Organometallics **2004,** *23,* 2995−3002

Synthesis and Characterization of (Mono)pentamethylcyclopentadienyl Lutetium Complexes: Formation of Bipyridyl-Stabilized Alkyls, Anilides, and Terminal Acetylides

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Received March 31, 2004

The alkyl complex [Lu(CH_2SiMe_3)$_3$(THF)$_2$] reacts with pentamethylcyclopentadiene (Cp*H), giving [Cp*Lu(CH_2SiMe_3)$_2$(THF)] (**1**). Complex **1** reacts with 1,2-dimethoxyethane (DME), affording [Cp*Lu(CH_2SiMe_3)$_2$(DME)] (**2**). Complex **1** also reacts with 2,2′-bipyridine (bipy) to give [Cp*Lu(CH_2SiMe_3)$_2$(bipy)] (**3**). The dialkyl complex **3** reacts with 1.0 equiv of 2,6-diisopropylaniline to give the mixed alkyl-anilide [Cp*Lu(NHAr)(CH_2SiMe_3)(bipy)] (**4**) (Ar = 2,6-$Pr^i_2C_6H_3$) and the bis(anilide) [Cp*Lu(NHAr)$_2$(bipy)] (**5**) in a 1.0:0.09 ratio. Complex **5** can be independently synthesized in high yield by treatment of **3** with 2.0 equiv of 2,6-diisopropylaniline or **4** with 1.0 equiv of 2,6-diisopropylaniline. Complex **3** also reacts with 2.0 equiv of phenylacetylene to afford dimeric [{Cp*Lu(CCPh)(bipy)}$_2$(μ-η^2:η^2-PhC_4Ph)]·2(C_6H_6) (**6**). Complex **6** reacts with THF and pyridine (py), giving terminal (bis)acetylide complexes [Cp*Lu(CCPh)$_2$(bipy)(THF)] (**7**) and [Cp*Lu(CCPh)$_2$(bipy)(py)] (**8**), respectively. The solid-state structures of **1**, **2**, **4**, **5**, **6**, and **8** are reported.

Introduction

The cyclopentadienyl (Cp) family of ancillary ligands are common in trivalent organometallic lanthanide (Ln) chemistry, and examples of bis-Cp Ln derivatives have been well documented.[1] These complexes are important and have found use, for example, in catalytic hydroamination[2] and polymerization.[3] When compared with bis-Cp complexes, the properties of mono-ring compounds that are desirable include an increased potential for functionalization at the metal center, a result of having only one monoanionic ancillary ligand present. Reports of mono-ring compounds are less prevalent due partially to the matching of steric requirements between Ln metal center and Cp ligand needed to inhibit formation of bis-Cp species.[4] We are specifically interested in the straightforward preparation of lutetium (Lu) mono-ring dialkyl complexes in order to study the potential chemistry of these relatively unexplored species (Lu was chosen due to the ease with which products can be characterized by nonparamagnetic NMR spectroscopy).[5] Reports of neutral, mono-Cp Ln complexes bearing dialkyl groups are limited to [Cp*Gd(CH_2Ph)$_2$(THF)] (Cp* = pentamethylcyclopentadienyl),[6] [(η^5-$C_5Me_4SiMe_2X$)Y(CH_2SiMe_3)$_2$(THF)] (X = Me, Ph, C_6F_5),[7] [(η^5-$C_5Me_4SiMe_2CH_2CHCH_2$) Y(CH_2SiMe_3)$_2$],[8] [Cp*La{CH($SiMe_3$)$_2$}$_2$],[9] [Cp*Lu(CH_2SiMe_3){CH($SiMe_3$)$_2$}(THF)],[10,11] [Cp*Lu(CH_2CMe_3)$_2$(THF)],[11] [Lu{η^5:η^1-$C_5Me_4SiMe_2$(C_4H_3O-2)}(CH_2SiMe_3)$_2$(THF)],[12] and [Cp′Lu(CH_2SiMe_3)$_2$(THF)] (Cp′ = $C_5Me_4SiMe_3$),[13] of which only [Cp*Gd(CH_2Ph)$_2$(THF)], [Cp*La{CH($SiMe_3$)$_2$}$_2$], and [Lu{η^5:η^1-$C_5Me_4SiMe_2$(C_4H_3O-2)}(CH_2SiMe_3)$_2$(THF)] have been characterized by X-ray crystallography. Furthermore, the isolation of [Cp*Lu(CH_2SiMe_3){CH($SiMe_3$)$_2$}(THF)] and [Cp*Lu(CH_2CMe_3)$_2$(THF)] is complicated by the formation of "ate" complexes due to the salt elimination strategy employed, a common problem with this type of approach to alkyl complexes in Ln chemistry.[4] We herein report the synthesis and characterization of Cp* lutetium dialkyl complexes generated via a simple

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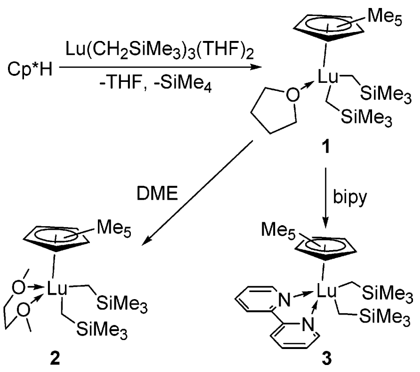
10.1021/om0497700 CCC: $27.50

Table 1. Summary of Crystallographic Data and Structure Refinement Details for 1, 2, and 4

	1	**2**	**4**
empirical formula	$C_{22}H_{45}OSi_2Lu$	$C_{22}H_{47}LuO_2Si_2$	$C_{36}H_{52}N_3LuSi\cdot 0.5$ THF
fw	556.73	574.75	765.92
space group	$P2_1/c$	$I4_1/a$	$P2_1/n$
a (Å)	18.531(4)	17.961(6)	10.837(5)
b (Å)	10.112(2)		20.678(9)
c (Å)	15.750(3)	34.786(15)	16.960(7)
β (deg)	112.973(4)		91.214(8)
V_c (Å^3)	2717.2(9)	11222(7)	3800(3)
D_c (Mg m^{-3})	1.361	1.361	1.339
Z	4	16	4
μ(Mo Kα) (mm^{-1})	3.729	3.617	2.659
final R indices[a]	R1 = 0.0329	R1 = 0.0727	R1 = 0.0790
	wR2 = 0.0733 [5839]	wR2 = 0.1651 [5032]	wR2 = 0.2346 [22 893]
a	0.0325	0.0550	0.0692

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (aP)^2]$.

Scheme 1



ligand protonolysis[7,13] (alkane elimination) procedure. The use of 2,2′-bipyridine (bipy) as an ancillary ligand in this system is explored. In contrast to conventional wisdom, the Ln metal retains its characteristic reactivity in the presence of this Lewis base (bipy). Furthermore, the chelating bipy has facilitated the isolation and complete characterization of the first, neutral, bis(terminal) acetylide Ln species.

Results and Discussion

Synthesis and Characterization of Lu Dialkyl Complexes [Cp*Lu(CH_2SiMe_3)$_2$(THF)] (1), [Cp*Lu(CH_2SiMe_3)$_2$(DME)] (2), and [Cp*Lu(CH_2SiMe_3)$_2$(bipy)] (3). Treatment of a toluene solution of Lu(CH_2SiMe_3)$_3$(THF)$_2$[14a] with an equimolar amount Cp*H over a 48 h period resulted in the formation of [Cp*Lu(CH_2SiMe_3)$_2$(THF)] (**1**), as determined by NMR spectroscopy (Scheme 1). Complex **1** was isolated as an off-white solid by removal of the toluene solvent under reduced pressure followed by crystallization of the resulting oil/wax from hexanes in 51% yield. This low isolated yield is due to the high solubility of **1** in hexanes. This crystallization step is unnecessary, and crude **1** can be used in subsequent chemistry, thus increasing the isolated yield. Repeated trituration of the crude oil/wax of **1** with hexanes results in the solidification of **1**, facilitating its manipulation. We highlight the ease with which this compound can be generated in contrast to the salt elimination, anionic complex forming route used to make similar complexes in the past[10,11] and point out that others have recently used the protonolysis approach to mono-ring Ln dialkyl complexes.[7,12,13]

Resonances for the coordinated THF are observed at 1.11 ppm (4H, β-protons) and 3.46 ppm (4H, α-protons), and the Cp**Me* groups resonate at 2.04 ppm (^{1}H NMR; C_6D_6; 25 °C). The alkyl group resonances appear as singlets at −0.87 ppm (4H, CH_2SiMe_3) and 0.31 ppm (18H, CH_2SiMe_3) in the ^{1}H NMR spectrum of **1**. Similar chemical shifts have been reported for lanthanide complexes bearing related alkyl groups.[7,8,10−13] The apparent equivalency of the $C_{\alpha-H}$ protons in the ^{1}H NMR spectrum of **1** at room temperature is interesting, as the complex, as drawn in Scheme 1, should display diastereotopic protons. Rapid dissociation of THF from **1** generating a pseudo-three-coordinate THF-free system could explain these results.[15] The variable-temperature ^{1}H NMR spectrum of **1**, however, does not change from 25 to −80 °C (C_7D_8). If there is an exchange process involving THF, it must still be rapid at −80 °C. A THF exchange process has been observed by ^{1}H NMR spectroscopy for Cp-based lutetium and yttrium complexes.[14] Another explanation assumes slow dissociation of THF on the NMR time scale. In this case the singlet could be explained by an A_2 spin system, the result of the difference in chemical shift of the $C_{\alpha-H}$ protons in question being equal to zero over the range of temperatures investigated.

A single-crystal X-ray study of **1** was carried out on a crystal grown from a concentrated hexanes solution, and the crystal details are presented in Table 1. The thermal ellipsoid plot of **1** is shown in Figure 1 and confirms the structure of **1** as shown in Scheme 1. Complex **1** adopts a distorted tetrahedral geometry. The Lu(1)−C(11) and Lu(1)−C(15) bond lengths of 2.342(4) and 2.322(4) Å, respectively, are within the expected range for Lu−C bonds in complexes containing a Lu-CH_2SiMe_3 functionality.[11,12,16] The Lu(1)−Cp^*_{cent} (cent = centroid) distance of 2.317 Å is also similar to Cp−metal distances in related lutetium compounds.[14a]

When complex **1** was dissolved in DME, the quantitative formation of **2** was observed by ^{1}H NMR spectros-

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(15) Exchange via a rapid associative pathway forming [Cp*Lu(CH_2SiMe_3)$_2$(THF)$_2$] due to adventitious THF could also explain the ^{1}H NMR spectrum of **1**.

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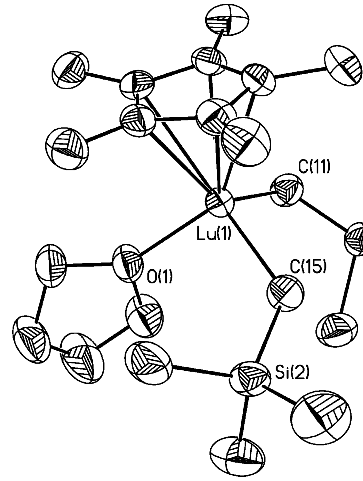


Figure 1. Thermal ellipsoid plot of **1** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Lu(1)−O(1) 2.255(3), Lu(1)−C(11) 2.342(4), Lu(1)−C(15) 2.322(4), Lu(1)−Cp*$_{cent}$ 2.317, O(1)−Lu(1)−C(11) 99.4(1), C(11)−Lu(1)−C(15) 102.7(1), O(1)−Lu(1)−Cp*$_{cent}$ 117.2.

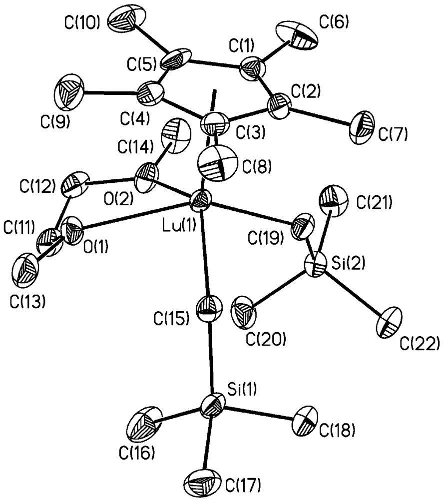
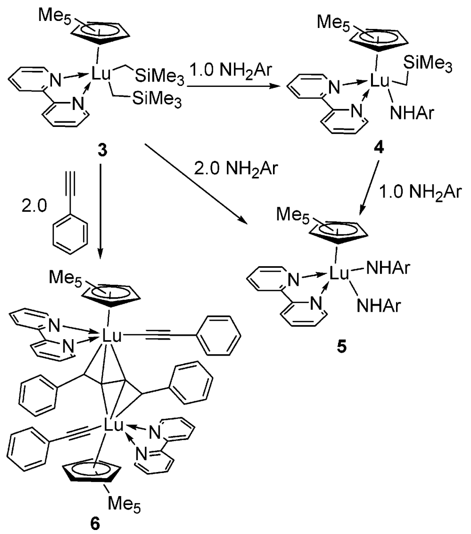


Figure 2. Thermal ellipsoid plot of **2** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Lu(1)−Cp*$_{cent}$ 2.362, Lu(1)−C(19) 2.40(1), Lu(1)−C(15) 2.391(9), Lu(1)−O(1) 2.460(6), Lu(1)−O(2) 2.396(7), Cp*$_{cent}$−Lu(1)−C(19) 111.5, Cp*$_{cent}$−Lu(1)−O(2) 110.6, Cp*$_{cent}$−Lu(1)−O(1) 108.2, Cp*$_{cent}$−Lu(1)−C(15) 111.5, O(2)−Lu(1)−C(19) 87.3(3), O(2)−Lu(1)−O(1) 65.4(2), O(1)−Lu(1)−C(15) 83.9(3), C(15)−Lu(1)−C(19) 94.5(4).

copy after appropriate workup. An X-ray crystallographic study was carried out on a single crystal of **2** grown from a DME/hexanes solution at −35 °C. The crystal data and details of the structure refinement are summarized in Table 1. The thermal ellipsoid plot of **2** with selected bond lengths and angles is shown in Figure 2. The geometry around the metal center is best described as distorted square pyramidal with O(1), O(2), C(15), and C(19) defining the base of the pyramid. The Lu(1)−C(19) and Lu(1)−C(15) bond lengths of 2.40(1) and 2.391(9) Å, respectively, are similar to the analogous Lu−C lengths in **1**. The Lu(1)−Cp*$_{cent}$ distance of 2.362 Å is, as in **1**, similar to Cp−metal distances in related lutetium compounds.[14a]

The solution structure of **2** is consistent with the solid-state structure of **2**. The diastereotopic alkyl $C_{\alpha-H}$ protons appear in the ^1H NMR spectrum of **2** as doublets at −1.11 and −0.96 ppm with a 12.0 Hz geminal coupling constant. The singlet resonance at 0.36 ppm has been assigned to the Si*Me*$_3$ group, and the Cp**Me* groups resonate at 2.03 ppm in the ^1H NMR spectrum of **2**.

Scheme 2[a]



[a] Ar = 2,6-diisopropyl.

The reaction of **1** with another potential chelate, bipy, was explored. Addition of 1.0 equiv of bipy to a toluene solution of **1** resulted in an immediate color change from pale yellow to dark red-orange. Concentration of the solution in vacuo followed by crystallization at −35 °C gave red-orange crystals that were isolated by filtration and dried under reduced pressure. The ^1H NMR spectroscopic data support the structure of **3** as shown in Scheme 1. The asymmetric nature of the compound results in diastereotopic $C_{\alpha-H}$ protons that display doublet resonances at −0.70 and −0.44 ppm ($^2J_{H-H}$ = 11.5 Hz). The silylmethyl resonance at 0.28 ppm and the Cp* resonance at 1.88 ppm in the ^1H NMR also support the proposed structure for **3**.

Complex **3** is an easily synthesized starting material that allows for the straightforward reactivity study of a Lu dialkyl complex containing only one ancillary Cp* ligand. We have focused our initial study on the reaction of **3** with compounds containing acidic N−H or C−H bonds. The results between reaction of **3** and 2,6-diisopropylaniline and phenylacetylene are shown in Scheme 2. Reaction of **3** with 1.0 equiv of NH_2Ar (Ar = 2,6-diisopropyl) gave **4** as a major product (92% by ^1H NMR spectroscopy) along with minor amounts (8% by ^1H NMR spectroscopy) of **5**. Complex **5** was independently prepared by treatment of **3** with 2.0 equiv of NH_2-Ar or treatment of **4** with 1.0 equiv of NH_2Ar. When **3** was treated with 2.0 equiv of phenylacetylene, the dimeric complex **6** was formed in good yield. The solid-state structures of **4**, **5**, and **6** were confirmed by single-crystal X-ray structure determination.

Complex **4** crystallized from THF in a monoclinic unit cell with two molecules of THF per unit cell. The thermal ellipsoid plot of **4** is shown in Figure 3 with selected bond lengths and angles, and the crystal data and details of the structure refinement are summarized in Table 1. The coordination environment about Lu(1)

Table 2. Summary of Crystallographic Data and Structure Refinement Details for 5, 6, and 8

	5	**6**	**8**
empirical formula	$C_{44}H_{56}N_4Lu$	$C_{72}H_{66}Lu_2N_4 \cdot 2(C_6H_6)$	$C_{41}H_{33}N_3Lu \cdot C_4H_8O$
fw	815.90	1493.44	814.78
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	22.058(5)	10.802(5)	9.485(2)
b (Å)	10.368(2)	12.607(5)	11.204(2)
c (Å)	18.363(4)	13.302(5)	22.304(5)
α (deg)		86.74(2)	96.360(4)
β (deg)	109.127(4)	77.70(2)	101.884(4)
γ (deg)		77.47(2)	98.837(5)
V_c (Å^3)	3967.6(1)	1727.6(1)	2266.9(9)
D_c (Mg m^{-3})	1.366	1.435	1.194
Z	4	1	2
μ(Mo Kα) (mm^{-1})	2.522	2.888	2.209
final R indices[a]	R1 = 0.0773	R1 = 0.0428	R1 = 0.0439
	wR2 = 0.1567 [29 002]	wR2 = 0.1116 [8016]	wR2 = 0.1059 [5077]
a	0.0796	0.0640	0.0700

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (aP)^2]$.

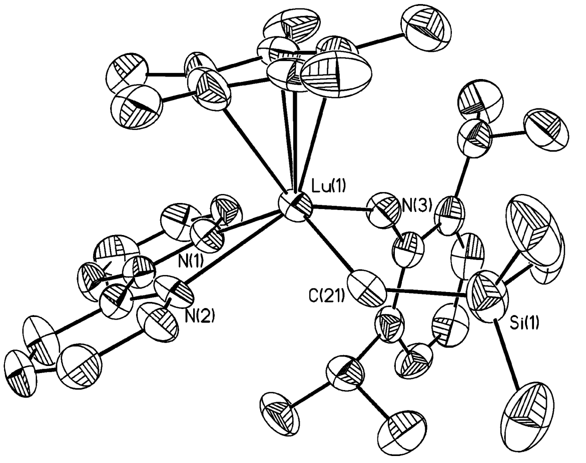


Figure 3. Thermal ellipsoid plot of **4** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Lu(1)−Cp*$_{cent}$ 2.340, N(1)−Lu(1) 2.47(1), N(2)−Lu(1) 2.48(1), N(3)−Lu(1) 2.22(1), C(21)−Lu(1) 2.40(1), N(1)−Lu(1)−N(3) 82.8(4), N(3)−Lu(1)−C(21) 100.2(4), C(21)−Lu(1)−N(2) 83.3(4), N(2)−Lu(1)−N(1) 65.1(3).

is best described as a pseudo-five-coordinate distorted square pyramid. The Lu(1)−N(3) distance of 2.22(1) Å is within the expected range for a lutetium anilide interaction.[17] The remainder of the metal to ligand bond lengths also fall within the expected ranges.

The ^{1}H NMR spectrum of **4** is consistent with the structure shown in Figure 3. Two doublets ($^2J_{H-H} = 10.5$ Hz) are observed in the ^{1}H NMR spectrum of **4** at −0.73 and −0.43 ppm for the $C_{\alpha-H}$ protons, while the $N_{\alpha-H}$ proton resonance for **4** appears at 4.89 ppm. The resonances for the $SiMe_3$ and Cp* groups fall within the expected ranges at 0.50 and 1.89 ppm, respectively, in the ^{1}H NMR spectrum of **4**. While the conversion of **3** to **4** was high yielding, samples of **4** were constantly contaminated with small amounts of **5**. Attempts to purify **4** by recrystallization were not fully successful due to the poor solubility of **5**. The best results obtained reduced the amount of **5** in the mixture to approximately 1% (by ^{1}H NMR spectroscopy) after one recrystallization. While subsequent recrystallizations could reduce the amount of **5** present, this would come with substantial loss of product.

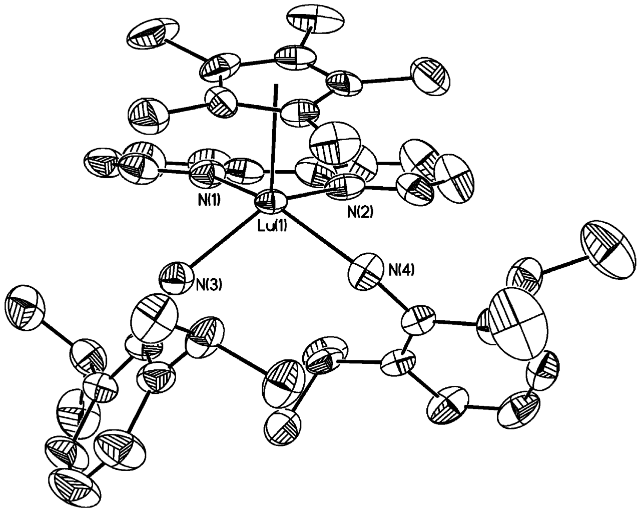


Figure 4. Thermal ellipsoid plot of **5** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Lu(1)−Cp*$_{cent}$ 2.344, N(1)−Lu(1) 2.500(7), N(2)−Lu(1) 2.472(7), N(3)−Lu(1) 2.208(7), N(4)−Lu(1) 2.209(7), N(1)−Lu(1)−N(2) 64.7(3), N(2)−Lu(1)−N(4) 82.6(2), N(4)−Lu(1)−N(3) 101.8(3), N(3)−Lu(1)−N(1) 80.6(3).

Although separation of **4** from **5** proved difficult, **4** represents a rare example of the preferred formation of a mixed alkyl anilide containing an anilide $N_{\alpha-H}$ proton, a possible precursor to a terminal imido complex. We propose that the high ratio of **4** to **5** is because the steric bulk at the metal center slows the second protonation reaction that affords **5**. A similar Nacnac-based scandium complex has recently been reported in the literature.[18]

When **3** or **4** is treated with appropriate amounts of $ArNH_2$ in benzene at 50 °C, **5** crystallizes from solution. Red crystals of **5** were isolated in 71% yield by filtration of the reaction mixture. One of these crystals was selected for a single-crystal X-ray diffraction study. The thermal ellipsoid plot of **5** is shown in Figure 4 with selected bond lengths and angles, and the crystal data are summarized in Table 2. The geometry around the metal in **5** is distorted square pyramidal and similar to that in **4**. Other structural parameters in **5** such as the

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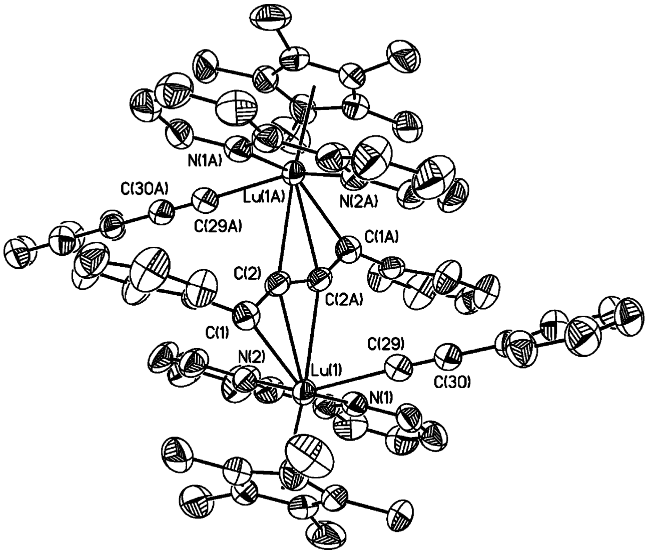


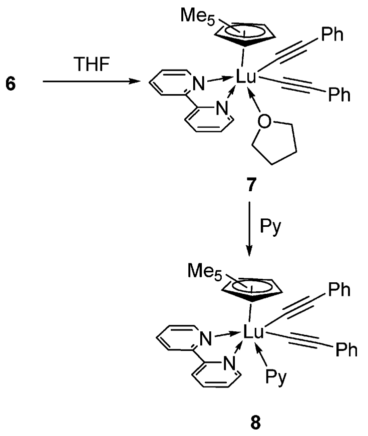
Figure 5. Thermal ellipsoid plot of **6** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): C(1)−C(2) 1.301(9), C(2)−C(2A) 1.33(1), Lu(1)−C(1) 2.388(6), Lu(1)−C(2) 2.569(6), Lu(1)−C(2A) 2.743(6), Lu(1)−N(1) 2.431(5), Lu(1)−N(2) 2.464(6), Lu(1)−Cp*$_{cent}$ 2.343, Lu(1)−C(29) 2.376(7), C(29)−C(30) 1.212(9), C(1)−C(2)−C(2A) 150.1(8).

Lu(1)−N(1) through N(4) bond lengths and the Lu(1)−Cp*$_{cent}$ bond length are comparable to similar interactions in **4**.

The formulation of **5** as a bis(anilide) is also borne out by ^{1}H NMR spectroscopy. The two inequivalent 2,6-Pr$^i{}_2$C$_6$H$_3$ methyl groups resonate at 0.83 and 1.02 ppm, while the equivalent 2,6-Pr$^i{}_2$C$_6$H$_3$ methine protons appear as a septet at 2.99 ppm. The Cp* and anilide N$_{\alpha-H}$ proton resonances show up at 1.77 and 4.09 ppm, respectively, and all aromatic proton resonances in the ^{1}H NMR spectrum of **5** have been assigned.

When benzene solutions of **3** were treated with phenylacetylene, single crystals of **6** formed and were isolated in 40% yield. An X-ray study was carried out on a single crystal of **6**. The summary of crystallographic data and structure refinement details for **6** are included in Table 2, and the thermal ellipsoid plot of **6** is shown in Figure 5. Complex **6** crystallizes with two benzene molecules of solvate in a triclinic unit cell, and the molecule sits on an inversion center. The Lu metal centers are bridged through a butatrienediyl fragment. The bond lengths C(1)−C(2) and C(2)−C(2A), within the butatrienediyl fragment, of 1.301(9) and 1.33(1) Å, respectively, are comparable to corresponding bond lengths in the related Sm,[19] Ce,[20] and La[21] bis((pentamethyl)cyclopentadienyl) systems.[22] The closest metal-to-butatrienediyl carbon contact is between Lu(1) and C(1) (2.388(6) Å). This is within the range expected for a Lu−C single bond and compares well with the Lu−C single bond lengths of 2.40(1) and 2.391(9) Å in **2**. The Lu(1)−C(2) and Lu(1)−C(2A) bond lengths of 2.569(6) and 2.743(6) Å are considerably longer than expected for Lu−C single bonds, implying weakening Lu−C interactions upon progression from the end to the center of the butatrienediyl fragment. Similar trends have been noted for the aforementioned Ln complexes.[19−21] The acetylide fragment Lu(1)−C(29) bond length of 2.376(7) Å is within the range of a lutetium carbon single bond. The acetylide C(29)−C(30) bond length of 1.212(9) Å is comparable to the usual carbon−carbon bond distance of 1.20 Å for alkynes, meaning there is a considerable amount of triple bond character between C(29) and C(30).[22] Having both terminal acetylide and bridging butatrienediyl fragments in the same molecule allows for a direct comparison of the carbon−carbon bond lengths. It is clear that there is little remaining triple bond character within the butatrienediyl fragment, as the C(1)−C(2) (1.301(9) Å) and C(2)−C(2A) (1.33(1) Å) bond lengths are considerably longer than the acetylide C(29)−C(30) (1.212(9) Å) bond distance.

Scheme 3



Complex **6** is unique among neutral, trivalent, lanthanide carbyls. Solid-state structures of complexes containing bridging butatrienediyl fragments have been reported,[19−21] as have those that contain terminal acetylide ligands.[23] To our knowledge, **6** is the first example of a neutral, trivalent, structurally characterized, Ln complex containing both butatrienediyl and terminal acetylide ligands.[24,25]

Crystals of **6** either are insoluble (C$_6$D$_6$, C$_6$D$_5$Cl, C$_7$D$_8$, CH$_3$CN) or react with (CD$_2$Cl$_2$, CD$_3$NO$_2$, OC(CD$_3$)$_2$) most conventional NMR solvents. While crystals of complex **6** do dissolve in d_8-THF, the ^{1}H NMR spectrum of the resulting solution is not consistent with the structure of **6** as shown in Figure 5. The ^{1}H and ^{13}C NMR data are consistent with the formation of a terminal bis(acetylide) THF complex (**7**), as shown in Scheme 3.

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[19] Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628.

[20] Heeres, H. J.; Nijhoff, J.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1993**, *12*, 2609.

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[22] For comparison the usual carbon−carbon distance in an alkene is 1.34 Å: *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986; Table F-158.

[23] (a) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618. (b) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124. (c) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506. (d) Lin, G.; McDonald, R.; Takats, J. *Organometallics* **2000**, *19*, 1814.

[24] An example of a related La complex with terminal and bridging acetylides has recently been reported: Tazelaar, C. G. J.; Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2004**, *23*, 936.

[25] A somewhat related complex, [CpLu(DME)]$_2$[1,1-μ-4,4-μ-(Ph)C-(Ph)C=C(Ph)C(Ph)], containing a tetracharged bridging ligand formed by the coupling of diphenylacetylene has been reported: Bochkarev, M. N.; Protchenko, A. V.; Zakharov, L. N.; Fukin, G. K.; Struchkov, Y. T. *J. Organomet. Chem.* **1995**, *501*, 123.

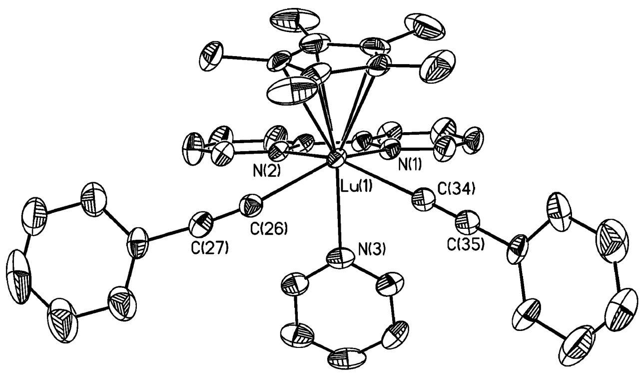

Figure 6. Thermal ellipsoid plot of **8** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Lu(1)−N(1) 2.453(6), Lu(1)−N(2) 2.455(5), Lu(1)−N(3) 2.580(8), Lu(1)−C(26) 2.397(7), Lu(1)−C(34) 2.383(7), C(26)−C(27) 1.19 (1), C(34)−C(35) 1.21(1), Lu(1)−Cp*$_{cent}$ 2.374, N(1)−Lu(1)−N(2) 66.4(2), N(2)−Lu(1)−C(26) 85.3(2), C(26)−Lu(1)−C(34) 106.8(2), C(34)−Lu(1)−N(1) 89.2(2), N(3)−Lu(1)−Cp*$_{cent}$ 175.6.

Growing single crystals of **7** proved to be difficult; however single crystals of the corresponding pyridine adduct (**8**) were grown from a THF/pyridine solution, allowing for a single-crystal X-ray study. The thermal ellipsoid plot of **8** is shown in Figure 6 with selected bond lengths and angles. The crystal parameters and structure refinement details appear in Table 2. Complex **8** crystallizes in a monoclinic unit cell with the ligands adopting a distorted octahedral geometry around Lu(1). The Lu(1)−C(26) and Lu(1)−C(34) acetylide bond lengths of 2.397(7) and 2.383(7) Å, respectively, are comparable to the Lu−acetylide bond length (Lu(1)−C(29)) of 2.376(7) Å in **6**. The multiple bond interaction between C(26)−C(27) and C(34)−C(35) in **8** is best described as a triple bond interaction with C(26)−C(27) and C(34)−C(35) distances of 1.19(1) and 1.21(1) Å, respectively. A similar interaction between C(29) and C(30) in complex **6** was discussed above. While some monomeric lanthanide complexes containing one terminal acetylide ligand have been synthesized,[23,24] to our knowledge, **8** represents the *first structurally characterized neutral, monomeric, lanthanide, bis(acetylide) species*.

Complexes **7** and **8** were fully characterized by NMR spectroscopy (HMQC and HMBC, the full assignments are included in the Experimental Section).[26] The proton and carbon chemical shifts of analogous fragments of **7** and **8** are very similar. Of interest are the acetylide resonances in the ^{13}C NMR spectra. The acetylide C_α and C_β resonances appear at 159.8 and 108.6 ppm for **7** and 159.9 and 108.6 ppm for **8**, respectively. The similarity in chemical shifts between **7** and **8** is consistent with analogous solution structures for the two molecules.

The potential reversibility involving the conversion of **6** to **7** was explored and found to depend on THF. When samples of **7**, dissolved in THF, were diluted with benzene or toluene, crystals of **6** formed over the course of 12 h, as determined by X-ray crystallography. Similarly when solid samples of **7**, isolated from THF solutions, were taken up in benzene or toluene, **6** crystallized from the resulting solution over the course of approximately 3 h. Solid samples of **6** isolated from the above two processes could be converted back to **7** by addition of THF. Attempts to study this potential equilibrium in more detail were hindered by the insolubility of **6**; however a similar process has been reported in the literature.[20]

The facile synthesis of (mono)pentamethylcyclopentadienyl lutetium dialkyl complexes as described herein allows for easy access to a variety of reactive molecules with only one anionic ancillary ligand (Cp*). We have structurally characterized many interesting derivatives including dialkyl complexes **1** and **2**, mixed alkyl-anilide **4**, and bis(anilide) **5**. We have also structurally characterized the first monomeric bis(acetylide) complex (**8**).

Experimental Section

General Methods. All reactions were conducted under a dry argon atmosphere using standard Schlenk techniques or in an argon-filled drybox. All solvents were distilled under argon from sodium or sodium benzophenone ketyl or passed over activated alumina, stored over molecular sieves, and degassed prior to use. The $Lu(CH_2SiMe_3)_3(THF)_2$ used was prepared according to a literature procedure.[14a] All NMR spectra were obtained on a Bruker AV300 instrument with C_6D_6, C_7D_8, CD_2Cl_2, or d_8-THF as solvent and referenced to residual solvent peaks. Elemental analyses were performed by the Micro-Mass Facility, University of California, Berkeley. In many cases the results obtained were not satisfactory and were inconsistent from run to run. Difficulties in characterizing organolanthanide compounds by elemental analysis have also been encountered by other researchers.[14a,27]

Crystallography. The crystal structures of all compounds were determined as follows, with exceptions noted below: A crystal was mounted onto a glass fiber using a spot of silicone grease. Due to air sensitivity, the crystal was mounted from a pool of mineral oil under argon gas flow. The crystal was placed on a Bruker P4/CCD diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The instrument was equipped with a sealed, graphite-monochromatized Mo Kα X-ray source ($\lambda = 0.71073$ 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.[28] Frame integration, including Lorentz−polarization corrections, and final cell parameter calculations were carried out using SAINT software.[29] The data were corrected for absorption using the SADABS program.[30] Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.[31] Additional details of data collection and structure refinement are listed in Tables 1 and 2. Compound **2**: The methylene hydrogen atom positions were found on the difference map and refined with their temperature factors fixed at 0.08 Å^2.

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[26] (a) Hurd, R. E.; John, B. K. *J. Magn. Reson.* **1991**, *91*, 648. (b) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

[27] Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

[28] *SMART-NT 4*; Bruker AXS, Inc.: Madison, WI 53719, 1996.

[29] *SAINT-NT 5.050*; Bruker AXS, Inc.: Madison, WI 53719, 1996.

[30] Sheldrick, G. *SADABS*, first release; University of Göttingen: Germany.

[31] *SHELXTL NT Version 5.10*; Bruker AXS, Inc.: Madison, WI 53719, 1997.

Compound **4**: The electron density of a disordered THF molecule was removed from the unit cell using PLATON/SQUEEZE.[32] This resulted in four THF molecules per cell being removed (89 e$^-$/cell and 450 Å^3). Compound **6**: A benzene solvent molecule was found on the difference map and refined with anisotropic temperature factors and idealized hydrogen atom positions. Compound **8**: One of the CCPh ligand phenyl groups, C36 to C41, was disordered and refined as two one-half occupancy phenyl groups (C36 to C41 and C36′ to C41′). Each ring was constrained to be rigid with fixed C−C bond distances. The anisotropic temperature factors were constrained to be equivalent on corresponding disordered atoms. Hydrogen atom positions were not refined on the disordered rings. The electron density of a disordered THF molecule was removed from the unit cell using PLATON/SQUEEZE.[32] This resulted in two THF molecules per cell being removed (147 e$^-$/cell and 742 Å^3).

Synthesis of [Cp*Lu(CH$_2$SiMe$_3$)$_2$(THF)] (1). To a stirring solution of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (1.20 g, 2.07 mmol) in toluene was added Cp*H (0.32 mL, 0.28 g, 2.07 mmol). The reaction was left to stir at 25 °C for 48 h and was then concentrated under reduced pressure, affording crude **1** in 77% yield. Complex **1** can be crystallized at −35 °C from concentrated hexanes solutions. ^{1}H NMR (C$_6$D$_6$; 25 °C): δ −0.87 (4H, C*H*$_2$SiMe$_3$), 0.31 (18H, CH$_2$Si*Me*$_3$), 1.11 (4H, br, THF β-protons), 2.04 (15H, Cp**Me*), 3.46 (4H, br, THF α-protons). ^{13}C{^{1}H} NMR (C$_6$D$_6$; 25 °C): δ 5.1 (q, $^1J_{C-H}$ = 117 Hz, Si*Me*$_3$), 11.8 (q, $^1J_{C-H}$ = 125 Hz, Cp**Me*), 25.2 (t, $^1J_{C-H}$ = 134 Hz, THF β-carbon), 39.2 (t, $^1J_{C-H}$ = 100 Hz, *C*H$_2$SiMe$_3$), 71.1 (t, $^1J_{C-H}$ = 152, THF α-carbon), 117.4 (Cp* *ipso*). Anal. Calcd for C$_{22}$H$_{45}$LuOSi$_2$: C, 47.46; H, 8.14. Found: C, 44.94; H, 7.97.

Synthesis of [Cp*Lu(CH$_2$SiMe$_3$)$_2$(DME)] (2). Complex **1** (0.200 g, 0.348 mmol) was added to 5 mL of DME at room temperature. Removal of the solvent under reduced pressure afforded **2** in quantitative yield. Single crystals of **2** were grown from a DME/hexanes solution at −35 °C. ^{1}H NMR (C$_6$D$_6$; 25 °C): δ −1.11 (2H, br, d, 12.0 Hz, C*H*$_2$SiMe$_3$), −0.96 (2H, br, d, 12.0 Hz, C*H*$_2$SiMe$_3$), 0.36 (18H, CH$_2$Si*Me*$_3$), 2.03 (15H, Cp**Me*), 2.55 (4H, br, DME), 2.98 (6H, br, DME). ^{13}C{^{1}H} NMR (C$_6$D$_6$; 25 °C): δ 5.6 (q, $^1J_{C-H}$ = 117.0 Hz, Si*Me*$_3$), 12.2 (q, $^1J_{C-H}$ = 124.0 Hz, Cp**Me*), 34.7 (t, $^1J_{C-H}$ = 98.0 Hz, Lu*C*H$_2$), 62.8 (q, $^1J_{C-H}$ = 147.0 Hz, DME, *C*H$_3$), 70.5 (t, $^1J_{C-H}$ = 147.0 Hz, DME, *C*H$_2$), 116.3 (Cp* *ipso* carbon). Anal. Calcd for C$_{22}$H$_{44}$LuO$_2$Si$_2$: C, 45.98; H, 8.24. Found: C, 45.93; H, 8.00.

Synthesis of [Cp*Lu(CH$_2$SiMe$_3$)$_2$(bipy)] (3). To a stirring solution of **1** (1.09 g, 1.96 mmol, toluene solution) was added 1.0 equiv of bipy (0.30 g, 1.96 mmol). The reaction was left to stir for 10 h, at which point the toluene solution was layered with hexanes and placed at −35 °C for 12 h. Crystals of **3** were isolated from this cold mixture by filtration in 68% yield. ^{1}H NMR (C$_6$D$_6$; 25 °C): δ −0.70 (2H, d, 11.5 Hz, C*H*$_2$SiMe$_3$), −0.44 (2H, d, 11.5 Hz, C*H*$_2$SiMe$_3$), 0.28 (18H, CH$_2$Si*Me*$_3$), 1.88 (15H, Cp**Me*), 6.64 (2H, mult, bipy), 6.90 (4H, mult, bipy), 8.88 (2H, d, 5.0 Hz, bipy). ^{13}C NMR (CDCl$_3$; 25 °C): δ 4.7, 11.6, 34.9, 115.8, 121.9, 125.8, 140.5, 153.1, 153.5. Anal. Calcd for C$_{28}$H$_{45}$LuN$_2$Si$_2$: C, 52.48; H, 7.07; N, 4.37. Found: C, 50.88; H, 6.65; N, 4.21.

Synthesis of [Cp*Lu(NHAr)(CH$_2$SiMe$_3$)(bipy)] (4) (Ar = 2,6-Pr$^i_2$C$_6$H$_3$). To a stirring toluene solution of **3** (0.100 g, 0.156 mmol) was added 1.0 equiv of NH$_2$Ar (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) (0.027 g, 0.156 mmol). After 10 h of stirring the solution was layered with hexanes and placed at −35 °C for 12 h. Solid **4** was isolated from this cold mixture by filtration in 75% yield. ^{1}H NMR (C$_6$D$_6$; 25 °C): δ −0.73 (1H, d, 10.5 Hz, C*H*$_2$SiMe$_3$), −0.43 (1H, d, 10.5 Hz, C*H*$_2$SiMe$_3$), 0.50 (9H, CH$_2$Si*Me*$_3$), 0.82 (6H, br, NHArPr^i *Me*), 1.45 (6H, d, 6.5 Hz, NHArPr^i *Me*), 1.89 (15H, Cp**Me*), 3.06 (2H, br, NHArPr^i C*H*), 4.89 (1H, N*H*ArPr^i), 6.26 (1H, d, 6.5 Hz, aromatic), 6.51 (1H, d, 6.5 Hz, aromatic), 6.7−7.1 (7H, ov, mult, aromatic), 8.71 (1H, d, 5.0 Hz, aromatic), 9.00 (1H, d, 5.5 Hz, aromatic). ^{13}C NMR (C$_6$D$_6$; 25 °C): δ 6.3, 12.1, 23.9, 25.7, 30.7, 32.5, 114.2, 116.0, 120.7, 120.9, 123.7, 125.1, 125.8, 133.4, 138.8, 139.5, 152.4, 153.2, 153.7, 154.0, 154.5.

Synthesis of [Cp*Lu(NHAr)$_2$(bipy)] (5) (Ar = 2,6-Pr$^i_2$C$_6$H$_3$). To a benzene solution of **4** (0.042 g, 0.058 mmol) was added 1.0 equiv of NH$_2$Ar (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) (0.010 g, 0.058 mmol). The solution was heated at 50 °C in a sealed vessel for 10 h. During the heating period crystals of **5** formed. These crystals were isolated by filtration in 71% yield. The procedure for the synthesis of **5** from **3** uses 2.0 equiv of NH$_2$Ar but is otherwise identical. ^{1}H NMR (CD$_2$Cl$_2$; 25 °C): δ 0.83 (12H, d, 6.5 Hz, NHArPr^i *Me*), 1.02 (12H, d, 7.0 Hz, NHArPr^i *Me*), 1.77 (15H, Cp**Me*), 2.99 (4H, sept, 6.5 Hz, NHArPr^i C*H*), 4.09 (2H, N*H*ArPr^i), 6.25 (2H, t, 7.5 Hz, NHArPr^i aromatic), 6.70 (4H, d, 7.5 Hz, NHArPr^i aromatic), 7.55 (2H, d of d of d, 7.5 Hz, 5.5 Hz, 1.0 Hz, bipy), 8.09 (2H, “t of d”, 8.0 Hz, 1.5 Hz, bipy), 8.25 (2H, d, 8.0 Hz, bipy), 8.99 (2H, mult, bipy). ^{13}C NMR (CD$_2$Cl$_2$; 25 °C): δ 11.5, 24.3, 24.7, 29.5, 113.1, 116.5, 122.0, 122.9, 125.7, 134.1, 140.5, 153.0, 153.4, 154.4. Anal. Calcd for C$_{44}$H$_{59}$LuN$_4$: C, 64.53; H, 7.26; N, 6.84. Found: C, 63.06; H, 6.92; N, 6.50.

Synthesis of [{Cp*Lu(CCPh)(bipy)}$_2$(μ-η^2:η^2-PhC$_4$Ph)]·2(C$_6$H$_6$) (6). To a benzene solution of **3** (0.100 g, 0.156 mmol) was added 2.0 equiv of phenylacetylene (0.032 g, 0.312 mmol). After 12 h with no stirring dark red single crystals of **6** formed and were isolated by filtration in 40% yield. The X-ray crystallographic study was carried out on one of these single crystals. Complex **6** is extremely insoluble in most nonreactive NMR solvents. These include d_6-benzene, d_8-toluene, d_5-pyridine, d_8-THF, d_3-nitromethane, and d_3-acetonitrile. Furthermore, **6** reacts with CD$_2$Cl$_2$ over the course of several hours to give an unidentified product. Due to the insoluble nature of **6**, NMR data cannot be collected. Anal. Calcd for C$_{72}$H$_{66}$Lu$_2$N$_4$·C$_6$H$_6$: C, 66.19; H, 5.12; N, 3.95. Found: C, 65.88; H, 5.11; N, 3.86.

Synthesis of [Cp*Lu(CCPh)$_2$(bipy)(THF)] (7). ^{1}H NMR (d_8-THF; 25 °C; assigned by HMQC and HMBC): δ 1.78 (15H, Cp**Me*), 7.02 (2H, t of t, 7.0 Hz, 1.5 Hz, acetylide *para* proton), 7.13 (4H, t, 7.0 Hz, acetylide *meta* proton), 7.33 (4H, d, 7.0 Hz, acetylide *ortho* proton), 7.70 (2H, d of d of d, 7.5 Hz, 5.0 Hz, 1.0 Hz, bipy 5 and 5′ protons), 8.12 (2H, t of d, 8.0 Hz, 2.0 Hz, bipy 4 and 4′ protons), 8.41 (2H, d, 8.0 Hz, bipy 3 and 3′ protons), 9.67 (2H, d of d of d, 5 Hz, 1.5 Hz, 1.0 Hz, bipy 6 and 6′ protons) (THF resonances not observed). The ^{1}H NMR spectrum of **7** remains unchanged from 25 to −100 °C. ^{13}C NMR (d_8-THF; 25 °C; assigned by HMQC and HMBC): δ 12.5 (Cp**C*H$_3$), 108.6 (LuC*C*Ph), 116.3 (Cp* *ipso*), 122.7 (bipy 3 and 3′ carbons), 125.4 (acetylide *para* carbons), 126.2 (bipy 5 and 5′ carbons), 128.5 (acetylide *meta* carbons), 130.1 (acetylide *ipso* carbons), 132.1 (acetylide *ortho* carbons), 140.4 (bipy 4 and 4′ carbons), 153.3 (bipy 6 and 6′ carbons), 154.3 (bipy 2 and 2′ carbons), 159.8 (Lu*C*CPh).

Synthesis of [Cp*Lu(CCPh)$_2$(bipy)(py)] (8). ^{1}H NMR (d_8-THF; 25 °C; assigned by HMQC and HMBC): δ 1.59 (15H, Cp**Me*), 6.83 (2H, t of d, 7.0 Hz, 2.5 Hz, acetylide *para* proton), 6.93 (4H, t, 7.0 Hz, acetylide *meta* protons), 7.02 (2H, d of d, 8.0 Hz, 5.0 Hz, pyridine *meta* protons), 7.12 (4H, d, 7.0 Hz, acetylide *ortho* protons), 7.43 (1H, ov, pyridine *para* proton), 7.48 (2H, “t”, 6.5 Hz, bipy 5 and 5′ protons), 7.92 (2H, t of d, 8.0 Hz, 1.5 Hz, bipy 4 and 4′ protons), 8.17 (2H, d, 8.0 Hz, bipy 3 and 3′ protons), 8.36 (2H, br, pyridine *ortho* protons), 9.46 (2H, d of d, 5.0 Hz, 1.0 Hz, bipy 6 and 6′ protons). ^{13}C NMR (d_8-THF; 25 °C; assigned by HMQC and HMBC): δ 12.6 (Cp**C*H$_3$), 108.6 (LuC*C*Ph), 116.3 (Cp* *ipso*), 122.7 (bipy 3 and 3′ carbons), 124.4 (pyridine *meta* carbons), 125.5 (acetylide *para* carbons), 126.2 (bipy 5 and 5′ carbons), 128.5 (acetylide

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(32) Spek, A. L. *Acta. Crystallogr.* **1990**, *A46*, C34.

meta carbons), 130.1 (acetylide *ipso* carbons), 132.0 (acetylide *ortho* carbons), 136.4 (pyridine *para* carbon), 140.4 (bipy 4 and 4′ carbons), 151.0 (pyridine *ortho* carbons), 153.2 (bipy 6 and 6′ carbons), 154.3 (bipy 2 and 2′ carbons), 159.9 (Lu*C*CPh).

Acknowledgment. We thank the Los Alamos National Laboratory LDRD program for support of this work. T.M.C. thanks the LDRD office for a Directors Funded Postdoctoral Fellowship.

Supporting Information Available: CIF files for the structures of **1**, **2**, **4**, **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0497700