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Neutral Monocyclopentadienyllutetium Alkyls: In Search of Steric Unsaturation

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Addition of a THF solution of NaC_5Me_5 (1 equiv) to a refluxing THF solution of $LuCl_3(THF)_3$ affords after workup $[Na(THF{\cdot}OEt_2)]Lu(\eta^5\text{-}C_5Me_5)Cl_3$ (**1**) in ca. 70% yield. Compound **1** reacts cleanly with $LiCH(SiMe_3)_2$ in diethyl ether, in the presence of THF (5 equiv) to afford the monoalkyl complex $[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2$ (**2**) in 69% yield. Addition of tetramethylethylenediamine (TMEDA) to the supernatant liquor after isolation of **2** affords an additional 16% of $[Li(TMEDA)]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2$ (**3**). A LiCl-free, mixed alkyl complex, **8**, was prepared from reaction of **3** with $LiCH_2SiMe_3$ giving initially a mixture of $[Li(THF)_3]Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}Cl$ (**7**) and $Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)$ (**8**). Recrystallization (once) from hexane gave neutral, LiCl-free **8**. This is the first reported neutral "mixed" alkyl organolanthanide complex. The single-crystal X-ray structure determinations of **3** and **7** are reported. In each case the lutetium atom shows a three-legged piano-stool coordination geometry, with the lithium atom in a tetrahedral coordination and linked to the lutetium by one (in **7**) or two (in **3**) bridging chloride ligands. The lutetium–alkyl bond lengths are 2.367 (6) Å in **3** and 2.394 (16) and 2.344 (18) Å for $Lu{-}CH(SiMe_3)_2$ and 2.353 (17) and 2.314 (18) Å for $Lu{-}CH_2SiMe_3$ for the two distinct molecules of **7**, present in the crystal.

Introduction

The recent growth in organolanthanide chemistry has produced a wealth of fascinating reactions including propylene oligomerization,[1] methane transmetalation,[2] and β-methyl elimination[3] by $Lu(\eta^5\text{-}C_5Me_5)_2Me$. Furthermore $[M(\eta^5\text{-}C_5Me_5)_2H]_2$ (M = La, Nd, Lu) have been shown to be excellent olefin hydrogenation and ethylene oligomerization catalysts.[4]

Despite this recent increase of interest in organolanthanide chemistry few[5-15] monoligand-supported lanthanide complexes have been prepared. Limitations to the potential scope of bis(pentamethylcyclopentadienyl) lanthanide species may exist, however, in that they possess only one reactive metal–carbon or metal–hydride bond. In seeking new catalytic hydrocarbon and alkene transformations we rationalized that neutral, salt- and solvent-free organolanthanide alkyl complexes containing only *one* supporting cyclopentadienyl ligand[8-11] would allow greater flexibility in their reactivity toward simple alkenes. We have recently reported the synthesis and X-ray structure determinations of $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2$ and $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2(THF)$[8] and the synthesis of the former compound's cerium congener has also been briefly described.[9] Additionally, the synthesis of mixed bis(alkyl) complexes of the type $Lu(\eta^5\text{-}C_5Me_5)R'R''{\cdot}L$ would allow the generation of a chiral lutetium center. We report here our approach toward these goals in organolutetium chemistry.

Experimental Section

All compounds are extremely sensitive to air and moisture, and therefore all manipulations were performed under either argon by using standard Schlenk techniques or in a nitrogen-filled drybox. Anhydrous $LuCl_3$ was purchased from Cerac Inc., Milwaukee, WI. Elemental analyses were performed at Analytische Laboratorien, Elbach, Germany, or at the University of Groningen, Groningen, The Netherlands, under the supervision of A. F. Hamminga. For the more unstable, salt-free complexes we have sometimes observed low carbon analysis. We ascribe this either to partial decomposition in transit or to the metal-catalyzed formation of silicon carbide, which does not burn completely during combustion analysis. $LuCl_3(THF)_3$ was always preisolated prior to use by Soxhlet extraction of $LuCl_3$ with THF. The alkylating agents $LiCH_2CMe_3$, $LiCH_2SiMe_3$, and $MCH(SiMe_3)_2$ (M = Li, K) were isolated prior to use as white powders and stored in the drybox. Nuclear magnetic resonance spectroscopy were recorded on Varian XL-200 (200 MHz, ^1H) and Varian VXR-300 (300 MHz, ^1H, or 75 MHz, ^{13}C) spectrometers. Chemical shifts are reported in parts per million and referenced to the residual protons in deuteriated solvents. Coupling constants are quoted in hertz. Obvious multiplicities and routine couplings are not listed. Solvents were P.A grade and were distilled from sodium benzophenone ketyl under argon prior to use. Deuteriated solvents were dried over activated 4-Å molecular sieves. All isolated organolutetium complexes were white in color.

Preparation of $[Na(THF{\cdot}OEt_2)]Lu(\eta^5\text{-}C_5Me_5)Cl_3$ (1). To a refluxing solution of 7.5 g (15.08 mmol) of $LuCl_3(THF)_3$ in 250 mL of THF was slowly added 2.2 g (13.87 mmol) of NaC_5Me_5 in 150 mL of THF, and the solution refluxed for 16 h. After being

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cooled to room temperature, the solution was filtered and the filtrate evaporated until almost dry (ca. 3 mL of THF remained), whereupon 120 mL of ether was added. Compound **1** precipitates as a white powder that was isolated by filtration to give 5.7 g (9.77 mmol, 70%) of **1**, which was used without further purification. A small quantity (5%) of [Na(THF)$_2$]Lu(η^5-C$_5$Me$_5$)$_2$Cl$_2$ is observed in the crude reaction mixture, which remained in the diethyl ether solution on crystallization of the product. The product is very slightly contaminated with what we believe to be the binuclear species Lu$_2$(η^5-C$_5$Me$_5$)Cl$_5$(THF)$_2$, in which unreacted LuCl$_3$(THF)$_2$ acts as a Lewis base, instead of NaCl(THF)$_2$, to a Lu(η^5-C$_5$Me$_5$)Cl$_2$ fragment.

An alternative workup procedure that gave a purer product but only in 20–50% yield involved cooling of the crude reaction mixture to room temperature and evaporation until only ca. 10 mL of THF remained, followed by addition of ether. The solution was *rapidly* filtered to remove residual solvated LuCl$_3$ and NaCl. When the clear filtrate was allowed to stir for 10–20 min, **1** precipitated as a white crystalline powder.

If the residual solid obtained after evaporation of the THF from the crude reaction mixture was extracted with a noncoordinating solvent such as toluene, a large amount of material that was inert to further reactions and insoluble in THF was obtained. We assume this to be a dimeric or polymeric species based on [Lu(η^5-C$_5$Me$_5$)Cl$_2$]$_n$. In the absence of coordinating solvents **1** slowly decomposed to ill-defined products. ^{1}H NMR (THF-d_8, 25 °C): δ 2.01 (C$_5$Me$_5$).

Preparation of Lu(η^5-C$_5$Me$_3$Ph$_2$)Cl$_2$(THF)(OEt$_2$) (1a). To a refluxing solution of 4.6 g (9.25 mmol) LuCl$_3$(THF)$_3$ in 300 mL of THF was slowly added 2.58 g (9.25 mmol) of NaC$_5$Me$_3$Ph$_2$ dissolved in 100 mL of THF. The solution was refluxed for 5 h. After being cooled, the mixture was filtered and the solvent removed in vacuo until ca. 3 mL of THF remained. The resulting yellow-brown oily solid was stirred vigorously with 150 mL of hexane and 5 mL of diethyl ether to give 3.7 g (5.68 mmol, 61%) of Lu(η^5-C$_5$Me$_3$Ph$_2$)Cl$_2$(THF)(OEt$_2$): ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.61 (4 H, d, H$_o$), 7.45 (4 H, t, H$_m$), 7.27 (2 H, d, H$_p$), 3.72 (4 H, m, THF), 3.50 (4 H, q, OEt$_2$), 2.48 (6 H, s, 2Me), 2.39 (3 H, s, Me), 1.87 (4 H, m, THF), 1.22 (6 H, t, OEt$_2$). Anal. Calcd for C$_{28}$H$_{35}$O$_2$Cl$_2$Lu: C, 51.61; H, 5.68; Cl, 10.91; Lu, 26.88; Na, 0.0. Found: C, 50.26; H, 5.38; Cl, 10.74; Lu, 26.55; Na, 0.08.

Preparation of [Li(THF)$_2$]Lu(η^5-C$_5$Me$_5$){CH(SiMe$_3$)$_2$}Cl$_2$ (2) and [Li(TMEDA)]Lu(η^5-C$_5$Me$_5$){CH(SiMe$_3$)$_2$}Cl$_2$ (3). To a suspension of 4.34 g (7.44 mmol) of **1** in 200 mL of hexane and 1.5 mL of THF at 20 °C was added 1.23 g (7.4 mmol) of LiCH(SiMe$_3$)$_2$ in 100 mL of hexane. After being stirred for 2 h, the mixture was concentrated to ca. 150 mL and the solution filtered. Further concentration of the solution to 40 mL and cooling to −70 °C gave 3.5 g (5.07 mmol, 69%) of **2** as a white powder. Addition of 387 mg (3.3 mmol) of TMEDA to the remaining supernatant liquor and cooling to −70 °C gave an additional 0.8 g (1.21 mmol, 16%) of [Li(TMEDA)]Lu(η^5-C$_5$Me$_5$){CH(SiMe$_3$)$_2$}Cl$_2$ (**3**). **2**: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 3.48 (8 H, m, THF), 2.31 (15 H, s, C$_5$Me$_5$), 1.32 (8 H, m, THF), 0.49 (18 H, s, SiMe$_3$), −0.26 (1 H, s, CH). Anal. Calcd for C$_{25}$H$_{50}$LiO$_2$Cl$_2$Si$_2$Lu: C, 43.49; H, 7.28; Cl, 10.25; Lu, 25.30; Li, 1.00. Found: C, 43.41; H, 6.92; Cl, 10.39; Lu, 25.25; Li, 0.93. **3**: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 2.29 (15 H, s, C$_5$Me$_5$), 1.90 (12 H, s, NMe$_2$), 1.57 (4 H, s, CH$_2$), 0.49 (18 H, s, SiMe$_3$), −0.22 (1 H, s, CH); ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 119.2 (C$_5$Me$_5$), 57.1 (CH$_2$N), 45.8 (NMe$_2$), 39.7 {d, ^1J(CH) = 93 Hz, *C*H}, 12.0 (C$_5$*Me*$_5$), 5.6 (SiMe$_3$).

Preparation of [Li(THF)$_2$]Lu(η^5-C$_5$Me$_5$)(CMe$_3$)$_2$Cl (4) and Lu(η^5-C$_5$Me$_5$)(CMe$_3$)$_2$(THF). To a refluxing solution of 1.94 g (3.9 mmol) of LuCl$_3$(THF)$_3$ in 200 mL of THF was slowly added a solution of 660 mg (4.18 mmol) of NaC$_5$Me$_5$ in 50 mL of THF. After being refluxed for 2 h, the solution was cooled to −78 °C and 5.6 mL of a 1.4 M (7.8 mmol) Li^{t}Bu solution added. The reaction mixture was slowly allowed to warm to 25 °C and then filtered. The solvent was removed under vacuum and the residue dissolved in hexane and filtered to remove any remaining solids. Workup involved dissolution of the mixture in hexane, centrifugation, and decanting of the supernatant liquor. Removal of the solvent under vaccum affords a mixture of **4** and Lu(η^5-C$_5$Me$_5$)(CMe$_3$)$_2$(THF). **4**: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 2.43 (C$_5$Me$_5$), 1.58 (CMe$_3$); ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 115.9 (C$_5$Me$_5$), 68.0 (THF), 48.1 (*C*Me$_3$), 33.4 (C*Me*$_3$), 24.4 (THF), 11.8 (C$_5$*Me*$_5$). Lu(η^5-C$_5$Me$_5$)(CMe$_3$)$_2$(THF): ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 2.06 (C$_5$Me$_5$), 1.30 (CMe$_3$); ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 117.1 (C$_5$Me$_5$), 70.3 (THF), 46.5 (CMe$_3$), 32.3 (CMe$_3$), 25.1 (THF), 11.3 (C$_5$Me$_5$). Data were extracted from mixtures of **4** and Lu(η^5-C$_5$Me$_5$)(CMe$_3$)$_2$(THF). Data for **4** are in agreement with those in the literature.[13]

Preparation of [Li(THF)$_2$]Lu(η^5-C$_5$Me$_5$)(CH$_2$CMe$_3$)$_2$Cl (5) and Lu(η^5-C$_5$Me$_5$)(CH$_2$CMe$_3$)$_2$·THF (6). To a refluxing solution of 540 mg (1.09 mmol) of LuCl$_3$(THF)$_3$ in 100 mL of THF was slowly added a solution of 171 mg (1.08 mmol) of NaC$_5$Me$_5$ in 30 mL of THF. After being refluxed for 2 h, the solution was cooled to −78 °C and 168 mg (2.15 mmol) of LiCH$_2$CMe$_3$ added. The reaction mixture was slowly allowed to warm to 25 °C and then filtered. The solvent was removed under vacuum and the residue dissolved in hexane and filtered to remove any remaining solids. Workup involved dissolution of the mixture in hexane, centrifugation, and decantation of the supernatant liquor from the remaining solids. Removal of the solvent under vacuum affords a mixture of **5** and **6**. This procedure was repeated several times (ca. 10) to finally yield LiCl-free **6** in ca. 10% yield. Due to its thermal instability the yield of **6** and its degree of contamination by **5** are dependent on the number of repetitions of this purification procedure. **6**: ^{1}H NMR δ 2.11 (15 H, s, C$_5$Me$_5$), 1.36 (18 H, s, CMe$_3$), 0.15 (4 H, s, CH$_2$); ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 116.6 (C$_5$Me$_5$), 74.9 {t, ^1J(CH) = 100 Hz, CH$_2$}, 70.3 (THF), 37.0 (*C*Me$_3$), 35.4 (C*Me*$_3$), 24.9 (THF), 11.5 (C$_5$Me$_5$). Rapid LiCl exchange in solutions containing both **5** and **6** gave broadened NMR spectra; thus no spectrum of pure **5** could be obtained. Chloride analysis indicates ca. 14% of the LiCl adduct **5** to be present in this particular analysis sample (after three recrystallizations). Calcd for C$_{24}$H$_{45}$OLu: C, 54.95; H, 8.64; Lu, 33.35. Found: C, 50.5; H, 7.99; Cl, 1.2; Lu, 36.5.

Preparation of [Li(THF)$_3$]Lu(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$){CH(SiMe$_3$)$_2$}Cl (7) and Lu(η^5-C$_5$Me$_5$)(CH$_2$SiMe$_3$){CH(SiMe$_3$)$_2$}(THF) (8). To 2.5 g (3.62 mmol) of [Li(THF)$_2$]Lu(η^5-C$_5$Me$_5$){CH(SiMe$_3$)$_2$}Cl$_2$ (**2**) dissolved in 150 mL of diethyl ether at 20 °C was added 340 mg (3.62 mmol) of LiCH$_2$SiMe$_3$ in 25 mL of diethyl ether. After the solution was stirred for 1 h, the solvent was removed in vacuo and 50 mL of hexane added. Filtration, concentration of the solution, and cooling yielded 1.81 g (2.89 mmol, 79%) of **8** contaminated with a small amount of the LiCl adduct **7**. Recrystallization from hexane gave pure **8**. **8**: ^{1}H NMR (C$_7$D$_8$, 25 °C) δ 3.88 (4 H, m, THF), 2.07 (15 H, s, C$_5$Me$_5$), 1.29 (4 H, s, THF), 0.24 {18 H, br, CH(Si*Me*$_3$)$_2$}, 0.17 (9 H, s, CH$_2$Si*Me*$_3$), −0.89 (1 H, s, CH), CH$_2$ not found; ^{1}H NMR (C$_7$D$_8$ −65 °C) δ 3.68 (4 H, m, THF), 2.00 (15 H, s, C$_5$Me$_5$), 1.00 (4 H, s, THF), 0.41 (9 H, s, SiMe$_3$), 0.20 (9 H, s, CH$_2$SiMe$_3$), 0.18 (9 H, s, Si*Me*$_3$), −0.33 {1 H, d, ^2J(HH) = 11.6 Hz, C*H*$_2$}, −0.82 (1 H, s, C*H*), −0.86 {1 H, d, ^2J(HH) = 11.6 Hz, C*H*$_2$}; ^{13}C NMR (C$_6$D$_6$, 25 °C) δ 117.9 (C$_5$Me$_5$), 70.6 (THF), 41.9 {t, ^1J(CH) = 100 Hz, CH$_2$}, 37.2 {d, ^1J(CH) = 88 Hz, CH}, 25.0 (THF), 12.0 (C$_5$Me$_5$), 5.7 {CH(Si*Me*$_3$)$_2$}, 5.2 (CH$_2$Si*Me*$_3$). Anal. Calcd for C$_{25}$H$_{53}$OSi$_3$Lu: C, 47.75; H, 8.50; Si, 13.4; Lu, 27.82. Found: C, 46.60; H, 8.00; Si, 10.25; Lu, 32.50. The low silicon content suggests loss of SiMe$_4$. Calcd for C$_{21}$H$_{41}$OSi$_2$Lu: C, 46.57; H, 7.92; Si, 10.15; Lu, 32.45. Another analysis of this compound gave the following: C, 47.96; H, 8.56.

Preparation of [K(OEt$_2$)$_{0.5}$]Lu(η^5-C$_5$Me$_3$Ph$_2$){CH(SiMe$_3$)$_2$}Cl$_2$ (9). To a suspension of 1.10 g (1.69 mmol) of **1a** in 100 mL of hexane and 1.0 mL of THF in a double Schlenk tube at −78 °C was added 0.33 g (1.67 mmol) of KCH(SiMe$_3$)$_2$ in 30 mL of ether. After being stirred for 0.5 h at −78 °C the mixture was allowed to warm to 22 °C where it was stirred for an additional 2 h. The solvent was then removed under vacuum and the resulting white solid washed with 25 mL of hexane. The remaining solid was extracted with a mixture of 150 mL of hexane and 20 mL of ether and filtered and the solvent evaporated to dryness. This solid was dissolved in 30 mL of hexane, 1 mL of THF, and 20 mL of ether and the solvent mixture slowly removed under vacuum whereupon [K(THF)]Lu(η^5-C$_5$Me$_3$Ph$_2$){CH(SiMe$_3$)$_2$}Cl$_2$ crystallized from solution and was isolated by filtration. Recrystallization from ether afforded [K(OEt$_2$)$_{0.5}$]Lu(η^5-C$_5$Me$_3$Ph$_2$){CH(SiMe$_3$)$_2$}Cl$_2$. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.68 (4 H, d, H$_o$), 7.31 (4 H, t, H$_m$), 7.10 (2 H, d, H$_p$), 3.27 (2 H, q, OEt$_2$), 2.51 (3 H, s, Me), 2.50 (6 H, s, 2Me), 1.11 (3 H, t, OEt$_2$) 0.411 (18 H, s, SiMe$_3$), −0.379 (1 H, s, CH). Anal. Calcd for C$_{27}$H$_{38}$Cl$_2$KLuSi$_2$: C, 46.08; H, 5.40; Cl, 10.1; K, 5.55; Lu, 24.89; Si, 7.96. Found: C, 44.98; H, 5.48; Cl, 10.76; K, 6.07; Lu, 24.10;

Si, by difference 8.61. The sample apparently did not contain ether on analysis.

Preparation of $\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_3Ph_2})(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})$ (10). To 0.24 g (0.369 mmol) of **1a** dissolved in 20 mL of benzene at 20 °C, was added 93 mg (2 equiv) of $\mathrm{KCH_2SiMe_3}$ in 10 mL of benzene. After the solution was stirred for 0.5 h, the solvent was removed in vacuo to give a slightly off-white solid/foam. This was extracted with 40 mL of hexane. Filtration and evaporation of the colorless solution afforded **10**. Attempts at crystallization failed due to its high solubility in hexane. ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C): δ 7.68 (4 H, d, $\mathrm{H_o}$), 7.31 (4 H, t, $\mathrm{H_m}$), 7.10 (2 H, d, $\mathrm{H_p}$), 3.30 (4 H, m, THF), 2.45 (3 H, s, Me), 2.25 (6 H, s, 2Me), 0.903 (4 H, m, THF), 0.261 (18 H, s, $\mathrm{SiMe_3}$), −0.610 (4 H, s, $\mathrm{2CH_2}$). As we have no good analysis for **10**, we cannot be absolutely certain that it is KCl-free.

X-ray Structure Analysis for $[\mathrm{Li(TMEDA)}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})\{\mathrm{CH(SiMe_3)_2}\}\mathrm{Cl_2}$ (3) and $[\mathrm{Li(THF)_3}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{CH_2SiMe_3})\{\mathrm{CH(SiMe_3)_2}\}\mathrm{Cl}$ (7). Single crystals of **3** and **7** were mounted under nitrogen in thin-walled glass capillaries in a drybox and held in place by using silicone grease. That for **7** was an irregular block cleaved from a larger crystal that had substantially lost crystallinity (presumably through loss of THF) during storage. All diffraction experiments were carried out at 200 K on a Nicolet four-circle diffractometer fitted with a LT-1 crystal cooling device using graphite-monochromated Mo Kα X-radiation (λ = 0.710 69 Å). Unit cell dimensions were determined from 23 and 17 centered reflections in the ranges $29.0° < 2\theta < 31.0°$ and $29.5° < 2\theta < 30.0°$ for **3** and **7**, respectively, and confirmed by partial rotation photographs taken about the *a*, *b*, and *c* axis. Details of crystal data collection and reduction are given in Table III. Data collection for **7** was terminated at $2\theta = 40°$ following partial decomposition and inadvertent destruction of the crystal. No absorption correction or high angle data collection for **7** was therefore possible. The absorption correction for **3** was based on 272 azimuthal scan data, maximum and minimum transmission coefficients being 0.258 and 0.165, respectively. Structure solution was by conventional heavy atom (Patterson and difference Fourier methods) and refinement by blocked-cascade full-matrix least squares (with weights w set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics). All hydrogen atoms were assigned idealized geometries (C–H = 0.96 Å; H–C–H = 109.5°) and fixed isotropic displacement parameters, except for the $C\mathrm{H(SiMe_3)_2}$ hydrogen of **3** which was refined without positional constraints. Residuals of convergence are listed in Table III. Final difference electron density maps show their largest features near the metal atoms. For **7** the size and anisotropy of the anisotropic displacement parameters for the $\mathrm{C_5Me_5}$ ligand attached to Lu(2) and some of the THF ligands are indicative of disorder. Given the limited resolution of the data it is not surprising that it was not possible to model such disorder by distinct multiple sites for the atoms involved. The large features in the final difference map for **7** are a consequence of the lack of an absorption correction, coupled with partial crystal decomposition. The quality of the data is further reflected in the size of the esd's in parameter values for **7**. Listings of the non-hydrogen coordinates are provided in Tables I and II for **3** and **7**, respectively. All calculations were carried out with Nicolet proprietary software using complex scattering factors taken from ref 16.

Results and Discussion

Synthesis of Monocyclopentadienyl- and Indenyllutetium Complexes. Reaction of $\mathrm{LuCl_3}$ with $\mathrm{LiC_5Me_5}$ in refluxing THF has been previously reported[15] to afford $[\mathrm{Li(OEt_2)_2}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{Cl_2}$ in 40% isolated yield. The monopentamethylcyclopentadienyl species $[\mathrm{Li(OEt_2)}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cl_3}$ was occasionally isolated in low yield from this reaction mixture.

Table I. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 3

	x	*y*	*z*	*U*(eq)[a]
Lu	2184 (1)	7678 (1)	434 (1)	22 (1)
Cl(1)	933 (2)	8912 (1)	92 (1)	30 (1)
Cl(2)	2689 (2)	7991 (1)	1817 (1)	31 (1)
Si(1)	−1281 (2)	7011 (1)	−691 (1)	30 (1)
Si(2)	132 (2)	6287 (1)	926 (1)	29 (1)
C(1)	389 (7)	6752 (4)	102 (4)	23 (2)
C(2)	−2536 (9)	7610 (5)	−392 (5)	45 (3)
C(3)	−791 (9)	7520 (4)	−1438 (4)	37 (3)
C(4)	−2382 (11)	6207 (5)	−1211 (5)	58 (4)
C(5)	1918 (8)	5938 (5)	1583 (4)	38 (3)
C(6)	−665 (8)	6906 (4)	1477 (4)	37 (3)
C(7)	−1107 (9)	5463 (5)	672 (5)	44 (3)
C(8)	4537 (8)	7000 (4)	490 (4)	35 (3)
C(9)	4977 (7)	7702 (5)	781 (4)	34 (2)
C(10)	4424 (7)	8214 (4)	177 (4)	30 (2)
C(11)	3644 (7)	7842 (4)	−475 (4)	29 (2)
C(12)	3690 (8)	7087 (4)	−307 (4)	37 (3)
C(13)	4973 (11)	6295 (6)	897 (6)	66 (4)
C(14)	5984 (8)	7888 (5)	1588 (4)	46 (3)
C(15)	4703 (9)	9030 (4)	225 (6)	48 (3)
C(16)	2983 (9)	8179 (6)	−1263 (5)	59 (4)
C(17)	3194 (9)	6488 (5)	−852 (6)	55 (4)
Li	1641 (12)	9142 (7)	1410 (7)	31 (4)
N(1)	−20 (6)	9519 (3)	1728 (3)	27 (2)
N(2)	2923 (6)	10016 (3)	1914 (3)	33 (2)
C(18)	458 (8)	10276 (4)	1945 (4)	33 (3)
C(19)	2076 (8)	10316 (4)	2370 (4)	37 (3)
C(20)	−1470 (8)	9517 (4)	1138 (4)	37 (3)
C(21)	−116 (10)	9098 (5)	2369 (5)	47 (3)
C(22)	4412 (8)	9828 (5)	2415 (5)	46 (3)
C(23)	2996 (10)	10546 (5)	1353 (5)	50 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In order to obtain an effective entry into monocyclopentadienyllutetium chemistry we hypothesized that use of homogeneous conditions would enable us to direct the reaction to a monocyclopentadienyllutetium species rather than to $[\mathrm{Li(OEt_2)_2}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{Cl_2}$,[15] previously prepared by use of insoluble $\mathrm{LiC_5Me_5}$. Thus, addition of a THF solution of $\mathrm{NaC_5Me_5}$ (1 equiv) to a refluxing THF solution of $\mathrm{LuCl_3(THF)_3}$ affords, after workup with ether, $[\mathrm{Na(THF{\cdot}OEt_2)}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cl_3}$ (1) in up to 70% yield. It is necessary to preisolate $\mathrm{LuCl_3(THF)_3}$ by Soxhlet extraction of $\mathrm{LuCl_3}$ with THF. In situ generation of the THF adduct yields a product that proved to be unsuitable in the synthesis of **1**.

$$\mathrm{LuCl_3(THF)_3} + \mathrm{NaC_5Me_5} \rightarrow \underset{\mathbf{1}}{[\mathrm{Na(THF{\cdot}OEt_2)}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cl_3}} \qquad (1)$$

We have attempted to extend the range of ligands known to support organolanthanide complexes from the ubiquitous, but very useful and versatile pentamethylcyclopentadienyl ligand. These efforts were not particularly successful although we were able to prepare the monoligand-substituted precursors. For example, reaction of $\mathrm{LuCl_3(THF)_3}$ with (1,3-diphenyl-2,4,5-trimethylcyclopentadienyl)sodium[17] in THF affords salt-free $\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_3Ph_2})\mathrm{Cl_2(THF)_2}$. Reaction of (neopentyltetramethylcyclopentadienyl)sodium with $\mathrm{LuCl_3(THF)_3}$ in THF followed by treatment with diethyl ether resulted in a mixture of products.[18] However, in subsequent reactions these behaved as would be expected for a $[\mathrm{Na(L_2)}]\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5Me_4CH_2CMe_3})\mathrm{Cl_3}$ (L = THF or $\mathrm{Et_2O}$) type species. The related 1,3-diphenyl-2-methylindenyl[17b] (Ind″) complex could not be prepared in THF. Instead it was prepared by reacting $\mathrm{LuCl_3(THF)_3}$ with 1 equiv of KInd″ in toluene at 25 °C. A small quantity of a toluene/THF

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(16) *International Tables for X-ray Crystallography*; Vol IV, 1974, Kynoch Press: Birmingham, England, 1974, Vol. IV.

(17) Prepared by modification of a literature procedure. *Org. Synth.* **1978**; *58*, 56. (b) Miller, W. G.; Pittman, C. U., Jr. *J. Org. Chem.* **1974**, *39*, 1955.

(18) Van der Heijden, H.; Pasman, P.; De Boer, E. J. M.; Schaverien, C. J., unpublished results.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 7

	x	y	z	U(eq)^a		x	y	z	U(eq)^a
Lu(1)	1071 (1)	2020 (1)	490 (1)	27 (1)	C(46)	4957 (12)	1394 (15)	−407 (14)	154 (18)
Lu(2)	6354 (1)	2241 (1)	560 (1)	34 (1)	C(47)	5950 (21)	2113 (11)	−1124 (10)	181 (24)
Cl(1)	1882 (3)	1515 (3)	1389 (2)	62 (2)	C(48)	7401 (16)	1701 (16)	−535 (18)	209 (25)
Cl(2)	7173 (3)	1962 (3)	1539 (2)	59 (2)	C(49)	7294 (19)	662 (18)	530 (15)	238 (25)
Si(1)	574 (3)	2913 (3)	1807 (3)	50 (2)	C(50)	5773 (20)	487 (12)	680 (11)	199 (27)
Si(2)	394 (3)	3741 (3)	556 (3)	63 (3)	C(51)	6684 (9)	3312 (9)	187 (9)	50 (8)
Si(3)	2679 (3)	2754 (3)	247 (3)	61 (2)	C(52)	5418 (9)	2301 (10)	1016 (9)	52 (8)
Si(4)	7488 (3)	3668 (3)	588 (2)	46 (2)	C(53)	8194 (10)	3006 (11)	627 (9)	71 (10)
Si(5)	6044 (3)	3936 (3)	−127 (2)	51 (2)	C(54)	7802 (10)	4501 (10)	245 (10)	72 (10)
Si(6)	5179 (3)	2890 (3)	1607 (3)	58 (2)	C(55)	7467 (11)	3913 (10)	1421 (8)	66 (9)
O(1)	1922 (7)	−72 (7)	2245 (6)	61 (6)	C(56)	5987 (11)	4655 (10)	469 (10)	75 (10)
O(2)	3235 (7)	326 (7)	1783 (7)	64 (6)	C(57)	5216 (10)	3563 (10)	−330 (9)	63 (9)
O(3)	2780 (8)	1161 (7)	2810 (6)	71 (6)	C(58)	6189 (12)	4423 (12)	−880 (10)	85 (11)
O(4)	6947 (8)	1261 (8)	2917 (7)	71 (7)	C(59)	4730 (11)	3682 (10)	1251 (10)	79 (10)
O(5)	8354 (7)	1134 (7)	2604 (6)	65 (6)	C(60)	4627 (11)	2431 (12)	2083 (10)	89 (11)
O(6)	7944 (7)	2574 (7)	3033 (6)	60 (6)	C(61)	5920 (11)	3218 (13)	2139 (10)	96 (12)
C(1)	937 (9)	1045 (8)	−369 (7)	32 (7)	C(70)	1289 (12)	−2 (11)	2438 (11)	84 (12)
C(2)	788 (10)	712 (9)	181 (9)	47 (8)	C(71)	881 (12)	−618 (13)	2191 (12)	88 (12)
C(3)	199 (9)	1020 (9)	301 (8)	38 (7)	C(72)	1383 (13)	−1145 (13)	2162 (13)	96 (13)
C(4)	−22 (8)	1507 (9)	−141 (8)	30 (7)	C(73)	2002 (13)	−797 (12)	2116 (15)	111 (15)
C(5)	411 (9)	1505 (9)	−571 (8)	37 (7)	C(74)	3894 (12)	393 (24)	2091 (13)	197 (25)
C(6)	1490 (10)	846 (10)	−686 (9)	60 (9)	C(75)	4334 (15)	206 (23)	1630 (15)	162 (22)
C(7)	1154 (10)	114 (10)	521 (9)	69 (9)	C(76)	3945 (15)	189 (15)	1075 (14)	114 (16)
C(8)	−127 (10)	760 (10)	836 (8)	63 (9)	C(77)	3270 (14)	79 (16)	1182 (15)	146 (18)
C(9)	−674 (9)	1888 (11)	−219 (10)	64 (9)	C(78)	2923 (17)	1888 (13)	2868 (13)	136 (16)
C(10)	338 (10)	1922 (10)	−1153 (8)	62 (9)	C(79)	3367 (22)	1949 (19)	3435 (14)	212 (26)
C(11)	454 (9)	2876 (9)	946 (8)	42 (7)	C(80)	3325 (22)	1341 (20)	3767 (13)	249 (28)
C(12)	1802 (9)	2610 (10)	−42 (7)	50 (8)	C(81)	2922 (16)	865 (14)	3381 (11)	119 (15)
C(13)	1414 (9)	3233 (10)	2157 (8)	60 (8)	C(82)	8629 (13)	878 (16)	2123 (11)	119 (15)
C(14)	−18 (11)	3485 (15)	2119 (10)	119 (14)	C(83)	9154 (13)	344 (13)	2364 (12)	97 (13)
C(15)	478 (13)	2032 (12)	2160 (10)	99 (12)	C(84)	9307 (15)	526 (18)	2986 (11)	134 (17)
C(16)	1184 (11)	4257 (11)	714 (9)	75 (10)	C(85)	8757 (14)	879 (15)	3149 (11)	111 (14)
C(17)	189 (15)	3644 (12)	−301 (10)	128 (15)	C(86)	6584 (24)	1428 (23)	3293 (25)	320 (41)
C(18)	−285 (15)	4333 (14)	765 (17)	178 (22)	C(87)	6051 (28)	991 (25)	3258 (24)	252 (42)
C(19)	3146 (9)	1942 (13)	322 (10)	86 (11)	C(88)	6069 (18)	503 (20)	2871 (22)	179 (25)
C(20)	2823 (10)	3164 (13)	1047 (9)	82 (10)	C(89)	6646 (29)	659 (20)	2664 (18)	254 (37)
C(21)	3094 (11)	3357 (14)	−238 (10)	104 (13)	C(90)	7576 (12)	3075 (13)	3325 (10)	79 (11)
C(41)	5691 (11)	1381 (11)	−234 (11)	58 (10)	C(91)	7921 (21)	3713 (17)	3359 (17)	184 (25)
C(42)	6115 (13)	1693 (9)	−562 (8)	45 (9)	C(92)	8510 (15)	3618 (16)	3150 (15)	121 (16)
C(43)	6771 (13)	1512 (13)	−323 (12)	63 (11)	C(93)	8566 (12)	2836 (15)	2968 (14)	112 (15)
C(44)	6748 (15)	1054 (13)	161 (12)	77 (12)	Li(1)	2463 (17)	351 (16)	2057 (13)	51 (13)
C(45)	6075 (16)	960 (10)	238 (10)	66 (11)	Li(2)	7607 (19)	1719 (18)	2580 (15)	64 (15)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

soluble complex, $[K(THF_x)]Lu(Ind'')Cl_3$ was isolated, the remainder being toluene/THF insoluble, possibly indicative of dimeric products, which could not be used in further reactions. Changes in the reaction conditions and/or solvent did not result in an improvement in yield.[18]

Use of these sterically more demanding cyclopentadienyl ligands did not result in significantly better behaved alkyllutetium complexes, although they did possess greater thermal stability. It appears that in monoligand-supported organolutetium chemistry cyclopentadienyl or, especially indenyl anions, can act as effective leaving groups, particularly if they possess anion stabilizing substituents. Thus, alkylation of $[K(THF_x)]Lu(Ind'')Cl_3$ with $KCH(SiMe_3)_2$ in hexane/ether results in the formation of KInd″ and also $[K(THF)]Lu\{CH(SiMe_3)_2\}_3Cl$. This species was identified by comparison of its NMR data with $KLu\{CH(SiMe_3)_2\}_3Cl$, which we have previously prepared and characterized.[19]

$$[K(THF_x)]Lu(Ind'')Cl_3 + 2KCH(SiMe_3)_2 \rightarrow KInd'' + [K(THF)]Lu\{CH(SiMe_3)_2\}_3Cl$$

Attempts to prepare a mono(3,5-dimethylpyrazolylborato)lutetium precursor that might be amenable to alkylation by reaction of $LuCl_3(THF)_3$ with 1 equiv of $KBH(3,5\text{-}C_3HN_2Me_2)_3$ were unsuccessful.

In further efforts, we rationalized that a monocyclopentadienyl species containing an additional chelating ligand would help to stabilize the lutetium center. Thus reaction of 1,2,3,4-tetramethylcyclopentenone with $Li(o\text{-}CH_2C_6H_4NMe_2)$ followed by the usual acidic workup procedure and deprotonation gave the new substituted cyclopentadienyl ligand $Li(o\text{-}C_5Me_4CH_2C_6H_4NMe_2)$.[18] Unfortunately, we were unable to cleanly isolate the anticipated cyclopentadienyllutetium complex. Teuben[20] has prepared a species containing a pyridine-substituted pentamethylcyclopentadienyl ligand that acts as a chelate to a titanium center, in $Ti(\eta^5\text{-}C_5Me_5)\{\eta^5\text{-}C_5Me_4CH_2C_5H_3(Me)N\}H$, by treatment of the tetramethylfulvene complex $Ti(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)$ with 2-methylpyridine. Bercaw and Shapiro have successfully prepared $Sc(C_5Me_4SiMe_2N^tBu)CH(SiMe_3)_2$, presumably via use of the dianion $Li_2(C_5Me_4SiMe_2N^tBu)$.[21] Use of a chelating side

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[19] Schaverien, C. J., unpublished results. For $[K(THF)]Lu\{CH(SiMe_3)_2\}_3Cl$: ^1H NMR (C_6D_6) δ 3.428 (THF), 1.375 (THF), 0.544 ($SiMe_3$), −0.662 (CH). For $KLu\{CH(SiMe_3)_2\}_3Cl$: ^1H NMR (C_6D_6) δ 0.578 ($SiMe_3$), −0.674 (CH). Anal. Calcd for $C_{21}H_{57}ClLuKSi_6$. C, 34.69; H, 7.84; K, 5.38. Found. C, 33.44; H, 7.41; K, 6.47.

[20] Pattiasina, J. W.; van Bolhuis, F.; Teuben, J. H. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 330.

[21] Shapiro, P. J.; Bercaw, J. E. Abstracts of Papers, 3rd Chemical Congress of North America, Toronto, 1988; INORG 584.

Table III. Crystal Data and Data Collection Parameters for 3 and 7

	3	7
	a. Crystal Data	
chemical formula	$C_{23}H_{50}Cl_2LiLuN_2Si$	$C_{33}H_{69}ClLiLuO_3Si_3$
mol wt	592.8	815.5
cryst system	monoclinic	monoclinic
space group, No.	$P2_1/c$, 14	$P2_1/c$, 14
a, Å	9.778 (2)	20.481 (8)
b, Å	18.374 (5)	19.178 (8)
c, Å	18.853 (4)	21.954 (7)
β, deg	110.28 (2)	100.06 (3)
V, Å^3	3177 (1)	8490 (5)
Z	4	8
D_{calcd}, g cm^{-3}	1.24	1.28
F(000), electrons	1351.7	3392
μ(Mo Kα), cm^{-1}	33.7	24.7
approx cryst dimen, mm	0.7 × 0.4 × 0.3	0.35 × 0.7 × 0.8
	b. Data Collection	
check reflctns	(1,3,12)	(4,3,14), (5,13,−2), (13,1,15)
cryst decay (%) during data collectn	0	5
$\theta/2\theta$ range	4.0° < 2θ < 50.0°	4.0° < 2θ < 40.0°
scan method	Wyckoff w	$\theta/2\theta$
total data	6151	8563
total unique data	5608	7954
obsd $I > 3\sigma(I)$	4399	5984
	c. Refinement	
no. of refined parameters	328	757
weighting factor, g	0.0003	0.0010
R	0.035	0.069
R_w	0.036	0.085
goodness of fit, S	1.59	2.02
min/max residual densities in final Fourier map, e/Å^3	−1.0, 0.7	−3.7, 2.6
max shift/esd in final cycle	0.06	0.14

chain containing an oxygen donor functionality rather than a dimethylamine group would clearly appear advantageous, given the known oxophilicity of these organolanthanide systems. So far we have been unable to synthesize the appropriately substituted pentamethylcyclopentadienyl ligand.

Because of the unexpected complications associated with these ligands we have consequently concentrated on the reactivity of $[Na(THF{\cdot}OEt_2)]Lu(\eta^5\text{-}C_5Me_5)Cl_3$ (1) and $Lu(\eta^5\text{-}C_5Me_3Ph_2)Cl_2(THF)_2$ (1a).

Synthesis of Alkyl Derivatives. Compound 1 reacts cleanly with $LiCH(SiMe_3)_2$ in diethyl ether in the presence of THF (5 equiv)[22] to afford the monoalkyl complex $[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2$ (2) in 69% yield (Scheme I). Addition of tetramethylethylenediamine (TMEDA) to the supernatant liquor after isolation of 2 affords an additional 16% of $[Li(TMEDA)]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2$ (3), the X-ray crystal structure of which was determined (Figure 1). Complex 3 displays, as well as resonances due to TMEDA and singlets for the C_5Me_5 and $SiMe_3$ protons at 2.29 and 0.49 ppm respectively, a resonance at −0.22 ppm attributable to the methyne proton. In the coupled ^{13}C NMR spectrum this methyne carbon occurs at 39.7 ppm with a carbon–hydrogen coupling constant of 93 Hz. This is indicative of some interaction with the electron-deficient lutetium center, even though coordinated LiCl(TMEDA) tends to reduce the electrophilicity of the lutetium center. However, X-ray structural data (vide infra) are inconclusive concerning the presence of such an interaction.

Scheme I

$$\underset{1}{[Na(THF{\cdot}OEt_2)]Lu(\eta^5\text{-}C_5Me_5)Cl_3} + LiCH(SiMe_3)_2 \rightarrow$$

$$\underset{2}{[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2} \xrightarrow{TMEDA}$$

$$\underset{3}{[Li(TMEDA)]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2}$$

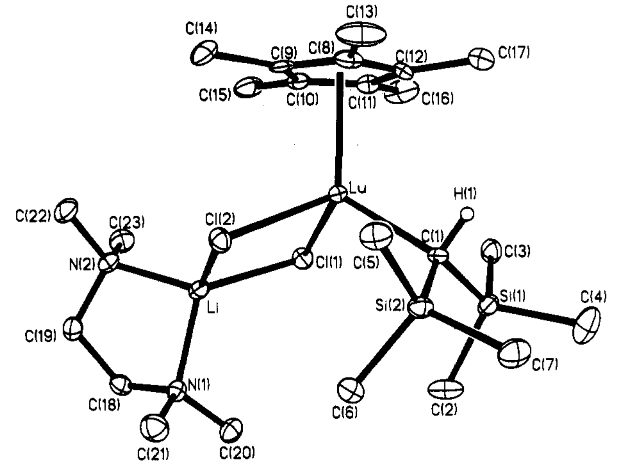

Figure 1. Molecular structure for 3 showing 30% probability ellipsoids with methyl and methylene hydrogen atoms omitted for clarity.

Coordinating solvents preferentially bind to coordinated LiCl or NaCl, if present, rather than the lutetium center. The propensity for LiCl dissociation and the thermal stability of the LiCl-free product depend strongly on the ligand environment around lutetium. For example, preparation of $[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)(CMe_3)_2Cl$[13] (4) could only be achieved by using in situ methodology; however, attempts to remove LiCl from 4 were thwarted due to the thermal instability of the LiCl-free product; thus $Lu(\eta^5\text{-}C_5Me_5)(CMe_3)_2(THF)$ could not be completely separated from 4 by successive recrystallizations. Similarly, reaction of 1 with $LiCH_2CMe_3$ (2 equiv; ether/THF, 99:1) affords a mixture of $[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2Cl$ (5) and $Lu(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2(THF)$ (6). Repeated (ca. 10 times) dissolution of the mixture in hexane and centrifugation to precipitate LiCl·THF, followed by decantation of the supernatant liquor and drying under vacuum affords LiCl-free $Lu(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2(THF)$ (6), albeit in significantly reduced yield, due to the latter's low thermal stability in solution at room temperature. In the presence of solvated LiCl, an equilibrium apparently exists between 5 and 6 in hexane. The limited solubility of LiCl·THF in hexane allows isolation of LiCl-free 6.

$$\underset{5}{[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2Cl} \rightleftarrows$$

$$\underset{6}{Lu(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2(THF)} + LiCl{\cdot}THF$$

Attempts at stabilizing the sterically unsaturated lutetium center with two bis(trimethylsilyl)methyl groups were unsuccessful because $[Li(THF{\cdot}OEt_2)]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2$ (2) does not react with $LiCH(SiMe_3)_2$ or is decomposed by $KCH(SiMe_3)_2$ to liberate $(Me_3Si)_2CH_2$ (ca. 1 equiv). Our inability to isolate a bis(alkyl) complex may be related to steric crowding in putative $Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2$, although we have reported the synthesis and structure of its lanthanum analogue.[8] An in situ reaction of $LuCl_3THF_3$ with NaC_5Me_5 followed by cooling to −78 °C and addition of $LiCH(SiMe_3)_2$ (2 equiv) gave a mixture containing $Lu\{CH(SiMe_3)_2\}_3THF_x$, $[Li(THF_x)]Lu\{CH$-

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[22] The presence of a small additional quantity of THF proved necessary.

$(SiMe_3)_2\}_4$, and ca. 30% (relative yield) of 2. There is no reaction between $Lu(\eta^5\text{-}C_5Me_5)_2CH(SiMe_3)_2$ and $LiCH(SiMe_3)_2$ indicating that this product distribution originates from a monocyclopentadienyllutetium precursor.[18]

Use of a less sterically demanding alkyl group enabled a LiCl-free, mixed alkyl complex 8 to be prepared from reaction of 3 with $LiCH_2SiMe_3$ to give a mixture of $[Li(THF)_3]Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}Cl$ (7) and $Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)$ (8). Compound 7 loses LiCl on dissolution in noncoordinating solvents; thus recrystallization of this mixture (once) from hexane gave neutral, LiCl-free 8 (see Scheme II). This represents the first reported neutral "mixed" alkyl organolanthanide complex.

Scheme II

$$\underset{\mathbf{1}}{[Na(THF{\cdot}OEt_2)]Lu(\eta^5\text{-}C_5Me_5)Cl_3} \xrightarrow{LiCH(SiMe_3)_2}$$

$$\underset{\mathbf{2}}{[Li(THF)_2]Lu(\eta^5\text{-}C_5Me_5)CH(SiMe_3)_2Cl_2} \xrightarrow{LiCH_2SiMe_3}$$

$$\underset{\mathbf{7}}{[Li(THF)_3]Lu(\eta^5\text{-}C_5Me_5)(CHSiMe_3)\{CH(SiMe_3)_2\}Cl}$$

$$\xrightarrow[-LiCl{\cdot}THF]{hexane} \underset{\mathbf{8}}{Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)}$$

Consistent with the expected chirality of the Lu center in 8, the α-methylene protons of the CH_2SiMe_3 ligand and the two $SiMe_3$ groups of the $CH(SiMe_3)_2$ ligand are diastereotopic at −65 °C, although variable-temperature ^1H NMR studies indicate equilibration at 25 °C, possibly via reversible THF association–dissociation. An approximate racemization energy of 28 kcal mol^{-1} has been calculated for this THF exchange process.[23] However, THF is strongly coordinated and indispensable for the stability of 8. Efforts to remove this coordinated THF resulted in decomposition. For example, by analogy with our[8] method to remove coordinated THF from $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2(THF)$[8] by reaction with Me_3SiI, treatment of 8 with Me_3SiI did not lead to any new organolutetium species, although $Me_3SiO(CH_2)_4I$ was observed by NMR monitoring of the reaction mixture.

In solution the ^{13}C NMR spectrum for salt-free 8 displayed reduced one-bond α-carbon–hydrogen coupling constants: 100 and 88 Hz for the α-CH and α-CH_2 groups, respectively; these values appear to be consistent with agostic interactions[24] and compare favorably with those obtained for the significantly distorted $CH(SiMe_3)_2$ groups in $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2$,[8] $La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}_2(THF)$,[8] and $Y(\eta^5\text{-}C_5Me_5)_2\{CH(SiMe_3)_2\}$[25] of 100, 92, and 84 Hz, respectively, although the structural data for both 3 and 7 do not conclusively support such interactions.

These salt-free bis(alkyl) complexes are white, crystalline solids that are extremely sensitive to air and moisture. They also have limited thermal stability, with slow deterioration being observed in the solid state at 20 °C. They decompose rapidly in solution above 40 °C. Use of the 1,3-diphenyl-2,4,5-trimethylcyclopentadienyl ligand gave greater thermal stability to the lutetium alkyl complexes $[K(OEt_2)_{0.5}]Lu(\eta^5\text{-}C_5Me_3Ph_2)\{CH(SiMe_3)_2\}Cl_2$ (**9**) and $Lu(\eta^5\text{-}C_5Me_3Ph_2)(CH_2SiMe_3)_2(THF)$ (**10**). These proved to be more thermally robust and were stable in solution at 50–60 °C for short periods.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Lu–Cl(1)	2.552 (2)	Lu–Cl(2)	2.546 (2)
Lu–C(1)	2.367 (6)	Lu–C(8)	2.586 (8)
Lu–C(9)	2.579 (6)	Lu–C(10)	2.595 (8)
Lu–C(11)	2.601 (8)	Lu–C(12)	2.593 (9)
Cl(1)–Li	2.375 (12)	Cl(2)–Li	2.359 (12)
Si(1)–C(1)	1.855 (6)	Si(1)–C(2)	1.874 (10)
Si(1)–C(3)	1.886 (9)	Si(1)–C(4)	1.890 (9)
Si(2)–C(1)	1.864 (8)	Si(2)–C(5)	1.869 (7)
Si(2)–C(6)	1.882 (9)	Si(2)–C(7)	1.893 (9)
C(1)–H(1)	0.939 (82)	C(8)–C(9)	1.410 (11)
C(8)–C(12)	1.451 (10)	C(8)–C(13)	1.489 (13)
C(9)–C(10)	1.431 (10)	C(9)–C(14)	1.537 (9)
C(10)–C(11)	1.381 (9)	C(10)–C(15)	1.522 (11)
C(11)–C(12)	1.420 (11)	C(11)–C(16)	1.531 (11)
C(12)–C(17)	1.469 (12)	Li–N(1)	2.038 (15)
Li–N(2)	2.057 (13)	N(1)–C(18)	1.479 (9)
N(1)–C(20)	1.468 (8)	N(1)–C(21)	1.465 (11)
N(2)–C(19)	1.491 (11)	N(2)–C(22)	1.477 (9)
N(2)–C(23)	1.456 (11)	C(18)–C(19)	1.507 (10)
Cl(1)–Lu–Cl(2)	87.9 (1)	Cl(1)–Lu–C(1)	109.0 (2)
Cl(2)–Lu–C(1)	107.2 (2)	Cl(1)–Lu–C(8)	141.3 (2)
Cl(2)–Lu–C(8)	102.3 (2)	C(1)–Lu–C(8)	103.4 (2)
Cl(1)–Lu–C(9)	114.9 (2)	Cl(2)–Lu–C(9)	85.6 (2)
C(1)–Lu–C(9)	134.7 (2)	C(8)–Lu–C(9)	31.7 (2)
Cl(1)–Lu–C(10)	88.7 (2)	Cl(2)–Lu–C(10)	103.2 (2)
C(1)–Lu–C(10)	145.1 (2)	C(8)–Lu–C(10)	52.7 (2)
C(9)–Lu–C(10)	32.1 (2)	Cl(1)–Lu–C(11)	93.1 (2)
Cl(2)–Lu–C(11)	133.9 (1)	C(1)–Lu–C(11)	115.8 (2)
C(8)–Lu–C(11)	53.0 (2)	C(9)–Lu–C(11)	52.4 (2)
C(10)–Lu–C(11)	30.8 (2)	Cl(1)–Lu–C(12)	123.2 (2)
Cl(2)–Lu–C(12)	134.6 (1)	C(1)–Lu–C(12)	93.7 (2)
C(8)–Lu–C(12)	32.5 (2)	C(9)–Lu–C(12)	52.8 (2)
C(10)–Lu–C(12)	52.0 (2)	C(11)–Lu–C(12)	31.7 (2)
Lu–Cl(1)–Li	87.3 (3)	Lu–Cl(2)–Li	87.8 (3)
C(1)–Si(1)–C(2)	113.1 (3)	C(1)–Si(1)–C(3)	110.5 (3)
C(2)–Si(1)–C(3)	107.2 (4)	C(1)–Si(1)–C(4)	113.6 (4)
C(2)–Si(1)–C(4)	107.5 (4)	C(3)–Si(1)–C(4)	104.3 (4)
C(1)–Si(2)–C(5)	110.2 (4)	C(1)–Si(2)–C(6)	112.6 (3)
C(5)–Si(2)–C(6)	108.2 (3)	C(1)–Si(2)–C(7)	114.5 (3)
C(5)–Si(2)–C(7)	105.2 (4)	C(6)–Si(2)–C(7)	105.8 (4)
Lu–C(1)–Si(1)	113.2 (3)	Lu–C(1)–Si(2)	114.3 (3)
Si(1)–C(1)–Si(2)	117.1 (4)	Lu–C(1)–H(1)	98.4 (46)
Si(1)–C(1)–H(1)	108.1 (37)	Si(2)–C(1)–H(1)	103.3 (45)
Cl(1)–Li–Cl(2)	96.7 (5)	Cl(1)–Li–N(1)	113.3 (5)
Cl(2)–Li–N(1)	120.6 (6)	Cl(1)–Li–N(2)	122.1 (6)
Cl(2)–Li–N(2)	115.1 (5)	N(1)–Li–N(2)	91.1 (6)
Li–N(1)–C(18)	101.1 (6)	Li–N(1)–C(20)	115.8 (6)
C(18)–N(1)–C(20)	110.0 (5)	Li–N(1)–C(21)	110.4 (6)
C(18)–N(1)–C(21)	112.0 (6)	C(20)–N(1)–C(21)	107.6 (6)
Li–N(2)–C(19)	100.6 (6)	Li–N(2)–C(22)	114.9 (6)
C(19)–N(2)–C(22)	109.8 (6)	Li–N(2)–C(23)	111.3 (6)
C(19)–N(2)–C(23)	110.4 (6)	C(22)–N(2)–C(23)	109.6 (6)
N(1)–C(18)–C(19)	111.4 (6)	N(2)–C(19)–C(18)	111.4 (6)

The Crystal and Molecular Structure of $[Li(TMEDA)]Lu(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}Cl_2$ (3). Molecules of 3 exist as monomeric species in the solid state separated by normal van der Waals' contacts. Selected molecular dimensions are given in Table IV. The overall geometry around the lutetium atom is approximately tetrahedral of the three-legged piano-stool type (see Figure 1). The chlorine atoms are in addition coordinated to the lithium atom, which is in turn chelated by a tetramethylethylenediamine (TMEDA) ligand, thereby achieving a distorted tetrahedral coordination geometry. The $Lu(\mu\text{-}Cl)_2Li$ moiety is near planar with intra-ring torsion angles of ±3.6° and ±3.9°, the ring being folded by 5.4° about the Cl(1)⋯Cl(2) vector. The distortions from tetrahedral geometry at lithium and the acute Cl–Lu–Cl angle appear to be general features in organolanthanide species containing $M(\mu\text{-}Cl)_2Li$ moieties. Thus Cl(1)–Li–Cl(2) is 96.7

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(23) Calculated from the chemical shift separation of the two diastereotopic trimethylsilyl groups at −65 °C and their coalescence temperature.

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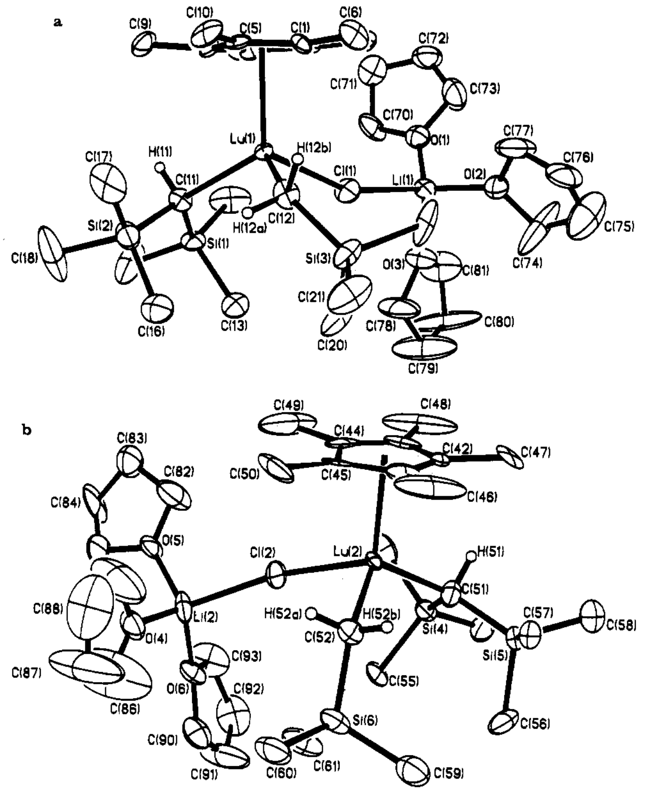

Figure 2. a. Molecular structure of the first of the two crystallographically independent molecules of **7**, showing 30% probability ellipsoids, with methyl group and THF ligand hydrogen atoms omitted for clarity. b. Molecular structure of the second of the two crystallographically independent molecules of **7**, drawn as for a.

(4)° in **3**, 97.2 (9)° in $[Li(THF)_2]Nd\{C_5H_3(SiMe_3)_2\}_2Cl_2$[26] (A), 95.4 (2)° in $[Li(OEt_2)_2]Yb(\eta^5\text{-}C_5Me_5)_2Cl_2$[15] (B) and 96.3° in $[Li(OEt_2)_2]Yb(\eta^5\text{-}C_5H_4SiMePh_2)_2Cl_2$[15] (C). The angle Cl(1)–M–Cl(2) is equal to 87.9 (1)° in **3** (M = Lu), 82.1° in A (M = Nd), 85.95 (2)° in B (M = Yb), and 87.13 (3)° in C (M = Yb). The Lu–Cl distances in **3** are rather shorter than the Nd–Cl and Yb–Cl bond lengths in the dicyclopentadienyl species A–C {Lu–Cl(1) = 2.552 (1) Å, Lu–Cl(2) = 2.546 (2) Å, cf. Nd–Cl = 2.744 Å in A and Yb–Cl = 2.596 (1) Å in B and 2.594 (2) Å in C}. Likewise the Li–Cl distances in **3** are also shorter than in A–C, Li–Cl(1) = 2.375 (12) Å and Li–Cl = 2.359 (12) Å {cf. 2.405 Å in A, 2.390 (6) and 2.412 (6) Å in B, and 2.390 Å in C). As a result the transannular Lu⋯Li distance is shorter in **3** than the M⋯Li distances in A–C at 3.404 (8) Å {cf. 3.63 (3), 3.478 (6), and 3.506 Å for A, B, and C, respectively}. The $Lu\text{–}CH(SiMe_3)_2$ bond length of 2.367 (6) Å is similar to that in other Lu–C sp³ bonds.[27] In contrast to the distorted bis(trimethylsilyl)methyl (disyl) groups observed[27-29] in other organolanthanide complexes, the Lu–C–Si angles are only slightly larger than the ideal tetrahedral values {Lu–C(1)–Si(1) = 113.2 (3)°; Lu–C(1)–Si(2) = 114.3(3)°} and the α-hydrogen shows little indication from the structural data of bonding to lutetium in an agostic manner {Lu–C(1)–H(1) = 98 (5)° and Lu⋯H(1) = 2.67 (8) Å}.

Molecular Structure of $[Li(THF)_3]Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}Cl$. The molecular structure of the two crystallographically independent molecules of **7** are shown in parts a and b of Figure 2, and selected molecular dimensions are listed in Table V (see Experimental Section for further details). The crystal structure, being centrosymmetric, consists of a racemic mixture of chiral molecules of **7**; parts a and b of Figure illustrate molecules of opposite hand. The gross molecular geometry at Lu is similar to that of **3** with both representing three-legged piano stools. As in **3** the angles at lutetium are much closer to tetrahedral than is the case for most d-block elements in, e.g., d⁶ $CpML_3$ complexes. Thus in **7** the Cp–Lu(1)–Cl(1), Cp–Lu(1)–C(11), and Cp–Lu(1)–C(12) angles are 112.6, 117.1, and 112.1°, respectively (Cp being the centroid of the pentamethylcyclopentadienyl ring), corresponding values for Lu(2) are 110.9, 114.7, and 111.1°, and for **3** 113.7 and 113.5° for Cl(1) and Cl(2) and 120.6° for the disyl carbon. As in **3** the Li atom achieves approximately tetrahedral coordination by coordination to a bridging chlorine {Cl(1)} and three oxygen atoms of the THF ligands. The two independent molecules of **7** are chemically similar, differing significantly only in respect of their conformations and showing variation in some bond angles. Bond lengths in the two independent molecules show no significant differences. Inter-bond angles at lutetium between the chloride, $CH(SiMe_3)_2$, and CH_2SiMe_3 [(trimethylsilyl)methyl (tmsm)] ligands show some variation between the two independent molecules of **7** present in the crystal: values for Lu(1) (with those for Lu(2) in braces) are Cl(1)–Lu(1)–C(11) = 105.0 (4)° {106.9 (4)°}, Cl(1)–Lu(1)–C(12) = 100.6 (4)° {96.9 (5)°} and C(11)–Lu(1)–C(12) = 107.9 (6)° {114.7 (6)°}. The marked increase in disyl–Lu–tmsm angle in molecule 2 may be linked to the different conformation of the tmsm group; in molecule 1 the tmsm $SiMe_3$ group almost eclipses Cl(1) while in molecule 2 they are more staggered bringing the tmsm $SiMe_3$ group closer to the disyl group {torsion angles are Cl(1)–Lu(1)–C(12)–Si(1) = −9.8°, Cl(2)–Lu(2)–C(52)–Si(6) = 63.4°, Cp–Lu(1)–C(12)–Si(3) = −129.7°, Cp–Lu(2)–C(52)–Si(6) = 179.0°}. As a further consequence of this conformational change, the Cl–Lu–tmsm angle is larger in molecule 1 than in molecule 2 and the Lu–C–Si angle of the tmsm ligand smaller {125.2 (8)° versus 132.4 (9)°}. The methylene or methyne hydrogen atoms were not directly located, but there is little structural evidence for agostic interactions between the α-CH groups of the (trimethylsilyl)methyl or bis(trimethylsilyl)methyl ligands and lutetium. In particular, the disyl group shows little flattening (sums of the Lu–C–Si and Si–C–Si angles are 346.6° and 347.0° in **3** and **7**, respectively) or abnormally large Lu–C–Si angles {values are 114.6 (8)–118.3 (9)°}. The Lu–C–Si angles of the tmsm ligand are considerably larger but do not give rise to particularly short calculated Lu⋯H contacts (all >2.68 Å). In contrast $Th(\eta^5\text{-}C_5Me_5)_2(CH_2SiMe_3)_2$[30] contains a highly unsymmetrical $Th(CH_2SiMe_3)_2$ fragment.

Reaction of Monocyclopentadienyl Alkyl Complexes with Small Molecules. An important goal was formation of lutetium hydride species. In the related $M(\eta^5\text{-}C_5Me_5)_2CH(SiMe_3)_2$[31] chemistry the dimeric hydride is prepared via facile hydrogenolysis. The salt-free complexes $Lu(\eta^5\text{-}C_5Me_2)(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)$ (**8**)

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Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for 7

Lu(1)–Cl(1)	2.539 (5)	Lu(1)–C(1)	2.638 (15)	O(3)–Li(1)	1.932 (29)	O(4)–C(86)	1.245 (37)
Lu(1)–C(2)	2.638 (16)	Lu(1)–C(3)	2.604 (16)	O(4)–C(89)	1.379 (37)	O(4)–Li(2)	1.871 (38)
Lu(1)–C(4)	2.610 (15)	Lu(1)–C(5)	2.670 (15)	O(5)–C(82)	1.372 (24)	O(5)–C(85)	1.417 (23)
Lu(1)–C(11)	2.394 (16)	Lu(1)–C(12)	2.344 (18)	O(5)–Li(2)	1.890 (40)	O(6)–C(90)	1.437 (25)
Lu(2)–Cl(2)	2.541 (5)	Lu(2)–C(41)	2.603 (18)	O(6)–C(93)	1.400 (24)	O(6)–Li(2)	1.978 (39)
Lu(2)–C(42)	2.645 (16)	Lu(2)–C(43)	2.652 (18)	C(1)–C(2)	1.445 (24)	C(1)–C(5)	1.403 (22)
Lu(2)–C(44)	2.617 (18)	Lu(2)–C(45)	2.593 (18)	C(1)–C(6)	1.479 (23)	C(2)–C(3)	1.411 (24)
Lu(2)–C(51)	2.353 (17)	Lu(2)–C(52)	2.314 (18)	C(2)–C(7)	1.494 (25)	C(3)–C(4)	1.366 (22)
L(1)–Li(1)	2.388 (29)	Cl(2)–Li(2)	2.350 (32)	C(3)–C(8)	1.532 (23)	C(4)–C(5)	1.405 (23)
Si(1)–C(11)	1.865 (17)	Si(1)–C(13)	1.862 (19)	C(4)–C(9)	1.504 (23)	C(5)–C(10)	1.493 (23)
Si(1)–C(14)	1.853 (21)	Si(1)–C(15)	1.884 (22)	C(41)–C(42)	1.360 (26)	C(41)–C(45)	1.433 (29)
Si(2)–C(11)	1.860 (18)	Si(2)–C(16)	1.876 (21)	C(41)–C(46)	1.484 (28)	C(42)–C(43)	1.397 (28)
Si(2)–C(17)	1.866 (22)	Si(2)–C(18)	1.911 (26)	C(42)–C(47)	1.464 (27)	C(43)–C(44)	1.386 (31)
Si(3)–C(12)	1.819 (19)	Si(3)–C(19)	1.820 (22)	C(43)–C(48)	1.492 (30)	C(44)–C(45)	1.429 (33)
Si(3)–C(20)	1.901 (19)	Si(3)–C(21)	1.874 (22)	C(44)–C(49)	1.469 (32)	C(45)–C(50)	1.535 (31)
Si(4)–C(51)	1.857 (18)	Si(4)–C(53)	1.916 (21)	C(70)–C(71)	1.492 (29)	C(71)–C(72)	1.452 (29)
Si(4)–C(54)	1.923 (19)	Si(4)–C(55)	1.896 (17)	C(72)–C(73)	1.452 (29)	C(74)–C(75)	1.511 (36)
Si(5)–C(51)	1.818 (18)	Si(5)–C(56)	1.920 (19)	C(75)–C(76)	1.334 (34)	C(76)–C(77)	1.458 (32)
Si(5)–C(57)	1.822 (20)	Si(5)–C(58)	1.965 (21)	C(78)–C(79)	1.411 (35)	C(79)–C(80)	1.386 (37)
Si(6)–C(52)	1.851 (18)	Si(6)–C(59)	1.876 (21)	C(80)–C(81)	1.410 (32)	C(82)–C(83)	1.512 (30)
Si(6)–C(60)	1.885 (22)	Si(6)–C(61)	1.855 (21)	C(83)–C(84)	1.391 (31)	C(84)–C(85)	1.413 (30)
O(1)–C(70)	1.440 (23)	O(1)–C(73)	1.435 (24)	C(86)–C(87)	1.369 (49)	C(87)–C(88)	1.268 (46)
O(1)–Li(1)	1.864 (37)	O(2)–C(74)	1.405 (26)	C(88)–C(89)	1.374 (46)	C(90)–C(91)	1.409 (34)
O(2)–C(77)	1.416 (28)	O(2)–Li(1)	1.894 (36)	C(91)–C(92)	1.376 (36)	C(92)–C(93)	1.562 (34)
O(3)–C(78)	1.426 (25)	O(3)–C(81)	1.361 (23)				

C(1)–Lu(1)–Cl(1)	104.9 (4)	C(2)–Lu(1)–Cl(1)	85.5 (4)	C(58)–Si(5)–C(56)	105.6 (10)	C(58)–Si(5)–C(57)	104.6 (10)
C(2)–Lu(1)–C(1)	31.8 (5)	C(3)–Lu(1)–Cl(1)	100.4 (4)	C(59)–Si(6)–C(52)	111.8 (9)	C(60)–Si(6)–C(52)	111.2 (9)
C(3)–Lu(1)–C(1)	51.7 (5)	C(3)–Lu(1)–C(2)	31.2 (5)	C(60)–Si(6)–C(59)	108.2 (10)	C(61)–Si(6)–C(52)	111.2 (9)
C(4)–Lu(1)–Cl(1)	130.7 (4)	C(4)–Lu(1)–C(1)	51.7 (5)	C(61)–Si(6)–C(59)	105.9 (11)	C(61)–Si(6)–C(60)	108.3 (11)
C(4)–Lu(1)–C(2)	51.4 (5)	C(4)–Lu(1)–C(3)	30.4 (5)	C(73)–O(1)–C(70)	106.7 (16)	Li(1)–O(1)–C(70)	126.6 (16)
C(5)–Lu(1)–Cl(1)	134.4 (4)	C(5)–Lu(1)–C(1)	30.6 (5)	Li(1)–O(1)–C(73)	125.8 (18)	C(77)–O(2)–C(74)	106.2 (19)
C(5)–Lu(1)–C(2)	50.9 (5)	C(5)–Lu(1)–C(3)	50.2 (5)	Li(1)–O(2)–C(74)	127.0 (18)	Li(1)–O(2)–C(77)	126.0 (18)
C(5)–Lu(1)–C(4)	30.8 (5)	C(11)–Lu(1)–Cl(1)	105.0 (4)	C(81)–O(3)–C(78)	108.5 (18)	Li(1)–O(3)–C(78)	127.2 (16)
C(11)–Lu(1)–C(1)	142.1 (6)	C(11)–Lu(1)–C(2)	130.7 (6)	Li(1)–O(3)–C(81)	124.3 (17)	C(89)–O(4)–C(86)	102.0 (25)
C(11)–Lu(1)–C(3)	100.0 (6)	C(11)–Lu(1)–C(4)	90.8 (6)	Li(2)–O(4)–C(86)	134.3 (23)	Li(2)–O(4)–C(89)	122.4 (23)
C(11)–Lu(1)–C(5)	113.2 (6)	C(12)–Lu(1)–Cl(1)	100.6 (4)	C(85)–O(5)–C(82)	105.6 (17)	Li(2)–O(5)–C(82)	129.1 (17)
C(12)–Lu(1)–C(1)	88.9 (6)	C(12)–Lu(1)–C(2)	117.4 (6)	Li(2)–O(5)–C(85)	125.3 (17)	C(93)–O(6)–C(90)	111.3 (17)
C(12)–Lu(1)–C(3)	139.1 (6)	C(12)–Lu(1)–C(4)	118.7 (6)	Li(2)–O(6)–C(90)	127.9 (17)	Li(2)–O(6)–C(93)	119.2 (19)
C(12)–Lu(1)–C(5)	90.7 (6)	C(12)–Lu(1)–C(11)	107.9 (6)	Si(1)–C(11)–Lu(1)	117.6 (8)	Si(2)–C(11)–Lu(1)	114.6 (8)
C(41)–Lu(2)–Cl(2)	128.5 (6)	C(42)–Lu(2)–Cl(2)	133.7 (5)	Si(2)–C(11)–Si(1)	114.8 (9)	H(11)–C(11)–Lu(1)	100.8 (4)
C(42)–Lu(2)–C(41)	30.0 (6)	C(43)–Lu(2)–Cl(2)	104.9 (7)	H(11)–C(11)–Si(1)	100.7 (6)	H(11)–C(11)–Si(2)	105.1 (6)
C(43)–Lu(2)–C(41)	51.1 (6)	C(43)–Lu(2)–C(42)	30.6 (6)	Si(3)–C(12)–Lu(1)	125.2 (8)	H(12A)–C(12)–Lu(1)	105.5 (4)
C(44)–Lu(2)–Cl(2)	84.4 (5)	C(44)–Lu(2)–C(41)	51.6 (7	H(12A)–C(12)–Si(3)	105.5 (6)	H(12B)–C(12)–Lu(1)	105.3 (4)
C(44)–Lu(2)–C(42)	50.2 (6)	C(44)–Lu(2)–C(43)	30.5 (7)	H(12B)–C(12)–Si(3)	105.3 (6)	Si(4)–C(51)–Lu(2)	116.2 (8)
C(45)–Lu(2)–Cl(2)	96.5 (6)	C(45)–Lu(2)–C(41)	32.0 (6)	Si(5)–C(51)–Lu(2)	118.3 (9)	Si(5)–C(51)–Si(4)	117.2 (9)
C(45)–Lu(2)–C(42)	51.1 (6)	C(45)–Lu(2)–C(43)	52.0 (7)	H(51)–C(51)–Lu(2)	99.3 (5)	H(51)–C(51)–Si(4)	101.7 (6)
C(45)–Lu(2)–C(44)	31.8 (7)	C(51)–Lu(2)–Cl(2)	106.9 (4)	H(51)–C(51)–Si(5)	98.0 (7)	Si(6)–C(52)–Lu(2)	132.4 (9)
C(51)–Lu(2)–C(41)	117.9 (7)	C(51)–Lu(2)–C(42)	92.3 (6)	H(52A)–C(52)–Lu(2)	103.4 (5)	H(52A)–C(52)–Si(6)	103.4 (6)
C(51)–Lu(2)–C(43)	93.2 (7)	C(51)–Lu(2)–C(44)	121.2 (10)	H(52B)–C(52)–Lu(2)	103.5 (5)	H(52B)–C(52)–Si(6)	103.5 (6)
C(51)–Lu(2)–C(45)	142.6 (7)	C(52)–Lu(2)–Cl(2)	96.9 (5)	C(71)–C(70)–O(1)	107.2 (17)	C(72)–C(71)–C(70)	102.2 (20)
C(52)–Lu(2)–C(41)	86.9 (7)	C(52)–Lu(2)–C(42)	112.9 (7)	C(73)–C(72)–C(71)	108.4 (20)	C(72)–C(73)–O(1)	107.5 (20)
C(52)–Lu(2)–C(43)	137.6 (6)	C(52)–Lu(2)–C(44)	121.0 (10)	C(75)–C(74)–O(2)	106.9 (24)	C(76)–C(75)–C(74)	106.7 (26)
C(52)–Lu(2)–C(45)	90.3 (8)	C(52)–Lu(2)–C(51)	114.7 (6)	C(77)–C(76)–C(75)	106.7 (28)	C(76)–C(77)–O(2)	107.8 (21)
Li(1)–Cl(1)–Lu(1)	158.5 (7)	Li(2)–Cl(2)–Lu(2)	161.1 (10)	C(79)–C(78)–O(3)	104.6 (24)	C(80)–C(79)–C(78)	107.7 (26)
C(13)–Si(1)–C(11)	112.3 (9)	C(14)–Si(1)–C(11)	114.7 (9)	C(81)–C(80)–C(79)	108.2 (24)	C(80)–C(81)–O(3)	106.9 (21)
C(14)–Si(1)–C(13)	105.6 (10)	C(15)–Si(1)–C(11)	112.2 (9)	C(83)–C(82)–O(5)	109.6 (20)	C(84)–C(83)–C(82)	101.4 (21)
C(15)–Si(1)–C(13)	106.4 (10)	C(15)–Si(1)–C(14)	104.9 (12)	C(85)–C(84)–C(83)	108.4 (23	C(84)–C(85)–O(5)	108.9 (20)
C(16)–Si(2)–C(11)	113.6 (9)	C(17)–Si(2)–C(11)	111.1 (9)	C(87)–C(86)–O(4)	111.5 (35)	C(88)–C(87)–C(86)	112.1 (41)
C(17)–Si(2)–C(16)	105.9 (12)	C(18)–Si(2)–C(11)	114.3 (11)	C(89)–C(88)–C(87)	100.8 (33)	C(88)–C(89)–O(4)	113.5 (34)
C(18)–Si(2)–C(16)	106.4 (12)	C(18)–Si(2)–C(17)	104.9 (14)	C(91)–C(90)–O(6)	107.9 (21)	C(92)–C(91)–C(90)	109.1 (27)
C(19)–Si(3)–C(12)	111.9 (10)	C(20)–Si(3)–C(12)	111.7 (8)	C(93)–C(92)–C(91)	108.7 (25)	C(92)–C(93)–O(6)	102.0 (21)
C(20)–Si(3)–C(19)	106.0 (10)	C(21)–Si(3)–C(12)	114.4 (9)	O(1)–Li(1)–Cl(1)	113.6 (15)	O(2)–Li(1)–Cl(1)	112.8 (16)
C(21)–Si(3)–C(19)	107.2 (10)	C(21)–Si(3)–C(20)	104.9 (11)	O(2)–Li(1)–O(1)	112.7 (16)	O(3)–Li(1)–Cl(1)	103.4 (13)
C(53)–Si(4)–C(51)	112.2 (9)	C(54)–Si(4)–C(51)	116.7 (9)	O(3)–Li(1)–O(1)	108.1 (17)	O(3)–Li(1)–O(2)	105.3 (16)
C(54)–Si(4)–C(53)	105.5 (9)	C(55)–Si(4)–C(51)	112.4 (9)	O(4)–Li(2)–Cl(2)	107.5 (17)	O(5)–Li(2)–Cl(2)	108.2 (17)
C(55)–Si(4)–C(53)	105.3 (9)	C(55)–Si(4)–C(54)	103.8 (9)	O(5)–Li(2)–O(4)	110.3 (17)	O(6)–Li(2)–Cl(2)	111.4 (14)
C(56)–Si(5)–C(51)	109.9 (9)	C(57)–Si(5)–C(51)	114.3 (8)	O(6)–Li(2)–O(4)	113.7 (20)	O(6)–Li(2)–O(5)	105.6 (18)
C(57)–Si(5)–C(56)	106.5 (9)	C(58)–Si(5)–C(51)	115.2 (10)				

and Lu(η^5-C_5Me_2)(CH_2CMe_3)$_2$(THF) (6) are hydrogenated with H_2 (2 h, 3 bar of H_2, hexane or C_6D_6, 25 °C) to give the free alkanes; however, no new organolutetium complex could be isolated or identified. In contrast, the LiCl-containing alkyl species did not react with hydrogen under similar conditions. The reactions of the neutral bis(alkyl) species 6 or 8 with ethylene, CO, 2-butyne, and 1,2-propadiene were attempted. Due to their thermal instability the products of these reactions could not be unambiguously characterized, and so these reactions were mainly studied as sealed NMR tube reactions. Reaction products were tentatively identified by their ^1H NMR spectra and by hydrolysis reactions that liberated the organic ligands which were subsequently identified by their ^1H NMR spectra and by comparison with authentic samples.

Treatment of the salt-free bis(neopentyl) species with 2-butyne in C_6D_6 or C_6D_{12} resulted in liberation of 1 equiv of neopentane (also with excess 2-butyne) and formation of a new lutetium species. The same species is also obtained from reaction with 1,2-butadiene and with release of neopentane. We propose that this species contains a Lu–CH_2CCMe moiety. Reaction of the bis(neopentyl) species with 1 equiv of CO resulted in insertion and formation of a single product that appears to contain an oxycarbene-type ligand.

Conclusions

We have developed a methodology to prepare the first neutral, monocyclopentadienyllutetium bis(alkyl) complexes. Stepwise metathesis of the chlorides in $LuCl_3(THF)_3$, first with sodium cyclopentadienides and subsequently with lithium alkyls, allows the rational synthesis of this new class of organometallic compound. Earlier results that suggested a strong preference toward the formation of bis(cyclopentadienyl) complexes can be explained by use of ill-defined starting materials, e.g. $(LuCl_3)_n$ and/or insoluble LiC_5Me_5.

The synthesis of 1 was hampered by considerable experimental difficulties. Use of sterically more demanding cyclopentadienyl or indenyl ligands has attracted relatively little attention, and we note that the alkyl complexes derived from $[K(THF)_x]Lu(\eta^5\text{-}C_9H_4MePh_2)Cl_3$ and $Lu(\eta^5\text{-}C_5Me_3Ph_2)Cl_2(THF)_2$ possess significantly more thermal stability than their pentamethylcyclopentadienyl counterparts. Unfortunately, difficulties in the synthesis and alkylation of these starting materials prevented us from further exploiting their chemistry, although it is probable that these phenyl-substituted ligands will have an analogously greater stabilizing effect in early-transition-metal chemistry than their pentamethylcyclopentadienyl analogues.

Investigation of this chemistry has been hindered by the prevalence of salt coordination. Removal of this coordinated salt, while possible, results in major product losses due to the poor thermal stability of the salt-free systems.

The first "mixed" alkyl neutral organolanthanide complex $Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)$ has been prepared. Efforts are continuing to prepare and separate a chiral $Lu(\eta^5\text{-}C_5Me_5)R'R''\cdot L$ species that may possess interesting properties.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters and full listings of bond distances and angles (20 pages); listings of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

3-Alkylidenethiagermiranes

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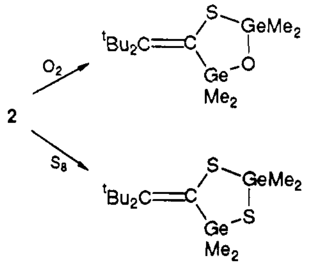
Dimethyl- and diphenylgermylenes react with di-*tert*-butylthioketene to give 4-alkylidene-1,2,3-thiadigermetanes **2** and **4**, the products of the insertion of germylenes into 3-alkylidenethiagermiranes. Dimesitylgermylene generated by the thermolysis of hexamesitylcyclotrigermane (**12**) at 80 °C reacts with di-*tert*-butylthioketene to produce a stable 3-alkylidenethiagermirane, **13**. Photolysis of **13** produces dimesitylgermylene and di-*tert*-butylthioketene via germathiocarbonyl ylide **17**, which is intensely blue in color with a maximum band at 580 nm. **13** reacts with dimethylgermylene to yield the corresponding 4-alkylidene-1,2,3-thiadigermetane **22**. Oxidation of **13** by *m*-chloroperbenzoic acid gives 3-alkylidene-1,2,4-oxathiagermetane *S*-oxide **23**.

Introduction

Special interest has been focused on the synthesis of three-membered rings bearing exocyclic double bonds because the introduction of an exomethylene group to a three-membered ring is expected to increase the strain energy.[1] Some metal–group 14 three-membered heterocycles have been isolated,[2-9] but, in contrast to rather extensive studies on alkylidenecyclopropanes and their heterocyclic analogues, there is no report on the chemistry of the germanium analogues. We recently reported the synthesis and chemical properties of thiagermiranes prepared by the reaction of germylenes with thioketones.[6] To synthesize the exomethylene-containing thiagermiranes "3-alkylidenethiagermiranes", we attempted reactions of germylenes with thioketenes. We report here the synthesis of the first type of these compounds 3-alkylidenethiagermiranes, and some of the chemical properties of these.

Scheme I



Results and Discussion

Reactions of Dimethyl- and Diphenylgermylenes with Thioketenes.[10] Thermolysis of a benzene solution

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