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Bis(pentamethylcyclopentadienyl) Complexes of Cerium(III). Crystal Structure of $(C_5Me_5)_2CeCH(SiMe_3)_2$

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$CeCl_3 \cdot x$THF ($1 < x < 2$) reacts with 2 equiv of Cp*Li[1] in THF forming $Cp^*{}_2CeCl_2Li(THF)_{2.5}$ (**1**). The coordinated THF can easily be displaced by DME to form $Cp^*{}_2CeCl_2Li(DME)$ (**2**). When **1** is heated to 250 °C (0.01 mmHg), $(Cp^*{}_2CeCl)_n$ (**4**) sublimes. A number of adducts, $Cp^*{}_2CeCl \cdot L_n$ (**5**, L = THF, n = 1; **6**, L = t-BuCN, n = 2), are accessible starting from **4**. Metathesis of **4** with $LiCH(SiMe_3)_2$ and $NaN(SiMe_3)_2$ in toluene gives $Cp^*{}_2CeCH(SiMe_3)_2$ (**8**) and $Cp^*{}_2CeN(SiMe_3)_2$ (**11**), respectively. Compound **8** reacts with LiCl in the presence of TMEDA to form $Cp^*{}_2CeCl_2Li(TMEDA)_2$ (**3**) and $LiCH(SiMe_3)_2$. Addition of t-BuCN to **8** affords the adduct $Cp^*{}_2CeCH(SiMe_3)_2 \cdot t$-BuCN (**9**). $(Cp^*{}_2CeH)_2$ (**10**) can be made by hydrogenolysis of **8** under mild conditions. $Cp^*{}_2CeNH$-t-Bu$\cdot NH_2$-t-Bu (**12**) and also **11** are prepared by the reaction of **8** with the corresponding amines. **8** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.061 (3) Å, b = 23.46 (1) Å, c = 11.692 (5) Å, and β = 102.99 (2)° (Z = 4). Least-squares refinement leads to a final R (based on F) of 0.038 for 5534 independent reflections. The molecular structure consists of monomeric $Cp^*{}_2CeCH(SiMe_3)_2$ units with a bent sandwich configuration. The average (ring centroid)–Ce–(ring centroid) angle is 134°. The $CH(SiMe_3)_2$ fragment is coordinated in a highly unsymmetrical fashion with a Ce–C σ-bond distance of 2.536 (5) Å.

Introduction

The recent development of organolanthanide chemistry has been focused almost exclusively on the small, late lanthanides. Cp_3Ln, Cp_2LnX, and $CpLnX_2$ complexes and homologues with substituted cyclopentadienyl ligands have been studied extensively. The chemistry of the early lanthanides (Ln = La, Ce, Pr) has been severely limited by the failure to synthesize mono- and bis(cyclopentadienyl) complexes.[2] In general, these metals seem to require more bulky ligands to achieve stable configurations. A number of $(C_5R_5)_2LnX$ (Ln = La–Nd) complexes have been reported that contain bridged dicyclopentadienyl[3] or substituted cyclopentadienyl ligands.[4] Especially the pentamethylcyclopentadienyl (Cp*) group is a very suitable ligand, and a number of $Cp^*{}_2LnX$[5] together with a few Cp^*LnX_2[6] complexes have been prepared.

Our group has reported extensively on the chemistry of $Cp^*{}_2MR$ complexes (M = Ti,[7] Y[8]), and this work stimulated our interest in lanthanide organometallics and especially in monomeric, coordinatively unsaturated pentamethylcyclopentadienyl complexes of the early lanthanides. Because of the large ionic radius of early lanthanides and a consequently large coordination sphere, these metals are expected to show unique chemical behavior. In the following we will focus on the synthesis and characterization of a number of bis(pentamethylcyclopentadienyl)cerium(III) halide, carbyl, amide, and hydride complexes. A preliminary account of part of this work has been published recently.[9]

Experimental Section

General Considerations. All compounds are extremely air-sensitive, and therefore manipulations were carried out by using Schlenk, vacuum line, or glovebox techniques under nitrogen or argon. Solvents were distilled from Na/K alloy under nitrogen prior to use. TMEDA, DME, $HN(SiMe_3)_2$, H_2N-t-Bu, and t-BuCN were distilled under nitrogen and stored over molecular sieves (3 Å). MeI (Merck) was vacuum transferred from KOH. Hydrogen (Hoek-Loos, 99.9995%) and deuterium (Matheson, C.P.) were used without further purification. CeO_2 (Aldrich) was used as purchased. Cp*H was synthesized by Burger's method[10] and converted to Cp*Li according to ref 11. $NaN(SiMe_3)_2$[12] and $LiCH(SiMe_3)_2$[13] were prepared following published procedures and the latter was sublimed at 90 °C (0.01 mmHg) before use. IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on Nicolet NT-200, Bruker WH-90, and Varian VXR-300 spectrometers. Chemical shifts are reported in parts per million and referenced to residual protons in deuteriated solvents (benzene-d_6, δ 7.15; THF-d_8, δ 1.72; toluene-d_8, δ 7.02; cyclohexane-d_{12}, δ 1.36). ^{13}C NMR chemical shifts were referenced to benzene-d_6 (δ 127.96) or cyclohexane-d_{12} (δ 26.60). Gas chromatography was performed with a HP 5890-A GC instrument using a Porapak Q packed column and a HP 3390 integrator. Vacuum sublimations were carried out by using a homemade sublimation apparatus equipped with a Philips IR lamp (375W/220V) connected to a variable resistor.[14] Elemental

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[1] In this paper the following abbreviations are used: Cp, η^5-C_5H_5; Cp*, η^5-C_5Me_5; Ln, 4f element; lw, line width at half-maximum.

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analyses were performed at the Microanalytical Department of this institute under supervision of A. F. Hamminga. All found percentages are the average of at least two independent determinations.

Preparation of CeCl$_3$·xTHF. CeO$_2$ (43.9 g, 0.255 mol), 500 mL of hydrochloric acid (37%), and 5.0 mL (0.13 mol) of HCOOH were stirred under reflux for 24 h. The resulting clear solution was evaporated to dryness. The remaining solid was dehydrated under vacuum (0.01 mmHg) at ca. 170 °C for 48 h. Yield: 60.5 g (0.245 mol, 96%). Anal. Calcd for CeCl$_3$: Ce, 56.85; Cl, 43.15. Found: Ce, 56.83; Cl, 43.48. CeCl$_3$·xTHF ($1 < x < 2$) was prepared by continuous extraction of CeCl$_3$ with THF.[15] The THF content was determined by elemental analysis.

Preparation of Cp*$_2$CeCl$_2$Li(THF)$_n$ (1). CeCl$_3$·xTHF (5.65 g, x = 1.95, 14.6 mmol) was suspended in 250 mL of THF, and 4.33 g (30.5 mmol) of Cp*Li was added at room temperature. After being stirred for 8 h under reflux, the clear yellow solution was dried in vacuo. The residue was extracted with two 50-mL portions of pentane. The extract was concentrated to ca. 50 mL and cooled to −80 °C to give 7.39 g (11.1 mmol, 76%) of **1** as yellow crystals. IR (cm^{-1}): 2710 (w), 2110 (w), 1045 (s), 910 (m), 890 (m), 790 (vw), 715 (w), 670 (vw). Anal. Calcd for C$_{30}$H$_{50}$CeCl$_2$LiO$_{2.5}$: C, 53.30; H, 7.52; Ce, 20.96; Cl, 10.60. Found: C, 53.35; H, 7.25; Ce, 20.78; Cl, 10.79. Yellow Cp*$_2$CeCl$_2$Li(DME) (**2**) was prepared by addition of an excess of DME to a solution of in situ prepared **1**. Crystallization from toluene gave **2** in 34% yield. IR (cm^{-1}): 2720 (w), 1375 (m), 1280 (w), 1245 (w), 1190 (m), 1120 (m), 1080 ns), 1020 (m), 875 (m), 805 (w), 725 (w). Anal. Calcd for C$_{24}$H$_{40}$CeCl$_2$LiO$_2$: C, 49.82; H, 6.97. Found: C, 49.86; H, 6.90.

Preparation of Cp*$_2$CeCl$_2$Li(TMEDA)$_2$ (3). **8** (0.42 g, 0.7 mmol), 0.07 g (1.7 mmol) of LiCl, and TMEDA (0.22 mL, 1.5 mmol) were stirred in 20 mL of pentane for 2 h at room temperature. The color of the suspension gradually changed from red to yellow. After removal of the volatiles in vacuo, the residue was extracted with Et$_2$O (40 mL). Concentration and crystallization at −80 °C gave **3** as yellow crystals. Yield: 0.30 g (0.4 mmol, 57%). IR (cm^{-1}): 2790 (m), 2710 (w), 2110 (w), 1380 (m), 1360 (m), 1290 (s), 1250 (m), 1185 (m), 1160 (m), 1130 (m), 1100 (w), 1070 (m), 1040 (s), 1020 (s), 950 (s), 855 (w), 790 (s), 595 (w), 500 (m), 445 (m). Anal. Calcd for C$_{32}$H$_{62}$CeCl$_2$LiN$_4$: C, 53.32; H, 8.67; Cl, 9.84. Found: C, 52.92; H, 8.50; Cl, 10.24.

Preparation of (Cp*$_2$CeCl)$_n$ (4). **4** sublimed on heating 3.97 g (6.3 mmol) of **1** at 250 °C (0.01 mmHg). After being washed with two portions of pentane (10 mL), **4** was isolated as an orange solid. Yield: 2.06 g (4.6 mmol, 73%). IR (cm^{-1}): 2720 (w), 2360 (w), 2130 (w), 1380 (m), 1260 (w), 1055 (w), 1020 (m), 800 (w). Anal. Calcd for C$_{20}$H$_{30}$CeCl: C, 53.85; H, 6.78; Cl, 7.95. Found: C, 54.21; H, 7.02; Cl, 8.24.

Preparation of Cp*$_2$CeCl·THF (5). **4** (8.48 g, 19.0 mmol) was dissolved in THF (100 mL). After stirring for 30 min at room temperature, the resulting clear yellow solution was concentrated and cooled to −80 °C. Isolation gave **5** as yellow needles. Yield: 8.53 g (16.5 mmol, 87%). IR (cm^{-1}): 2705 (w), 2130 (w), 1375 (m), 1340 (w), 1040 (m), 1020 (s), 910 (w), 855 (s), 795 (w). Anal. Calcd for C$_{24}$H$_{38}$CeClO: C, 55.63; H, 7.40; Ce, 27.04, Cl, 6.84; mol wt, 518. Found: C, 55.38; H, 7.37; Ce, 27.08; Cl, 6.88; mol wt (C$_6$H$_6$), 513 ± 21.

Preparation of Cp*$_2$CeCl·2-*t*-BuCN (6). **4** (0.80 g, 1.8 mmol) was suspended in a mixture of pentane (15 mL) and toluene (10 mL). *t*-BuCN (2.0 mL, 18.3 mmol) was added at room temperature, and the mixture was stirred for 70 h. The yellow suspension was vacuum dried, and the remaining solid was dissolved in Et$_2$O (50 mL). This solution was cooled to −80 °C, and yellow crystals of **6** separated. Yield: 0.70 g (1.1 mmol, 61%). IR (cm^{-1}): 2710 (w), 2260 (s), 1480 (m), 1375 (m), 1240 (s), 1205 (m), 1025 (m), 800 (w), 695 (m). ^{13}C NMR (toluene-d_8, 21 °C): δ 205.4 (s, *C*$_5$Me$_5$), 131.2 (s, *C*N), 25.7 (s, *C*Me$_3$), 22.4 (q, C*Me*$_3$, $^1J_{C-H}$ = 130 Hz), 11.2 (q, C$_5$*Me*$_5$, $^1J_{C-H}$ = 125 Hz). Anal. Calcd for C$_{30}$H$_{48}$CeClN$_2$: C, 58.85; H, 7.90; Ce, 22.89; mol wt, 621. Found: C, 58.71; H, 7.84; Ce, 22.93; mol wt (C$_6$H$_6$), 423 ± 10.

Preparation of Cp*$_2$CeCH(SiMe$_3$)$_2$ (8). **4** (15.98 g, 35.8 mmol) and 5.90 g (35.5 mmol) of LiCH(SiMe$_3$)$_2$ were suspended in 400 mL of toluene. After stirring for 5 h at room temperature, the deep red suspension was evaporated to dryness. The resulting solid was extracted with pentane (200 mL). Concentration to ca. 50 mL and cooling to −80 °C gave **8** as deep-red crystals (11.22 g, 19.7 mmol, 55%). IR (cm^{-1}): 2715 (w), 1375 (m), 1250 (s), 1240 (s), 1040 (m), 1020 (m), 860 (vs), 825 (s), 760 (m), 660 (w), 575 (m). ^{13}C NMR (benzene-d_6, 20 °C): δ 301.4 (multiplicity not observed, *C*H), 194.5 (s, *C*$_5$Me$_5$), 191.6 (s, *C*$_5$Me$_5$), 10.0 (q, C$_5$*Me*$_5$, $^1J_{C-H}$ = 124 Hz), 9.1 (q, C$_5$*Me*$_5$, $^1J_{C-H}$ = 124 Hz), −0.6 (q, Si*Me*$_3$, $^1J_{C-H}$ = 116 Hz). Anal. Calcd for C$_{27}$H$_{49}$CeSi$_2$: C, 56.89; H, 8.67; Ce, 24.58. Found: C, 56.89; H, 8.60; Ce, 24.58.

Preparation of Cp*$_2$CeCH(SiMe$_3$)$_2$·*t*-BuCN (9). *t*-BuCN (0.45 mL, 0.4 mmol) was added to a solution of 0.21 g (0.4 mmol) of **8** in 10 mL of pentane. The solution turned orange immediately after the admission of *t*-BuCN. After stirring for 30 min at room temperature, the clear solution was concentrated and cooled to −80 °C. Isolation gave 0.12 g (0.2 mmol, 50%) of **9** as gold crystals. IR (cm^{-1}): 2730 (w), 2250 (m), 1400 (w), 1375 (m), 1245 (s), 1230 (s), 1200 (w), 1020 (s), 850 (vs), 830 (vs), 765 (m), 675 (m), 660 (m), 580 (m). Anal. Calcd for C$_{32}$H$_{58}$CeNSi$_2$: C, 58.85; H, 8.95; Ce, 21.46; N, 2.14. Found: C, 59.05; H, 9.01; Ce, 21.40; N, 2.41.

Preparation of (Cp*$_2$CeH)$_2$ (10). **8** (2.99 g, 5.3 mmol) was dissolved in 40 mL of pentane and stirred for 2 h under an atmosphere of hydrogen (1 atm) at room temperature. The resulting green suspension was filtered, and the green residue was washed with pentane (20 mL). Yield: 1.66 g (4.0 mmol, 75%) of **10**. IR (cm^{-1}): 2705 (w), 1370 (m), 1120 (s, br), 1010 (m), 940 (m, br), 800 (w), 770 (m, br), 570 (m). ^{13}C NMR (cyclohexane-d_{12}, 20 °C): δ 210.2 (s, *C*$_5$Me$_5$), 7.4 (q, $^1J_{C-H}$ = 125 Hz, C$_5$*Me*$_5$). Anal. Calcd for C$_{20}$H$_{31}$Ce: C, 58.36; H, 7.59; Ce, 34.04; mol wt, 823. Found: C, 58.27; H, 7.94; Ce, 33.83; mol wt (C$_6$H$_6$), 816 ± 90.

(Cp*$_2$CeD)$_2$ was prepared via an analogous procedure using D$_2$. IR (cm^{-1}): 2700 (w), 1365 (m), 1015 (w), 795 (br, m), 660 (br, w), 540 (br, m), 405 (m).

Preparation of Cp*$_2$CeI·THF (7). (a) Toepler Pump Experiment. Benzene (5 mL) was vacuum transferred onto 45 mg (0.055 mmol) of (Cp*$_2$CeH)$_2$. 0.11 mmol of MeI was admitted at room temperature, and the reaction mixture was stirred for 90 min during which a pink deposit formed. Toepler pump gas analysis gave the formation of 0.115 mmol (1.05 mol/mol of Ce) gas which analyzed as 100% methane (GC and MS).

(b) Preparative Scale. **10** (1.27 g, 1.5 mmol) was suspended in pentane (25 mL), and 0.2 mL (3.2 mmol) of MeI was syringed into the solution at room temperature. Immediately after admission a pink deposit formed. After washing with two portions of pentane (40 mL), the residue was dissolved in THF (20 mL). Filtration and slowly cooling to −80 °C gave **7** as orange crystals. Yield: 1.05 g (1.8 mmol, 60%). IR (cm^{-1}): 2720 (w), 2140 (w), 1345 (w), 1040 (m), 1025 (s), 925 (w), 860 (s), 835 (m), 800 (w), 675 (w). Anal. Calcd for C$_{24}$H$_{38}$CeIO: C, 47.29; H, 6.28; Ce, 22.99; I, 20.82. Found: C, 47.23; H, 6.22; Ce, 23.02; I, 20.96.

Preparation of Cp*$_2$CeN(SiMe$_3$)$_2$ (11). (a) **8** (0.59 g, 1.0 mmol) was dissolved in toluene (25 mL). HN(SiMe$_3$)$_2$ (0.50 mL, 2.4 mmol) was syringed into the red solution. After stirring for 120 h at 90 °C, the resulting light red solution was concentrated. Crystallization at −80 °C gave **11** as red crystals. Yield: 0.37 g (0.7 mmol, 70%). (b) **4** (9.68 g, 21.7 mmol) was suspended in toluene (150 mL). NaN(SiMe$_3$)$_2$ (3.98 g, 21.7 mmol) was added at room temperature. After stirring at room temperature for 60 h, the red suspension was dried in vacuo. Sublimation of the residue at 220–250 °C (0.01 mmHg) gave 10.03 g (17.6 mmol, 81%) of **11** as red crystals. IR (cm^{-1}): 2715 (w), 1380 (m), 1255 (s), 1240 (s), 1040 (vs), 935 (w), 865 (s), 820 (vs), 760 (s), 675 (m), 600 (s). ^{13}C NMR (benzene-d_6, 25 °C): δ 178.5 (s, *C*$_5$Me$_5$), 8.4 (q, C$_5$*Me*$_5$, $^1J_{C-H}$ = 125 Hz), −5.6 (q, Si*Me*$_3$, $^1J_{C-H}$ = 116 Hz). Anal. Calcd for C$_{26}$H$_{48}$CeNSi$_2$: C, 54.69; H, 8.47; Ce, 24.54; N, 2.45; mol wt, 571. Found: C, 54.75; H, 8.54; Ce, 24.57; N, 2.36; mol wt (C$_6$H$_6$), 607 ± 54.

Preparation of Cp*$_2$CeNH-*t*-Bu·NH$_2$-*t*-Bu (12). **8** (0.66 g, 1.2 mmol) was dissolved in pentane (20 mL). *t*-BuNH$_2$ (0.25 mL, 2.4 mmol) was syringed into the solution at room temperature. After stirring for 60 h at room temperature, the resulting light

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Table I. ^{1}H NMR Data for All New $Cp^*_2CeR \bullet L_n$ Complexes[a]

compound	solv[b]	δ(Cp*)	δ(R)	δ(L)
$Cp^*_2CeCl_2Li(THF)_2$[c] (**1**)	1	4.05 (50)		1.10 (27); 0.76 (35)
$Cp^*_2CeCl_2Li(DME)$ (**2**)	1	4.28 (44)		1.17 (44); −0.58 (18)
$Cp^*_2CeCl_2Li(TMEDA)_2$ (**3**)	3	4.13 (25)		2.24 (8); 2.09 (12)
$Cp^*_2CeCl \cdot THF$[c] (**5**)	2	3.50 (80)		−5.92 (75); −18 (500)
$Cp^*_2CeCl \cdot 2\text{-}t\text{-}BuCN$ (**6**)	1	3.67 (20)		−1.97 (5)
$Cp^*_2CeI \cdot THF$ (**7**)	3	5.16 (50)		
$Cp^*_2CeCH(SiMe_3)_2$[c] (**8**)	2	3.64 (10, 3.29 (10)	−10.5 (9), $SiMe_3$; 39.4 (70), CH	
$Cp^*_2CeCH(SiMe_3)_2 \cdot t\text{-}BuCN$[c] (**9**)	2	4.63 (20), 3.97 (20)	−5.58 (190), $SiMe_3$; 40.1 (60), CH	−4.81 (10)
$(Cp^*_2CeH)_2$ (**10**)	4	−0.90 (35)	168 (1300)	
$Cp^*_2CeN(SiMe_3)_2$ (**11**)	1	3.54 (5)	−11.26 (18)	
$Cp^*_2CeNH\text{-}t\text{-}Bu \cdot NH_2\text{-}t\text{-}Bu$[d] (**12**)	1	2.24 (5)	10.5 (400)	−64 (340)

[a] All signals are singlets and show correct intensities; temperature is 25 °C (unless stated otherwise); values in parentheses are the width (Hz) at half-maximum. [b] Solvent: 1, benzene-d_6; 2, toluene-d_8, 3, THF-d_8; 4, cyclohexane-d_{12}. [c] Temperature is 20 °C. [d] Amine protons not observed.

brown solution was concentrated. Crystallization at −80 °C gave **12** as gold-brown crystals. Yield: 0.32 g (0.6 mmol, 50%). IR (cm^{-1}): 3320 (w), 3260 (w), 2720 (w), 2190 (w, br), 1580 (w), 1370 (m), 1345 (m), 1260 (w), 1210 (s), 1060 (m), 1010 (w), 990 (s), 965 (s), 900 (m), 800 (w), 770 (m), 740 (w), 505 (m), 470 (w). Anal. Calcd for $C_{28}H_{51}CeN_2$: C, 60.50; H, 9.25; Ce, 25.21; mol wt, 556. Found: C, 60.52; H, 9.09; Ce, 25.22; mol wt (C_6H_6), 475 ± 21.

X-ray Diffraction: Crystal and Molecular Structure of 8. A suitable red block-shaped crystal, obtained by cooling a saturated pentane solution to −30 °C, was glued on the top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit mounted on a Enraf-Nonius CAD4F diffractometer interfaced to a PDP-11/23. Crystal data and other details of the structure determination are collected in Table II. Unit-cell parameters and their standard deviations were derived from the angular settings of 22 reflections in the range 8.75° < θ < 13.89°. Three reference reflections measured every 200 min of the X-ray exposure time showed a small decay. The net intensities of the data were corrected for the decay, Lorentz, and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics and the term (P^2I^2) where P (= 0.036) is the instability constant as derived from the excess variance in the reference reflections.[16] The cell constants of the title compound were virtually identical with those of the analogous neodymium[5c] compound. Therefore we assumed that both structures are isomorphous and the coordinates of the non-hydrogen atoms of the neodymium compound were used in the preliminary stage of the refinement and refined satisfactorily. The C(6) and C(7) atoms showed large thermal parameters and were constrained to silicon at 1.85 Å. The Cp* rings were found to be disordered in two staggered positions relative to each other. In the final refinement all Cp* atoms were assigned fixed site occupation factors of 0.5 (refinement of the occupation factor of the Cp* rings revealed a factor of 0.5 within the esd's). After completion of the isotropic refinement, empirical absorption corrections based on $F_o - F_c$ differences were applied.[17] Refinement of F was done by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogens located on a difference Fourier map were used to introduce the remaining hydrogens assuming idealized configuration (all C–H set to 1.0 Å) and refined with fixed geometry with respect to their carrier atoms and with an overall isotropic temperature factor. Isotropic secondary extinction[18] correction was applied. The final values of the refined positional parameters are presented in Table III. The largest peaks in the final difference Fourier map are located in the vicinity of the Ce atom. Scattering atoms were taken from Cromer and Mann.[19] Anomalous dispersions from Cromer and Liberman.[20] All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program XTAL,[21] the EUCLID[22] package, and a locally modified version of the PLUTO[23] program.

Table II. Crystal Data and Details of the Structure Analysis for $Cp^*_2CeCH(SiMe_3)_2$ (8)

a. Crystal Data

chemical formula	$C_{27}H_{49}CeSi_2$
mol wt	569.98
cryst system	monoclinic
space group, No.	$P2_1/n$, 14
a, Å	11.061 (3)
b, Å	23.46 (1)
c, Å	11.692 (5)
β, deg	102.99 (2)
V, Å^3	2956 (2)
Z	4
D_{calcd}, g·cm^{-3}	1.28
$F(000)$, electrons	1188
μ(Mo K$\bar{\alpha}$), cm^{-1}	16.5
approx cryst dimen, mm	0.13 × 0.38 × 0.40

b. Data Collection

diffractometer	Enraf-Nonius CAD-4F
radiatn, Å	Mo K$\bar{\alpha}$, 0.710 73
monochromator	graphite
temperature, K	130
θ range (min, max), deg	1.74, 28.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.96 + 0.35 \tan\theta$
data set	h, $-14 \rightarrow 14$; k, $0 \rightarrow 30$; l, $-15 \rightarrow 15$
cryst to receiving aperture dist, mm	173
horizontal, vertical aperture, mm	3.2 + tan θ, 4.0
reference reflcns, rms dev in %	$03\bar{5}$, 2.3 $13\bar{6}$, 1.7 $10\bar{5}$, 2.2
drift correctn	0.995–1.225
min and max abs corr fac	0.85–1.13
R_1 (= $\sum(I - \bar{I})/\sum I$)	0.025
R_2 (= $\sum\sigma/\sum I$)	0.044
X-ray exposure time, h	321.4
total data	14505
total unique	7084
obsd $F > 4.0\sigma(F)$	5534

c. Refinement

no. of reflcns	5534
no. of refined parameters	447
isotropic secondary extinctn coefft, g	5.4 (5) × 10^{-4}
final $R_F = \sum(\|\|(F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.038
final $wR = [\sum(w(\|F_o\| - \|F_c\|)^2)/\sum\|wF_o^2\|]^{1/2}$	0.047
weighting scheme (rms dev reflctn on unit wt)	$1/\sigma^2(F)$
$(\sum w(\|F_o\| - \|F_c\|)^2/(m - n)^{1/2}$[a]	2.092
min and max residual densities in final Fourier map, e/Å^3	−1.56, 1.02
max (shift/σ) final cycle	0.60
av (shift/σ) final cycle	0.046

[a] m = number of observations; n = number of variables.

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Table III. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms with esd's in Parentheses

	x	y	z	U_{eq} (Å^2)^a
Ce(1)	0.30648 (2)	0.14520 (1)	0.12856 (2)	0.01890 (0)
Si(1)	0.3342 (1)	0.14332 (7)	0.4195 (1)	0.0420 (4)
Si(2)	0.1293 (1)	0.04884 (8)	0.3318 (2)	0.0727 (5)
C(1)	0.2395 (4)	0.1011 (2)	0.3024 (4)	0.047 (2)
C(2)	0.4336 (5)	0.1944 (2)	0.3526 (4)	0.049 (2)
C(3)	0.4490 (6)	0.1032 (4)	0.5321 (5)	0.079 (3)
C(4)	0.2485 (6)	0.1893 (4)	0.5026 (5)	0.110 (4)
C(5)	0.2015 (8)	−0.0114 (4)	0.4184 (9)	0.139 (5)
C(6)	0.0294 (1)	0.01575 (8)	0.2004 (2)	0.26 (1)
C(7)	0.0093 (1)	0.07645 (8)	0.4050 (2)	0.31 (2)
C(18)	0.4692 (6)	0.1170 (4)	−0.0137 (7)	0.025 (2)
C(19)	0.5341 (7)	0.1107 (4)	0.1040 (7)	0.030 (2)
C(110)	0.4892 (7)	0.0641 (4)	0.1556 (6)	0.025 (2)
C(111)	0.3876 (6)	0.0425 (3)	0.0713 (6)	0.023 (2)
C(112)	0.3744 (7)	0.0737 (4)	−0.0312 (6)	0.026 (2)
C(113)	0.4963 (9)	0.1551 (5)	−0.1043 (8)	0.045 (3)
C(114)	0.6508 (7)	0.1443 (5)	0.1506 (9)	0.046 (3)
C(115)	0.5497 (9)	0.0408 (5)	0.2750 (7)	0.046 (3)
C(116)	0.3150 (8)	−0.0123 (4)	0.0858 (9)	0.044 (3)
C(117)	0.2814 (8)	0.0565 (4)	−0.1452 (8)	0.045 (3)
C(118)	0.0846 (6)	0.2129 (4)	0.0997 (6)	0.031 (3)
C(119)	0.0753 (7)	0.1811 (4)	−0.0074 (6)	0.029 (2)
C(120)	0.1664 (8)	0.2085 (4)	−0.0620 (7)	0.036 (3)
C(121)	0.2326 (7)	0.2513 (4)	0.0172 (7)	0.029 (2)
C(122)	0.1828 (7)	0.2530 (4)	0.1178 (7)	0.031 (3)
C(123)	−0.0036 (7)	0.2068 (5)	0.1819 (8)	0.042 (3)
C(124)	−0.0198 (9)	0.1389 (5)	−0.0551 (9)	0.051 (4)
C(125)	0.174 (1)	0.2001 (5)	−0.1859 (7)	0.055 (4)
C(126)	0.3312 (8)	0.2882 (4)	−0.0108 (9)	0.050 (3)
C(127)	0.2144 (8)	0.2967 (4)	0.2094 (8)	0.047 (3)
C(28)	0.4419 (5)	0.1002 (3)	−0.0243 (5)	0.018 (2)
C(29)	0.5347 (6)	0.1229 (4)	0.0660 (7)	0.028 (2)
C(210)	0.5423 (7)	0.0895 (4)	0.1668 (7)	0.034 (3)
C(211)	0.4547 (7)	0.0453 n4)	0.1405 (7)	0.030 (2)
C(212)	0.3873 (6)	0.0524 (4)	0.0177 (6)	0.026 (2)
C(213)	0.4170 (9)	0.1148 (6)	−0.1549 (7)	0.050 (4)
C(214)	0.6197 (8)	0.1716 (5)	0.048 (1)	0.049 (3)
C(215)	0.6438 (8)	0.0959 (6)	0.2743 (8)	0.053 (4)
C(216)	0.439 (1)	−0.0045 (5)	0.2149 (9)	0.057 (4)
C(217)	0.2936 (8)	0.0130 (5)	−0.0436 (9)	0.052 (3)
C(218)	0.1268 (7)	0.2273 (4)	0.1126 (6)	0.031 (2)
C(219)	0.0777 (6)	0.1876 (3)	0.0250 (6)	0.023 (2)
C(220)	0.1454 (7)	0.1887 (4)	−0.0635 (6)	0.028 (2)
C(221)	0.2329 (7)	0.2331 (4)	−0.0315 (7)	0.031 (2)
C(222)	0.2201 (7)	0.2555 (4)	0.0746 (7)	0.031 (2)
C(223)	0.0715 (9)	0.2411 (5)	0.2139 (8)	0.051 (3)
C(224)	−0.0349 (7)	0.1466 (4)	0.0165 (9)	0.042 (3)
C(225)	0.1092 (9)	0.1570 (5)	−0.1802 (8)	0.057 (4)
C(226)	0.3173 (9)	0.2572 (5)	−0.1078 (9)	0.055 (4)
C(227)	0.291 (1)	0.3081 (5)	0.131 (1)	0.064 (4)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

Results and Discussion

Bis(pentamethylcyclopentadienyl)cerium(III) Halides. The tetrahydrofuran adduct of cerium trichloride, $CeCl_3 \cdot x$THF ($1 < x < 2$), reacts in THF with (pentamethylcyclopentadienyl)lithium in a 1:2 ratio to give $Cp^*_2CeCl_2Li(THF)_n$ (1) (eq 1). 1 is isolated as intensely

$$CeCl_3 \cdot x\mathrm{THF} + 2\mathrm{Cp^*Li} \xrightarrow{\mathrm{THF}} \underset{\mathbf{1}}{\mathrm{Cp^*_2CeCl_2Li(THF)}_n} + \mathrm{LiCl} \quad (1)$$

yellow crystals in good yield. Instead of a stoichiometry with 2 mol of THF/cerium as reported earlier,[6] elemental analysis and signal intensities in ^{1}H NMR spectra indicate the presence of about 2.5 molecules of THF/cerium atom. The coordinated THF can easily be displaced by other Lewis bases such as diethyl ether[5d] or DME (eq 2; DME = 1,2-dimethoxyethane). Similar facile exchange of co-

$$\underset{\mathbf{1}}{\mathrm{Cp^*_2CeCl_2Li(THF)}_n} + \mathrm{DME} \rightarrow \underset{\mathbf{2}}{\mathrm{Cp^*_2CeCl_2Li(DME)}} + n\mathrm{THF} \quad (2)$$

ordinated solvent is observed in related bis(pentamethylcyclopentadienyl) late lanthanide[4b,5b] and yttrium[24] halides.

On heating 1 at 250 °C under vacuum (0.01 mmHg) an orange complex with the empirical formula Cp^*_2CeCl (4) sublimes. A similar synthetic procedure for 4, starting with $Cp^*_2CeCl_2Li(OEt_2)_2$, has been reported earlier.[5d] Compound 4 is insoluble in pentane and sparingly soluble in benzene and toluene. The solid-state structure has not been solved, but its low solubility suggests an oligomeric structure. The structure of the corresponding Sm complex, $(Cp^*_2SmCl)_3$, a chlorine-bridged trimer, has been reported recently.[25]

Compound 4 is a convenient starting material for a number of soluble and salt-free bis(pentamethylcyclopentadienyl)cerium chloride complexes. The oligomeric structure can be broken up by Lewis bases such as THF or *t*-BuCN (eq 3). Both 5 and 6 are yellow, very air-

$$(1/n)(\mathrm{Cp^*_2CeCl})_n + m\mathrm{L} \rightarrow \mathrm{Cp^*_2CeCl \cdot L}_m \quad (3)$$
$$\mathbf{5}\text{: L = THF, } m = 1$$
$$\mathbf{6}\text{: L = } t\text{-BuCN, } m = 2$$

sensitive, crystalline solids. A number of $Cp^*_2LnCl \cdot$THF (L_n = Nd,[5b], Sm,[26] Ho,[5e] Yb,[5b] Lu,[27] Y,[24,26] Sc[28]) complexes are reported, although synthesized by different procedures. The samarium, holmium, lutetium, and yttrium compounds are structurally characterized, and all are monomeric in the solid state. A similar structure is expected for 5, and a molecular weight determination (cryoscopy in benzene) reveals that 5 indeed is monomeric in solution. Compound 6 illustrates how large the coordination sphere around the cerium atom is, and is the first example of a bis(pentamethylcyclopentadienyl)lanthanide(III) halide complex with two additional ligands, giving a formal coordination number of nine. In solution however, partial dissociation of *t*-BuCN takes place, resulting in a substantial lowering of the apparent molecular weight (calcd, 612; found, 423 ± 10, cryoscopy in benzene, $K_{diss} = 7\ (\pm\ 3) \times 10^{-3}$ mol/L).

Hydrocarbon and Hydrido Derivatives. A useful ligand for the synthesis of salt-free bis(pentamethylcyclopentadienyl)lanthanide carbyl complex[5c,8] is the bulky bis(trimethylsilyl)methyl group. Analytically pure $Cp^*_2CeCH(SiMe_3)_2$ (8) can be obtained as intense red crystals by reaction of 4 with $LiCH(SiMe_3)_2$ in toluene followed by crystallization from pentane (eq 4). 8 can also be prepared starting from $Cp^*_2CeCl_2Li(THF)_n$ (1) and

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$$(1/n)\underset{\mathbf{4}}{(\mathrm{Cp^*_2CeCl})_n} + \mathrm{LiCH(SiMe_3)_2} \rightarrow \underset{\mathbf{8}}{\mathrm{Cp^*_2CeCH(SiMe_3)_2}} + \mathrm{LiCl} \quad (4)$$

$\mathrm{LiCH(SiMe_3)_2}$ (eq 5). However, this route is less convenient because the yields are rather poor on larger scale syntheses (>5 g).

$$\underset{\mathbf{1}}{\mathrm{Cp^*_2CeCl_2Li(THF)}_n} + \mathrm{LiCH(SiMe_3)_2} \xrightleftharpoons[+n\mathrm{THF}]{-n\mathrm{THF}} \underset{\mathbf{8}}{\mathrm{Cp^*_2CeCH(SiMe_3)_2}} + 2\mathrm{LiCl} \quad (5)$$

The reverse reaction of eq 5 is observed when reacting **8** with LiCl in the presence of TMEDA, forming **3** and $\mathrm{LiCH(SiMe_3)_2}$ (eq 6). This demonstrates that **8** can act as an alkylating reagent, even toward LiCl, and this reaction is probably responsible for the synthetic problems when the procedure is used as given in eq 5.

$$\underset{\mathbf{8}}{\mathrm{Cp^*_2CeCH(SiMe_3)_2}} + 2\mathrm{LiCl} \xrightarrow{\mathrm{TMEDA}} \underset{\mathbf{3}}{\mathrm{Cp^*_2CeCl_2Li(TMEDA)_2}} + \mathrm{LiCH(SiMe_3)_2} \quad (6)$$

Related reactivity was already reported in 1956 when Wilkinson synthesized ferrocene by reaction of $\mathrm{Cp_3Ce}$ and $\mathrm{FeCl_2}$.[29] Recently Bruno et al.[6] found that $\mathrm{Cp^*_2CeCl_2Li(OEt_2)_2}$ reacts with $\mathrm{(CpCo(NCMe)_3)(BF_4)_2}$ forming $\mathrm{(CpCp^*Co)BF_4}$, indicating Cp* transfer from cerium to cobalt.

Compound **8** reacts with *t*-BuCN to give the adduct $\mathrm{Cp^*_2CeCH(SiMe_3)_2}$·*t*-BuCN (**9**). With other Lewis bases, e.g. THF or $\mathrm{Et_2O}$, no adduct formation is observed at room temperature. The formation of stable coordination complexes of **8** seems to be restricted to small molecules only, like the rod-shaped cyanide part of *t*-BuCN. In contrast to related bis(pentamethylcyclopentadienyl) alkyls of Sc[30] and Y,[31] insertion of the cyanide function in the Ce–C bond is not observed at room temperature. Since Ce is much larger than Sc and Y, steric reasons for these differences are not likely.

Hydrogenolysis of Ln–C σ-bonds has proven a very useful method to synthesize metal hydrides[5c] and was also successful to synthesize a new organocerium hydride. A solution of $\mathrm{Cp^*_2CeCH(SiMe_3)_2}$ in pentane reacts quickly at room temperature with hydrogen (1 atm) to give $\mathrm{(Cp^*_2CeH)_2}$ (**10**) and $\mathrm{CH_2(SiMe_3)_2}$ (eq 7). Toepler pump analyses shows an uptake of 1.06 mol of $\mathrm{H_2}$ per mol of Ce, confirming the stoichiometry of the reaction.

$$\underset{\mathbf{8}}{\mathrm{Cp^*_2CeCH(SiMe_3)_2}} + \mathrm{H_2} \xrightarrow{\text{pentane}} \tfrac{1}{2}\underset{\mathbf{10}}{\mathrm{(Cp^*_2CeH)_2}} + \mathrm{CH_2(SiMe_3)_2} \quad (7)$$

Compound **10** is a green crystalline solid which is soluble in toluene and benzene but nearly insoluble in pentane. The compound is dimeric in solution (cryoscopy in benzene). The related neodymium hydride is also dimeric, in contrast to late lanthanide bis(pentamethylcyclopentadienyl) hydrides complexes which are significantly dissociated in solution.[5c] The exact structure of the dimer and especially the locations of the hydride ligands remains uncertain. The only structurally characterized bis(pentamethylcyclopentadienyl)lanthanide hydride is $\mathrm{(Cp^*_2SmH)_2}$,[32] but unfortunately the hydrogen atoms were not located in the X-ray analysis.

Chemical evidence for the presence of metal hydrogen bonds is obtained by reaction with MeI[26] (eq 8). Toepler pump determination and GC analyses of the gas formed showed the formation of 1.05 mol of $\mathrm{CH_4}$/mol of Ce.

$$\underset{\mathbf{10}}{\mathrm{(Cp^*_2CeH)_2}} + 2\,\mathrm{MeI} \xrightarrow[2.\ \mathrm{THF}]{1.\ \text{benzene}} 2\mathrm{MeH} + 2\underset{\mathbf{7}}{\mathrm{Cp^*_2CeI{\cdot}THF}} \quad (8)$$

The initially formed pink deposit dissolves in THF, giving a clear orange reaction mixture from which $\mathrm{Cp^*_2CeI{\cdot}THF}$ (**7**) is isolated.

Amido Derivatives. Bercaw et al. prepared a number of bis(pentamethylcyclopentadienyl)scandium amido complexes by reaction of $\mathrm{Cp^*_2ScH}$ or $\mathrm{Cp^*_2ScMe}$ with primary and secondary amines.[30] We successfully used this method to synthesize salt-free $\mathrm{Cp^*_2Ce}$ amides (eq 9).

$$\underset{\mathbf{8}}{\mathrm{Cp^*_2CeCH(SiMe_3)_2}} + \mathrm{HN(SiMe_3)_2} \xrightarrow{90\ ^\circ\mathrm{C}} \underset{\mathbf{11}}{\mathrm{Cp^*_2CeN(SiMe_3)_2}} + \mathrm{CH_2(SiMe_3)_2} \quad (9a)$$

$$\underset{\mathbf{8}}{\mathrm{Cp^*_2CeCH(SiMe_3)_2}} + 2\mathrm{H_2N}\text{-}t\text{-}\mathrm{Bu} \xrightarrow{20\ ^\circ\mathrm{C}} \underset{\mathbf{12}}{\mathrm{Cp^*_2NH}\text{-}t\text{-}\mathrm{Bu{\cdot}NH_2}\text{-}t\text{-}\mathrm{Bu}} + \mathrm{CH_2(SiMe_3)_2} \quad (9b)$$

$\mathrm{Cp^*_2CeN(SiMe_3)_2}$ (**11**) is a red crystalline solid which sublimes at 220–250 °C (0.01 mmHg), demonstrating its high thermal stability. Similar to the corresponding yttrium compound,[8] it is monomeric in solution (cryoscopy in benzene). Compound **12** forms gold-brown crystals, and like **6** it is partly dissociated in solution (cryoscopy in benzene). Both amides **11** and **12** are soluble in common solvents like toluene, benzene, pentane, and $\mathrm{Et_2O}$. In contrast with its scandium congener,[30] the coordination sphere of **12** is completed by coordination of a $\mathrm{NH_2}$-*t*-Bu molecule.

These reactions probably occur by interaction of the nitrogen lone pair of the amine with cerium followed by a four-center elimination of $\mathrm{CH_2(SiMe_3)_2}$ (σ-bond metathesis[28]). A mechanism involving "tucked-in" permethylcyclopentadienyls cannot a priori be excluded,[33] but the fact that higher reaction temperatures and prolonged reaction times are needed for reaction with the bulky $\mathrm{HN(SiMe_3)_2}$ amine compared to $\mathrm{H_2N}$-*t*-Bu favor a four center mechanism.

Although the synthesis of **11** following eq 9a is quite satisfactory, the metathesis of **4** with $\mathrm{NaN(SiMe_3)_2}$ in toluene is more convenient. After solvent removal **11** is easily sublimed out.

Spectroscopic Characterization. All new complexes reported here have the regular bent metallocene structure with two η^5-Cp* ligands. This follows from IR, NMR, and the molecular structure of $\mathrm{Cp^*_2CeCH(SiMe_3)_2}$ (vide infra). IR spectra display the characteristic η^5-Cp* absorptions at 2720, 1365, 1025, and 800 $\mathrm{cm^{-1}}$. Due to the paramagnetic character of the compounds ($\mathrm{Ce^{3+}}$ is a $4f^1$ system), the NMR signals are broadened and isotropically shifted.[34] For all compounds, except **8** and **9**, the resonances of the

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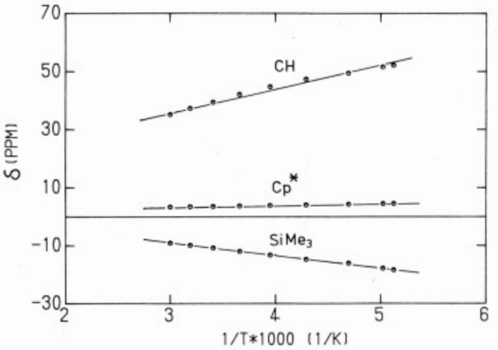

Figure 1. Paramagnetic shifts versus the reciprocal temperature for the ^{1}H NMR resonances of $Cp^*_2CeCH(SiMe_3)_2$ (**8**). For clarity, only one Cp* resonance has been shown.

Cp* protons are observed as singlets between δ 5.16 and –0.9. The line width at half-maximum varies between 5 and 80 Hz. In compound **8** and **9** the Cp* resonances are observed as two signals (1:1) showing inequivalent Cp* ligands, as expected for a bis(trimethylsilyl)methyl ligand with hindered rotation around the Ce–C σ-bond. The ^{1}H NMR data for all new compounds are given in Table I.

IR is a very useful identification technique when dealing with paramagnetic compounds.[7] The absorptions of DME and TMEDA in compounds **2** and **3** clearly demonstrate that these ligands are coordinated to the lithium atom and are superimposable on the corresponding yttrium complexes.[8] Beside characteristic Li^+–THF absorptions in complex **1** at 1045 and 890 cm^{-1}, also free THF is present (910 cm^{-1}), which accounts for the nonstoichiometric amount of THF as determined by elemental analyses.[35]

Especially noteworthy is a sharp absorption in the IR spectra between 2140 and 2110 cm^{-1} in the halide-containing compounds **1**, **2**, **3**, **4**, **5**, **7**, and $(Cp^*_2CeH)_2$ (**10**). This absorption is assigned to the splitting of the ^2F ground state of Ce^{3+} ($^2F_{5/2}$ and $^2F_{7/2}$) and has been observed in a number of organocerium(III) compounds.[36] According to Blasse,[37] the energy separation for this transition is about 2200 cm^{-1}. All other compounds display rather broad and weak absorptions in this specific IR region. A more elaborate discussion, in combination with results obtained from luminescence measurements, will be published elsewhere.[38]

The IR spectrum of $(Cp^*_2CeH)_2$ (**10**) displays one intense, broad absorption at 1120 cm^{-1} and two weaker absorptions at 940 and 770 cm^{-1}, which are assigned to metal–hydrogen vibrations. On deuteriation these bands shift to 795, 660, and 540 cm^{-1}, respectively, in accordance with the predicted $\nu_H/\nu_D = \sqrt{2}$ ratio. The hydride resonance is, despite the paramagnetic character of the compound, observed in ^{1}H NMR (cyclohexane-d_{12}) as a broad signal (lw = 1300 Hz) at 168 ppm with the expected intensity.

The temperature dependence of the ^{1}H NMR resonances of **8** are as expected for a paramagnetic compound, showing the linear Curie–Weiss relation between chemical shift and the reciprocal temperature (Figure 1). Some compounds show interesting dynamic behavior in solution.[39] The SiMe$_3$ groups in $Cp^*_2CeCH(SiMe_3)_2$·*t*-BuCN (**8**) are observed as a singlet at –5.58 ppm at 20 °C. Because rotation about the cerium–carbon σ-bond is restricted, as follows from nonequivalent Cp* groups, equivalent SiMe$_3$ groups can be explained by assuming fast exchange of *t*-BuCN between the two possible positions for coordination in the equatorial plane between the Cp* ligands. Indeed, addition of a second mole of *t*-BuCN per mol cerium results in a single resonance for the *t*-Bu groups, indicating fast exchange between coordinated and free *t*-BuCN on ^{1}H NMR time scale. Cooling down a pure sample of **9** (toluene-d_8, 300 MHz) to –20 °C results in two broad separate peaks for both SiMe$_3$ groups at 0.9 and –13.9 ppm, indicating slow exchange of *t*-BuCN at this temperature.

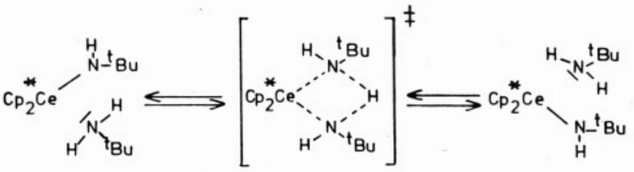

Figure 2. Proposed mechanism to explain the equivalence of the *t*-Bu groups in **12** at 70 °C.

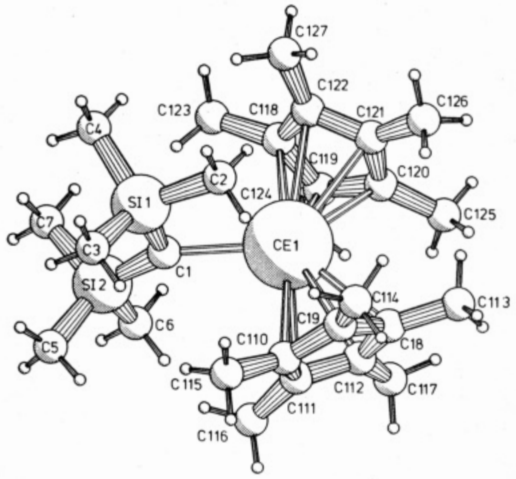

Figure 3. Perspective PLUTO view with adopted numbering scheme of $Cp^*_2CeCH(SiMe_3)_2$ (**8**). For clarity, only one orientation of each disordered Cp* ligand has been shown.

The Cp* protons of Cp^*_2CeNH-*t*-Bu·NH_2-*t*-Bu (**12**) are observed as a sharp singlet at 2.25 ppm (toluene-d_8, 300 MHz). Two broad signals (lw = 400 and 260 Hz) are observed for the *t*-Bu groups at room temperature with considerable differences in chemical shift. The signals coalescence on heating between 50 and 70 °C giving a singlet at 1.71 ppm. A likely mechanism to explain the equivalence of the *t*-Bu groups is given in Figure 2. It is based on "σ-bond metathesis" proposed by Bercaw et al. for C–H and H–H activations in bis(pentamethylcyclopentadienyl)scandium systems.[28]

On the basis of molecular weight determinations, Cp^*_2CeCl·2-*t*-BuCN is significantly dissociated in solution (vide supra). The *t*-BuCN resonance of this complex (^{1}H NMR toluene-d_8) is observed as a singlet at room temperature and also at –80 °C, indicating fast exchange of *t*-BuCN.

^{13}C NMR spectra are, despite the paramagnetic character of the compounds, informative and readily interpreted. The line widths of the signals are comparable to those observed in ^{1}H NMR spectra, and because of the

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(35) ^{1}H NMR spectra of **1** (toluene-d_8, 20 °C and also –80 °C) show two distinct signals for the THF ligands, indicating fast exchange between free and coordinated THF.

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Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $Cp^*_2CeCH(SiMe_3)_2$ (8)[a]

a. Bond Distances			
Ce(1)–C(1)	2.535 (5)	Si(1)–C(2)	1.909 (5)
Ce(1)–C(2)	2.917 (5)	Si(1)–C(3)	1.865 (7)
C(1)–Si(1)	1.819 (5)	Si(1)–C(4)	1.849 (8)
C(1)–Si(2)	1.815 (5)	Si(2)–C(5)	1.82 (1)
Ce(1)–C(18)	2.791 (8)	Ce(1)–C(28)	2.785 (6)
Ce(1)–C(19)	2.721 (8)	Ce(1)–C(29)	2.830 (7)
Ce(1)–C(110)	2.742 (9)	Ce(1)–C(210)	2.861 (8)
Ce(1)–C(111)	2.707 (7)	Ce(1)–C(211)	2.846 (9)
Ce(1)–C(112)	2.738 (8)	Ce(1)–C(212)	2.782 (9)
Ce(1)–C(118)	2.879 (8)	Ce(1)–C(218)	2.744 (9)
Ce(1)–C(119)	2.819 (8)	Ce(1)–C(219)	2.735 (7)
Ce(1)–C(120)	2.832 (9)	Ce(1)–C(220)	2.731 (8)
Ce(1)–C(121)	2.843 (9)	Ce(1)–C(221)	2.781 (9)
Ce(1)–C(122)	2.865 (9)	Ce(1)–C(222)	2.781 (9)
C(18)–C(19)	1.41 (1)	C(28)–C(29)	1.40 (1)
C(19)–C(110)	1.39 (1)	C(29)–C(210)	1.40 (1)
C(110)–C(111)	1.41 (1)	C(210)–C(211)	1.41 (1)
C(111)–C(112)	1.38 (1)	C(211)–C(212)	1.47 (1)
C(112)–C(18)	1.44 (1)	C(212)–C(28)	1.41 (1)
C(118)–C(119)	1.44 (1)	C(218)–C(219)	1.40 (1)
C(119)–C(120)	1.46 (1)	C(219)–C(220)	1.41 (1)
C(120)–C(121)	1.45 (1)	C(220)–C(221)	1.41 (1)
C(121)–C(122)	1.41 (1)	(C221)–C(222)	1.38 (1)
C(122)–C(118)	1.42 (1)	C(222)–C(218)	1.38 (1)
C(18)–C(113)	1.47 (1)	C(28)–C(213)	1.53 (1)
C(19)–C(114)	1.51 (1)	C(29)–C(214)	1.52 (1)
C(110)–C(115)	1.51 (1)	C(210)–C(215)	1.49 (1)
C(111)–C(116)	1.55 (1)	C(211)–C(216)	1.49 (1)
C(112)–C(117)	1.54 (1)	C(212)–C(217)	1.45 (1)
C(118)–C(123)	1.52 (1)	C(218)–C(223)	1.49 (1)
C(119)–C(124)	1.46 (1)	C(219)–C(224)	1.56 (1)
C(120)–C(125)	1.48 (1)	C(220)–C(225)	1.53 (1)
C(121)–C(126)	1.49 (1)	C(221)–C(226)	1.54 (1)
C(122)–C(127)	1.47 (1)	C(222)–C(227)	1.53 (1)
b. Bond Angles			
Ce1–C1–Si1	99.1 (2)	C1–Si1–C3	116.2 (3)
Ce1–C1–Si2	139.2 (2)	C1–Si1–C4	115.9 (3)
Si1–C1–Si2	121.5 (3)	C3–Si1–C4	105.8 (3)
C1–Si1–C2	108.7 (2)		

[a] The two different Cp* rotamers are differentiated by the first digit (1 or 2) of the atom labeling.

larger differences in chemical shifts for ^{13}C NMR signals, the resolution is increased and carbon–hydrogen coupling constants are clearly observed. ^{13}C NMR spectra of **6**, **8**, **10**, and **11** give the ring and methyl resonances of the Cp* ligand between 211 and 178 and 12 and 7 ppm, respectively. The $^1J_{C-H}$ coupling constants of about 125 Hz for the methyl protons of the Cp* ligand of **6**, **8**, **10**, and **11** are as expected for sp^3-carbon atoms. The resonance of the $SiMe_3$ protons in **8** and **11** are observed as quartets at 0.6 (**8**) and –5.6 (**11**) ppm. The first-order carbon hydrogen coupling constant for these protons are 116 Hz in both compounds, identical as observed for the diamagnetic yttrium analogues.[8] These rather low coupling constants are a result of γ-agostic interactions of the carbyl and amido group with the metal center[8] (vide infra). The carbon–hydrogen coupling constant of the α-carbon atom in **8** is not observed.

The Molecular Structure of $Cp^*_2CeCH(SiMe_3)_2$ (8). The molecular structure of 8 (Figure 3) was determined by single-crystal X-ray analysis. The crystals are built from monomeric $Cp^*_2CeCH(SiMe_3)_2$ units at normal van der Waals distances. Relevant bond lengths and angles with estimated standard deviations are given in Table IV. Unfortunately disorder of the Cp* rings, similar to that observed in $Cp^*_2NdCH(SiMe_3)_2$,[5c] limits the accuracy of the structure determination. The Cp* rings are η^5-bonded, the values of the C–C in the rings average 1.41 (1) Å, and the average values of ring to methyl–carbon bonds, $C-CH_3$, are 1.51 (1) Å for the two pairs of rings. The cerium–internal carbon Cp* distances vary between 2.729 (7) and 2.879 (8) Å. These distances are similar with another structurally characterized, eight-coordinate Ce^{3+} compound, $Cp^*CeI_2\cdot 3THF$,[6] where they vary between 2.749 (13) and 2.844 (14) Å. The average ring centroid–metal–ring centroid angle is 134° for the two pairs of rings, which is the same as found for $Cp^*_2NdCH(SiMe_3)_2$ (134.5°)[5c] and falls within the 131–138° range as observed for most di- and trivalent bis-Cp* compounds.[40] The Ce–C(1) σ-bond distance is 2.535 (5) Å. Metrical data for Ce–C σ-bond distances have not been reported yet. If we compare this value with the Nd–C σ-bond distances of 2.506 (7) and 5.517 (7) Å in $Cp^*_2NdCH(SiMe_3)_2$[5c] and $Me_2SiCp^*_2NdCH(SiMe_3)_2$,[41] respectively, and correct for the differences in eight-coordinate ionic radii (0.034 Å)[42] between Ce^{3+} and Nd^{3+}, the Ce–C σ-bond distance seems quite normal. Noteworthy is the unsymmetrical coordination of the σ-bonded carbyl ligand. The Ce, C(1), Si(1), and Si(2) atoms are coplanar within 0.031 Å. The Ce–C(2) distance is 2.917 (5) Å, which is only 0.382 Å longer than the Ce–C(1) bond and significantly shorter than the sum of the methyl van der Waals radius (2.0 Å)[43] and the eight-coordinate ionic radius of Ce^{3+} (1.143 Å).[42] The Ce–C(1)–Si(1) angle is 99.1 (2)° and the Ce–C(1)–Si(2) angle of 139.2 (2)° clearly demonstrate the asymmetrically bonded carbyl group. A similar distortion of the $CH(SiMe_3)_2$ ligand is observed in other electron-deficient metal complexes, e.g., $Cp^*_2MCH(SiMe_3)_2$ (M = Y[8] and Nd[5c]) and $Me_2SiCp^*_2NdCH(SiMe_3)_2$.[41] A recent theoretical study for $Ti(C(SiH_2CH_3){=}CH_2)Cl_2^+$ shows an optimized structure with a distorted alkenyl ligand, a small Ti–C–Si bond angle, a long Si–γ-C bond, and a short Ti–γ-C distance, in agreement with the molecular structure of $Cp_2Ti(C(Si(CH_3)_3){=}C(CH_3))(C_6H_5)^+$.[44] The origin of this distortion is a donative interaction of the Si–C σ-bond (a so-called β-SiC agostic interaction) to a vacant Ti d orbital, assisted by γ-CH agostic interactions. The structural features of the $CH(SiMe_3)_2$ ligand in **8** resemble that of the alkenyl group in $Ti(C(SiH_2CH_3){=}CH_2)Cl_2^+$; a small Ce–C–Si angle and a short Ce–γ-C distance. However, the Si(1)–C(2) distance 1.909 (5) Å) is only slightly longer than the Si(1)–C(3) distance (1.865 (7) Å), the Si(1)–C(4) distance (1.849 (5) Å), and the Si-C distance in CH_3SiH_3 (1.867 Å),[45] in contrast to the Si–γ-C distance in $Cp_2Ti(C(Si(CH_3)_3){=}C(CH_3))(C_6H_5)^+$ (2.01 Å) and the theoretical value for the optimized geometrie (2.00 Å). It seems that the γ-CH agostic interactions are the major origin of the distortion in **8** and that the β-SiC agostic interaction is less important. Definite conclusions about the presence of an α-agostic interaction as observed in $Cp^*_2YCH(SiMe_3)_2$[8] and $Me_2SiCp^*_2NdCH(SiMe_3)_2$[41] cannot be made because the α-H atom could not be located.

Conclusions. $(Cp^*_2CeCl)_n$ (**4**) is a convenient starting material for the syntheses of monomeric Cp^*_2CeR complexes. The Ce–C σ-bond in the carbyl **8** is extremely reactive, and with substrates containing active hydrogens such as dihydrogen and amines σ-bond metathetical reactions are observed with the formation of $(Cp^*_2CeH)_2$ (**10**)

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and Cp^*_2Ce(amido) complexes (**11**, **12**), respectively. Reaction of **8** with LiCl in the presence of basic ligands; e.g., TMEDA gives $Cp^*_2CeCl_2Li(TMEDA)_2$ (**3**) and $LiCH(SiMe_3)_2$, indicating that alkylation of Ce–Cl bonds by metathetical reactions with a main-group hydrocarbyl is thermodynamically very critical. Despite the paramagnetic character of these bis(pentamethylcyclopentadienyl)cerium complexes, ^{13}C NMR spectra are readily interpreted and provide valuable information.

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Note Added in Proof. After submission of this paper Evans et al. reported the synthesis of **4** and **5**.[46]

Registry No. **1**, 106043-06-5; **2**, 116635-57-5; **3**, 116635-58-6; **4**, 98789-69-6; **5**, 111559-69-4; **6**, 116635-59-7; **7**, 113132-51-7; **8**, 106333-13-5; **9**, 116635-60-0; **10**, 106433-89-0; **11**, 116635-61-1; **12**, 116635-62-2; $CeCl_3$, 7790-86-5; CeO_2, 1306-38-3; Cp*Li, 51905-34-1; $LiCH(SiMe_3)_2$, 41823-71-6; *t*-BuCN, 630-18-2; $(Cp^*_2CeD)_2$, 116635-63-3; $HN(SiMe_3)_2$, 999-97-3; $NaN(SiMe_3)_2$, 1070-89-9; *t*-$BuNH_2$, 75-64-9.

Supplementary Material Available: An ORTEP drawing and tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates for **8** (23 pages); a listing of structure factors for **8** (21 pages). Ordering information is given on any current masthead page.

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Photoexcitation of Tungsten Hexacarbonyl in Solutions Containing Pyridine-2-carbaldehyde Imine Ligands. Spectral Characterization and Reaction Kinetics of the Photoproduced Monodentate $W(CO)_5L$ Intermediate

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UV photolyses of $W(CO)_6$ in solutions containing pyridine-2-carbaldehyde N-substituted imine (R-pyca) or 6-methyl-pyridine-2-carbaldehyde N-substituted imine (R-pyca′) ligands produce transient species that are attributed to $W(CO)_5L$ complexes, where the normally chelating ligands are coordinated in a monodentate configuration. Electronic absorption and Fourier transform infrared spectra recorded immediately following light excitation using rapid scanning techniques have enabled characterization of this monodentate $W(CO)_5L$ species. Kinetic data have been obtained for the chelation reactions of $W(CO)_5L$ to form $W(CO)_4L$ and CO; in each case the ring closure reaction proceeds via a first-order mechanism. From the ligand dependence of the kinetic data it is inferred that R-pyca scavenges the primary photoproduct exclusively at the pyridine nitrogen atom whereas R-pyca′ initially coordinates at the aliphatic nitrogen atom. These kinetic results are discussed in terms of steric hindrance during the ligand scavenging process.

Introduction

Photochemical studies of metal carbonyl complexes have been greatly stimulated by the importance of these molecules as models in mechanistic organometallic chemistry and in the design of homogeneous catalytic processes.[1] Although unsaturated species are believed to be involved in a number of these processes, direct spectral observation and quantitative measurements of their reactivity have rarely been reported. In fact, our current knowledge of the identity and reactivity of intermediates involved in ligand substitution events at low-valent transition-metal centers remains fairly limited.

Recently, several reports have appeared concerned with the nature of reaction intermediates that are produced during the photochemical formation of chelated $M(CO)_4L$ complexes from $M(CO)_6$ (M = Cr, Mo, W) solutions containing bidentate ligands (L).[2–4] Spectral data obtained using rapid-scanning Fourier transform infrared spectroscopy[3] and diode-array UV–visible spectroscopy[4] have provided a direct characterization of the monodentate $M(CO)_5L$ intermediate, where L is a series of substituted 2,2′-bipyridine, 1,4-diazabutadiene, or pyridine-2-carbaldehyde imine ligands. Consequently, the photochemical formation of the chelated $M(CO)_4L$ complex is believed to proceed according to eq 1 and 2. In a further extension

$$M(CO)_6 \xrightarrow[L]{h\nu} M(CO)_5L + CO \tag{1}$$

$$M(CO)_5L \xrightarrow{\Delta} M(CO)_4L + CO \tag{2}$$

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