

ACS PRF 57668-DNI3

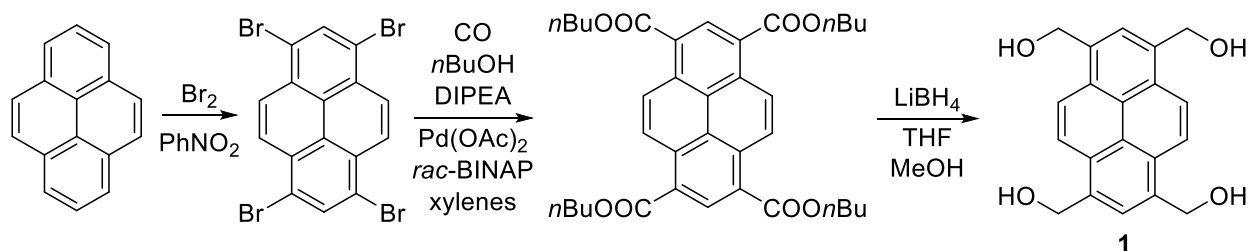
Narrative report

Low-valent dilanthanide complexes for alkane activation

Reminder of the goals of the project:

- *isolate* reduced dilanthanide complexes.
- *examine* these complexes for the activation of the C–H bond of methane.
- *convert* the activated methane into methanol.

I) Ligand synthesis challenges.



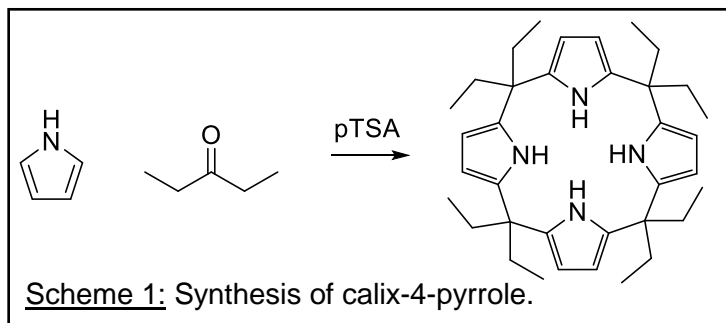
The ligand synthesis was proposed from intermediate **1**. During the first semester of the funding period, compound **1** was obtained in low yields (~4-6% over 3 steps).

The synthesis of the ligand “arm” namely 2-adamantyl-4-methylphenol was also successful in high yields (87%), however the coupling of both intermediate **1** and the ligand “arm” was unsuccessful.

The small amount of intermediate **1** available limit possible explorations of the ligand platform, and current optimization are underway.

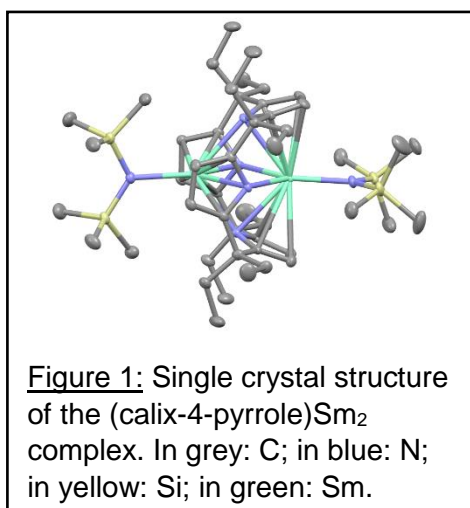
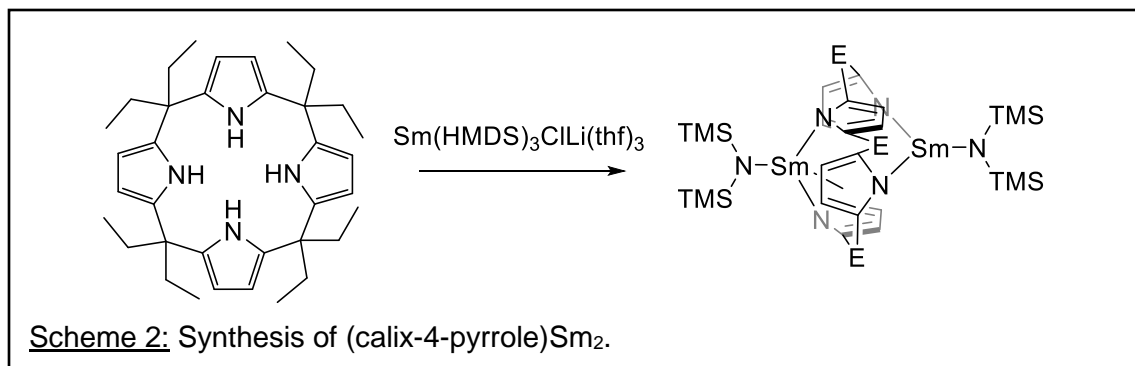
II) Design of a suitable ligand platform.

To progress in the synthesis of low-valent dilanthanide complexes, we have turned our attention to calix-4-pyrrole ligands. The ligand was synthesized from pyrrole and pentanone in high yield (Scheme 1).



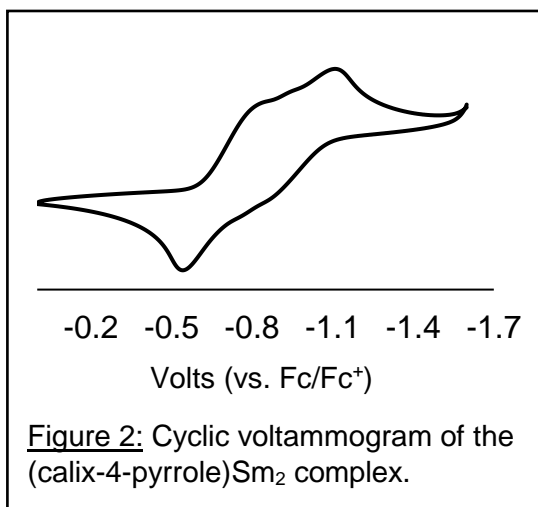
Coordination of the ligand to lanthanides was achieved by mixing the free ligand with lanthanide-hexamethyldisilazide salts (Scheme 2). Interestingly, we found that the lithium chloride adduct was required to obtain

the desired product. No metal complexes could be obtained from the simple lanthanide-hexamethyldisilazide salt.



A bis-samarium complex was obtained during the second semester of the funding period as yellow crystals. Its solid-state structure was determined by single crystal X-ray diffraction (Figure 1). The samarium atoms are each bound to the four pyrrole moieties of our ligand. Two pyrroles are bound through the nitrogen atom, while the other two pyrroles are bound in an η^5 -manner.

We collected cyclic voltammetry data for the samarium complex and observed a reversible reduction event at -0.8 V (vs Fc/Fc⁺) (Figure 2).



Chemical reduction of the calix-4-pyrrole complex yielded a dark-red compound that was paramagnetic. Crystallization attempts have been unsuccessful at the moment, and full characterization of the complex are still underway.

We are also exploring the coordination of other lanthanides and will probe the reactivity of the reduced complex towards small molecules during the third semester of the funding period.