Organometallics 1991, *10*, 2585–2592

Organometallic Compounds of the Lanthanides. 64.[1] Synthesis and X-ray Crystal Structures of Dimethylgermyl Bis(tetramethylcyclopentadienyl) Halide and Alkyl Derivatives of the Lanthanides

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Received January 10, 1991

Metathesis of Me_2GeCl_2 or Me_2SnCl_2 with 2 equiv of LiC_5Me_4H affords $Me_2Ge(C_5Me_4H)_2$ (**1**) and $Me_2Sn(C_5Me_4H)_2$ (**2**), respectively. The subsequent deprotonation of **1** with MeLi yields only the desired dilithium salt $Me_2Ge(C_5Me_4Li)_2$ (**3**) whereas **2** forms Me_4Sn and two LiC_5Me_4H. The trichlorides of neodymium, samarium, holmium, and lutetium react with the dilithium salt **3** with the formation of $Me_2Ge(C_5Me_4)_2LnCl_2Li(THF)_2$ (Ln = Nd (**4**), Sm (**5**), Ho (**6**), Lu (**7**)). The reaction of **4** and **6** with $LiCH(SiMe_3)_2$ produces $Me_2Ge(C_5Me_4)_2LnCH(SiMe_3)_2$ (Ln = Nd (**8**), Ho (**9**)). The new compounds have been characterized by elemental analysis, mass and NMR spectra, as well as X-ray structural analysis of **5**, **7**, and **9**. The halides **5** and **7** crystallize in the monoclinic space group $P2_1/c$ (No. 14) with $a = 9.7284$ (9), $b = 19.397$ (1), $c = 16.610$ (2) Å, $\beta = 98.963$ (9)°; Z = 4 or $a = 9.578$ (3), $b = 19.218$ (4), $c = 16.525$ (4) Å, $\beta = 99.73$ (2)°; Z = 4, respectively. Least-squares refinement led to a final *R* value of 0.020 ($F_o > 4\sigma(F_o)$) for 5554 independent reflections for **5** or of 0.028 ($F_o > 3\sigma(F_o)$) for 5822 independent reflections for **7**. Compound **9** crystallizes in the monoclinic space group $P2_1/m$ (No. 11) with $a = 9.2621$ (8), $b = 14.216$ (2), $c = 11.839$ (2) Å, $\beta = 107.79$ (1)°, $Z = 2$, and $R = 0.023$ ($F_o > 4\sigma(F_o)$) for 2954 reflections. The structure of **9** shows a short Ho–C(methyl) contact of 2.774 (4) Å.

Introduction

The successful synthesis, isolation, and structural characterization of a great number of organolanthanides[2-12] was achieved by the exchange of C_5H_5 ligands for the sterically more demanding C_5Me_5 units. Thus an almost complete series of alkalimetal chloride adducts of the type $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2MB_2$ can be obtained for both, large and small lanthanide cations (Ln = La, Ce, and Pr,[3,4] Nd,[3,5,7] Sm,[6,7] Gd, Tb, Dy, Ho, Er, and Tm,[3] Yb,[3,7,8] and Lu;[3] M = Li, Na, K; B = Et_2O, THF, DME, or TMED). The advantage of such a bis(pentamethylcyclopentadienyl) ligation with respect to the stability of such complexes has been deeply researched. On the other hand, the increase in stability may cause a decrease in reactivity with respect to hydrogenation processes[9-12] as reported for the complexes $(C_5Me_5)_2LnR$ (R = H, $CH(SiMe_3)_2$). In preserving the main positive aspects of C_5Me_5 ligation, the steric conditions can be effectively influenced by bridging the two C_5Me_5 ligands via atoms having a definite hybridization and forcing the cyclopentadienyl ligands in otherwise unusual positions to the central lanthanide. Thus complexes like the dimer $[Me_2Si(C_5Me_4)_2LnH]_2$, or the monomer $Me_2Si(C_5Me_4)_2LnCH(SiMe_3)_2$[11] (Ln = La, Nd, Sm, or Lu) and even their precursors $Me_2Si(C_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$ and $[Me_2Si(C_5Me_4)_2NdCl]_2ClLi(THF)_2$[11] exhibit interesting structural and chemical features due to the opening of the metal coordination sphere by the fixation of C_5Me_4 rings at the silicon atom. Here we present the results which we obtained by replacing the silicon atom in the $C_5Me_4\text{–}Si\text{–}C_5Me_4$ ligand bridge with its larger congener germanium and the effect of this substitution on the properties of the organolanthanide complexes.

Experimental Section

All compounds described below are extremely air and moisture sensitive, thus all manipulations were conducted under purified, oxygen-free argon by using Schlenk and vacuum line techniques. Solvents were distilled from sodium (toluene) or sodium benzophenone ketyl (ether and tetrahydrofuran (THF)) under argon prior to use. NMR spectra were recorded on a Bruker WP-80 (^1H, 80 MHz) or Bruker WH-270 (^1H, 270 MHz; ^{13}C, 67.9 MHz) instrument. Low-temperature NMR spectra were recorded on a Bruker AM-300 instrument. ^1H chemical shift values are reported in parts per million and referenced to residual protons in deuteriated solvents benzene-d_6 $\delta = 7.15$ ppm, toluene-d_8 $\delta = 2.09$ ppm, and THF-d_8 $\delta = 1.73$ ppm. ^{13}C chemical shift values were referenced to benzene-d_6 $\delta = 128$ ppm and THF-d_8 $\delta = 67.39$ ppm. Elemental analyses were performed by using a Perkin-Elmer CHN analyzer 240C. Mass spectra were obtained on a Varian MAT 311A.

Dimethylgermanium dichloride was prepared according to the description of Rochow[13] from powdered germanium with methyl chloride at 380 °C with copper used as a catalyst. The

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0276-7333/91/2310-2585$02.50/0

crude product was purified by fractional distillation until the purity of the dimethylgermanium dichloride fraction (bp 124 °C) exceeded 90% according to its NMR spectrum. **Dimethyltin dichloride** was obtained by the facile disproportionation[14] of equimolar amounts of $SnCl_4$ and $SnMe_4$ with subsequent recrystallization from THF. **(Bis(trimethylsilyl)methyl)lithium** was prepared according to literature procedures.[15] **1,2,3,4-Tetramethylcyclopentadiene** was prepared by using a modification of the synthesis of pentamethylcyclopentadiene, first described by Burger, Delay, and Mazenod.[16] The most recent and detailed preparation of tetramethylcyclopentadiene ($C_5Me_4H_2$) was published by Marks et al.[12]

$Me_2Ge(C_5Me_4H)_2$ (1). A 250-mL round-bottomed flask, equipped with a mechanical stirrer was charged with 5.27 g (43.1 mmol) tetramethylcyclopentadiene, dissolved in 100 mL of THF. The flask was cooled in ice. *n*-BuLi (24 mL, 43.2 mmol, 1.8 M in hexane) was syringed into it over a 5-min period. The thick yellow slurry was next stirred for 12 h, while the temperature was slowly increased to ambient temperature. After the intense yellow color had disappeared, the white mixture was cooled to −78 °C. Dimethylgermanium dichloride (2.3 mL, 19.7 mmol) was subsequently syringed into the flask. The mixture instantly turned into a clear solution; it was allowed to warm up to room temperature and was next refluxed over a 5-h period. The solvent was removed in vacuo, and the resulting solid was extracted with 55 mL of pentane. The pale yellow solution was concentrated in vacuo, and the product was purified by repeated recrystallization at −30 °C. Yield: 1.45 g (21%). ^1H NMR (270 MHz, C_6D_6): δ 3.37 (br, 2 H), 2.03 (s, 12 H), 1.94 (s, 12 H), 0.03 (s, 6 H). ^{13}C NMR (67.9 MHz, C_6D_6): δ 135.22, 132.86, 54.45, 14.49, 11.3, −5.21. MS (EI, 70 eV, 15 °C): *m/z* 346 (6.5) M^+, 225 (76.9) $Me_2Ge(C_5Me_4H)^+$, 195 (6.7), $C_5Me_4HGe^+$, 121 (100) $C_5Me_4H^+$. Anal. Calcd for $C_{20}H_{32}Ge$: C, 69.62; H, 9.35. Found: C, 68.93; H, 9.35.

$Me_2Sn(C_5Me_4H)_2$ (2). To a white slurry of LiC_5Me_4H in 50 mL of THF at −78 °C, prepared in the same way as described above, from 2.4 g (19.7 mmol) tetramethylcyclopentadiene and 12 mL (19.0 mmol) *n*-BuLi (1.5 M in hexane), was added a solution of 2.23 g (10 mmol) Me_2SnCl_2 in 10 mL THF in drops. The mixture turned into a clear yellow solution, which was then stirred at room temperature for 3 h. The solvent was removed in vacuo. The resulting solid was extracted with pentane. Pale yellow crystals were obtained by cooling a concentrated solution to −30 °C. Yield: 0.88 g (25%). ^1H NMR (270 MHz, C_6D_6): δ 3.54 (br, 2 H), 1.94 (s, 12 H), 1.89 (s, 12 H), −0.18 (s, 6 H). ^{13}C NMR (67.9 MHz, C_6D_6): δ 133.2, 130.4, 57.3, 13.9, 11.3, −10.4. MS (EI, 70 eV, 15 °C): *m/z* 392 (7) M^+, 271 (93.5) $Me_2Sn(C_5Me_4H)^+$, 241 (77.2) $C_5Me_4HSn^+$, 135 (8.8), $MeSn^+$, 121 (100) $C_5Me_4H^+$. Anal. Calcd for $C_{20}H_{32}Sn$: C, 61.35; H, 8.24. Found: C, 61.28; H, 8.32.

$Me_2Ge(C_5Me_4)_2NdCl_2Li(THF)_2$ (4). A 100-mL flask, equipped with a magnetic stirring bar, was charged with 0.66 g (1.9 mmol) $Me_2Ge(C_5Me_4H)_2$ (1) dissolved in 15 mL of ether. The clear, colorless solution was cooled to 0 °C and 2.7 mL (3.8 mmol) of MeLi (1.44 M in ether) was syringed into it. The solution turned into a white slurry and was stirred for 12 h at room temperature. A fine white precipitate had formed and the above solvent was decanted off. The solid was washed with 10 mL of ether and carefully dried in vacuo. The addition of 50 mL of THF and 0.75 g (1.9 mmol) $NdCl_3{\cdot}2THF$, followed by refluxing over a 5-h period resulted in a clear blue solution. The solvent was removed and the resulting greenish-blue residue was extracted three times with a mixture of 15 mL of ether and 3 mL of THF. Blue needle-shaped crystals were formed by cooling the concentrated solution to −30 °C. Yield: 0.52 g (38.6%). ^1H NMR (270 MHz, C_4D_8O): δ 21.62 (s, 12 H), 3.50 (m, 8 H), 1.73 (m, 8 H), −3.22 (s, 6 H), −6.39 (s, 12 H). ^{13}C NMR (67.9 MHz, C_4D_8O): δ 259.8, 161.4, 67.4, 25.3, 13.15, −20.20, −29.98. Anal. Calcd for $C_{28}H_{46}Cl_2GeLiNdO_2$: C, 47.41; H, 6.54. Found: C, 47.72; H, 6.64.

$Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$ (5). This compound was prepared from 0.95 g (2.5 mmol) of $SmCl_3{\cdot}1.7THF$ and 2.78 mmol $Me_2Ge(C_5Me_4Li)_2$ (3), which was freshly prepared by the reaction of 0.96 g (2.78 mmol) of $Me_2Ge(C_5Me_4H)_2$ (1) and 4.4 mL of MeLi (5.59 mmol, 1.27 M in ether) in 10 mL of Et_2O according to the description above. The reaction was carried out in 50 mL of THF. The clear amber solution was refluxed for 5 h. Removal of the solvent was followed by extraction of the yellow solid with ether (3 × 15 mL). Yellow crystals were obtained by cooling the concentrated ethereal solution to −30 °C. Yield: 0.77 g (43%). ^1H NMR (80 MHz, C_6D_6): δ 4.44 (m, 12 H), 2.94 (m, 12 H), 1.91 (s, 12 H), 1.76 (s, 6 H), −2.22 (s, 12 H). Anal. Calcd for $C_{28}H_{46}Cl_2GeLiO_2Sm$: C, 47.00; H, 6.48. Found: C, 46.78; H, 6.53.

$Me_2Ge(C_5Me_4)_2HoCl_2Li(THF)_2$ (6). This compound was prepared analogously to the description above, from 0.44 g (1.27 mmol) of $Me_2Ge(C_5Me_4H)_2$ (1) and 1.77 mL of MeLi (2.55 mmol, 1.44 M) at 0 °C and stirred for 12 h at room temperature. The solvent was replaced by 50 mL of THF. The reaction was completed by adding 0.35 g (1.28 mmol) of $HoCl_3$, stirring at room temperature for 12 h, and refluxing for 3 h. The solvent was removed in vacuo, and the remaining yellow solid was extracted with ether (2 × 10 mL). Crystals were obtained from a concentrated solution at −30 °C. Yield: 0.50 g (53.5%). ^1H NMR (80 MHz, C_6D_6): δ 52 (s, 12 H), 15 (m, 8 H), 13.6 (m, 8 H), −31.6 (s, 6 H), −165 (s, 12 H). Anal. Calcd for $C_{28}H_{46}Cl_2GeHoLiO_2$: C, 46.07; H, 6.35. Found: C, 46.33, H, 6.40.

$Me_2Ge(C_5Me_4)_2LuCl_2Li(THF)_2$ (7). This compound was prepared by addition of 0.56 g (1.99 mmol) of $LuCl_3$ to a slurry of 2.09 mmol of $Me_2Ge(C_5Me_4Li)_2$ (3) which had been prepared from 0.72 g (2.09 mmol) of $Me_2Ge(C_5Me_4H)_2$ dissolved in 10 mL of ether and 5.5 mL of MeLi (4.18 mmol, 0.76 M in ether). The workup was identical with that described above. Yield: 0.75 g (51%). ^1H NMR (270 MHz, C_6D_6): δ 3.55 (m, 8 H), 2.38 (s, 12 H), 2.29 (s, 12 H), 1.39 (m, 8 H), 1.21 (s, 6 H). ^{13}C NMR (67.9 MHz, C_6D_6): δ 125.1, 118.7, 102.9, 68.3, 25.3, 14.5, 12.4, 4.3. Anal. Calcd for $C_{28}H_{46}Cl_2GeLiLuO_2$: C, 45.44; H, 6.26; Ge, 9.81; Li, 0.94. Found C, 46.05; H, 6.24; Ge, 8.54; Li, 1.04.

$Me_2Ge(C_5Me_4)_2NdCH(SiMe_3)_2$ (8). A blue solution of 0.40 g (0.51 mmol) of 4 in 20 mL of toluene was allowed to react with 95 mg (0.57 mmol) of $LiCH(SiMe_3)_2$ at −78 °C. The temperature was allowed rise to room temperature overnight. The solvent was removed in vacuo, and the green solid was extracted with hexane (3 × 5 mL). Green crystals could be obtained from a concentrated solution at −30 °C. Yield: 0.18 g (54%). ^1H NMR (80 MHz, $C_6D_5CD_3$): δ 126 (s, 1 H), 16.8 (s, 6 H), 9.9 (s, 6 H), 8.8 (s, 6 H), −9.4 (s, 6 H), −14.0 (s, 18 H), −16.6 (s, 6 H). Anal. Calcd for $C_{27}H_{49}GeNdSi_2$: C, 50.15; H, 7.64. Found: C, 50.71; H, 7.77.

$Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$ (9). In an analogous manner to that described above, a solution of 0.42 g (0.58 mmol) of $Me_2Ge(C_5Me_4)_2HoCl_2Li(THF)_2$ (6) in 20 mL of toluene was cooled to −78 °C. $LiCH(SiMe_3)_2$ (0.14 g, 0.84 mmol) was added to the orange solution. The mixture was stirred overnight, allowing the temperature to rise to room temperature. The removal of toluene in vacuo was followed by extraction of the residue with pentane (3 × 8 mL). The pale yellow solution yielded orange crystals on cooling to −30 °C. Suitable crystals for X-ray investigations can be obtained from toluene. Yield: 0.21 g (54%). ^1H NMR (80 MHz, $C_6D_5CD_3$, $T = 303$ K): δ 69.61 (s, 6 H), 69.15 (s, 6 H), 50.27 (s, 6 H), −195.7 (s, 6 H), −199.5 (s, 18 H), −224.9 (s, 6 H). (The signal for the proton of the $CH(SiMe_3)_2$ residue could not be observed.) MS (EI, 70 eV, 30 °C): *m/z* 667 (0.2) $M - H^+$, 509 (100) $M - CH(SiMe_3)_2{}^+$. Anal. Calcd for $C_{27}H_{49}GeHoSi_2$: C, 48.59; H, 7.40. Found: C, 48.57; H, 7.49.

Crystal Structure Determination and Refinement of 5. Suitable crystals of 5 were obtained by recrystallization from toluene. A small amount of the toluene solution, containing some crystals of 5 was dropped into a device similar to that reported by Veith and Bärninghausen.[17] A yellow block-shaped crystal of 5 measuring 0.30 × 0.33 × 0.18 mm was selected, glued on the top of a glass fiber and transferred onto a goniometer head mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a low-temperature device. Lattice parameters were determined initially from the angular setting of 25 reflections and refined by a least-squares fit of 94 accurately centered reflections with $28 \le 2\theta \le 35°$. All intensity profiles were measured at 150 K and stored. The crystal data and some data collection parameters

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Table I. Crystal and Data Collection Parameters[a] for 5, 7 and 9

	$Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$ (5)	$Me_2Ge(C_5Me_4)_2LuCl_2Li(THF)_2$ (7)	$Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$ (9)
formula	$C_{28}H_{46}Cl_2GeLiO_2Sm$	$C_{28}H_{46}Cl_2GeLiLuO_2$	$C_{27}H_{49}GeHoSi_2$
fw	715.47	740.07	667.38
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/m$ (No. 11)
a, Å	9.7284 (9)	9.578 (3)	9.2621 (8)
b, Å	19.397 (1)	19.218 (4)	14.216 (2)
c, Å	16.610 (2)	16.525 (4)	11.839 (2)
β, deg	98.963 (9)	99.73 (2)	107.79 (1)
V, Å^3	3096.1 (5)	2998 (2)	1484.3 (4)
Z	4	4	2
D_{calcd}, g/cm^3	1.54	1.64	1.56
crystal dimensions, mm	0.30 × 0.33 × 0.18	0.17 × 0.25 × 0.34	0.35 × 0.40 × 0.45
μ(Mo Kα), cm^{-1}	30.4	44.7	37.7
F(000), e	1444	1480	676
diffractometer		Enraf-Nonius CAD-4	
radiatn, Å		MoK$_\alpha$, $\lambda = 0.71073$	
monochromator		graphite	
temp, K	150 (5)	138 (5)	140 (5)
θ range, deg	$0 \leq 2\theta \leq 53$	$2 \leq 2\theta \leq 55$	$1 \leq 2\theta \leq 53$
data set, hkl	0–12, 0–24, −20 to 20	−9 to 0, 0–18, −15 to 15	−11 to 0, −17 to 0, −14 to 14
scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
decay of std, %	1.4	4.6	0.5
total no. of data	6597	7500	3400
no. of unique data	6118	6462	3122
no. of obsd data	5554 ($F_o > 4\sigma(F_o)$)	5822 ($F_o > 3\sigma(F_o)$)	2954 ($F_o > 4\sigma(F_o)$)
max shift/error (Δ/σ)	≤0.001	≤0.008	≤0.003
no. of params	500	500	170
$R(F)$[b]	0.020	0.024	0.023
$R_w(F)$[b]	0.023	0.028	0.037
weighting scheme	$1.21/[\sigma_F^2 + 0.0001(F_o)^2]$	$1.28/[\sigma_F^2 + 0.000373(F_o)^2]$	$1/[\sigma_F^2 + 0.0015(F_o)^2]$

[a] Estimated standard deviations are given in Parentheses. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

are given in Table I. Three intensity control monitors were measured every 7200 s of X-ray exposure time and showed only a small decay (1.4%). The net intensities were corrected for Lorentz and polarization effects but not for decay. A semiempirical absorption correction (ψ scans) with min 77.8% and max 100% transmission was carried out. Since the cell constants of 5 and 7 are virtually identical, we assumed that both structures are isomorphous. By using all fractional coordinates of 7, the structure was refined satisfactorily by full-matrix least-squares (500 parameters) calculations. The final difference Fourier map showed no electron density greater than 0.43 or less than −0.37 e Å^{-3}. X-ray scattering factors were taken from Cromer and Mann[18] and were corrected for anomalous dispersion.[19] Data reduction and all corrections were performed by using the SDP.[20] Structure refinement was carried out on a Cray X-MP with use of the program SHELX-76.[21]

Crystal Structure Determination and Refinement of 7. Crystal choice and treatment was virtually identical with that described above. An almost colorless crystal of 7 with the approximate dimensions 0.17 × 0.25 × 0.34 mm, was placed into the cold nitrogen stream of an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions and their standard deviations were determined from the angular setting of 25 reflections. Raw intensities and standard deviations were measured at 138 K. Details are given in Table I. Intensities were corrected for decay and Lorentz and polarization effects. Analysis of the Patterson map revealed the location of the heavy atom. The positions of all non-hydrogen atoms were located on difference Fourier maps. Hydrogen atoms were introduced in calculated positions, but refined without further constraints. An empirical absorption correction (DIFABS[22] correction factor: min 0.927, max 1.176) was applied to the structure factors, and refinement proceeded with anisotropical thermal parameters for all non-hydrogen atoms by using blocked-matrix least-squares methods. The final difference Fourier map showed no peak higher than 0.6 e Å^{-3}. Scattering factors were taken from refs 18 and 19. All computations were carried out on a MicroVAX II employing the programs SDP[20] and SHELX-76[21] as described above.

Crystal Structure Determination and Refinement of 9. In an analogous manner to that described above, a light-yellow single crystal of 9, grown in pentane, was placed into the cold nitrogen stream of an Enraf-Nonius CAD-4 diffractometer. Unit cell dimensions were derived from the angular setting of 25 reflections. The crystal system was found to be monoclinic primitive. Crystal data and data collection parameters are given in Table I. Intensities were corrected for Lorentz and polarization effects but not for decay. A semiemperical absorption correction (ψ scans) with min 89.0% and max 100% transmission was carried out. Systematically absent reflections with $0k0$ ($k = 2n + 1$) reduced the choice of possible space groups to $P2_1$ and $P2_1/m$ with $Z = 2$. Since the molecule expected cannot adopt a C_s site symmetry, it was assumed that $P2_1$ was the correct choice. Structure solution and the identification of all non-hydrogen atoms was achieved by Patterson and Fourier techniques. Since the refinement of 9, however, did not improve the model, but rather led to unacceptable bond distortions along with considerable correlations between the matrix elements of the two C_5Me_4 rings, further refinement was carried out in the centrosymmetric space group $P2_1/m$. As a consequence of the mirror plane imposing C_s site symmetry on the molecule 9, the site occupation of atoms C12 and H121 was taken into account by assuming a disorder of the $CH(SiMe_3)_2$ residue by 50%. The hydrogen atoms H121, H131, H132, H151, and H152 were located on the difference Fourier map and refined with constant isotropic thermal parameter $U = 0.05$ Å^2. The remaining hydrogen atoms were placed on calculated positions (d(C–H) = 0.95 Å)[23] and refined with respect to their carrier atoms with fixed isotropic thermal parameter $U = 0.05$ Å^2. The final difference Fourier map showed no peak greater than 0.91 e Å^{-3} or less than −1.2 e Å^{-3}. Refinement by full-matrix least-squares fitting converged to $R = 0.023$. Reasonable bond distances proved $P2_1/m$ to be the correct choice.[24] Scattering factors were taken from refs 18 and 19.

The final atomic parameters are given in Tables II (5), III (7), and IV (9). Bond distances and angles are summarized in Tables V–VIII. Further details of the structure investigations are available on request from the Fachinformationszentrum Karlsruhe,

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Table II. Positional Parameters and Their Estimated Standard Deviations in $Me_2GeCp''_2SmCl_2Li(THF)_2$ (5)[a]

atom	*x/a*	*y/b*	*z/c*	B_{eq}[b]
Sm	0.16188 (1)	0.07483 (1)	0.29542 (1)	1.20
Ge	0.43147 (3)	0.12903 (1)	0.44186 (2)	1.52
C1	0.6209 (3)	0.1566 (2)	0.4298 (2)	2.60
C2	0.4278 (3)	0.1432 (2)	0.5575 (2)	2.48
C3	0.2886 (2)	0.1824 (1)	0.3708 (1)	1.46
C4	0.2924 (3)	0.1961 (1)	0.2859 (1)	1.65
C5	0.1563 (3)	0.2117 (1)	0.2469 (1)	1.77
C6	0.0657 (3)	0.2083 (1)	0.3056 (1)	1.74
C7	0.1458 (2)	0.1899 (1)	0.3814 (1)	1.51
C8	0.4176 (3)	0.2017 (2)	0.2434 (2)	2.64
C9	0.1177 (4)	0.2344 (2)	0.1597 (2)	2.50
C10	−0.0858 (3)	0.2267 (2)	0.2932 (2)	2.45
C11	0.0837 (3)	0.1837 (1)	0.4585 (2)	2.04
C12	0.3768 (2)	0.0361 (1)	0.4023 (1)	1.48
C13	0.2629 (2)	−0.0017 (1)	0.4258 (1)	1.54
C14	0.2196 (2)	−0.0525 (1)	0.3659 (1)	1.64
C15	0.3053 (2)	−0.0473 (1)	0.3050 (1)	1.62
C16	0.4018 (2)	0.0068 (1)	0.3265 (1)	1.56
C17	0.2027 (3)	0.0060 (2)	0.5036 (2)	2.26
C18	0.1083 (3)	−0.1059 (1)	0.3681 (2)	2.32
C19	0.3031 (3)	−0.0954 (2)	0.2340 (2)	2.45
C20	0.5152 (3)	0.0246 (2)	0.2783 (2)	2.48
Cl1	0.1099 (1)	0.04760 (3)	0.13395 (4)	2.22
Cl2	−0.1055 (1)	0.04158 (3)	0.29791 (4)	2.06
Li	−0.1119 (4)	0.0117 (2)	0.1600 (3)	2.13
O1	−0.1404 (2)	−0.0850 (1)	0.1475 (1)	2.45
C21	−0.2523 (3)	−0.1181 (2)	0.1805 (2)	2.91
C22	−0.3649 (3)	−0.1275 (2)	0.1089 (2)	3.74
C23	−0.2860 (4)	−0.1371 (2)	0.0375 (2)	3.60
C24	−0.1362 (3)	−0.1203 (2)	0.0714 (2)	2.79
O2	−0.2540 (2)	0.0627 (1)	0.0910 (1)	2.78
C25	−0.3397 (4)	0.1166 (2)	0.1145 (2)	3.35
C26	−0.3214 (4)	0.1784 (2)	0.0616 (2)	3.24
C27	−0.2367 (5)	0.1515 (2)	−0.0017 (2)	4.01
C28	−0.2464 (4)	0.0748 (2)	0.0061 (2)	3.34

[a] Estimated standard deviations are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$ [Å²].

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Results and Discussion

Ligand Synthesis. Compounds $Me_2Ge(C_5Me_4H)_2$ (**1**) and $Me_2Sn(C_5Me_4H)_2$ (**2**) were obtained in yields of ca. 25% by the reaction of Me_2GeCl_2 or Me_2SnCl_2 with 2 equiv of LiC_5Me_4H in THF (eq 1). **1** is a colorless solid and **2** a yellow crystalline solid melting at 78 or 70 °C, respectively.

$$Me_2ECl_2 + 2LiC_5Me_4H \rightarrow \underset{\substack{\mathbf{1},\ E = Ge \\ \mathbf{2},\ E = Sn}}{Me_2E(C_5Me_4H)_2} + 2LiCl \quad (1)$$

Unsuccessful attempts were made to prepare **1** and **2** in a manner similar to the synthesis of $Me_2Si(C_5Me_4H)_2$,[12] starting with the reaction of ECl_4 with LiC_5Me_4H (eq 2), followed by methylation of $Cl_2E(C_5Me_4H)_2$ with MeLi (eq 3) and subsequent protonation of the methylated product by CH_3OH (eq 4).

$$ECl_4 + 2LiC_5Me_4H \rightarrow Cl_2E(C_5Me_4H)_2 + 2LiCl \quad (2)$$
$$E = Si, Ge, Sn$$

$$Cl_2E(C_5Me_4H)_2 + 4MeLi \rightarrow Me_2E(C_5Me_4Li)_2 + 2LiCl + 2CH_4 \quad (3)$$
$$E = Si; E \neq Ge, Sn$$

$$Me_2E(C_5Me_4Li)_2 + 2CH_3OH \rightarrow Me_2E(C_5Me_4H)_2 + 2LiOCH_3 \quad (4)$$
$$E = Si; E \neq Ge, Sn$$

Table III. Positional Parameters and Their Estimated Standard Deviations in $Me_2Ge(C_5Me_4)_2LuCl_2Li(THF)_2$ (7)[a]

atom	*x/a*	*y/b*	*z/c*	B_{eq}[b]
Lu	0.16684 (1)	0.07597 (1)	0.29737 (1)	1.00
Ge	0.43537 (3)	0.12917 (2)	0.44375 (2)	1.24
C1	0.6266 (4)	0.1577 (2)	0.4330 (2)	2.05
C2	0.4314 (4)	0.1427 (2)	0.5597 (2)	2.07
C3	0.2895 (3)	0.1816 (1)	0.3706 (2)	1.34
C4	0.2934 (3)	0.1931 (1)	0.2855 (2)	1.52
C5	0.1531 (3)	0.2082 (1)	0.2446 (2)	1.37
C6	0.0615 (3)	0.2046 (1)	0.3026 (2)	1.37
C7	0.1437 (3)	0.1877 (1)	0.3802 (2)	1.27
C8	0.4198 (4)	0.2001 (2)	0.2435 (2)	2.38
C9	0.1149 (4)	0.2306 (2)	0.1565 (2)	2.20
C10	−0.0930 (4)	0.2232 (2)	0.2885 (2)	2.03
C11	0.0800 (4)	0.1831 (2)	0.4570 (2)	1.70
C12	0.3780 (3)	0.0364 (1)	0.4023 (2)	1.22
C13	0.2600 (3)	−0.0002 (1)	0.4241 (2)	1.37
C14	0.2123 (3)	−0.0506 (1)	0.3620 (2)	1.46
C15	0.3004 (3)	−0.0449 (1)	0.3015 (2)	1.40
C16	0.4010 (3)	0.0085 (1)	0.3248 (2)	1.30
C17	0.2017 (4)	0.0060 (2)	0.5027 (2)	1.91
C18	0.0998 (4)	−0.1040 (2)	0.3635 (2)	1.91
C19	0.2953 (4)	−0.0931 (2)	0.2291 (2)	1.88
C20	0.5183 (4)	0.0243 (2)	0.2788 (2)	1.92
Cl1	0.12204 (9)	0.05110 (4)	0.14157 (4)	1.72
Cl2	−0.09198 (8)	0.04364 (4)	0.30054 (4)	1.63
Li	−0.1037 (6)	0.0122 (3)	0.1626 (3)	2.13
O1	−0.1319 (3)	−0.0853 (1)	0.1492 (1)	2.00
C21	−0.2414 (4)	−0.1192 (2)	0.1836 (2)	2.58
C22	−0.3611 (4)	−0.1279 (2)	0.1114 (3)	3.05
C23	−0.2833 (4)	−0.1382 (2)	0.0385 (2)	2.79
C24	−0.1303 (4)	−0.1193 (2)	0.0721 (2)	2.21
O2	−0.2501 (3)	0.0615 (1)	0.0909 (1)	2.46
C25	−0.3412 (4)	0.1147 (2)	0.1132 (2)	2.62
C26	−0.3261 (4)	0.1769 (2)	0.0594 (2)	2.48
C27	−0.2390 (5)	0.1496 (2)	−0.0038 (3)	3.20
C28	−0.2446 (5)	0.0724 (2)	0.0054 (2)	2.60

[a] Estimated standard deviations are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$ [Å²].

Table IV. Positional Parameters and Their Estimated Standard Deviations in $Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$ (9)[a]

atom	*x/a*	*y/b*	*z/c*	B_{eq}[b]
Ho	−0.13030 (2)	0.25	−0.21874 (1)	1.23
Ge	0.17667 (5)	0.25	0.03046 (4)	1.71
C1	0.1844 (6)	0.25	0.1962 (4)	3.05
C2	0.3906 (5)	0.25	0.0402 (5)	2.87
C3	0.0593 (3)	0.1460 (2)	−0.0632 (2)	1.65
C4	0.0711 (3)	0.1156 (2)	−0.1755 (2)	1.68
C5	−0.0615 (3)	0.0658 (2)	−0.2355 (3)	1.81
C6	−0.1580 (3)	0.0662 (2)	−0.1638 (3)	2.07
C7	−0.0859 (3)	0.1152 (2)	−0.0587 (2)	1.81
C8	0.2077 (4)	0.1202 (2)	−0.2180 (3)	2.29
C9	−0.0860 (4)	0.0116 (2)	−0.3494 (3)	2.47
C10	−0.3022 (3)	0.0112 (2)	−0.1857 (3)	3.13
C11	−0.1495 (4)	0.1221 (2)	0.0438 (3)	2.86
C12	−0.2670 (6)	0.2288 (3)	−0.4266 (5)	1.62
Si1	−0.4564 (1)	0.25	−0.4124 (1)	1.75
C13	−0.4389 (5)	0.25	−0.2473 (4)	1.93
C14	−0.5708 (5)	0.1442 (3)	−0.4737 (3)	4.67
Si2	−0.2257 (1)	0.25	−0.5673 (1)	2.00
C15	−0.0150 (6)	0.25	−0.5410 (5)	3.36
C16	−0.3016 (5)	0.1441 (3)	−0.6617 (4)	3.50
H121	−0.2364	0.1723	−0.4073	4
H131	−0.5339	0.25	−0.2336	4
H132	−0.3854	0.2041	−0.2095	4
H151	0.0087	0.25	−0.6088	4
H152	0.0346	0.2001	−0.4943	4

[a] Estimated standard deviations are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$ [Å²].

The treatment of **1** and **2** with MeLi causes the formation of the desired dilithium salt, $Me_2E(C_5Me_4Li)_2$, only in the case of E = Ge (eq 5), as a colorless solid, whereas

Table V. Selected Bond Distances (Å) in $Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$[a] (5) and $Me_2Ge(C_5Me_4)_2LuCl_2Li(THF)_2$[a] (7)

	complex	
bond	5 (Ln = Sm)	7 (Ln = Lu)
Ln···Ge[b]	3.4514 (5)	3.378 (1)
Ln···Li[b]	3.433 (4)	3.350 (5)
Ln–Cl1	2.703 (1)	2.582 (1)
Ln–Cl2	2.686 (1)	2.565 (2)
Ln–C3	2.638 (2)	2.547 (3)
Ln–C4	2.690 (2)	2.580 (3)
Ln–C5	2.773 (2)	2.682 (3)
Ln–C6	2.767 (2)	2.676 (3)
Ln–C7	2.667 (2)	2.576 (3)
Ln–Cp_{1g}[c]	2.421	2.315
Ln–C12	2.632 (2)	2.547 (3)
Ln–C13	2.684 (2)	2.587 (3)
Ln–C14	2.753 (2)	2.662 (3)
Ln–C15	2.742 (2)	2.647 (3)
Ln–C16	2.661 (2)	2.565 (3)
Ln–Cp_{2g}	2.408	2.302
Ge–C1	1.958 (3)	1.948 (4)
Ge–C2	1.946 (3)	1.940 (3)
Ge–C3	1.971 (2)	1.964 (3)
Ge–C12	1.964 (2)	1.955 (3)
Li–Cl1	2.371 (4)	2.368 (6)
Li–Cl2	2.354 (4)	2.342 (6)
Li–O1	1.903 (5)	1.902 (6)
Li–O2	1.925 (5)	1.926 (6)
C3–C4	1.442 (3)	1.431 (4)
C3–C7	1.434 (3)	1.436 (4)
C4–C5	1.413 (3)	1.428 (4)
C5–C6	1.414 (3)	1.405 (5)
C6–C7	1.418 (3)	1.424 (4)
C12–C13	1.433 (3)	1.428 (4)
C12–C16	1.436 (3)	1.441 (4)
C13–C14	1.417 (3)	1.428 (4)
C14–C15	1.411 (3)	1.417 (5)
C15–C16	1.417 (3)	1.415 (4)
C4–C8	1.504 (4)	1.500 (5)
C5–C9	1.506 (3)	1.503 (4)
C6–C10	1.499 (4)	1.502 (5)
C7–C11	1.503 (3)	1.502 (5)
C13–C17	1.507 (3)	1.503 (5)
C14–C18	1.503 (3)	1.491 (5)
C15–C19	1.500 (4)	1.508 (5)
C16–C20	1.501 (3)	1.490 (5)
C21–C22	1.497 (5)	1.517 (5)
C21–O1	1.444 (3)	1.431 (5)
C22–C23	1.522 (5)	1.534 (6)
C23–C24	1.515 (4)	1.521 (5)
C24–O1	1.444 (3)	1.435 (4)
C25–C26	1.513 (4)	1.511 (5)
C25–O2	1.428 (3)	1.432 (5)
C26–C27	1.525 (5)	1.534 (6)
C27–C28	1.499 (5)	1.493 (6)
C28–O2	1.444 (3)	1.437 (4)

[a] Estimated standard deviations are given in parentheses. [b] Nonbonded distance. [c] Cp_{1g} and Cp_{2g} denotes the centroids of the cyclopentadienyl group C3–C4–C5–C6–C7 and C12–C13–C14–C15–C16, respectively.

for E = Sn the products were Me_4Sn and $2LiC_5Me_4H$ (eq 6).

$$1 + 2MeLi \rightarrow \underset{(3)}{Me_2Ge(C_5Me_4Li)_2} + 2CH_4 \qquad (5)$$

$$2 + 2MeLi \rightarrow Me_4Sn + 2LiC_5Me_4H \qquad (6)$$

The course of the reaction demonstrated by eq 6 could not be changed by variation of the reaction conditions, including lowering of the reaction temperature to −100 °C, or by the substitution of MeLi by bulkier organolithium bases.

Synthesis of Organolanthanide Halide and Organolanthanide Alkyl Complexes. The lanthanide trichlorides $NdCl_3$, $SmCl_3$, $HoCl_3$, and $LuCl_3$ react in THF with equimolar amounts of the new chelating ligand **3** to give the complexes $Me_2Ge(C_5Me_4)_2LnCl_2Li(THF)_2$ (**4**–**7**) (eq 7).

Compounds **4** and **7** are solids which are readily soluble in THF and moderately soluble in ether, benzene, or toluene. Their analytical and spectroscopic data as well as the X-ray structural analysis of **5** and **7** confirm the proposed structure.

Table VI. Selected Bond Angles (deg) in $Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$[a] (5) and $Me_2Ge(C_5Me_4)_2LuCl_2Li(THF)$[a] (7)

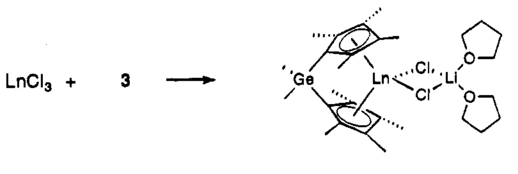
	complex	
bond	5 (Ln = Sm)	7 (Ln = Lu)
Cp_{1g}–Ln–Cp_{2g}[b]	124.5	127.9
Cp_{1g}[b]–Ln–Cl1	110.2	108.5
Cl1–Ln–Cl2	86.36 (2)	88.69 (3)
C1–Ge–C2	103.0 (1)	103.1 (2)
C1–Ge–C3	112.5 (1)	112.4 (1)
C1–Ge–C12	115.2 (1)	116.0 (1)
C2–Ge–C3	113.4 (1)	114.1 (1)
C2–Ge–C12	114.5 (1)	114.6 (1)
C3–Ge–C12	98.8 (1)	97.1 (1)
C4–C3–C7	105.9 (2)	106.4 (2)
C3–C4–C5	108.8 (2)	108.5 (3)
C4–C5–C6	108.3 (2)	108.3 (3)
C5–C6–C7	107.9 (2)	108.1 (3)
C3–C7–C6	109.0 (2)	108.6 (3)
C13–C12–C16	106.3 (2)	106.7 (2)
C13–C13–C14	108.7 (2)	108.9 (3)
C12–C14–C15	108.1 (2)	107.4 (3)
C14–C15–C16	108.3 (2)	108.9 (3)
C12–C16–C15	108.6 (2)	108.2 (3)
Ln–Cl1–Li	84.9 (1)	85.1 (1)
Ln–Cl2–Li	85.6 (1)	86.0 (2)
Cl1–Li–Cl2	102.6 (2)	99.6 (2)
Cl1–Li–O1	113.0 (2)	114.2 (3)
Cl1–Li–O2	109.3 (2)	110.0 (3)
Cl2–Li–O1	109.3 (2)	110.5 (3)
Cl2–Li–O2	111.1 (2)	112.5 (3)
O1–Li–O2	111.3 (2)	109.8 (3)
C21–O1–C24	104.3 (2)	105.3 (3)
O1–C21–C22	104.7 (2)	104.2 (3)
C21–C22–C23	103.8 (3)	103.2 (3)
C22–C23–C24	104.9 (3)	104.4 (3)
O1–C24–C23	105.7 (2)	106.2 (3)
C25–O2–C28	105.6 (2)	106.0 (3)
O2–C25–C26	107.1 (2)	106.8 (3)
C25–C26–C27	104.8 (3)	104.4 (3)
C26–C27–C28	103.4 (3)	103.7 (4)
O2–C28–C27	105.0 (3)	104.6 (3)

[a] Estimated standard deviations are given in parentheses. [b] See note *c* of Table V.

Table VII. Selected Interatomic Distances (Å) in $Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$[a] (9)

Ho–C12	2.418 (5)	Si1–C14	1.855 (4)
Ho···C13[b]	2.774 (4)	Si2–C12	1.844 (6)
Ho···Si1[b]	3.185 (1)	Si2–C15	1.880 (6)
Ho–C3	2.586 (3)	Si2–C16	1.879 (4)
Ho–C4	2.609 (3)	C3–C4	1.435 (4)
Ho–C5	2.716 (3)	C3–C7	1.431 (4)
Ho–C6	2.723 (3)	C4–C5	1.408 (4)
Ho–C7	2.637 (3)	C5–C6	1.407 (5)
Ho–Cp_g[c]	2.366	C6–C7	1.404 (4)
Ge–C1	1.942 (5)	C4–C8	1.499 (4)
Ge–C2	1.950 (5)	C5–C9	1.509 (4)
Ge–C3	1.964 (3)	C6–C10	1.501 (4)
Si1–C12	1.837 (5)	C7–C11	1.505 (4)
Si–C13	1.911 (4)	Ho···H121	2.41

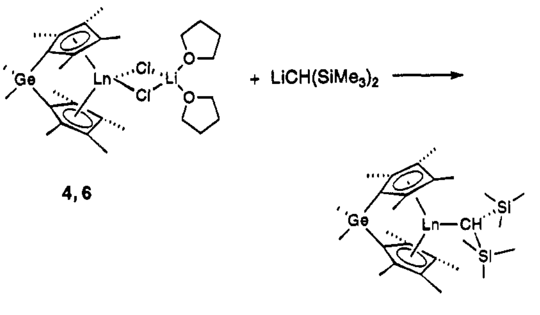
[a] Estimated standard deviations are given in parentheses. [b] Nonbonded distance. [c] Cp_g denotes the centroids of the cyclopentadienyl group (C3–C4–C5–C6–C7). Cp_g', C14′, and C16′ are mirror related to Cp_g, C14, and C16, respectively. Symmetry transformation (*x*, 0.5 − *y*, *z*).



(7)

Ln = Nd (**4**), Sm (**5**), Ho (**6**), Lu (**7**)

The reaction of **4** and **6** with $LiCH(SiMe_3)_2$ in toluene at −78 °C afforded the monomeric and base-free alkyl complexes **8** and **9** (eq 8).



(8)

4, 8: Ln = Nd

6, 9: Ln = Ho

8 and **9** are air- and moisture-sensitive compounds which are readily soluble in pentane and toluene. Enclosed in argon-filled glass capillaries, **8** decomposes at 180 °C whereas **9** is stable up to 234 °C. Elemental analysis, ^1H NMR and mass spectra, and X-ray structural analysis of **9** prove the suggested molecular formula and structure. The ^1H NMR spectra reveal large chemical shifts ranging from +126 to −17 ppm for **8**, and from +70 to −225 ppm for **9**. Similar values of +136 to −17 ppm have been reported for $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$[11] for which the resonance at 136 ppm was assigned to the hydrogen atom in closest proximity to the Nd^{3+} ion, the $CHSi_2$ hydrogen. The corresponding signal in **9** could not be located, probably due to a large dipolar shift and/or loss of intensity by an extremely short relaxation time, which often is observed for protons in vicinity of a paramagnetic metal ion.

Molecular Structure of 5 and 7. The structures of **5** and **7** show both compounds to belong to the most commonly encountered type of bent metallocenes of the general formula $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2MB_2$, (Ln = lanthanide element, M = alkali metal, B = hard Lewis base). Figure 1 shows an ORTEP[25] plot of the molecule **5** with the atomic numbering scheme, which is exactly the same for the isostructural **7**. In fact the lanthanide to element (carbon and chlorine) bonds differ by 0.10 ± 0.02 Å which matches the difference (Δr = 0.102 Å) in ionic radii[26] of eight-coordinate Sm^{3+} (r = 1.079 Å) and Lu^{3+} (r = 0.977 Å).

Compounds **5** and **7** are in good agreement with special structural features of ring-bridged complexes such as $[Me_2Si(C_5Me_4)_2NdCl]_2ClLi(THF)_2$[11] and $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$[11] with respect to the considerable dispersion, e.g. in the Sm–C_{ring} bond distances, ranging from 2.632 (3) to 2.773 (3) Å and the remarkable contraction by 3–9° of the (ring centroid)–Sm–(ring centroid) angle (124.5°) for **5**. For the latter, values of 134.5, 138.5, and 128.2° were reported for $(C_5Me_5)_2SmCl(THF)$,[6] $(C_5Me_5)_2Sm(C_6H_5)(THF)$,[27] and $((C_5Me_5)_2SmCl)_3$.[28]

Table VIII. Selected Interatomic Angles (deg) in $Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$ (9)[a]

Cp_g–Ho–Cp_g'[c]	125.9	C3–Ge–C3′[c]	97.6 (1)
Cp_g–Ho–C12[c]	108.0	Ge–C3–Cp_g[c]	162.2
Cp_g–Ho···C13[b,c]	107.1	C4–C3–C7	106.3 (2)
Cp_g'–Ho–C12[c]	122.1	C3–C4–C5	108.5 (2)
C12–Ho···C13[b]	71.1 (2)	C3–C4–C8	127.6 (3)
Ho–C12–Si1	96.0 (2)	C5–C4–C8	123.3 (3)
Ho–C12–Si2	135.2 (3)	C4–C5–C6	108.1 (2)
Si1–C12–Si2	121.5 (3)	C4–C5–C9	125.3 (3)
Ho–C12–H121	80 (6)	C6–C5–C9	126.2 (3)
C12–Si1–C13	108.0 (2)	C5–C6–C7	108.6 (2)
C12–Si1–C14	106.1 (2)	C5–C6–C10	126.1 (3)
C14–Si1–C14′[c]	108.3 (2)	C7–C6–C10	124.6 (3)
C13–Si1–C14	105.1 (1)	C3–C7–C6	108.5 (2)
C12–Si2–C15	110.0 (2)	C3–C7–C11	127.8 (3)
C12–Si2–C16	105.2 (2)	C6–C7–C11	123.4 (3)
C16–Si2–C16′[c]	106.5 (1)	C8–C4–Cp_g[c]	172.9
C15–Si2–C16	106.2 (2)	C9–C5–Cp_g[c]	173.9
C1–Ge–C2	102.6 (2)	C10–C6–Cp_g[c]	172.7
C1–Ge–C3	114.4 (1)	C11–C7–Cp_g[c]	174.6
C2–Ge–C3	114.2 (1)		

[a] Estimated standard deviations are given in parentheses. [b] Nonbonded distance. [c] Cp_g denotes the centroids of the cyclopentadienyl group (C3–C4–C5–C6–C7). C3′, Cp_g', C14′, and C16′ are mirror related to C3, Cp_g, C14, and C16, respectively. Symmetry transformation (x, 0.5 − y, z).

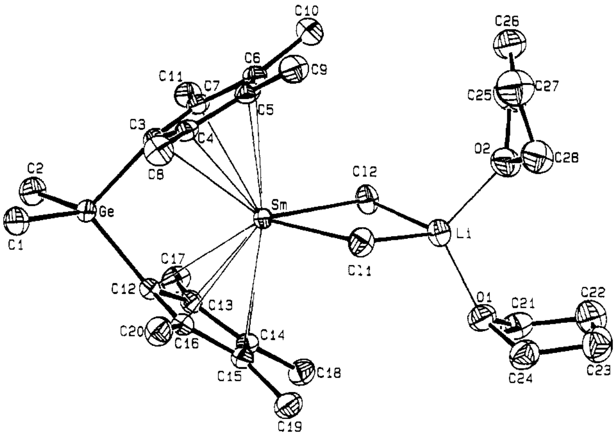


Figure 1. ORTEP drawing[25] of the molecular structure of $Me_2Ge(C_5Me_4)_2SmCl_2Li(THF)_2$ (**5**) with the numbering scheme. Thermal ellipsoids scaled at 50% probability level. Hydrogen atoms omitted for clarity.

Taking other $(C_5Me_5)_2Sm$ compounds into account such as $(C_5Me_5)_2Sm(THF)_2$,[29] $(C_5Me_5)_2Sm$,[30] and $(C_5Me_5)_{10}Sm_5Cl_5$(tetraglyme)[28] having (ring centroid)–Sm–(ring centroid) angles of 137, 140.1, and 133–136°, a value of 128.2° appears to be exceptional, so that a contraction as high as 9–12° seems to come closest to the truth. This contraction is stronger with the Me_2Si group as a ring bridge as shown in $[Me_2Si(C_5Me_4)_2NdCl]_2ClLi(THF)_2$ which has an angle of 121.3°.[11] The difference observed in the angle (ring centroid)–Nd–(ring centroid) between $(C_5Me_5)_2NdR$[9] and $Me_2Si(C_5Me_4)_2NdR$[11] (R = $CH(SiMe_3)_2$) is 12.8°. While internal C_5Me_4 ring parameters (average $\bar{d}$ (C_{ring}–C_{ring}) = 1.424 (3) Å and $\bar{d}$ (C_{ring}–C_{methyl}) = 1.503 (3) Å) fall in the usual range, the Sm–(ring centroid) distance of 2.415 Å appears to be shorter by 0.04 Å than expected. Typical values are close to 2.45–2.46 Å.[27-30] However the average Sm–Cl bond distance of 2.695 Å falls

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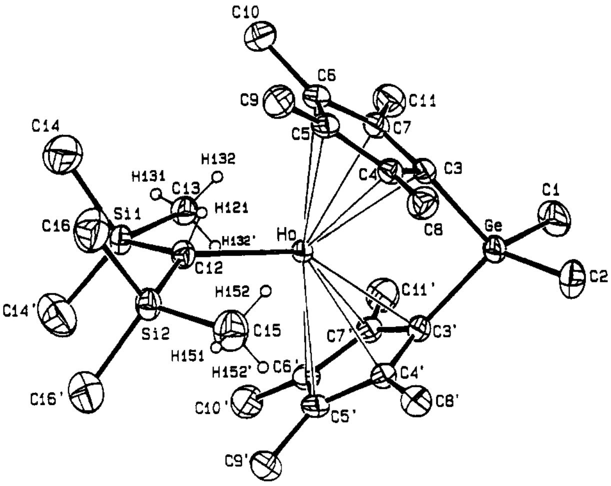

Figure 2. ORTEP drawing[25] of the molecular structure of $Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$ (**9**) with the numbering scheme. Thermal ellipsoids scaled at 50% probability level. Only one position of the disordered atoms C12 and H121 is shown. Less important hydrogen atoms omitted for clarity.

in the range of 2.689–2.719 Å which is the calculated magnitude for a Sm–Cl bond in $Ln(\mu\text{-}Cl)_2M$ systems. This estimate is based on the sum of the ionic radii of Sm^{3+} (r = 1.079 Å) and the "effective" ionic radii of $\mu^2\text{-}Cl^-$ (r = 1.61–1.64 Å) as derived by Evans.[31] In accordance with the smaller radial size of Lu^{3+}, the average Lu–Cl bond distance of 2.574 (2) Å in **7** is shorter than the Sm–Cl distance by 0.121 Å and the Cl_1–Lu–Cl_2 angle of 88.68 (3)° is consequently widened by 2.33° (∠ (Cl_1–Sm–Cl_2) = 86.36 (2)°).

Noteworthy is the pronounced dependence of the important (ring centroid)–Ln–(ring centroid) angle on the radial size of the complexed lanthanide ion in the Me_2Ge–ring-bridged compounds **5**, **7**, and **9** compared with related nonbridged $(C_5Me_5)_2$ analogues. The latter increases by a total of 3° from 134° for $(C_5Me_5)_2CeCH(SiMe_3)_2$[32] to 137° for $(C_5Me_5)_2LuCl(THF)$[33] as the size of the Ln^{3+} ion decreases by 0.163 Å, while an angle expansion of 3.4° is being observed from 124.5° for **5** to 127.9° for **7** along with a markedly smaller decrease in the radial size from Sm^{3+} to Lu^{3+} by only 0.102 Å.

Molecular Structure of 9. Compound **9** is made up of monomeric molecules of the bent metallocene type and is bisected by a crystallographic mirror plane. This plane m imposes C_s symmetry on **9** with C1, C2, Ge, Ho, Si1, C13, Si2, and C15 lying on it. The tetramethylcyclopentadienyl ring (C_5Me_4) and one methyl group on each silicon atom is duplicated by m and thus metrical data for mutually mirror-related structure elements of **9** are identical. Hence, two (mirror-related) C_5Me_4 rings are bonded to Ho^{3+} in an η^5 fashion and do not evidence any unusual internal parameters:[34] $\bar{d}$ (C_{ring}–C_{ring}) = 1.417 (4) Å and $\bar{d}$(C_{ring}–C_{methyl}) = 1.504 (4) Å (Figure 2). The Me_2Ge bridge enforces a considerable dispersion in Ho–C_{ring} distances, ranging from 2.586 (3) to 2.723 (3) Å with the shortest distance being to the carbon atom C3, which is also connected to the bridge Me_2Ge. The mentioned ring linkage causes a (ring centroid)–Ho–(ring centroid) angle contraction to 125.9°. The most important feature of **9**, however, is the extremely asymmetrical conformation of the carbyl ligand $CH(SiMe_3)_2$. Naturally, C12 and H121 have no mirror image within one molecule. Consequently, C12 does not lie in the plane m but 0.302 (5) Å above it. The deviation of the sp^3 hybridized C12 from an ideally tetrahedral arrangement of its substituents can best be seen by inspecting the angles between the three non-hydrogen atoms Ho, Si1, and Si2: ∠(Ho–C12–Si1) = 96.0 (2)°, ∠(Ho–C12–Si2) = 135.2 (3)° and ∠(Si1–C12–Si2) = 121.5 (3)°. A total of 352.7° suggests a substantial approach to a pseudo-trigonal planar geometry. The Ho–C12 distance of 2.418 (5) Å is significantly shorter than the value observed in $[Li(TMED)]_3[Ho(CH_3)_6]$[35] of 2.563 (20) Å, which is explained by the different type of holmium to carbon bond in both structures. Bridging methyl groups, as in the latter case, are less strongly bonded to the Ln^{3+} and therefore these bonds are elongated by roughly 0.1 Å.[31] We find a shortening of 0.145 (25) Å. Short intramolecular contacts between Ho and Si1 (3.185 (3) Å) and Ho and C13 (2.774 (4) Å) are particularly noteworthy. The significance of 2.774 (4) Å for a Ho–methyl contact becomes obvious if one compares this value with 2.723 (3) Å which is assigned to the Ho–C7 bond. This kind of interaction between a coordinatively unsaturated lanthanide Ln^{3+}(Ho^{3+}, CN = 7) and C13 is supposedly not the result of an agostic, electron deficient Ho···H–C bond, as observed in organo transition metal complexes,[36] but more likely a γ-agostic Ho···C(methyl) interaction. If a hydrogen bridge between Ho and C13 is responsible for the short distance observed, it would be most likely to find this hydrogen atom (here H132) on the mirror plane, because this would ensure the strongest possible bond. On the contrary, the situation (Figure 3) is reminiscent of the quasi planar transition state for a β-alkyl elimination.[11] Such a distortion of the $CH(SiMe_3)_2$ ligand has attracted considerable attention.[9a,11,32,37-40] Moreover, H121 is bent back to the Ho^{3+} ion (∠(Ho–C12–H121) = 80 (6)°), indicating an α-agostic interaction. For $(C_5Me_5)_2YCH(SiMe_3)_2$,[37] $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$,[11] $(C_5Me_5)La[CH(SiMe_3)_2]_2$,[38] and

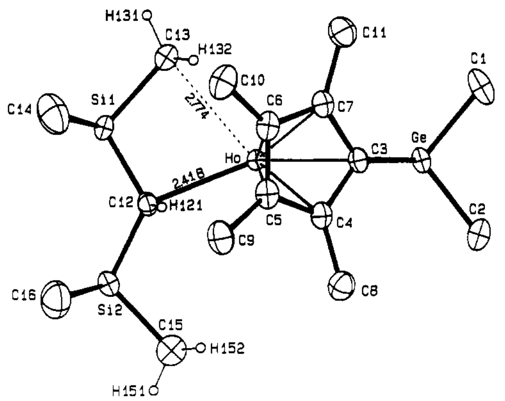

Figure 3. ORTEP drawing[25] of a view down the b axis in **9**. This picture illustrates the unsymmetrical conformation of the $CH(SiMe_3)_2$ ligand. Important hydrogen atoms are included. The dashed line indicates the γ-agostic Ho···C13 interaction.

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$(C_5Me_5)La(THF)[CH(SiMe_3)_2]_2$,[38] the following respective values have been reported: 84 (3)°; 76°; 86 (3)°, 85 (3)°; and 81 (5)°, 106 (8)°. In order to prove the γ-agostic interaction Ho···C13 to be sufficiently strong enough to be detected by other analytical methods (especially in solution) and to distinguish it from crystal packing effects, attempts to record ^{1}H NMR spectra were undertaken. Room-temperature ^{1}H NMR spectra show 18 equivalent protons for all six methyl groups of the $C(Si(C\mathit{H}_3)_3)_2$ ligand at −199.5 ppm. Four peaks are detected for the eight methyl groups of the two C_5Me_4 rings, while we find only one signal for the two methyl groups bonded to Ge (69.61 ppm). This is clearly a time-averaged spectrum, indicating that the "bond" energy of the γ-agostic Ho···C13 bond is much smaller than at room temperature. Low-temperature ^{1}H NMR spectra of **9**, recorded in toluene, showed a rapid decrease of the intensity of the peak for the $C(Si(C\mathit{H}_3)_3)_2$ group along with a high-field shift. At about 213 K this particular resonance disappeared. Unfortunately **9** becomes increasingly less soluble in toluene and forms a precipitate as one lowers the temperature to 203 K.

After submission of this paper, Marks et al.[40] reported on the synthesis and structural analysis of some Me_2Si–ring bridged dicyclopentadienyllutetium complexes. The coordination of the π-ligand in $Me_2Si(C_5Me_4)(C_5H_4)LuCH(SiMe_3)_2$ is similar to that in **7** and the overall geometry of the carbyl ligand $CH(Si(CH_3)_3)_2$ compares favorably with that of **9**.

Acknowledgment. Financial support by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and the Bundesminister für Bildung und Wissenschaft (Graduiertenkolleg "Synthese und Strukturaufklärung niedermolekularer Verbindungen", Doktoranden-Stipendium für L.E.) is gratefully acknowledged. This work was also supported by a special grant of the TU Berlin within the exchange program TU Berlin/University of Oklahoma. We thank Prof. J. Pickardt for giving us access to the MicroVax II, Dr. C. Mügge (Humboldt Universität, Berlin) for low-temperature NMR, and A. Kucht for mass spectra.

Supplementary Material Available: Tables of thermal parameters and hydrogen parameters for **5**, **7**, and **9** (6 pages); listings of observed and calculated structure factors for **5**, **7**, and **9** (61 pages). Ordering information is given on any current masthead page.

Convenient Synthesis of Cationic (η^3-Allyl)palladium Complexes. Preparative and Stereochemical Aspects

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Received November 28, 1990

The oxidative addition of allylic trifluoroacetates to $Pd(dba)_2$ (dba = dibenzylideneacetone) gives (η^3-allyl)palladium trifluoroacetates in excellent yields. The stereochemistry of the reaction is solvent dependent; i.e., predominant trans addition is observed in a THF/MeCN mixture, whereas cis addition dominates in pure THF. By addition of a neutral ligand the trifluoroacetates can be converted to cationic complexes either directly (giving trifluoroacetate salts) or by in situ ion exchange with tetrafluoroboric acid (giving tetrafluoroborate salts). The syn–anti stereochemistry of the cationic η^3-allyl complexes can be largely controlled by the use of the hindered ligand 2,9-dimethyl-1,10-phenanthroline under the appropriate preparative conditions. Cationic complexes with phenanthroline ligands can also be prepared in good yields by acid-assisted oxidative addition of allylic acetates and alcohols to $Pd(dba)_2$.

Introduction

Methods for selective preparation of (*Z*)-alkenes are of considerable interest in synthetic organic chemistry. We have recently found that a route via cationic (η^3-allyl)palladium complexes may be feasible. This is based on the ability of ligands such as 2,9-disubstituted phenanthrolines to induce an unusual thermodynamic preference for the anti configuration over the syn configuration (Scheme I).[1] Nucleophilic addition to the anti complex can then lead to the desired (*Z*)-alkene.

During our continued studies of the influence of ligands on the syn–anti equilibrium, we felt the need for a simple and general synthesis of cationic (η^3-allyl)palladium complexes. Although alternative routes have sometimes been used,[2] such complexes have been prepared from the corresponding chloride bridged dimers, generally by treatment with metal salts and the appropriate neutral ligands.[3] The chloride-bridged dimers, in turn, have been prepared by

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