\mathrm{C}\mathit{Me}_3$), 30.46 (s, $\mathrm{C}\mathit{Me}_3$), 30.36 (s, $\mathrm{C}\mathit{Me}_3$), 11.41 (s, $\mathrm{C_5}\mathit{Me}_5$), 0.48 (s, $\mathrm{CH_2Si}\mathit{Me}_3$). ^{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 $\mathrm{C_{47}H_{62}N_4F_5LuSi}$ (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 ($\mathrm{M^+}$), 893 ($\mathrm{M^+ - SiMe_4}$), 799 ($\mathrm{M^+ - NH(C_6F_5)}$). 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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