

# Formation of a Ce(IV) Oxo Complex via Inner Sphere Nitrate Reduction

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**S** Supporting Information

**ABSTRACT:** Reaction of  $\text{Ce}(\text{NO}_3)_3(\text{THF})_4$  with  $\text{Li}_3(\text{THF})_3(\text{NN}'_3)$  ( $\text{NN}'_3 = \text{N}(\text{CH}_2\text{CH}_2\text{NR})_3$ ,  $\text{R} = \text{Si}^t\text{BuMe}_2$ ) in  $\text{Et}_2\text{O}$ , in the presence of 12-crown-4, results in the formation of  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{O})]$  (**1**) in 36% yield. This transformation proceeds via formation of a Ce(III) nitrate intermediate,  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\kappa^2\text{-O}_2\text{NO})]$  (**2**), which undergoes inner sphere nitrate reduction. In addition, reaction of **1** with  $^t\text{BuMe}_2\text{SiCl}$  results in the formation of  $(\text{NN}'_3)\text{Ce}(\text{OSi}^t\text{BuMe}_2)$  (**3**), confirming the nucleophilic character of its oxo ligand. Natural bond orbital and quantum theory of atoms-in-molecules data reveal the Ce–O interaction in **1** to be significantly covalent, and strikingly similar to analogous U–O bonding.

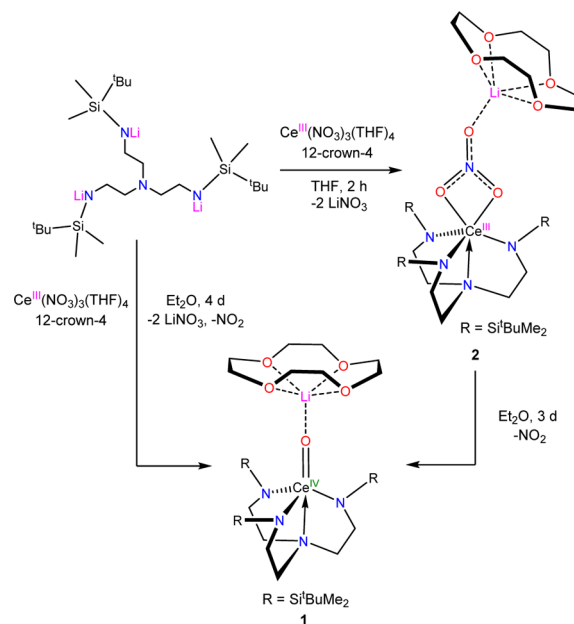
The need to understand the role of the valence *f*- and *d*-orbitals in the bonding of the *f* elements, primarily for improved liquid–liquid extraction during nuclear fuel processing, has resulted in renewed interest in actinide–ligand multiple bonding,<sup>1–6</sup> an area which is proving to be an excellent laboratory for exploring orbital participation in the *Sf* series. However, while many examples of actinide–ligand multiple bonding are now known,<sup>7,8</sup> instances of lanthanide–ligand multiple bonding are rare.<sup>9–11</sup> Examples include the isolation, by Leung and co-workers, of a Ce<sup>IV</sup> oxo complex ligated by the tripodal Kläui ligand,  $(\text{L}_{\text{OEt}})_2\text{Ce}(\text{O})(\text{H}_2\text{O})$  ( $\text{L}_{\text{OEt}} = \text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3$ ).<sup>12–14</sup> Similarly, Lappert and co-workers reported the Ce<sup>IV</sup> oxo complexes,  $[\mu\text{-M}]_2[\text{Ce}(\mu\text{-O})(\text{NR}_2)_3]_2$  formed in low yields by reaction of  $\text{Ce}(\text{NR}_2)_3$  ( $\text{R} = \text{SiMe}_3$ ) with dioxygen, in the presence of  $\text{MNR}_2$  ( $\text{M} = \text{Na}, \text{K}$ ).<sup>15</sup> More recently, Anwander and co-workers reported the preparation of the first terminal lanthanide imido complexes,  $[(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ln}(=\text{NAr})(\text{dmap})]$  ( $\text{Ln} = \text{Y}, \text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ;  $\text{Ln} = \text{Lu}, \text{Ar} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ).<sup>16</sup> This was followed by the synthesis of a cerium(IV) terminal imido,  $[\text{K}(\text{DME})_2][\text{Ce}=\text{N}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)(\text{TriNOx})]$ , by Schelter and co-workers.<sup>17</sup> Also of note is the Ce(IV) methanediide complex,  $[\text{Ce}(\text{BIPM}^{\text{TMS}})(\text{ODipp})_2]$  ( $\text{BIPM}^{\text{TMS}} = \text{C}(\text{PPh}_2\text{NSiMe}_3)_2$ ;  $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ), reported by Liddle and co-workers.<sup>18,19</sup>

This paucity of lanthanide examples has been rationalized by the mismatch in the energies of the metal and ligand frontier orbitals, which results in poor orbital overlap.<sup>20–22</sup> However, recent XAS studies have demonstrated that the 4*f* orbitals can participate in cerium–ligand bonding, at least for the Ce(IV) oxidation state, suggesting that some covalency within

lanthanide–ligand bonding is possible.<sup>23</sup> Indeed,  $[\text{CeCl}_6]^{2-}$  features more *f* orbital participation in its metal–ligand bonds than does  $[\text{UCl}_6]^{2-}$ . If this observation is general, it suggests that Ce(IV) should be as adept at forming multiple bonds as U(IV). In an effort to test this hypothesis, we have begun to explore the synthesis of cerium(IV)–ligand multiple bonds. Herein, we describe the synthesis and characterization of a rare cerium oxo complex.

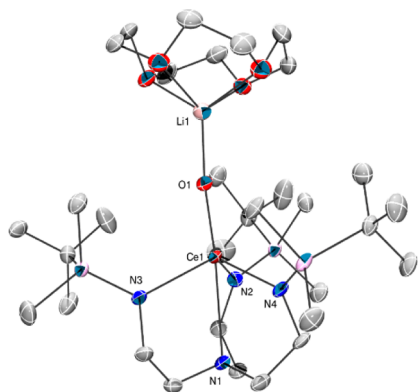
Reaction of  $\text{Ce}(\text{NO}_3)_3(\text{THF})_4$  with  $\text{Li}_3(\text{THF})_3(\text{NN}'_3)$  ( $\text{NN}'_3 = \text{N}(\text{CH}_2\text{CH}_2\text{NR})_3$ ,  $\text{R} = \text{Si}^t\text{BuMe}_2$ ) in  $\text{Et}_2\text{O}$ , in the presence of 12-crown-4, results in the formation of a red-orange solution after 4 d. Crystallization of this material from concentrated  $\text{Et}_2\text{O}$ , layered with hexanes, results in the deposition of  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\text{O})]$  (**1**), which was isolated in a 36% yield as yellow blocks (Scheme 1). In the solid state, complex **1** features a distorted trigonal bipyramidal geometry about the Ce ion (Figure 1). Its Ce–O bond length (1.902(2) Å) is somewhat shorter than that observed in  $[(\text{L}_{\text{OEt}})_2\text{Ce}(\text{O})(\text{MeC}(\text{O})\text{NH}_2)][\text{Na}(\text{L}_{\text{OEt}})]$  (1.953(4) Å),<sup>14</sup> but slightly longer than the Ce–O distance observed for  $(\text{L}_{\text{OEt}})_2\text{Ce}(\text{O})(\text{H}_2\text{O})$  (1.857(3) Å)<sup>12</sup> and the

**Scheme 1. Synthetic Routes to Complex 1**



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**Figure 1.** ORTEP diagram of **1** shown with 50% probability ellipsoids. Hydrogen atoms and one molecule of benzene are omitted for clarity. Selected bond distances (Å) and angles (deg): Ce1–O1 = 1.902(2), Ce1–N1 = 2.716(3), Ce1–N2 = 2.316(3), Ce1–N3 = 2.361(3), Ce1–N4 = 2.331(3), O1–Li1 = 1.827(6), O1–Ce1–N1 = 174.83(9), Li1–O1–Ce1 = 170.9(2).

distance predicted for  $\text{Cp}_2\text{Ce}(\text{O})$  (1.814 Å).<sup>9</sup> This distance is also much shorter than the  $\text{Ce}=\text{N}$  distance in  $[\text{K}(\text{DME})_2][\text{Ce}=\text{N}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)(\text{TriNOx})]$  (2.119(3) Å).<sup>17</sup> The oxo ligand in **1** is also coordinated by the  $\text{Li}^+$  ion of the  $[\text{Li}(12\text{-crown-4})]^+$  moiety. The Li–O bond length is 1.827(6) Å, which is within the range of those exhibited by  $\text{Li}^+$  cations bound by an organic carbonyl.<sup>24–26</sup> Finally, it is interesting to note the similarity between the capping  $[\text{Li}(12\text{-crown-4})]^+$  cation in **1** and the capping  $[\text{K}(18\text{-crown-6})]$  moiety found in  $[\text{K}(18\text{-crown-6})][\text{M}(\text{E})(\text{NR}_2)_3]$  (M = Th, U; E = O, S, Se, Te; R =  $\text{SiMe}_3$ ),<sup>27–30</sup> which can be viewed as its actinide analogues.

Complex **1** is soluble in  $\text{Et}_2\text{O}$ , THF, toluene, and benzene; however, it decomposes in the presence of  $\text{CH}_2\text{Cl}_2$  or MeCN. Its  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  features a sharp singlet at 1.41 ppm, assignable to the  $^t\text{Bu}$  groups of the TREN ligand. The chemical shift, along with its sharp appearance, is indicative of a diamagnetic  $\text{Ce}^{\text{IV}}$  complex. Most significantly, resonances at 3.07 and 2.40 ppm, each integrating for 8 protons, are assigned to the *endo* and *exo* environments for the methylene groups of the oxo-bound  $[\text{Li}(12\text{-crown-4})]^+$  cation. The observation of two chemical shifts for 12-crown-4 can be rationalized by assuming that the O(oxo)–Li interaction is maintained over the time scale of the NMR experiment and demonstrates that the solid state structure is conserved in solution. For comparison, the related actinide complex,  $[\text{K}(18\text{-crown-6})][\text{Th}(\text{O})(\text{NR}_2)_3]$ , does not exhibit *endo* and *exo* environments for its 18-crown-6 methylene groups in  $\text{C}_6\text{D}_6$ ,<sup>29</sup> suggesting that a stronger alkali metal–oxygen interaction is present in complex **1**. Finally, the solid state Raman spectrum of **1** displays two bands assigned to  $\nu(\text{Ce}=\text{O})$  stretching modes at 783 and 719  $\text{cm}^{-1}$ . For comparison,  $\nu(\text{Ce}=\text{O})$  in  $^3\text{CeO}$  and  $^1\text{H}_2\text{CeO}$  were determined to be 808 and 849  $\text{cm}^{-1}$ , respectively, by IR spectroscopy.<sup>31</sup>

To better understand the solution phase properties of **1**, we recorded its  $^1\text{H}$  and  $^7\text{Li}\{^1\text{H}\}$  NMR spectra in  $\text{THF-}d_8$ . Interestingly, in this solvent, the  $^1\text{H}$  resonance attributable to the 12-crown-4 moiety appears as a sharp singlet at 3.59 ppm, which is suggestive of the formation of a separated ion pair. However, the  $^7\text{Li}$  resonance of this sample appears at  $-3.68$  ppm, which is nearly identical to the chemical shift observed for **1** in  $\text{C}_6\text{D}_6$  ( $-3.92$  ppm), suggesting similar chemical environments in both solvents. We also recorded a  $^7\text{Li}\{^1\text{H}\}$  NMR spectrum of a 1:1 mixture of complex **1** and  $[\text{Li}][\text{PF}_6]$  in  $\text{THF-}d_8$  (Figure S14). This

spectrum reveals the appearance of two broad resonances: one at  $-0.85$  ppm, which we have assigned to  $[\text{Li}(\text{THF})_x][\text{PF}_6]_x$ , and one at  $-3.66$  ppm, which we have assigned to complex **1**. The appearance of two resonances in this spectrum, along with the similar  $^7\text{Li}$  chemical shift values in polar and nonpolar solvents, demonstrates that the Li cation in complex **1** is likely coordinated to the oxo ligand in both solvents.

To rationalize the formation of **1**, we speculate that, during the reaction of  $\text{Ce}(\text{NO}_3)_3(\text{THF})_4$  with  $\text{Li}_3(\text{THF})_3(\text{NN}'_3)$ , the Ce(III) nitrate complex,  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\kappa^2\text{-O}_2\text{NO})]$  (**2**), is generated transiently. The  $[\text{NO}_3]^-$  ligand in this complex is then reduced by  $1e^-$ , generating the oxo moiety and releasing  $\text{NO}_2$ . To test this hypothesis, we attempted to isolate this material from the reaction of  $\text{Ce}(\text{NO}_3)_3(\text{THF})_4$  with  $\text{Li}_3(\text{THF})_3(\text{NN}'_3)$ . Thus, workup of this reaction mixture after only 2 h resulted in the isolation of  $[\text{Li}(12\text{-crown-4})][(\text{NN}'_3)\text{Ce}(\kappa^2\text{-O}_2\text{NO})]$  (**2**), as an orange-red solid in 47% yield (Scheme 1). Complex **2** was characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography. Its solid state molecular structure reveals  $\kappa^2$  coordination of the nitrate moiety to the cerium center, with Ce–O distances (2.724(6) and 2.745(6) Å; see SI) within the range of those reported for other  $\text{Ce}^{\text{III}}$ –nitrate complexes.<sup>32,33</sup> In addition, the  $[\text{Li}(12\text{-crown-4})]^+$  cation is ligated to the terminal oxygen atom of the nitrate moiety. The resulting Li–O distance is 2.01(2) Å.

Gratifyingly, upon dissolution in  $\text{Et}_2\text{O}$ , complex **2** converts to **1** over the course of 3 d. Synthesized via this route, **1** can be isolated in 43% yield (Scheme 1). This result demonstrates that **2** is an intermediate in the formation of **1** during the reaction of  $\text{Ce}(\text{NO}_3)_3(\text{THF})_4$  with  $\text{Li}_3(\text{THF})_3(\text{NN}'_3)$ . Interestingly, there are only a few other examples of oxo ligand formation via nitrate reduction.<sup>34</sup> For example, reaction of  $\text{MoOCl}_2(\text{bipy})$  with  $[\text{NO}_3]^-$  results in the formation of  $\text{MoO}_2\text{Cl}_2(\text{bipy})$  and  $\text{NO}_2$ .<sup>35,36</sup> Similarly, photolysis of either  $(\text{TPP})\text{Mn}(\text{NO}_3)$  or  $\text{Ru}_2(\text{chp})_4(\text{NO}_3)$  ( $\text{chp} = 6\text{-chloro-2-hydroxypyridinate}$ ) generates a metal oxo and  $\text{NO}_2$ .<sup>37,38</sup>

We recently employed dispersion-corrected density functional theory (DFT) at the PBE level to study the geometric and electronic structures of  $[\text{K}(18\text{-crown-6})][\text{M}(\text{O})(\text{NR}_2)_3]$  (M = Th, U; R =  $\text{SiMe}_3$ )<sup>29</sup> and have here applied the same approach to the fictitious Ce analogue of these systems, and to complex **1**. The bond lengths between the Ce and ligating atoms in the latter are well reproduced computationally, with the largest difference between experiment and theory being  $<0.06$  Å (for the Ce–O bond, which is slightly overestimated by DFT). The bending along Ce–O–Li (to  $167.9^\circ$ ) is very close to that found experimentally. The Raman data for **1** are well supported by the DFT calculations, which find three Raman active vibrational modes with significant Ce–O stretching character, at 524, 708, and 762  $\text{cm}^{-1}$ , the latter two modes lying within 11 and 21 wavenumbers, respectively, of the experimental bands.

As in our previous study, we have analyzed the metal–oxygen bonding using the natural bond orbital (NBO) and quantum theory of atoms-in-molecules (QTAIM) approaches. In all cases NBO finds the M–O interaction to be a  $\sigma + 2\pi$  triple bond, and the compositions of the  $\pi$  natural localized molecular orbitals (NLMOs) are given in Table 1. It is striking how similar the data are for  $[\text{K}(18\text{-crown-6})][\text{U}(\text{O})(\text{NR}_2)_3]$  and  $[\text{K}(18\text{-crown-6})][\text{Ce}(\text{O})(\text{NR}_2)_3]$ , which both feature a slightly more covalent interaction than in either the Th system or complex **1**, which are rather similar to one another.

The QTAIM states that there is a bond critical point (BCP) between every two atoms bonded to each other, with the BCP

**Table 1. Averaged Compositions (%) of the Two M–O  $\pi$  Bonding NLMOs of [K(18-crown-6)][M(O)(NR<sub>2</sub>)<sub>3</sub>] (M = Th, U, Ce; R = SiMe<sub>3</sub>) and **1**<sup>a</sup>**

	O	M
[K(18-crown-6)][Th(O)(NR <sub>2</sub> ) <sub>3</sub> ]	86.86 (99.97 p)	11.75 (65.36 d, 34.48 f)
[K(18-crown-6)][U(O)(NR <sub>2</sub> ) <sub>3</sub> ]	83.72 (99.96 p)	16.67 (61.31 d, 38.41 f)
[K(18-crown-6)][Ce(O)(NR <sub>2</sub> ) <sub>3</sub> ]	83.48 (99.94 p)	15.27 (54.31 d, 45.68 f)
<b>1</b>	85.55 (99.85 p)	12.96 (56.92 d, 42.92 f)

<sup>a</sup>Data for [K(18-crown-6)][M(O)(NR<sub>2</sub>)<sub>3</sub>] (M = Th, U) taken from ref 29.

located at the minimum in the electron density along the bond path, the line of maximum electron density between the two atoms.<sup>39</sup> The values of the electron and energy densities  $\rho$  and  $H$  at the BCP can be used in analyzing the nature of the bond. Large  $\rho$  values are associated with covalent bonds, and  $H$  is negative for interactions with sharing of electrons, with its magnitude indicating the covalency of the interaction.<sup>40</sup> A bond is cylindrically symmetric when the bond ellipticity  $\epsilon$  is 0, such as in single and triple bonds, with higher values otherwise. The delocalization index ( $\delta$ ) between two bonded atoms indicates the bond order between them.

QTAIM M–O BCP and delocalization index data are collected in Table 2. The ellipticity values are all very close to zero, as

**Table 2. QTAIM BCP Electron ( $\rho$ ) and Energy ( $H$ ) Densities (au), Ellipticities ( $\epsilon$ ) and Delocalization Indices ( $\delta(M, O)$ ) for [K(18-crown-6)][M(O)(NR<sub>2</sub>)<sub>3</sub>] (M = Th, U, Ce; R = SiMe<sub>3</sub>) and **1**<sup>a</sup>**

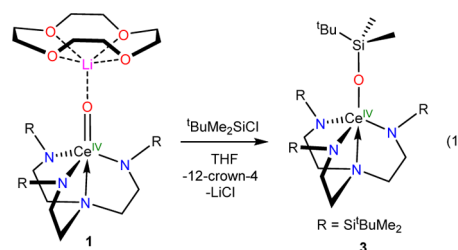
	$\rho$	$H$	$\epsilon$	$\delta(M, O)$
[K(18-crown-6)][Th(O)(NR <sub>2</sub> ) <sub>3</sub> ]	0.175	−0.094	0.000	1.387
[K(18-crown-6)][U(O)(NR <sub>2</sub> ) <sub>3</sub> ]	0.199	−0.119	0.062	1.575
[K(18-crown-6)][Ce(O)(NR <sub>2</sub> ) <sub>3</sub> ]	0.196	−0.111	0.000	1.643
<b>1</b>	0.168	−0.079	0.008	1.458

<sup>a</sup>Data for [K(18-crown-6)][M(O)(NR<sub>2</sub>)<sub>3</sub>] (M = Th, U) taken from ref 29.

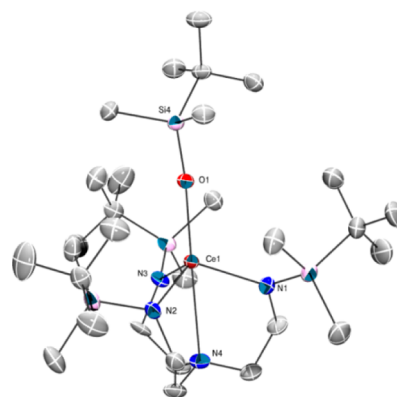
expected for cylindrically symmetric triple bonds. As with the  $\pi$  NLMO compositions, the other QTAIM metrics for the analogous U and Ce systems are very similar to one another and indicate a significantly covalent M–O interaction, with  $\rho$  and  $H$  values among the largest (in an absolute sense) seen for f element bonds. Indeed, the present  $\rho$  and  $H$  are approximately double the value of the equivalent metrics of the M(IV)–C multiple bonds recently reported by Liddle et al.<sup>18</sup> Pleasingly, the covalency trend  $Ce \approx U > Th$  is the same in both our system and the BIPM<sup>TMS</sup> compounds.

The QTAIM data for **1** are smaller (in an absolute sense) than those for the U and Ce K-based systems and are more similar to those for the Th complex. This is most likely a consequence of the O atom in **1** being bonded to the more polarizing Li<sup>+</sup> vs K<sup>+</sup> for the other three systems calculated.

Finally, we explored the reactivity of complex **1** with electrophiles. Thus, reaction of **1** with <sup>t</sup>BuMe<sub>2</sub>SiCl in THF results in rapid formation of (NN′<sub>3</sub>)Ce(OSi<sup>t</sup>BuMe<sub>2</sub>) (**3**), which can be isolated as a red solid in 32% yield by crystallization from hexamethyldisiloxane (eq 1). The low yield of **3** can be rationalized by its extremely high solubility in nonpolar solvents.



More importantly, this result demonstrates the nucleophilic nature of the oxo ligand in **1**. Interestingly, reaction of **1** with <sup>t</sup>BuMe<sub>2</sub>SiCl in C<sub>6</sub>D<sub>6</sub> is substantially slower, only reaching 50% completion after 24 h (Figure S12). The much slower rate in this solvent demonstrates that the barrier of Li<sup>+</sup> exchange is greatly increased in nonpolar solvents. Complex **3** was characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography (Figure 2). Its Ce–O distance (2.169(2) Å) is consistent with



**Figure 2.** ORTEP diagram of **3** shown with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ce1–O1 = 2.169(2), Ce1–N1 = 2.223(3), Ce1–N2 = 2.229(3), Ce1–N3 = 2.225(3), Ce1–N4 = 2.731(3), Si4–O1 = 1.641(3), O1–Ce1–N4 = 178.6(1), Si4–O1–Ce1 = 167.2(2).

single bond character<sup>41–45</sup> and is significantly longer than the Ce–O distance observed in **1**, confirming multiple bond character in the latter. In addition, the Ce–O–Si angle is 167.2(2)°. Also of note, its average Ce–N(amide) distance is 0.1 Å shorter than that observed in complex **1**. This may be a consequence of the weaker donating ability of the silyloxo ligand (vs oxo), which allows for a strengthening of the Ce–N bonds.

The <sup>1</sup>H NMR spectrum of **3**, in C<sub>6</sub>D<sub>6</sub>, reveals resonances at 1.21 and 1.02 ppm, in a 1:3 ratio. These resonances are assignable to <sup>t</sup>Bu environments of the silyloxo and NN′<sub>3</sub> ligands, respectively, consistent with the proposed formula. Interestingly, complex **3** often appears as a minor impurity in crude reaction mixtures of complex **1** (see Figure S10). In these cases, the <sup>t</sup>BuMe<sub>2</sub>Si group is likely derived from cannibalization of the TREN ligand. The formation of **3** in these reactions also helps to account for the modest yields of **1**.

In summary, we have isolated and structurally characterized a rare example of a Ce(IV) oxo complex, [Li(12-crown-4)]-[(NN′<sub>3</sub>)Ce(O)], which is generated by inner sphere nitrate reduction by a Ce(III) precursor. These results suggest that nitrate reduction could be a useful tool for f element oxo formation. In this regard, we note that many Ln(II) complexes are, in principle, sufficiently reducing to effect nitrate reduction (the [NO<sub>3</sub>]<sup>−</sup>/[NO<sub>3</sub>]<sup>2−</sup> redox couple has been measured at  $E^\circ =$

−0.89 V vs NHE), providing a potential route to Ln(III) oxos.<sup>46,47</sup> In addition, NBO and QTAIM analysis of the metal–oxygen interaction in complex **1**, and the fictitious Ce analogue of our previously reported complexes  $[K(18\text{-crown-}6)][M(O)(NR_2)_3]$  ( $M = \text{Th, U}$ ), reveals the Ce=O interaction to be rather covalent. The data for the analogous U and Ce systems are strikingly similar, reinforcing our hypothesis that Ce(IV) should be as adept as U(IV) in forming multiple bonds. The Ce–O interaction in **1** has NBO and QTAIM metrics more similar to those in  $[K(18\text{-crown-}6)][Th(O)(NR_2)_3]$ , presumably as a result of the more polarizing  $Li^+$  vs  $K^+$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07932.

X-ray crystallographic details (CIF)

Experimental and computational details, spectral data, additional figures and tables (PDF)

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### Notes

The authors declare no competing financial interest.

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