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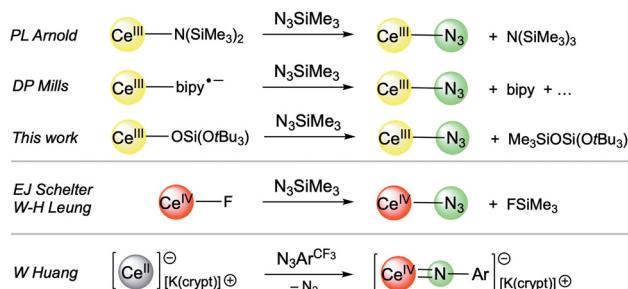
Trimethylsilylhalogenides and -pseudohalogenides are frequently used reactants for (pseudo)halogen transfer, including derivatizations of cerium compounds. The present study describes the facile ligand exchange of cerium(III) complex $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$ with Me_3SiN_3 generating the mixed azido/siloxy Ce^{III} complexes $\text{Ce}_2[\text{OSi}(\text{OtBu})_3]_5(\text{N}_3)_4$ and $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_2(\text{N}_3)]_4$. Although cerium siloxide complexes are a topical research field, thermal or photolytic ligand degradation as described in Ce^{IV} alkoxide chemistry has not been described. The activation of the azide complexes by irradiation with UV-visible light is easily achieved for such mixed azido/siloxy cerous complexes, as revealed by the identification of the homoleptic ceric complex $\text{Ce}[\text{OSi}(\text{OtBu})_3]_4$.

Organoazide-promoted formation of organoimide and nitride complexes has emerged as a productive/popular synthesis protocol in uranium 5f chemistry.^{1,2} Such redox transformations build on the release of N_2 according to photolytic and thermal pathways as well as the facile accessibility of uranium in high oxidation states ($\text{U}^{\text{IV-VI}}$).^{1,2} Reinforcing similarities between $\text{U}^{\text{III/IV}}$ and $\text{Ce}^{\text{III/IV}}$ ions,^{3,4} it was recently shown that the 4f-element cerium can engage in a similar redox transformation. For example, anionic cerium(IV) terminal imide was obtained by two-electron oxidation of a “Ce^{II}” complex supported by a tripodal tris(amido)arene ligand using organoazide $\text{N}_3\text{Ar}^{\text{CF}_3}$ ($\text{Ar}^{\text{CF}_3} = \text{C}_6\text{H}_3(\text{CF}_3)_2-3,5$).⁵ In contrast, the only molecular cerium nitride $[(\text{TriNO}_x)\text{Ce}(\text{Li}_2\mu-\text{N})\text{Ce}(\text{TriNO}_x)][\text{BAr}^{\text{F}}_4]$ did not involve an azide derivative but a reaction sequence comprising the cationization of the chloride precursor in liquid ammonia and subsequent exhaustive deprotonation of the formed ammonia complex with $\text{Li}[\text{N}(\text{SiMe}_3)_2]$.⁶ The few reported molecular Ce^{III} and Ce^{IV} azide complexes were accessed *via* salt-

metathesis protocols with an inorganic azide, AgN_3 or NaN_3 (ref. 7–10), but also by applying organoazide-promoted trans-silylation (Scheme 1).^{11–14} The latter include the terminal Ce^{IV} species $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3(\text{N}_3)$ ¹² and the terminal and bridging Ce^{III} complexes ($\text{Tp}^{\text{Me}^2})_2\text{Ce}(\text{N}_3)$ ($\text{Tp}^{\text{Me}^2} = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$)¹³ and $[\text{LCe}[\text{N}(\text{SiMe}_3)_2](\mu-\text{N}_3)]_2$ ($\text{L} = \text{alkoxy-N-heterocyclic carbene } \text{Me}_3\text{Si}\{\text{C}(\text{NDippCH}_2\text{CH}_2\text{N})\}\text{CH}_2\text{CMe}_2\text{O}$).¹⁴

Given that the monoanionic tris(*tert*-butoxy)siloxy ligand $[\text{OSi}(\text{OtBu})_3]$ was successfully employed by Mazzanti *et al.* for the syntheses of uranium imido-, imino- and nitride complexes^{1e} and because it provides a stabilizing platform for both ceric and cerous chemistry,^{15,16} we set out to examine $[\text{OSi}(\text{OtBu})_3]/\text{N}_3\text{SiMe}_3$ exchange reactions driven by silicon oxophilicity. In this communication, a stepwise azide transfer *via* trans-silylation of cerous tris(*tert*-butoxy)siloxide is presented, affording well-defined mixed azido/siloxy cerium complexes of distinct aggregation. Preliminary experiments revealed that the heteroleptic Ce^{III} complexes are potential precursors for photolytic and thermal oxidation generating Ce^{IV} compounds.

Treatment of a slurry of $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$ (ref. 15) in *n*-hexane with one equiv. of Me_3SiN_3 gave a clear solution (Scheme 2). The ambient temperature ^1H NMR spectrum in C_6D_6 of the obtained colourless reaction product revealed dis-



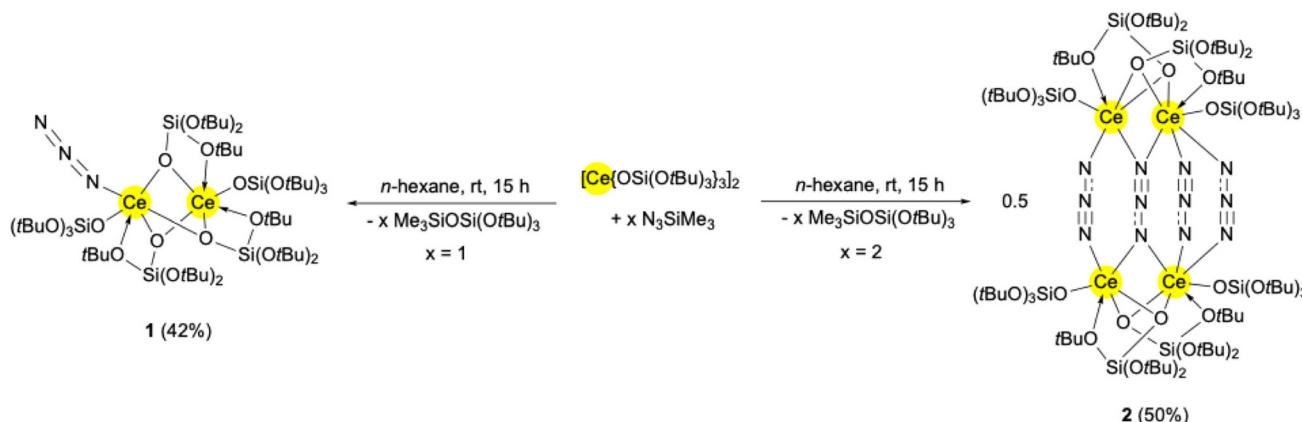
Scheme 1 Organoazide-promoted formation of cerium azides and organoimides.

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Scheme 2 Stepwise functionalization of $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$ with azido ligands *via* a trans-silylation reaction with Me_3SiN_3 .

tinct paramagnetic resonances in the range from 10.31 to -8.77 ppm (Fig. S1†). These were accompanied by diamagnetic signals, attributable to the side-product $\text{Me}_3\text{SiOSi}(\text{OtBu})_3$ (1.39, 0.28 ppm). Recrystallization at -40 °C from a toluene solution allowed for the effective removal of the silyl ether and isolation of complex $\text{Ce}_2[\text{OSi}(\text{OtBu})_3]_5(\text{N}_3)$ (**1**), with the composition as suggested by elemental analysis. In non-coordinating solvents, slow ligand rearrangement was observed, as confirmed by formation of the complex $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_2(\mu\text{-N}_3)]$ (**2**, *vide infra*). Complex **2** also appeared in the supernatants of crystallization attempts of **1** (see also Fig. S1†). The ambient temperature ^1H NMR spectrum of crystalline **1** showed paramagnetically broadened resonances at 10.31/9.75 and -6.02 ppm (ratio 6 : 9) for the *t*Bu protons (Fig. S2†) in accordance with distinct siloxy ligands. FT IR spectroscopy showed a vibration band at $\nu = 2076$ cm^{-1} (Fig. S17†), characteristic of cerium-coordinated azido ligands. The X-ray structural analysis of complex **1** revealed a binuclear structural motif slightly different from that of the dimeric precursor $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$.¹⁵ In the solid state, bimetallic complex **1** displays two 6-coordinate cerium atoms asymmetrically bridged by three siloxy ligands, each involving a κ^2 -bonding mode (Fig. 1 and Scheme 2). Whereas Ce(2) completes its coordination sphere with one terminal siloxy ligand, Ce(1) bears a terminal siloxy and a terminal azido ligand. For comparison, the cerium centres in the dimeric homoleptic precursor are 5-coordinate with two terminal and two bridging κ^2 -bonded siloxy ligands.

The terminal azido ligand in **1** features a Ce(1)-N bond length of 2.375(6) Å, quite similar to the 2.340(6) Å reported for trivalent $[(\text{Tp}^{\text{Me}^2})_2\text{Ce}(\text{N}_3)]$.¹³ Further metrics of the Ce-N₃ moiety include the interatomic angles Ce1-N1-N2 (166.8(6)°) and N1-N2-N3 (179.4(9)°), while the distances N1-N2 (1.194 (8) Å) and N2-N3 (1.137(8) Å) are in accordance with an ionic azido bonding.^{17,18} The terminal Ce-O(siloxyl) distances of 2.223(4) and 2.215(4) Å are slightly longer than those reported for $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$ reflecting the higher coordination number of complex **1**.¹⁵ The bridging Ce-O(siloxyl) distances range from 2.306(4) to 2.634(4) Å. For comparison, the bridging distances in $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$ were detected as 2.532(2)

and 2.396(2) Å. The Ce-OtBu donor distances in **1** amount to 2.547(4), 2.572(4) and 2.597(4) Å, and match those in $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$.¹⁵

Treatment of $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_3]_2$ with two equiv. of Me_3SiN_3 in *n*-hexane again led to the complete dissolution of the cerous siloxide upon stirring overnight (Scheme 2). The ambient temperature ^1H NMR spectrum of the obtained colourless product in C_6D_6 indicated distinct paramagnetic resonances, as well as diamagnetic signals of the side-product $\text{Me}_3\text{SiOSi}(\text{OtBu})_3$. Once more, the silyl ether could be effectively separated *via* recrystallization from a toluene solution at -40 °C. The ambient temperature ^1H NMR spectrum of pure $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_2(\mu\text{-N}_3)]_4$ (**2**) in C_6D_6 (Fig. S3†) showed broad paramagnetic resonances at 8.24 and -8.77 ppm (ratio 54 : 54), indicative of two chemically inequivalent tris(*tert*-butoxy)siloxyl ligand environments.

The results obtained from elemental analysis displayed CHN values as expected for a compound of composition $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_2(\text{N}_3)]$ (**2**). In contrast to compound **1**, the IR spectrum of **2** revealed distinct azido vibration bands at $\nu = 2144$ and 2076 cm^{-1} (Fig. S8†), indicative of different azido bondings. The X-ray structural analysis of complex **2** revealed a tetrametallic complex of composition $[\text{Ce}_4(\text{OSi}(\text{OtBu})_3)_4(\mu_2\text{-OSi}(\text{OtBu})_3)_4(\mu_2\text{-N}_3)_3(\mu_4\text{-N}_3)]$ (**2**) (Fig. 1). The asymmetric unit consists of a bimetallic entity in which each cerium ion is coordinated by one terminal, as well as two bridging siloxy ligands adopting the κ^2 -bonding mode (Fig. 1). The asymmetric units are connected by four azido moieties (Scheme 2 and Fig. 1), which display two distinct coordination modes. While three of the azido ligands each bridge two of the four cerium atoms asymmetrically in a $\mu_{2(1,3)}$ -fashion, the fourth one connects to all four cerium centres in a $\mu_{4(1,1',3,3')}$ fashion.¹⁹ As a consequence, both 6- and 7-coordinate cerium atoms are present. In complex **2**, the terminal Ce-O siloxyl bonds are 2.1931(13) and 2.2007(13) Å, while the bridging ones range from 2.3128(14) to 2.5665(13) Å. The donor Ce-OtBu moieties show interatomic Ce-O distances of 2.4934(14) and 2.6340(14) Å. As expected, the Ce-N distances of the bridging azido moieties are significantly elongated (2.5475(18)–

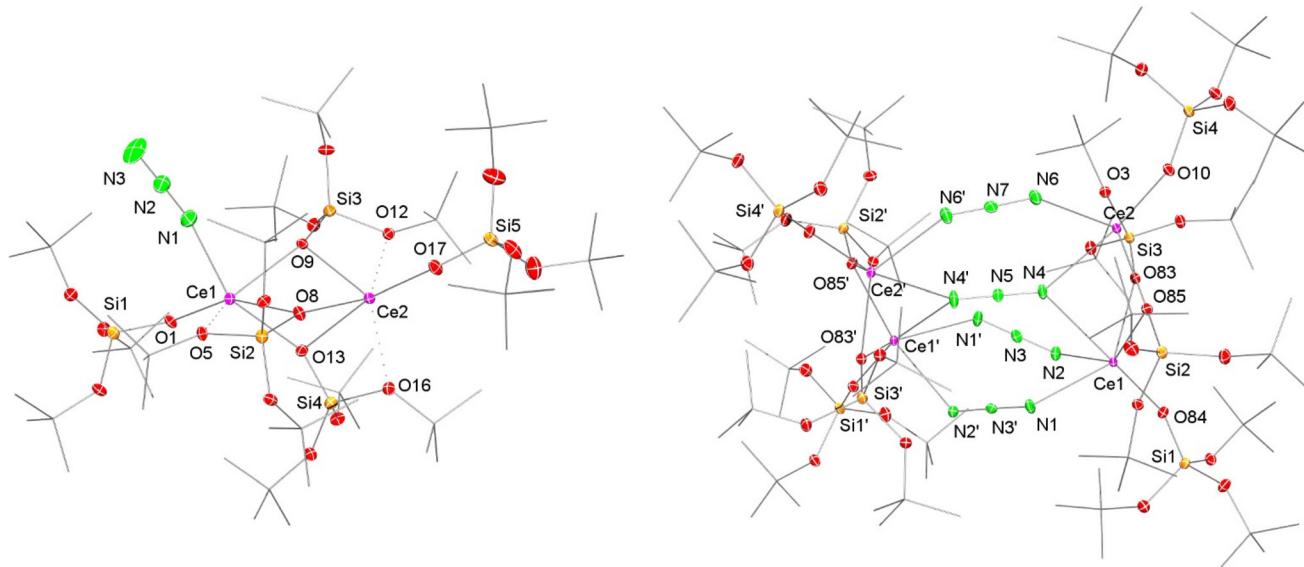


Fig. 1 ORTEP representations of the molecular structure of $[\text{Ce}(\text{OSi}(\text{OtBu})_3)\{\mu\text{-OSi}(\text{OtBu})_3\}_3\text{Ce}(\text{OSi}(\text{OtBu})_3)\text{N}_3]$ (**1**, left) and of complex $[\{\text{Ce}_2\{\mu_2\text{-OSi}(\text{OtBu})_3\}_2\{\text{OSi}(\text{OtBu})_3\}_2\{\mu_{2(1,3)}\text{-N}_3\}_3\{\mu_{4(1,1',3,3')}\text{-N}_3\}]$ (**2**, right). The asymmetric unit of molecule **1** is shown in the ESI (Fig. S10).[†] Thermal ellipsoids are set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: 1: Ce1–O1 2.223(4), Ce1–O5 2.572(4), Ce1–O8 2.634(4), Ce1–O9 2.391(4), Ce1–O13 2.436(4), Ce2–O8 2.306(4), Ce2–O9 2.407(4), Ce2–O12 2.597(4), Ce2–O13 2.560(4), Ce2–O16 2.547(4), Ce2–O17 2.215(4), Ce1–N1 2.375(6), N1–N2 1.194(8), N2–N3 1.137(8), O1–Si1 1.598(4), O8–Si2 1.606(4), O9–Si3 1.605(4), O13–Si4 1.594(4), O17–Si5 1.597(4), Ce1–N1–N2 166.8(6), N1–N2–N3 179.4(9), O1–Ce1–O8 156.03(14), O1–Ce1–O9 126.53(14), O1–Ce1–O13 100.45(14), O9–Ce1–N1 83.08(18), O8–Ce2–O17 105.47(15), O9–Ce2–O17 123.63(14), O13–Ce2–O17 167.45(14). 2: Ce1–O74 2.6340(14), Ce1–O83 2.4019(14), Ce1–O84 2.2007(13), Ce1–O85 2.5665(13), Ce2–O3 2.4934(14), Ce2–O10 2.1931(13), Ce2–O83 2.5054(13), Ce2–O85 2.3128(14), Ce1–N1 2.5578(18), Ce1–N2 2.5569(17), Ce1–N4 2.7528(18), Ce2–N4 2.6198(18), Ce2–N6 2.5475(18), N1–N3 1.177(2), N1–N3' 1.176(2), N2–N3 1.173(2), N4–N5 1.1693(17), N6–N7 1.1717(18), O84–Si1 1.5998(15), O85–Si2 1.6098(15), O83–Si3 1.6061(15), O10–Si4 1.6037(15), Ce1–N1–N3' 132.82(15), Ce1–N2–N3 126.21(14), Ce2–N6–N7 143.83(17), N2–N3–N1' 178.8(2), N4–N5–N4' 179.2(3), N6–N7–N6' 178.5(3), Ce1–O84–Si1 157.12(9), Ce2–O10–Si4 154.36(9), O10–Ce1–O83 125.03(5), O10–Ce1–O85 107.65(5), O83–Ce1–O84 107.11(5), O84–Ce1–O85 120.59(5). ' = $-x, y, -z + 3/2$.

2.7528(18) Å) in agreement with those reported for the 5-coordiante Ce^{III} complex $[\text{LCe}\{\text{N}(\text{SiMe}_3)_2\}\{\mu\text{-N}_3\}]_2$ (*vide supra*, 2.538 (2) and 2.585(2) Å).¹⁴ The N–N distances are slightly enlarged (1.169(2)–1.177(2) Å) as a result of the end-on coordination to cerium.

Exposing the colourless complex **1** to ambient light resulted in a colour change within hours. The ambient temperature ¹H NMR spectrum of the obtained yellow substance in C₆D₆ displayed resonances of unknown diamagnetic species (1.64–1.60 ppm), with Ce[OSi(OtBu)₃]₄ emerging (Fig. S4†), and presumably HOSi(OtBu)₃ (1.40 ppm). Interestingly, excitation of a C₆D₆ solution containing complex **1** with UV light (254 nm) for 17 h allowed the generation of the aforementioned diamagnetic intermediate product (1.61 ppm) more selectively (see ESI Fig. S5†). The photoreaction also produced isobutene. After prolonged treatment for 3.5 days, complete decomposition was observed, which was revealed by undefined paramagnetically shifted resonances in the ambient temperature ¹H NMR spectrum (Fig. S6†). Short exposure times of 10 min to UV irradiation (260–330 nm) revealed almost complete consumption of complex **1** with isobutene as the main decomposition product detectable (Fig. S7†). The degradation reaction was revealed by the DRIFT spectrum, which showed almost complete disappearance of the azido bands (Fig. S19†). Applying this short UV irradiation to complex **2** produced

significant amounts of both isobutene and homoleptic complex Ce[OSi(OtBu)₃]₄ (Fig. S8 and S21†). Unfortunately, any other cerium- or nitrogen-containing product could neither be identified spectroscopically nor isolated. Overall, our observations are similar to those of the thermal decomposition study of the uranium(IV) siloxide congener $[\text{U}\{\text{OSi}(\text{OtBu})_3\}_3]_2$ reported by Mazzanti *et al.* which led to the isolation of the mixed siloxy/silanediolato uranium(IV) complex $[\text{U}\{\text{OSi}(\text{OtBu})_3\}_2\{\mu\text{-O}_2\text{Si}(\text{OtBu})_2\}_2]$.^{20,21} The formation of the latter uranium(IV) complex takes place at ambient temperature both in the solid state and in solution, and is accompanied by the elimination of isobutene.

Thermal activation of an azido moiety was also suggested by the treatment of complex **1** dissolved in C₆D₆ at 50 °C. Over a period of 5 days increasing resonances of diamagnetic Ce[OSi(OtBu)₃]₄ (Fig. S9†) and HOSi(OtBu)₃ (1.40 ppm) were detected. These were accompanied by low intensity paramagnetically shifted resonances of complex **2** occurring from concomitant ligand rearrangement. Conducting the thermal treatment of complexes **1** and **2** at 80 °C in toluene for 38 h showed only negligible decomposition, and formation of significant amounts of Ce[OSi(OtBu)₃]₄ was not detected by NMR/DRIFT spectroscopy (Fig. S10, S11 and S21†). Furthermore, performing such prolonged heating on homoleptic cerium tris(*tert*-butoxy)siloxide complexes, trivalent $[\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_3]_2$ as well

as tetravalent $\text{Ce}[\text{OSi}(\text{OtBu})_3]_4$, did not result in any significant decomposition (Fig. S13 and S14[†]). In contrast, isobutene formation features a prominent thermal decomposition path of both cerous alkoxide $\text{Ce}(\text{OCtBu})_3$ (ref. 22) and dimeric ceric complex $[\text{Ce}(\text{OtBu})_3(\mu\text{-}\text{OtBu})]_2$.²³

In conclusion, mixed ligand siloxy/azido complexes of cerium(III) are readily accessible *via* a trans-silylation protocol. Complexes $[\text{Ce}_2\{\text{OSi}(\text{OtBu})_3\}_5\text{N}_3]$ and $[\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_2\text{N}_3]_4$ can be isolated in good yields but possess limited stability under light. It is revealed that both moderate thermal and photolytic treatment can lead to the oxidation of Ce^{III} ions, as corroborated by the identification of ceric complex $\text{Ce}[\text{OSi}(\text{OtBu})_3]_4$. Intermediate products generated from the photolytic path tend to slow ligand degradation, while the thermally activated product is prone to rearrangement reactions. Given the stabilizing effect of siloxy ligands on rare-earth-metal complexes, such transazidation reactions might provide a new avenue for cerium redox transformations.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.[†] Crystallographic data for the compounds have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers 2448269 and 2448270[†]).

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