

Narrative report

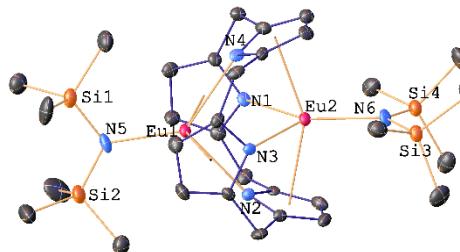
Low-valent dilanthanide complexes for alkane activationProgress prior to the third and fourth semester:

Due to the synthetic difficulties encountered with the originally proposed ligand, a calix-4-pyrrole ligand was chosen to continue the proposed work on low-valent dilanthanide complexes. A bis-samarium complex was obtained during the second semester of the funding period as yellow crystals, and cyclic voltammetry studies determined that reduction into low-valent dilanthanide complexes was possible.

Progress towards low- and mixed-valent dilanthanide complexes:

We envisioned an alternative strategy for small molecule activation utilizing mixed-valent (Ln(III)/Ln(II)) dilanthanide complexes. Our goal involve the synergistic utilization of a strong base bound to the Ln(III), and one-electron reduction from the Ln(II). As a proof of concept, we chose to utilize the calix[4]pyrrole ligand platform, well-known to stabilized low-valent Ln(II)/Ln(II) and mixed-valent Ln(III)/Ln(II) complexes.

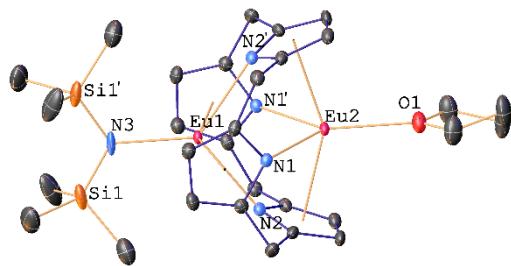
Complexes (Et₈-calix[4]pyrroly)Ln₂(HMDS)₂ (Ln = Sm, Eu) were obtained in moderate yields from octaethylcalix[4]pyrrole and Ln(HMDS)₃(μ -Cl)Li(thf)₃. The samarium complex LSm₂(HMDS)₂ was characterized by ¹H NMR spectroscopy, four paramagnetically shifted signals were observed indicative of the high symmetry of the complex in solution. Due to the higher paramagnetism of europium, a meaningful ¹H NMR spectrum of LEu₂(HMDS)₂ could not be obtained. The identity of both complexes was confirmed by single crystal X-ray diffraction studies. Both complexes crystallized in the P-1 space group. Each lanthanide ion is coordinated by a hexamethyldisilazide ligand, two η^5 -pyrroles and two η^1 -pyrroles.



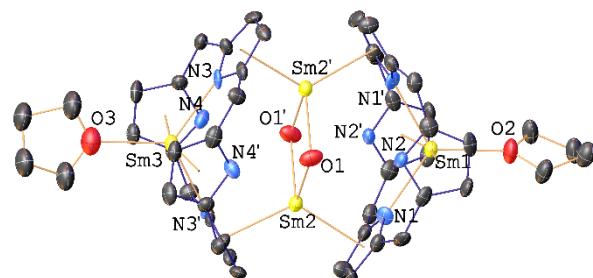
Reduction of LSm₂(HMDS)₂ with one equivalent of sodium amalgam yielded a new complex in moderate yield. The ¹H NMR spectrum displayed nine paramagnetically shifted resonances suggesting the presence of two inequivalent samarium centers. Unfortunately, single crystals of the complex could not be

grown, however combustion analyses of the purified material are consistent with a mixed-valent LSm₂(HMDS)(thf) complex. The electronic absorption spectrum of the mixed-valent LSm₂(HMDS)(thf) complex show two new bands centered at 400 and 560 nm, consistent with the presence of a Sm(II) center. Interestingly, both LSm₂(HMDS)₂ and LSm₂(HMDS)(thf) are weakly

emissive, displaying the expected $^4G_{5/2} \rightarrow ^6H_J$ ($J = 5/2, 7/2, 9/2$) transitions. This result confirms the presence of a Sm(III) center in the mixed-valent $LSm_2(HMDS)(thf)$ complex.



Similarly, reduction of $LEu_2(HMDS)_2$ with one equivalent of sodium amalgam yielded a crystalline compound in good yield. Single crystals were grown from a concentrated pentane solution, and single crystal X-ray diffraction studies confirmed the mixed-valent structure of $LEu_2(HMDS)(thf)$. The molecular arrangement of $LEu_2(HMDS)(thf)$ is similar to the one of $LEu_2(HMDS)_2$, both europium ions being coordinated by two η^5 -pyrroles and two η^1 -pyrroles, however, one europium ion is bound to a hexamethyldisilazide while the other is bound to a tetrahydrofuran. The europium bound to the hexamethyldisilazide can therefore be assigned the +III oxidation state, and the europium bound to the tetrahydrofuran is in its +II oxidation state. Accordingly, the distances between the η^5 -pyrrole centroid and europium are slightly elongated for the Eu(+II) (2.66 Å) vs. the Eu(+III) (2.60 Å), and the distances between the nitrogen of the η^1 -pyrrole and europium follow the same trend (Eu(+II): 2.74 Å vs. Eu(+III): 2.63 Å).



To elucidate the dual reactivity of the mixed valent complex (as base and reductant), we reacted $LLn_2(HMDS)(thf)$ with one equivalent of water, and observed the formation of the μ -oxo bridged complex. This compound can be obtained by subsequent reduction and deprotonation of water. To confirm the reduction pathway, $LLn_2(HMDS)(thf)$ were treated with one equivalent of silanol, and the same μ -oxo bridged complex was obtained. The presence of disilane was detected by 1H NMR, suggesting that a silyl radical was generated in the course of the reaction.

Outlook:

Significant progress was made utilizing the calix-4-pyrrole framework supporting low-valent dilanthanide species. This work will be submitted for publication in the next few months. Continuation of the work will be done on other lanthanides. The preliminary results obtained have also been integrated in grant proposals.