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Synthesis, Characterization, and Reactivity of the Thermally Stable Lutetium Tris(alkyl) Complex (^{t}Bu$_2$bpy)Lu(CH$_2$SiMe$_3$)$_3$

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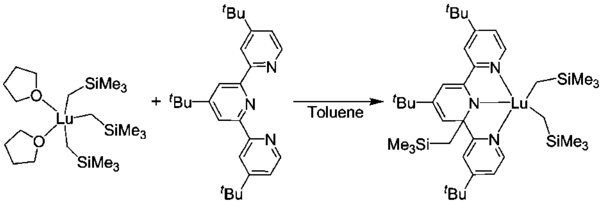
4,4′-Di-*tert*-butyl-2,2′-bipyridyl (^{t}Bu$_2$bpy) stabilizes the thermally sensitive [Lu(CH$_2$SiMe$_3$)$_3$] unit, giving the isolable lutetium(III) (trimethylsilyl)methyl complex (^{t}Bu$_2$bpy)Lu(CH$_2$SiMe$_3$)$_3$ (**4**). This tris(alkyl) complex does not undergo alkane elimination, and it readily reacts with Ph$_3$COH, H$_2$N-2,6-^{i}Pr$_2$-C$_6$H$_3$, H$_2$N-2,4,6-^{t}Bu$_3$-C$_6$H$_2$, and *N*,*N*′-dicyclohexylcarbodiimide (DCHCDI) to afford a variety of Lu(III) tris(alkoxide), tris(amide), mono(amide) bis(alkyl), and amidinate bis(alkyl) compounds. Reaction of the amide bis(alkyl) complex (^{t}Bu$_2$bpy)Lu(NH-2,4,6-^{t}Bu$_3$-C$_6$H$_2$)(CH$_2$SiMe$_3$)$_2$ (**7**) with triphenylphosphine oxide gives (Ph$_3$P=O)$_2$Lu(NH-2,4,6-^{t}Bu$_3$-C$_6$H$_2$)(CH$_2$SiMe$_3$)$_2$ (**9**), showing that the bidentate ^{t}Bu$_2$bpy ligand can be displaced.

Introduction

Terminal alkylidene (M=CR$_2$), imido (M=NR), phosphinidene (M=PR), and oxo (M=O) complexes are pervasive in transition-metal chemistry.[1] Although there have been reports of lanthanide systems containing bridging or capping imido[2] and oxo[3] ligands, as well as numerous lanthanide carbene complexes,[4] terminal oxo, phosphinidene, and alkylidene functional groups are noticeably absent for the lanthanide elements.[5] Recently, however, the lutetium imido complexes LuCl$_2$(ImN$^{\text{Dipp}}$)(THF)$_3$ and (C$_8$H$_8$)Lu(ImN$^{\text{Dipp}}$)(THF)$_2$ (where ImN$^{\text{Dipp}}$ = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imide), were reported by Tamm and co-workers.[6] The overall lack of these species is curious, since the related actinide series displays numerous examples of complexes containing An=N, An=P, and An=O linkages.[1,7]

In our recent efforts to prepare robust lanthanide tris(alkyl) complexes as precursors to alkylidene complexes,[8] we discovered that lutetium(III) alkyl fragments supported by terpyridines are not stable and undergo facile 1,3-alkyl migration, resulting in dearomatization and functionalization of the terpyridine ligand, as illustrated in eq 1.



1 **2** **3** (1)

Although this observation clearly demonstrated that the terpyridine ligand is not an ideal platform for this chemistry, density functional theory calculations suggested that the formation of a lutetium alkylidene functional group is energetically viable from a thermodynamic standpoint.[8] Toward this goal, we now report that 4,4′-di-*tert*-butyl-2,2′-bipyridyl (^{t}Bu$_2$bpy)

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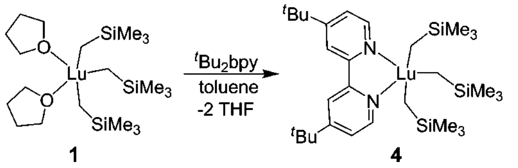
enables the stabilization of the thermally sensitive $[Lu(CH_2SiMe_3)_3]$ unit, giving the isolable lutetium(III) tris(alkyl) complex $(^tBu_2bpy)Lu(CH_2SiMe_3)_3$ (**4**). Herein, we describe the preparation, characterization, and chemistry of this new lutetium tris(alkyl) system and its ability to stabilize multiply bonded functional groups.

Results and Discussion

Reaction of $[Lu(CH_2SiMe_3)_3(THF)_2]$ (**1**) with 1 equiv of 4,4′-di-*tert*-butyl-2,2′-bipyridyl ($^tBu_2bpy$) at ambient temperature affords the neutral lutetium tris(alkyl) complex $(^tBu_2bpy)Lu(CH_2SiMe_3)_3$ (**4**) as an orange powder in 83% isolated yield (eq 2).



(2)

Diagnostic ^1H NMR spectroscopic data (benzene-d_6, 23 °C) demonstrate the formation of **4** with resonances centered at δ 9.06, 7.67, and 6.86 ppm for the three pyridyl protons, a singlet at δ 0.96 ppm for the two ^tBu groups on the bipyridyl ligand, and signals at δ 0.31 and -0.08 ppm corresponding to the methyl and methylene protons, respectively, on the three equivalent $-CH_2SiMe_3$ groups. Whereas the THF complex **1** is thermally sensitive, decomposing if not stored below -35 °C,[9] $(^tBu_2bpy)Lu(CH_2SiMe_3)_3$ (**4**) is stable as a solid at room temperature for at least 3 months and for 2 weeks in solution (benzene-d_6). However, the complex does decompose over a 24 h period when heated at 60 °C in benzene-d_6. For comparison purposes, even the recently reported $(^iPr\text{-trisox})Lu(CH_2SiMe_3)_3$ was observed to decompose over a few days at ambient temperature.[10] The neutral lutetium tris(alkyl) system [(12-crown-4)$Lu(CH_2SiMe_3)_3$] has also been noted to have enhanced thermal stability relative to the THF complex **1**.[11] Thus, complex **4** may serve as a complement to the crown ether derivative.

Single crystals of complex **4** suitable for X-ray diffraction analysis were obtained from a concentrated pentane solution at -35 °C. Similar to $[Lu(CH_2SiMe_3)_3(THF)_2]$ (**1**),[12] the molecular structure of **4** reveals a five-coordinate geometry about the lutetium(III) center, which is best described as distorted trigonal bipyramidal with the equatorial plane being defined by two metal-bound (trimethylsilyl)methyl groups and one of the bipyridyl nitrogens (Figure 1). The two $Lu-N_{bpy}$ dative bonds have distances of 2.437(7) and 2.427(7) Å, which are comparable to those reported for other structurally characterized lutetium bipyridyl complexes. For example, $[(C_5Me_5)Lu(NH\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(CH_2SiMe_3)(bpy)]$, $[(C_5Me_5)Lu(NH\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)_2(bpy)]$, $[(C_5Me_5)Lu(C{\equiv}CPh)_2(bpy)(NC_5H_5)]$, $[\{(C_5Me_5)Lu(C{\equiv}CPh)(bpy)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)]$, $[(C_5Me_5)Lu(NH\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)\{OCH(CH_2SiMe_3)(C_{10}H_7N_2)\}]$, and $[(C_5Me_5)Lu\{OC(SiMe_3){=}CH_2\}\{OCH(CH_2SiMe_3)(C_{10}H_7N_2)\}]$ have $Lu-N_{bpy}$ bond distances ranging between 2.360(3) and 2.500(7) Å.[13] The $Lu-CH_2$ distances (Lu(1)−C(19) = 2.369(8) Å, Lu(1)−C(20) = 2.358(9) Å, Lu(1)−C(21) = 2.318(9) Å) and $Lu-CH_2-Si$ angles (Lu(1)−C(19)−Si(2) = 139.5(5)°, Lu(1)−C(21)−Si(1) = 126.1(5)°, Lu(1)−C(20)−Si(3) = 120.8(4)°) are within previously reported ranges of 2.30–2.40 Å and 115–149° typically observed for $Lu-CH_2SiMe_3$ complexes.[8–12,13a,14]

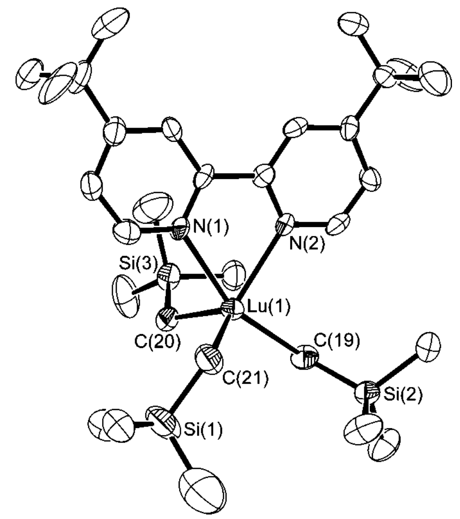


Figure 1. Molecular structure of **4** (left) with thermal ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (deg): Lu(1)−N(1) = 2.437(7), Lu(1)−N(2) = 2.427(7), Lu(1)−C(19) = 2.369(8), Lu(1)−C(20) = 2.358(9), Lu(1)−C(21) = 2.318(9); N(1)−Lu(1)−N(2) = 65.7(2), Lu(1)−C(19)−Si(2) = 139.5(5), Lu(1)−C(20)−Si(3) = 120.8(4), Lu(1)−C(21)−Si(1) = 126.1(5).

The reactivity of the lutetium tris(alkyl) system **4** was probed, and a summary of its behavior is presented in Scheme 1. As evidenced by ^1H NMR spectroscopy, thermolysis of **4** (benzene-d_6, 60 °C, 24 h) results in the formation of $SiMe_4$ and decomposition to intractable materials even in the presence of pyridine, 2,2′-bipyridine, and 2-(diphenylphosphino)-2′-(dimethylamino)biphenyl (to capture any potential $(^tBu_2bpy)Lu({=}CHR)$ species).

The alkyl groups in **4** are susceptible to protonation by amines, as demonstrated by the reaction of **4** with 3 equiv of $H_2N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3$ in toluene to give the tris(amide) complex **5** in 76% isolated yield. No evidence was seen for the formation of any imido-containing lutetium complexes, even at elevated temperatures (toluene-d_8, 90 °C, 24 h). Attempts were made to prepare the corresponding mono- and bis(amide) species $(^tBu_2bpy)Lu(NHAr)(CH_2SiMe_3)_2$ and $(^tBu_2bpy)Lu(NHAr)_2(CH_2SiMe_3)$ (Ar = $2,6\text{-}^iPr_2\text{-}C_6H_3$); however, ^1H NMR spectroscopy showed that the tris(amide) **5** was produced irrespective of the amount of aniline reacted with complex **4**. Similar chemistry was observed between **4** and alcohols, with reaction

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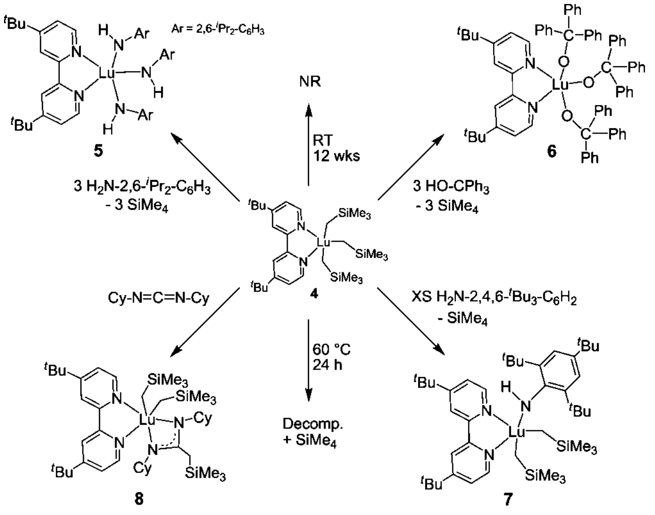
Scheme 1. Reactivity Displayed by the Lu(III) Tris(alkyl) Complex (^{t}Bu$_2$bpy)Lu(CH$_2$SiMe$_3$)$_3$ (4)



of **4** and 3 equiv of Ph$_3$COH affording the tris(alkoxide) derivative **6**.

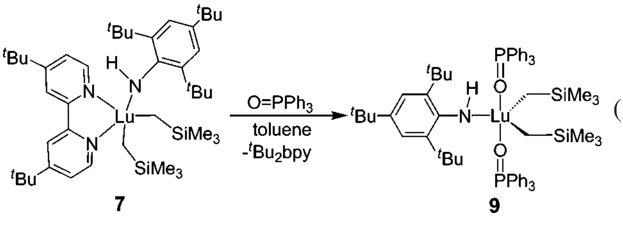
Figure 2 displays the molecular structures for both the tris(amide) and tris(alkoxide) complexes **5** and **6**, respectively, which both feature a lutetium(III) metal center coordinated in a distorted-trigonal-bipyramidal fashion by a bidentate ^{t}Bu$_2$bpy and three amide or alkoxide ligands, respectively. In both complexes, the Lu−N$_{\mathrm{bpy}}$ dative bond distances (**5**, 2.423(4) and 2.444(4) Å; **6**, 2.456(3) and 2.432(3) Å) compare favorably with those observed in the tris(alkyl) complex **4**. The Lu−N$_{\mathrm{anilide}}$ bond distances (2.167(4), 2.207(4), 2.167(4) Å) and Lu−N−C$_{\mathrm{Ar}}$ angles (142.5(4), 145.6(4), 153.5(4)°) in complex **5** are comparable to the Lu−N$_{\mathrm{anilide}}$ interactions reported for the structurally related [(C$_5$Me$_5$)Lu(NH-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CH$_2$SiMe$_3$)(bpy)] (2.22(1) Å, 145.8(9)°), [(C$_5$Me$_5$)Lu(NH-2,6-^{i}Pr$_2$-C$_6$H$_3$)$_2$(bpy)] (2.208(7) Å, 150.9(6)°; 2.209(7) Å, 143.2(5)°), and [(C$_5$Me$_5$)Lu(NH-2,6-^{i}Pr$_2$-C$_6$H$_3$){OCH(CH$_2$SiMe$_3$)(C$_{10}$H$_7$N$_2$)}] (2.238(4) Å, 135.8(3)°).[13]

Similarly, the metrical parameters for the Lu−O interactions in **6** (2.030(2), 2.032(2), 2.059(2) Å) are also in agreement with those found in other crystallographically characterized lutetium alkoxide complexes and can be compared to the average Lu−O distances of 2.044(4), 2.052(5), and 2.077(9) Å found in Lu(O-2,6-^{i}Pr$_2$-C$_6$H$_3$)$_3$(THF)$_2$,[15] Lu(O-2,6-Ph$_2$-C$_6$H$_3$)$_3$,[16] and [(Me$_3$SiCH$_2$)$_2$-Lu(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)$_2$][Li(THF)$_4$](THF)$_2$,[17] respectively. The Lu−O−C$_{\mathrm{Ar}}$ angles are almost linear (164.7(3), 161.1(2), 155.8(2)°) and are typical of those seen in other early-transition-metal, lanthanide, and actinide complexes bearing bulky alkoxide or aryloxide ligands.[18]

The aminolysis chemistry can be controlled by using sterically demanding amide ligands such as H$_2$N-2,4,6-^{t}Bu$_3$-C$_6$H$_2$. Reaction of complex **4** with excess H$_2$N-2,4,6-^{t}Bu$_3$-C$_6$H$_2$ resulted in loss of SiMe$_4$ with concomitant formation of the mono(amide) bis(alkyl) lutetium complex **7** in 84% isolated yield. Most of the lanthanide bis(alkyl) complexes reported to date have been stabilized by multidentate ancillary ligands such as cyclopentadienyls,[13,14c,19] amidinates,[20] bis(oxazolinates),[21] β-diketiminates,[22] amido−phosphines,[14d,g,23] anilido−pyridine−imines,[11] amido−pyridines,[8] and imino−pyrrolides.[14e] As such, complex **7** represents a rare example of a lanthanide bis(alkyl) complex supported by a monodentate anionic ancillary ligand and, to the best of our knowledge, the first example of a lutetium metal center supported by the sterically demanding 2,4,6-tri-*tert*-butylamide ligand. Other examples are limited to the aryloxide-supported lutetium bis(alkyl) ate complex [(Me$_3$SiCH$_2$)$_2$Lu(O-2,6-^{t}Bu$_2$-C$_6$H$_3$)$_2$][Li(THF)$_4$](THF)$_2$ mentioned above,[17] the silanolate-supported bis(alkyl) complexes [(Me$_3$SiCH$_2$)$_2$Ln-{μ,η^2-OSi(O^{t}Bu)$_3$}]$_2$ (Ln = Tb, Lu),[24] and the anilide-supported bis(alkyl) complexes [2,6-^{i}Pr$_2$-C$_6$H$_3$N(SiMe$_3$)]Ln(CH$_2$Si-Me$_3$)$_2$(THF) (Ln = Ho, Lu).[25]

Single crystals of **7** suitable for X-ray diffraction analysis were obtained from a concentrated pentane/toluene solution at −35 °C. The molecular structure of compound **7** is available in Figure 3 and shows that the lutetium metal center is coordinated in a distorted-trigonal-bipyramidal fashion by the bidentate ^{t}Bu$_2$bpy, two alkyl groups, and the bulky amide ligand. Clearly, this geometry seems to be common to all the (^{t}Bu$_2$bpy)LuX$_3$ systems presented in this work and the Lu−N$_{\mathrm{bpy}}$ dative bond distances (2.467(3) and 2.453(3) Å) are in agreement with those observed in the other (^{t}Bu$_2$bpy)LuX$_3$ systems discussed above. The most interesting aspect of the structure is the Lu−N$_{\mathrm{anilide}}$ interaction, with a bond distance of 2.144(3) Å and the nearly linear Lu−N−C$_{\mathrm{Ar}}$ angle of 157.7(2)°, which compare well with those reported for other structurally characterized lutetium aryl amide complexes, including complex **5**.[13] Finally, the metrics associated with the two Lu−CH$_2$SiMe$_3$ fragments (2.345(4), 2.363(4) Å and 116.25(17), 128.68(18)°) are similar to those found in other lutetium bis(alkyl) complexes.[8,14c,d,17,19–25]

Efforts to promote alkane elimination from **7** were unsuccessful. Whereas no reaction was observed upon heating **7** (benzene-d_6, 60 °C) for 24 h, thermolysis for 72 h resulted in the formation of SiMe$_4$ and decomposition, as monitored by ^{1}H NMR spectroscopy. Interestingly, in the presence of Ph$_3$P=O, alkane elimination is also not observed but rather displacement of the bidentate ^{t}Bu$_2$bpy ligand to give complex **9** (eq 3).



(3)

Clearly, this reaction sequence demonstrates the limitations of the ^{t}Bu$_2$bpy as a supporting ligand on lutetium in competition with stronger donor ligands such as Ph$_3$P=O. Although the yield

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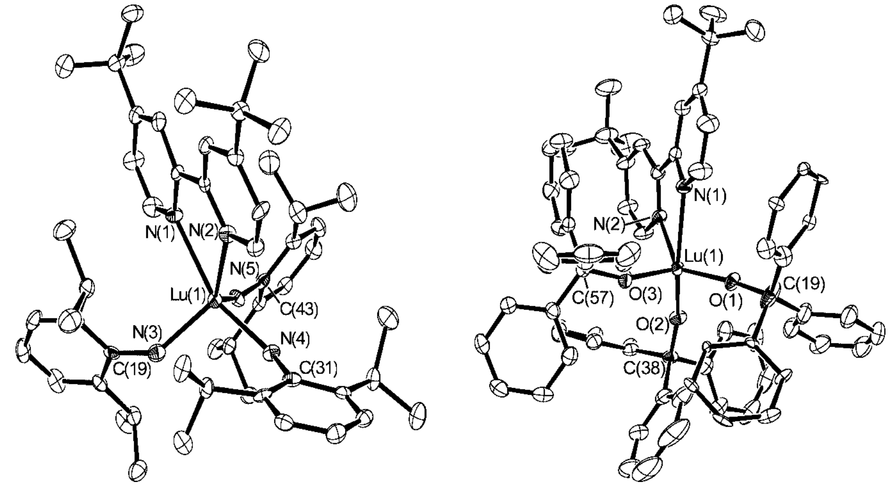

Figure 2. Molecular structures of **5** (left) and **6** (right) with ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (deg) for **5**: Lu(1)−N(1) = 2.423(4), Lu(1)−N(2) = 2.444(4), Lu(1)−N(3) = 2.167(4), Lu(1)−N(4) = 2.207(4), Lu(1)−N(5) = 2.167(4); N(1)−Lu(1)−N(2) = 65.16(14), Lu(1)−N(3)−C(19) = 142.5(4), Lu(1)−N(4)−C(31) = 145.6(4), Lu(1)−N(5)−C(43) = 153.5(4). Selected bond distances (Å) and angles (deg) for **6**: Lu(1)−N(1) = 2.456(3), Lu(1)−N(2) = 2.432(3), Lu(1)−O(1) = 2.030(2), Lu(1)−O(2) = 2.059(2), Lu(1)−O(3) = 2.030(2); N(1)−Lu(1)−N(2) = 65.60(10), Lu(1)−O(1)−C(19) = 164.7(3), Lu(1)−O(2)−C(38) = 161.1(2), Lu(1)−O(3)−C(57) = 155.8(2).

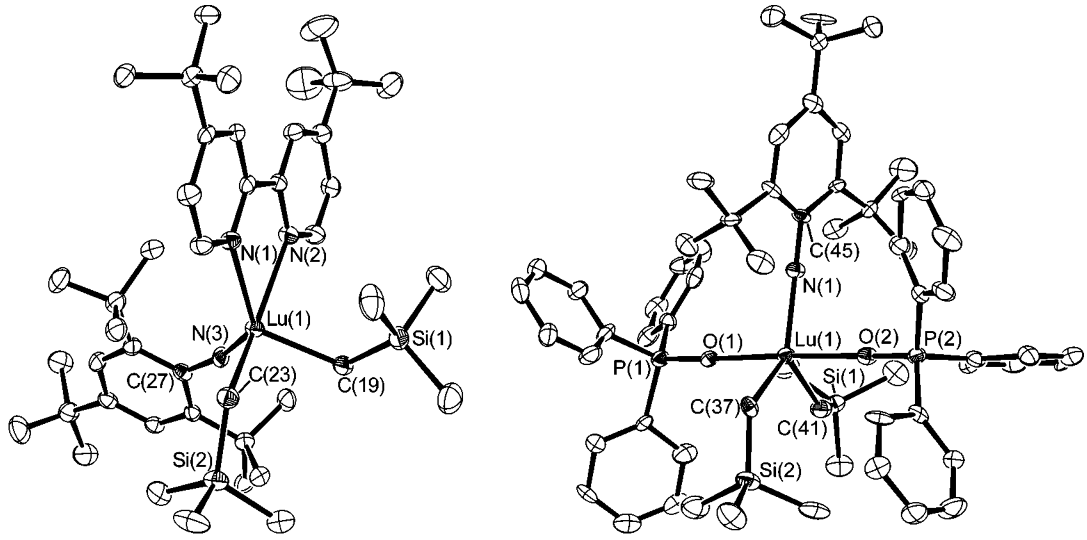

Figure 3. Molecular structures of **7** (left) and **9** (right) with ellipsoids projected at the 50% probability level. Selected bond distances (Å) and angles (deg) for **7**: Lu(1)−N(1) = 2.467(3), Lu(1)−N(2) = 2.453(3), Lu(1)−N(3) = 2.144(3), Lu(1)−C(19) = 2.345(4), Lu(1)−C(23) = 2.363(4); N(1)−Lu(1)−N(2) = 65.12(10), Lu(1)−N(3)−C(27) = 157.7(2), Lu(1)−C(19)−Si(1) = 116.25(17), Lu(1)−C(23)−Si(2) = 128.68(18). Selected bond distances (Å) and angles (deg) for **9**: Lu(1)−O(1) = 2.217(6), Lu(1)−O(2) = 2.239(6), Lu(1)−N(1) = 2.224(7), Lu(1)−C(37) = 2.401(8), Lu(1)−C(41) = 2.346(9), P(1)−O(1) = 1.499(6), P(2)−O(2) = 1.506(6); O(1)−Lu(1)−O(2) = 177.7(2), Lu(1)−O(1)−P(1) = 176.0(4), Lu(1)−O(2)−P(2) = 167.5(4), Lu(1)−N(1)−C(45) = 156.6(6), Lu(1)−C(37)−Si(2) = 125.6(4), Lu(1)−C(41)−Si(1) = 138.4(5).

was not optimized, the formation of **9** was easily apparent from ^{1}H NMR spectroscopy (benzene-d_6, 23 °C), which showed the release of free ^{t}Bu$_2$bpy (δ 9.05, 8.63, 6.93, 1.14 ppm) and the appearance of diagnostic signals centered at δ 7.50 ppm for the two aromatic anilide protons and at δ 4.15 ppm for the N−H (upfield from δ 5.52 ppm for **7**), singlets at δ 1.64 and 1.56 ppm for the ^{t}Bu groups on the anilide ligand, and resonances at δ 0.24 and −0.46 ppm corresponding to the methyl and methylene protons, respectively, on the two $-$CH$_2$SiMe$_3$ groups. The ^{31}P NMR spectrum for **9** shows a peak at δ 33.14 ppm for the two coordinated Ph$_3$P=O ligands. Formation of **9** was confirmed by a single-crystal X-ray diffraction study, and the molecular structure is presented in Figure 3. The metrical parameters for the ligands in the compound are all within expected ranges.

Finally, as Scheme 1 illustrates, complex **4** also participates in insertion chemistry and reacts smoothly with 1 equiv of *N,N′*-dicyclohexylcarbodiimide (DCHCDI) in toluene at room temperature to form the monoinsertion product **8**, which is a rare example of a lutetium amidinate complex.[14g,23] Although a crystal suitable for X-ray diffraction studies could not be obtained, the ^{1}H and ^{13}C{^{1}H} NMR spectra confirm the formation of the amidinate fragment. In addition, similar

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insertion chemistry was recently reported for (amidophosphine)$\mathrm{Lu(CH_2SiMe_3)_2}$ complexes and (*N,N′*)-diisopropylcarbodiimide.[14g]

Conclusion

The 4,4′-di-*tert*-butyl-2,2′-bipyridyl ($^t\mathrm{Bu_2bpy}$) ligand stabilizes the thermally sensitive $[\mathrm{Lu(CH_2SiMe_3)_3}]$ unit, giving the isolable lutetium(III) (trimethylsilyl)methyl complex $(^t\mathrm{Bu_2bpy})\mathrm{Lu(CH_2SiMe_3)_3}$ (**4**), though it is not able to support lutetium complexes containing multiply bonded functional groups. Nevertheless, complex **4** does participate in a variety of protonolysis and insertion reactions, affording Lu(III) tris(alkoxide), tris(amide), mono(amide) bis(alkyl), and amidinate bis(alkyl) compounds. This work forms the basis for exploring complex **4** and the bis(alkyl) derivatives **7** and **8** as starting materials for the synthesis of new organolanthanide derivatives such as cationic alkyl complexes. As such, we intend to extend this chemistry to other lanthanide derivatives and examine their potential as polymerization and hydroamination catalysts.

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 techniques. Glassware was dried at 150 °C before use. ^{1}H, ^{13}C{^{1}H}, DEPT-135, and 2-D ^{13}C{^{1}H}−^{1}H NMR spectra were collected in benzene-d_6 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 NMR) and δ 128.39 ppm (^{13}C{^{1}H} NMR) or external $\mathrm{H_3PO_4}$ (^{31}P NMR). ^{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), pentane (Aldrich), and hexanes (Aldrich) were dried over KH for 24 h, passed through a column of activated alumina, 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. 2,6-Diisopropylaniline (Aldrich) was passed through a column of activated alumina and stored over activated 4 Å molecular sieves prior to use. 4,4′-Di-*tert*-butyl-2,2′-bipyridyl (Aldrich), 2,4,6-tri-*tert*-butylaniline (Aldrich), triphenylmethanol (Aldrich), and triphenylphosphine oxide (Aldrich) were purified by recrystallization from toluene at −35 °C. $[\mathrm{Lu(CH_2SiMe_3)_3(THF)_2}]$ (**1**) was prepared according to the literature procedure.[9b]

Synthesis of $(^t\mathrm{Bu_2bpy})\mathrm{Lu(CH_2SiMe_3)_3}$ (4). A 125-mL side-arm flask equipped with a stir bar was charged with $\mathrm{Lu(CH_2SiMe_3)_3(THF)_2}$ (**1**; 0.469 g, 0.81 mmol) and toluene (30 mL). To the resulting clear, colorless solution was added dropwise a 10 mL toluene solution of $^t\mathrm{Bu_2bpy}$ (0.217 g, 0.81 mmol) with stirring. The reaction mixture immediately turned orange and was stirred for 1 h at ambient temperature. The volatiles were then removed under reduced pressure to give complex **4** as an analytically pure orange powder (0.470 g, 0.67 mmol, 83%). ^{1}H NMR (benzene-d_6, 298 K): δ 9.06 (d, 2H, 5.5 Hz, $\mathrm{C_{Ar}}$ *H*), 7.67 (s, 2H, $\mathrm{C_{Ar}}$ *H*), 6.86 (d, 2H, 5.5 Hz, $\mathrm{C_{Ar}}$ *H*), 0.96 (s, 18H, C*Me*$_3$), 0.31 (s, 27H, Si*Me*$_3$), −0.08 (s, 6H, Lu−C*H*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 165.84 (s, C_{Ar}), 154.47 (s, C_{Ar}), 152.04 (s, C_{Ar}), 123.75 (s, C_{Ar}), 118.15 (s, C_{Ar}), 46.15 (s, Lu−*C*H$_2$), 35.59 (s, *C*Me$_3$), 30.34 (s, C*Me*$_3$), 5.03 (s, Si*Me*$_3$). Anal. Calcd for $\mathrm{C_{30}H_{57}N_2LuSi_3}$ (mol wt 705.01): C, 51.11; H, 8.15; N, 3.97. Found: C, 51.18; H, 8.26; N, 4.08. Mp = 99–100 °C.

Synthesis of $(^t\mathrm{Bu_2bpy})\mathrm{Lu(NH\text{-}2,6\text{-}^{\mathit{i}}Pr_2\text{-}C_6H_3)_3}$ (5). A 20-mL scintillation vial was charged with $(^t\mathrm{Bu_2bpy})\mathrm{Lu(CH_2SiMe_3)_3}$ (**4**; 0.208 g, 0.29 mmol) and hexanes (18 mL). To the resulting orange solution was added dropwise 2,6-diisopropylaniline (0.17 mL, 0.157 g, 0.88 mmol) with stirring. An orange solid immediately precipitated from the reaction solution. The reaction mixture was filtered through a Celite-padded coarse frit to remove the filtrate. The collected orange solid was washed with pentane (3 × 1 mL). Using a clean 125-mL side-arm flask, the frit was placed on top of the empty side-arm flask and THF was used (until washings were colorless) to pass the product through the Celite. The filtrate was collected, and the volatiles were removed under reduced pressure. The resulting oily product was triturated with pentane, and the pentane was removed under reduced pressure to give complex **5** as an analytically pure bright orange powder (0.216 g, 0.22 mmol, 76%). ^{1}H NMR (benzene-d_6, 298 K): δ 8.89 (d, 2H, 5.8 Hz, $\mathrm{C_{Ar}}$ *H*), 7.82 (s, 2H, $\mathrm{C_{Ar}}$ *H*), 7.16 (s, 3H, $\mathrm{C_{Ar}}$ *H*), 7.14 (s, 3H, $\mathrm{C_{Ar}}$ *H*), 6.83 (t, 3H, 7.41 Hz, $\mathrm{C_{Ar}}$ *H*), 6.60 (dd, 2H, 5.8 and 1.7 Hz, $\mathrm{C_{Ar}}$ *H*), 5.07 (s, 3H, N*H*), 3.36 (sep, 6H, 6.6 Hz, C*H*Me$_2$), 1.24 (d, 36H, 6.6 Hz, CH*Me*$_2$), 0.85 (s, 18H, C*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 166.16 (s, quat C_{Ar}), 154.07 (s, quat C_{Ar}), 153.90 (s, quat C_{Ar}), 152.79 (s, C_{Ar}), 134.15 (s, quat C_{Ar}), 124.09 (s, C_{Ar}), 123.45 (s, C_{Ar}), 117.79 (s, C_{Ar}), 115.73 (s, C_{Ar}), 35.55 (s, *C*Me$_3$), 30.73 (s, *C*HMe$_2$), 30.10 (s, C*Me*$_3$), 23.99 (s, CH*Me*$_2$). Anal. Calcd for $\mathrm{C_{54}H_{78}N_5Lu}$ (mol wt 972.20): C, 66.71; H, 8.09; N, 7.20. Found: C, 66.68; H, 8.19; N, 6.97. MS (EI, 70 eV): *m/z* 795 ($\mathrm{M^+ - NH\text{-}2,6\text{-}^{\mathit{i}}Pr_2C_6H_3}$). Mp = 183–184 °C.

Synthesis of $(^t\mathrm{Bu_2bpy})\mathrm{Lu[OC(C_6H_5)_3]}$ (6). A 50-mL side-arm flask equipped with a stir bar was charged with $(^t\mathrm{Bu_2bpy})\mathrm{Lu(CH_2SiMe_3)_3}$ (**4**; 0.172 g, 0.244 mmol) and hexanes (15 mL). To the resulting orange solution was added dropwise a solution (10 mL of toluene and 10 mL of hexanes) of $\mathrm{Ph_3COH}$ (0.190 g, 0.244 mmol) with stirring. The resultant reaction solution turned yellow, and a yellow precipitate was deposited upon stirring overnight. The volatiles were removed under reduced pressure, and the resulting product was triturated with pentane (6 mL). Upon removal of the pentane solution by decantation and drying under reduced pressure, complex **6** was isolated as an analytically pure yellow powder (0.274 g, 0.224 mmol, 92%). ^{1}H NMR (benzene-d_6, 298 K): δ 8.40 (d, 2H, 5.7 Hz, $\mathrm{C_{Ar}}$ *H*), 7.63 (br s, 9H, $\mathrm{C_{Ar}}$ *H*), 7.44 (s, 1H, $\mathrm{C_{Ar}}$ *H*), 7.43 (s, 1H, $\mathrm{C_{Ar}}$ *H*), 6.98 (m, 36H, $\mathrm{C_{Ar}}$ *H*), 6.52 (dd, 2H, 5.7 and 1.7 Hz, $\mathrm{C_{Ar}}$ *H*), 0.89 (s, 18H, C*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 163.95 (s, quat C_{Ar}), 153.69 (s, quat C_{Ar}), 153.10 (s, C_{Ar}), 152.90 (s, quat C_{Ar}), 129.41 (s, C_{Ar}), 128.00 (s, C_{Ar}), 126.22 (s, C_{Ar}), 122.55 (s, C_{Ar}), 117.09 (s, C_{Ar}), 35.17 (s, *C*Me$_3$), 30.26 (s, C*Me*$_3$). Anal. Calcd for $\mathrm{C_{81}H_{83}LuN_2O_3}$ (mol wt 1307.50): C, 74.41; H, 6.40; N, 2.14. Found: C, 74.48; H, 6.83; N, 1.94. Mp = 197–198 °C.

Synthesis of $(^t\mathrm{Bu_2bpy})\mathrm{Lu(NH\text{-}2,4,6\text{-}^{\mathit{t}}Bu_3\text{-}C_6H_2)(CH_2SiMe_3)_2}$ (7). A 50-mL side-arm flask equipped with a stir bar was charged with $(^t\mathrm{Bu_2bpy})\mathrm{Lu(CH_2SiMe_3)_3}$ (**4**; 0.207 g, 0.293 mmol) and toluene (15 mL). To the resulting clear orange solution was added dropwise a 5 mL toluene solution of $\mathrm{H_2N\text{-}2,4,6\text{-}^{\mathit{t}}Bu_3\text{-}C_6H_2}$ (0.069 g, 0.293 mmol) with stirring. The resultant reaction solution gradually turned red overnight. The volatiles were removed under reduced pressure, and the resulting product was triturated with 10 mL of pentane. The pentane solution was removed, and the remaining solids were dried under reduced pressure to give **7** as an analytically pure red powder (0.215 g, 0.245 mmol, 84%). ^{1}H NMR (benzene-d_6, 298 K): δ 9.07 (d, 2H, 5.7 Hz, C_{Ar} *H*), 7.74 (s, 1H, C_{Ar} *H*), 7.73 (s, 1H, C_{Ar} *H*), 7.47 (s, 2H, C_{Ar} *H*), 6.75 (dd, 2H, 5.6 and 1.7 Hz, C_{Ar} *H*), 5.52 (s, 1H, N*H*), 2.10 (s, 18H, C*Me*$_3$), 1.76 (s, 9H, C*Me*$_3$), 0.91 (s, 18H, C*Me*$_3$), 0.27 (s, 18H, CH$_2$Si*Me*$_3$), −0.07 (s, 4H, C*H*$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 165.67 (s, quat C_{Ar}), 154.49 (s, quat C_{Ar}), 153.86 (s, quat C_{Ar}), 152.67 (s, C_{Ar}), 135.01 (s, C_{Ar}), 134.54 (s, quat C_{Ar}), 123.85 (s, C_{Ar}), 122.23 (s, C_{Ar}), 118.12 (s, C_{Ar}), 41.47 (s, *C*H$_2$SiMe$_3$), 35.80 (s, *C*Me$_3$), 35.52 (s, *C*Me$_3$), 34.86 (s, *C*Me$_3$), 32.73 (s, C*Me*$_3$), 32.19 (s, C*Me*$_3$), 30.18 (s, C*Me*$_3$), 4.91 (s, CH$_2$Si*Me*$_3$). Anal. Calcd for $C_{44}H_{76}N_3LuSi_2$ (mol wt 878.23): C, 60.17; H, 8.72; N, 4.78. Found: C, 60.23; H, 8.52; N, 4.36. Mp = 161–162 °C.

Synthesis of (^{t}Bu$_2$bpy)Lu[CyNC(CH$_2$SiMe$_3$)NCy](CH$_2$SiMe$_3$)$_2$ (8). A 125-mL side-arm flask equipped with a stir bar was charged with (^{t}Bu$_2$bpy)Lu(CH$_2$SiMe$_3$)$_3$ (**4**; 0.302 g, 0.428 mmol) and toluene (30 mL). To the resulting clear orange solution was added dropwise a 10 mL toluene solution of CyN=C=NCy (0.088 g, 0.428 mmol) with stirring. The resultant reaction solution gradually turned dark red overnight. The volatiles were removed under reduced pressure, the resulting oily product was redissolved in pentane, and the solvent was removed under reduced pressure to give **8** as an analytically pure orange powder (0.202 g, 0.221 mmol, 52%). ^{1}H NMR (benzene-d_6, 298 K): δ 9.34 (d, 2H, 5.4 Hz, C_{Ar} *H*), 7.94 (s, 1H, C_{Ar} *H*), 7.93 (s, 1H, C_{Ar} *H*), 6.97 (dd, 2H, 5.7 and 1.7 Hz, C_{Ar} *H*), 3.06 (br s, 2H, Cy C*H*), 1.93 (s, 2H, C*H*$_2$SiMe$_3$), 1.77 (br s, 4H, Cy C*H*$_2$), 1.64 (br s, 4H, Cy C*H*$_2$), 1.52 (br s, 1H, Cy C*H*$_2$), 1.48 (br s, 1H, Cy C*H*$_2$), 1.14–1.36 (m, 10H, Cy C*H*$_2$), 0.99 (s, 18H, C*Me*$_3$), 0.27 (s, 18H, CH$_2$Si*Me*$_3$), 0.13 (s, 9H, CH$_2$Si*Me*$_3$), −0.31 (s, 4H, C*H*$_2$SiMe$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 173.85 (s, quat C_{Ar}), 164.77 (s, quat C_{Ar}), 155.11 (s, quat C_{Ar}), 151.59 (s, C_{Ar}), 123.07 (s, C_{Ar}), 117.97 (s, C_{Ar}), 57.31 (s, *C*H), 37.61 (s, *C*H$_2$), 37.48 (s, *C*H$_2$), 35.50 (s, *C*Me$_3$), 30.40 (s, C*Me*$_3$), 26.97 (s, *C*H$_2$), 26.75 (s, *C*H$_2$), 17.07 (s, *C*H$_2$), 5.42 (s, CH$_2$Si*Me*$_3$), 0.38 (s, CH$_2$Si*Me*$_3$). Anal. Calcd for $C_{48}H_{91}N_4LuSi_3$ (mol wt 983.49): C, 58.62; H, 9.33; N, 5.70. Found: C, 58.42; H, 9.06; N, 5.99. Mp = 111–113 °C.

Crystallographic Details for Complexes 4–7 and 9. A crystal of **4** was mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. The crystal was placed on a Bruker P4 diffractometer with 1k CCD and cooled to 203 K using a Bruker LT-2 liquid nitrogen vapor low-temperature device. The instrument was equipped with a sealed, graphite-monochromated Mo Kα X-ray source (λ = 0.710 73 Å). A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.[26] Frame integration, including Lorentz−polarization corrections, and final cell parameter calculations were carried out using SAINT software.[27] The data were corrected for absorption using the SADABS program.[28] Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. One of the SiMe$_3$ groups (Si(1), C(22)−C(24)) and one of the ^{t}Bu groups (C(11)−C(14)) were disordered, and the methyl groups were refined in two positions at half-occupancy. The C−C and Si−C bond distances were restrained to chemically reasonable values. All hydrogen atom positions were idealized and rode on the atom to which they were attached.

Crystals of **5**−**7** and **9** were mounted in a nylon cryoloop from Paratone-N oil under argon gas flow. The data were collected on a Bruker D8 APEX II charge-coupled-device (CCD) diffractometer, with a KRYO-FLEX liquid nitrogen vapor cooling device. The instrument was equipped with graphite-monochromated Mo Kα X-ray source (λ= 0.710 73 Å), with MonoCap X-ray source optics. A hemisphere of data was collected using ω scans, with 5 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[29] Frame integration, including Lorentz−polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[30] The data were corrected for absorption using the SADABS program.[31] Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. In **6**, one of the −CPh$_3$ groups was disordered and was refined in two half-occupancy positions. Also, in **6**, four disordered toluene molecules per unit cell were removed using PLATON/SQUEEZE:[32] 1266 Å^3 and 1227 electrons/cell. All hydrogen atom positions were idealized and rode on the atom to which they were attached. Hydrogen atom positions were not included on disordered atoms. The final refinement included anisotropic temperature factors on all non-hydrogen atoms.

Structure solution, refinement, and creation of publication materials were performed using SHELXTL.[33] All figures were made using ORTEP-3 for Windows.[34] Additional details of the data collection and structure refinement and tables of bond lengths and angles are given in the Supporting Information.

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Supporting Information Available: Tables and CIF files giving X-ray crystallographic data for complexes **4**–**7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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