

An Indian-Australian research partnership

**Project Title:** **Low-coordinate monomeric lanthanoid chalcogenolates**

**Project Number** **IMURA0242** (will be inserted by The Academy)

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## Research Academy Themes:

**Highlight which of the Academy's Theme(s) this project will address?**

(Feel free to nominate more than one. For more information, see [www.iitbmonash.org](http://www.iitbmonash.org))

- Advanced computational engineering, simulation and manufacture
- Infrastructure Engineering
- Clean Energy
- Water
- Nanotechnology**
- Biotechnology and Stem Cell Research

## The research problem

Complexation reaction of lanthanoid with simple chalcogenolates such as  $\text{PhSe}^-$  is known to form nanosized clusters with interesting photophysical properties.<sup>1</sup> The synthesis of monomeric chalcogenides has been a challenging area of research. The studies on the synthesis, photophysical and magnetic properties of the monomeric chalcogenolates are not well explored. Generally, the synthesis of monomeric chalcogenolates is achieved using sterically demanding groups.<sup>2</sup> The stabilization of such species using intramolecular coordination approach has not been systematically investigated. Secondly, the conventional high temperature syntheses of these lanthanoid chalcogenide material are difficult and are often hindered by impurities incorporated due to the high oxophilicity of the rare earth centers. The conversion of molecular precursor complexes of type,  $\text{Ln}(\text{ER})_x$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$  or  $\text{R} = \text{alkyl/aryl}$ ;  $\text{Ln} = \text{Lanthanoid}$ ) to rare earth monochalcogenides,  $\text{LnE}$ , with the elements combined at the molecular level in the correct stoichiometry, is highly desired. Moreover, these monomeric chalcogenolates could also serve as precursor for the semiconductors.

- Moore, B. F.; Kumar, A.; Tan, M. -C.; Kohl, J.; Riman, R. E.; Brik, M. G.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **2010**, <http://pubs.acs.org/doi/pdf/10.1021/ja1069322>.
- Hauber, S. -O.; Niemeyer, M. *Chem. Commun.*, **2007**, 275-277.

## Project aims

The main aim of the proposal is to synthesize low molecularity lanthanoid chalcogenolates and to systematically investigate the nature of the molecular lanthanoid-chalcogen bonds using ligands having either intramolecular coordinating groups or having the intramolecular coordinating groups along with the sterically hindered groups.

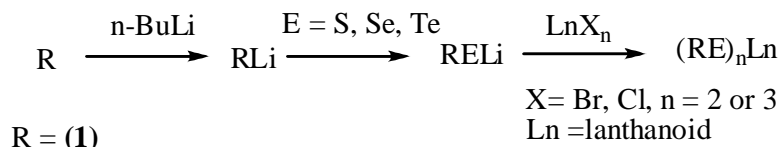
## Expected outcomes

We believe that the presence of the steric hindered and intramolecularly coordinating groups should enable: (i) the isolation of low molecularity lanthanoid chalcogenolates, and (ii) these chalcogenolates can be used as precursors for the preparation of semiconducting materials.

## How will the project address the Goals of the above Themes?

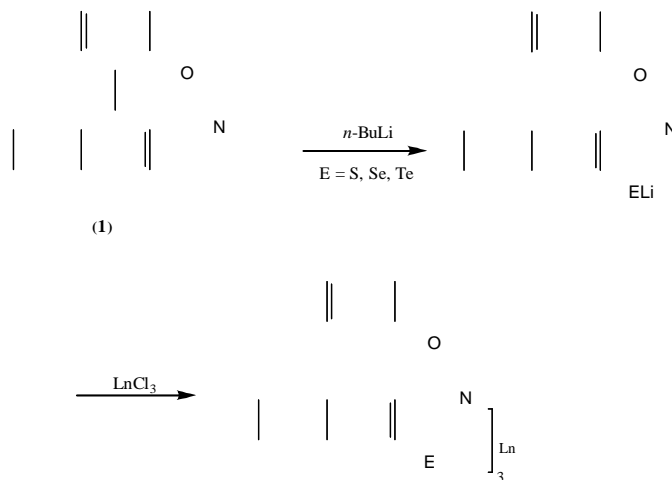
The following synthetic strategies are proposed to achieve the goal.

a). **Directed lithiation method:** The lanthanoid chalcogenolates can be synthesized by the *ortho*-lithiation route. The reaction of lanthanoid halides with lithium arenechalcogenolate, in turn, prepared by the treatment of [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] with *n*-BuLi followed by the addition of chalcogens can afford the expected stable monomeric lanthanoid chalcogenolates (**Scheme 1**).



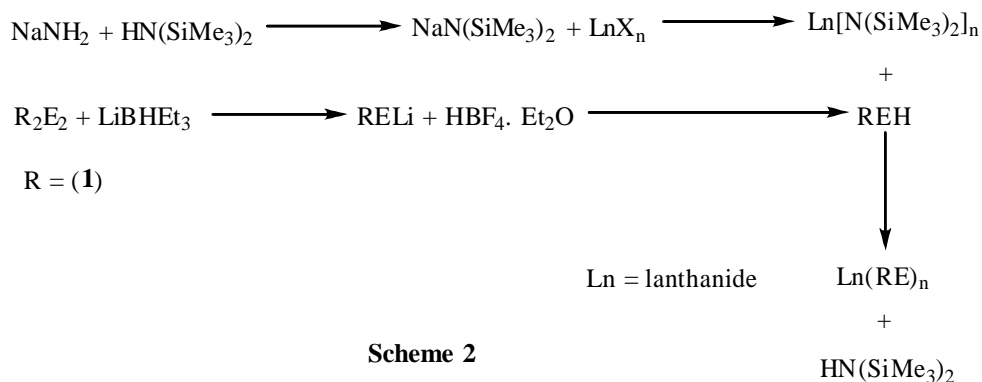
**Scheme 1**

For example,



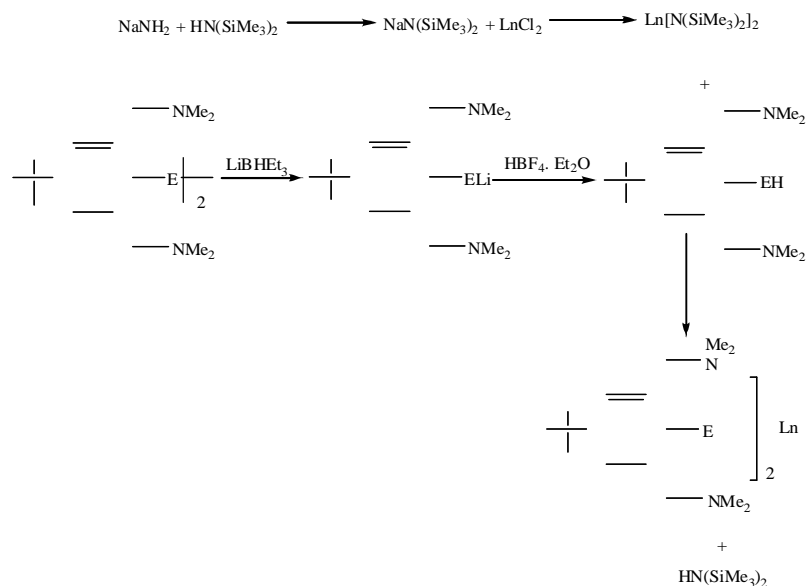
In some cases, the lanthanoid chalcogenolates could undergo reductive elimination to give dichalcogenides and lanthanoid metal. Also due to poor solubility of metal halides the complicated mixtures of uncharacteristic products are expected to form. In such cases, the lanthanoid chalcogenolates, alternatively, can be prepared by the chalcogenolysis method.

b). **Chalcogenolysis method:** The reaction of lanthanoid amide derivatives with the corresponding chalcogenol (**Scheme 2**) gives the expected lanthanoid chalcogenolates. Compared to directed lithiation approach, the chalcogenolysis method has several advantages; i) The chalcogenols and metal amide derivatives are soluble in non-polar solvents. ii) The product can be isolated conveniently in pure form as other side products are volatile liquid. ii) Yield of the products is also high in this method.

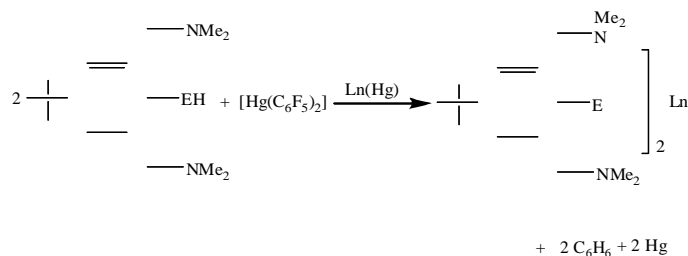


**Scheme 2**

For example

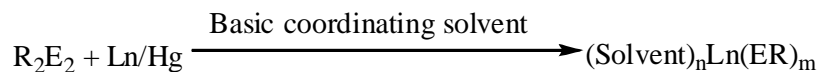


Alternatively, the chalcogenol generated above can be used for the protolytic agent in redox transmetallation/protolytic reaction reactions.



c). **Direct Reduction of Se-Se Bond by Lanthanoid Amalgam**

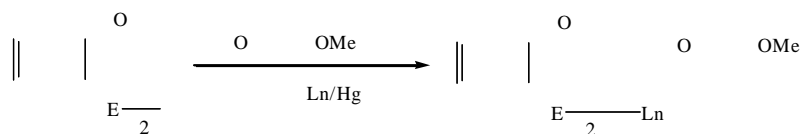
Lanthanoid chalcogenolates can be prepared by the direct reduction of dichalcogenide with Ln/Hg amalgam (Scheme 3).



R = (1)  
 E = S, Se, Te  
 Ln = lanthanide

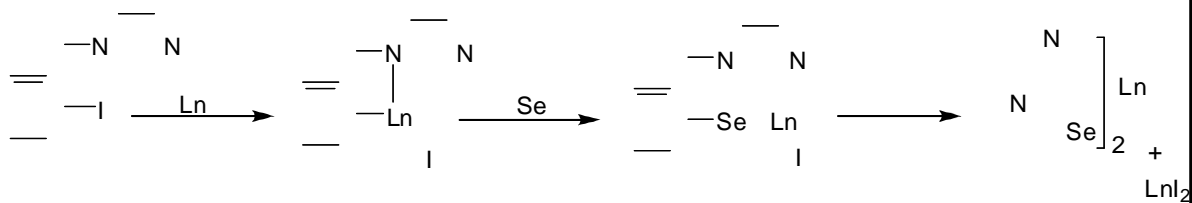
**Scheme 3**

For example



d). **Insertion Across C-X Bond**

Lanthanoid metals are known to undergo insertion reaction across C-X (Br and I) bonds. The insertion reaction can be exploited to synthesize lanthanum chalcogenides. The representative example proposed for the synthesis is given below (Scheme 4).



**Scheme 4**