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Abstract

The reactivity of the cerium(IV) oxo complex $[(L_{OEt})_2Ce^{IV}(=O)(H_2O)]\cdot MeC(O)NH_2$ (**1**) (L_{OEt}^- = $[CoCp\{P(O)(OEt)_2\}_3]^-$ where Cp = η^5-C_5H_5) toward electrophiles and Brønsted acids has been investigated. Treatment of **1** with acetic anhydride afforded the diacetate complex $[Ce^{IV}(L_{OEt})_2(O_2CMe)_2]$ (**2**). Reaction of **1** with $B(C_6F_5)_3$ yielded $[Ce^{IV}(L_{OEt})_2(Me_2CONH_2)_2][B(C_6F_5)_3(OH)]_2$ (**3**), in which the $[B(C_6F_5)_3(OH)]^-$ anions are H-bonded to the O-bound acetamide ligands. Treatment of **1** with HCl and HNO_3 afforded $[Ce^{IV}(L_{OEt})_2Cl_2]$ and $[Ce^{IV}(L_{OEt})_2(NO_3)_2]$, respectively. Protonation of **1** with triflic acid (HOTf) gave the diaqua complex $[Ce^{IV}(L_{OEt})_2(H_2O)_2](OTf)_2$ (**4**), in which the triflate anions are H-bonded to the two aqua ligands. Treatment of **1** with phenol afforded the phenoxide complex $[Ce^{IV}(L_{OEt})_2(OPh)_2]$ (**5**). The oxo-bridged bimetallic complex $[(L_{OEt})_2(Me_2CONH_2)Ce^{IV}(O)NaL_{OEt}]$ (**6**) with the Ce-O_{oxo} and Na-O_{oxo} distances of 1.953(4) and 2.341(4) Å, respectively was obtained from the reaction of **1** with $[NaL_{OEt}]$. Density functional theory calculations showed that the model complex $[(L_{OMe})_2Ce^{IV}(Me_2CONH_2)(O)NaL_{OMe}]$ (L_{OMe}^- = $[CoCp\{P(O)(OMe)_2\}_3]^-$) (**6A**) contains a polarized Ce=O multiple bond. The energy for dissociation of the $\{NaL_{OMe}\}$ fragment from **6A** in acetonitrile was calculated to be +33.7 kcal/mol, which is higher than that for the dissociation of the H-bonded acetamide from $[(L_{OMe})_2Ce^{IV}(=O)(H_2O)]\cdot MeC(O)NH_2$ (**1A**) (calculated to be +17.4 kcal/mol). While the Ce/Na complex **6** is stable in solution, complex **1**, upon dissociation of the H-bonded acetamide, converts easily to a mixture of a tetranuclear Ce(IV) oxo cluster, $[Ce^{IV}_4(L_{OEt})_4(\mu_4\text{-}O)(\mu_2\text{-}O)_4(\mu_2\text{-}OH)_2]\cdot MeC(O)NH_2$ (**7**), and a Ce(III) complex, $[Ce^{III}(L_{OEt})_2(H_2O)_2][L_{OEt}]$ (**8**(L_{OEt})), in hexanes. The crystal structures of **3**, **4**·H_2O, **6**, and **8**(L_{OEt}) have been determined.

Introduction

Metal complexes containing metal-ligand multiple bonds are of significance due to their

applications in atom transfer and metathesis reactions.[1] Of particular importance are metal-oxo complexes that are involved as active intermediates in metal-catalyzed oxidations and biological transformations.[2,3] Although transition-metal complexes with terminal oxo, nitrido, imido, and carbene ligands are well documented,[1a,4] very few analogues of the 4*f* elements have been isolated. This is in contrast with the 5*f* congeners that display rich chemistry of metal-ligand multiple bonding.[5] Notably, the organometallic chemistry of uranium oxo, imido, and nitrido complexes has received much attention recently, owing to their potential applications in catalysis and activation of small molecules.[6]

The paucity of stable isolated lanthanide (Ln) compounds with multiply bonded ligands can be attributed to the mismatch between the d_π(Ln) and p_π(X) (X = O, N, *etc*.) orbital energy that results in polar Ln-X bonds (i.e. Ln$^+$-X$^-$).[7] As such, Ln=X complexes are kinetically unstable and liable to electrophilic/nucleophilic attack. Thus, early attempts to prepare lanthanide-imido complexes led to isolation of dimeric/polymeric bridged imido complexes.[8]

The most extensively explored Ln=X complexes are trivalent rare earth metal complexes with π-conjugated chelating carbene ligands such as bis(iminophosphorano)methanediide.[9] Non-chelated terminal organoimido complexes of Sc(III),[10] and more recently Lu(III) and Y(III),[11] that contain short M-N bonds and linear M-N-R (R = aryl group) linkages have been synthesized and structurally characterized. Novel organometallic reactivity of Sc(III) imido complexes, e.g. cycloaddition with unsaturated substrates and C-H activation, has been reported.[12]

With an accessible +4 oxidation state, Ce is anticipated to be the most likely 4*f* element that forms stable metal-ligand multiple bonds. A theoretical study pointed out that [Cp$_2$Ce^{IV}=X] (X = oxo, imido, carbene, etc.; Cp = cyclopentadienyl) complexes are feasible synthetic targets.[13] It may be noted that analogous tetravalent metallocene oxo and imido complexes of actinides (e.g. U, Th)[14] and group 4 metals (Ti, Zr, Hf)[15] are well documented.

Recently, Liddle and coworkers reported that the Ce-C$_{carbene}$ bond in a Ce(IV) bis(iminophosphorano)carbene complex can be formulated as a multiple bond.[16] Nevertheless, prior to our recent work, Ce(IV) complexes with terminal oxo ligands remain elusive. Isolated Ce(IV) oxo compounds, which were usually obtained from hydrolysis of the Ce(IV) alkoxides/carboxylate or oxidation of Ce(III) precursors, are mostly dinuclear and polynuclear complexes with bridged oxo ligands.[17]

It is well-known that oxygen ligands can stabilize the +4 oxidation state of cerium.[18] We are particularly interested in metal complexes with the π-donating Kläui tripodal oxygen ligand [CpCo{P(O)(OEt)$_2$}$_3$]$^-$ (L$_{OEt}^-$, Chart 1) that has been recognized as an oxygen analogue of cyclopentadienyl.[19] Tetravalent cerium complexes of the types [Ce^{IV}(L$_{OEt}$)$_2$X$_2$] and [Ce^{IV}(L$_{OEt}$)X$_3$] (X$^-$ = monoanionic ligands) have been isolated.[20] The reduction potentials of [(L$_{OEt}$)$_2$Ce(NO$_3$)$_2$] and [(L$_{OEt}$)Ce(NO$_3$)$_3$] in MeCN of ca. +0.05 and +0.4 V vs. Fc$^{+/0}$ (Fc = ferrocene), respectively are considerably less anodic than that for (n-Bu$_4$N)$_2$[Ce(NO$_3$)$_6$] (ca. +0.62 V vs. Fc$^{+/0}$, MeCN),[21] demonstrating the ability of the tripodal oxygen ligand in stabilizing Ce(IV).
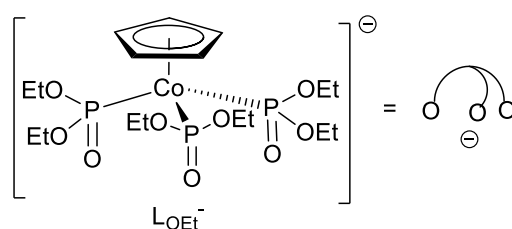
Chart 1. Structure of the Kläui Tripodal Ligand L$_{OEt}^-$

Recently, we reported the synthesis of a Ce(IV) terminal oxo complex, [(L$_{OEt}$)$_2$Ce^{IV}(=O)(H$_2$O)]·Me$_2$C(O)NH$_2$ (**1**) (Scheme 1), by metathesis reaction of [(L$_{OEt}$)$_2$CeCl$_2$] with Ag$_2$O in the presence of acetamide.[22] The Ce-O$_{oxo}$ bond distance in **1** of 1.857(3) Å, which is the shortest known Ce-O distance, is close to the sum of Pyykko's triple bond radii for Ce and O (1.84 Å).[23] Density functional theory (DFT) calculations revealed

that the occupied bonding molecular orbitals relevant to the Ce-O π and σ bonds in **1** are mostly localized on the oxo group. Thus, the Ce-oxo bond in **1** is best described as a polarized multiple bond, i.e. Ce=O $\leftrightarrow$ Ce^{+}-O^{-}. Consistent with this bonding description, **1** is highly nucleophilic and reacts with the CO_2 in air rapidly to give a Ce(IV) carbonate complex. In addition, **1** is redox-active and can be reduced by CO to a dinuclear Ce(III) carbonate complex (Scheme 1). To further explore the chemistry of nucleophilic lanthanide terminal oxo complexes, we systematically studied the reactivity of the Ce=O multiple bond in **1** toward Lewis and Brønsted acids. Also, the effect of protonation on the redox property of **1** has been investigated.
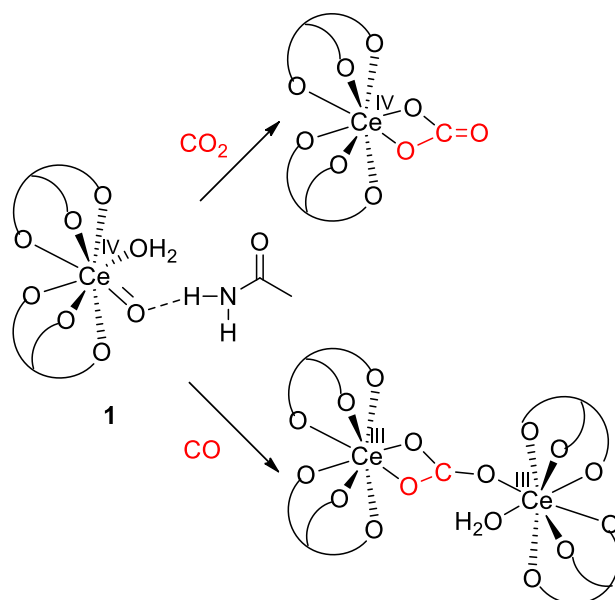
Scheme 1. Reactions of the Ce(IV) oxo complex **1** with CO_2 and CO[22]

In previous work, we found that the hydrogen bond between the co-crystallized acetamide and the oxo plays an important role in stabilizing the Ce=O moiety in **1** in the solid state. It is therefore of interest to examine the effect of redox-inactive metal ions on the stability/reactivity of the Ce=O moiety in **1**. Recent studies have shown that redox-inactive metal cations can modulate the redox chemistry and reactivity of transition-metal oxo complexes.[24] For example, the binding of Sc^{3+} has a profound influence on the electron and

oxo transfer chemistry of iron-oxo species.[25] Bimetallic Ce^{IV}-O-M (M = Li, Na, K) complexes have been prepared by oxidation of the Ce(III) amides $[Ce(NR_2)_3]$ (R = trialkylsilyl) with oxidants at low temperature by Lappert and coworkers. However, these Ce(IV)-O-M complexes are highly air and thermally unstable, and their reactivity has not been studied.[17a] Herein, we report the isolation and structure of a bimetallic Ce/Na oxo complex $[(L_{OEt})_2(Me_2CONH_2)Ce^{IV}(O)NaL_{OEt}]$ that features a polarized Ce-O multiple bond. The electronic structure and stability of this tripod-supported Ce(IV)-O-Na complex has been analyzed by DFT calculations.

Results and Discussion

Reactions of 1 with Electrophiles. As reported previously, **1** possesses a polarized Ce=O multiple bond and exhibits nucleophilic behavior. Since **1** decomposes easily in nonpolar solvents such as hexanes but is stable in MeCN (vide infra), the reactions of **1** with electrophiles (Scheme 2) in MeCN were investigated.
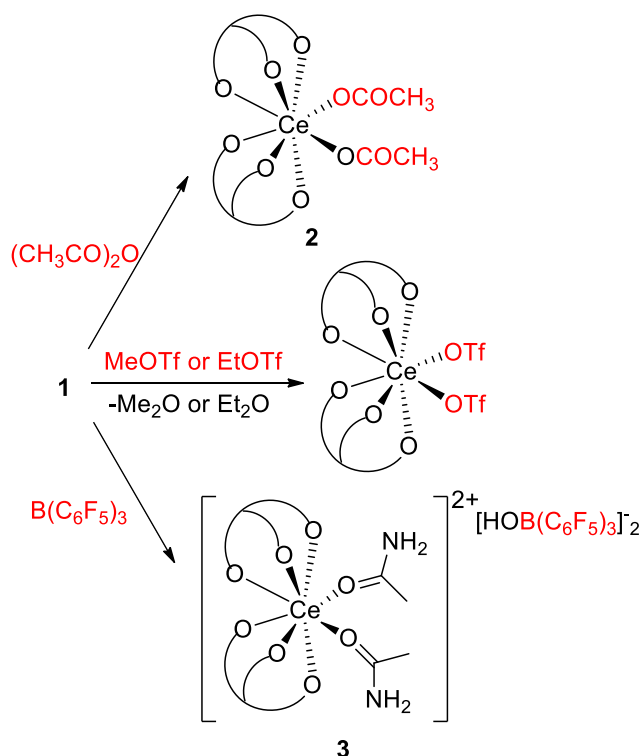
Scheme 2. Reactivity of **1** toward Electrophiles

Treatment of **1** in acetonitrile with acetic anhydride afforded the diacetate complex [Ce^{IV}(L$_{OEt}$)$_2$(O$_2$CMe)$_2$] (**2**), apparently via the nucleophilic attack of acetic anhydride by Ce=O and subsequent coordination of the dissociated acetate to Ce. The ^{1}H NMR spectrum of **2** displayed well-resolved signals corresponding to the L$_{OEt}^-$ ligands and a singlet at δ 2.0 ppm due to the acetate ligands. The IR spectrum showed the ν(C-O) bands of the acetate ligands at 1574 and 1641 cm^{-1}. Similarly, upon treatment with methyl triflate at -40 ^{o}C, a yellow acetonitrile solution of **1** turned red immediately. Recrystallization from hexanes afforded red crystals that were identified as the ditriflate complex [Ce^{IV}(L$_{OEt}$)$_2$(OTf)$_2$] in 38% yield. A higher yield (>80%) of [Ce^{IV}(L$_{OEt}$)$_2$(OTf)$_2$] was obtained if 2 equiv or more methyl triflate was employed. It seems likely that the reaction of **1** with methyl triflate initially gave a methoxy intermediate, "Ce(L$_{OEt}$)$_2$(OMe)(OTf)", that further reacted with methyl triflate to yield the ditriflate product. Although we were not able to identify the gaseous by-product Me$_2$O, Et$_2$O has been detected in the reaction of **1** with ethyl triflate in CD$_3$CN by ^{1}H NMR spectroscopy.

The treatment of **1** in acetonitrile with BPh$_3$ resulted in the formation of an intractable material. On the other hand, **1** reacted with 2 equiv of B(C$_6$F$_5$)$_3$ to give the dicationic complex [Ce(L$_{OEt}$)$_2$(MeCONH$_2$)$_2$][B(C$_6$F$_5$)$_3$(OH)]$_2$ (**3**) containing two [B(C$_6$F$_5$)$_3$(OH)]$^-$ anions. The formation of **3** possibly involved the electrophilic attack of the oxo ligand in **1** by B(C$_6$F$_5$)$_3$. Subsequent cleavage of the Ce-OB(C$_6$F$_5$)$_3$ bond and binding of the co-crystallized acetamide in **1** yielded the bis(acetamide) product **3**. It should be noted that cationic Ce(IV) complexes are rather rare, owing to the facile Ce(IV/III) reduction.[26] Apparently, the electron-releasing ability of the acetamide ligand together with the hydrogen bond between the acetamide ligands and the [B(C$_6$F$_5$)$_3$(OH)]$^-$ anions (vide infra) helps stabilize the dicationic complex **3**. Figure 1 shows the crystal structure of **3**. The Ce-O(L$_{OEt}$) bond distances in **3** (av. 2.306 Å) are shorter than that of the charge-neutral [Ce^{IV}(L$_{OEt}$)$_2$Cl$_2$] (av. 2.341 Å). The acetamide

ligands are O-bonded, and the Ce-O(acetamide) distances in **3** are 2.390(2) Å that are shorter than that in $[Ce^{III}\{MeC(O)NH_2\}_4(H_2O)_4][I]_3$ (av. 2.418 Å).[27] The B-OH bond distances in **3** [1.468(5) and 1.476(5) Å] are normal by comparison with that in $[K(dibenzo-18-crown-6)][HOB(C_6F_5)_3]$ [1.480(11) Å].[28] The NH_2 groups in the acetamide ligands are H-bonded to the $[(HO)B(C_6F_5)_3]^-$ anions with an average N⋯O separation of 2.792 Å.
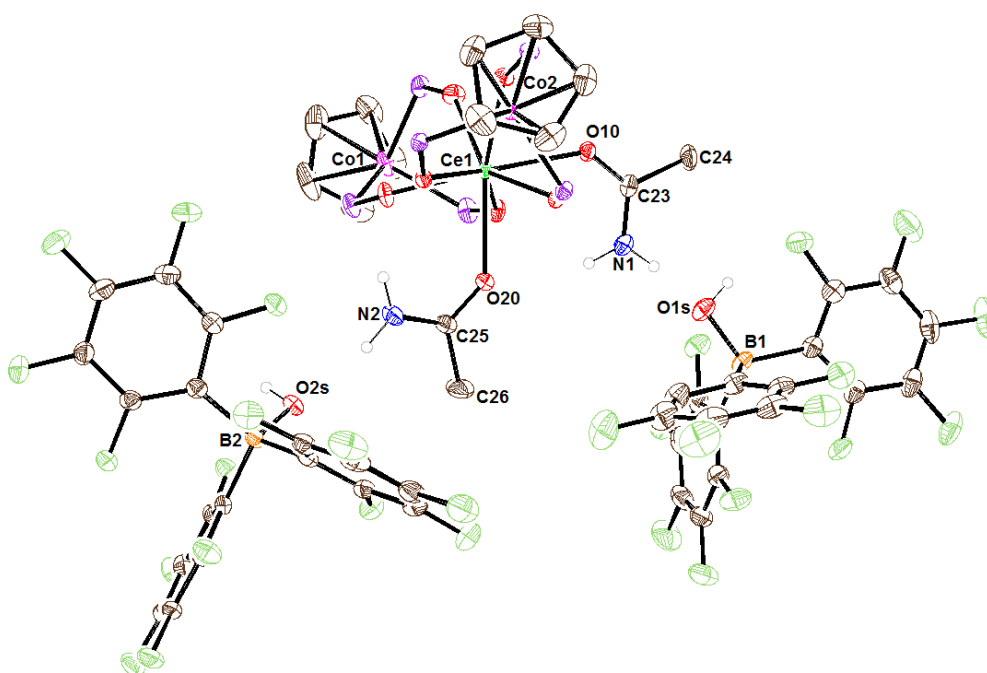
Figure 1. Molecular structure of **3**. Ethoxy groups of L_{OEt}^- and hydrogen atoms (except those of the hydroxide and acetamide) are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Ce(1)-O(7) 2.298(2), Ce(1)-O(8) 2.341(2), Ce(1)-O(9) 2.275(3), Ce(1)-O(17) 2.330(2), Ce(1)-O(18) 2.316(2), Ce(1)-O(19) 2.275(2), Ce(1)-O(10) 2.390(2), Ce(1)-O(20) 2.390(2); O(10)-Ce(1)-O(20) 101.41(8); H-bond distances (Å): N(1) ⋯O(1S) 2.732(4), N(2) ⋯O(2S) 2.852(4).

Similar to Ti(IV) terminal oxo complexes,[29] **1** is reactive toward aldehydes such as benzaldehyde, as evidenced by NMR spectroscopy. However, we were not able to crystallize and characterize the product of the reaction of **1** with benzaldehyde. No reaction was found between **1** and ketones (e.g. acetophenone) or alkynes (e.g. diphenylacetylene).

Reactions of 1 with Brønsted Acids. The oxo ligand in **1** is basic and can be easily protonated by Brønsted acids (Scheme 3).
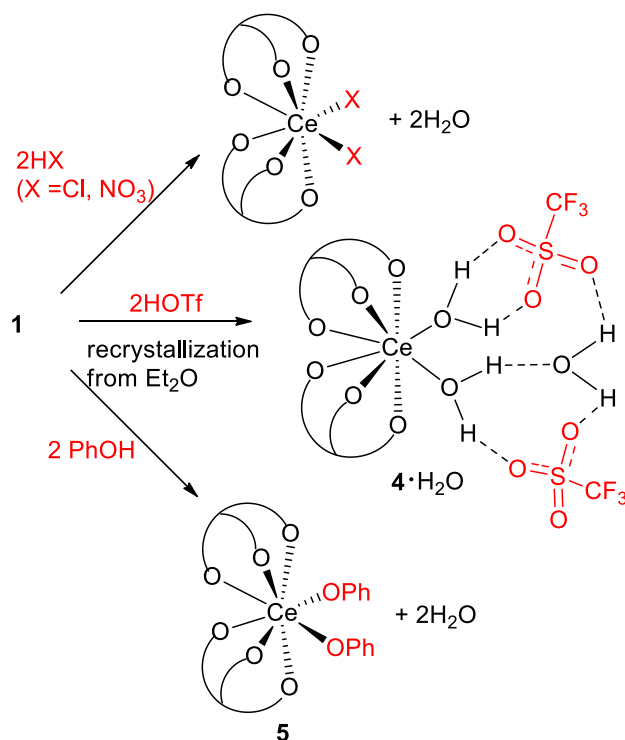
Scheme 3. Reactions of **1** with Brønsted Acids

Protonation of **1** with strong acids such as HCl and HNO_3 gave the reported chloride $[Ce^{IV}(L_{OEt})_2Cl_2]$ and nitrate $[Ce^{IV}(L_{OEt})_2(NO_3)_2]$ complexes, respectively. On the other hand, the treatment of **1** with triflic acid, followed by recrystallization from Et_2O led to isolation of the diaqua compound $[Ce^{IV}(L_{OEt})_2(H_2O)_2](OTf)_2$ (**4**). Complex **4** is soluble in both water and common organic solvents except hexanes. To our knowledge, **4** is the first dicationic Ce(IV) aqua complex characterized by X-ray diffraction. The ^1H NMR spectrum of **4** displayed a sharp singlet at δ 2.69 ppm attributable to the aqua ligands. The crystal structure of **4**·H_2O is

shown in Figure 2. The average Ce-O(L_{OEt}) bond distance (2.285 Å) is similar to those in **3**. The Ce-OH$_2$ distances [2.475(4) and 2.466(4) Å] are shorter than that of the charge-neutral complex **1** [2.572(3) Å], but within the range for reported Ce(IV) aqua complexes [2.379(2) - 2.597(9) Å].[30] The triflate anions are H-bonded to the aqua ligands and a co-crystallized water molecule.
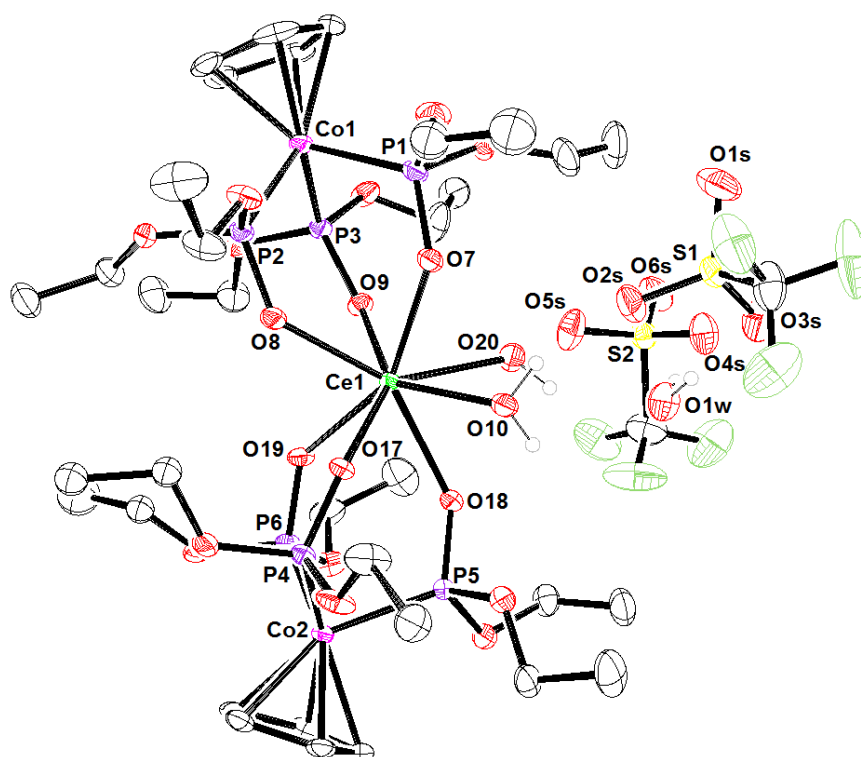
Figure 2. Molecular structure of **4**·H$_2$O. Hydrogen atoms (except those of the aqua ligands) are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Ce(1)-O(7) 2.262(4), Ce(1)-O(8) 2.298(4), Ce(1)-O(9) 2.265(3), Ce(1)-O(17) 2.285(3), Ce(1)-O(18) 2.310(4), Ce(1)-O(19) 2.291(4), Ce(1)-O(10) 2.475(4), Ce(1)-O(20) 2.466(4); O(10)-Ce(1)-O(20) 73.81(14); H-bond distances (Å): O(10)···O(2S) 2.695(6), O(20)···O(5S) 2.837(6), O(20)···O(1W) 2.711(6), O(1W)···O(3S) 2.855(7), O(1W)···O(4S) 2.876(7).

1 can also be protonated with weaker oxo acids such as phenol. For example, the reaction of **1** with 2 equiv of phenol resulted in an immediate color change from yellow to deep purple. Recrystallization from hexanes yielded a purple crystalline solid characterized as the phenoxide complex $[Ce^{IV}(L_{OEt})_2(OPh)_2]$ (**5**). No reactions were found between **1** and aliphatic alcohols such as ethanol and isopropanol.

Redox Reactions. The redox potential of **1** has not been determined because the compound decomposes rapidly in supporting electrolytes such as $[nBu_4N]PF_6$ in acetonitrile. No reaction was found between **1** and ferrocene (Fc) or 1,1'-dimethylferrocene ($E_{1/2}$ = -0.11 V vs. $Fc^{+/0}$, MeCN), but **1** can be reduced to a Ce(III) species by decamethylferrocene ($E_{1/2}$ = -0.48 V vs. $Fc^{+/0}$, MeCN), indicating that the redox potential of **1** lies between -0.11 and -0.48 V vs. $Fc^{+/0}$. However, upon protonation with acids such as triflic acid, **1** can oxidize ferrocene to ferrocenium. This is understandable as protonation of **1** gives a cationic Ce(IV) aqua species that is a stronger oxidizing agent than **1**. For example, the Ce(IV/III) redox potential for **4** in acetonitrile was determined to be +0.20 V vs. $Fc^{+/0}$. Accordingly, complex **4** is readily reduced by ferrocene to afford a Ce(III) complex (δ^P 170.8 ppm). **1** cannot oxidize organic substrates such as triphenylphosphine, phenyl methylsulfide, styrene, and dihydroanthracene.

Bimetallic Ce/Na Oxo Complex. To study the influence of redox-inactive metal ions on the bonding and reactivity of the Ce=O complex, efforts have been made to synthesize bimetallic Ce(IV)-O-Na compounds. The treatment of **1** with $[NaL_{OEt}]$ afforded the oxo-bridged bimetallic Ce/Na oxo complex $[(L_{OEt})_2(Me_2CONH_2)Ce^{IV}(O)NaL_{OEt}]$ (**6**) (Scheme 4), which was obtained as yellow crystals after recrystallization from hexanes. Alternatively, **6** could be synthesized in high yield (>80%) by reacting $[Ce(L_{OEt})_2Cl_2]$ with Ag_2O and acetamide in acetonitrile, followed by treatment with $[NaL_{OEt}]$.
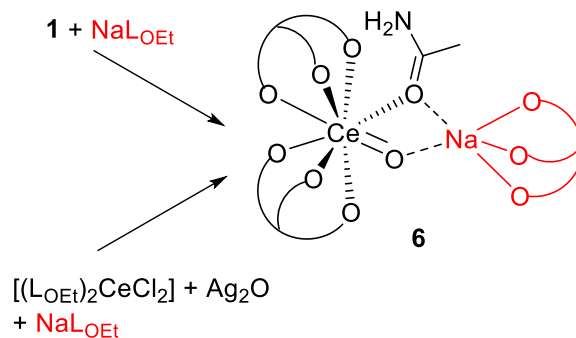
Scheme 4. Synthesis of Bimetallic Ce/Na oxo complex **6**

The ^{31}P $\{^1H\}$ NMR spectrum of **6** displayed two resonances at δ 112.7 and 105.2 ppm that are assigned to the Ce- and Na-bound L$_{OEt}^-$ ligands, respectively.[31] The solid-state structure of **6** is depicted in Figure 3. The $\{NaL_{OEt}\}$ fragment binds to the $\{(L_{OEt})_2Ce(=O)(MeCONH_2)\}$ moiety via the oxo and acetamide oxygen atom. As expected, the binding of the $\{NaL_{OEt}\}$ fragment results in lengthening of the Ce-O(oxo) bond. The Ce-O(oxo) distance in **6** of 1.953(4) Å is longer than that in **1** [1.857(3) Å] but comparable to that in a related oxo-bridged Ce/Na amido complex [$\{(R_2N)_3Ce\}_2(\mu$-ONaONa)] (R = SiMe$_3$)] [1.948(4) Å].[17a] The Ce-O(acetamide) distance in **6** [2.507(3) Å] is longer than that in **3** that contains terminal acetamide ligands. The Na-O(oxo) and Na-O(acetamide) distances are 2.341(4) and 2.511(4) Å, respectively.
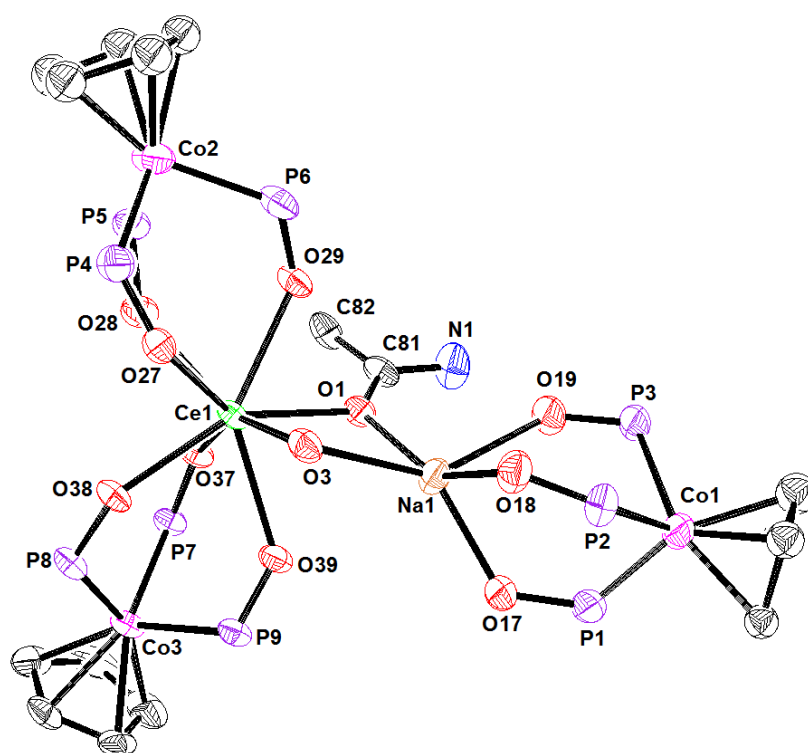
Figure 3. Molecular structure of **6**. Ethoxy groups of the tripodal ligands and hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Ce(1)-O(3) 1.953(4), Ce(1)-O(1) 2.507(3), Na(1)-O(3) 2.341(4), Na(1)-O(1) 2.511(4), Ce(1)-O(L_{OEt}) 2.402(3)-2.574(4), Na(1)-O(L_{OEt}) 2.266(6)-2.393(7), O(1)-C(81) 1.259(6), N(1)-C(81) 1.289(8), C(82)-C(81) 1.470(9); O(3)-Ce(1)-O(1) 81.93(14), O(3)-Na(1)-O(1) 74.91(15), Ce(1)-O(3)-Na(1) 111.18(19), Ce(1)-O(1)-Na(1) 90.03(13).

DFT Calculations. DFT calculations were performed in order to understand the influence of the {NaL$_{OEt}$} moiety on the electronic structure and stability of the Ce=O complex. The natural bond orbital (NBO) analysis on the basis of the DFT calculated wavefunctions shows a double bond associated with the cerium-oxo moiety in the model compound [(L$_{OMe}$)$_2$Ce^{IV}(Me$_2$CONH$_2$)(O)NaL$_{OMe}$] (**6A**), similar to what we found earlier for [(L$_{OMe}$)$_2$Ce(O)(H$_2$O)(Me$_2$CONH$_2$)] (**1A**), which is a model of **1**.[22] The NBO results also show that the Ce-oxo σ- and π-bonds in **6A** are mostly localized on the oxygen [σ: Ce 5*d*/4*f* (6.3%

13

5d and 11.1% 4f) and O 2p (83.7%); π. Ce 5d/4f (6.9% 5d and 9.1% 4f) and O 2p (79.9%)].

Like **1A**, the Ce-oxo moiety in **6A** can be described as a polarized Ce=O multiple bond. Consistent with this bonding description, **6** exhibits nucleophilic behavior. For example, as described above, **6** reacts with CO_2 and acetic anhydride to give $[Ce^{IV}(L_{OEt})_2(CO_2)]$ and $[Ce^{IV}(L_{OEt})_2(CH_3CO_2)_2]$, respectively. Also, **6** can be reduced by decamethylferrocene but does not react with 1,1'-dimethyferrocene. Treatment of **6** with CO gave a Ce(III) carbonate species. Therefore, it appears that the binding of the {NaL$_{OEt}$} fragment does not have a big influence on the nucleophilic and redox properties of the Ce(IV)-oxo complex.

To understand the factors affecting the stability of the Ce=O complex in solution (see later section), the dissociation energy of the {NaL$_{OMe}$} fragment from **6A** was calculated (Scheme 5). The energy for dissociation of the {NaL$_{OMe}$} fragment from **6A** was calculated to be +33.7 kcal/mol (eq 1). On the other hand, the dissociation energy for the H-bonded acetamide in $[(L_{OMe})_2Ce(O)(H_2O)(Me_2CONH_2)]$ (**1A**) was calculated to be +17.4 kcal/mol (eq 2). These results show the binding of the {NaL$_{OMe}$} fragment in **6A** is much stronger than the binding of H-bonded acetamide in **1A**, and may explain why **1**, upon dissociation of the H-bonded acetamide, is not stable in hexanes and rearranges to a tetranuclear cluster readily (vide infra), whereas the Ce-O-Na complex **6** is stable in solution.
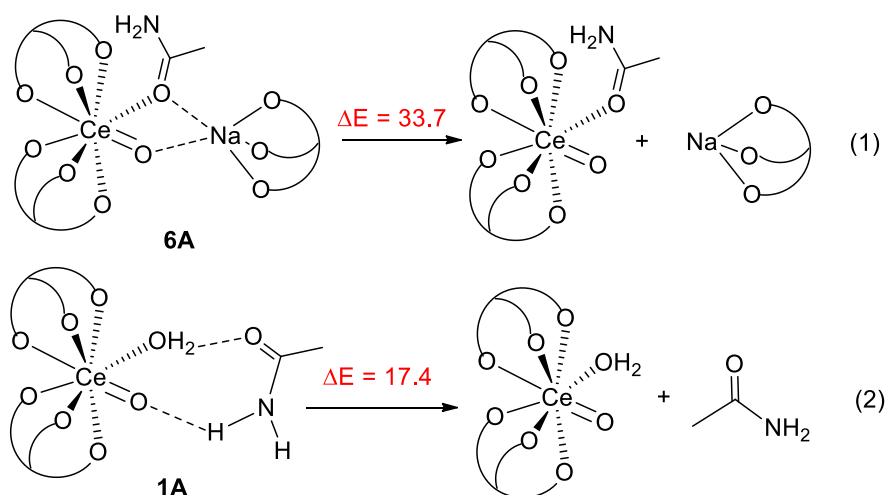
Scheme 5. Calculated Dissociation Energies ΔE (kcal/mol) for **6A** and **1A**

Our previous DFT study showed that the dihydroxy compound $[Ce(L_{OMe})_2(OH)_2]$ is slightly more stable than the oxo-aqua analogue $[Ce(L_{OMe})_2(O)(H_2O)]$ by just ca. 0.9 kcal/mol in the gas phase (0.1 kcal/mol taking into account the solvation effect), whereas in the presence of an H-bonded acetamide the latter is more stable than the former by 3.1 kcal/mol (3.6 kcal/mol taking into account the solvation effect).[22] The relatively small energy difference between the oxo-aqua and dihydroxy forms indicate that these two species can be in equilibrium in solution. This may raise a question as to whether the observed reactivity of **1** is originated from the Ce=O or Ce-OH functionality. The finding that the aqua-free complex **6** that possesses a polarized Ce=O multiple bond but does not equilibrate with a hydroxy species exhibits the same reactivity as **1** lends further support that the nucleophilic reactivity of the Ce-oxo complex is originated from the Ce=O group.

Decomposition of 1 in Nonpolar Solvents. Although **1** is quite stable in polar solvents such as acetonitrile and acetone, it decomposes easily in non-polar, non-coordinating solvents such as hexanes and benzene, as evidenced by NMR spectroscopy. The stability of **1** in polar solvents is presumably due to solvation effects and H-bonding between the polar Ce=O group and solvent. Close examination revealed that the degradation of **1** in hexanes is critically dependent upon adventitious water present in the solvent/glassware. In fact, **1** was found to be reasonably stable in vigorously dried hexanes under strictly anhydrous conditions,[32] but it decomposes readily if water is added (vide infra). By contrast, water has no effect on the stability of **1** in acetonitrile under the same conditions. It seems possible that water plays a role in the Ce=O/Ce-OH tautomerization of the Ce=O complex in hexanes that facilitates the conversion of **1** to a cluster (vide infra).

The decomposition of **1** in hexanes (containing adventitious water) at room temperature has been monitored by ^{31}P NMR spectroscopy (see Supporting Information). During the course of the decomposition, the signal of **1** (δ^P 112.7 ppm) dropped while new signals due to

a diamagnetic Ce(IV) species (**7**, δ^P 115.7 ppm) and a paramagnetic Ce(III) species (**8**, δ^P 154.3 ppm) appeared. In addition, a singlet corresponding to free L_{OEt}^- (δ^P 104.4 ppm) along with some unidentified weak peaks were observed. The signal of **1** disappeared completely in ca. 4 h. The resulting solution was found to contain mainly **7**, **8**, and free L_{OEt}^-. The degradation of **1** in hexanes appeared to display very complex kinetics dependent on many factors that are not well understood at this point. The degradation is obviously accelerated by water. If water (0.01 mL) was added to the reaction mixture, the conversion of **1** into **7**, **8**, and L_{OEt}^- in hexanes completed within 5 min. The MALDI mass spectrum of the decomposition product mixture showed signals at *m/z* 2814 and 1210 corresponding to $[(L_{OEt})_4Ce_4(\mu_4\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-OH})_2]^+$ and $[Ce(L_{OEt})_2]^+$, respectively. The ^{31}P NMR resonance for **7** at δ^P 115.7 ppm is identical with that of the tetranuclear oxo cluster $[(L_{OEt})_4Ce_4(\mu_4\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-OH})_2]$ that was synthesized previously by reaction of $[Ce(L_{OEt})(NO_3)_3]$ with Et_4NOH in MeCN,[33] whereas the resonance for **8** (δ^P 154.3 ppm) is close to that of the Ce(III) aqua compound $[Ce^{III}(L_{OEt})_2(H_2O)_2]Cl$ (δ^P 157 ppm).[33]

Cooling the final reaction mixture at -10 ℃ led to isolation of yellow crystals that were identified as an inseparable mixture of a tetranuclear cluster, $[(L_{OEt})_4Ce_4(\mu_4\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-OH})_2]\cdot MeC(O)NH_2$, and a mononuclear Ce(III) compound, $[Ce^{III}(L_{OEt})_2(H_2O)_2](L_{OEt})$, by X-ray diffraction (Scheme 6). These two species have very similar solubility and we have not been able to separate them cleanly by recrystallization. The molecular structure of $[Ce^{III}(L_{OEt})_2(H_2O)_2](L_{OEt})$ containing a L_{OEt}^- anion that is H-bonded to the aqua ligands is shown in Figure 4. Unfortunately, due to severe disorder problems, the crystal structure of $[(L_{OEt})_4Ce_4(\mu_4\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-OH})_2]\cdot MeC(O)NH_2$ (see Supporting Information) has not been refined satisfactorily. Nevertheless, the identity of the tetranuclear cluster that features a $\{Ce_4(\mu_4\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-OH})_2\}$ core has been established. It should be noted that the structure of a related acetamide-free tetranuclear Ce(IV) oxo cluster, $[(L_{OEt})_4Ce_4(\mu_4\text{-O})(\mu_2\text{-O})_4(\mu_2\text{-OH})_2]$, has been reported by us recently.[33] On the basis of NMR

spectroscopy, mass spectrometry, and X-ray crystallography, the diamagnetic species **7** formed by the degradation of **1** in hexanes is assigned as $[(L_{OEt})_4Ce_4(\mu_4\text{-}O)(\mu_2\text{-}O)_4(\mu_2\text{-}OH)_2]$ that was co-crystallized with an acetamide molecule, whereas the paramagnetic species **8** is assigned as $[Ce^{III}(L_{OEt})_2(H_2O)_2]^+$ that was isolated as the L_{OEt}^- salt.

The conversion of **1** into the cluster **7** possibly involves a dihydroxy intermediate, $[Ce^{IV}(L_{OEt})_2(OH)_2]$ derived from the oxo-aqua tautomer, $[Ce^{IV}(L_{OEt})_2(O)(H_2O)]$, which is formed by dissociation of acetamide from **1**. Water may play a role in the oxo-aqua/dihydroxy tautomerization of **1** (vide supra). Ligand re-distribution of $[Ce^{IV}(L_{OEt})_2(OH)_2]$ gives "$[Ce^{IV}(L_{OEt})(OH)_3]$" and "$[Ce^{IV}(L_{OEt})_2(OH)](L_{OEt})$". Condensation of the former complex with elimination of water affords the tetranuclear cluster $[(L_{OEt})_4Ce_4(\mu_4\text{-}O)(\mu_2\text{-}O)_4(\mu_2\text{-}OH)_2],$[33] which is co-crystallized with an acetamide molecule. Reduction of "$[Ce^{IV}(L_{OEt})_2(OH)](L_{OEt})$" yields the Ce(III) aqua compound **8**(L_{OEt}). The nature of the reducing agent involved is not clear at this point. Attempts have been made to generate the reactive dihydroxy intermediate $[Ce^{IV}(L_{OEt})_2(OH)_2]$ by (a) reaction of the diqua compound **4** with 2 equiv Et₄NOH and (b) treatment of $[Ce^{IV}(L_{OEt})_2(NO_3)_2]$ with 2 equiv of Et₄NOH. Both reactions produced a mixture of $[(L_{OEt})_4Ce_4(\mu_4\text{-}O)(\mu_2\text{-}O)_4(\mu_2\text{-}OH)_2]$ and **8**(L_{OEt}) according to NMR spectroscopy, lending support for the involvement of the Ce(IV) hydroxy species in the decomposition of **1** in hexanes.
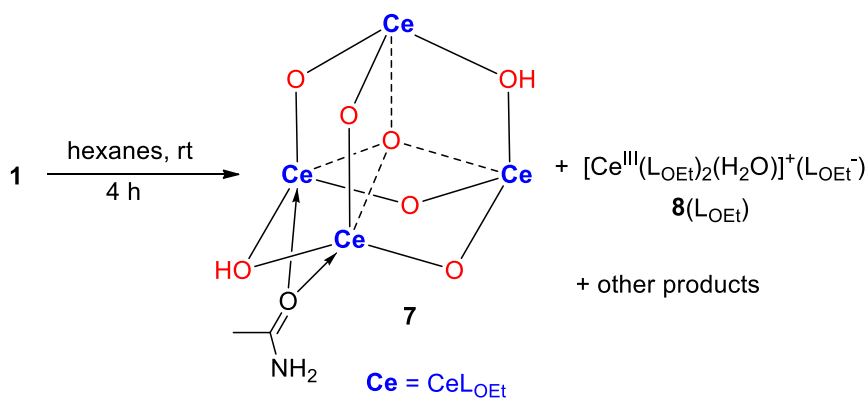
Scheme 6. Decomposition of **1** in Hexanes
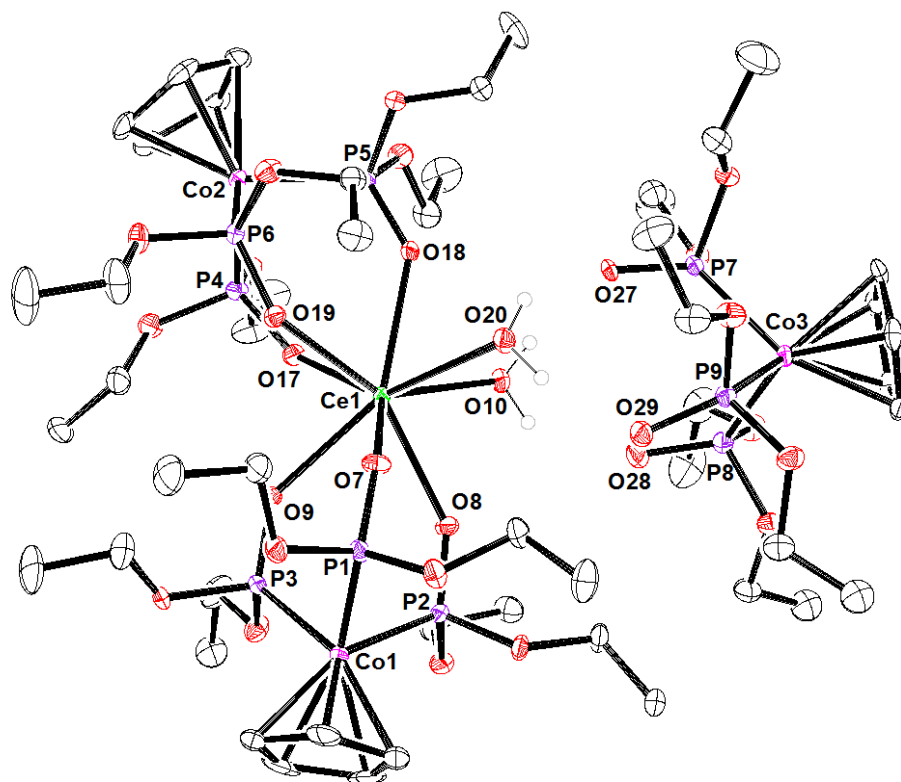
Figure 4. Molecular structure of **8**(L_{OEt}). Hydrogen atoms (except those on coordinated aqua ligands) are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): Ce(1)-O(L_{OEt}) 2.404(3)-2.516(3), Ce(1)-O(10) 2.531(3), Ce(1)-O(20) 2.579(3); H-bond distances (Å): O(10)···O(28) 2.682(5), O(10)···O(27) 2.792(5), O(20)···O(27) 2.843(4), O(20)···O(29) 2.678(5).

Concluding Remarks

In summary, we have investigated the reactivity of the Ce(IV)=O complex **1** toward electrophiles and Brønsted acids. Whereas an acetate complex was isolated from the acylation of **1** with acetic anhydride, further reactions were found for the electrophilic attack of **1** with the stronger electrophiles methyl triflate and B(C_6F_5)$_3$, which led to the formation of Ce(IV)

triflate and acetamide complexes, respectively. The oxo group in **1** can be protonated by Brønsted acids, including phenol, but is inert toward aliphatic alcohols. Protonation of **1** with triflic acid led to isolation of a cationic Ce(IV) aqua complex, which is a stronger oxidizing agent than the starting oxo complex. Treatment of **1** with NaL_{OEt} afforded an oxo-bridged Ce/Na bimetallic complex, **6**. DFT calculations indicated that **6** contains a polarized Ce=O multiple bond and the oxo group exhibits nucleophilic behavior. Like **1**, **6** reacted with CO_2 and CO to give Ce(IV) and Ce(III) carbonate complexes, respectively, thus indicating that the binding of the $\{NaL_{OEt}\}$ moiety does not have a big influence on the nucleophilic and redox properties of the Ce^{IV}=O complex. While **1** is reasonably stable in acetonitrile, it decomposes easily to a tetranuclear Ce(IV) oxo cluster, **7**, along with a Ce(III) aqua compound in hexanes, especially in the presence of water. It is believed that upon dissociation of the co-crystallized acetamide, the Ce=O complex is in equilibrium with a hydroxy species that condenses to the tetranuclear cluster **7** rapidly. By contrast, the Ce/Na oxo complex **6** is stable in hexanes presumably because the coordination of the $\{NaL_{OEt}\}$ moiety to Ce=O inhibits the Ce=O/Ce-OH tautomerization. The stabilization of polar metal-ligand multiple bonds with main group metal ions is well precedented.[34] For example, K-stabilized nucleophilic Ti(IV) terminal nitrido complexes have been isolated recently.[34a,b] It is anticipated that analogous unknown Ce(IV) terminal nitrido complexes stabilized with main group metal ions can be stable enough for isolation.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400, 376.5, and 162 MHz for ^1H, ^{19}F and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H), $CF_3C_6H_5$ (^{19}F) and H_3PO_4 (^{31}P), respectively. Infrared spectra were

recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, UK. Mass spectrum was recorded on a Waters Mass Spectrometer, with MALDI Micro MX module. The compounds $[(L_{OEt})_2Ce(=O)(H_2O)] \cdot MeC(O)NH_2$ (**1**),[22] $[NaL_{OEt}]$,[35] and $[Ce(L_{OEt})_2Cl_2]$[22] were prepared according to literature methods.

Synthesis of $[Ce(L_{OEt})_2(CH_3CO_2)_2]$ (2). To a solution **1** (50 mg, 0.038 mmol) in acetonitrile (10 mL) was added acetic anhydride (3.8 μL, 0.040 mmol) at 0 °C. The reaction mixture was stirred for 10 min and the solvent was removed in vacuo. Extraction of the residue with hexanes and cooling at -20 °C afforded yellow crystals. Yield: 44 mg (85 %). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.24 (t, J = 7.2 Hz, 36H, CH$_3$), 2.00 (s, 6H, CH_3CO$_2$), 4.11 (m, 24H, CH$_2$), 5.03 (s, 10H, Cp). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): δ 117.03 (s). IR (KBr, cm^{-1}): 1574 and 1641 [v(C-O)]. Anal. Calcd for $C_{38}H_{76}CeCo_2O_{22}P_6 \cdot H_2O$: C, 33.89; H, 5.84. Found: C, 33.49; H, 5.66.

Reaction of 1 with Methyl Triflate. To a solution of **1** (50 mg, 0.038 mmol) in acetonitrile (10 mL) was added methyl triflate (4.3 μL, 0.038 mmol) at 0 °C. The color of the solution changed from yellow to red immediately. Evaporation of the solvent gave a red solid, which was washed with hexanes and then extracted with CH$_2$Cl$_2$. Recrystallization from CH$_2$Cl$_2$/hexanes afforded red crystals. Yield: 21.8 mg (38 %). The product was characterized as $[Ce(L_{OEt})_2(OTf)_2]$ by NMR spectrosocpy and elemental analysis. ^{1}H NMR (400 MHz, CD$_3$CN, 25 °C): δ 1.28 (t, J = 7.2 Hz, 36H, CH$_3$), 4.08 (m, 24H, CH$_2$), 5.20 (s, 10H, Cp). ^{31}P {^{1}H} NMR (162 MHz, CD$_3$CN, 25 °C): δ 122.28 (s). ^{19}F {^{1}H} NMR (376.5 MHz, CD$_3$CN, 25 °C): δ -79.36 (s). Anal. Calcd for $C_{36}H_{70}CeCo_2F_6O_{24}P_6S_2$: C, 28.66; H, 4.68; Found: C, 28.34; H, 4.75. Alternatively, $[Ce(L_{OEt})_2(OTf)_2]$ has been prepared by the reaction of $[Ce(L_{OEt})_2Cl_2]$ and 2 equiv of AgOTf in MeCN in 88% yield. The NMR data of the product were identical with that prepared from **1** and methyl triflate.

NMR Reaction of 1 with Ethyl Triflate. To a solution of **1** (5 mg, 3.8 μmol) in CD$_3$CN

(0.4 mL) was added ethyl triflate (1.0 μL, 7.6 μmol) at 0 °C. The resulting red solution was shaken for 5 min and analyzed by NMR spectroscopy. ^{1}H NMR (400 MHz, CD$_3$CN, 25 °C): δ 1.12 (t, J = 7.2 Hz, 6H, O(CH$_2$$CH_3$)$_2$), 1.29 (t, J = 7.2 Hz, 36H, CH$_3$), 3.42 (q, J = 7.2 Hz, 4H, O(CH_2CH$_3$)$_2$), 4.09 (m, 24H, CH$_2$), 5.18 (s, 10H, Cp). ^{31}P {^{1}H} NMR (162 MHz, CD$_3$CN, 25 °C): δ 122.38 (s). ^{19}F {^{1}H} NMR (376.5 MHz, CD$_3$CN, 25 °C): δ -79.32 (s).

[Ce(L$_{OEt}$)$_2${MeC(O)NH$_2$}$_2$][B(C$_6$F$_5$)$_3$(OH)]$_2$ (3). To a solution of **1** (100 mg, 0.040 mmol) in acetonitrile (10 mL) was added B(C$_6$F$_5$)$_3$ (20.5 mg, 0.040 mmol) at room temperature. The color of the solution changed from yellow to orange immediately. Evaporation of the solvent gave an orange solid. Recrystallization from CH$_2$Cl$_2$/hexanes afforded orange single crystals. Yield: 38 mg (40 %). ^{1}H NMR (400 MHz, CD$_3$CN, 25 °C): δ = 1.28 (t, J = 7.2 Hz, 36H, CH$_3$), 1.87 (s, 6H, MeC(O)NH$_2$), 4.07 (m, 12H, CH$_2$), 5.19 (s, 10H, Cp), 5.69 (br., 2H, NH), 6.32 (br., 2H, NH). ^{31}P {^{1}H} NMR (162 MHz, CD$_3$CN, 25 °C): δ 122.18 (s). ^{19}F {^{1}H} NMR (376.5 MHz, CD$_3$CN, 25 °C): δ -167.88 (t), -164.05 (t), -136.61 (d). Anal. Calcd for C$_{74}$H$_{82}$B$_2$CeCo$_2$F$_{30}$N$_2$O$_{22}$P$_6$: C, 37.24; H, 3.46; N, 1.17. Found: C, 37.26; H, 3.52; N, 1.23.

Reaction of 1 with HCl. To a solution of **1** (50 mg, 0.038 mmol) in acetonitrile (10 mL) was added HCl (0.76 mL of a 0.1 M solution in Et$_2$O, 0.076 mmol) at 0 °C. The color of the solution changed from yellow to red immediately. Evaporation of the solvent gave a red solid. Recrystallization from hexanes afforded red crystals that were identified as the known compound [Ce(L$_{OEt}$)$_2$Cl$_2$][22] by NMR spectroscopy. Yield: 43 mg (88 %). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ 1.25 (t, J = 7.2 Hz, 36H, CH$_3$), 4.24 (m, 24H, CH$_2$), 5.05 (s, 10H, Cp). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): δ 118.4 (s).

Reaction of 1 with HNO$_3$. To a solution of **1** (50 mg, 0.038 mmol) in acetonitrile (10 mL) was added 0.1 M HNO$_3$ (0.76 mL, 0.076 mmol) at 0 °C. The color of the solution changed from yellow to red immediately. Evaporation of the solvent and recrystallization from hexanes afforded red crystals that were identified as the known compound

$[Ce(L_{OEt})_2(NO_3)_2]^{20}$ by NMR and IR spectroscopy. Yield: 37 mg (73 %). ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C): δ 1.31 (t, 36H, J = 7.2 Hz, CH$_3$), 4.14 (m, 24H, CH$_2$), 5.17 (s, 10H, Cp). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$, 25 ^{o}C): δ 123.4 (s). IR (KBr, cm^{-1}): 1384 [v(NO$_3$)].

Synthesis of [Ce(L$_{OEt}$)$_2$(OH$_2$)$_2$](OTf)$_2$ (4). To a solution of **1** (50 mg, 0.038 mmol) in acetonitrile (10 mL) was added triflic acid (7.0 μL, 0.076 mmol) at 0 ^{o}C. The color of the solution changed from yellow to red immediately. Evaporation of the solvent and recrystallization from Et$_2$O afforded red single crystals that were identified as **4**·H$_2$O. Yield: 53 mg (86 %). ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C): δ 1.29 (t, J = 7.2 Hz, 36H, CH$_3$), 2.69 (s, 4H, H$_2$O), 4.12 (m, 24H, CH$_2$), 5.13 (s, 10H, Cp). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$, 25 ^{o}C): δ 121.16 (s). ^{19}F {^{1}H} NMR (376.5 MHz, CDCl$_3$, 25 ^{o}C): δ -78.33 (s). Anal. Calcd for C$_{36}$H$_{74}$CeCo$_2$O$_{26}$P$_6$S$_2$·H$_2$O: C, 27.67; H, 4.90. Found: C, 27.45; H, 5.01.

Synthesis of [Ce(L$_{OEt}$)$_2$(OPh)$_2$] (5). To a solution of **1** (50 mg, 0.038 mmol) in acetonitrile (10 mL) was added phenol (7.5 mg, 0.080 mmol) at room temperature. The color of the solution changed from yellow to deep purple immediately. Evaporation of the solvent and recrystallization from hexanes afforded dark purple crystals. Yield: 45 mg (81 %). ^{1}H NMR (400 MHz, CD$_3$CN, 25 ^{o}C): δ 1.12 (t, J = 7.2 Hz, 36H, CH$_3$), 3.96 (m, 12H, CH$_2$), 4.08 (m, 12H, CH$_2$), 4.99 (s, 10H, Cp), 6.26 (tt, J = 7.2, 1.2 Hz, 2H, H$_p$), 6.67 (dt, J = 8.6, 1.0 Hz, 4H, H$_o$), 6.98 (t, J = 7.2, 1.2 Hz, 4H, H$_m$). ^{31}P {^{1}H} NMR (162 MHz, CD$_3$CN, 25 ^{o}C): δ 114.17 (s). Anal. Calcd for C$_{46}$H$_{80}$CeCo$_2$O$_{20}$P$_6$: C, 39.55; H, 5.77. Found: C, 39.76; H, 5.74.

[(L$_{OEt}$)$_2$(MeC(O)NH$_2$)Ce(O)Na(L$_{OEt}$)] (6). A mixture of [Ce(L$_{OEt}$)$_2$Cl$_2$] (100 mg, 0.078 mmol), Ag$_2$O (18 mg, 0.078 mmol), acetamide (23 mg, 0.39 mmol), and NaL$_{OEt}$ (43.5 mg, 0.078 mmol) in acetonitrile (10 mL) containing 0.1 mL of water was stirred at room temperature for 1 h. The AgCl formed was filtered off. The solvent was removed in vacuo, and the residue was extracted with hexanes. Concentration afforded a yellow crystalline solid. recrystallization from hexanes at -20 ^{o}C afforded yellow single crystals. Yield: 131 mg (91 %). ^{1}H NMR (400 MHz, CD$_3$CN, 25 ^{o}C): δ1.18 (t, J = 7.2 Hz, 18H, CH$_3$ of NaL$_{OEt}$), 1.20 (t, J

= 7.2 Hz, 36H, CH$_3$ of CeL$_{OEt}$), 1.77 (br., 6H, *Me*C(O)NH$_2$), 3.93 (m, 12H, CH$_2$ of NaL$_{OEt}$), 4.05 (m, 24H, CH$_2$ of CeL$_{OEt}$), 4.92 (s, 5H, Cp of NaL$_{OEt}$), 5.05 (s, 10H, Cp of CeL$_{OEt}$), 5.47 (br., 2H, NH), 6.01 (br., 2H, NH). ^{31}P {^{1}H} NMR (162 MHz, CD$_3$CN, 25 ^{o}C): δ 105.18 (s, NaL$_{OEt}$), 112.67 (s, CeL$_{OEt}$). Anal. Calcd for C$_{53}$H$_{110}$CeCo$_3$NNaO$_{29}$P$_9$·MeC(O)NH$_2$: C, 34.71; H, 6.09; N, 1.47. Found: C, 34.63; H, 6.89; N, 1.37. Alternatively, **6** could be synthesized by the treatment of **1** (50 mg, 0.038 mmol) with NaL$_{OEt}$ (21 mg, 0.038 mmol) in acetonitrile (5 mL). The mixture was stirred at room temperature for 15 min. The solvent was removed in vacuo and the residue was extracted with hexanes. Concentration afforded a yellow crystalline solid. Yield: 63 mg, 90%.

Reaction of 6 with Acetic Anhydride. To a solution of **6** (50 mg, 0.026 mmol) in acetonitrile (10 mL) was added acetic anhydride (2.5 μL, 0.026 mmol) at 0 ^{o}C. The reaction mixture was stirred for 10 min and the solvent was removed in vacuo. Extraction of the residue with hexanes and slow evaporation of the solvent gave a yellow solid in ca. 87 % yield (with respect to **6**) that was identified as an inseparable mixture of **2** and [NaL$_{OEt}$] by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C): δ 1.17 (t, *J* = 7.2 Hz, 18H, CH$_3$ of NaL$_{OEt}$), 1.24 (t, *J* = 7.2 Hz, 36H, CH$_3$ of CeL$_{OEt}$), 2.00 (s, 6H, *CH$_3$*CO$_2$), 3.93 (m, 12H, CH$_2$ of NaL$_{OEt}$), 4.11 (m, 24H, CH$_2$ of CeL$_{OEt}$), 4.92 (s, 5H, Cp of NaL$_{OEt}$), 5.03 (s, 10H, Cp of CeL$_{OEt}$). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$, 25 ^{o}C): δ 105.21 (s, NaL$_{OEt}$), 117.03 (s, CeL$_{OEt}$).

Reaction of 6 with HCl. To a solution of **6** (50 mg, 0.026 mmol) in acetonitrile (10 mL) was added HCl (0.52 mL of a 0.1 M solution in Et$_2$O, 0.052 mmol) at 0 ^{o}C. The color of the solution changed from yellow to red immediately. The solvent was removed in vacuo, extraction of the residue with hexanes and slow evaporation of the solvent gave an orange solid in ca. 88% yield (with respect to **6**) that was identified as an inseparable mixture of the known compound [Ce(L$_{OEt}$)$_2$Cl$_2$][22] and [NaL$_{OEt}$] by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C): δ 1.17 (t, *J* = 7.2 Hz, 18H, CH$_3$ of NaL$_{OEt}$), 1.25 (t, *J* = 7.2 Hz, 36H, CH$_3$ of CeL$_{OEt}$), 3.92 (m, 12H, CH$_2$ of NaL$_{OEt}$), 4.24 (m, 24H, CH$_2$ of CeL$_{OEt}$), 4.92 (s, 5H, Cp of

NaL_{OEt}), 5.05 (s, 10H, Cp of CeL_{OEt}). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 105.21 (s, NaL_{OEt}), 118.40 (s, CeL_{OEt}).

Reaction of 6 with CO₂. A solution of **6** (50 mg, 0.026 mmol) in acetonitrile (10 mL) was bubbled with carbon dioxide for 3 min at room temperature. The color of the solution changed from yellow to orange immediately. The solvent was removed in vacuo, and the residue was extracted with hexanes. Slow evaporation of the solvent gave an orange solid in ca. 85% yield (with respect **6**) that was identified as an inseparable mixture of the reported carbonate compound $[Ce(L_{OEt})_2(CO_3)]\cdot MeC(O)NH_2$ and $[NaL_{OEt}]$ by NMR spectroscopy. ^1H NMR (400 MHz, CD_3CN, 25 °C): δ 1.18 (t, J = 7.2 Hz, 18H, CH_3 of NaL_{OEt}), 1.23 (t, J = 7.2 Hz, 36H, CH_3 of CeL_{OEt}), 1.81 (s, 3H, $MeC(O)NH_2$), 3.93 (m, 12H, CH_2 of NaL_{OEt}), 4.08 (m, 24H, CH_2 of CeL_{OEt}), 4.92 (s, 5H, Cp of NaL_{OEt}), 5.06 (s, 10H, Cp of CeL_{OEt}), 5.52 (br., 1H, NH), 6.10 (br., 1H, NH). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 105.27 (s, NaL_{OEt}), 116.46 (s, CeL_{OEt}).

Reaction of 6 with CO. A solution of **6** (50 mg, 0.026 mmol) in acetonitrile (10 mL) was bubbled with carbon monoxide for 15 min at room temperature. The color of the solution changed from yellow to pale yellow. The solvent was removed in vacuo, and the residue was extracted with hexanes. Concentration (to ca. 2 mL) and cooling the solution at 0 °C afforded a yellow solid in ca. 76% yield (with respect to **6**) that was identified as an inseparable mixture of the reported Ce(III) carbonate compound $[(L_{OEt})_2Ce(\mu\text{-}CO_3)Ce(H_2O)(L_{OEt})_2]$ and $[NaL_{OEt}]$ by NMR spectroscopy. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ -0.12 (br., 72H, CH_3 of CeL_{OEt}), 1.18 (t, J = 7.2 Hz, 36H, CH_3 of NaL_{OEt}), 1.91 (br., 24H, CH_2 of CeL_{OEt}), 2.33 (br., 24H, CH_2 of CeL_{OEt}), 3.94 (m, 24H, CH_2 of NaL_{OEt}), 4.92 (s, 10H, Cp of NaL_{OEt}), 10.84 (br., 20H, Cp of CeL_{OEt}). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 105.26 (s, NaL_{OEt}), 154.45 (s, CeL_{OEt}).

Decomposition of 1 in Hexanes. To **1** (10 mg) in a 5-mm NMR tube sealed with a septum was added hexanes (1 mL) via a syringe. The reaction mixture was left to stand at

During the course of the reaction, the signal due to **1** dropped while new signals attributable to a Ce(IV) (δ^P 115.7 ppm) species, a Ce(III) (δ^P 154.3 ppm) species, and free L_{OEt}^- (δ^P 104.4 ppm) appeared. The signals of **1** disappeared in ca. 4 h. Cooling the product mixture at -10 ^{o}C led to isolation of yellow crystals (ca. 20 mg) that were identified as an inseparable mixture of [Ce$_4$(L$_{OEt}$)$_4$(μ_4-O)(μ-O)$_4$(μ-OH)$_2${MeC(O)NH$_2$}] (**7**) and [Ce(L$_{OEt}$)$_2$(H$_2$O)$_2$](L$_{OEt}$) (**8**(L$_{OEt}$)) by X-ray crystallography. Another crop of yellow crystals could be obtained after cooling the mother liquor at -10 ^{o}C for a couple of days. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ^{o}C): δ -0.33 (br., 144H, CH$_3$ (**8$^+$**)), 1.16 (t, J = 7.2 Hz, 72H, CH$_3$ (L$_{OEt}^-$)), 1.23 (t, J = 7.2 Hz, 72H, CH$_3$ (**7**)), 1.46 (br., 48H, CH$_2$ (**8$^+$**)), 1.88 (br., 48H, CH$_2$ (**8$^+$**)), 2.00 (s, 3H, *Me*C(O)NH$_2$), 3.91 (m, 48H, CH$_2$ (L$_{OEt}^-$)), 4.00 (m, 48H, CH$_2$ (**7**), 4.94 (s, 20H, Cp (L$_{OEt}^-$)), 5.03 (s, 20H, Cp (**7**)), 11.60 (br., 40H, Cp (**8$^+$**)). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$, 25 ^{o}C): δ 106.65 (s, L$_{OEt}^-$), 117.50 (s, **7**), 157.90 (br., **8$^+$**). MALDI-MS: *m/z*: 2814 [(L$_{OEt}$)$_4$Ce$_4$(μ_4-O)(μ_2-O)$_4$(μ_2-OH)$_2$]$^+$, 1210 [Ce(L$_{OEt}$)$_2$]$^+$.

Attempted Synthesis of "[Ce^{IV}(L$_{OEt}$)$_2$(OH)$_2$]". *Method A*: To a solution of [Ce(L$_{OEt}$)$_2$(NO$_3$)$_2$] (50 mg, 0.037 mmol) in MeCN (10 mL) was added Et$_4$NOH (55 μL of a 1.37 M solution in water, 0.075 mmol) at -40 ^{o}C and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was pumped off and the residue was extracted with hexanes. Slow evaporation of the filtrate afforded a yellow solid (ca. 30 mg). The ^{31}P NMR spectrum of the yellow solid showed signals corresponding to **7** and **8$^+$** (see above section).

Method B: To a solution of **4** (50 mg, 0.032 mmol) in MeCN (10 mL) was added Et$_4$NOH (47 μL of a 1.37 M solution in water, 0.064 mmol) at -40 ^{o}C and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was pumped off and the residue was extracted with hexanes. Slow evaporation afforded a yellow solid (ca. 28 mg) that was found to contain **7** and **8$^+$** according to ^{31}P NMR spectroscopy.

DFT Calculations. Geometry optimizations have been performed at the Becke3LYP (B3LYP) level of the density functional theory.[36] Stuttgart/Dresden effective core potential and the associated basis sets were used to describe Co, Ce, Ag and P atoms.[37] Polarization functions were added for Ag (ζ_f = 1.611) and P (ζ_d = 0.387).[38] For simplicity, the methoxy substituted tripodal ligand $[CoCp\{P(O)(OMe)_2\}_3]^-$ (L_{OMe}^-) ligand was used to model L_{OEt}^-, and the STO-3G basis set was used for the C, O and H atoms in the L_{OMe} ligand except those O atoms directly bonded with the Ce center. The 6-31G(d) basis set was used for all of the other atoms. The calculations were performed with the Gaussian 09 software packages.[39] Natural population analysis was done by the NBO 6.0 program based on the optimized structures.[40]

X-ray Crystallography. Crystallographic data and refinement details for **3**, **4**, **6** and **8**(L_{OEt}) are listed in Supporting Information (Table S1). The diffraction intensity data of **3** was collected with a Rigaku SuperNova Atlas Ultra X-ray Diffractometer with monochromatized Cu-Kα radiation (λ = 1.54178 Å) at 173K. The diffraction intensity data of **4** was collected with a Rigaku Gemini™ S X-ray Diffractometer with monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 173 K. The diffraction intensity data of **6** was collected with a Rigaku SuperNova Atlas X-ray Diffractometer with monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The diffraction intensity data of **8**(L_{OEt}) was collected with a Rigaku Gemini™ S Ultra X-ray Diffractometer with monochromatized Cu-Kα radiation (λ = 1.54178 Å) at 143 K. Diffraction data of **3**, **4**, **6** and **8**(L_{OEt}) were collected and processed using the CrysAlisPro software (Rigaku, 2012). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all complexes were performed using the Olex2 software package[41] (which embedded SHELXTL[42]). All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms

were refined anisotropically with a riding model for the hydrogen atoms except noted separately. All the pictures of molecules were made using ORTEP. CCDC 1448803, 1448804, 1448805 and 1448806 contain the supplementary crystallography data for complexes **3**, **4**, **6** and **8**(L_{OEt}) respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxx.

Crystallographic data and experimental details for **3**, **4**, **6**, and **8**(L_{OEt}) (Table S1)

Cartesian coordinates and electronic energies for the calculated (optimized) structures

NMR monitoring of decomposition of **1** in hexanes (Figure S1)

Acknowledgment

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Table of Contents Entry

Probing the Reactivity of the Ce=O Multiple Bond in a Cerium(IV) Oxo Complex

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The reactivity of the Ce(IV) oxo complex $[(L_{OEt})_2Ce^{IV}(=O)(H_2O)] \cdot MeC(O)NH_2$ (**1**) (L_{OEt}^- = $[CoCp\{P(O)(OEt)_2\}_3]^-$) toward electrophiles and Brønsted acids has been investigated. The influence of the $\{NaL_{OEt}\}$ moiety on the electronic structure and stability of the Ce/Na bimetallic complex $[(L_{OEt})_2Ce^{IV}(Me_2CONH_2)(O)NaL_{OEt}]$ has been analyzed by density functional theory calculations.