

# Reactivity of $(C_5Me_5)Lu(CH_2SiMe_3)_2(THF)$ with Pyridine Ring Systems: Synthesis and Structural Characterization of an $\eta^2$ -(N,C)-Pyridyl (Mono)pentamethylcyclopentadienyl Lutetium(III) Complex

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Reaction of  $(C_5Me_5)Lu(CH_2SiMe_3)_2(THF)$  with pyridine results in the activation of an ortho C–H bond to form the corresponding  $\eta^2$ -(N,C)-pyridyl complex with elimination of  $SiMe_4$ . This is a rare example of pyridine metalation at a lanthanide metal center in the absence of a bent metallocene framework. The  $\eta^2$ -(N,C)-pyridyl coordination mode was confirmed by X-ray crystallographic analysis. The pyridyl complex adopts a distorted square-pyramid geometry with the  $C_5Me_5$  unit residing in the apical position and the pyridyl ligand and remaining ligands residing in the basal plane. Isotopic labeling studies suggest that C–H bond activation is consistent with a  $\sigma$ -bond metathesis mechanism.

## Introduction

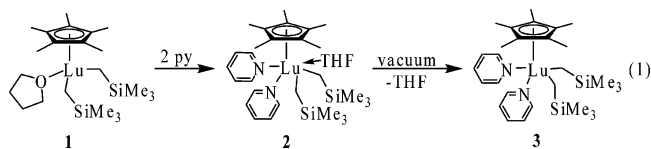
Although ample precedent exists for transition metals that form  $\eta^2$ -pyridyl complexes upon reaction with pyridine, reports of similar complexes for the f-elements remain scarce.<sup>1</sup> In 1999, Scott and co-workers reported the first structurally characterized example of an f-element  $\eta^2$ -pyridyl complex obtained from the reaction of pyridine with a highly strained uranium(IV) metallocycle.<sup>2</sup> Earlier work by Watson demonstrated that reaction of pyridine with  $(C_5Me_5)_2Lu(CH_3)$  resulted in C–H bond activation of pyridine and concomitant elimination of methane to form the  $\eta^2$ -pyridyl complex  $(C_5Me_5)_2Lu[\eta^2$ -(N,C)-NC<sub>5</sub>H<sub>4</sub>].<sup>3</sup> This complex was characterized solely by NMR spectroscopy, and to date, no structural data for this or any other lanthanide  $\eta^2$ -pyridyl complex have been described. These examples of f-element  $\eta^2$ -pyridyl coordination occur in an environment containing either a bent metallocene or bulky ligand framework.

We recently demonstrated that reaction of pyridine N-oxide ring systems with thorium(IV) and uranium(IV) alkyl and aryl

complexes either mediate facile ring-opening of pyridine N-oxide (forming thorium  $\eta^2$ -(O,N) oximate complexes)<sup>4</sup> or activate  $sp^2$  and  $sp^3$  C–H bonds of pyridine N-oxide and lutidine N-oxide, respectively (forming the corresponding cyclometalated complexes).<sup>5</sup> Additionally, reaction of  $(C_5Me_5)_2An(CH_3)_2$  ( $An = U, Th$ ) with pyridine derivatives results in C–H bond activation and formation of the corresponding  $\eta^2$ -pyridyl complexes.<sup>6</sup> Given these diverse and unusual modes of reactivity for 5f-element complexes, we were interested in extending our studies to include representatives of the 4f-series. Herein, we describe the reactivity of the mono(pentamethylcyclopentadienyl) lutetium(III) complex  $(C_5Me_5)Lu(CH_2SiMe_3)_2(THF)$  with pyridine ring systems. We report a synthetic method for the preparation of the pyridine adduct  $(C_5Me_5)Lu(NC_5H_5)_2(CH_2SiMe_3)_2$ , which undergoes further reactivity to give  $SiMe_4$  and the corresponding  $\eta^2$ -(N,C)-pyridyl complex  $(C_5Me_5)Lu[\eta^2$ -(N,C)-NC<sub>5</sub>H<sub>4</sub>]( $CH_2SiMe_3$ )(NC<sub>5</sub>H<sub>5</sub>). Both the pyridine adduct and  $\eta^2$ -(N,C)-pyridyl complexes were characterized by NMR spectroscopy and X-ray crystallography.

## Results and Discussion

As illustrated in eq 1, reaction of a colorless hexanes solution of  $(C_5Me_5)Lu(CH_2SiMe_3)_2(THF)$  (**1**)<sup>7</sup> with 2 equiv of pyridine at ambient temperature instantly produced the bright yellow-colored bis( $\eta^1$ -pyridine) complex  $(C_5Me_5)Lu(NC_5H_5)_2(CH_2SiMe_3)_2(THF)$  (**2**) in greater than 95% yield (based on internal standard). The molecule of THF is in a dynamic equilibrium, as indicated by <sup>1</sup>H NMR spectroscopy experiments.



Complex **2** is not readily isolable; removal of volatile materials using dynamic vacuum resulted in the loss of THF

(4) Pool, J. A.; Scott, B. L.; Kiplinger, J. L. *Chem. Commun.* **2005**, 2591–2593.

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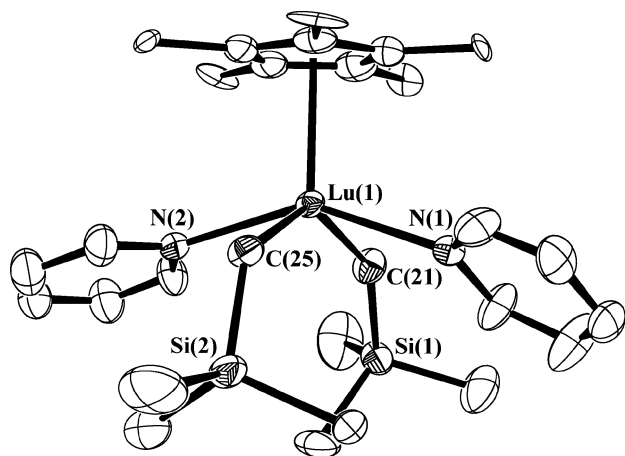
<sup>†</sup> Los Alamos National Laboratory.

<sup>‡</sup> Simon Fraser University.

(1) Lanthanides in the strictest sense include the elements from lanthanum to lutetium. Some representative transition metal, Sc, and Y examples include: (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219. (b) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053–2060. (c) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546–1557. (d) Deelman, B. J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881–3891. (e) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291–2302. (f) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415–4420. (g) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506–5516. (h) Zhu, G.; Tanski, J. M.; Churchill, D. G.; Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2002**, *124*, 13658–13659. (i) Bradley, C. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 8110–8111. (j) Ozerov, O. V.; Pink, M.; Watson, L. A.; Caulton, K. G. *J. Am. Chem. Soc.* **2004**, *126*, 2105–2113. (k) Arndt, S.; Elvidge, B. R.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, *25*, 793–795.

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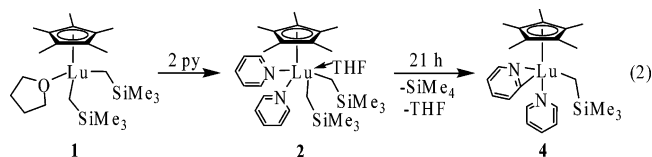
**Figure 1.** Molecular structure of complex **3** with thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (deg): Lu(1)–C<sub>5</sub>Me<sub>5</sub>(cent), 1.997(6); Lu(1)–N(1), 2.506(8); Lu(1)–N(2), 2.505(9); Lu(1)–C(21), 2.406(11); Lu(1)–C(25), 2.398(9); N(1)–Lu(1)–N(2), 146.9(3); N(1)–Lu(1)–C(21), 84.1(3); N(1)–Lu(1)–C(25), 81.1(3); N(2)–Lu(1)–C(21), 86.8(3); N(2)–Lu(1)–C(25), 84.2(3); Lu(1)–C(21)–Si(1), 141.3(7); Lu(1)–C(25)–Si(2), 125.7(5); C(21)–Lu(1)–C(25), 137.1(4).

and formation of (C<sub>5</sub>Me<sub>5</sub>)Lu(NC<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (**3**) as a bright yellow solid in 73% isolated yield (eq 1). Complex **3** is indefinitely stable at –35 °C; however, complete decomposition is observed within 2 days at room temperature. The aryl region of the <sup>1</sup>H NMR spectrum of **3** displays three multiplets at δ 8.28, 6.83, and 6.56 ppm corresponding to the ortho, para, and meta pyridyl protons, respectively. The alkyl group resonances are observed as singlets at δ 0.25 (18H, CH<sub>2</sub>SiMe<sub>3</sub>) and –0.63 (4H, CH<sub>2</sub>SiMe<sub>3</sub>) ppm, respectively, and exhibit chemical shift values comparable to other trivalent lutetium complexes that contain a –CH<sub>2</sub>SiMe<sub>3</sub> group.<sup>7,8</sup>

Single crystals of **3** suitable for X-ray diffraction analysis were obtained overnight at –35 °C from a concentrated hexanes solution. As shown in Figure 1, the molecular structure of **3** exhibits distorted square-pyramidal geometry about the metal center, with the pyridine ligands oriented in a trans configuration, and bent away from the C<sub>5</sub>Me<sub>5</sub> moiety. The Lu(1)–N(1) and Lu(1)–N(2) bond distances of 2.506(8) and 2.505(9) Å, respectively, are in good agreement with Lu–N bond distances reported for other lutetium(III) complexes containing an η<sup>1</sup>-pyridine functionality.<sup>7,9</sup> Specifically, the cationic complexes [Lu<sub>2</sub>(py)<sub>5</sub>][I] and [Lu(μ-O<sup>i</sup>Pr)(py)<sub>5</sub>][I] have Lu–N bond distances in the range 2.443(6)–2.54(2) Å, and the neutral complex [(C<sub>5</sub>Me<sub>5</sub>)Lu(C≡CPh)<sub>2</sub>(bipy)(py)] has a distance of 2.580(8) Å. The Lu(1)–C(21) and Lu(1)–C(25) bond distances of 2.406(11) and 2.398(9) Å, respectively, also fall within the expected range for a Lu–CH<sub>2</sub>SiMe<sub>3</sub> linkage.<sup>10</sup>

Treating a toluene solution of **1** with 2 equiv of pyridine at room temperature resulted in C–H bond activation at the ortho

position of one of the pyridine ligands, with concomitant elimination of SiMe<sub>4</sub>, to afford the corresponding η<sup>2</sup>-pyridyl complex (C<sub>5</sub>Me<sub>5</sub>)Lu[η<sup>2</sup>-(N,C)-NC<sub>5</sub>H<sub>4</sub>](CH<sub>2</sub>SiMe<sub>3</sub>)(NC<sub>5</sub>H<sub>5</sub>) (**4**) (eq 2). This complex was not isolated due to its instability under dynamic vacuum; however, monitoring by <sup>1</sup>H NMR spectroscopy revealed that complex **4** was generated in 64% yield (based on internal standard). The moderate yield is due to the presence of some unreacted starting material in the reaction mixture. Complex **4** slowly decomposes at room temperature, with total decomposition and the formation of intractable materials occurring after ~2 days. Most prominent in the <sup>1</sup>H NMR spectrum of **4** are four distinct multiplets at δ 8.47, 7.95, 7.16, and 6.72 ppm, corresponding to the η<sup>2</sup>-(N,C)-pyridyl protons. The η<sup>1</sup>-pyridine ligand resonances are observed at δ 8.56, 6.68, and 6.95 ppm for the ortho, meta, and para protons, respectively.



This is a rare example of pyridine metalation at a neutral lanthanide metal center in the absence of a metallocene framework. It is interesting that the observed pyridine C–H activation occurs in a half-metallocene environment and in the presence of THF, which is a coordination environment quite different from the known bent metallocene (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ln–R (R = H, alkyl) systems.<sup>1a,3</sup> Additionally, in contrast to the chemistry observed with (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>An(CH<sub>3</sub>)<sub>2</sub> (An = Th, U),<sup>4–6</sup> reaction of complex **1** with 2 equiv of either 2-picoline, 2-picoline *N*-oxide, or pyridine *N*-oxide leads to intractable materials. Presumably, this difference in reactivity is a reflection of the electronically and coordinatively more unsaturated monopen-tamethylcyclopentadienyl lutetium metal center compared to the bent metallocene actinide systems.<sup>8e</sup>

Due to the thermal sensitivity of complexes **2–4**, low-temperature <sup>13</sup>C{<sup>1</sup>H} NMR studies were performed and assignment of the chemical shifts was confirmed through the use of DEPT-135 and 2D-COSY experiments. The <sup>13</sup>C{<sup>1</sup>H} NMR resonances for **4** are comparable to the η<sup>2</sup>-(N,C)-pyridyl ligand resonances reported for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Lu[η<sup>2</sup>-(N,C)-NC<sub>5</sub>H<sub>4</sub>], with the exception of a significant upfield shift for the C–H activated quaternary carbon of complex **4** observable at δ 115.66 ppm as compared to δ 234.26 ppm in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Lu[η<sup>2</sup>-(N,C)-NC<sub>5</sub>H<sub>4</sub>], which indicates a more electron-rich lutetium metal center in complex **4**.

The η<sup>2</sup>-(N,C)-pyridyl binding mode to the lutetium center in **4** was unambiguously confirmed by a single-crystal X-ray diffraction study (Figure 2). Suitable crystals of **4** were grown overnight at –35 °C from a pentane/toluene (5:3) solution of **4**. Complex **4** represents a rare structurally characterized lanthanide complex supporting an η<sup>2</sup>-(N,C)-pyridyl linkage.<sup>1,3</sup> As observed for **3**, the overall geometry about the metal center is best described as distorted square pyramidal with the C<sub>5</sub>Me<sub>5</sub> unit residing in the apical position and the remaining three ligands residing in the basal plane. Two pyridine ligands are

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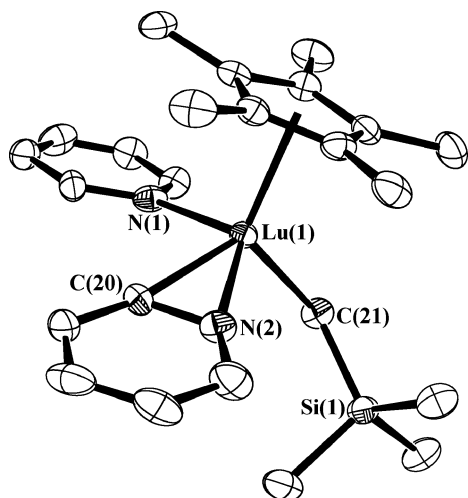
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(10) For example, see the following: (a) (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>LuCH<sub>2</sub>SiMe<sub>3</sub>·THF, Lu–C = 2.376(17) Å; Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194–1200. (b) [Lu(μ-Cl){2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Lu–C = 2.39(3) Å; Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem.–Eur. J.* **1995**, *1*, 343–350. (c) [2-{(2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CMe}-6-{(2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NCMe<sub>2</sub>}C<sub>5</sub>H<sub>3</sub>N-Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Lu–C = 2.329(6), 2.349(6) Å; Cameron, T. M.; Gordon, J. C.; Michalczyk, R.; Scott, B. L. *Chem. Commun.* **2003**, 2282–2283.



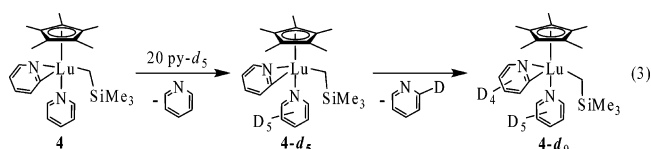
**Figure 2.** Molecular structure of **4** with thermal ellipsoids at the 33% probability level. Selected bond distances (Å) and angles (deg): Lu(1)–C<sub>5</sub>Me<sub>5</sub>(cent), 1.939(9); Lu(1)–N(1), 2.396(8); Lu(1)–N(2), 2.270(6); Lu(1)–C(20), 2.340(8); Lu(1)–C(21), 2.379(9); N(2)–C(20), 1.356(13); Lu(1)–C(21)–Si(1), 119.4(4), N(2)–Lu(1)–C(20), 34.2(3); C(21)–Lu(1)–C(20), 120.0(3); C(21)–Lu(1)–N(1), 92.4(3).

bound to the lutetium center, one in a dative  $\eta^1$ -fashion and the other in an  $\eta^2$ -(N,C) coordination mode. The  $\eta^2$ -pyridyl unit has a Lu(1)–N(2) distance of 2.270(6) Å, which is significantly shorter than the  $\eta^1$ -pyridine Lu(1)–N(1) distance of 2.396(8) Å. The Lu(1)–N(1) distance in **4** is shorter than the analogous distance in **3** and in previously reported  $\eta^1$ -pyridine lutetium complexes.<sup>7,9</sup> The pyridyl N(2)–C(20) bond distance of 1.356(13) Å falls within the range (1.25–1.47 Å) of N–C distances previously reported for other structurally characterized  $\eta^2$ -(N,C)-pyridyl complexes.<sup>1,2,6</sup>

The formation of **4** likely occurs through a  $\sigma$ -bond metathesis mechanism in a fashion similar to that observed for other electropositive early transition metal,<sup>1a,b</sup> lanthanide, and actinide complexes. That is, pyridine initially coordinates in a  $\eta^1$ -fashion to the lutetium metal center in complex **1** (yielding **2**), followed by intramolecular activation of the ortho C–H bond on the pyridine to give the cyclometalated  $\eta^2$ -pyridyl product **4** and SiMe<sub>4</sub> (eq 2). Accordingly, reaction of **1** with pyridine-*d*<sub>5</sub> in toluene-*d*<sub>8</sub> initially produced the bright yellow (C<sub>5</sub>Me<sub>5</sub>)Lu(NC<sub>5</sub>D<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (**2-d**<sub>10</sub>), as determined using <sup>1</sup>H NMR spectroscopy. Over the course of 7 days at ambient temperature, the reaction mixture darkened to a brownish-orange color and resonances consistent with the formation of (C<sub>5</sub>Me<sub>5</sub>)Lu[ $\eta^2$ -(N,C)-NC<sub>5</sub>D<sub>4</sub>](CH<sub>2</sub>SiMe<sub>3</sub>)(NC<sub>5</sub>D<sub>5</sub>) (**4-d**<sub>9</sub>) were apparent in the <sup>1</sup>H NMR spectrum. The most diagnostic feature highlighting this conversion is a 1:1:1 triplet at  $\delta$  –0.02 ppm (<sup>2</sup>J<sub>HD</sub> = 2.0 Hz) corresponding to SiMe<sub>3</sub>CH<sub>2</sub>D as the eliminated product. The same reaction with pyridine-*d*<sub>5</sub> was performed in protio toluene and monitored using <sup>2</sup>H NMR. After standing at room temperature for 23 h, a 1:2:1 triplet at  $\delta$  0.21 ppm (<sup>2</sup>J<sub>HD</sub> = 2.0 Hz) again assignable to SiMe<sub>3</sub>CH<sub>2</sub>D was observed. The deuterium labeling studies are consistent with the mechanism outlined in eq 2 for the C–H activation chemistry.

Complex **4** undergoes pyridyl ligand exchange upon addition of pyridine-*d*<sub>5</sub>. As shown in eq 3, addition of 20 equiv of pyridine-*d*<sub>5</sub> to **4** resulted in the loss of pyridine and formation of **4-d**<sub>9</sub> and pyridine-2-*d*<sub>1</sub> (at low conversions),<sup>11</sup> implying the

intermediacy of (C<sub>5</sub>Me<sub>5</sub>)Lu[ $\eta^2$ -(N,C)-NC<sub>5</sub>H<sub>4</sub>](CH<sub>2</sub>SiMe<sub>3</sub>)(NC<sub>5</sub>D<sub>5</sub>) (**4-d**<sub>5</sub>) and suggesting that the pyridyl ligand exchange also proceeds by way of the  $\sigma$ -bond metathesis mechanism outlined in eq 2. Similar observations have been reported for related scandium chemistry with (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sc[ $\eta^2$ -(N,C)-NC<sub>5</sub>H<sub>4</sub>] and pyridine-*d*<sub>5</sub>, which afforded (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sc[ $\eta^2$ -(N,C)-NC<sub>5</sub>D<sub>4</sub>] and pyridine-*d*<sub>1</sub>.<sup>1a</sup> Notably, no deuterium incorporation into the methyl groups of the C<sub>5</sub>Me<sub>5</sub> ligand was observed in any of the labeling studies, indicating that a “tuck-in” complex, ( $\eta^1, \eta^5$ -CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)(NC<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(THF), is not an intermediate in the formation of **4** or the pyridyl ligand exchange chemistry.<sup>12</sup>



### Concluding Remarks

In summary, we have demonstrated that pyridine can be metalated by the mono-ring lutetium system (C<sub>5</sub>Me<sub>5</sub>)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (**1**) to yield the corresponding  $\eta^2$ -(N,C)-pyridyl complex. C–H activation chemistry at lanthanide metal centers has been conventionally supported by bis(cyclopentadienyl) ligand frameworks. However, the present work shows that the electronically unsaturated and sterically more open monopentamethylcyclopentadienyl can also serve as a useful platform for productive  $\sigma$ -bond metathesis chemistry and the elaboration of pyridine ring systems.

### Experimental Section

**Methods and Materials.** Reactions and manipulations were performed at 21 °C in a recirculating MBraun 150 B-G atmosphere drybox (N<sub>2</sub>) or using standard Schlenk techniques. Glassware was dried at 150 °C before use. NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Chemical shifts were referenced to the protio solvent impurity in benzene-*d*<sub>6</sub> at  $\delta$  7.15 ppm or toluene-*d*<sub>8</sub> at  $\delta$  2.09 ppm (<sup>1</sup>H NMR) and 20.4 ppm (<sup>13</sup>C-{<sup>1</sup>H} NMR). <sup>1</sup>H and <sup>13</sup>C NMR assignments were confirmed through the use of DEPT-135 and two-dimensional <sup>13</sup>C{<sup>1</sup>H}-<sup>1</sup>H NMR experiments. All <sup>2</sup>H NMR spectra were referenced to external toluene-*d*<sub>8</sub> at  $\delta$  2.09 (<sup>1</sup>H).

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Anhydrous toluene (Aldrich), hexanes (Aldrich), tetrahydrofuran (Aldrich), pyridine (Aldrich), pyridine-*d*<sub>1</sub> (CDN Isotopes), pyridine-*d*<sub>5</sub> (Aldrich), benzene-*d*<sub>6</sub> (Aldrich), and toluene-*d*<sub>8</sub> (Cambridge Isotope Laboratories) were passed through a column of activated alumina under nitrogen and stored over 4 Å activated molecular sieves prior to use. Ferrocene (Acros) was purified by recrystallization from toluene at –35 °C. Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub><sup>13</sup> and (C<sub>5</sub>Me<sub>5</sub>)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (**1**) were prepared according to literature procedures.

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(13) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690–4700.

(11) Pyridine-2-*d*<sub>1</sub>: <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 298 K, 300 MHz)  $\delta$  8.50 (m, 1H, ortho H), 7.07 (m, 1H, para H), 6.74 (m, 2H, meta H); <sup>2</sup>H NMR (toluene, 298 K, 300 MHz)  $\delta$  8.69 (br s).

**Synthesis of  $(C_5Me_5)Lu(NC_5H_5)_2(CH_2SiMe_3)_2(THF)$  (**2**).** This compound was not isolable, as loss of the THF occurred upon removal of the solvent under reduced pressure. Complex **2** was generated by charging a 20 mL scintillation vial with **1** (0.024 g, 0.043 mmol), toluene- $d_8$  (0.4 mL), and pyridine (7.1 mg, 7.3  $\mu$ L, 0.98 g/mL, 0.091 mmol). The reaction mixture immediately turned bright yellow in color upon addition of pyridine. After 1 min of standing at ambient temperature, a toluene- $d_8$  solution (0.4 mL) of ferrocene (0.008 g, 0.043 mmol) was added as an internal standard and the resulting reaction mixture was loaded into a NMR tube. A  $^1H$  NMR spectrum was collected 12 min after addition of pyridine to **1**, and the yield of **2** was determined as >95%. The following NMR data are reported without added ferrocene.  $^1H$  NMR (toluene- $d_8$ , 298 K):  $\delta$  8.50 (m, 4H, ortho H), 7.03 (m, 2H, para H), 6.74 (m, 4H, meta H), 3.55 (m, 4H,  $\alpha$  THF H), 1.88 (s, 15H,  $C_5Me_5$ ), 1.48 (m, 4H,  $\beta$  THF H), 0.14 (s, 18H,  $CH_2SiMe_3$ ), -0.75 (s, 4H,  $CH_2SiMe_3$ ).  $^1H$  NMR (toluene- $d_8$ , 243 K):  $\delta$  8.75 (m, 4H, ortho H), 6.88 (m, 2H, para H), 6.64 (m, 4H, meta H), 3.56 (m, 4H,  $\alpha$  THF H), 1.81 (s, 15H,  $C_5Me_5$ ), 1.42 (m, 4H,  $\beta$  THF H), 0.21 (s, 18H,  $CH_2SiMe_3$ ), -0.71 (s, 4H,  $CH_2SiMe_3$ ).  $^{13}C\{^1H\}$  NMR (toluene- $d_8$ , 243 K):  $\delta$  150.46 (s, ortho C), 137.54 (s, para C), 123.70 (s, meta C), 115.83 (s,  $C_5Me_5$ ), 67.73 (s,  $\alpha$  THF C), 36.57 (s,  $CH_2SiMe_3$ ), 25.63 (s,  $\beta$  THF C), 11.70 (s,  $C_5Me_5$ ), 5.03 (s,  $CH_2SiMe_3$ ).

**Synthesis of  $(C_5Me_5)Lu(NC_5H_5)_2(CH_2SiMe_3)_2$  (**3**).** A 50 mL sidearm flask equipped with a stir bar was charged with **1** (0.394 g, 0.71 mmol) and hexanes (20 mL). To the clear, colorless solution was added dropwise pyridine (0.12 g, 0.12 mL, 0.98 g/mL, 1.49 mmol) with stirring. The reaction mixture immediately turned bright yellow in color and was stirred at ambient temperature for 1 min. The volatiles were removed under reduced pressure to give **3** as a pale yellow powder (0.334 g, 0.52 mmol, 73%). Crystals suitable for X-ray diffraction analysis were obtained overnight from a concentrated hexanes solution at -35 °C.  $^1H$  NMR (benzene- $d_6$ , 298 K):  $\delta$  8.28 (m, 4H, ortho H), 6.83 (m, 2H, para H), 6.56 (m, 4H, meta H), 1.96 (s, 15H,  $C_5Me_5$ ), 0.25 (s, 18H,  $CH_2SiMe_3$ ), -0.63 (s, 4H,  $CH_2SiMe_3$ ).  $^1H$  NMR (toluene- $d_8$ , 298 K):  $\delta$  8.24 (m, 4H, ortho H), 6.85 (m, 2H, para H), 6.58 (m, 4H, meta H), 1.96 (s, 15H,  $C_5Me_5$ ), 0.22 (s, 18H,  $CH_2SiMe_3$ ), -0.67 (s, 4H,  $CH_2SiMe_3$ ).  $^1H$  NMR (toluene- $d_8$ , 248 K):  $\delta$  8.38 (m, 4H, ortho H), 6.77 (m, 2H, para H), 6.51 (m, 4H, meta H), 1.92 (s, 15H,  $C_5Me_5$ ), 0.26 (s, 18H,  $CH_2SiMe_3$ ), -0.65 (s, 4H,  $CH_2SiMe_3$ ).  $^{13}C\{^1H\}$  NMR (toluene- $d_8$ , 248 K):  $\delta$  148.82 (s, ortho C), 138.82 (s, para C), 124.32 (s, meta C), 116.52 (s,  $C_5Me_5$ ), 38.70 (s,  $CH_2SiMe_3$ ), 11.46 (s,  $C_5Me_5$ ), 4.79 (s,  $CH_2SiMe_3$ ).

**Synthesis of  $(C_5Me_5)Lu[\eta^2-(N,C)-NC_5H_4](CH_2SiMe_3)(NC_5H_5)$  (**4**).** This compound was not isolable, as decomposition occurred upon removal of the solvent under reduced pressure. Complex **4** was generated by charging a 20 mL scintillation vial with **1** (0.036 g, 0.065 mmol) and toluene- $d_8$  (0.4 mL). To the clear, colorless solution was added pyridine (11 mg, 11  $\mu$ L, 0.98 g/mL, 0.14 mmol) by syringe. The reaction mixture immediately turned bright yellow in color. After 1 min of standing at ambient temperature, a toluene- $d_8$  solution (0.4 mL) of ferrocene (0.012 g, 0.065 mmol) was added as an internal standard, and the resulting reaction mixture was loaded into an NMR tube. Over a period of 21 h, the reaction mixture turned dark orange in color and the yield of **4** was determined as 64%. The following NMR data are reported without added ferrocene.  $^1H$  NMR (toluene- $d_8$ , 298 K):  $\delta$  8.56 (br s, 2H, ortho H), 8.47 (dt, 1H, 5.2 Hz, 1.4 Hz, Ar H), 7.95 (dt, 1H, 7.4 Hz, 1.4 Hz, Ar H), 7.16 (td, 1H, 7.4 Hz, 1.4 Hz, Ar H), 6.95 (br m, 1H, para H), 6.72 (ddd, 1H, 7.4 Hz, 5.2 Hz, 1.4 Hz, Ar H), 6.68 (br m, 2H, meta H), 1.92 (s, 15H,  $C_5Me_5$ ), -0.07 (s, 9H,  $CH_2SiMe_3$ ), -0.69 (s, 2H,  $CH_2SiMe_3$ ).  $^1H$  NMR (toluene- $d_8$ , 248 K):  $\delta$  8.56 (m, 2H, ortho H), 8.45 (m, 1H, Ar H), 8.01 (m, 1H, Ar H), 7.16 (m, 1H, Ar H), 6.84 (m, 1H, para H), 6.69 (m, 1H, Ar H), 6.59 (m, 2H, meta H), 1.95 (s, 15H,  $C_5Me_5$ ), 0.02 (s, 9H,  $CH_2$ -

$SiMe_3$ ), -0.72 (s, 2H,  $CH_2SiMe_3$ ).  $^{13}C\{^1H\}$  NMR (toluene- $d_8$ , 248 K):  $\delta$  149.88 (s, ortho C), 145.26 (s, Ar H), 137.72 (s, para C), 132.96 (s, Ar C), 131.62 (s, Ar C), 123.81 (s, meta C), 121.39 (s, Ar C), 115.66 (s, quat Ar C), 114.98 (s,  $C_5Me_5$ ), 36.62 (s,  $CH_2SiMe_3$ ), 11.22 (s,  $C_5Me_5$ ), 4.14 ( $CH_2SiMe_3$ ).

X-ray quality crystals of **4** were obtained by charging a 20 mL scintillation vial equipped with a stir bar with **1** (0.214 g, 0.42 mmol), pentane (5 mL), and toluene (3 mL). To the clear, colorless solution was added pyridine (0.07 g, 0.07 mL, 0.98 g/mL, 0.88 mmol) by syringe. The reaction mixture immediately turned bright yellow in color and was stirred at ambient temperature for 5 min and then allowed to stand for 21 h. After this time the reaction vial was placed in a -35 °C freezer, and orange block-shaped crystals of **4** suitable for X-ray analysis were grown overnight.

**Reaction of Complex **1** with Pyridine- $d_5$  in Toluene- $d_8$ .** An NMR tube was charged with **1** (0.019 g, 0.034 mmol), pyridine- $d_5$  (6.0 mg, 5.7  $\mu$ L, 1.1 g/mL, 0.072 mmol), and toluene- $d_8$  (0.5 mL). The reaction mixture immediately turned bright yellow in color. After 30 min at ambient temperature, the  $^1H$  NMR spectrum was recorded and displayed resonances consistent with the formation of the pyridine complex  $(C_5Me_5)Lu(CH_2SiMe_3)_2(NC_5D_5)_2(THF)$  (**2-d<sub>10</sub>**).  $^1H$  NMR (298 K):  $\delta$  3.55 (m, 4H,  $\alpha$  THF H), 1.94 (s, 15H,  $C_5Me_5$ ), 1.45 (m, 4H,  $\beta$  THF H), 0.21 (s, 18H,  $CH_2SiMe_3$ ), -0.69 (s, 4H,  $CH_2SiMe_3$ ). Upon standing at ambient temperature, the reaction mixture darkened to a brownish-orange color and resonances consistent with the formation of  $SiMe_3CH_2D$  were apparent after 1 day.  $^1H$  NMR (298 K):  $\delta$  0.00 (s,  $SiMe_3CH_2D$ ), -0.02 (t, 2.0 Hz,  $SiMe_3CH_2D$ ). Complete conversion to the  $\eta^2$ -pyridyl complex  $(C_5Me_5)Lu[\eta^2-(N,C)-NC_5D_4](CH_2SiMe_3)(NC_5D_5)$  (**4-d<sub>9</sub>**) was not observed even after 11 days at ambient temperature, due to the instability of **4-d<sub>9</sub>**.  $^1H$  NMR of **4-d<sub>9</sub>** (toluene- $d_8$ , 298 K):  $\delta$  1.90 (s, 15H,  $C_5Me_5$ ), -0.07 (s, 9H,  $CH_2SiMe_3$ ), -0.71 (s, 2H,  $CH_2SiMe_3$ ).

**Reaction of Complex **1** with Pyridine- $d_5$  in Toluene.** An NMR tube was charged with **1** (0.019 g, 0.034 mmol), pyridine- $d_5$  (6.0 mg, 5.7  $\mu$ L, 1.1 g/mL, 0.072 mmol), and toluene (0.5 mL). The reaction mixture immediately turned bright yellow in color. Upon standing at ambient temperature, the reaction mixture darkened to a brownish-orange color and  $^2H$  NMR resonances consistent with the formation of  $SiMe_3CH_2D$  were apparent after 1 day.  $^2H$  NMR (298 K):  $\delta$  0.21 (t, 1D, 2.0 Hz,  $SiMe_3CH_2D$ ).

**Reaction of Complex **4** with Pyridine- $d_5$  in Toluene- $d_8$ .** An NMR tube was charged with **1** (0.020 g, 0.036 mmol), pyridine (5.9 mg, 6  $\mu$ L, 0.98 g/mL, 0.075 mmol), and toluene- $d_8$  (0.5 mL). The reaction mixture was allowed to stand at ambient temperature for 21 h to generate complex **4**, and then pyridine- $d_5$  (61 mg, 58  $\mu$ L, 1.1 g/mL, 0.72 mmol) was added by syringe. Approximately 10 min after the addition of pyridine- $d_5$ , resonances consistent with the formation of pyridine-2- $d_1$ , pyridine, and  $(C_5Me_5)Lu[\eta^2-(N,C)-NC_5D_5](CH_2SiMe_3)(NC_5D_5)$  (**4-d<sub>9</sub>**) were evident.  $^1H$  NMR of **4-d<sub>9</sub>** (toluene- $d_8$ , 298 K):  $\delta$  1.90 (s, 15H,  $C_5Me_5$ ), -0.07 (s, 9H,  $CH_2SiMe_3$ ), -0.71 (s, 2H,  $CH_2SiMe_3$ ).

**Crystallographic Details for  $(C_5Me_5)Lu(NC_5H_5)_2(CH_2SiMe_3)_2$  (**3**).** A yellow crystal of **3** was mounted from Paratone N oil (Hampton Research) onto a glass fiber under argon gas flow and placed on a Bruker P4/CCD diffractometer, equipped with a Bruker LT-2 temperature device. A hemisphere of data was collected using  $\varphi$  scans, with 30 s frame exposures, and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.<sup>14</sup> Frame integration and final cell parameter calculations were carried out using SAINT software.<sup>15</sup> The data were corrected for absorption using the SADABS program.<sup>16</sup> Decay of reflection data was monitored by analysis of redundant frames.

(14) SMART-NT 4; Bruker AXS, Inc.: Madison, WI 53719, 1996.

(15) SAINT-NT 5.050; Bruker AXS, Inc.: Madison, WI 53719, 1998.

(16) Sheldrick, G. SADABS, first release; University of Göttingen: Germany.

The structure was solved using direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares procedures. One of the  $C_5Me_5$  ligands, C29 to C38, was disordered and subsequently refined as two half-occupancy  $C_5Me_5$  groups (C29 to C38 and C29' to C38'). Each  $C_5Me_5$  was constrained to be rigid with fixed C–C bond distances. In addition, several methyl groups and one pyridine carbon atom were disordered and refined anisotropically as two half-occupancy positions (C24/C24', C26/C26', C27/C27', C46/C46', and C54/C54'). The anisotropic temperature factors were constrained to be equivalent on corresponding disordered atoms. Hydrogen atom positions were not included on any of the disordered positions. The absorption coefficient was  $3.214 \text{ mm}^{-1}$ . The least-squares refinement converged normally with residuals of  $R1 = 0.0705$  ( $I > 2(I)$ ),  $wR2 = 0.1598$ , and  $GOF = 1.033$  ( $F^2$ );  $C_{28}H_{47}N_2LuSi_2$  (642.82 g/mol), space group  $P2_1/n$ , monoclinic  $a = 16.225(3) \text{ \AA}$ ,  $b = 11.999(3) \text{ \AA}$ ,  $c = 32.866(6) \text{ \AA}$ ,  $\beta = 97.654(4)^\circ$ ,  $V = 6342(2) \text{ \AA}^3$ ,  $Z = 8$ ,  $F(000) = 2888$ ,  $\rho_{\text{calcd}} = 1.491 \text{ g cm}^{-3}$ . Structure solution, refinement, and creation of publication materials were performed using SHELXTL.<sup>17</sup>

**Crystallographic Details for  $(C_5Me_5)Lu[\eta^2$ -(N,C)-NC $_5$ H $_5$ ]- $(CH_2SiMe_3)(NC_5H_5)$  (**4**).** A dark orange crystal of **4** was mounted from Paratone N oil (Hampton Research) onto a glass fiber under argon gas flow and placed on a Bruker P4/CCD diffractometer, equipped with a Bruker LT-2 temperature device. A hemisphere of data was collected using  $\varphi$  scans, with 30 s frame exposures, and  $0.3^\circ$  frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.<sup>14</sup> Frame integra-

tion and final cell parameter calculations were carried out using SAINT software.<sup>15</sup> The data were corrected for absorption using the SADABS program.<sup>16</sup> Decay of reflection data was monitored by analysis of redundant frames. The structure was solved using Patterson techniques, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions. The absorption coefficient was  $3.994 \text{ mm}^{-1}$ . The least-squares refinement converged normally with residuals of  $R1 = 0.0413$  ( $I > 2(I)$ ),  $wR2 = 0.0957$ , and  $GOF = 1.034$  ( $F^2$ );  $C_{24}H_{35}N_2LuSi$  (554.60 g/mol), space group  $P2_1$ , monoclinic  $a = 10.734(3) \text{ \AA}$ ,  $b = 7.955(2) \text{ \AA}$ ,  $c = 15.068(5) \text{ \AA}$ ,  $\beta = 102.850(4)^\circ$ ,  $V = 1254.4(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $F(000) = 556$ ,  $\rho_{\text{calcd}} = 1.468 \text{ g cm}^{-3}$ . Structure solution, refinement, and creation of publication materials were performed using SHELXTL.<sup>17</sup>

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**Supporting Information Available:**  $^1\text{H}$  NMR spectra of compounds **2**, **3**, and **4** and X-ray crystallographic data for **3** and **4** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) SHELXTL Version 5.10; Bruker AXS, Inc.: Madison, WI 53719, 1997.