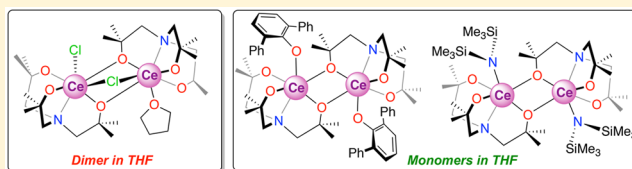


Exploration of the Solid- and Solution-State Structures and Electrochemical Properties of Ce^{IV}(atrane) ComplexesLukman A. Solola,[†] Thibault Cheisson,[†] Qiaomu Yang,[‡] Patrick J. Carroll, and Eric J. Schelter^{*‡}

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, United States

Supporting Information

ABSTRACT: Chemical oxidation of cerium complexes can be unpredictable because of labile metal–ligand bonds leading to ligand redistribution. The use of tripodal frameworks such as silyl-substituted tren ligands ($\text{NN}'_3 = [\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_2\text{tBu}))_3]^{3-}$) and a tris(hydroxylamino) ligand, $[(2\text{-tBuNO})\text{C}_6\text{H}_4\text{CH}_2]_3\text{N}^{3-}$ (TriNOx^{3-}), has been shown to mitigate ligand redistribution effects to allow access to tetravalent cerium complexes with different apical ligands. In the current work, the coordination chemistry of Ce^{IV} with the related tripodal atrane³⁻ ($\text{H}_3\text{atrane} = [\text{N}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH})_3]$) ligand framework was examined. A series of Ce^{IV}(atrane) complexes with supporting chloride, silylamide, and aryloxy ligands were synthesized and characterized by X-ray crystallography. The solution-state behaviors of these complexes were studied using ¹H and diffusion-ordered (DOSY) NMR spectroscopies. The electrochemical stabilization of the Ce^{IV} cation within the atrane³⁻ framework was examined. Our results showed that a combination of suitable apical ligands and the atrane framework provided excellent stabilization for the Ce^{IV} cation.

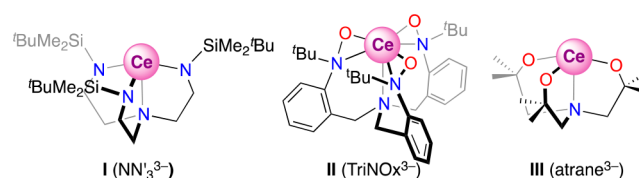


INTRODUCTION

Lanthanide complexes generally exhibit low barriers toward ligand redistribution reactions because of the nondirectional and ionic natures of their metal–ligand bonds.¹ While lability and typically fast rates of ligand exchange are beneficial in lanthanide catalysis,^{2,3} ligand redistribution effects pose a significant synthetic challenge in the rational design and isolation of metal complexes. These challenges are especially severe in the isolation of Ce^{IV} coordination complexes through oxidative routes.⁴ For example, oxidation of the Ce^{III} complex $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_3$ with the hypervalent iodine reagent PhICl_2 led to the isolation of $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_4$ instead of the expected $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_3\text{Cl}$.^{4–6} Similarly, Lappert and co-workers reported the isolation of a homoleptic bis(cyclohexyl)-amide complex, $\text{Ce}(\text{NCy}_2)_4$, from the aerobic oxidation of $\text{Ce}(\text{NCy}_2)_3$.⁵ Bulky, multidentate ligand frameworks have been shown to mitigate ligand redistribution pathways by exploiting the chelate effect.^{7–9} Scott and co-workers synthesized tetravalent cerium halide complexes using the silyl-substituted triamidoamine ligand $[\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_2\text{tBu}))_3]^{3-}$ (**I**, NN'_3^{3-} ; Chart 1).⁷ Our group has also shown that the tripodal, anionic hydroxylamino ligand framework $[(2\text{-tBuNO})\text{C}_6\text{H}_4\text{CH}_2]_3\text{N}^{3-}$ (**II**, TriNOx^{3-} ; Chart 1) allows access to a series of Ce^{IV} complexes through controlled oxidative synthetic routes.⁸ Despite these promising results, the study of the coordination chemistry of cerium within tripodal, trianionic, ligand frameworks is still underdeveloped.

In recent work from our group, we reported the synthesis of atrane³⁻-stabilized, cationic cerium complexes with multiple open coordination sites (Chart 1, **III**).¹⁰ Solution electro-

Chart 1. Tripodal, Trianionic, Ligand Frameworks Relevant in Ce^{IV} Coordination Chemistry



chemical studies conducted on these complexes showed that the atrane ligand conferred thermodynamic stabilization on the Ce^{III} oxidation with $E_{\text{pc}} < -1.00$ V versus ferrocene/ferrocenium, rendering them mild reductants.¹¹ Herein we report on a series of neutral Ce^{IV}(atrane) complexes with halide, amide, and aryloxy supporting ligands, characterized by solution-state NMR spectroscopy, electrochemical methods, and single-crystal X-ray analyses.

RESULTS AND DISCUSSION

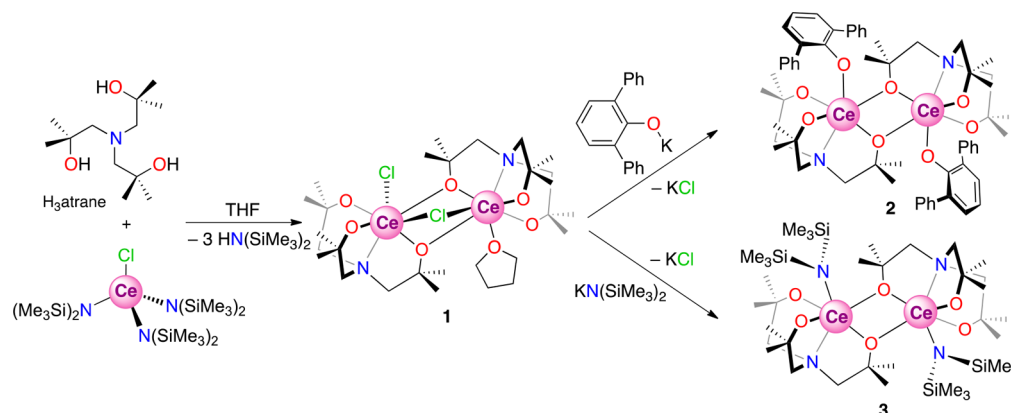
Synthesis and Characterization. To develop the chemistry of Ce^{IV}(atrane) complexes, we sought a suitable Ce^{IV} precursor that would enable chemistry through a protonolysis route. Treating a tetrahydrofuran (THF) solution of the Ce^{IV} complex $\text{Ce}[\text{N}(\text{SiMe}_2)_2]_3\text{Cl}$ ¹² with H_3atrane led to the rapid formation of a yellow solution (Scheme 1). Subsequent workup and crystallization of the solid from a

Received: March 29, 2018

Published: August 23, 2018



Scheme 1. Synthesis of Complexes 1–3



THF/*n*-hexane mixture led to the deposition of yellow $\{[\text{Ce}(\text{atrane})\text{Cl}](\mu\text{-Cl})[\text{Ce}(\text{atrane})(\text{THF})]\}$ (**1**) in 65% yield.

Complex **1** crystallized in the form of the THF solvate in the monoclinic space group $C2/c$ (Figure 1). In contrast to the

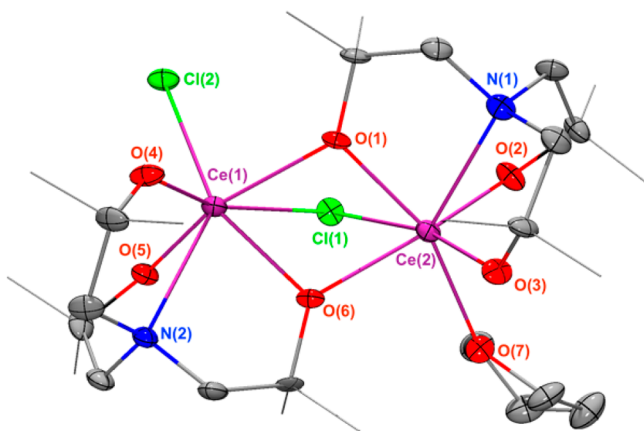


Figure 1. Thermal ellipsoid plot of **1**·THF shown at the 50% probability level. The interstitial THF molecule and H atoms have been omitted for clarity. Methyl groups are depicted using a wire model. Selected bond distances (Å) and angle (deg): Ce(1)–O(1) 2.260(5), Ce(1)–O(2) 2.098(6), Ce(1)–O(3) 2.104(7), Ce(1)–Cl(1) 2.832(3), Ce(2)–Cl(1) 2.879(2), Ce(2)–Cl(2) 2.677(2); Ce(1)–Cl(1)–Ce(2) 79.26(7).

previously reported cationic $\text{Ce}(\text{atrane})$ complexes $[\text{Ce}(\text{atrane})(\text{THF})_3][\text{I}_3]$ and $[\text{Ce}(\text{atrane})(\text{THF})_3][\text{BAr}^{\text{F}}_4]$ ($\text{BAr}^{\text{F}}_4 = \text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4^-$),¹⁰ X-ray analysis of **1** revealed an unsymmetrical bimetallic structure, in which the atrane^{3−} ligands bridged the two Ce ions through anionic O atoms, O(1) and O(6). The chloride ligands were bound in the terminal $[\text{Cl}(2)]$ and bridging $[\text{Cl}(1)]$ modes. The structural metrics in **1** were consistent with those in the previously reported Ce^{IV} complexes.^{8,10,13} The Ce–Cl_{terminal} bond length of 2.677(2) Å was shorter than that of 2.7436(8) Å found in $\text{Ce}(\text{TriNOx})\text{Cl}$,⁸ presumably because of the relatively less steric bulk of the atrane ligand. The Ce–Cl_{bridging} bond lengths of 2.832(3) and 2.879(2) Å were also significantly shorter than that of 3.0080(2) Å reported for $[\{\text{Ce}(\text{NN}'_3)\}_2(\mu\text{-Cl})]$.⁷ This observation can be attributed to both the reduced steric bulk of atrane compared to NN'_3 and the mixed-valent nature of $[\{\text{Ce}(\text{NN}'_3)\}_2(\mu\text{-Cl})]$.

With complex **1** in hand, the substitution chemistry of the apical, anionic ligand and its impact on the solution- and solid-state structures, and the solution electrochemical properties, of the corresponding complexes were investigated. For this study, we chose silylamide and aryloxide apical ligands because they have been shown to offer considerable stabilization for Ce^{IV} .^{14,15} Complex **1** proved to be a useful precursor for the synthesis of amide- and aryloxide-capped $\text{Ce}^{\text{IV}}(\text{atrane})$ complexes.

Treating a THF solution of **1** with 1 equiv of KOAr [$\text{Ar} = 2,6\text{-(C}_6\text{H}_5)_2\text{-C}_6\text{H}_3$] and $\text{KN}(\text{SiMe}_3)_2$, followed by subsequent workup and crystallization from *n*-pentane, afforded the isolation of $\{\text{Ce}(\text{atrane})(\text{OAr})\}_2$ (**2**; 29% yield) and $\{\text{Ce}(\text{atrane})[\text{N}(\text{SiMe}_3)_2]\}_2$ (**3**; 24% yield), respectively (Scheme 1). The low yields of these complexes were due to their high solubilities in most organic solvents. Compounds **1**, **3**, and **2** were respectively yellow, pale orange, and red/orange (in THF, see the UV–vis spectra in Figure S19). This color change arises from a gradual shift of a putative ligand-to-metal charge-transfer band, consistent with previous studies on related homoleptic compounds.^{15,16}

Both complexes **2** and **3** were crystallized as dimeric complexes similar to **1** (Figure 2). However, in contrast to the solid-state structure of **1**, which included a bridging chloride ligand, the amide and aryloxide ligands in both **2** and **3** were terminal. The Ce–O_{bridging} bond lengths for **2** ranged from 2.347(3) to 2.372(3) Å and were shorter than those for complex **3** [2.379(1)–2.399(1) Å] possibly because of the increased steric profile of the amide ligand compared to that of the aryloxide. The Ce–O_{aryloxide} bond lengths in **2** were 2.189(3) and 2.222(3) Å and were longer than those found in the homoleptic complex $\text{Ce}(\text{OAr})_4$ [2.101(3)–2.125(3) Å].¹⁵ The propensity of $\text{Ce}^{\text{IV}}(\text{atrane})$ complexes for dimerization can be understood in terms of the smaller steric profile of atrane^{3−} in comparison, for example, with the NN'_3 ^{3−} framework.⁷ This observation was confirmed by the percent buried volume calculations with $\%V_{\text{Bur}} = 45.9$ for atrane^{3−} and 76.0 for NN'_3 ^{3−} (see the Supporting Information for details).^{10,17}

Solution-State ¹H NMR Studies. Complex **1** was soluble in coordinating solvents such as THF, diethyl ether, and pyridine. The ¹H NMR spectrum of **1** in pyridine-*d*₅ showed two sharp resonances at 1.37 and 3.44 ppm. The resonance at 1.37 ppm was assigned to the methyl proton of the atrane^{3−} ligand and was downfield-shifted compared to those in the cationic complexes $[\text{Ce}(\text{atrane})(\text{THF})_3]^+$ (1.29 ppm measured in pyridine-*d*₅).¹⁰ Conversely, the methylene resonance at 3.44

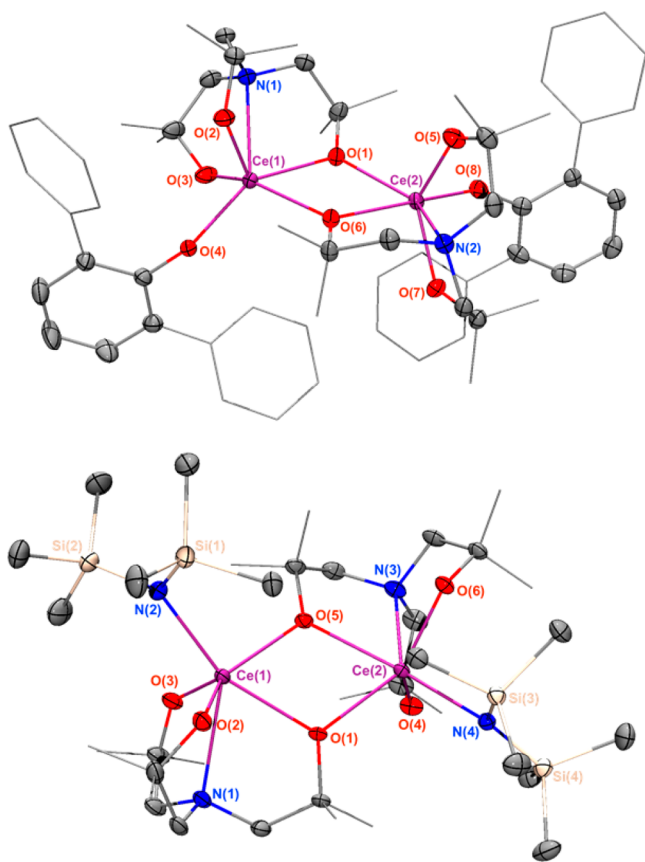


Figure 2. Thermal ellipsoid plots of **2** (top) and **3** (bottom) shown at the 50% probability level. Interstitial *n*-pentane and H atoms have been omitted for clarity. Methyl and phenyl groups are depicted using a wire model. Selected bond distances (Å) and angle (deg) for **2**: *n*-pentane: Ce(1)–O(1) 2.372(3), Ce(1)–O(2) 2.078(3), Ce(1)–O(3) 2.103(3), Ce(1)–O(4) 2.189(3), Ce(2)–O(8) 2.222(3); Ce(1)–O(1)–Ce(2) 111.4(1). Selected bond distances (Å) and angle (deg) for **3**: *n*-pentane: Ce(1)–O(1) 2.399(1), Ce(1)–O(2) 2.120(1), Ce(1)–O(3) 2.084(1), Ce(1)–N(2) 2.360(2), Ce(1)–N(4) 2.345(2); Ce(1)–O(1)–Ce(2) 112.89(5).

ppm in **1** was upfield-shifted compared to the corresponding cationic complexes (3.57 ppm for [Ce(atrane)(THF)₃]⁺I₃[−] and 3.59 ppm for [Ce(atrane)(THF)₃][BAR^F₄][−], both of which were measured in pyridine-*d*₅).¹⁰ We conclude that the Lewis basicity promotes a solvated, monometallic structure of **1** in pyridine-*d*₅, as confirmed by ¹H DOSY NMR studies (vide infra).

A difference was noted between the ¹H NMR spectrum of **1** recorded in pyridine-*d*₅ and that in THF-*d*₈. The ¹H NMR spectrum of **1** in THF-*d*₈ at room temperature exhibited broad resonances centered at 1.23 and 3.36 ppm, possibly indicating fluxional behavior. Indeed, the ¹H NMR spectrum measured at 330 K (THF-*d*₈) showed a sharpening of both the methyl and methylene resonances (Figures 3 and S3) in agreement with a C_{2v}-symmetric complex at the NMR time scale. At 270 K, decoalescence of both the methyl and methylene resonances was observed. The former were split into six resonances, while the latter formed a complicated pattern of diastereotopic protons, as confirmed by ¹H COSY NMR. This result agrees with a lowering of the symmetry to a C₂- or C_s-symmetric dimer presumably because of fast Cl[−] and THF exchange between the Ce cations. At 210 K, with further decoalescence, a C₁-symmetric structure consisting of ~10 resonances for the

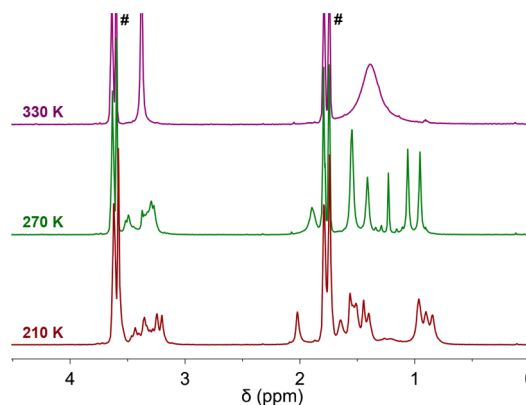


Figure 3. Partial variable-temperature ¹H NMR spectra of **1** in THF-*d*₈ (#, proteo solvent peaks; see Figure S6 for the full range).

methyl groups (corresponding to 12 total overlapping peaks) and a complex pattern of superimposed diastereotopic methylene protons was identified (see Figure 3 and S4 and S5 for details). Overall, the variable-temperature solution-state ¹H NMR study confirmed that the solid-state bimetallic structure of **1** was conserved in THF.

In contrast to complex **1**, the solution-state ¹H NMR spectra of complexes **2** and **3** exhibited sharp resonances in both THF-*d*₈ and pyridine-*d*₅. The atrane^{3−} methyl resonances were observed at 1.19 ppm for complex **2** and 1.29 ppm for **3**. These values were upfield-shifted compared to those observed for **1**. Likewise, the atrane methylene resonances observed at 3.22 ppm for **2** and 3.26 ppm for **3** were upfield-shifted compared to that for **1**. Our hypothesis from these series of experiments was that complexes **2** and **3** were monomeric in both THF and pyridine because of the steric bulk of the ancillary aryloxy or amide ligands and because of probable coordination of the Lewis basic solvent molecules to the Ce^{IV} cation.

¹H diffusion-ordered (DOSY) NMR spectroscopy (see the Supporting Information for details) was used to determine the speciation of **1**–**3** in THF and pyridine (Table 1). We have

Table 1. ¹H DOSY NMR Measurement Results for Compounds **1**–**3**

complex	<i>D</i> ₀ ^a	<i>r</i> _H (exp) ^b	<i>r</i> _H (theo)mono ^c	<i>r</i> _H (theo)dimer ^c
1 (THF- <i>d</i> ₈)	8.2 ± 0.1	6.3 ± 0.6	5.2	6.3
1 (Pyr- <i>d</i> ₅)	1.9 ± 0.1	4.9 ± 0.6	5.2	6.3
2 (THF- <i>d</i> ₈)	8.0 ± 0.1	6.0 ± 0.2	5.8	8.3
3 (THF- <i>d</i> ₈)	9.1 ± 0.1	5.0 ± 0.9	5.6	7.5

^aDiffusion coefficient (×10^{−10} m² s^{−1}). ^bAveraged hydrodynamic radius (in Å) value from calculations using *D*₀ and *r*_H of the internal references (benzene, ferrocene, and tetramethylsilane). ^cRadii of the monometallic or dimeric structure as determined from crystal structures (in Å).

previously used DOSY to ascertain the speciation of cerium complexes in solution.^{18,19} The determined hydrodynamic radius (*r*_H) of **1** was 6.3 ± 0.6 Å in THF-*d*₈. This result correlates well with the retention of a bimetallic structure upon a comparison of values from the crystal structures of the respective complexes. When dissolved in pyridine-*d*₅, ¹H DOSY NMR experiments returned *r*_H = 4.9 ± 0.6 Å, in agreement with a monometallic form in this solvent. As expected from the ¹H NMR spectroscopy data, the hydrodynamic radii of both complexes **2** (6.0 ± 0.2 Å) and **3** (5.0 ±

0.9 Å) were consistent with the presence of monomeric species in a THF solution.

Solution Electrochemistry. With a better understanding of the speciation of all three complexes, solution electrochemical studies were performed on 1–3 to ascertain the stabilizing effect of the anionic apical ligands on the Ce^{IV} cation. All measurements were carried out in 0.1 M THF solutions of $[\text{Pr}_4\text{N}][\text{BAR}^{\text{F}}_4]$ with ferrocene as an internal standard (Figure 4). The cyclic voltammogram of complex 1

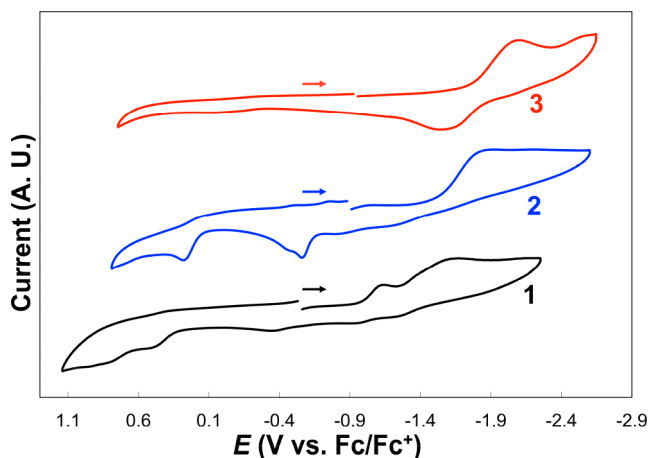


Figure 4. Electrochemical measurements of 1–3 performed in 0.1 M $[\text{Pr}_4\text{N}][\text{BAR}^{\text{F}}_4]/\text{THF}$ (scan rate = 100 mV s^{-1}).

exhibited two poorly-defined metal-based, quasi-reversible reduction waves at $E_{\text{pc}} = -1.14$ and -1.67 V versus ferrocene. This observation supports the formulation of 1 as a bimetallic complex under the electrochemical measurement conditions, consistent with the results obtained from the DOSY measurements in THF.

Complex 2 showed an irreversible metal-based r feature at $E_{\text{pc}} = -1.86$ V versus an internal ferrocene standard (Figure 4). This value represents a stabilization of -1.36 V compared to the homoleptic complex, $\text{Ce}(\text{OAr})_4$ $E_{\text{pc}} = -0.50$ V vs ferrocene).¹⁵ A return wave(s) was observed at $E_{\text{pa}} = -0.56$ V and assigned as cerium oxidation; however, the difference in the current and large peak separation suggested a chemical process associated with the reduced form of 2. A second oxidation, independent of the cerium reduction, was observed at $+0.26$ V and tentatively assigned to oxidation of the coordinated aryloxy ligand (Figure S14). Complex 3 showed the best degree of electrochemical reversibility in the series. The metal-based feature for 3 was poorly reversible (Figures 3 and S18) with cathodic and anodic peaks at -1.90 and -1.47 V, respectively. The reason for the better electrochemical reversibility observed in 3 compared to 1 and 2 can be attributed to the increased steric profile of the $\text{N}(\text{SiMe}_3)_2^-$ ligand compared to Cl^- and ArO^- . We propose that complexes 1 and 2 exhibited irreversible electrochemical features because of an electrochemical process facilitated by the formation of oligomeric Ce^{III} species in solution. However, the more sterically demanding amide ligand allowed the generated $\text{Ce}^{\text{III}}(\text{atrane})$ complex to maintain its monomeric structure in solution, thus allowing for better electrochemical reversibility.

CONCLUSIONS

Tripodal, trianionic, ligand frameworks provide excellent steric and electronic stabilization for the synthesis of stable Ce^{IV}

complexes. Indeed, recent reports on the isolation of rare cerium–ligand multiple bonds were achieved using these classes of ligands.^{13,20,21} However, despite the obvious synthetic advantages that these ligands offer, a detailed study of their coordination chemistry with cerium is lacking.

We have prepared the first examples of neutral $\text{Ce}^{\text{IV}}(\text{atrane})$ complexes with anionic halide, aryloxy, and amide ligands. Solution-state NMR measurements showed that the Lewis basic chloride apical ligand enforced a bimetallic solution-state structure in THF, but the stronger Lewis basicity of pyridine was sufficient to access monometallic species. However, because of the increased steric bulk of the aryloxy and amide apical ligands, complexes 2 and 3 were monomers in both THF and pyridine. Electrochemical measurements on all three complexes showed that the atrane ligand in conjunction with an ancillary ligand effectively stabilizes the Ce^{IV} cation, with the silylamide ligand providing the best stabilization ($E_{1/2} = -1.68$ V vs ferrocene). These results show that tripodal trianionic ligand frameworks with O-donor atoms are ideal for effectively stabilizing the Ce^{IV} ion while limiting the effects of ligand reorganization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00712.

Details of the experimental procedures, crystallographic data, ^1H DOSY NMR spectroscopic characterization, UV–vis spectra, percent buried volume calculations, and supplementary electrochemistry data (PDF)

Accession Codes

CCDC 1833327–1833329 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: schelter@sas.upenn.edu.

ORCID

Thibault Cheisson: 0000-0003-4359-5115

Qiaomu Yang: 0000-0002-4231-1355

Eric J. Schelter: 0000-0002-8143-6206

Author Contributions

[†]L.A.S. and T.C. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Science Foundation (Grant CHE-1664928) and University of Pennsylvania for financial support of this work. L.A.S. thanks the NSF Graduate Research Fellowship program for support. We thank G. Panetti (University of Pennsylvania) for assistance in recording the variable-temperature NMR data.

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