122648-16-2; **3a** (X = 1,2,3,4,5-Me, R = Ph), 122648-24-2; **3a** (X = 1,2,3,4,5-Me, R = Me), 95344-72-2; **3a** (X = 1,2,4,5-Me, R = Ph), 95344-74-4; **3b** (X = 1,2,3,4,5-Me, R = Ph), 122648-18-4; **3b** (X = 1,2,3,4,5-Me, R = Me), 122648-20-8; **3b** (X = 1,2,3,4,5,6-Me, R = Me), 122648-22-0; **4a** (X = 1,2,3,4,5-Me, R = Me), 122741-55-3; **4a** (X = 1,2,4,5-Me, R = Ph), 122742-51-2; **4b** (X = 1,2,3,4,5-Me, R = Ph), 122648-25-3; **4b** (X = 1,2,3,4,5-Me, R = Me), 122648-26-4; $Re(CO)_5Br$, 14220-21-4; $[(C_6H_6)Re(CO)_3]AlCl_3Br$, 122648-27-5; $(C_6Me_7)Re(CO)_3$, 122648-28-6; Ph_4AsCN, 21154-65-4; Et_4NCN, 13435-20-6; PBu_3, 998-40-3; $CH(CO_2Me)_2^-$, 13435-20-6.

Mono(pentamethylcyclopentadienyl) Complexes of Cerium(III). Synthesis, Molecular Structure, Thermal Stability, and Reactivity of $(C_5Me_5)CeX_2$ (X = 2,6-Di-*tert*-butylphenoxo, $CH(SiMe_3)_2$, and $N(SiMe_3)_2$) Complexes

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Reaction of $Ce(OAr)_3$[1] (**1**) with LiR (R = C_5Me_5, 1,3-diphenyl-2-methylindene) affords novel $RCe(OAr)_2$ (R = C_5Me_5, **2**; R = 1,3-diphenyl-2-methylindene, **3**) compounds. Metathesis of the remaining aryloxide ligands in **2** with bulky main-group alkyl and amide compounds ($LiCH(SiMe_3)_2$ and $NaN(SiMe_3)_2$) provide neutral $C_5Me_5CeR_2$ complexes (R = $CH(SiMe_3)_2$, **5**; R = $N(SiMe_3)_2$, **6**). Compound **5** is a polymerization catalyst for ethylene but not for propylene. Compounds **2** and **6** disproportionate in solution with formation of equilibrium mixtures containing $C_5Me_5CeX_2$, $(C_5Me_5)_2CeX$, and CeX_3 complexes. Structural studies on **2**, **5**, and **6** show monomeric, formally five-coordinate compounds in the solid state. Compound **2** crystallizes in the monoclinic space group $P2_1$ with $a = 9.575$ (1) Å, $b = 17.026$ (2) Å, $c = 11.530$ (1) Å, $\beta = 112.02$ (1)°, and $Z = 2$. Compound **5** crystallizes in the hexagonal space group $P6_3$ with $a = 18.477$ (2) Å, $c = 15.991$ (3) Å, and $Z = 6$. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with $a = 19.252$ (6) Å, $b = 13.430$ (4) Å, $c = 12.503$ (3) Å, $\beta = 90.28$ (2)°, and $Z = 4$. All compounds display interesting secondary interactions of the metal with C–H and/or Si–C bonds in the solid state.

Introduction

The last decade, organometallic compounds of group 3 and lanthanide elements with unprecedented structural features and spectacular reactivity have been reported.[2] Especially worth mentioning are methane activation and β-methyl transfer reactions with lutetium compounds $(C_5Me_5)_2LuR$.[3] Lanthanide compounds $[(C_5Me_5)_2LnH]_2$ (Ln = La, Nd, Sm, Lu) have been shown to be extremely active catalysts for olefin hydrogenation and ethylene polymerization reactions.[4]

The reported chemistry deals mainly with cyclopentadienyl and substituted cyclopentadienyl compounds with the bis(pentamethylcyclopentadienyl) compounds $(C_5Me_5)_2LnR$ as the most extensively studied.[2] The two bulky pentamethylcyclopentadienyl ligands strongly influence the reactivity. An outstanding feature of this specific geometry is a dramatic improvement of stability, thus allowing detailed kinetic and mechanistic studies. However, the reactivity can also be decreased by the two bulky ligands. For example, propylene is neither polymerized nor oligomerized by $(C_5Me_5)_2ScMe$, whereas oligomers do form when the cyclopentadienyl ligands are bridged, e.g., by a $SiMe_2$ group.[5] The effect of the bridge is to open the wedge of the $(C_5Me_5)_2ScMe$ compound, thus allowing the propylene molecules to enter the coordination sphere and insert repeatedly into the Sc–C bond. It was shown by Marks et al. that ring-bridged hydrides, $[Me_2Si(C_5Me_4)_2LnH]_2$ (Ln = Nd, Sm, Lu), are ca. 10 times more active for the polymerization of ethylene than the corresponding $[(C_5Me_5)_2LnH]_2$ hydrides.[4b] This observation was also attributed to an increase of the coordination space around the metal by bridging the C_5Me_5 rings.

With these dramatic spatial effects in mind, we reasoned that mono(pentamethylcyclopentadienyl) complexes $(C_5Me_5)LnX_2$ may show interesting chemistry and we decided to investigate compounds of the type $(C_5Me_5)LnX_2$ (X = alkoxide, amide, carbyl). Because of our experience with bis(pentamethylcyclopentadienyl) derivatives of early

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(1) In this paper the following abbreviations are used: Ln = lanthanide or group 3 element; Ind* = 1,3-diphenyl-2-methylindenyl; OAr = 2,6-di-*tert*-butylphenoxo.

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lanthanides La and Ce,[6] we focused our attention on these elements.

A complication that hampers the synthesis of well-defined compounds considerably is the nonstoichiometric incorporation of salt and/or solvent molecules. This is common for $(C_5Me_5)_2LnX$ systems and may be expected to be even more dominant for $(C_5Me_5)LnX_2$ compounds. Another synthetic complication is the possibility of disproportionation (eq 1).[2d]

$$2C_5Me_5LnX_2 \rightleftarrows (C_5Me_5)_2LnX + LnX_3 \qquad (1)$$

Only a few monomeric pentamethylcyclopentadienyl complexes of the early lanthanides have been reported to date, e.g. $(C_5Me_5)LnI_2\cdot 3THF$ (Ln = La, Ce),[7] $(C_5Me_5)La[CH(SiMe_3)_2]_2$,[8a] $(C_5Me_5)La[CH(SiMe_3)_2]_2\cdot THF$[8a] $[(C_5Me_5)LnCl_3][Na(OEt_2)_n]$ (Ln = Pr, Nd),[9] and $(C_5Me_5)Nd[N(SiMe_3)_2]_2$,[9a] and systematic synthetic routes are lacking.

We here report the use of homoleptic aryloxides, $Ln(OAr)_3$, as starting materials for the synthesis of monocyclopentadienyl lanthanide compounds. These aryloxides have been used successfully to synthesize neutral homoleptic carbyls, $Ln[CH(SiMe_3)_2]_3$ (Ln = La, Sm,[10] and Ce[11]), by metathesis of the appropriate aryloxide and $LiCH(SiMe_3)_2$. A preliminary account of part of this work has been published recently.[12]

Experimental Section

General Considerations. All compounds are extremely air-sensitive, and manipulations were carried out by using Schlenk, vacuum line, or glovebox (Braun MB-20) techniques under nitrogen or argon. Vacuum sublimations were carried out by using a homemade sublimation apparatus with IR heating.[13] Solvents were distilled from Na/K alloy prior to use. 2,6-Di-*tert*-butylphenol, $HN(SiMe_3)_2$, and $HC{\equiv}C(t\text{-Bu})$ were dried before use (molecular sieves, 4 Å). Ethylene and propylene were used as purchased (Ucar, C.P.). $Li(OAr)\cdot OEt_2$ was prepared from *n*-BuLi and 2,6-di-*tert*-butylphenol in Et_2O.[14] C_5Me_5H was synthesized by Burger's method[15] and converted to C_5Me_5Li according to ref 16. $NaN(SiMe_3)_2$[17] and $LiCH(SiMe_3)_2$[18] were prepared following published procedures and sublimed (90–100 °C, 0.01 mmHg) before use. $KCH(SiMe_3)_2$ was synthesized by the reaction of $LiCH(SiMe_3)_2$ with KO(*t*-Bu) in hexane.[8b] 1,3-Diphenyl-2-methylindene[19] was converted into (1,3-diphenyl-2-methylindenyl)lithium by reaction with *n*-BuLi in Et_2O. $Ce[NSiMe_3)_2]_3$ was synthesized according to ref 20 and sublimed (110 °C, 0.01 mmHg) before use. IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer using Nujol mulls between KBr disks. NMR samples were prepared in a glovebox and sealed under vacuum. NMR spectra were recorded on a Bruker WH-90 or a Varian VXR-300 spectrometer. Chemical shifts are reported in parts per million and referenced to residual protons in deuterated solvents (^1H NMR (benzene-d_6) δ 7.15; ^1H NMR (THF-d_8) δ 1.72; ^1H NMR (toluene-d_8) δ 6.98; ^{13}C NMR (benzene-d_6) δ 127.96). Elemental analyses were performed at the Micro-Analytical Department of the University of Groningen. All listed data are the average of at least two independent determinations.

Table I. ^1H NMR Spectra for All New Compounds (Benzene-d_6, 21 °C)

compd	assignt		δ[a]	lw[b]	m[c]	coupling[d]
$(C_5Me_5)Ce(OAr)_2$ (**2**)	C_6H_3	4 H	9.91	23	s	
	C_6H_3	2 H	9.02	18	s	
	C_5Me_5	15 H	2.71	80	s	
	t-Bu	36 H	−4.6	200	s	
$(Ind^*)Ce(OAr)_2$ (**3**)	CH	4 H	12.63	<5	d	7.5
	CH	2 H	11.13	<5	t	7.5
	CH	4 H	10.41	30	s	
	CH	4 H	8.52	15	s	
	CH	2 H	8.10	<5	t	7.1
	CH	2 H	5.92	30	s	
	CH_3	3 H	2.02	7	s	
	CH	2 H	−0.23	12	s	
	t-Bu	36 H	−5.03	18	s	
$(C_5Me_5)Ce(OAr)CH(SiMe_3)_2$[e] (**4**)	C_6H_3	2 H	15.83	10	d	6.0
	C_6H_3	1 H	13.50	25	s	
	C_5Me_5	15 H	2.44	25	s	
	t-Bu	18 H	−0.76	60	s	
	$SiMe_3$	18 H	−11.6	25	s	
$(C_5Me_5)Ce[CH(SiMe_3)_2]_2$[e] (**5**)	C_5Me_5	15 H	2.84	28	s	
	$SiMe_3$	36 H	−7.61	300	s	
$(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (**6**)	C_5Me_5	15 H	3.45	12	s	
	$SiMe_3$	36 H	−7.00	13	s	

[a] Referenced to residual protons in benzene-d_6 (δ 7.15 ppm). [b] lw = line width of the signals at half width. [c] Abbreviations: m, multiplicity; s, singlet; d, doublet; t, triplet. [d] In Hz. [e] α-CH protons not observed.

Preparation of $Ce(OAr)_3$ (1). A suspension of 10.13 g (35.4 mmol) of $Li(OAr)\cdot OEt_2$ and 2.91 g (11.8 mmol) of $CeCl_3$ in THF (200 mL) was stirred at reflux for 96 h. The resulting pale yellow suspension was evaporated to dryness and sublimed at about 150 °C (0.01 mmHg) to give 5.81 g (7.7 mmol, 65%) of **1** as yellow crystals. IR (cm^{-1}): 3060 (w), 1585 (m), 1410 (s), 1360 (m), 1240 (s), 1190 (m), 1120 (m), 1100 (m), 890 (m), 865 (s), 820 (m), 750 (s), 655 (s), 555 (m), 460 (m). ^1H NMR (benzene-d_6, 300 MHz, 21 °C): δ 10.85 (6 H, d, $^3J_{HH}$ = 10 Hz, C_6H_3), 9.59 (3 H, t, $^3J_{HH}$ = 10 Hz, C_6H_3), −3.05 (54 H, s, lw = 18 Hz, *t*-Bu). ^{13}C NMR (benzene-d_6, 75.4 MHz, 21 °C): δ 208.4 (s, OC_6H_3), 155.6 (s, OC_6H_3), 130.5 (d, $^1J_{CH}$ = 155 Hz, OC_6H_3), 124.5 (d, $^1J_{CH}$ = 158 Hz, OC_6H_3), 36.5 (s, *t*-Bu), 23.9 (q, $^1J_{CH}$ = 125 Hz, *t*-Bu). Anal. Calcd for $C_{42}H_{63}CeO_3$: C, 66.72; H, 8.40; Ce, 18.53. Found: C, 67.00; H, 8.48; Ce, 18.48.

Preparation of $(C_5Me_5)Ce(OAr)_2$ (2). A suspension of 9.33 g (12.3 mmol) of **1** and 1.76 g (12.6 mmol) of C_5Me_5Li in toluene (150 mL) was stirred at 80 °C for 20 h. The resulting yellow-orange suspension was dried in vacuo, and the residue was extracted with pentane (120 mL). After filtration, concentration, and cooling to −80 °C, 4.70 g (6.9 mmol) of **2** was isolated as yellow crystals. Further workup gave a second crop (1.73 g, 2.5 mmol) of **2**. Yield: 6.43 g (9.4 mmol, 76%). IR (cm^{-1}): 3040 (m), 2720 (w), 2120 (m), 1580 (m), 1400 (s), 1355 (m), 1240 (s), 1200 (m), 1115 (w), 1090 (m), 1015 (w), 880 (m), 860 (s), 820 (m), 745 (s), 640 (m), 625 (w), 540 (w), 450 (w). ^1H NMR data are given in Table I. Anal. Calcd for $C_{38}H_{57}CeO_2$: C, 66.53; H, 8.38; Ce, 20.43. Found: C, 66.63; H, 8.37; Ce, 20.42.

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Table II. Crystal Data, Summary of Intensity Data Collection, and Structure Refinement for $(C_5Me_5)Ce(OAr)_2$ (2), $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (5), and $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (6)

	2	5	6
color/shape	yellow, block-shaped	red, block-shaped	orange, parallelepiped
formula	$C_{38}H_{57}CeO_2$	$C_{24}H_{53}CeSi_4$	$C_{22}H_{51}CeN_2Si_4$
mol wt	685.99	594.14	596.1
cryst system	monoclinic	hexagonal	monoclinic
space group	$P2_1$	$P6_3$	$P2_1/c$
a, Å	9.575 (1)	18.477 (2)	19.252 (6)
b, Å	17.026 (2)		13.430 (4)
c, Å	11.530 (1)	15.991 (3)	12.503 (3)
β, deg	112.02 (1)		90.28 (2)
V, Å^3	1742.6 (3)	4728 (1)	3233
Z	2	6	4
cryst dimens, mm	0.10 × 0.12 × 0.25	0.10 × 0.12 × 0.24	0.23 × 0.28 × 0.40
d_{calcd}, g/cm^3	1.307	1.252	1.22
radiatn, Å	Mo K$\bar{\alpha}$, 0.71073	Mo K$\bar{\alpha}$, 0.71073	Mo K$\bar{\alpha}$, 0.71073
monochromator	graphite	graphite	graphite
temp, K	130	130	293
θ range, deg	$1.20 < \theta < 27.0$	$1.27 < \theta < 27.0$	$1 < \theta < 25.0$
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.85 + 0.35 \tan\theta$	$\Delta\omega = 0.70 + 0.35 \tan\theta$	$\Delta\omega = 0.80 + 0.35 \tan\theta$
decay of stds	4%	2%	2%
no. of data collected	4819	3911	6168
no. of unique data	3927	3573	4926
obsd data, criterion	3703, $I \geq 2.5\sigma(I)$	2821, $I \geq 2.5\sigma(I)$	3914, $F_o > 5\sigma(F_o)$
μ(Mo K$\bar{\alpha}$), linear abs coeff, cm^{-1}	13.5	16.3	14.6
no. of parameters refined	541	421	262
R_F^{a}	0.021	0.032	0.047
R_w^{b}	0.026	0.026	0.052
GOF^c	1.476	1.222	1.7
largest feature final diff map, e/Å	0.62	0.99	0.6

$^a R_F = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum(w(|F_o| - |F_c|)^2)/\sum w|F_o|^2]^{1/2}$. $^c \mathrm{GOF} = [\sum(w|F_o| - |F_c|)^2/(m - n)]^{1/2}$; m = number of observations; n = number of variables.

Preparation of $(Ind^*)Ce(OAr)_2$ (3). 1 (1.40 g, 1.9 mmol) and 0.51 g (1.8 mmol) of (1,3-diphenyl-2-methylindenyl)lithium were suspended in toluene (50 mL). After the solution was stirred for 21 h at 80 °C, a yellow-orange suspension had formed. The volatiles were removed in vacuo, and pentane (80 mL) was added. Filtration and subsequent cooling to −20 °C gave 0.51 g (0.6 mmol, 31%) of 3 as orange crystals. IR (cm^{-1}): 3060 (w), 3020 (w), 1600 (m), 1585 (w), 1500 (m), 1400 (s), 1350 (w), 1335 (w), 1240 (s), 1200 (m), 1120 (w), 1100 (w), 1000 (w), 860 (s), 820 (m), 770 (m), 750 (s), 650 (m), 550 (w), 500 (w), 460 (w). ^{1}H NMR data are given in Table I. ^{13}C NMR (benzene-d_6, 75.4 MHz, 21 °C): δ 222.3 (s, OC_6H_3), 161.8 (s, OC_6H_3), numerous resonances in the 135–110 ppm region, 37.8 (s, *t*-Bu), 23.1 (q, $^1J_{CH}$ = 122 Hz, *t*-Bu), 12.4 (q, $^1J_{CH}$ = 125 Hz, Me). Anal. Calcd for $C_{50}H_{59}CeO_2$: C, 72.17; H, 7.15; Ce, 16.84. Found: C, 72.15; H, 7.27; Ce, 16.85.

Preparation of $(C_5Me_5)Ce(OAr)(CH(SiMe_3)_2)$ (4). 2 (0.50 g, 0.73 mmol) and 0.25 g (1.28 mmol) of $KCH(SiMe_3)_2$ were suspended in pentane (50 mL). After the solution was stirred at room temperature for 5 days, an orange suspension had formed. Filtration, concentration, and cooling to −80 °C gave 0.22 g (0.35 mmol, 48%) of 4 as orange crystals. IR (cm^{-1}): 3060 (w), 2730 (w), 2115 (w), 1590 (w), 1410 (s), 1360 (w), 1250 (s), 1200 (w), 1100 (w), 1025 (m), 870 (s), 860 (s), 835 (s), 750 (s), 680 (w), 650 (m), 580 (w), 550 (w), 460 (w). ^{1}H NMR data are given in Table I. Anal. Calcd for $C_{31}H_{55}CeOSi_2$: C, 58.17; H, 8.66; Ce, 21.89. Found: C, 58.74; H, 8.69; Ce, 21.73.

Preparation of $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (5). 2 (2.06 g, 3.00 mmol) and 1.00 g (6.00 mmol) of $LiCH(SiMe_3)_2$ were suspended in pentane (100 mL). After the solution was stirred for 16 h at room temperature an orange suspension had formed, which was filtered and subsequently evaporated to dryness. Crystallization from Et_2O at −80 °C gave 0.55 g (0.93 mmol, 31%) of 5 as orange crystals. Analytically pure material was obtained by recrystallization from pentane. IR (cm^{-1}): 2750 (w), 2720 (w), 1255 (s), 1240 (s), 1050 (w), 1010 (s), 855 (vs), 830 (vs), 780 (m), 760 (s), 710 (m), 680 (m), 660 (m), 650 (m), 580 (m). ^{1}H NMR spectral data are given in Table I. Anal. Calcd for $C_{24}H_{53}CeSi_4$: C, 48.51; H, 9.00; Ce, 23.58. Found: C, 48.67; H, 9.00; Ce, 23.61.

Preparation of $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (6). 2 (0.95 g, 1.4 mmol) and 0.50 g (2.7 mmol) of $NaN(SiMe_3)_2$ were suspended in toluene (50 mL). After the solution was stirred at 70 °C for 48 h, an orange suspension had formed. The solvent was removed in vacuo, and 50 mL of pentane was added. Filtration, concentration, and cooling to −80 °C gave 0.38 g (0.5 mmol, 36%) of 6 as orange crystals. Analytically pure material was obtained by recrystallization from Et_2O. IR (cm^{-1}): 2715 (w), 2140 (w), 1240 (s), 1000 (s), 875 (s), 855 (s), 830 (s), 760 (s), 725 (m), 675 (m), 600 (m), 370 (m). ^{1}H NMR data are given in Table I. ^{13}C NMR (benzene-d_6, 75.4 MHz, 21 °C): δ 152.9 (s, C_5Me_5), 4.71 (q, $^1J_{CH}$ = 117 Hz, Si*Me*$_3$), δ 4.66 (q, $^1J_{CH}$ = 125 Hz, C_5*Me*$_5$). Anal. Calcd for $C_{22}H_{51}CeN_2Si_4$: C, 44.32; H, 8.62. Found: C, 44.65; H, 8.79.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)Ce(OAr)_2$ (2) and $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (5). Suitable crystals of 2 and 5, obtained by cooling saturated pentane solutions to −30 °C, were glued on top of a glass fiber and transferred into the cold nitrogen stream of the low temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Precise lattice parameters and their standard deviation were derived from the angular setting of 25 reflections in the range $10.12° < \theta < 16.98°$ for 2 and 21 reflections in the range $11.68° < \theta < 16.91°$ for 5. Crystal data and experimental details of the structure determinations are given in Table II. The net intensities of data were corrected for scale variation and Lorentz and polarization effects but not for absorption. Standard deviations in the intensities based on counting statistics[21] were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (PI)^2$ (P = 0.030 for 2 and 0.0175 for 5). The cerium atom of both compounds was located by Patterson techniques (SHELX86).[22] Extension of the model for 2 was accomplished by direct methods applied to difference structure factors by using the program DIRDIF[23] and for 5 was accomplished by using standard Fourier techniques. Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of all the hydrogen atoms of 2 and most of the hydrogen

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(22) Sheldrick, G. M. SHELXS86, program for crystal structure solution; University of Göttingen: Göttingen Federal Republic of Germany, 1986.

(23) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; van den Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Gould, R. O.; Parthasarathi, V. In *Conformation in Biology*; Srinivasan, R., Sarma, R. H., Eds.; Adenine Press: New York, 1982; p 389.

atoms of **5**. The remaining hydrogen atoms were initially placed at calculated positions and all refined satisfactorily. Weights were introduced in the final refinement cycles ($w = 1/\sigma^2(F)$). Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one common isotropic thermal parameter for the hydrogen atoms converged at $R_F = 0.021$ ($R_w = 0.026$) for **2** and $R_F = 0.032$ ($R_w = 0.026$) for **5**. The alternative absolute structures were rejected on the basis of the resulting higher R values ($R_F = 0.025$, $R_w = 0.032$ for **2**, and $R_F = 0.035$, $R_w = 0.028$ for **5**, obtained by introducing negative anomalous dispersion factors ($-i\Delta f''$). The 002 reflection of **5** with a $w\Delta F/\sigma(F)$ ratio of -24.6, probably suffering from severe extinction, was excluded from the final refinement. Scattering factors were taken from Cromer and Mann[24] and anomalous dispersion factors from Cromer and Liberman.[25] All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL[26] and EUCLID (calculation of geometric data)[27] and a locally modified version of the program PLUTO.[28]

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (6). An orange single crystal of the title compound, obtained by cooling a saturated OEt_2 solution to −40 °C, was mounted in a thin-walled glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer. Precise lattice parameters and their standard deviation were derived from the angular setting of 25 reflections with $\theta > 20°$. The space group was determined to be the centric $P2_1/c$ from the systematic absences. A summary of data collection parameters is given in Table II. The intensities were corrected for Lorentz and polarization effects and for absorption (empirical, psi scan). The cerium atom was located by Patterson techniques (SHELX76).[29] Least-squares refinement with isotropic thermal parameters led to $R = 0.081$. High thermal motion, but no resolvable disorder was noted for the methyl carbons of the C_5Me_5 ligand and for the amide methyls except for C(4) and C(7). Due to this relatively high thermal motion, the hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic thermal factors led to the final values of $R = 0.047$ and $R_w = 0.052$. Neutral scattering factors and anomalous dispersion corrections were taken from ref 30.

Results and Discussion

Synthesis. Recently Sen et al. published the synthesis of the first neutral, homoleptic, hydrocarbon-soluble cerium aryloxide, $Ce(OAr)_3$ (OAr = 2,6-di-*tert*-butylphenoxo) (**1**), by reaction of $Ce[N(SiMe_3)_2]_3$ with 2,6-di-*tert*-butylphenol in pentane.[31] A convenient alternative, using more readily available starting materials, is given in eq 2. After removal of the solvent, **1** is obtained by vacuum sublimation in 65% yield.

$$CeCl_3 + 3LiOAr{\cdot}OEt_2 \xrightarrow{THF} \underset{\mathbf{1}}{Ce(OAr)_3} + 3LiCl \quad (2)$$

The reactivity of **1** toward various substituted cyclopentadienyl anions was investigated in more detail. To avoid coordination of solvent molecules and to prevent the formation of soluble adducts of main-group aryloxides, the reactions were carried out in apolar, noncoordinating solvents. Stirring **1** and $(C_5Me_5)Li$ in toluene at 80 °C for 20 h resulted in the formation of an intense yellow-orange suspension. Workup gave yellow crystals of **2** in 76% yield (eq 3). ^{1}H NMR indicates the presence of one C_5Me_5 ligand per two aryloxide ligands, in accordance with elemental analysis. Compound **2** is soluble in common solvents (Et_2O, THF, pentane, benzene, and toluene).

$$Ce(OAr)_3 + (C_5Me_5)Li \xrightarrow{toluene} \underset{\mathbf{2}}{(C_5Me_5)Ce(OAr)_2} + LiOAr \quad (3)$$

The key to the successful synthesis of **2** is the combination of the appropriate starting materials and solvent. Alternative attempts to synthesize $(C_5Me_5)CeX_2$ compounds, e.g., by reaction of $Ce[N(SiMe_3)_2]_3$ with $(C_5Me_5)Li$ gave only unreacted $Ce[N(SiMe_3)_2]_3$ after workup.

We tried to estimate the minimal size of the π-ligand needed to obtain stable complexes of the type $RCe(OAr)_2$ (R = C_5R_5 ligand). All attempts to introduce MeC_5H_4 ligands resulted in the formation of dark brown, intractable mixtures. Hence, it seems that a ligand set of one MeC_5H_4 and two 2,6-di-*tert*-butylphenoxo ligands is not capable of stabilizing the large cerium atom to give a mononuclear compound. In contrast, a bulky Ind* (Ind* = 1,3-diphenyl-2-methylindenyl) ligand is easily introduced (eq 4), using a similar synthetic procedure as for **2**. (Ind*)Ce(OAr)$_2$ (**3**) is obtained as orange crystals in 31% yield. The compound is poorly soluble in aliphatic hydrocarbons but soluble in aromatics.

$$Ce(OAr)_3 + (Ind^*)Li \xrightarrow{toluene} \underset{\mathbf{3}}{(Ind^*)Ce(OAr)_2} + LiOAr \quad (4)$$

The reactions of **2** with main-group alkyls and amides were studied in order to synthesize novel mono(pentamethylcyclopentadienyl)cerium complexes containing Ce–C and Ce–N σ-bonds. We decided to use bulky $CH(SiMe_3)_2$ and $N(SiMe_3)_2$ groups to achieve kinetic stabilization for stable, salt-free complexes $(C_5Me_5)CeR_2$. Surprisingly, the degree of OAr/R exchange in the reactions of **2** with main-group carbyls $MCH(SiMe_3)_2$ (M = Li or K) strongly depends on the counterion M. The reaction of **2** with 2 mol of $KCH(SiMe_3)_2$ resulted in partial OAr substitution and formation of $(C_5Me_5)Ce(OAr)CH(SiMe_3)_2$ (**4**) (eq 5). Compound **4** was isolated as orange crystals

$$(C_5Me_5)Ce(OAr)_2 + KCH(SiMe_3)_2 \rightarrow \underset{\mathbf{4}}{(C_5Me_5)Ce(OAr)(CH(SiMe_3)_2)} + KOAr \quad (5)$$

in ca. 50% yield. However, it appeared to contain small amounts of **2** (less than 10%, ^{1}H NMR). Attempts to obtain analytically pure **4** (e.g. using excess of $KCH(SiMe_3)_2$) were unsuccessful. The reaction of **2** with 2 mol of $LiCH(SiMe_3)_2$ in pentane at ambient temperature (eq 6) produced an orange solution and a white precipitate of LiOAr. Filtration, solvent removal, and crystallization from Et_2O provided orange crystals of $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (**5**), the first isolated neutral mono(pentamethylcyclopentadienyl)cerium carbyl complex.

$$(C_5Me_5)Ce(OAr)_2 + 2LiCH(SiMe_3)_2 \rightarrow \underset{\mathbf{5}}{(C_5Me_5)Ce[CH(SiMe_3)_2]_2} + 2LiOAr \quad (6)$$

$(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (**6**) was prepared by the reaction of **2** with 2 equiv of $NaN(SiMe_3)_2$ in toluene at 70 °C (eq 7). Compound **6** was isolated as extremely air-sensitive

$$(C_5Me_5)Ce(OAr)_2 + 2NaN(SiMe_3)_2 \rightarrow \underset{\mathbf{6}}{(C_5Me_5)Ce[N(SiMe_3)_2]_2} + 2NaOAr \quad (7)$$

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(24) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(25) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(26) *XTAL 2.2 User Manual*; Hall, S. R., Stewart, J. H., Eds.; Universities of Western Australia and Maryland.

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(28) (a) Meetsma, A. Extended version of the program PLUTO; University of Groningen; Groningen The Netherlands, 1986 (unpublished). (b) Motherwell, W. D. S.; Clegg, W. PLUTO, program for plotting molecular and crystal structures; University of Cambridge: Cambridge, England, 1978 (unpublished).

(29) Sheldrick, G. M. SHELX76, a system of computer programs for X-ray structure determination as locally modified; University of Cambridge: Cambridge, England, 1976.

(30) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149.

(31) Stecker, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 1132.

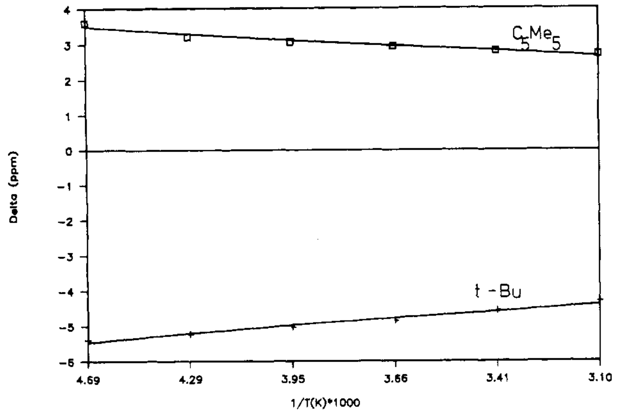

Figure 1. Plot of paramagnetic shifts against the reciprocal temperature for the *t*-Bu and C_5Me_5 ^1H NMR resonances of $(C_5Me_5)Ce(OAr)_2$ (**2**) (toluene-d_8).

orange crystals that are readily soluble in hydrocarbons, aromatic hydrocarbons, and aliphatic ethers (OEt_2 and THF).

Spectroscopic Characterization. Ce(III) is paramagnetic ($4f^1$) and consequently all NMR resonances are shifted and broadened.[32] However, ^1H NMR spectra are readily interpreted because the shift range is relatively narrow (100 ppm) and line widths are nearly always smaller than 300 Hz. Except for most α-CH protons, all resonances are clearly observed and have the expected intensities. For example, the C_5Me_5 ring resonances for **2**, **4**, **5**, and **6** are only slightly shifted compared with the diamagnetic C_5Me_5 positions (1.5–2.0 ppm) and are observed as singlets between 2.44 and 3.45 ppm. ^1H NMR data for all compounds are given in Table I.

Suitable ^{13}C NMR spectra were obtained for **3** and **6** only. Compounds **2** and **5** display rather broad lines without resolvable coupling patterns which preclude detailed assignment. The C_5Me_5 internal ring carbon atoms of **6** are present as a singlet at 152.9 ppm, which is somewhat low compared to the 178–211 ppm range observed for a number of $(C_5Me_5)_2Ce$ complexes.[6] The methyl ring carbons are observed as a quartet at 4.66 ppm with a normal sp^3 CH coupling constant of 125 Hz. Both $SiMe_3$ groups are equivalent and give a quartet at 4.71 ppm with $^1J_{CH} = 117$ Hz.

The ^1H NMR spectra of **2** between −60 and 50 °C show a single *t*-Bu resonance for the aryloxide ligands (Figure 1). The solid-state structure (vide infra) shows two distinct aryloxide ligands with essentially four inequivalent *t*-Bu groups. It is clear that both aryloxide ligands rapidly exchange in solution, even at −60 °C. The molecular structure of **5** and **6** in the solid state show inequivalent $SiMe_3$ groups as well (vide infra). Again, ^1H NMR resonances of the supporting carbyl and amide ligands are observed as singlets at −7.61 and −7.00 ppm, respectively (room temperature). Attempts to freeze out the exchanging groups of **6** by cooling down a solution sample (toluene-d_8) were not successful. The $SiMe_3$ groups are still observed as a slightly broadened singlet (lw = 53 Hz) at −80 °C. Hence, solution NMR indicates that the observed secondary interactions in the solid state are relatively weak.

Thermolysis Studies. All compounds described in this paper are thermally stable in the solid state and can be stored in an inert atmosphere at room temperature for months without noticeable decomposition. The thermolyses of **2**, **5**, and **6** in solution were studied in detail by monitoring the reactions by ^1H NMR.

Table III. Equilibrium Constants for 2 and 6[a]

compd	solv	temp, °C	K^b
2	THF-d_8	70	$(3.1 \pm 1.2) \times 10^{-3}$
2	benzene-d_6	70	$(3.1 \pm 1.2) \times 10^{-2}$
2	THF-d_8	120	$(9.1 \pm 3.6) \times 10^{-3}$
6	THF-d_8	120	$\gg 90$

[a] All concentrations are ca. 0.1 M. [b] Based on the equilibrium given in eq 8.

Compounds **2** and **6** disproportionate slowly in solution forming equilibrium mixtures containing CeX_3, $(C_5Me_5)_2CeX$, and starting compound $(C_5Me_5)CeX_2$ (eq 8).

$$2(C_5Me_5)CeX_2 \underset{K}{\rightleftharpoons} (C_5Me_5)_2CeX + CeX_3 \qquad (8)$$

The reaction is very slow at room temperature where it takes months for completion. At elevated temperatures (70–120 °C), the disproportionation rate is as expected much faster. The solvent dramatically influences the rate. In benzene-d_6 (70 °C) about 16% of **2** had disappeared following eq 8 after 24 h. In a coordinating solvent like THF the process is much slower and after 50 h at 70°C still 95% of **2** was present. This effect indicates a competing activity of basic solvent molecules, likely by coordination of THF to coordinatively very unsaturated **2** (or **6**). Transfer of ligands between two metal centers, which most probably proceeds via formation of dimers of **2** (or **6**), will be hindered, thus causing a rate suppression.

The extent of disproportionation, i.e. the value of equilibrium constant *K*, depends strongly on the nature of ligands X in $(C_5Me_5)CeX_2$. While **6** disproportionates completely (120 °C, THF-d_8), compound **2** forms under similar conditions an equilibrium mixture with 84% of original **2** present. Table III gives data for the disproportionation reaction of **2** and **6** in benzene-d_6 and THF-d_8 at various temperatures. A more elaborate investigation on the diamagnetic lanthanum analogue of **2**, $(C_5Me_5)La(OAr)_2$, will be published separately.[33]

The dialkyl **5** starts to thermolyze already at room temperature (benzene-d_6), and conditions to observe disproportionation could not be achieved. By analogy with **2** and **6** this is expected to proceed at elevated temperatures. The room-temperature thermolysis in benzene-d_6 (half-life ca. 30 h) proceeds with formation of 1 mol of $CH_2(SiMe_3)_2$/mol of **5**. Numerous broad resonances in the ^1H NMR spectra between −30 and 15 ppm and a brown precipitate imply formation of a complex mixture of organocerium species. Identification of individual components was not attempted. The formation of $CH_2(SiMe_3)_2$ suggests abstraction of either an α- or γ-hydrogen from a $CH(SiMe_3)_2$[34] group or hydrogen abstraction from a C_5Me_5 ring.[35] Solvent participation can be excluded since incorporation of deuterium in the bis(trimethylsilyl)methane was not observed when working in benzene-d_6 or THF-d_8.

A remarkable slowing down of the thermolysis of **5** was observed in the presence of excess of propylene (solvent benzene-d_6). After 21 days at room temperature free

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[32] Fischer, R. D. In *Fundamental and Technological Aspects of Organo-f-element Chemistry*; Marks, T. J.; Fragalà, I. L., Eds.; D. Reidel: Dordrecht, 1985; p 277.

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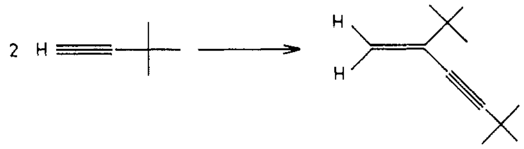
[35] (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682.

Scheme I



$CH_2(SiMe_3)_2$ was present together with 70% of the original amount of **5** and 15% of $(C_5Me_5)_2CeCH(SiMe_3)_2$. The other disproportionation product, $Ce[CH(SiMe_3)_2]_3$, could not be detected. This is not unexpected since in previous investigations we have observed[11] that this compound is thermally unstable under the conditions applied and gives, inter alia, $CH_2(SiMe_3)_2$. Comparison of NMR spectra of the thermolyzing solutions of **5** in the presence and absence of propylene makes clear that propylene slows down the low-temperature thermolysis of **5** completely and allows disproportionation (eq 8) to proceed. Because of the complexity of the whole process, no attempts were made to study the thermolysis of **5** in more detail.

Reactivity of $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (5). The reactivity of **5** toward olefins and acetylenes was studied in order to explore the catalytic properties of this compound. **5** slowly polymerizes ethylene (1 atm, room temperature, toluene solution). The uptake of ethylene decreased in time, and polymerization stopped after ca. 45 min. The average polymerization rate was determined by workup of the polyethylene formed as (230 mmol/mmol of **5**)/h. These results imply that the space around the metal is large enough to allow ethylene molecules to enter the coordination sphere of the metal. In contrast, $(C_5Me_5)_2CeCH(SiMe_3)_2$ is inactive toward ethylene under the same conditions, in line with a more crowded metal center.[36] It is clear that the mono(pentamethylcyclopentadienyl) complexes as reported here indeed have more space available around the metal center compared to their $(C_5Me_5)_2Ce$ analogues.

The reaction of **5** with propylene (11 mmol of propylene/mmol of **5**) was monitored with ^1H NMR (benzene-d_6, room temperature). Polymerization was not observed over a period of 21 days. Instead, disproportionation took place, and a mixture of **5** and $(C_5Me_5)_2CeCH(SiMe_3)_2$ was formed together with free $CH_2(SiMe_3)_2$ (vide supra).

With excess of HC≡C(*t*-Bu), **5** reacts at room temperature in benzene-d_6 with quick and quantitative formation of $CH_2(SiMe_3)_2$. ^1H NMR shows broadened resonances at δ 4.34 and −6.45 ppm that correspond to those of the product obtained from the reaction between **5** and 2 mol of HC≡C(*t*-Bu) which was identified as $[(C_5Me_5)Ce(C{\equiv}C(t\text{-Bu}))_2]_n$ (vide infra). When left standing at room temperature, the reaction goes on slowly and after several days all alkyne has been dimerized to exclusively 2,4-di-*tert*-butyl-1-buten-3-yne (Scheme I).[37] The presence of various broad resonances in the range −30 to 25 ppm in the final solution indicates a complex mixture of organocerium compounds. It is not possible to identify the organocerium species responsible for the catalytic reaction. In an attempt to obtain more information 2 mol of HC≡C(*t*-Bu) was added to 1 mol of **5**. In ca. 8 h at room temperature all alkyne had been consumed and 2 mol of $CH_2(SiMe_3)_2$ had been liberated. Resonances at δ 5.34 (15 H) and −6.45 ppm (18 H) represented over 90% of the organocerium species present and were assigned to a dialkynyl, $[(C_5Me_5)Ce(C{\equiv}C(t\text{-Bu}))_2]_n$. This compound is not stable and could not be isolated. It decomposes gradually giving a complex mixture of organocerium compounds and also dimerized alkyne, 2,4-di-*tert*-butyl-1-buten-3-yne. This type of acetylene dimerization has also been observed for the bis(pentamethylcyclopentadienyl) derivative $(C_5Me_5)_2CeCH(SiMe_3)_2$ and related systems.[36] The activity for the latter is much higher than observed here. It is likely that formation of a bis(pentamethylcyclopentadienyl)cerium(III) species is a condition for the catalytic reaction to start. It is, however, very difficult to design experiments to solve this question. Considering the fact that exchange of ligands and disproportionation are observed in all cases studied so far, it was decided not to continue our research on the catalytic properties of $(C_5Me_5)CeX_2$ compounds.

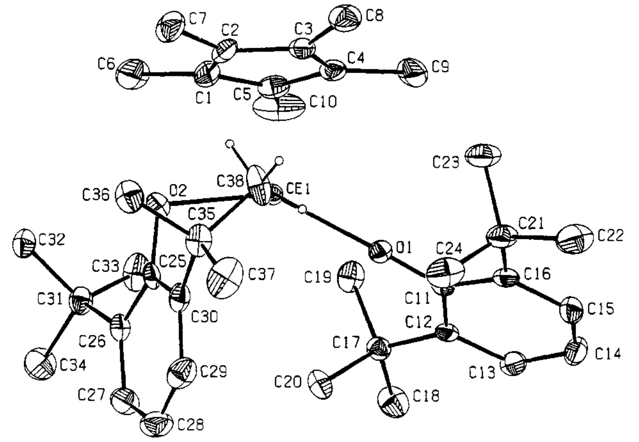


Figure 2. Perspective ORTEP[54] view with adopted numbering scheme of $(C_5Me_5)Ce(OAr)_2$ (**2**) (hydrogen atoms, except for C(38), omitted for clarity).

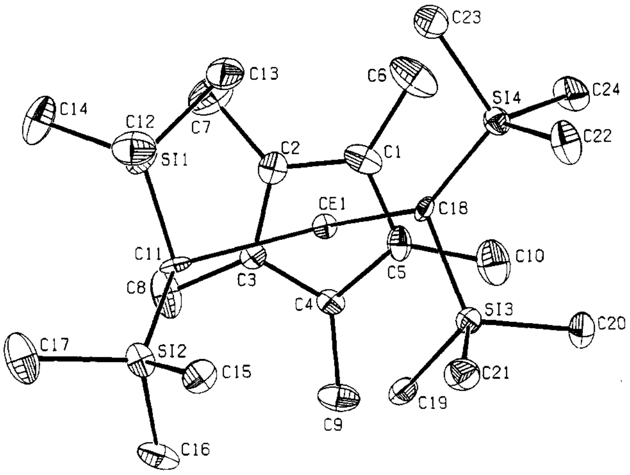


Figure 3. Perspective ORTEP[54] view with adopted numbering scheme of $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (**5**) (hydrogen atoms omitted for clarity).

Molecular Structures of $(C_5Me_5)Ce(OAr)_2$, $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$, and $(C_5Me_5)Ce[N(SiMe_3)_2]_2$

General Features. The molecular structures of the highly unsaturated compounds **2**, **5**, and **6** were determined by single-crystal X-ray diffraction. All complexes crystallize in monomeric units, resulting in formally five-coordinate cerium ions (assuming a C_5Me_5 ring occupies three coordination positions). The molecular geometries and the labeling schemes are given in Figure 2–4.

The C_5Me_5 rings of compound **2** and **6** are η^5-coordinated to cerium and dish-shaped (the methyl groups are directed

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(36) Heeres, H. J.; Heeres, A.; Teuben, J. H., to be submitted for publication.

(37) ^1H NMR data for 2,4-di-*tert*-butyl-1-buten-3-yne (benzene-d_6): δ 1.16 (9 H, s, *t*-Bu), 1.19 (9 H, s, *t*-Bu), 5.10 (1 H, d, $^2J_{HH}$ = 1.6 Hz, CH), 5.32 (1 H, d, $^2J_{HH}$ = 1.6 Hz, CH).

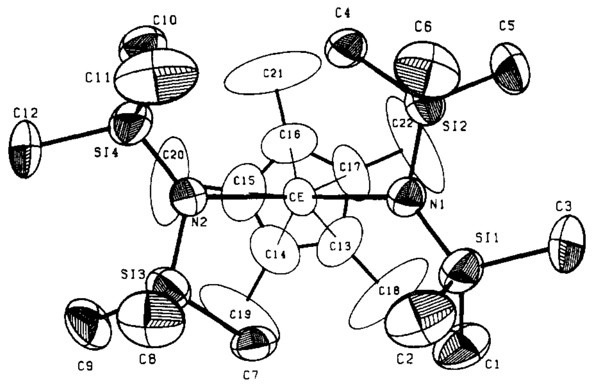

Figure 4. Perspective ORTEP[54] view with adopted numbering scheme of $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (**6**).

Table IV. Average Ce–C(ring) Distances for a Number of Mono(pentamethylcyclopentadienyl)cerium Compounds

compd[a]	Ce–C(ring), Å	CN[b]	ref
$(C_5Me_5)Ce(OAr)_2$	2.76 (1)	5	this work
$(C_5Me_5)CeR_2$	2.79 (3)	5	this work
$(C_5Me_5)CeNR_2$	2.77 (1)	5	this work
$[(C_5Me_5)Ce(\mu\text{-}I)NR_2]_2$	2.75 (1)	6	39
$[(C_5Me_5)Ce(O\text{-}t\text{-}Bu)_2]_2$	2.82 (2)	6	40
$(C_5Me_5)Ce(OAr)Ma$	2.78 (2)	6	41
$(C_5Me_5)CeI_2{\cdot}3THF$	2.78	8	7

[a] OAr = 2,6-di-*tert*-butylphenoxo; R = $CH(SiMe_3)_2$; NR_2 = $N(SiMe_3)_2$; Ma = [(dimethylamino)methyl]phenyl. [b] CN = formal coordination number.

away from the metal with average out of plane deviations of 0.13 and 0.11 Å, respectively). In contrast, the C_5Me_5 ring of **5** is slightly distorted. Here, the Ce–C(1) and Ce–C(5) distances are relatively short (2.721 (8) and 2.713 (8) Å, respectively) whereas the Ce–C(3) distance is substantially longer (2.871 (7) Å). The internal carbon atoms (C(1)–C(5)) of the C_5Me_5 ring are planar within 0.03 Å, and all C–C internal ring distances are equal within the estimated standard deviation and indicate a fully delocalized π-system. It seems that the ring is tilted to relieve unfavorable steric interactions with one of the carbyl ligands. Indeed, the hydrogen atom on C(11) (H(111)) is pointing toward the C_5Me_5 ring. This results in a close C(8)···H(111) contact of 2.69 (6) Å, which is less than the normal van der Waals contact (2.90 Å).[38]

Average Ce–C(ring) distances for **2**, **5**, **6**, and a number of other structurally characterized mono(pentamethylcyclopentadienyl) compounds are given in Table IV. It seems that this specific distance is independent of the coordination number of the cerium center. A similar pattern was observed by Evans et al. for two $(C_5Me_5)_2SmI{\cdot}L$ adducts (L = THF, eight-coordinate; L = 1,5-pentamethylenetetrazole, nine-coordinate) with different coordination numbers.[42]

These monomeric, electronically unsaturated compounds are expected to form agostic interactions with available C–H or Si–C bonds.[43] Indeed, the solid-state structures for all complexes reveal the presence of these interesting secundary interactions. A more elaborate discussion for each individual compound is given below.

Table V. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms for $(C_5Me_5)Ce(OAr)_2$ (2)

	x	y	z	U_{eq},[a] Å^2
Ce(1)	0.11328 (2)	0.49854 (0)	0.24353 (2)	0.01500 (9)
O(1)	0.1168 (2)	0.4454 (2)	0.1510 (2)	0.0186 (7)
O(2)	0.2202 (3)	0.5837 (2)	0.4023 (2)	0.0203 (7)
C(1)	0.4130 (4)	0.4912 (5)	0.2636 (4)	0.026 (1)
C(2)	0.4035 (4)	0.4405 (3)	0.3569 (4)	0.024 (1)
C(3)	0.3111 (4)	0.3756 (2)	0.2982 (4)	0.021 (1)
C(4)	0.2628 (4)	0.3861 (2)	0.1666 (4)	0.023 (1)
C(5)	0.3245 (4)	0.4583 (3)	0.1449 (4)	0.025 (1)
C(6)	0.5156 (4)	0.5601 (3)	0.2860 (5)	0.042 (2)
C(7)	0.4886 (4)	0.4509 (3)	0.4941 (4)	0.036 (1)
C(8)	0.2856 (5)	0.3027 (3)	0.3617 (4)	0.033 (1)
C(9)	0.1691 (5)	0.3298 (3)	0.0681 (5)	0.039 (2)
C(10)	0.3148 (5)	0.4908 (5)	0.0207 (4)	0.047 (2)
C(11)	−0.2448 (4)	0.4234 (2)	0.0583 (4)	0.018 (1)
C(12)	−0.3020 (4)	0.4695 (2)	−0.0532 (4)	0.0178 (9)
C(13)	−0.4279 (4)	0.4428 (3)	−0.1528 (4)	0.024 (1)
C(14)	−0.4984 (4)	0.3726 (3)	−0.1455 (4)	0.030 (1)
C(15)	−0.4476 (4)	0.3305 (3)	−0.0360 (5)	0.030 (1)
C(16)	−0.3233 (4)	0.3536 (2)	0.0686 (4)	0.023 (1)
C(17)	−0.2291 (4)	0.5482 (2)	−0.0619 (3)	0.020 (1)
C(18)	−0.3120 (5)	0.5909 (3)	−0.1860 (4)	0.032 (1)
C(19)	−0.0656 (4)	0.5335 (3)	−0.0555 (4)	0.027 (1)
C(20)	−0.2334 (4)	0.6036 (2)	0.0416 (4)	0.026 (1)
C(21)	−0.2771 (4)	0.3080 (2)	0.1917 (4)	0.029 (1)
C(22)	−0.3844 (5)	0.2398 (3)	0.1856 (6)	0.045 (2)
C(23)	−0.1181 (4)	0.2737 (3)	0.2265 (5)	0.036 (1)
C(24)	−0.2841 (5)	0.3620 (3)	0.2961 (5)	0.036 (2)
C(25)	0.1056 (4)	0.6291 (2)	0.4051 (4)	0.018 (1)
C(26)	0.0776 (4)	0.7034 (2)	0.3429 (4)	0.021 (1)
C(27)	−0.0542 (5)	0.7425 (3)	0.3316 (4)	0.030 (1)
C(28)	−0.1524 (5)	0.7132 (3)	0.3829 (5)	0.034 (2)
C(29)	−0.1182 (4)	0.6444 (3)	0.4519 (4)	0.031 (1)
C(30)	0.0123 (4)	0.6008 (2)	0.4662 (4)	0.022 (1)
C(31)	0.1940 (4)	0.7381 (2)	0.2916 (4)	0.023 (1)
C(32)	0.3491 (4)	0.7396 (2)	0.3937 (4)	0.025 (1)
C(33)	0.1926 (5)	0.6922 (3)	0.1768 (4)	0.032 (1)
C(34)	0.1534 (5)	0.8236 (3)	0.2495 (5)	0.039 (1)
C(35)	0.0602 (4)	0.5299 (2)	0.5555 (4)	0.025 (1)
C(36)	0.2081 (5)	0.5501 (3)	0.6633 (4)	0.030 (1)
C(37)	−0.0576 (5)	0.5124 (4)	0.6137 (4)	0.041 (2)
C(38)	0.0849 (5)	0.4532 (2)	0.4940 (4)	0.031 (1)

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

Table VI. Selected Bond Distances and Angles for $(C_5Me_5)Ce(OAr)_2$ (2)[a]

	Bond Distances (Å)		
Ce(1)–O(1)	2.247 (2)	Ce(1)–O(2)	2.258 (2)
Ce(1)–C(1)	2.794 (4)	Ce(1)–C(2)	2.772 (4)
Ce(1)–C(3)	2.733 (4)	Ce(1)–C(4)	2.730 (4)
Ce(1)–C(5)	2.753 (4)	O(1)–C(11)	1.343 (5)
O(2)–C(25)	1.352 (5)	C(1)–C(2)	1.409 (8)
C(1)–C(5)	1.427 (7)	C(1)–C(6)	1.489 (9)
C(2)–C(3)	1.419 (6)	C(2)–C(7)	1.494 (6)
C(3)–C(4)	1.422 (6)	C(3)–C(8)	1.507 (6)
C(4)–C(5)	1.426 (6)	C(4)–C(9)	1.506 (7)
C(5)–C(10)	1.505 (7)	C(35)–C(36)	1.533 (6)
C(35)–C(37)	1.542 (7)	C(35)–C(38)	1.546 (5)
Ce–Cent	2.478 (2)		
	Bond Angles (deg)		
O(1)–Ce(1)–O(2)	135.2 (1)	Ce(1)–O(1)–C(11)	158.5 (2)
Ce(1)–O(2)–C(25)	105.1 (2)	C(30)–C(35)–C(36)	108.4 (4)
C(30)–C(35)–C(37)	111.0 (4)	C(30)–C(35)–C(38)	114.4 (3)
Cent–Ce–O(1)	121.67 (7)	Cent–Ce–O(2)	99.26 (8)

[a] Cent = centroid of the C_5Me_5 ring.

Molecular Structure of 2. The final fractional coordinates for **2** are given in Table V. Selected bond distances and angles are presented in Table VI.

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Another way of looking at the geometry of 2 is to consider it as a quasi-three-coordinate complex with the C_5Me_5 ring occupying one coordination site and bound to the cerium atom by its center of gravity. The geometry of 2 is rather pyramidal than trigonal planar with the metal 0.26 Å above the plane of the ligating atoms O1, O2, and the C_5Me_5 centroid.

Of great interest is the bonding of the aryloxide ligands. The Ce(1)–O(1)–C(11) angle of 158.5 (2)° is in the range observed for O-bonded lanthanide, actinide, and early-transition-metal aryloxide complexes.[44] However, the bonding of the other aryloxide ligand is unprecedented. It shows an extremely small Ce(1)–O(2)–C(25) angle of 105.1 (2)°, which is even smaller than observed for main-group aryloxides (125–150°).[45] Surprisingly, the Ce–O bond distances, 2.247 (2) and 2.258 (2) Å, do not differ significantly. These data do not fit the pattern observed for a number of lanthanide, actinide, and transition-metal aryloxides/alkoxides: large M–O–C angles are coupled with short M–O distances, rationalized by assuming partial multiple-bond character in the M–O–C linkage.[44,46] Apparently, steric factors and/or metal aryloxide secondary interactions (vide infra) instead of $M \overset{\leftarrow}{=} O — C$ π-donative interactions determine the nature of the M–O–C linkage.

The Ce–O distances are identical compared with five-coordinate $Ce(OAr)_3 \cdot (t\text{-}BuCN)_2$ (average 2.23 Å)[31] and as expected somewhat longer than the average value of three-coordinate $Ce(OAr)_3$ (average 2.14 Å).[31]

In addition to the oxygen–cerium coordination, there is an interaction of cerium with a *t*-Bu methyl group of one of the aryloxide ligands. Methyl group C(38) is pointing directly toward the metal, a situation that would be expected to maximize unfavorable steric interactions. The Ce···C(38) distance is very short (3.098 (4) Å), compared to 3.533 (5) Å for the closest contact of the methyl group on the opposite *t*-Bu group. Furthermore, two of the refined hydrogen atoms have close contacts with the cerium center, viz., 2.67 (4) and 2.86 (4) Å.

Structural studies on organometallic compounds containing *tert*-butyl-substituted aryloxide ligands have indicated similar conformations of the *t*-Bu groups with short metal–carbon contacts for three other cases: (4-methoxy-2,6-di-*tert*-butylphenoxo)$Zr(OAr)(CH_2Ph)_2$,[47] $(OAr)_2TaCl_3$,[48] and $(OAr)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2$.[49] It seems that these close contacts are a result of agostic CH interactions which help to decrease the electron deficiency of these Lewis acid metal centers.

The origin of the strong distortion of one of the aryloxide ligands, which leads to an extremely small Ce–O–C angle, remains unclear. Reduction of the Ce–O–C angle increases the steric pressure of an aryloxide ligand, resulting in a more efficient filling of the coordination sphere around the metal. However, electronic effects, i.e. the Ce–O–C angle is decreased to force the interacting *t*-Bu group close to the cerium center in order to optimize C–H metal agostic interactions, cannot be excluded.

Table VII. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms for $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (5)

	x	y	z	U_{eq},[a] Å^2
Ce(1)	0.37890 (2)	0.33788 (2)	0.00000 (0)	0.0143 (1)
Si(1)	0.1948 (1)	0.2400 (1)	−0.0972 (1)	0.0236 (6)
Si(2)	0.1538 (1)	0.2214 (1)	0.0963 (1)	0.0218 (6)
Si(3)	0.4186 (1)	0.5092 (1)	0.1115 (1)	0.0184 (5)
Si(4)	0.4593 (1)	0.5710 (1)	−0.0749 (1)	0.0184 (5)
C(1)	0.4974 (4)	0.3029 (4)	−0.0551 (4)	0.024 (2)
C(2)	0.4250 (4)	0.2230 (4)	−0.0613 (4)	0.020 (2)
C(3)	0.3970 (3)	0.1933 (4)	0.0201 (3)	0.014 (2)
C(4)	0.4513 (4)	0.2541 (4)	0.0765 (4)	0.015 (2)
C(5)	0.5147 (4)	0.3222 (4)	0.0315 (4)	0.023 (2)
C(6)	0.5497 (5)	0.3579 (5)	−0.1257 (5)	0.041 (3)
C(7)	0.3906 (5)	0.1750 (5)	−0.1413 (5)	0.039 (3)
C(8)	0.3271 (4)	0.1083 (4)	0.0425 (5)	0.034 (2)
C(9)	0.4488 (4)	0.2426 (4)	0.1702 (4)	0.029 (2)
C(10)	0.5864 (4)	0.4003 (4)	0.0651 (5)	0.037 (3)
C(11)	0.2257 (3)	0.2347 (3)	0.0122 (5)	0.016 (2)
C(12)	0.1324 (4)	0.2932 (5)	−0.1088 (4)	0.035 (3)
C(13)	0.2917 (4)	0.3043 (4)	−0.1628 (4)	0.030 (2)
C(14)	0.1379 (5)	0.1365 (4)	−0.1490 (5)	0.039 (3)
C(15)	0.1502 (4)	0.3184 (4)	0.1195 (4)	0.027 (2)
C(16)	0.1873 (4)	0.1895 (4)	0.1927 (5)	0.035 (3)
C(17)	0.0431 (4)	0.1362 (4)	0.0749 (5)	0.043 (3)
C(18)	0.4007 (3)	0.4858 (3)	−0.0022 (6)	0.014 (1)
C(19)	0.3920 (4)	0.4082 (4)	0.1701 (4)	0.023 (2)
C(20)	0.5300 (4)	0.5823 (4)	0.1397 (5)	0.029 (2)
C(21)	0.3526 (4)	0.5482 (4)	0.1594 (4)	0.028 (2)
C(22)	0.4662 (4)	0.6726 (4)	−0.0447 (5)	0.033 (3)
C(23)	0.4084 (5)	0.5420 (4)	−0.1805 (5)	0.037 (3)
C(24)	0.5699 (4)	0.5929 (4)	−0.0873 (4)	0.028 (2)

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

Table VIII. Selected Bond Distances and Angles for $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ (5)[a]

Bond Distances (Å)			
Ce(1)···Si(1)	3.332 (2)	Si(1)–C(14)	1.855 (7)
Ce(1)···Si(3)	3.378 (2)	Si(2)–C(11)	1.819 (8)
Ce(1)–C(1)	2.721 (8)	Si(2)–C(15)	1.864 (7)
Ce(1)–C(2)	2.828 (7)	Si(2)–C(16)	1.863 (8)
Ce(1)–C(3)	2.871 (7)	Si(2)–C(17)	1.887 (8)
Ce(1)–C(4)	2.784 (8)	Si(3)–C(18)	1.86 (1)
Ce(1)–C(5)	2.713 (8)	Si(3)–C(19)	1.920 (7)
Ce(1)–C(11)	2.508 (6)	Si(3)–C(20)	1.867 (8)
Ce(1)···C(13)	2.959 (7)	Si(3)–C(21)	1.865 (8)
Ce(1)–C(18)	2.556 (5)	Si(4)–C(18)	1.816 (7)
Ce(1)···C(19)	2.972 (6)	Si(4)–C(22)	1.879 (7)
Si(1)–C(11)	1.858 (8)	Si(4)–C(23)	1.876 (8)
Si(1)–C(12)	1.861 (9)	Si(4)–C(24)	1.885 (8)
Si(1)–C(13)	1.894 (8)	Ce–Cent	2.512 (3)
Bond Angles (deg)			
Ce(1)–C(11)–Si(1)	98.4 (3)	Ce(1)–C(18)–Si(3)	98.6 (3)
Ce(1)–C(11)–Si(2)	129.1 (3)	Ce(1)–C(18)–Si(4)	130.0 (4)
Ce(1)–C(11)–H(111)	90 (3)	Ce(1)–C(18)–H(118)	93 (3)
Si(1)–C(11)–Si(2)	118.7 (4)	Si(3)–C(18)–Si(4)	117.7 (3)
Cent–Ce–C(11)	108.4 (2)	Cent–Ce–C(18)	142.2 (2)

[a] Cent = centroid of the C_5Me_5 ring.

Molecular Structures of 5 and 6. Crystals of 5 consist of monomeric $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$ units at normal van der Waals distances. The final fractional coordinates are given in Table VII. Relevant bond distances and angles with estimated standard deviations are given in Table VIII. Compound 5 is isostructural with the lanthanum analogue.[8a] The unit cell of 6 contains discrete molecules separated by normal van der Waals distances (Figure 4). The final fractional coordinates are given in Table IX. Selected bond distances and bond angles are given in Table X.

The $CH(SiMe_3)_2$ ligands of compound 5 are bound primarily by Ce–C σ-bonds (Ce(1)–C(18) = 2.556 (5) Å and Ce(1)–C(11) = 2.508 (6) Å) and adopt different confor-

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Table IX. Final Fractional Atomic Coordinates for $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (6)

atom	x/a	y/b	z/c	B(eq),[a] Å^2
Ce	0.25009 (3)	0.01743 (4)	0.33709 (4)	2.65
Si(1)	0.4160 (1)	−0.0171 (2)	0.1907 (3)	4.24
Si(2)	0.3671 (1)	−0.1588 (2)	0.3596 (2)	3.64
Si(3)	0.1487 (2)	0.0211 (2)	0.1267 (2)	3.87
Si(4)	0.1004 (2)	−0.1434 (2)	0.2718 (3)	4.30
N(1)	0.3578 (4)	−0.0513 (5)	0.2871 (6)	3.20
N(2)	0.1539 (3)	−0.0455 (5)	0.2427 (6)	3.08
C(1)	0.4235 (6)	0.1232 (8)	0.182 (1)	5.56
C(2)	0.3857 (6)	−0.0612 (8)	0.0530 (8)	5.70
C(3)	0.5075 (5)	−0.066 (1)	0.215 (1)	7.30
C(4)	0.2856 (5)	−0.1724 (7)	0.4467 (8)	3.84
C(5)	0.4422 (5)	−0.1561 (8)	0.4588 (9)	4.86
C(6)	0.3699 (6)	−0.2762 (7)	0.2762 (9)	5.23
C(7)	0.2272 (5)	0.1118 (7)	0.1266 (7)	3.85
C(8)	0.1574 (6)	−0.0551 (8)	−0.0008 (8)	5.40
C(9)	0.0671 (6)	0.1022 (8)	0.114 (1)	5.66
C(10)	0.0886 (5)	−0.1563 (8)	0.4224 (8)	4.50
C(11)	0.1398 (7)	−0.2647 (8)	0.2236 (9)	6.63
C(12)	0.0092 (6)	−0.127 (1)	0.214 (1)	8.11
C(13)	0.2815 (7)	0.1961 (9)	0.438 (1)	4.84
C(14)	0.2131 (8)	0.2045 (9)	0.410 (1)	5.08
C(15)	0.1730 (7)	0.143 (1)	0.469 (1)	5.39
C(16)	0.2167 (8)	0.0891 (8)	0.5382 (9)	4.96
C(17)	0.2861 (6)	0.122 (1)	0.520 (1)	4.67
C(18)	0.3394 (9)	0.261 (1)	0.398 (1)	11.29
C(19)	0.1813 (9)	0.285 (1)	0.334 (1)	10.23
C(20)	0.0919 (6)	0.132 (1)	0.464 (1)	9.82
C(21)	0.190 (1)	0.018 (1)	0.623 (1)	11.22
C(22)	0.3517 (8)	0.094 (1)	0.574 (1)	12.34

[a] $B(\mathrm{eq}) = {}^4/_3[a^2b(11) + b^2b(22) + c^2b(33) + (ab)(\cos\gamma)b(12) + (ac)(\cos\beta)b(13) + (bc)(\cos\alpha)b(23)]$.

Table X. Selected Bond Distances and Angles for $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ (6)[a]

Bond Distances (Å)			
Ce–N(1)	2.357 (7)	Ce–N(2)	2.349 (7)
Ce–C(13)	2.77 (1)	Ce–C(14)	2.77 (1)
Ce–C(15)	2.79 (1)	Ce–C(16)	2.77 (1)
Ce–C(17)	2.77 (1)	Si(1)–N(1)	1.713 (7)
Si(1)–C(1)	1.89 (1)	Si(1)–C(2)	1.91 (1)
Si(1)–C(3)	1.90 (1)	Si(2)–N(1)	1.712 (7)
Si(2)–C(4)	1.922 (9)	Si(2)–C(5)	1.90 (1)
Si(2)–C(6)	1.89 (1)	Si(3)–N(2)	1.707 (7)
Si(3)–C(7)	1.941 (9)	Si(3)–C(8)	1.90 (1)
Si(3)–C(9)	1.92 (1)	Si(4)–N(2)	1.710 (7)
Si(4)–C(10)	1.91 (1)	Si(4)–C(11)	1.90 (1)
Si(4)–C(12)	1.91 (1)	C(13)–C(14)	1.36 (2)
C(13)–C(17)	1.44 (2)	C(13)–C(18)	1.50 (1)
C(14)–C(15)	1.35 (2)	C(14)–C(19)	1.56 (2)
C(15)–C(16)	1.40 (2)	C(15)–C(20)	1.57 (2)
C(16)–C(17)	1.43 (2)	C(16)–C(21)	1.51 (1)
C(17)–C(22)	1.48 (1)	Ce–Cent	2.51
Bond Angles (deg)			
Ce–N(1)–Si(1)	131.4 (4)	Ce–N(2)–Si(3)	106.3 (3)
Ce–N(1)–Si(2)	106.2 (3)	Ce–N(2)–Si(4)	130.0 (4)
N(1)–Ce–N(2)	114.7 (2)	N(1)–Si(2)–C(4)	107.2 (4)
N(1)–Si(2)–C(5)	114.0 (4)	N(1)–Si(2)–C(6)	114.5 (4)
N(2)–Si(3)–C(7)	106.7 (4)	N(2)–Si(3)–C(8)	115.1 (4)
N(2)–Si(3)–C(9)	114.3 (5)	Cent–Ce–N(1)	125.0
Cent–Ce–N(2)	120.2		

[a] Cent = centroid of the C_5Me_5 ring.

mations with endo and exo α-CH groups with respect to the C_5Me_5 ring. These distances are nearly the same as observed for $(C_5Me_5)_2CeCH(SiMe_3)_2$ (2.535 (5) Å).[6] The cerium atom in 6 is bound to two amide nitrogen atoms at an average distance of 2.353 (4) Å, and this is slightly longer compared to the Ce–N bond distance in $[(C_5Me_5)Ce(I)N(SiMe_3)_2]_2$ (2.308 (4) Å).[39]

The electron deficiency of the cerium atom in both compounds is relieved by a number of secondary interactions. The $CH(SiMe_3)_2$ groups of 5 are distorted in such a way that two of the methyl groups, C(13) and C(19), are oriented toward the cerium atom (Ce(1)···C(13) = 2.959 (7) Å, Ce(1)···C(19) = 2.972 (6) Å). Consequently, these ligands are skewed so that the overall geometry of 5 can be described as a four-legged piano stool. These interactions are clearly expressed by the differences in Ce–C–Si angles: Ce(1)–C(11)–Si(1) = 98.4 (3)°, Ce(1)–C(11)–Si(2) = 129.1 (3)°, Ce(1)–C(18)–Si(3) = 98.6 (3)°, Ce(1)–C(18)–Si(4) = 130.0 (4)°.

Also noteworthy is the position of the refined α-hydrogen atoms. Both are pointing toward the metal (Ce(1)–C(18)–H(181) = 93 (3)° and Ce(1)–C(11)–H(111) = 90 (3)°), and this results in short Ce–H distances (Ce(1)–H(181) = 2.82 (6) Å and Ce(1)–H(111) = 2.71 (5) Å). Similar α-CH agostic interactions have been observed for a number of lanthanide and actinide carbyls[50] and reflect the high electron deficiency of these compounds.

The geometry of compound 6 can also be considered as a four-legged piano stool with trans nitrogen and carbon atoms, similar as observed for $(C_8H_8)Th[N(SiMe_3)_2]_2$.[53] The Ce···C(4) and Ce···C(7) distance are 2.972 (9) and 2.952 (9) Å, respectively, and are much shorter than the average of the remaining Ce–amide carbon distances (3.78 (2) Å). The Ce–N–Si angles clearly show the distorted amide ligands: Ce(1)–N(1)–Si(1) = 131.4 (4)°, Ce(1)–N(1)–Si(2) = 106.2 (3)°, Ce(1)–N(2)–Si(3) = 106.3 (3)°, Ce(1)–N(2)–Si(4) = 130.0 (4)°.

There is a growing body of literature dealing with close methyl-metal contacts.[8a,50] Recent ab initio calculations for $Ti(C(SiH_2Me){=}CH_2)Cl_2^+$ show an optimized structure with a distorted alkenyl ligand: a small Ti–C–Si angle, a long Si–γ–C bond distance, and a short Ti–γ–C distance,[51] in agreement with the molecular structure of $Cp_2Ti(C(SiMe_3){=}C(Me)Ph)^+$.[52] This distortion is explained as a donative interaction of the Si–C σ-bond (a β-SiC agostic interaction) to a vacant Ti d orbital, assisted by γ-CH agostic interactions. However, the β-Si–Me bond lengths of the interacting methyl groups of 5 (Si(1)–C(13) = 1.894 (8) Å and Si(3)–C(19) = 1.920 (7) Å) are only marginally longer compared with the other Si–Me bonds (average 1.87 (1) Å) and a similar situation is observed for 6 (Si(2)–C(4) = 1.922 (9) Å; Si(3)–C(7) = 1.941 (9) Å and the average Si–C bond = 1.90 (1) Å). Hence, it is tempting to suggest that here the γ-CH bonds are the major origin of the observed distortion. However, the refined hydrogens on C(13) and C(19) in 5 are oriented to place two of the hydrogen atoms close to the metal, a situation which is favored in order to diminish steric repulsion. This is in marked contrast with β-CH agostic interactions, in which the C–H bond is invariably directed toward the metal.[43] Conclusions about the presence of γ-CH interactions in compound 6 cannot be made because the hydrogen atoms could not be located. However, it is noted that C(4) and C(7) are best behaved of any of the methyl carbons. The thermal motion of these atoms is well below that observed

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for the other methyl groups. γ-CH interactions would be expected to dampen the thermal motion of these atoms. A definitive explanation for these close methyl–metal contacts will have to wait for further, accurate structural (e.g. neutron diffraction) studies.

Conclusions

$Ce(OAr)_3$ is a convenient precursor for the preparation of neutral monopentamethylcyclopentadienyl organocerium(III) complexes containing Ce–O, Ce–N, and Ce–C bonds. Disproportionation with the formation of $(C_5Me_5)_2CeX$ and CeX_3 compounds is observed frequently and seems a general feature of this class of compounds. This lability of ancillary ligands hampers detailed reactivity and mechanistic studies. The molecular structures of **2**, **4**, and **5** display interesting secondary interactions that relieve the electron deficiency of the highly unsaturated cerium center. Some indication for β-SiC agostic interaction is obtained from the slightly longer Si–C bonds.

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Registry No. **1**, 113034-77-8; **2**, 121934-76-7; **3**, 122923-71-1; **4**, 122923-72-2; **5**, 121934-77-8; **6**, 122923-73-3; $CeCl_3$, 7790-86-5; Li(OAr), 55894-67-2; (Ind*)Li, 122875-95-0; $KCH(SiMe_3)_2$, 118111-55-0; $LiCH(SiMe_3)_2$, 41823-71-6; $NaN(SiMe_3)_2$, 1070-89-9; $(C_5Me_5)_2CCH(SiMe_3)_2$, 106333-13-5; $HC{\equiv}C(t\text{-Bu})$, 917-92-0; $[(C_5Me_5)Ce(C{\equiv}C(t\text{-Bu}))_2]_n$, 122923-74-4; 1,3-diphenyl-2-methylidene, 51310-26-0; ethylene, 74-85-1; propylene, 115-07-1; 2,4-di-*tert*-butyl-1-buten-3-yne, 59474-22-5.

Supplementary Material Available: Tables of all atomic coordinates, thermal parameters, bond distances, and bond angles for **2**, **5**, and **6** and a table of least-squares planes for **6** (18 pages); listings of observed and calculated structure factors for **2**, **5**, and **6** (41 pages). Ordering information is given on any current masthead page.

Mono-, Poly-, and Permercuration in the Acetone–Mercury(II) System[†]

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Mercuration occurs spontaneously, if slowly, in acidic aqueous solutions of acetone and free mercuric ion to produce at least nine organomercury species, all of which can exist in equilibrium simultaneously. The reaction sequence was followed by ^1H and ^{199}Hg NMR; the order of appearance of the ^1H and ^{199}Hg spectra and the spin-coupling interactions therein suffice to distinguish a monomercury, two dimercury (symmetrical and unsymmetrical), two trimercury, two tetramercury (symmetrical and unsymmetrical), one pentamercury, and one hexamercury species. The $^2J_{HgCH}$ coupling in the previously unreported $-CHHg_2$ moiety is 190–200 Hz.

Polymercuration of aromatic systems is well-known, and many such investigations have been reported in an extensive series of papers by Deacon[1a] et al.; a comprehensive review has been given by Wardell.[1b] While many monomercury derivatives of nonaromatic compounds have been prepared of the types RHgX or R_2Hg, including the monoacetone[2] $[(CH_3COCH_2)Hg]I$ and diacetone[3] $(CH_3COCH_2)_2Hg$ compounds, few polymercury derivatives have been described. Some dimercury derivatives of doubly activated methylene groups (i.e., diketones) have been reported,[4] and some compounds have been characterized by X-ray diffraction.[5,6] The first permercurated alkyl compounds were synthesized and identified by Matteson[8] as $C(HgI)_4$ and $C(HgC_2H_3O_2)_4$. A number of "mercarbides" prepared by Hoffmann[7] around 1900 have been elucidated in part as monomeric $[CHg_4{}^{4+}]$ and polymeric $[CHg_4O^{2+}]_n$ species by Grdenic[9] et al.

The present work uses ^1H and ^{199}Hg NMR spectra to investigate the mercuration of acetone in acidic aqueous solution where stepwise replacement of H^+ by Hg^{2+} is observed without C–C bond cleavage or other redox complications.

Table I. ^1H and ^{199}Hg NMR of the Nine Hg–Acetone Species

symbol	structure	^1H shift[a]	^{199}Hg shift[b]
I	$[(CH_3COCH_2)Hg]^+$	0.07, 0.86	571 t
IIA	$[Hg(CH_2COCH_2Hg]^{2+}$	0.94	567 t
IIB	$[(CH_3COCH)Hg_2]^{2+}$	0.17, 1.41	720 d of d
IIIA	$[Hg(CH_2COCH)Hg_2]^{3+}$	1.03, 1.64	562 t, 700 d of d
IIIB	$[(CH_3COC)Hg_3]^{3+}$	0.28	792 s
IVA	$[Hg_2(CHCOCH)Hg_2]^{4+}$	1.78	686 d
IVB	$[Hg(CH_2COC)Hg_3]^{4+}$	1.12	557 t, 785 s
V	$[Hg_2(CHCOC)Hg_3]^{5+}$	2.07	673 d, 773 s
VI	$[Hg_3(CCOC)Hg_3]^{6+}$		762 s

[a] In units from internal free acetone; shifts are given in order of position in structure. [b] In units from "free" mercuric ion. Abbreviations: s, singlet: d, doublet: t, triplet.

Results and Discussion

Qualitative Interpretation of Spectra. When acetone (e.g., 0.5 mL, 7 mmol) was added to aqueous mercuric nitrate solution (e.g., 10 mL of 1.4 M $Hg(NO_3)_2$—14 mmol—in 1 M HNO_3), a complex set of sequential reactions occurred over a period of about 50 h. The resulting

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[†] This work is dedicated to the memory of Dr. Charles B. Colburn, who died on August 2, 1988.

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