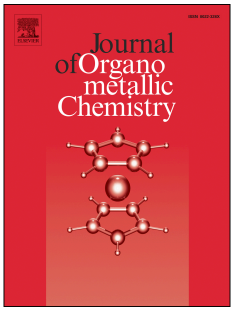

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Cationic Cerium(IV) Complexes with Multiple Open Coordination Sites

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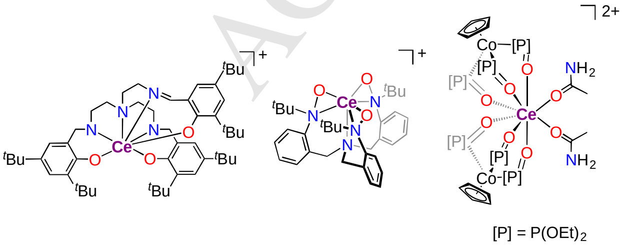
Dedicated to our friend and mentor, Prof. William J. Evans, on the occasion of his 70th birthday.

Supporting Information Placeholder

ABSTRACT: Oxidation of *in situ* generated Ce^{III}(atrane) (atrane = $[N(CH_2C(CH_3)_2O)_3]^{3-}$) with either iodine or FcBAr^F afforded the novel cationic tetravalent cerium salts [Ce^{IV}(atrane)(thf)$_3$][I$_3$] and [Ce^{IV}(atrane)(thf)$_3$][BAr^F], both of which showed multiple open coordination sites.

1. Introduction

The coordination chemistry of cerium has grown during the past few decades, and much of this effort has been focused on understanding the redox properties of the cerium ion within different ligand frameworks [1–3]. While the trivalent oxidation state is prevalent in lanthanide (Ln) complexes [4], cerium is the only lanthanide with an accessible tetravalent oxidation state in its molecular chemistry, with $E° = 1.74$ V *versus* NHE for the Ce$^{III/IV}$ couple [5]. The relative stability of the tetravalent oxidation of the cerium ion is due to its stable noble gas configuration of [Xe]4f^0. Eller and Penneman rationalized that ligands with electronegative hard donor atoms are best poised to stabilize high valent cerium [6]. Our group [2,3,7,8,9] and others [10–14] have isolated and characterized highly-stabilized tetravalent cerium complexes by using ligand frameworks with hard donor anions such as oxygen and nitrogen (Scheme 1).



I **II** **III**

Scheme 1. Previously reported cationic cerium complexes

While there has been a steady increase in the number of neutral tetravalent cerium complexes reported in recent years, there are limited reports of their cationic congeners. To date, only four examples of crystallographically characterized cationic Ce^{IV} complexes have been reported [3,15,16]. Notably, isolation of these compounds was made possible by the use of electron rich and sterically congested ligand frameworks such as H$_3$TRENDSAL ($N[CH_2CH_2N{=}CH(C_6H_2{}^tBu_2\text{-}3,5\text{-}OH\text{-}2]_3$) [15], H$_3$TriNOx ($[((2\text{-}{}^tBuNOH)C_6H_4CH_2)_3N]$) [3] and the Kläui ligand ($[CoCp\{P(O)(OEt)_2\}_3]^-$) [14] (Figure 1). However, a drawback of using these sterically encumbered ligand frameworks is that they coordinatively saturate the metal center. It is of interest to expand the library of cationic lanthanide complexes to take advantage of their Lewis acidic characteristics in reactivity [17–18].

We recently reported on the coordination chemistry of a tripodal trianionic hydroxylamine ligand framework, TriNOx^{3-} with cerium [3]. We also studied the redox properties of the Ce(III) ion within the TriNOx framework (Scheme 1, **II**). Our investigations showed that TriNOx^{3-} provided significant stabilization of the 4+ oxidation state with an experimentally determined $E_{½} = -0.96$V versus Fc/Fc$^+$. Chemical oxidations of a Ce^{III}(TriNOx) complex with ferrocenium salts, FcBAr^F and FcOTf, yielded rare examples of structurally characterized cationic cerium complexes with one open coordination site. In a bid to isolate stable cationic tetravalent cerium complexes with multiple open coordination sites, we chose tris(2-hydroxyisobutyl)amine (H$_3$atrane), a derivative of triethanolamine (TEA), as a suitable ligand. The coordination chemistries of TEA and its derivatives with main-group elements, transition metals and the lanthanides have been studied [19–21]. We hypothesized that the three hard anionic oxygen donors on atrane would provide sufficient stabilization of the tetravalent oxidation state of the cerium ion comparable to that of TriNOx^{3-}. Also, due to the small steric profile of atrane, the Ce^{IV} cation would be open, thereby