Supporting Information

Synthesis and derivatisation of ceric tris(tert-butoxy)siloxides

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1. Experimental Details

General Procedures. All operations were performed with rigorous exclusion of oxygen and moisture under an argon atmosphere. The syntheses were carried out either in a glovebox (*MBraun* MB200B; <1 ppm O_2 , <1 ppm H_2O) or according to standard Schlenk techniques. Anhydrous CeCl₃ (99.99% trace metal basis), KN(SiMe₃)₂ (95%), HOSi(OtBu)₃ (99.99% trace metal basis) and Ph₃CCI (98%) were purchased from Sigma-Aldrich and used as received. Cerium(III) chloride was activated via thf soxhlet extraction. $ZnMe_2$ (95%) was purchased from ABCR. $Ce[N(SiMe_3)_2]_3$ was synthesized according to literature procedures.¹ Toluene, *n*-hexane, dcm, and thf were dried and degassed prior to use and provided by an *MBraun* SPS-800. C_6D_6 , toluene- d_8 and thf- d_8 were obtained from *Euriso-top*, degassed, dried over NaK for at least 24 h, and filtered prior to use (thf-d₈ was distilled). NMR spectra were recorded on a Bruker AVII+400 spectrometer. Magnetic susceptibilities were determined in deuterated solvents according to the Evans method^{2,3} with hexamethylsiloxane as an internal reference. Infrared spectra were recorded on a Thermo Fisher Scientific NICOLET 6700 FTIR spectrometer using a DRIFT chamber with KBr windows. The samples were prepared in a glovebox and mixed with KBr powder. The collected data were refined by the Kubelka-Munk baseline correction. Elemental analyses were determined by an Elementar Vario Micro Cube. UV-Visible spectra were recorded on a PG Instruments T60 UV-Visible Spectrophotometer from 180 – 800 nm (1 nm slit width) in Hellma Analytics QS suprasil quarz cells with 1 cm path length. Autozero calibrations were performed prior each measurement against the pure solvent.

[MeZn{OSi(OtBu)₃**]**₂ was synthesized according to a slightly modified literature procedure.⁴ A chilled solution of HOSi(OtBu)₃ (27 mg, 0.10 mmol) in toluene (-40 °C) was added to a stirred solution of ZnMe₂ (10 mg, 0.10 mmol) in toluene (-40 °C). The reaction mixture was stirred for 1 h at -40 °C and then allowed to warm to ambient temperature. Evaporation of the solvent under reduced pressure gave a colourless solid and finally a colourless powder upon dissolving in toluene, filtration and drying (35 mg, 0.10 mmol, 99%). The spectroscopic data varied slightly to the previously published.^{4 1}H NMR (400.13 MHz, thf-*d*₈, 26 °C) δ [ppm]: 1.33 (s, 27H, *CH*₃), -0.66 (s, 3H, *CH*₃); ¹H NMR (400.13 MHz, tol-*d*₈, 26 °C) δ [ppm]: 1.39 (s, 27H, *CH*₃), -0.12 (s, 3H, *CH*₃); ¹H NMR (400.13 MHz, C₆D₆, 26 °C) δ [ppm]: 1.42 (s, 27H, *CH*₃), -0.04 (s, 3H, *CH*₃). Elemental analysis calculated for C₁₃H₃₀CeO₄SiZn [%]: C 45.41, H 8.79; found: C 45.77, H 9.09.

Synthesis of [Ce{OSi(OtBu)₃}₃]₂ (1): HOSi(OtBu)₃ (639.5 mg, 2.41 mmol) was dissolved in *n*-hexane (5 mL) and slowly added to a vigorously stirred solution of Ce[N(SiMe₃)₂]₃ (500 mg, 0.80 mmol) in *n*-hexane (5 mL). The reaction mixture was stirred for 12 h while a white precipitate formed. The mixture was centrifuged, washed with *n*-hexane (3x2mL) and evaporated to dryness in vacuum to afford **1** as a white solid (610 mg, 0.65 mmol, 82%). Compound **1** is insoluble in non-coordinating solvents. Colourless single crystals of **1** suitable for X-ray diffraction analysis were grown at -40 °C from a saturated solution in Et₂O (Figure S30). Colourless single crystals of [Ce{OSi(OtBu)₃}(thf)₃] (**1a-thf**) suitable for X-ray diffraction analysis were grown at -40 °C from a saturated solution in thf (Figure S31). ¹H NMR (400.13 MHz, thf-*d*₈, 26 °C) δ [ppm]: 1.69 (br, 81H, C(CH₃)₃). Elemental analysis calculated for: C₃₆H₈₁CeO₁₂Si₃ [%]: C 46.47, H 8.78; found: C 46.40, H 8.23. μ_{eff} (thf-*d*₈) = 2.44, c = 1.14 \cdot 10⁻⁵ mol/mL, Δ_{shift} = 62.4 Hz.

Synthesis of [Ce{OSi(OtBu)₃}₃(thf)₂] (1a): Compound 1 was dissolved in thf, filtered and evaporated to dryness in vacuum to afford bis(THF) adduct 1a as a white powder in quantitative yield. ¹H NMR (400.13 MHz, thf- d_8 , 26 °C) δ [ppm]: 3.62 (m, 8H, CH₂, thf), 1.78 (m, 8H, CH₂, thf), 1.70 (br, 81H, C(CH₃)₃). Elemental analysis calculated for: C₄₄H₉₇CeO₁₄Si₃ [%]: C: 49.18, H 8.88; found: C 49.20, H 8.91.

Synthesis of [Ce{OSi(OtBu]₃]₄] (2): Ph₃CCl (21 mg, 7.63·10⁻² mmol) was dissolved in toluene (2 mL) and added slowly to a slurry of 1 (71 mg, 7.63·10⁻² mmol) in toluene (2 mL). The slurry turned yellow and was vigorously stirred for 24 h. The mixture was centrifuged, the residue washed with cold toluene (3 x 2 mL) and evaporated to dryness in vacuum to afford 2 as a white powder (15 mg, $1.26 \cdot 10^{-2}$ mmol, 16%). The combined toluene extracts also contained 2, but separation from the by-product (Gomberg's dimer) failed. Colourless single crystals of 2 suitable for X-ray diffraction analysis were grown at -40 °C from a saturated solution in toluene. ¹H NMR (400.13 MHz, thf-*d*₈, 26 °C) δ [ppm]: 1.40 (s, 108H, CH₃); ¹H NMR (400.13 MHz, C₆D₆, 26 °C) δ [ppm]: 1.57 (s, 108H, C(CH₃)₃). ¹³C NMR (100.62 MHz,

C₆D₆, 26 °C) δ [ppm]: 73.21 (*C*(CH₃)₃), 32.21 (C(*C*H₃)₃). Elemental analysis calculated for: C₄₈H₁₀₈CeO₁₆Si₄ [%]: C 48.29, H 9.12; found: C 48.28, H 9.26. Evans (C₆D₆): χ_{mol} = 7.24·10⁻⁴ emu·mol⁻¹, χ_{mol} ·T = 0.22 emu·K·mol⁻¹, μ_{eff} = 1.32 μ_{B} , Δ_{Shift} = 1.93 Hz, c = 9.05·10⁻⁶ mol/mL.

Synthesis of [Ce{OSi(OtBu)₃}₃Cl(thf)] (3): A chilled solution of Ph₃CCl (61.2 mg, 2.15·10⁻¹ mmol) in toluene (2 mL) was slowly added to a slurry of **1a** (200 mg, 2.15·10⁻¹ mmol) in toluene (2 mL) at -40 °C. After complete addition, a greenyellow slurry had formed. The reaction mixture was stirred another 30 min and then its volume halved under vacuum. The remaining slurry in toluene was cooled overnight at -40 °C. The supernatant was removed and 2 mL of cold toluene was added. Cooling and two further extraction steps afforded **3** as a white solid (137 mg, 1.32·10⁻¹ mmol, 71%). Recrystallization from thf and evaporation to dryness in vacuum gave analytically pure **3**. Colourless single crystals of the bis(thf) adduct **3-thf** suitable for X-ray diffraction analysis were grown at -40 °C from a saturated solution in thf. ¹H NMR (400.13 MHz, thf-*d*₈, 26 °C) δ [ppm]: 1.38 (s, 81H, CH₃); ¹H NMR (400.13 MHz, C₆D₆, 26 °C) δ [ppm]: 3.61 (m, 4H CH₂, thf), 1.77 (m, 4H, CH₂, thf), 1.56 (s, 81H, C(CH₃)₃). ¹³C NMR (100.62 MHz, thf-*d*₈, 26 °C) δ [ppm]: 72.57 (*C*(CH₃)₃), 32.24 (*C*(CH₃)₃). Elemental analysis calculated for: C₄₀H₈₉CeClO₁₃Si₃ [%]: C: 46.29, H: 8.64; found: C 46.29, H 8.71. Evans (thf-*d*₈): $\chi_{mol} = 5.95 \cdot 10^{-4}$ emu·mol⁻¹, $\chi_{mol} \cdot T = 0.18$ emu·K·mol⁻¹, $\mu_{eff} = 1.19 \mu_B$, $\Delta_{shift} = 0.57$ Hz, c = 9.54·10⁻⁶ mol/mL.

Synthesis of [Ce{OSi(OtBu)₃}₃(OMe)(thf)₂] (4^{OMe}): [Ce{OSi(OtBu)₃}₃Cl(thf)] (**3**) (40 mg, 3.85·10⁻⁵ mol) was dissolved in 2 mL of Et₂O. Under stirring KOMe (2.7 mg, 3.85·10⁻⁵ mol) was added in 1.5 mL of Et₂O, while a slightly yellow solution was obtained which was stirred for another hour. Filtration and evaporation of the solvent left a yellow powder, which was extracted with *n*-pentane to yield the yellow-green product (36.4 mg, 3.78·10⁻⁵ mol, 98%). Crystallization from a concentrated solution in thf gave yellow-green crystals of **4**^{OMe} suitable for X-ray diffraction analysis. ¹H NMR (400.13 MHz, thf-*d*₈, 26 °C) δ [ppm]: 4.31 (s, 3H, [OCH₃]), 3.62 (s, 4H, *CH*₂, thf), 1.77 (s, 4H, *CH*₂, thf), 1.36 (s, 81H, [OSi(C(*CH*₃)₃)₃]).). ¹³C NMR (100.62 MHz, thf-*d*₈, 26 °C) δ [ppm]: 72.57 (*C*(CH₃)₃), 32.24 (C(*C*H₃)₃). Elemental analysis calculated for [Ce[OSi(OtBu)₃]₃(OMe)] C₃₇H₈₄CeO₁₃Si₃, considering complete loss of thf during the work-up in *n*-pentane: C 46.22, H 8.81; found: C 44.70, H 8.11. . Evans (thf-*d*₈): $\chi_{mol} = 6.84 \cdot 10^{-4}$ emu·mol⁻¹, χ_{mol} ·T = 0.20 emu·K·mol⁻¹, $\mu_{eff} = 1.22 \mu_{B}$, $\Delta_{Shift} = 1.88$ Hz, c = 2.06·10⁻⁵ mol/mL.

Synthesis of [Ce{OSi(OtBu)₃}₃(OtBu)(thf)] (4^{OtBu}): [Ce[OSiOtBu₃]₃Cl(thf)] (40 mg, $3.85 \cdot 10^{-5}$ mol) was dissolved in 2 mL of Et₂O. Under stirring KOtBu (4.4 mg, $3.85 \cdot 10^{-5}$ mol) was added in 1.5 mL of Et₂O, while a slightly yellow solution was obtained which was stirred for another hour. Filtration and evaporation of the solvent left a yellow powder, which was extracted with *n*-pentane to yield the yellow-green product (35.5 mg, $3.25 \cdot 10^{-5}$ mol, 84%). Yellow-green crystals of **4**^{OtBu} could been grown from a concentrated solution in toluene. ¹H NMR (400.13 MHz, C₆D₆, 26 °C) δ [ppm]: 3.85 (s, 4H, CH₂, thf), 1.57 and 1.56 (2x s, 81H, [OSi(C(CH₃)₃)₃]), 1.52 (s, 4H, CH₂, thf), 1.49 (s, 9H, [OC(CH₃)₃]).]). ¹³C NMR (100.62 MHz, C₆D₆, 26 °C) δ [ppm]: 72.95 ([OSi(C(CH₃)₃)₃]), 68.76 (CH₂, thf), 33.29 ([OC(CH₃)₃]), 32.10 ([OSi(C(CH₃)₃)₃])) 25.72 (CH₂, thf). Elemental analysis calculated for [Ce[OSiOtBu₃]₃(OtBu)(thf)] C₄₄H₉₈CeO₁₄Si₃: C 49.13, H 9.18; found C: 48.81, H 8.58. Evans (C₆D₆): $\chi_{mol} = 6.84 \cdot 10^{-4}$ emu·mol⁻¹, χ_{mol} ·T = 0.20 emu·K·mol⁻¹, $\mu_{eff} = 1.28 \mu_B$, $\Delta_{Shift} = 2.84$ Hz, c = 1.84 $\cdot 10^{-5}$ mol/mL.Elemental analysis calculated for [Ce[OSiOtBu₃]₃(OtBu)(thf)] C₄₄H₉₈CeO₁₄Si₃: C 49.13, H 9.18; found C: 48.81, H 8.58.

NMR-scale reactions of [Ce{OSi(OtBu)₃}₃Cl(thf)] (3) with ZnMe₂. 1 equiv. ZnMe₂: A solution of ZnMe₂ (2.4 mg, 2.40·10⁻² mmol, in C₆D₆ 0.1 mL) was injected to **3** (25 mg, 2.40·10⁻² mmol) overlaid with C₆D₆ (0.4 mL). 2 equiv. ZnMe₂: as aforementioned but involving ZnMe₂ (4.8 mg, 4.80·10⁻² mmol in C₆D₆ 0.2 mL). Exs. ZnMe₂: as aforementioned but involving two drops of ZnMe₂ (~26.6 mg, 2.65·10⁻¹ mmol). Strong shaking of each reaction ensured rapid mixing after injection of the methylation agent.

Reaction of [Ce{OSi(OtBu)₃}₃Cl(thf)] (3) with one equiv. of ZnMe₂: A solution of ZnMe₂ (7.4 mg, 7.70·10⁻² mmol) in *n*-hexane (1.5 mL) was added quickly and dropwise to a slurry of **3** (80 mg, 7.70·10⁻² mmol) in *n*-hexane (1.5 mL) which was stirred for 2 h. Evaporation to dryness and crystallization at -40 °C from a saturated solution in SiMe₄ afforded colourless crystals of ClZn[μ -OSi(OtBu)₃]₃Ce[OSi(OtBu)₃] (**5**^{Cl}, 34 mg, 2.63·10⁻² mmol, 34%) suitable for X-ray diffraction analysis (Figure S33). The supernatant was filtered and further crystallization at -40 °C gave another batch

of colourless single crystals identified as $MeZn[\mu-OSi(OtBu)_3]_2Ce[OSi(OtBu)_3]_2$ (5^{Me}) by X-ray diffraction analysis. Crude product: ¹H NMR (400.13 MHz, C₆D₆, 26 °C) δ [ppm]: 5.32 (br) 4.66 (br, 5^{Me}, CH₃), 3.46 (br), 1.44 (br), 1.01 (br, 5^{Me}, C(CH₃)₃), -0.05 (s), -0.76 (br), -3.30, -4.78 (Figure S 11, top).

Reaction of [Ce{OSi(OtBu)₃}₃Cl(thf)] (3) with ½ equiv. of ZnMe₂: applying the synthesis procedure described above, ZnMe₂ (3.7 mg, 3.85·10⁻² mmol) and **3** (80 mg, 7.70·10⁻² mmol), resulted in a colourless substance after evaporation of the solvent. Colorless single crystals of [Ce{OSi(OtBu)₃}Cl(thf)₄] (**6**) suitable for X-ray diffraction analysis were grown at -40 °C from a saturated solution in thf (Figure S34). Colorless single crystals of the dimeric (thf) adduct [Ce{OSi(OtBu)₃}Cl(thf)]₂ (**7**) suitable for X-ray diffraction analysis were grown at -40 °C from a saturated solution in *n*hexane (Figure S35). Cell data of [Ce{OSi(O^tBu)₂}Cl(thf)]₂ (**7**): a = 30.48, b = 10.07, c = 34.85, α = 90°, β = 104.66°, γ = 90°.

Synthesis of MeZn[μ -OSi(OtBu)₃]₂Ce[OSi(OtBu)₃]₂ (5^{Me}) from [Ce{OSi(OtBu)₃}₄] (2): A solution of ZnMe₂ (6.7 mg, 6.70·10⁻² mmol) in *n*-hexane (1.5 mL) was added dropwise to a solution of 2 (80 mg, 6.70·10⁻² mmol) in *n*-hexane (1.5 mL). Evaporation to dryness in vacuum resulted quantitatively in 5^{Me} (84 mg, 6.59·10⁻² mmol, 98%). Colourless single crystals of (5^{Me}) were grown at -40 °C from a saturated solution in *n*-hexane. ¹H NMR (400.13 MHz, C₆D₆, 26 °C) δ [ppm]: 4.65 (s, 3H, CH₃), 1.01 (s, 108H, C(CH₃)₃). Elemental analysis calculated for: C₄₉H₁₁₁CeO₁₉Si₄Zn [%]: C 46.19, H 8.78; C 46.56, H 8.88.

2. NMR Spectra

(* solvent; # minor impurities)



Figure S1. ¹H NMR spectrum (400.13 MHz, thf- d_8 , 26 °C) of [Ce{OSi(OtBu)₃}₃]₂ (**1**).



Figure S2. ¹H NMR spectrum (400.13 MHz, thf- d_8 , 26 °C) of Ce[OSi(OtBu)₃]₃(thf)₂ (1a).



Figure S3. ¹H NMR spectrum (400.13 MHz, C_6D_6 , 26 °C) of Ce[OSi(OtBu)₃]₄ (**2**).



Figure S4. ¹H NMR spectrum (400.13 MHz, thf- d_8 , 26 °C) of Ce[OSi(OtBu)₃]₄ (**2**). Shows minor impurities of HOSi(OtBu)₃ (#).



Figure S5. ¹H NMR spectrum (400.13 MHz, thf- d_8 , 26 °C) of Ce[OSi(OtBu)₃]₃Cl(thf) (**3**). Shows minor impurities of HOSi(OtBu)₃ (#).



Figure S6. ¹H NMR spectrum (400.13 MHz, C₆D₆, 26 °C) of Ce[OSi(OtBu)₃]₃Cl (thf) (**3**), recorded 30 min upon dissolvation. Emerging Ce{OSi(OtBu)₃}₄ (**2**) resonates at δ =1.57 ppm.



Figure S7. ¹H NMR spectra (400.13 MHz, C_6D_6 , 26 °C) of decomposing Ce[OSi(OtBu)₃]₃Cl(thf) (**3**). Black: recorded at ~24 h after dissolvation; red: 5 days after dissolvation; green: 15 days after dissolvation; blue: 29 days after dissolvation.



Figure S8. ¹H NMR spectrum (400.13 MHz, thf- d_{g_r} 26 °C) of Ce[OSi(OtBu)₃]₃(OMe)(thf)₂ (**4**^{OMe}).



Figure S9. ¹H NMR spectrum (400.13 MHz, C_6D_6 , 26 °C) of $Ce[OSi(OtBu)_3]_3(OtBu)(thf)$ (**4**^{0tBu}).



Figure S10. ¹H NMR spectrum (400.13 MHz, C₆D₆, 26 °C) of MeZn[μ -OSi(OtBu)₃]₂Ce[OSi(OtBu)₃]₂ (**5**^{Me}). *n*-exane (#) is contained as a minor impurity.



Figure S11. ¹H NMR spectra (400.13 MHz, C_6D_6 , 26 °C) of the NMR-scale reaction of Ce{OSi(OtBu)₃}₃Cl(thf) (**3**) with 1 equiv. of ZnMe₂ (bottom) and of the filtrated and solvent-evaporated crude reaction product (top). ***1**: presumably intermediate I; ***2**: **5**^{Me}; ***3**: C₂H₆.



Figure S12. ¹H NMR spectra (400.13 MHz, C_6D_6 , 26 °C). From bottom to top: NMR-scale reaction of Ce{OSi(OtBu)₃}₃Cl(thf) (**3**) with 1 equiv. of ZnMe₂ (bottom); + 1 equiv. ZnMe₂; + exs. ZnMe₂ (~10 equiv.); the filtrated and solvent-evaporated crude reaction product obtained after reacting for ~3d in the NMR tube (blue trace); MeZn[OSi(OtBu)₃] (green trace). ***1**: presumably intermediate **5**, ***2**: MeZn[OSi(OtBu)₃], ***3**: **5**^{Me}, ***4**: C₂H₆, ***5**: ZnMe₂, #: minor impurities of toluene.



Figure S13. Comparison of ¹H NMR spectra (400.13 MHz, C_6D_6 , 26 °C): crude reaction product from Ce{OSi(OtBu)₃}₃Cl(thf) (**3**) and 1 equiv. of ZnMe₂ (black trace); from crude reaction product crystallized substance which was characterized as ClZn[μ -OSi(OtBu)₃]₂Ce[OSi(OtBu)₃]₂ (**5**^{Cl}, 1st crop (blue trace)); from crude reaction product crystallized substance which was characterized as MeZn[μ -OSi(OtBu)₃]₂Ce[OSi(OtBu)₃]₂ (**5**^{Me}, 2nd crop (red trace)); pure MeZn[μ -OSi(OtBu)₃]₂Ce[OSi(OtBu)₃]₂ (**5**^{Me}, green trace).

Signal labeling: ***1**: Zn-Me; ***2**: OtBu(**5**^{Me}); ***3**: presumably intermediate **5**; ***4**: OtBu(**5**^{CI}); #: Impurities of SiMe₄.



Figure S14. ¹H NMR spectrum (400.13 MHz, thf- d_8 , 26 °C) of [Ce{OSi(OtBu)₂}Cl(thf)]₂ (7) with minor impurities.



Figure S15. Comparison of ¹H NMR spectra (400.13 MHz, thf- d_8 , 26 °C): crude product from the reaction of Ce{OSi(OtBu)₃}₃Cl(thf) (**3**) with 1 equiv. of ZnMe₂ (black); [Ce{OSi(OtBu)₃}₂Cl(thf)]₂ (**7**) (blue); [MeZn{OSi(OtBu)₃}]₂ (green).



Figure S16. ¹³C NMR spectrum (100.06 MHz, 900 scans, C_6D_6 , 26 °C) of Ce[OSi(OtBu)₃]₄ (2).



Figure S17. ¹³C NMR spectrum (100.06 MHz, 900 scans, thf-*d8*, 26 °C) of Ce[OSi(O*t*Bu)₃]₃Cl(thf) (**3**).



Figure S18. ¹³C NMR spectrum (100.06 MHz, 2000 scans, thf-*d8*, 26 °C) of Ce[OSi(O*t*Bu)₃]₃(OMe)(thf)₂ (**4**^{OMe}).



Figure S19. HSQC NMR spectrum (60 scans, thf-d8, 26 °C) of Ce[OSi(OtBu)₃]₃(OMe)(thf)₂ (**4**^{OMe}).



Figure S20. ¹³C NMR spectrum (100.06 MHz, 900 scans, thf-*d8*, 26 °C) of Ce[OSi(OtBu)₃]₃(OtBu)(thf) (**4**^{OtBu}).

3. UV/Vis Spectra



Figure S21. UV/Vis spectra of compounds [Ce{OSi(OtBu)₃}] (2) (blue; c = $1.42 \cdot 10^{-4}$ mol L⁻¹; ε_{281} = 5141 L mol⁻¹ cm⁻¹, ε_{258} = 4824 L mol⁻¹ cm⁻¹), [Ce{OSi(OtBu)₃}Cl(thf)] (3) (black; c = $1.59 \cdot 10^{-4}$ mol L⁻¹; ε_{296} = 4628 L mol⁻¹ cm⁻¹, ε_{260} = 4752 L mol⁻¹ cm⁻¹, ε_{231} = 4739 L mol⁻¹ cm⁻¹), [Ce{OSi(OtBu)₃}(O^tBu)(thf)] (4^{OtBu}) (red; c = $8.11 \cdot 10^{-5}$ mol L⁻¹; ε_{278} = 6853 L mol⁻¹ cm⁻¹) measured in dichloromethane and [Ce{OSi(OtBu)₃}(OtBu)₃}(OMe)(thf)] (4^{OMe}) (green; c = $7.39 \cdot 10^{-5}$ mol L⁻¹; ε_{284} = 6551 L mol⁻¹ cm⁻¹) measured in tetrahydrofurane.

4. DRIFT Spectra



Figure S22. DRIFT spectrum of compound 1.



Figure S23. DRIFT spectrum of compound 1a.



Figure S24. DRIFT spectrum of compound 2.



Figure S25. DRIFT spectrum of compound **3**.



Figure S26. DRIFT spectrum of compound **4**^{OMe}.



Figure S27. DRIFT spectrum of compound **4**⁰*r*Bu.



Figure S28. DRIFT spectrum of compound **5**^{Me}.



Figure S29. DRIFT spectrum of compound **6**.

5. X-Ray Crystallography and Crystal Structure Determinations

Suitable single crystals for X-ray structure analyses were selected in a glovebox and coated with Paratone-N HR2-643 and fixed on a nylon loop fibre. Data for compounds **1**, **1a-thf**, **2**, **3-thf**, **4**^{OMe}, **5**^{Cl}, **6** and **7** were collected on a Bruker APEX DUO instrument equipped with an I μ S microfocus sealed tube and QUAZAR optics for Mo_{Ka} radiation ($\lambda = 0.71073 \text{ Å}$). The data collection strategy was determined using COSMO⁵ employing ω - and φ scans. Raw data were processed using APEX^{6,7} and SAINT,^{8,9} corrections for absorption effects were applied using SADABS.^{10,11} Data for compound **5**^{Me} was collected on a Bruker SMART APEX II instrument equipped with a fine focus sealed tube and curved graphite monochromator using Mo_{Ka} radiation ($\lambda = 0.71073 \text{ Å}$). The data collection strategy was determined using COSMO⁵ employing ω - and φ scans. Raw data were processed using APEX^{6,7} and SAINT,^{8,9} corrections for absorption effects were applied using scale tube and curved graphite monochromator using Mo_{Ka} radiation ($\lambda = 0.71073 \text{ Å}$). The data collection strategy was determined using COSMO⁵ employing ω - and φ scans. Raw data were processed using APEX^{6,7} and SAINT,^{8,9} corrections for absorption effects were applied using Sadabs.^{10,11} The structures were solved by direct methods (SHELXS-1997/2013)¹² and refined against all data by full-matrix least-squares methods on F2 (SHELXL-1997/2014).¹³ All graphics were produced employing ORTEP-3¹⁴ and POV-Ray.¹⁵ Further details of the refinement and crystallographic data are listed in Tables S1, S2, and S3 and in the CIF files. CCDC (**1**), (**1**a), (**2**), (**3-thf**), (**4**^{OMe}), (**5**^{Cl}), (**5**^{Me}), (**6**), and (**7**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

	1	1a-thf	2	3-thf
CCDC	1567496	1567503	1567498	1567499
Empirical formula	$C_{72}H_{162}Ce_2O_{24}Si_6$	C ₅₆ H ₁₂₁ CeO ₁₇ Si ₃	C ₄₈ H ₁₀₈ CeO ₁₆ Si ₄	C ₄₆ H ₁₀₁ CeClO _{14.5} Si ₃
M _w [g mol ⁻¹]	1860.79	1290.91	1193.82	1146.10
T [K]	100(2)	100(2)	200(2)	173(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C 2/c	P 2 ₁ /n	C 2/c	Cc
a [Å]	26.0279(10)	16.6416(9)	24.1857(6)	24.8822(13)
b [Å]	14.1706(5)	22.8253(13)	13.5705(3)	14.2617(8)
c [Å]	27.3540(10)	18.8236(10)	41.0143(10)	38.922(2)
α [°]	90	90	90	90
β[°]	97.351(2)	92.368(3)	96.5530(10)	107.3820(10)
γ [°]	90	90	90	90
Volume [ų]	10006.1(6)	7144.0(7)	13373.4(6)	13181.1(12)
Z	4	4	8	8
density (calculated) ρ [mg mm ⁻³]	1.235	1.200	1.186	1.155
Absorption coefficient $\mu \text{ [mm}^{-1}$]	1.030	0.745	0.806	0.836
R1 (obs) ^[a]	0.0453	0.0357	0.0403	0.0371
wR2 (all) ^[b]	0.0895	0.0896	0.0830	0.0883
Diffractometer	Bruker APEX DUO	Bruker APEX DUO	Bruker APEX DUO	Bruker APEX DUO

Table S1. Crystallographic data for compounds 1, 1a-thf, 2 and 3-thf

	۵ ^{OMe}	5 ^{CI}	5 ^{Me}
Empirical formula	$C_{45}H_{100}CeSi_{3}O_{15}x\frac{1}{2}(OC_{4}H_{8})$	C ₄₈ H ₁₀₈ CeClO ₁₆ Si ₄ Zn	C ₅₃ H ₁₂₃ CeO ₁₆ Si ₅ Zn
CCDC	1567501	1567497	1567502
$M_w[g mol^{-1}]$	1141.69	1294.64	1362.45
T [K]	103(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	P21/c	C 2/c
a [Å]	46.814(3)	13.237(2)	19.3644(15)
b [Å]	13.9872(9)	20.065(4)	20.0689(16)
c [Å]	19.1160(12)	28.704(5)	20.9286(18)
α [°]	90	90	90
β[°]	99.748(2)	90.639(10)	111.894(3)
γ [°]	90	90	90
Volume [Å ³]	12336.3(14)	7623(2)	7546.7(11)
Z	8	4	4
density (calculated) ρ [mg mm ⁻³]	1.229	1.128	1.199
Absorption coefficient μ [mm ⁻¹]	0.852	1.050	1.045
R1 (obs) ^[a]	0.0296	0.0557	0.0279
wR2 (all) ^[b]	0.0712	0.0983	0.0665
Diffractometer	Bruker APEX DUO	Bruker APEX DUO	Bruker APEX II DUO

Table S2. Crystallographic data for compounds ${\bf 4^{OMe}, 5^{Cl}}$ and ${\bf 5^{Me}}$

	6	7
Empirical formula	$C_{44}H_{94}CeClO_{13}Si_2$	$C_{56}H_{124}Ce_2Cl_2O_{18}Si_4$
CCDC	1567500	
$M_w[g mol^{-1}]$	1062.94	1549.04
T [K]	173(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	P 2/c	P2 ₁ /n
a [Å]	16.545(3)	19.923(7)
b [Å]	9.2664(15)	9.999(3)
c [Å]	20.324(3)	25.750(7)
α [°]	90	90
β[°]	115.236(10)	97.929(5)
γ [°]	90	90
Volume [ų]	2818.5(8)	5081(3)
Z	2	2
density (calculated) ρ	1.252	1.013
[mg mm ⁻³]		
Absorption coefficient	0.950	1.027
μ [mm ⁻¹]		
R1 (obs) ^[a]	0.0348	*
wR2 (all) ^[b]	0.0824	-
Diffractometer	Bruker APEX DUO	Bruker APEX DUO

Table S3. Crystallographic data for compounds 6 and 7

*Connectivity only.

^[a] Final R indices [I>2sigma(I)]; ^[b] R indices (all data)

Selected interatomic distances [Å] and angles [°] of complexes shown in Figures 1 and 2:

2: Ce1–O1 2.103(2), Ce1–O5 2.089(2), Ce1–O9 2.157(2), Ce1–O11 2.593(2), Ce1–O13 2.090(2), Si1–O1 1.617(2), Si2–O5 1.603(2), Si3–O9 1.604(2), Si3–O11 1.660(2), Si4–O13 1.614(2); Ce1–O1–Si1 170.7(1), Ce1–O5–Si2 155.6(1), Ce1–O9–Si3 111.03(9), Ce1–O11–Si3 91.57(7), Ce1–O13–Si4 170.7(1), O1–Ce1–O5 102.70(7), O1–Ce1–O13 112.82(7), O5–Ce1–O13 103.08(8) O1–Ce1–O9 122.98(7), O5–Ce1–O9 93.64(7), O9–Ce1–O13 115.83(7).

3: Ce1–O1 2.108(3), Ce1–O5 2.102(3), Ce1–O9 2.096(4), Ce1–O13 2.495(4), Ce1–O14 2.533(5), Ce2–O101 2.096(4), Ce2–O105 2.121(3), Ce2–O109 2.103(4), Ce1–Cl1 2.670(2), Ce2–Cl5 2.656(2), Si1–O1 1.596(4), Si2–O5 1.615(4), Si3–O9 1.612(4); Ce1–O1–Si1 165.1(3), Ce1–O5–Si2 170.6(3), Ce1–O9–Si3 172.7(2), O5–Ce1–Cl1 157.9 (1), O1–Ce1–O13 163.7(2), O9–Ce1–O14 165.2(2).

4^{OMe}: Ce1–O1 2.155(1), Ce1–O5 2.138(1), Ce1–O9 2.136(1), Ce1–O13 2.094(1), Ce1–O14 2.521(1), Ce1–O15 2.518(1), Si1–O1 1.604(1), Si2–O5 1.603(1), Si3–O9 1.604(1); Ce1–O1–Si1 163.61(8), Ce1–O5–Si2 154.28(8), Ce1–O9–Si3 169.23(8), O1–Ce1–O13 155.93(5), O5–Ce1–O14 163.32(5), O9–Ce1–O15 169.34(5).

5^{Me}: Ce1–O1 2.479(1), Ce1–O2 2.682(1), Ce1–O5 2.224(1), Zn1–O1 1.933(1), Zn1–C25 1.942(3), Si1–O1 1.602(1), Si1–O2 1.658(1), Si2–O5 1.593(1); O1–Ce1–O5 109.49(5), O1–Ce1–O5' 119.36(5), O1–Ce1–O1' 64.02(6), O5–Ce1–O5' 121.86(7), O1–Zn1–O1' 85.64(8), O1–Zn1–C25 137.18(4), Ce1–O1–Zn1 105.17(5).

6. Drawings of Molecular Structures



Figure S30. ORTEP representation of the molecular structure of $[Ce{\mu-OSi(OtBu)_3}OSi(OtBu)_3]_2]_2$ (1) with atomic displacement ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ce1–O1 2.202(3), Ce1–O5 2.532(2), Ce1–O5' 2.396(2), Ce1–O9 2.186(3), Ce1–O8 2.539(3), O1–Si1 1.602(3), O5–Si2 1.616(3), O9–Si3 1.595(3), Ce1–O1–Si1 164.1(2), Ce1–O5–Si2 101.9(1), Ce1–O9–Si3 171.5(2), Ce1–O5'–Si2' 148.1(1).



Figure S31. ORTEP representation of the molecular structure of $Ce[OSi(OtBu)_3]_3(thf)_3$ (**1a-thf**) with atomic displacement ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ce1–O1 2.243(2), Ce1–O5 2.246(2), Ce1–O9 2.249(2), Ce1–O13 2.603(2), Ce1–O14 2.578(2), Ce1–O15 2.594(2), O1–Si1 1.587(2), O5–Si2 1.582(2), O9–Si3 1.584(2), Ce1–O1–Si1 159.2(1), Ce1–O5–Si2 168.4(1), Ce1–O9–Si3 157.2(1), O1–Ce1–O13 153.96(6), O5–Ce1–O14 155.50(6), O9–Ce1–O15 159.61(6).¹⁶



Figure S32. ORTEP representation of the asymmetric unit of $Ce[OSi(OtBu)_3]_3Cl(thf)_2$ (3) with atomic displacement ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity.



Figure S33. ORTEP representation of the molecular structure of $CIZn[\mu-OSi(OtBu)_3]_3Ce[OSi(OtBu)_3]$ (5^{Cl}) with atomic displacement ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ce1–O1 2.233(4), Ce1–O5 2.636(4), Ce1–O9 2.469(4), Ce1–O10 2.201(4), Ce1–O14 2.492(3), Ce1–O15 2.624(3), Zn1–O9 1.953(4), Zn1–O14 1.961(4), Zn1–O12 2.131(3), Zn1–Cl1 2.1712(17), O1–Si1 1.599(4), O9–Si2 1.585(4), O5–Si2 1.675(4), O10–Si3 1.576(4), O12–Si3 1.691(4), O14–Si4 1.592(4), O15–Si4 1.672(4), O1–Ce1–O9 148.1(1), O1–Ce1–O10 99.9(1), O1–Ce1–O14 142.9(1), Ce1–O9–Zn1 96.9(1), Ce1–O14–Zn1 95.9(1), O9–Zn1–Cl1 116.3(1), O12–Zn1–Cl1 118.9(1), O14–Zn1–Cl1 116.5(1), O12–Zn1–O9 104.0(1), O12–Zn1–O14 105.7(1).



Figure S34. ORTEP representation of the molecular structure of Ce[OSi(OtBu)₃]₂Cl(thf)₄] (**6**) with atomic displacement ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ce1–O1 2.262(5), Ce1–O5 2.561(9), Ce1–O6 2.578(3), Ce1–Cl1 2.784(4), O1–Si1 1.584(2).



Figure S35. Connectivity structure of $[Ce{OSi(OtBu)_3}_2Cl(thf)]_2$ (7); hydrogen atoms are omitted for clarity. Data for the connectivity measurement of 7: $C_{56}H_{124}Ce_2Cl_2O_{18}Si_4$, M = 1549.04 g·mol⁻¹, monoclinic, a = 19.923(7), b = 9.999(3), c = 25.750(7) Å, β = 97.929(5)°, V = 5081(3) Å³, Z = 2, T = 100(2) K, space group P2₁/n, R1 (obs).

7. Literature

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