Organometallics **2005,** *24,* 6393−6397

The Elusive $(C_5Me_4H)_3Lu$: Its Synthesis and $LnZ_3/K/N_2$ Reactivity

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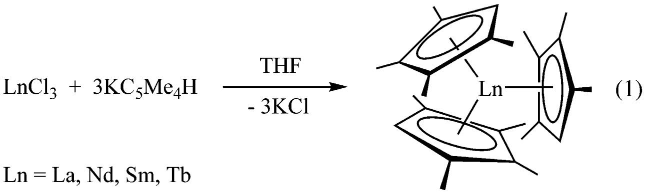
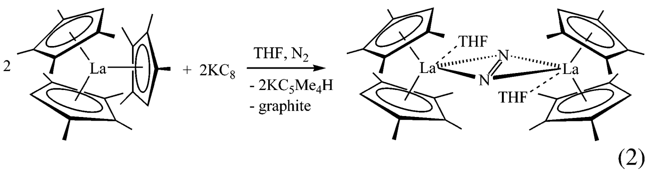
Received August 16, 2005

The previously inaccessible smallest member of the $(C_5Me_4H)_3Ln$ series, $(C_5Me_4H)_3Lu$, has been synthesized from $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ and KC_5Me_4H and reduced with potassium under dinitrogen to form $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.

Introduction

The tetramethylcyclopentadienyl complexes, $(C_5Me_4H)_3Ln$, constitute a desirable series of homoleptic organolanthanide precursors since they can be synthesized directly from $LnCl_3$ in one step according to eq 1 (Ln = La−Tb).[1,2] For example, $(C_5Me_4H)_3La$ was chosen as a starting material to determine if the $LnZ_3/K/N_2$ reduction system[3,4] was viable with organometallic LnZ_3 complexes and to obtain the first crystallographically characterizable $(N_2)^{2-}$ complex of lanthanum, eq 2.[5]





However, in the 12 years since the first examples of $(C_5Me_4H)_3Ln$ complexes were described,[1] a crucial member of the series, the lutetium analogue, has not been reported. It is unfortunate that the synthesis of this complex remained elusive since lutetium is the smallest lanthanide and is diamagnetic. The availability of both $(C_5Me_4H)_3La$ and $(C_5Me_4H)_3Lu$ would mean that metal size optimization in organolanthanide chemistry could be evaluated with an isomorphous pair of diamagnetic complexes that had the extremes in metal radial size. For example, $(C_5Me_4H)_3Lu$ could provide, via eq 2, the first pair of crystallographically characterized La^{3+} and Lu^{3+} $(N_2)^{2-}$ complexes with the same ligand set. The only La^{3+} and Lu^{3+} $(N_2)^{2-}$ complexes identified by X-ray crystallography to date are $\{[(Me_3Si)_2N]_2Lu(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$,[3] $[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$,[5] and $[(C_5Me_5)_2La(THF)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.[5]

$(C_5Me_4H)_3Lu$ was of interest for another reason. Recent studies have shown that $(C_5Me_5)_3M$ complexes can display unusual cyclopentadienyl reaction chemistry presumably due to the steric crowding and their unusually long M−C distances.[6,7] Similar chemistry is not observed for $(C_5Me_4H)_3M$ complexes,[1,2] but the most sterically crowded member of the lanthanide series, $(C_5Me_4H)_3Lu$, had never been made. Hence, it was of interest to see if $(C_5Me_4H)_3Lu$ would display any of the unusual chemistry of the long bond organometallic $(C_5Me_5)_3Ln$ complexes.

We sought to synthesize $(C_5Me_4H)_3Lu$ for use in the LnZ_3/alkali metal/N_2 system and for use in any other organometallic reactions to be examined with a complete LnZ_3 series in which Z = $(C_5Me_4H)^-$. We report here the synthesis of $(C_5Me_4H)_3Lu$, its X-ray crystal structure, and the $LnZ_3/K/N_2$ reduction chemistry of this complex and its precursor, $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$. These studies provide the first analogous pair of lanthanum and lutetium $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ complexes.

Experimental Section

General Comments. The manipulations described below were performed under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Potassium was purchased from Aldrich, washed with hexanes, and scraped to provide shiny pieces before use. KC_8 was prepared according to literature methods.[8,9] KH under mineral oil was purchased from Aldrich and used after washing with hexanes. KC_5Me_4H was prepared by mixing 1 equiv of KH with 1 equiv of 1,2,3,4-tetramethyl-1,3-cyclopentadiene in THF. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. NMR solvents were dried over sodium potassium alloy, degassed, and vacuum transferred before use. ^1H NMR, ^{13}C NMR, and ^{15}N NMR spectra were recorded with Bruker DRX 400 MHz

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10.1021/om050709k CCC: $30.25

or Bruker DRX 500 MHz spectrometers. ^{15}N NMR spectra were measured using as an external reference ^{15}N-formamide in DMSO (−268 ppm with respect to nitromethane at 0 ppm).[10] Melting points were taken using a Thomas-Hoover melting point apparatus in sealed capillary tubes. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Complexometric analyses were carried out as previously described.[11]

$(C_5Me_4H)_3Lu$, 1. Following the method of Schumann[1,2] $LuCl_3$ (0.532 g, 1.8 mmol) was reacted with KC_5Me_4H (0.923 g, 5.7 mmol) in 10 mL of THF, giving a yellow solution that was stirred for 12 h. Gray insoluble materials were removed by centrifugation, and solvent was removed via rotary evaporation. The resulting yellow powder was placed in a glass tube fitted with a vacuum adapter and attached to a high-vacuum line. At 150 °C at 1×10^{-4} Torr, a yellow powder began to sublime. The resulting yellow material was extracted into toluene and dried to a yellow powder (0.183 g, 18%). ^{1}H NMR (C_6D_6): 6.12 (s, $C_5Me_4\mathit{H}$, 1H), 2.05 (s, $C_5\mathit{Me}_4H$, 6H), 1.80 (s, $C_5\mathit{Me}_4H$, 6H). ^{13}C NMR (C_6D_6): 124.9 (C_5Me_4H), 114.3 (C_5Me_4H), 111.7 (C_5Me_4H), 12.9 ($C_5\mathit{Me}_4H$), 11.7 ($C_5\mathit{Me}_4H$). Anal. Calcd for $C_{27}H_{39}Lu$: C, 60.21; H, 7.30; Lu, 32.49. Found: C, 59.96; H, 7.22; Lu, 32.75. Crystals suitable for X-ray crystallography were grown from concentrated toluene solutions at −35 °C. Mp: 257 °C.

Alternative Synthesis of $(C_5Me_4H)_3Lu$, 1. $LuCl_3$ (0.4903 g, 1.74 mmol) and KC_5Me_4H (0.5587 g, 3.48 mmol) were stirred in THF for 24 h. The resulting white slurry was centrifuged to separate insoluble material. The pale yellow solution was evaporated under vacuum to yield $(C_5Me_4H)_2LuCl_2K(THF)_2$ (1.01 g, 86%). ^{1}H NMR (THF-d_8): 5.51 (s, $C_5Me_4\mathit{H}$, 1H), 1.93 (s, $C_5\mathit{Me}_4H$, 6H), 1.85 (s, $C_5\mathit{Me}_4H$, 6H). ^{13}C NMR (THF-d_8): 119.1 (C_5Me_4H), 114.5 (C_5Me_4H), 109.2 (C_5Me_4H), 14.0 ($C_5\mathit{Me}_4H$), 13.2 ($C_5\mathit{Me}_4H$). $ClMg(CH_2CHCH_2)$ (0.75 mL of a 2.0 M solution in THF, 1.50 mmol) was added to a stirred slurry of $(C_5Me_4H)_2LuCl_2K(THF)_2$ (1.01 g, 1.50 mmol) in toluene. The white slurry immediately became a yellow solution and was allowed to stir overnight. Evaporation of the solvent yielded a yellow powder. This yellow solid was triturated with a 2% dioxane/hexanes solution and was allowed to stir overnight. White insolubles were removed by centrifugation to yield a yellow solution. The solvent was removed under vacuum, and the product was redissolved in toluene. The solvent was removed under vacuum to yield $(C_5Me_4H)_2Lu(C_3H_5)(THF)$ as a bright yellow powder. ^{1}H NMR (THF-d_8): 6.49 (p, $CH_2C\mathit{H}CH_2$, 1H), 5.63 (s, $C_5Me_4\mathit{H}$, 2H), 2.44 (d, $C\mathit{H}_2CHC\mathit{H}_2$, 4H), 1.94 (s, $C_5\mathit{Me}_4H$, 12H), 1.92 (s, $C_5\mathit{Me}_4H$, 12H). ^{13}C NMR (THF-d_8): 152.4 ($CH_2\mathit{C}HCH_2$), 119.0 (C_5Me_4H), 115.8 (C_5Me_4H), 110.8 (C_5Me_4H), 72.2 ($\mathit{C}H_2CH\mathit{C}H_2$), 13.2 ($C_5\mathit{Me}_4H$), 11.9 ($C_5\mathit{Me}_4H$). The yellow powder was desolvated under high vacuum (1×10^{-5} Torr) for 24 h at 60 °C. The resulting material was extracted with hexanes to yield $(C_5Me_4H)_2Lu(C_3H_5)$ (0.596 g, 86%) as a bright yellow powder. ^{1}H NMR (toluene-d_8, 190 K): 7.33 (m, $CH_2C\mathit{H}CH_2$, 1H), 5.99 (s, $C_5Me_4\mathit{H}$, 1H), 5.70 (s, $C_5Me_4\mathit{H}$, 1H), 3.83 (d, $C\mathit{H}_2CHC\mathit{H}_2$, 2H), 2.07 (d, $C\mathit{H}_2CHC\mathit{H}_2$, 2H), 2.05 (s, $C_5\mathit{Me}_4H$, 6H), 2.02 (s, $C_5\mathit{Me}_4H$, 6H), 1.89 (s, $C_5\mathit{Me}_4H$, 6H), 1.56 (s, $C_5\mathit{Me}_4H$, 6H). $(C_5Me_4H)_2Lu(C_3H_5)$ (0.373 g, 0.81 mmol) and Et_3NHBPh_4 (0.360 g, 0.85 mmol) were stirred in benzene for 24 h. Excess Et_3NHBPh_4 was removed by centrifugation, yielding a colorless solution. $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$, **2**, was isolated as a white powder after removal of the solvent (0.563 g, 94%). ^{1}H NMR (C_6D_6): 7.84 (d, o-C_6H_5, 8H), 4.98 (s, $C_5Me_4\mathit{H}$, 2H), 1.62 (s, $C_5\mathit{Me}_4H$, 12H), 1.59 (s, $C_5\mathit{Me}_4H$, 12H). There is a set of resonances overlapping the lock solvent in the region from 7.10 to 7.16 that could not be unambiguously identified. ^{13}C NMR (C_6D_6): 123.9 (C_5Me_4H), 120.6 (C_5Me_4H), 115.6 (C_5Me_4H), 13.7 ($C_5\mathit{Me}_4H$), 11.8 ($C_5\mathit{Me}_4H$). Phenyl resonances could not be located. ^{1}H NMR (THF-d_8): 7.30 (d, o-C_6H_5, 8H), 6.87 (t, m-C_6H_5, 8H), 6.74 (t, p-C_6H_5, 8H), 5.82 (s, $C_5Me_4\mathit{H}$, 2H), 2.03 (s, $C_5\mathit{Me}_4H$, 12H), 1.95 (s, $C_5\mathit{Me}_4H$, 12H). ^{13}C NMR (THF-d_8): 137.3 (C_6H_5), 126.0 (C_6H_5), 123.4 (C_6H_5), 122.1 (C_5Me_4H), 119.5 (C_5Me_4H), 114.5 (C_5Me_4H), 13.2 ($C_5\mathit{Me}_4H$), 11.9 ($C_5\mathit{Me}_4H$). Anal. Calcd for $C_{42}H_{46}BLu$: Lu, 23.75. Found: Lu, 23.2. KC_5Me_4H (0.112 g, 0.70 mmol) and $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ (0.507 g, 0.69 mmol) were combined along with a stir bar in 10 mL of benzene. The reaction was stirred overnight, during which the color of the solution changed from colorless to yellow-orange. White solids were removed from the solution by centrifugation. Evaporation of the solvent left $(C_5Me_4H)_3Lu$ (0.3330 g, 90%), which was identified by ^{1}H NMR spectroscopy. The overall yield of **1** from $LuCl_3$ was 70%.

$[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 3, from 1. In a nitrogen-filled glovebox, a yellow solution of **1** (0.112 g, 0.21 mmol) in 10 mL of THF was added to a vial containing KC_8 (0.028 g, 0.21 mmol) and a stir bar. The mixture immediately became dark and was allowed to stir for 2 h. The mixture was centrifuged to remove black and white insoluble material (presumably graphite and KC_5Me_4H, respectively), and evaporation of the supernatant yielded a yellow powder. Extraction with 10 mL of toluene and removal of solvent gave a yellow powder (0.075 g, 72%). A concentrated toluene sample of **3** at −35° C produced pale blue crystals over one week. ^{1}H NMR (C_6D_6): 5.73 (s, $C_5Me_4\mathit{H}$, 1H), 3.63 (s, THF, 2H), 2.07 (s, $C_5\mathit{Me}_4H$, 6H), 2.01 (s, $C_5\mathit{Me}_4H$, 6H), 1.42 (s, THF, 2H). ^{13}C NMR (C_6D_6): 118.2 (C_5Me_4H), 116.2 (C_5Me_4H), 111.6 (C_5Me_4H), 68.6 (THF), 26.2 (THF), 12.6 ($C_5\mathit{Me}_4H$), 12.0 ($C_5\mathit{Me}_4H$). ^{15}N{^{1}H} NMR (C_6D_6): 521 (s). Anal. Calcd for $C_{44}H_{68}N_2O_2Lu_2$: Lu, 34.75. Found: Lu, 34.7. The complex is isomorphous with $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.[5] Mp: 195 °C (dec).

3 from 2. In a nitrogen-filled glovebox, a colorless solution of $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ (0.060 g, 0.81 mmol) in 10 mL of THF was added to a vial containing KC_8 (0.012 g, 0.88 mmol) and a stir bar. The mixture immediately became dark and was allowed to stir for 2 h. The mixture was centrifuged to remove black and white insoluble material (presumably graphite and $KBPh_4$, respectively), and evaporation of the supernatant yielded a yellow powder. Extraction with 10 mL of toluene and removal of solvent gave a yellow powder (0.033 g, 80%), which was identified as $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ by ^{1}H NMR spectroscopy.

X-ray Data Collection, Structure Solution, and Refinement for $(C_5Me_4H)_3Lu$, 1. A yellow crystal of approximate dimensions $0.32 \times 0.33 \times 0.44$ mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[12] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). The raw frame data were processed using SAINT[13] and SADABS[14] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[15] program. The systematic absences were consistent with the rhombohedral space groups $R3$ and $R\bar{3}$. It was later determined that the centrosymmetric space group $R\bar{3}$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[16] for neutral atoms were used throughout the analysis. The molecule was located on a 3-fold rotation axis. Hydrogen atoms were included using a riding model. At

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Table 1. X-ray Data Collection Parameters for Complexes 1, 2, and 3

empirical formula	$C_{27}H_{39}Lu$, **1**	$C_{42}H_{46}BLu \cdot ^1/_2(C_7H_8)$, **2**	$C_{44}H_{68}N_2O_2Lu_2 \cdot 2(C_7H_8)$, **3**
fw	538.55	782.64	1191.21
temperature (K)	158(2)	163(2)	163(2)
cryst syst	rhombohedral	monoclinic	monoclinic
space group	$R\bar{3}$	$P2_1/n$	$C2/c$
a (Å)	15.4695(8)	14.631(2)	15.123(5)
b (Å)	15.4695(8)	14.429(2)	13.951(5)
c (Å)	16.6565(12)	17.559(2)	25.662(8)
α (deg)	90	90	90
β (deg)	90	102.354(2)	105.263(5)
γ (deg)	120	90	90
volume Å^3	3452.0(4)	3621.0(9)	5223(3)
Z	6	4	4
ρ_{calcd} (Mg/m^3)	1.554	1.436	1.515
μ (mm^{-1})	4.299	2.757	3.800
R1 [$I > 2.0\sigma(I)$]	0.0244	0.0192	0.0439
wR2 (all data)	0.0650	0.0511	0.1362

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (C_5Me_4H)$_3$Lu, 1

Lu(1)−Cnt1	2.406	Lu(1)−C(4)	2.566(3)
Lu(1)−C(1)	2.800(4)	Lu(1)−C(5)	2.641(3)
Lu(1)−C(2)	2.798(3)	Lu(1)−C(3)	2.633(3)

Cnt1−Lu(1)−Cnt2	120

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [(C_5Me_4H)$_2$Lu][(μ-Ph)$_2$BPh$_2$], 2

Lu(1)−Cnt1	2.302	Lu(1)−C(13)	2.595(2)
Lu(1)−Cnt2	2.301	Lu(1)−C(14)	2.520(2)
Lu(1)−C(1)	2.576(2)	Lu(1)−C(20)	2.668(2)
Lu(1)−C(2)	2.621(2)	Lu(1)−C(21)	2.947(2)
Lu(1)−C(3)	2.630(2)	Lu(1)−C(26)	2.800(2)
Lu(1)−C(4)	2.618(2)	Lu(1)−C(27)	3.237(2)
Lu(1)−C(5)	2.550(2)	B(1)−C(19)	1.645(3)
Lu(1)−C(10)	2.559(2)	B(1)−C(25)	1.648(3)
Lu(1)−C(11)	2.640(2)	B(1)−C(31)	1.639(3)
Lu(1)−C(12)	2.673(2)	B(1)−C(37)	1.647(3)

Cnt1−Lu(1)−Cnt2	133.4	Cnt2−Lu(1)−C(20)	103.6
Cnt1−Lu(1)−C(20)	114.9	Cnt2−Lu(1)−C(21)	99.4
Cnt1−Lu(1)−C(21)	102.3	Cnt2−Lu(1)−C(26)	113.7
Cnt1−Lu(1)−C(26)	102.9	Cnt2−Lu(1)−C(27)	100.6

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [(C_5Me_4H)$_2$(THF)Lu]$_2$(μ-η^2:η^2-N$_2$), 3

Lu(1)−Cnt1	2.369	Lu(1)−C(11)	2.700(7)
Lu(1)−Cnt2	2.385	Lu(1)−C(12)	2.615(7)
Lu(1)−C(1)	2.637(7)	Lu(1)−C(13)	2.605(7)
Lu(1)−C(2)	2.684(7)	Lu(1)−C(14)	2.696(7)
Lu(1)−C(3)	2.698(7)	Lu(1)−N(1A)	2.290(6)
Lu(1)−C(4)	2.666(7)	Lu(1)−N(1)	2.311(6)
Lu(1)−C(5)	2.600(7)	Lu(1)−O(1)	2.462(17)
Lu(1)−C(10)	2.744(7)	N(1)−N(1A)	1.243(12)

Cnt1−Lu(1)−Cnt2	129.9	Cnt2−Lu(1)−N(1A)	104.7
Cnt1−Lu(1)−N(1)	109.7	N(1A)−Lu(1)−N(1)	31.3(3)
Cnt1−Lu(1)−N(1A)	104.5	N(1A)−Lu(1)−O(1)	114.3(4)
Cnt2−Lu(1)−N(1)	116.5	N(1)−Lu(1)−O(1)	83.1(4)

convergence, wR2 = 0.0650 and GOF = 1.221 for 85 variables refined against 1827 data. As a comparison for refinement on F, R1 = 0.0244 for those 1733 data with $I > 2.0\sigma(I)$. Experimental parameters for data collection and structure refinement for **1** are given in Table 1. Selected bond distances and angles for **1** are given in Table 2.

X-ray Data Collection, Structure Solution, and Refinement for [(C_5Me_4H)$_2$Lu][(μ-Ph)$_2$BPh$_2$], 2. A colorless crystal of approximate dimensions 0.19 × 0.24 × 0.29 mm was handled as described for **1**. The diffraction symmetry was 2/m, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later determined to be correct. Hydrogen atoms were located from a difference Fourier map and refined (x,y,z and U_{iso}). There was one-half molecule of toluene solvent present per formula unit. The toluene was disordered about an inversion center and was included with partial site-occupancy factors (0.50) for atoms C(43), C(45), and C(47). The hydrogen atoms associated with the solvent were not included in the refinement. At convergence, wR2 = 0.0511 and GOF = 1.062 for 626 variables refined against 8742 data. As a comparison for refinement on F, R1 = 0.0192 for those 7733 data with $I > 2.0\sigma(I)$. Experimental parameters for data collection and structure refinement for **2** are given in Table 1. Selected bond distances and angles for **2** are given in Table 3.

[(C_5Me_4H)$_2$(THF)Lu]$_2$(μ-η^2:η^2-N$_2$), 3. A pale blue crystal of approximate dimensions 0.30 × 0.38 × 0.39 mm was handled as described for **1**. The diffraction symmetry was 2/m, and the systematic absences were consistent with the monoclinic space groups Cc and $C2/c$. It was later determined that the centrosymmetric space group $C2/c$ was correct. Hydrogen atoms were included using a riding model. The molecule was located about a 2-fold rotation axis. There were two molecules of toluene solvent present per dimeric formula unit. Atoms O(1) and C(20) to C(30) were disordered and included using multiple components with partial site-occupancy factors. The tetramethylcyclopentadienyl ring defined by atoms C(10)−C(19) was also disordered. Atoms C(17) and C(19) exhibited short methyl−ring distances. The site-occupancy factors of these two atoms were set to 0.42 and 0.58, respectively, to account for the methyl carbon atom being disordered over two positions. The ring-hydrogen atom associated with the disordered tetramethylcyclopentadienyl ligand could not be located and was not included in the refinement. At convergence, wR2 = 0.1363 and GOF = 1.094 for 286 variables refined against 6233 data. As a comparison for refinement on F, R1 = 0.0439 for those 5577 data with $I > 2.0\sigma(I)$. Experimental parameters for data collection and structure refinement for **3** are given in Table 1. Selected bond distances and angles for **3** are given in Table 4.

Results and Discussion

Synthesis. (C_5Me_4H)$_3$Lu, **1**, was originally synthesized in this study from $LuCl_3$ and KC_5Me_4H following the method of Schumann for the other lanthanide analogues, La−Tb, according to eq 1. Unfortunately, the yield was too low to provide sufficient amounts for reactivity studies, and an alternative synthesis was sought. The route previously used to make (C_5Me_5)$_3$Ln complexes from [(C_5Me_5)$_2$Ln][(μ-Ph)$_2$BPh$_2$] and KC_5Me_5 seemed like a good alternative and proved to be successful.[7,17]

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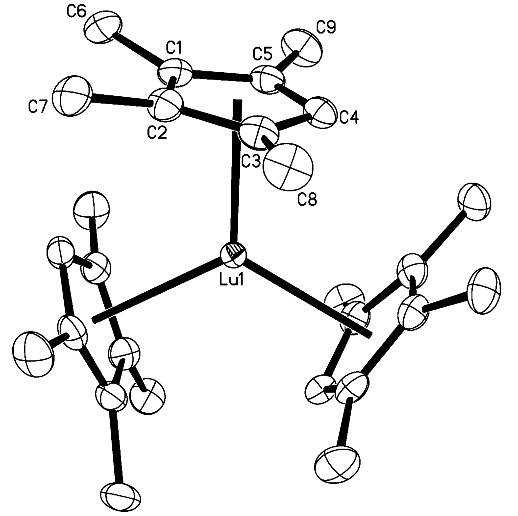

Figure 1. Thermal ellipsoid plot of $(C_5Me_4H)_3Lu$ drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

$(C_5Me_4H)_3Lu$ can be synthesized according to the reactions in eqs 3−6.

$$LuCl_3 + 2KC_5Me_4H \xrightarrow[\text{-KCl}]{\text{THF}} (C_5Me_4H)_2LuCl_2K(THF)_2 \quad (3)$$

$$(C_5Me_4H)_2LuCl_2K(THF)_2 + ClMg(C_3H_5) \xrightarrow[\substack{\text{2. hexanes/dioxane}\\ \text{-MgCl}\\ \text{-KCl}\\ \text{-THF}}]{\text{1. toluene}} (C_5Me_4H)_2Lu(C_3H_5) \quad (4)$$

$$(C_5Me_4H)_2Lu(C_3H_5) + Et_3NHBPh_4 \xrightarrow[\substack{\text{-propene}\\ \text{-Et}_3\text{N}}]{C_6H_6} [(C_5Me_4H)_2Lu][BPh_4] \quad (5)$$

$$[(C_5Me_4H)_2Lu][BPh_4] + KC_5Me_4H \xrightarrow[\text{-KBPh}_4]{C_6H_6} (C_5Me_4H)_3Lu \quad (6)$$

Although this requires several steps, each is in good yield and the overall yield from $LuCl_3$ is 70%.

Reactivity of $(C_5Me_4H)_3Lu$. $(C_5Me_4H)_3Lu$ shows none of the unusual reactivity of the sterically crowded $(C_5Me_5)_3Ln$ complexes.[6] Hence, in contrast to $(C_5Me_5)_3Sm$,[7,18] it does not ring open THF, it does not polymerize ethylene, and it does not reduce 1,3,5,7-cyclooctatetraene. This "normal" $(C_5R_5)_3Ln$ reactivity suggested that, even with the smallest metal in the lanthanide series, $(C_5Me_4H)_3Ln$ complexes were not sterically crowded.

However, $(C_5Me_4H)_3Lu$ did prove to be reactive in the $LnZ_3/K/N_2$ reaction. Addition of yellow $(C_5Me_4H)_3Lu$ to KC_8 in THF under nitrogen led to immediate darkening consistent with KC_8 reactivity. After 2 h, $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **3**, was isolated in 72% yield in a reaction analogous to that in eq 2. The ^1H and ^{13}C NMR spectra were normal for a $(C_5Me_4H)^-$ complex of lutetium, and the complex was fully identified by X-ray crystallography, Figure 3. $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ is isomorphous with $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$.[5] The NN bond distance is 1.243(12) Å and is consistent with the formation of an $(N{=}N)^{2-}$ moiety.

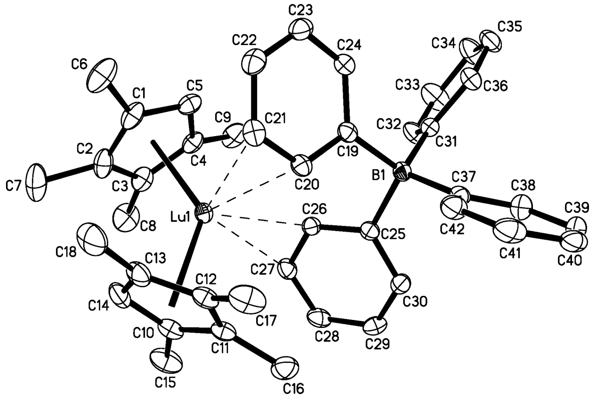

Figure 2. Thermal ellipsoid plot of $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

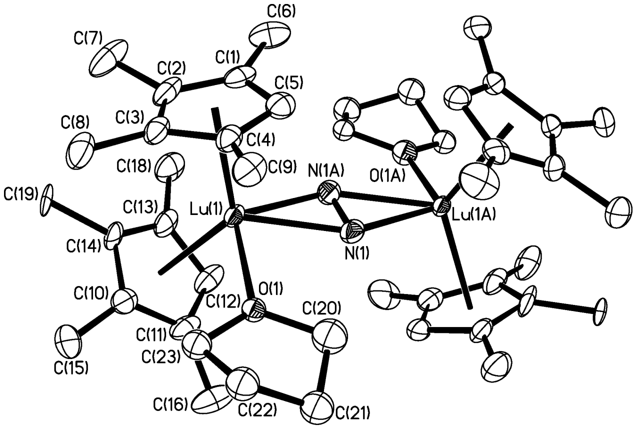

Figure 3. Thermal ellipsoid plot of $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 5. ^{15}N NMR Shifts for Lanthanide and Yttrium $(N{=}N)^{2-}$ Complexes

compound	^{15}N NMR shift referenced to $MeNO_2$	ref
$[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	569	5
$\{[(Me_3Si)_2N]_2(THF)Lu\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	557	3
$[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	521	this work
$\{[(Me_3Si)_2N]_2(THF)La\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	516	4
$\{[(Me_3Si)_2N]_2(THF)Y\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	513	3
$[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	495	5

The ^{15}N NMR spectrum of **3** showed a resonance at 521 ppm (with respect to $MeNO_2$ referenced at 0 ppm). This can be compared to the analogous resonances of $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ at 495 ppm and $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ at 513 (Y) and 557 (Lu) ppm, Table 5.

If $(C_5Me_4H)_3Lu$ were directly obtainable from $LuCl_3$ in high yield, the $(C_5Me_4H)_3Lu/K/N_2$ reaction would be the best route to $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$. However, since $(C_5Me_4H)_3Lu$ is made in a multistep route with $[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ as the immediate precursor, this latter complex is a preferable precursor to $[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ since one less step is required. It has previously been shown that $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ complexes can function in $LnZ_2Z'/K/N_2$ reactions analogous to $LnZ_3/K/N_2$ reductions.[5] Indeed, dinitrogen can be reduced by the $[(C_5Me_4H)_2Lu][(\mu\text{-}$

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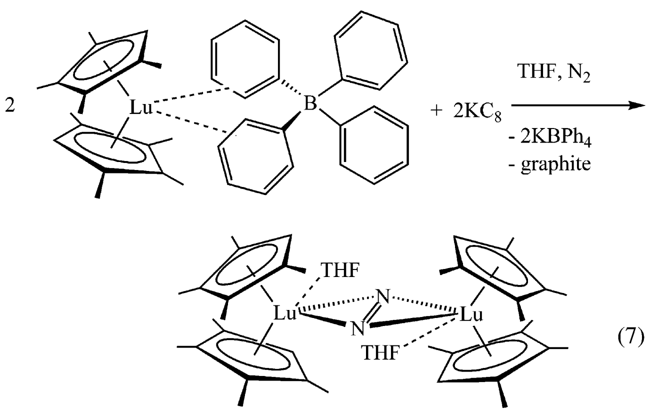
[18] Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 9273.

Table 6. Selected Metrical Data on Lutetium Metallocene Compounds

compound	(ring centroid)−M−(ring centroid) angle (deg)	M−(ring centroid) distances (Å)
$(C_5Me_4H)_3Lu$, **1**	120	2.406
$[(C_5Me_4H)_2Lu][(\mu\text{-}Ph)_2BPh_2]$, **2**	133.4	2.301, 2.302
$[(C_5Me_5)_2LuMe]_2$[20,21]	135.9, 138.8	2.278, 2.367
$[(C_5Me_5)_2Lu(\mu\text{-}S^tBu)_2Li(THF)_2]$[22]	131.5	2.364, 2.370
$(C_5Me_5)_2Lu[O(CH_2)_4C_5Me_5](THF)$[23]	136.1	2.362, 2.363
$[(C_5Me_4H)_2(THF)Lu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **3**	129.9	2.369, 2.385

Ph)$_2$BPh$_2$]/KC$_8$ combination to make [(C$_5$Me$_4$H)$_2$(THF)Lu]$_2$(μ-η^2:η^2-N$_2$) in 80% yield, eq 7.



(7)

Structural Studies. (C$_5$Me$_4$H)$_3$Lu was characterized by X-ray crystallography to confirm its existence and structure, Figure 1. The precursor, [(C$_5$Me$_4$H)$_2$Lu][(μ-Ph)$_2$BPh$_2$], **2**, was also structurally characterized, Figure 2, to confirm its identity, to provide comparisons with (C$_5$Me$_4$H)$_3$Lu, and to evaluate the arene metal interactions likely on the basis of the structures of the [(C$_5$Me$_5$)$_2$M][(μ-Ph)$_2$BPh$_2$] complexes (M = Sm, U).[17,19] The structure of [(C$_5$Me$_4$H)$_2$(THF)Lu]$_2$(μ-η^2:η^2-N$_2$), **3**, also provides comparisons with **1**. Accordingly, the structures of **2** and **3** are discussed first. Selected metrical parameters for all of these complexes are compared with those in other lutetium metallocene complexes in Table 6.[20−24]

The [(C$_5$Me$_4$H)$_2$Lu]$^+$ moiety in **2** has structural parameters typical of lanthanide metallocenes.[24] For example, the 133.4° (C$_5$Me$_4$H ring centroid)−Lu−(C$_5$Me$_4$H ring centroid) angle and 2.301 and 2.302 Å metal centroid distances are in the normal range. The Lu−C(C$_5$Me$_4$H) bond distances range from 2.520(2) to 2.673(2) Å and average 2.598(2) Å.

As in other [(C$_5$R$_5$)$_2$M][(μ-Ph)$_2$BPh$_2$] complexes,[17,19] two of the aryl rings of the [(μ-Ph)$_2$BPh$_2$]$^-$ anion in **2** are oriented toward the metal. The closest approach of ring C(20)−C(25) involves C(20) and C(21) with Lu−C distances of 2.668(2) and 2.947(2) Å. The other ring has analogous distances of 2.800(2) and 3.237(2) Å for C(26) and C(27), respectively. These distances are long compared to the Lu−C(C$_5$R$_5$) ring distances given above and are more similar to lanthanide arene distances in (C$_6$H$_5$Me)Yb(AlCl$_4$)$_3$,[25] 2.78(1) to 2.92(2) Å, and in Lu(OC$_6$H$_3$Ph$_2$-2,6)$_3$,[26] 2.787(8) to 3.087(12) Å. The pattern of metal arene interactions observed in **2** was also found in [(C$_5$Me$_5$)$_2$Sm][(μ-Ph)$_2$BPh$_2$][17] (2.825(3) and 3.059(3) Å from one ring, 2.917(3) and 3.175(3) Å from the other) and in [(C$_5$Me$_5$)$_2$U][(μ-Ph)$_2$BPh$_2$][19] (2.880(7) and 3.166(8) Å from one ring and 2.857(7) and 3.138(8) Å from the other).

The metallocene parameters in [(C$_5$Me$_4$H)$_2$(THF)Lu]$_2$(μ-η^2:η^2-N$_2$) are similar to those in **2**, as shown in Table 6. The Lu−N distances in **3**, 2.290(6) and 2.311(6) Å, are similar to those in {[(Me$_3$Si)$_2$N](THF)Lu}$_2$(μ-η^2:η^2-N$_2$),[3] 2.241(2) and 2.272(2) Å.

(C$_5$Me$_4$H)$_3$Lu has a trigonal planar arrangement of (C$_5$Me$_4$H)$^-$ ligands around Lu and is isomorphous with (C$_5$Me$_4$H)$_3$Tb.[1,27] The 2.406 Å Lu−(C$_5$Me$_4$H ring centroid) distance is shorter than the 2.445 Å value in the Tb complex as expected on the basis of the difference in ionic radii of the nine coordinate ions, 0.063 Å.[28] As shown in Tables 2−4, the Lu−C(1) and Lu−C(2) distances in **1** are long compared to the others in **1**−**3**. They are most distant from the hydrogen-substituted C(4) and lead to a tilt of the rings that minimizes steric crowding. As a consequence, (C$_5$Me$_4$H)$_3$Lu is not in the class of sterically crowded complexes that display unusual cyclopentadienyl reactivity.

Conclusion

The (C$_5$Me$_4$H)$_3$Ln complex of the smallest member of the lanthanide series, Lu, is synthetically accessible and has the same structure as its analogues. It displays bond distances and (C$_5$Me$_4$H)$^-$ reactivity typical of other lutetium metallocenes and is not sterically crowded. Treatment of (C$_5$Me$_4$H)$_3$Lu with K under nitrogen provides [(C$_5$Me$_4$H)$_2$(THF)Lu]$_2$(μ-η^2:η^2-N$_2$) in good yield, but a more efficient route uses [(C$_5$Me$_4$H)$_2$Lu][(μ-Ph)$_2$BPh$_2$] as a precursor. These reactions provide for the first time an analogous pair of (N=N)$^{2-}$ complexes of La^{3+} and Lu^{3+}.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, complete bond distances, and angles (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM050709K

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