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A homoleptic tetravalent cerium silylamide

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Treatment of Ce[N(SiHMe₂)₂]₃(thf)₂ with chlorinating agents PhICl₂, Ph₃CCl or C₂Cl₆ gave the homoleptic Ce(IV) silylamide Ce[N(SiHMe₂)₂]₄. When performed in the absence of donating (solvent) molecules, the trivalent cluster ¹⁰ Ce₅[N(SiHMe₂)₂]₈Cl₇ was isolated.

Silylamido groups are a well established ligand set in many s-, dand f-block metal complexes, first and foremost the ubiquitous monovalent hexamethyldisilazide N(SiMe₃)₂.¹ Less frequently, 15 but increasingly employed is the tetramethyl derivative N(SiHMe₂)₂ featuring the Si-H moiety as a spectroscopic probe and revealing superior reactivity in sterically demanding ligand exchange reactions.² Particularly, the trivalent rare-earth metal derivatives, Ln[N(SiHMe₂)₂]₃(thf)_x (Ln=Sc: x=1, Ln=Y, La-Lu: x $_{20}$ = 2) emerged as prominent synthesis precursors according to amine and amide elimination protocols.^{3,4} Although only a few heteroleptic tetravalent cerium amide complexes have been reported,5-9 including Lappert's Ce[N(SiMe₃)₂]₃Cl,^{7a} silylamide ligands seem to provide a stabilising environment for Ce(IV) 25 centres. Strikingly, Lappert et al. also described the X-ray structure analysis of the only homoleptic Ce(IV) amide complex, Ce(NCy₂)₄.¹⁰ The black bis(cyclohexyl)amido complex was obtained by air oxidation/redistribution of the corresponding Ce(III) complexes. In this report, we wish to illustrate the 30 synthesis of the homoleptic Ce(IV) silvlamide complex Ce[N(SiHMe₂)₂]₄ as well as the isolation of the trivalent complex $Ce_5[N(SiHMe_2)_2]_8Cl_7.$



Scheme 1 Synthesis of compounds 2 and 3 by reaction of $Ce[N(SiHMe_2)_2]_3(thf)_x$ (1: x = 2; 1a: x = 0) at ambient temperature in i) THF and ii) toluene.

Based on the successful synthesis of black tetravalent $_{40}$ (C₅H₅)₃CeCl, utilizing PhI(III)Cl₂ as the oxidant for Ce(C₅H₅)₃, ¹¹ we now treated Ce[N(SiHMe₂)₂]₃(thf)₂ (1) with 0.5 equivalents of the same chlorinating agent in THF at ambient temperature

⁵⁵ expected for N(SiHMe₂)₂ (Figure S2, ESI), whereas the ²⁹Si NMR spectrum ($\delta = -23.25$ ppm, ¹J_{SiH} = 167.73 Hz) points to the presence of very weak secondary Ce(IV)---SiH interactions in solution.³ However, CHN elemental analysis of **2** was not in agreement with the envisaged chlorinated reaction product ⁶⁰ Ce[N(SiHMe₂)₂]₃Cl and so an X-ray diffraction study was warranted.

Surprisingly, the homoleptic compound Ce[N(SiHMe₂)₂]₄ (2) was revealed[‡] (Fig. 1). The molecular structure shows a Ce(IV) centre adopting a distorted tetrahedral geometry with N-Ce-N ⁶⁵ angles in the range from 98.35(4)° to 116.33(4)° placing 2 in the middle of known redox-stable complexes Hf[N(SiHMe₂)₂]₄ (102°-105°)¹² and U[N(SiHMe₂)₂]₄ (99°-126°).¹³



Fig. 1 Molecular structure of 2 (ellipsoids set to 50%). All hydrogen 70 atoms except Si-H have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Ce(1)-N(1) 2.2438(11), Ce(1)-N(2) 2.2378(11), Ce(1)-N(3) 2.2488(11), Ce(1)-N(4) 2.2574(11), Ce(1)--Si(1) 3.2297(4), Ce(1)---Si(2) 3.4773(4), Ce(1)---Si(3) 3.6245(4), Ce(1)---Si(4) 3.1814(4), Ce(1)---Si(5) 3.1714(4), Ce(1)---Si(6) 3.5234(4), Ce(1)---Si(7)

⁽Scheme 1, i). An instant reaction was indicated by a colour change from pale yellow to deep red. Removal of the solvent ⁴⁵ produced an oily residue. Upon concentrating a hexane solution of this residue and cooling to -35 °C dark red crystals were produced. DRIFT spectroscopy of these crystals revealed the presence of the bis(dimethylsilyl)amido ligand in distinct environments. This can be derived from two well-resolved peaks ⁵⁰ for the Si-H stretching vibrations at 2100 and 2010 cm⁻¹, the latter being indicative of significant Ce(IV)---SiH β-agostic interactions in the solid state (Figure S1, ESI). ¹H NMR spectroscopy of this compound 2, in [D₆]benzene, showed a doublet at 0.34 and a septet at 6.01 ppm with a ratio of 6:1 as

3.5524(4), Ce(1)---Si(8) 3.1919(4), Ce(1)-N(1)-Si(1) 108.68(5), Ce(1)-N(1)-Si(2) 122.41(6), Ce(1)-N(2)-Si(3) 125.73(6), Ce(1)-N(2)-Si(4) 106.60(5), Ce(1)-N(3)-Si(5) 105.64(5), Ce(1)-N(3)-Si(6) 124.74(6), Ce(1)-N(4)-Si(7) 126.08(6), Ce(1)-N(4)-Si(8) 106.23(5), N(1)-Ce(1)-N(2) 5 113.89(4), N(1)-Ce(1)-N(3) 99.47(4), N(1)-Ce(1)-N(4) 116.33(4), N(2)-Ce(1)-N(3) 114.03(4), N(2)-Ce(1)-N(4) 98.35(4),), N(3)-Ce(1)-N(4) 115.70(4).

The average Ce-N bond length for 2 is 2.247 Å comparing similarly to other known tetravalent silylamide complexes 10 (Ce[N(SiMe₃)₂]₃Cl: 2.217 Å,^{7a} Ce(NHC)[N(SiMe₃)₂]₂Cl: 2.258 $Å^8$ and $\{Ce[N(SiMe_3)_2]_2(\mu-O)\}_2$ 2.245 Å)⁹ as well as to $Ce(NCy_2)_4$ (2.242 Å).¹⁰ For further comparison, trivalent $[Na(thf)_4(Et_2O)][Ce{N(SiMe_3)_2}_4]$, which features the only other structurally authenticated cerium tetrakis silylamide, exhibits ¹⁵ Ce(III)-N bond lengths in the range from 2.434(6) to 2.448(6) Å.¹⁴ The Ce(IV) ion in 2 appears to be coordinatively saturated due to the absence of donating THF in the structure despite it being used as the reaction solvent. Ce(IV)---SiH β-agostic interactions exclude THF donation (also seen for Sm(II))¹⁵ with 20 SiH bonds from each silvlamide ligand contributing to the coordination sphere. Ce---H contacts range from 2.81 Å-3.53 Å

(av. 3.08 Å) (av. 3.076 Å) and Ce---Si av. 3.170 Å. When sounding out less laborious chlorinating reagents, we found that Ph₃CCl and C₂Cl₆ produce compound 2 as well and in 25 better yields (PhICl₂ oxidation: crystallized yield 20%). While trityl chloride was previously shown to quantitatively convert $Ce[N(SiMe_3)_2]_3$ into $Ce[N(SiMe_3)_2]_3Cl_3^8$ hexachloroethane was mainly used for preparing CeCl₃(thf)₂ from metal powder.¹⁶ Although the Ce[N(SiHMe₂)₂]₃(thf)₂/C₂Cl₆ reaction, producing $_{30}$ C₂Cl₄ as the major product proceeds at a slower rate (crystallized yield 45%) than the Ph₃CCl-based one (60% yield calculated on the basis of NMR data, cf., Figure S3, ESI), product separation via crystallization is more straightforward.

- Interested in the role THF played in the oxidation of 1, the 35 reaction was repeated using donor-free starting material $[Ce{N(SiHMe_2)_2}_3]_2$ (1a) with toluene as the solvent (Scheme 1, ii). A similar colour change was observed as above, however, FTIR spectroscopy of the red residue showed a shift in the SiH peak centred at 2067 $\text{cm}^{\text{-1}}$ with a significantly more detailed $\beta\text{-H}$ ⁴⁰ agostic interaction shoulder. ¹H NMR spectroscopy produced broader peaks indicating the likelihood of a trivalent complex. Cooling a concentrated hexane solution of the residue to -35 °C produced colourless crystals that were used in an X-ray diffraction experiment. Figure 2 shows a representation of the
- ⁴⁵ molecular structure [{Ce[N(SiHMe₂)₂]}₄{Ce[N(SiHMe₂)₂]₂}(μ_2 - $Cl_{2}(\mu_{3}-Cl)_{4}\{\mu_{2}-N(SiHMe_{2})_{2}\}$ (3)§. To our knowledge complex 3 is the first donor-free rare-earth metal(III) complex featuring amido and halo ligands exclusively. It is noteworthy that trivalent cerium complexes and in particular $[Ce{N(SiMe_3)_2}_2(\mu_2 -$ 50 Cl)₂(thf)]₂ occurred as significant reaction products during the
- synthesis of Ce[N(SiMe₃)₂]₃Cl from Ce[N(SiMe₃)₂]₃ and TeCl₄. Compound 3 is a pentanuclear Ce(III) complex with each metal centre adopting a six-coordinate arrangement in a distorted
- octahedral geometry. Two metal coordination environments exist, 55 Ce(1) consists of two terminal amido groups and four (μ_3) chlorine atoms. The second environment, Ce(2) and Ce(3), are each surrounded by a terminal and a μ_2 -amido group. In addition, four chlorine atoms (1 μ_2 Cl(3); 2 μ_3 Cl(1 and 2); 1 μ_4 Cl(4)) bind to each metal centre. The terminal Ce-N bond lengths (av 2.285
- ⁶⁰ Å) are of similar length to the three neodymium-centred chlorosilylamido complex $[{Nd{N(SiHMe_2)_2}(hf)}_2(Nd{N(SiHMe_2)-})$ $_{2}_{2}(\mu_{2}-Cl)_{2}(\mu_{3}-Cl)_{2}\{\mu-N(SiHMe_{2})_{2}\}]$ (A).



As expected the Ce-Cl bond lengths are in the order μ_2 (av $2.957 \text{ Å} < \mu_3$ (av 2.968 Å) $< \mu_4$ (av 3.004 Å). Both SiH moieties belonging to the bridging bis(dimethylsilyl)amido ligands are involved in agostic interactions with short Ce---H contacts (av. 70 2.638 Å). The terminal amido groups exhibit longer metalhydrogen distances with asymmetrical Ce---H contacts averaging 2.786 Å and 3.392 Å, respectively.



Fig. 2 Molecular structure of 3 (ellipsoids set to 50%). All hydrogen and 75 carbon atoms have been omitted for clarity. The molecule has a 2-fold axis (^{\$}) along space diagonal Ce(1)---Cl(4). Selected interatomic distances (Å) and angles (°): Ce(1)-N(1) 2.305(2), Ce(2)-N(2) 2.280(2), Ce(2)-N(3) 2.628(2), Ce(3)-N(3)^{\$} 2.566(2), Ce(3)-N(4) 2.283(2), Ce(1)-Cl(1) 2.9438(4), Ce(1)-Cl(2) 3.1411(5), Ce(2)-Cl(1) 2.9476(4), Ce(2)-Cl(2) ⁸⁰ 2.8729(4), Ce(2)-Cl(3) 2.9129(4), Ce(2)-Cl(4) 2.9410(2), Ce(3)-Cl(1)^{\$}, 2.9185(4), Ce(3)-Cl(2) 2.8729(4), Ce(3)-Cl(3) 2.8483(5), Ce(3)-Cl(4) 3.0550(2), Ce(2)---Ce(3)^s 4.0708(2), Ce(1)---Si(1) 3.2284(6), Ce(2)---Si(3) 3.1570(5), Ce(2)---Si(6) 3.2412(5), Ce(3)---Si(5)^s 3.2472(5), Ce(3)---Si(8) 3.1429(6), Ce(1)-N(1)-Si(1) 106.7(1), Ce(1)-N(1)-Si(2) 117.3(1),

- 85 Ce(2)-N(2)-Si(3) 103.91(8), Ce(2)-N(2)-Si(4) 128.06(8), Ce(2)-N(3)-Si(5) 115.90(7), Ce(2)-N(3)-Si(6) 93.87(6), Ce(3)-N(3)-Si(5) 96.30(7), Ce(3)-N(3)-Si(6) 121.97(7), Ce(3)-N(4)-Si(7) 120.2(1), Ce(3)-N(4)-Si(8) 103.50(9), N(1)-Ce(1)-N(1)^s 96.4(1), N(2)-Ce(2)-N(3) 108.61(5), N(3)^s-Ce(3)-N(4) 115.5(6).
- In summary, the bis(dimethylsilyl)amido ligand facilitates an oxidation/redistribution sequence and the formation of homoleptic Ce[N(SiHMe₂)₂]₄, via reaction of Ce[N(SiHMe₂)₂](thf)₂ with chlorinating reagents. This is in contrast to the generation of heteroleptic complexes 95 Ce[N(SiMe₃)₂]₃X (X = Cl, Br) in the presence of a sterically more demanding silylamido ligand. In the absence of donating solvent molecules (here THF) reduction/redistribution reactions feature prominent side-reactions as shown for the formation of the
- silylamide-chloro $Ce_5[N(SiHMe_2)_2]_8Cl_7.$ Ce(III) complex 100 Unsurprisingly, such donor-free dimethylsilylamide complexes show significant Ce(IV)---SiH β-agostic interactions in the solid state. This work was funded by the University of Bergen (program Nanoscience@UiB) and the Meltzer Foundation. We are grateful to Prof. N. Å. Frøystein for technical assistance with ¹⁰⁵ the ²⁹Si NMR spectroscopy.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Experimental details, NMR and FTIR data presented. See DOI: 10.1039/b000000x/
- ¹⁰ Synthesis of Ce[N(SiHMe₂)₂]₄ **2**: A solution of **1** (0.266 g, 0.390 mmol) in THF (10 ml) was added to a solution of PhICl₂¹⁸ (0.053 g, 0.193 mmol) in THF (2 ml) in one portion in the dark. A colour change from yellow to red was observed immediately. This solution was allowed to stir for 1 hr. The volatiles were removed via vacuum leaving an oily solid. To this,
- 15 hexane (2 ml) was added and upon subsequent cooling to -35 °C dark red crystals suitable for X-ray diffraction were produced (yield 20%). In pure form, **2** can be sublimed at 80 °C/1.2×10⁻⁴ mbar. IR (DRIFT): $v_{max} = 2953$ m, 2900 w, 2102 m, 2009 m, 1942 vw sh, 1419 vw, 1248 s, 1020 s, 939 s, 889 vs, 841 s, 795 s, 768 m, 746 vw, 679 m, 631 w, 586 m, 409 w cm⁻¹.
- ²⁰ ¹H NMR (400 MHz, [D₆]benzene, 20 °C): $\sigma = 0.34$ (d, J = 7.4 Hz, 48H, Si(H)*Me*₂), 6.01 (septet, J = 2.9 Hz, 8H, Si(Me₂)*H*). *Anal.* Calc. for C₁₆H₃₆CeN₄Si₈: C, 28.71; H, 8.43; N, 8.37. Found: C, 28.30; H, 7.88; N, 6.43%.
- Alternative synthesis of Ce[N(SiHMe₂)₂]₄ **2**: A solution of trityl chloride 25 (0.099 g, 0.35 mmol) in toluene (3 ml) was slowly added to a solution of **1** (0.241 g, 0.35 mmol) in toluene (3 ml). A colour change from yellow to red was observed immediately. This solution was allowed to stir for 0.5 hr. The volatiles were removed via vacuum leaving a dark red solid (0.327 g). To this, toluene (0.5 ml) was added and upon subsequent
- 30 cooling to -40 °C dark red crystals of 2 suitable for X-ray diffraction were produced (along with colourless crystals of Gomberg's dimer). Yield calculated from NMR data (based on the Ce-content): 60%.
- Second alternative synthesis of Ce[N(SiHMe₂)₂]₄ **2**: A solution of hexachloroethane (0.174 g, 0.73 mmol) in toluene (5 ml) was slowly ³⁵ added to a solution of **1** (1.001 g, 1.47 mmol) in toluene (5 ml). A colour change from yellow via orange and bright red to dark red occurred within 18 hr, after which the volatiles were removed via vacuum leaving dark
- red sticky crystals (0.954 g). To this, toluene (1.5 ml) was added and upon subsequent cooling to -40 °C dark red crystals of **2** suitable for X-ray 40 diffraction were produced A solution of hexachloroethane (0.045 g, 0.19 mmol) in toluene (2 ml) was slowly added to a solution of **1** (0.257 g,
- 0.38 mmol) in toluene (5 ml). A colour change from yellow via orange and bright red to dark red occurred within 18 hr, after which the volatiles were removed via vacuum leaving dark red sticky crystals (0.240 g). To ⁴⁵ this, toluene (0.5 ml) was added and upon subsequent cooling to -40 °C
- dark red crystals of **2** suitable for X-ray diffraction were produced (yield of two crops combined: 0.116 g, 0.17 mmol, 45%). Synthesis of Ce[N(SiHMe₂)₂]₈Cl₇ **3**: A solution of **1a**¹⁹ (0.488 g, 0.910
- mmol) in toluene (10 ml) was added to a solution of PhICl₂ (0.125 g, so 0.454 mmol) in toluene (2 ml) in one portion in the dark. A colour change from yellow to red was observed immediately. This solution was allowed to stir for 1 hr. The volatiles were removed via vacuum leaving an oily
- solid. To this, hexane (2 ml) was added and upon subsequent cooling to -35 °C colourless crystals suitable for X-ray diffraction were produced 55 (yield 38%). IR (DRIFT): $v_{max} = 2952$ m, 2898 w, 2123 m sh, 2066 m, 2008 m sh, 1959 m sh, 1910 m sh, 1418 w, 1296 w sh, 1254 m, 1057 m
- sh, 1024 m sh, 1008 m sh, 959 m, 893 s, 837 m, 795 m, 769 m, 687 m, 591 m, 565 w, 410 m. ¹H NMR (400 MHz, [D₆]benzene, 20 °C): $\delta = 0.12$, 2.11, 4.71. *Anal.* Calc. for C₃₂H₁₁₂Ce₅Cl₇N₈Si₁₆: C, 19.15; H, 5.63; N, 60 5.59. Found: C, 17.53; H, 4.44; N, 4.57%.
- ⁺Crystal data for **2**: C₁₆H₅₆CeN₄Si₈, M = 669.49, monoclinic, a = 18.3037(9) Å, b = 11.1158(5) Å, c = 18.8563(9) Å, $\beta = 107.559(1)$ °, V = 3657.8(3) Å³, T = 103(2) K, space group $P2_1/c$, Z = 4, 65647 reflections measured, 12241 independent reflections ($R_{int} = 0.0443$). R_1 values = 65 0.0243 ($I > 2\sigma(I)$), wR(F^2) = 0.0662 (all data).
- §Crystal data for **3**: C₃₂H₁₁₂Ce₅Cl₇N₈Si₁₆, M = 2007.49, monoclinic, a = 17.2810(6) Å, b = 25.5225(9) Å, c = 19.8095(7) Å, $\beta = 100.2028(4)^\circ$, V = 8598.9(5) Å³, T = 100(2) K, space group C2/c, Z = 4, 71792 reflections measured, 12787 independent reflections ($R_{int} = 0.0292$). R_I values = 70 0.0210 ($I > 2\sigma(I)$). wR(F^2) values = 0.0549 (all data).

Data collection was done on a Bruker AXS Ultra TXS rotating anode CCD instrument using an Oxford Cryosystems series 700 N₂ cryostat. Data collection and reduction was done using the Bruker AXS APEX2 suite programs.²⁰ Structure solution and refinement was done using the SHELXS and SHELXL, respectively.²¹ CCDC codes. 904595

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