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The Impact of Ligand Reorganization on Cerium(III) Oxidation Chemistry**

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Among the lanthanides, La–Lu, Ce compounds have played a unique and important role in organic synthesis, inorganic chemistry, and materials science because of their distinct accessible tetravalent oxidation state.[1] As a result, there is keen interest in expanding Ce redox chemistry. Ce^{IV} compounds are best known as oxidants, while reductions with Ce^{III} are widely viewed as counterintuitive.[1a–e] Ideally, Ce^{III} complexes may serve as economical complements to the established Sm^{II} reduction systems. In order to apply Ce^{III} as a reductant, controlled redox behavior, which allows for prediction of the products, must be established.[1a,2] Furthermore, the results of these studies may enable the oxidative functionalization of Ce^{III} complexes, which has proven challenging.[3,4]

Typically, investigations of the coordination chemistry of the rare earths have relied on the use of sterically bulky ligands to coordinatively saturate the ions. However, these ligands can result in large activation barriers for metal oxidation reactions. This is exemplified in the case of $[Ce^{III}(N^*)_3]$ ($N^* = N(SiMe_3)_2^-$), where several groups have reported a lack of generality in its oxidation chemistry.[4] The electrochemistry of $[Ce^{IV}Cl(N^*)_3]$, which was measured as a point of reference for this study, shows a reversible $Ce^{III/IV}$ couple at $E_{1/2} = -0.30$ V vs. ferrocene (Fc) in THF (see the Supporting Information). It is noteworthy that the strong oxidants $AgBF_4$ ($E_{pc} = +0.41$ V vs. Fc in THF) and Cl_2 ($E_{pc} = +0.18$ V vs. Fc in CH_3CN) show no reaction with $[Ce^{III}(N^*)_3]$, however, trityl chloride reacts quantitatively.[4e,5] These results suggest that the outcomes of Ce^{III} oxidation reactions are difficult to predict solely on thermodynamic grounds, and that ligand reorganization could be a major determinant for these oxidations.[4a,6]

We hypothesized that controlling ligand reorganization would allow for the development of Ce^{III} oxidation chemistry in which the products can be predicted. Two of us,[7] and others,[8–10] have investigated Shibasaki's heterobimetallic framework, REMB (RE = rare earth; M = Li, Na, K; B = (*S*)-binolate; RE/M/B = 1:3:3; Figure 1). The REMB complexes have been used in asymmetric catalysis with great success.[10] A key feature is the role of the M in shaping the primary coordination environment at the RE; when M = Li the complex adopts an open conformation with one axial coordination site for a Lewis base; whereas when M = Na or K, the complex adopts a closed conformation with no space for a Lewis basic ligand bound at the RE ion in the solid or solution states.[8,9] Herein, we report previously unknown CeMB complexes where M = Li, Na, and K, all of which show variable oxidation reaction outcomes that are predicated on the identity of M. Through detailed electrochemical and chemical kinetics experiments we provide evidence that electron transfer rates from oxidation of the complexes fundamentally differ from their chemical oxidation rates, which implies a central role for ligand reorganization in Ce^{III} oxidation reactions.

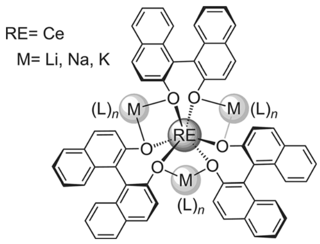

Figure 1. Molecular structure of REMB framework. RE = rare earth; M = Li, Na, K; B = (*S*)-binolate; RE/M/B = 1:3:3.

The syntheses of CeMB (where M = Li, Na, K) complexes were accomplished in 88–92 % yield through salt metathesis or protonolysis routes (see the Supporting Information). Single crystal X-ray diffraction data for $[M_3(thf)_x]$-$[(binolate)_3Ce^{III}(thf)_y]$ (**1**; M = Li, $x = 4$, $y = 1$); (**2**; M = Na, $x = 6$, $y = 0$), (**3**, M = K; $x = 6$, $y = 0$); showed that the CeMB complexes were isostructural to those reported for the early lanthanides.[7–10] The ^{1}H NMR data for **1**–**3** displayed D_3 symmetric structures with six paramagnetically shifted binolate resonances and chemical shifts ranging from +10 to −3 ppm. With confirmation of the solid state and solution structures of the CeMB complexes in hand, we investigated their electrochemical behavior to study the kinetic and thermodynamic contributions to the oxidations of **1**–**3**.

Cyclic voltammetry was performed for **1**–**3** in THF solutions using 0.1 M $[NPr_4][BAr^F_4]$ (BAr^F = tetrakis[3,5-(trifluoromethyl)phenyl]borate) as a supporting electrolyte (Figure 2). The three complexes display irreversible metal oxidation events with clear return reduction waves. The appearance of the $Ce^{III/IV}$ redox couples for **1**–**3** is noteworthy given the prediction that the Ce^{IV} ion is too strongly oxidizing

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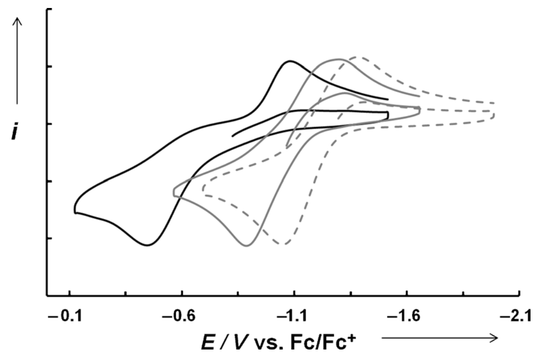


Figure 2. Normalized cyclic voltammograms of **1** (——), **2** (——), and **3** (-----) in THF. $\nu = 100\ \text{mV}\,\text{s}^{-1}$, [CeMB] = ca. 1 mM, $[n\text{Pr}_4\text{N}][\text{BAr}^{\text{F}}_4] = 0.1$ M.

to be supported by aryloxide ligands.[11] In fact, it is evident that the Ce^{IV} ion is strongly stabilized in the tris(binolate) framework; the Li$^+$ complex **1** is stabilized by ca. 1.8 V compared to the standard oxidation potential of the Ce^{III} ion,[12] and **1**–**3** are most accurately described as mild reductants, as per the classification system of Connelly and Geiger.[13] Interestingly, the presence of Li, Na, or K within the CeMB framework causes an unprecedented variance of the Ce$^{III/IV}$ oxidation wave for a given ligand system; the choice of alkali metal produces a ca. 600 mV range in potentials between **1**–**3**.

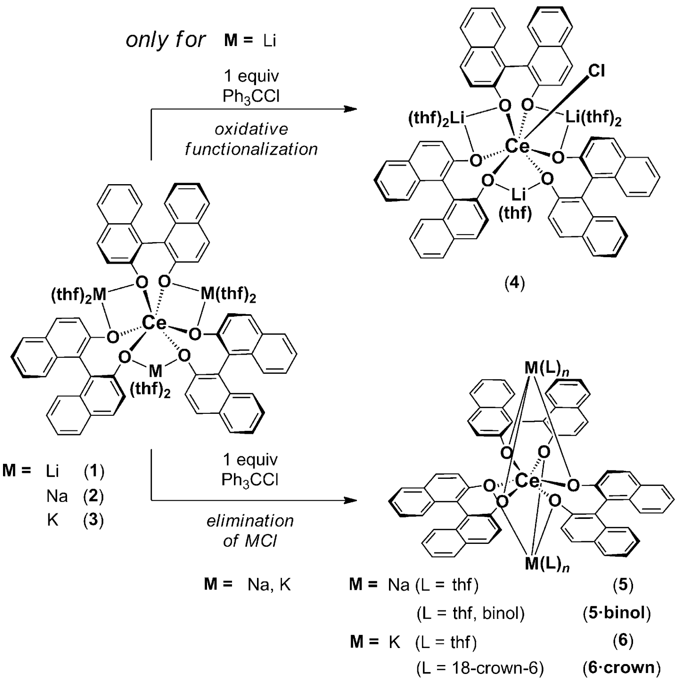
The identity of M is also a major determinant in the observed heterogeneous electron transfer kinetics. The complexes **1**–**3** show large anodic and cathodic wave separations, ΔE_p (Table 1), and reflect sluggish electron transfer rates, k_s.[14–16] Applying Kochi's extension[15] of the Nicholson method[16] (see the Supporting Information) the values of k_s were calculated and follow the order $k_s(\text{K}^+) > k_s(\text{Na}^+) > k_s(\text{Li}^+)$ (Table 1). According to Marcus–Hush theory, variations in electron transfer rate constants (k_s) depend on the thermodynamic driving force ($\Delta G°$) and the total reorganizational energy (λ).[17a] We expect variation of ligand reorganization energy, a component of λ,[17b] based on the identity of M. It is tempting to conclude that the slower heterogeneous electron transfer rate for complex **1** is due to a more robust heterobimetallic structure of that complex; however, the observed differences in driving forces for **1**–**3** make it problematic to assign the exact contribution from ligand reorganization to the value of k_s.

Table 1: Electrochemical data and electron transfer rates (k_s [$\times 10^{-4}$ cm s^{-1}]) for CeMB (**1**–**3**).

Entry	CeMB (M)	E_{pa} [V vs. Fc][a]	E_{pa} [V vs. Fc][a]	ΔE_p [V][a]	k_s[a,b]
1	**1** (Li)	−0.445	−1.085	0.640	4.84
2	**2** (Na)	−0.895	−1.295	0.400	5.97
3	**3** (K)	−1.045	−1.385	0.340	9.47

[a] $\nu = 100\ \text{mV}\,\text{s}^{-1}$. [b] Calculated by the method employed in Ref. [15b] (see the Supporting Information).

To elucidate the role of ligand reorganization in the outcomes of oxidation reactions, we investigated the chemical oxidations of **1**–**3**. The oxidations of **1**–**3** with trityl chloride proceed to Ce^{IV} products, as judged by ^{1}H NMR spectroscopy, with the consumption of Ce^{III} starting materials and the formation of Gomberg's dimer as a byproduct.[18] Two reaction pathways are suggested by the identity of the Ce^{IV} products (Scheme 1). Direct oxidative functionalization of **1** in coordinating and non-coordinating solvents produces only the intensely purple complex $[\text{Li}_3(\text{thf})_5][(\text{binolate})_3\text{Ce}^{\text{IV}}\text{Cl}]$ (**4**; Figure 3), which was isolated as a crystalline solid in 85% yield. Alternatively, elimination of one equivalent of MCl generates the dark red complexes $[\text{M}_2(\text{thf})_n][(\text{binolate})_3\text{Ce}^{\text{IV}}]$ (for M = Na (**5**) or K (**6**)) in 99 and 92% yield, respectively.



Scheme 1. Oxidation reactions of CeMB with trityl chloride.

Complexes **5** and **6** were crystallized by the addition of either one equivalent of (*S*)-binol (**5·binol**) or two equivalents of 18-crown-6 (**6·crown**), and were obtained as crystalline solids in 86 and 70% yield, respectively (Scheme 1). The solid-state structures of **5** (see the Supporting Information) and **6** (Figure 4) reveal a surprising structural rearrangement: the two M$^+$ ions migrate to cap the axial faces of the tris(binolate) framework, while the Ce^{IV}-aryloxide coordination sphere collapses into a closed octahedral arrangement. These represent new structural types for this widely studied class of catalysts.

The oxidation reactions of **1**–**3** are amongst the few reported from a Ce heterobimetallic framework, and, to our knowledge, represent the first system where the identity of the M co-cation results in selective oxidative functionalization or salt elimination within the same ligand framework.[19] Additionally, we qualitatively observed that the chemical

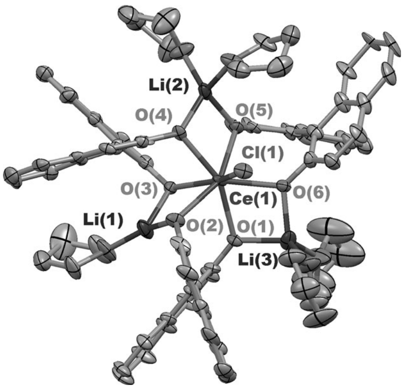


Figure 3. Thermal ellipsoid plot of $[Li_3(thf)_5][(binolate)_3CeCl]\cdot THF$ (**4**). Thermal ellipsoids set at 50% probability. An interstitial THF molecule has been removed for clarity. Selected bond distances [Å]: Ce(1)–Cl(1) 2.667(2), Ce(1)–O(1) 2.293(6), Ce(1)–O(2) 2.333(6), Ce(1)–O(3) 2.295(5), Ce(1)–O(4) 2.277(6), Ce(1)–O(5) 2.297(5), Ce(1)–O(6) 2.311(6), Li(1)–O(3) 1.93(2), Li(1)–O(2) 1.91(2), Li(2)–O(4) 1.953(17), Li(2)–O(5) 1.90(2), Li(3)–O(1) 1.922(18), Li(3)–O(6) 1.93(2)

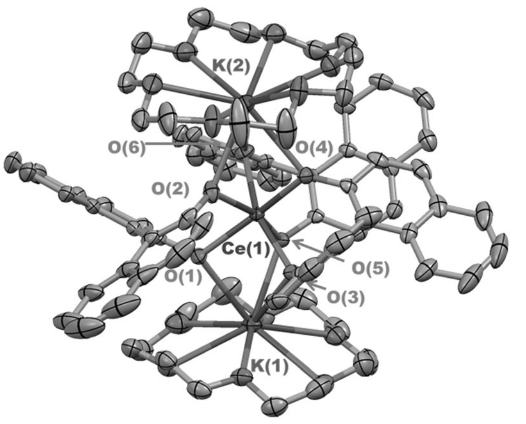


Figure 4. Thermal ellipsoid plot of $[K_2(18\text{-crown-}6)_2][(binolate)_3Ce]$ (**6·crown**). Thermal ellipsoids set at 50% probability. Selected bond distances [Å]: Ce(1)–O(1) 2.240(2), Ce(1)–O(2) 2.233(2), Ce(1)–O(3) 2.241(2), Ce(1)–O(4) 2.234(2), Ce(1)–O(5) 2.255(2), Ce(1)–O(6) 2.236(2), K(1)–O(1) 2.938(2), K(1)–O(3) 3.214(2), K(1)–O(5) 2.748(2), K(2)–O(2) 2.904(2), K(2)–O(4) 2.914(2), K(2)–O(6) 3.130(2).

oxidations proceeded in minutes for **1** and hours for **2** and **3**. Critically, this observation runs counter to the trend for k_s predicted by Marcus theory: $k_s(K^+) > k_s(Na^+) > k_s(Li^+)$, and prompted us to further explore oxidation rate studies in these complexes.

Rate studies for the oxidations of **1**–**3** with trityl chloride were performed by monitoring the characteristic absorption bands for **4**–**6** centered at 445–487 nm (see the Supporting Information) using UV/Vis absorption spectroscopy. The reactions with **1**–**3** were first order in the complexes and trityl chloride, thus indicating their involvement in the rate-determining step. Rate data obtained under pseudo-first order conditions for the complexes are displayed in Figure 5. The values of k_{obs} (Table 2) follow the trend k_{obs} $(K^+) < k_{obs}$ $(Na^+) \ll k_{obs}$ (Li^+), with a ca. 120-fold decrease in the observed rates comparing **1** and **3** (entries 1–3). Although **1** has the weakest driving force and smallest value for k_s, **1** exhibits the fastest reactivity for the homogeneous oxidation with Ph_3CCl (k_{obs}).

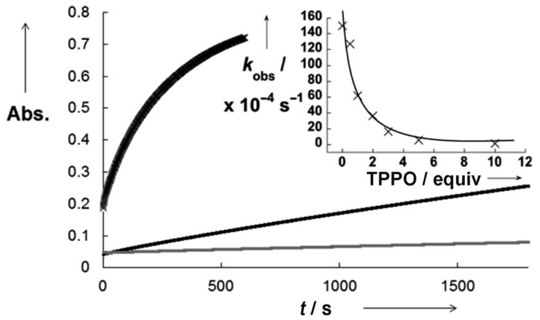


Figure 5. Pseudo-first order rate data for **1** (×), **2** (■), and **3** (■) in THF at 23 °C (10 equiv Ph_3CCl). Inset shows k_{obs} for **1** in toluene in the presence of varying equivalents of TPPO. Line in the inset is provided as a guide for the eye.

Table 2: Pseudo-first order rate data (k_s [$\times 10^{-4}$ cm s^{-1}] and k_{obs} [$\times 10^{-4}$ s^{-1}]) for the oxidations of **1**–**3** with trityl chloride.

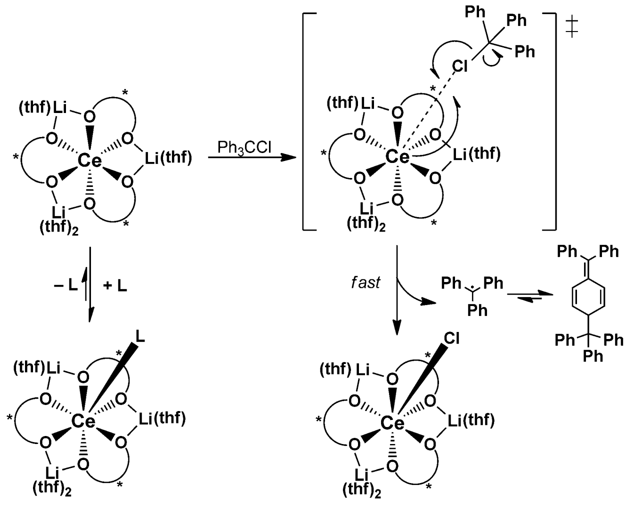
Entry	CeMB (M)	k_s[a]	Solvent	k_{obs}[b]
1	**3** (K)	9.45	THF	0.216
2	**2** (Na)	5.97	THF	1.93
3	**1** (Li)	4.84	THF	30.0
4	**1** (Li)	–	toluene	150
5[c]	**1** (Li)	–	toluene	5.46

[a] Obtained by cyclic voltammetry measurements in THF. [b] Obtained under pseudo-first order conditions using UV/Vis absorption spectroscopy; $[CeMB]/[Ph_3CCl] = 1{:}10$. [c] 5 equiv of triphenylphosphine oxide (TPPO) added.

The opposing trends between k_s and k_{obs} suggest that the heterogeneous and homogeneous electron transfer processes operate by different mechanisms;[20] that is, the homogeneous oxidation with Ph_3CCl proceeds by an inner sphere mechanism. Indeed, trends for k_{obs} follow the accessibility of the central RE^{III} ion towards Lewis base coordination; when M = Li there is easy access for binding to Ce^{III}, whereas when M = Na or K coordinative saturation of that ion is observed. Furthermore, one would expect an inner sphere process to be sensitive to competitive binding at the Ce ion. By conducting the oxidation reactions of **1** in toluene in the presence of triphenylphosphine oxide (TPPO), significant inhibition of the rate was observed (Figure 5, inset); the use of 5 equiv of TPPO resulted in a ca. 27-fold decrease in rate compared to the reaction in the absence of TPPO (entries 4 and 5), and is consistent with TPPO binding competitively to the Ce^{III} center.[21]

The differences in the chemical oxidation rates for **1**–**3** and in the structures of isolated products **4**–**6**, highlight the role of ligand reorganization in oxidation reactions with this system. While **1**–**3** display small and variable heterogeneous electron transfer rates, our key result is that chemical reaction rate does not track with heterogeneous electron transfer rate. Instead, rates of chemical oxidation follow the accessibility of the Ce^{III} ion with $k_{obs}(Li^+) \gg k_{obs}(Na^+) > k_{obs}(K^+)$, which is directly tied to reorganization of the coordination spheres of these complexes. To access the central Ce^{III} ion, displacement from the plane formed by the alkali metal cations[7,9] must occur, and this is much less favorable for **2** and **3**. The 0.14 Å reduction in the ionic radius from $Ce^{III} = 1.01$ Å to $Ce^{IV} = 0.87$ Å disfavors the seven coordinate geometry for CeMB when M = Na or K.[22] The related complexes YbMB ($Yb^{III} = 0.87$ Å, M = Na, K) do not bind solvent in the solid state or solution, which supports the hypothesis that reorganization to maintain a seven coordinate geometry is disfavored with small rare earth ions (for M = Na, K).[7b–d,8a]

The data support that heterobimetallic frameworks are beneficial to complex integrity in all cases; detrimental reactivity, such as ligand redistribution, was not observed upon oxidation of **1**–**3**. The Li framework of **1** sustains the overall structure of the complex and easily reorganizes between the six- and seven-coordinate geometries (Scheme 2) to afford direct oxidative functionalization. This is not the case for **2** and **3**, the seven-coordinate species is too energetically costly to be compensated for by the Ce^{IV}–Cl bond enthalpy, and salt elimination occurs, thus providing additional enthalpic driving force from the lattice energies of MCl.



Scheme 2. Proposed inner sphere oxidation mechanism of **1**.

In accordance with our experimental results, we propose that ligand reorganization plays an essential role in successful Ce^{III} oxidation reactions. Furthermore, oxidative functionalization reactions whose products can be predicted require ligand sets that provide an electron-donating ligand environment at the Ce^{III} ion, while allowing access to the Ce^{III} ion and maintaining the overall structure of the complex over the reaction pathway. Our results suggest that control of ligand reorganization using heterobimetallic frameworks should prove useful in this pursuit.

In summary, we have reported a unique family of Ce heterobimetallic complexes that have enabled the study of ligand reorganization on Ce^{III} oxidation reactions. The CeMB complexes exhibit properties and reactivity tunable by changing the identity of M, and selective chemical oxidations with trityl chloride furnish novel tetravalent frameworks in excellent yields. Kinetics studies reveal rates of chemical oxidation (k_{obs}) that run counter to those observed by cyclic voltammetry (k_s) and are consistent with an inner sphere oxidation pathway for **1**–**3**. These results suggest that reorganization plays a significant role in the oxidation reactions of **1**–**3**, and we propose new criterion for Ce^{III} oxidation reactions in which the product can be predicted. Expansion of this work in the context of stable platforms for the exploration of Ce redox chemistry and the investigation of these complexes in asymmetric catalysis are currently underway.

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