



1 Introduction

1.1 Chalcogen

1.1.1 General

The word "chalcogen" is derived from a combination of the Greek word *khalkós* principally meaning copper (the term was also used for bronze/brass, any metal in the poetic sense, ore or coin), and the latinized Greek word *genēs*, meaning born or produced.^[1] Chalcogens are known as oxygen, sulfur, selenium, tellurium and radioactive element polonium, which are group 16 elements. According to Emsley John, the chemically uncharacterized synthetic element livermorium (Lv) is predicted to be a chalcogen as well.^[2] Oxygen was recognized as an element in the 18th century. Sulfur has been known since antiquity as well. Selenium, tellurium and polonium were synthesized in the 19th century, and livermorium in 2000. Almost all the chalcogens can find their roles in biological functions. Typically, lighter chalcogens (oxygen and sulfur) are rarely toxic in their elemental form, and are often critical to life, while the heavier chalcogens (selenium and tellurium) are often toxic.^[3] Commercially, selenium is used for glassmaking and pigments. Moreover, selenium is a semiconductor used in photocells electronics. Tellurium is extremely rare in earth's crust. Compounds bearing tellurium were first discovered in Zlatna, Romania by Austrian mineralogist Franz-Joseph Müller von Reichenstein in 1782 in a gold mine, and subsequently, this new element was named by Martin Heinrich Klaproth in 1798. Tellurium has no biological function, although fungi can use it in place of sulfur and selenium in amino acids such as tellurocysteine and telluromethionine.^[4] The primary use of tellurium is in copper and steel alloys, in which it provides improved machinability. Other applications namely CdTe solar panels and semiconductors also consume a significant portion of tellurium production. Polonium was discovered by Marie and Pierre Curie in 1898 from uranium ore and identified solely by its strong radioactivity and this makes polonium dangerously toxic. Polonium has few applications (heaters in space probes, antistatic



devices, and sources of neutrons and alpha particles) except for those related to its radioactivity.

1.1.2 Physical and Chemical Properties

Table 1.1 shows selected physical properties of the group 16 elements. The trend in electronegativity values has important consequences as regards the ability of O-H bonds to form hydrogen bonds. This pattern follows that in group 15. Of all the group 16 elements, there are nonmetals (oxygen, sulfur, and selenium) and metalloid (tellurium).^[5] Polonium possesses some metallic properties, however, some sources also refer to polonium as a metalloid.^[3,6] It is also notable that some selenium allotropes show metalloid characteristics. Even though the group 16 is also named as the oxygen group. Oxygen has very different chemical properties from those of the other chalcogens. This owes not only to the fact that heavier chalcogens possess vacant *d*-orbitals, but also to oxygen's distinctly higher electronegativity, which makes the electric polarizability of oxygen multiple times lower compared to the other chalcogens.^[7] The most common oxidation number of chalcogens is -2, though chalcogens' tendency forming -2 state compounds decreases towards the heavier ones. The highest oxidation number is +6,^[8] found in sulfates, selenates, tellurates, polonates, and, their corresponding acids. In terms of oxygen, the second most electronegative element, it participates into the formation of compounds with almost all elements (namely water, metal/metalloid-oxide and ubiquitous organic oxygen compounds) with its common oxidation state being -2 and -1.^[8] When it comes to sulfur, whose most common oxidation states are -2, +2, +4 and, +6, the chemistry is in multiple ways similar to that of oxygen.

However, sulfur-sulfur double bonds are far weaker than that of oxygen-oxygen while the corresponding single bonds are just on the contrary. Organic sulfur compounds normally have obvious specific smell, and a good case in point is thiols. It is worth mentioning that some organic sulfur compounds are of great significance to humans and utilized by some organisms.^[3]

**Table 1.1** Some physical properties of the group 16 elements and their ions.^[9]

Property	O	S	Se	Te	Po
Atomic number, Z	8	16	34	52	84
Ground state electronic configuration	[He]2s ² 2p ⁴	[Ne]3s ² 3p ⁴	[Ar]3d ¹⁰ 4s ² 4p ⁴	[Kr]4d ¹⁰ 5s ² 5p ⁴	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
Enthalpy of atomization, $\Delta_a H^\circ(298\text{K})/\text{kJ mol}^{-1}$	249 [‡]	277	227	197	≈146
Melting point, mp/K	54	388	494	725	527
Boiling point, bp/K	90	718	958	1263*	1235
Standard enthalpy of fusion, $\Delta_{\text{fus}} H^\circ(\text{mp})/\text{kJ mol}^{-1}$	0.44	1.72	6.69	17.49	-
First ionization energy, $IE_1/\text{kJ mol}^{-1}$	1314	999.6	941.0	869.3	812.1
$\Delta_{\text{EA}} H^\circ_1(298\text{K})/\text{kJ mol}^{-1**}$	-141	-201	-195	-190	-183
$\Delta_{\text{EA}} H^\circ_2(298\text{K})/\text{kJ mol}^{-1**}$	+789	+640			
Covalent radius, r_{cov}/pm	73	103	117	135	-
Ionic radius, r_{ion} for X ²⁻ /pm	140	184	198	211	-
Pauling electronegativity, χ^{P}	3.4	2.6	2.6	2.1	2.0
NMR active nuclei(% abundance, nuclear spin)	¹⁷ O (0.04, $I = 5/2$)	³³ S (0.76, $I = 3/2$)	⁷⁷ Se (7.6, $I = 1/2$)	¹²³ Te (0.9, $I = 1/2$) ¹²⁵ Te (7.0, $I = 1/2$)	

[‡] For oxygen, $\Delta_a H^\circ = 1/2 \times$ dissociation energy of O₂.

* For amorphous Te.

** $\Delta_{\text{EA}} H^\circ_1(298\text{K})$ is the enthalpy change associated with the process X(g) + e⁻ → X⁻(g) ≈ - $\Delta U(0\text{ K})$; $\Delta_{\text{EA}} H^\circ_2(298\text{K})$ refers to the process X⁻(g) + e⁻ → X²⁻(g)

As is often the case, the most common oxidation states of selenium are -2, +4 and +6 and selenium can bond to oxygen.^[3] Organic selenium compounds do exist, for example, selenoproteins. Tellurium commonly possesses -2, +2, +4 and +6 oxidation states and forms tellurium mono/di/tri-oxide compounds. Polonium's oxidation states are +2 and +4.^[8] Although O, Se, Te, Po (and Lv) can be defined as chalcogens, oxygen and oxides are normally distinguished from chalcogens and chalcogenides. The term



“chalcogenides” is more commonly referred to sulfides, selenides, and tellurides. During the last decades, there has been an increasing interest in the chemistry of group 16 elements.^[10-11] The metal chalcogenide chemistry has been developing at a rapid speed and numerous complexes related are found in a broad spectrum of fields such as catalysis,^[12-13] nanomaterials,^[14-18] and bioinorganic chemistry.^[19] The search of novel synthetic methods to approach metal chalcogenide complexes with different physical and chemical properties applicable in multiple fields has become increasingly interesting and ever growing number of new and excellent results can be expected in the coming future.

1.2 Rare earth elements

1.2.1 General

Rare earth elements refer to a family of elements including scandium, yttrium and lanthanides, which are the 15 elements namely La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Normally, the term “lanthanides” shares exchangeable concepts with rare earth metals and thus “Ln” will be adopted to refer to all the rare earth metals throughout the presented work. On the contrary to the term “rare” implies, rare earth metals are not really less abundant than the other elements. Terrestrial abundance of rare earth metals ranges from 0.2 (for Tm) to 46 (for Ce) ppm, which is higher than that of Au (0.004 ppm), Hg (0.08 ppm), and Se (0.05 ppm).^[20-21] As a matter of fact, even the least common lanthanide thulium (except for the radioactive Pr) is more abundant than precious metals in the Earth’s crust.^[22] It is difficult to imagine life without rare earth elements and derived compounds with versatile applications not only as laser materials, luminescent probes and even shielding materials based on their neutron capture properties,^[23-28] but also as high-activity low-cost, low-toxicity Lewis acid catalysts in homogeneous reactions.^[29-32] Owing to the similar properties of these elements, people spent approximately 160 years to fully isolate all the elements. In 1787, Carl Axel Arrhenius (1757-1824) discovered a black mineral from a mine in Ytterby, near Stockholm, Sweden. Then a new oxide material was discovered in 1794 by Johan Gadolin (1760-1852) from the previously mentioned black mineral and later was named Yttria.^[33] Virtually, the so-called black mineral is a mixture of metal oxides and it was

over the whole next century that more Ln elements had been discovered from this mixture. Until the year 1947, the last lanthanide element, Pm, was isolated.^[34]

1.2.2 Physical and chemical properties

Lanthanides are different from transition metals due to the *f*-elements arising from successive occupation of the *f*-orbitals with electrons.

Table 1.2 Electronic configurations of the lanthanide atoms and derived ions.^[35]

	Atom	Ln ^{II}	Ln ^{III}	Ln ^{IV}
La	[Xe]5 <i>d</i> ¹ 6 <i>s</i> ²		[Xe]	
Ce	[Xe]4 <i>f</i> ¹ 5 <i>d</i> ¹ 6 <i>s</i> ²		[Xe]4 <i>f</i> ¹	[Xe]
Pr	[Xe]4 <i>f</i> ³ 6 <i>s</i> ²		[Xe]4 <i>f</i> ²	[Xe]4 <i>f</i> ¹
Nd	[Xe]4 <i>f</i> ⁴ 6 <i>s</i> ²	[Xe]4 <i>f</i> ⁴	[Xe]4 <i>f</i> ³	[Xe]4 <i>f</i> ²
Pm	[Xe]4 <i>f</i> ⁵ 6 <i>s</i> ²		[Xe]4 <i>f</i> ⁴	
Sm	[Xe]4 <i>f</i> ⁶ 6 <i>s</i> ²	[Xe]4 <i>f</i> ⁶	[Xe]4 <i>f</i> ⁵	
Eu	[Xe]4 <i>f</i> ⁷ 6 <i>s</i> ²	[Xe]4 <i>f</i> ⁷	[Xe]4 <i>f</i> ⁶	
Gd	[Xe]4 <i>f</i> ⁷ 5 <i>d</i> ¹ 6 <i>s</i> ²		[Xe]4 <i>f</i> ⁷	
Tb	[Xe]4 <i>f</i> ⁹ 6 <i>s</i> ²		[Xe]4 <i>f</i> ⁸	[Xe]4 <i>f</i> ⁷
Dy	[Xe]4 <i>f</i> ¹⁰ 6 <i>s</i> ²	[Xe]4 <i>f</i> ¹⁰	[Xe]4 <i>f</i> ⁹	[Xe]4 <i>f</i> ⁸
Ho	[Xe]4 <i>f</i> ¹¹ 6 <i>s</i> ²		[Xe]4 <i>f</i> ¹⁰	
Er	[Xe]4 <i>f</i> ¹² 6 <i>s</i> ²		[Xe]4 <i>f</i> ¹¹	
Tm	[Xe]4 <i>f</i> ¹³ 6 <i>s</i> ²	[Xe]4 <i>f</i> ¹³	[Xe]4 <i>f</i> ¹²	
Yb	[Xe]4 <i>f</i> ¹⁴ 6 <i>s</i> ²	[Xe]4 <i>f</i> ¹⁴	[Xe]4 <i>f</i> ¹³	
Lu	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ¹ 6 <i>s</i> ²		[Xe]4 <i>f</i> ¹⁴	

The similarity of these *f*-elements and their ions derive from the electronic configurations has been shown in Table 1.2. The core of lanthanides is an Xe (1*s*²2*s*²2*p*⁶3*s*²3*p*⁶3*d*¹⁰4*s*²4*p*⁶4*d*¹⁰5*s*²5*p*⁶) and the 4*f* orbitals of lanthanides are gradually filled from La to Lu.^[35] La possesses no 4*f* electron and its lower-energy (compared to its 4*f* orbital) 5*d* orbital is filled with one electron. Ce is the first lanthanide element to feature a 4*f* electron. Gd has a 5*d* orbital because of the stability of its half-filled 4*f* orbital. Full-filled 4*f* orbital can be observed for Lu, whose 5*d* orbital has only one electron. Additionally, an abrupt decrease of the energy and spatial extension of 4*f*



orbitals can be observed with the binding energy of a single 4f electron ranged from -0.95 eV (La) to -5 eV (Nd).^[35]

Another identical feature of lanthanides is known as lanthanide contraction (Table 1.3), meaning that the ionic radius decreases smoothly along with the increase of the atomic number (from 57 for La to 71 for Lu). It derives from the imperfect shielding of 4f electrons by other 4f electrons.^[36]

Table 1.3 Ionic radii for nine coordinate Ln^{III} ions.^[37]

Ln	Ionic radius [Å]	Ln	Ionic radius [Å]
La	1.216	Tb	1.095
Ce	1.196	Dy	1.083
Pr	1.179	Y	1.075
Nd	1.163	Ho	1.072
Pm	1.144	Er	1.062
Sm	1.132	Tm	1.052
Eu	1.120	Yb	1.042
Gd	1.107	Lu	1.032

The most stable oxidation state of the rare earth elements is +3. Ce^{IV}, Sm^{II}, Eu^{II} and Yb^{II} used to be the only non-trivalent lanthanide ions that are accessible in coordination chemistry.^[38-39] Until very recently, discovery shows that all lanthanides can form divalent derivatives as long as a proper ligand environment is provided.^[40-45] Lanthanides are a series of elements exhibiting similar reactivity but possess different ionic radii. This makes lanthanides perfect candidates in the application of homogeneous catalysis because it allows for the control of catalytic reactions by precisely altering the size of center metal, more than simply varying ligands. Being strong Lewis acids, Ln^{III} normally tend to possess large coordination numbers (owing to their large ionic radii) and are very sensitive to moisture and air. The coordination chemistry of lanthanides had been dominated by cyclopentadienyl (-derivatives) for decades since pioneering work from Wilkinson *et al.*^[46-47] His work showed that there was no 18-rule for the Ln^{III}-cyclopentadienyl system. Early development of organolanthanide chemistry witnessed the preparation of Cp₂LnCl and CpLnCl₂.^[48-49]



Subsequently, numerous cyclopentadienyl lanthanide complexes were isolated.^[50-55] In recent decades, alternatives for cyclopentadienyl ligands have been successfully developed to give rise the post-metallocenes.^[56-61] When it comes to divalent lanthanides, the ionic radii are remarkably similar to those of corresponding alkaline earth metal ions (*e.g.* for six-coordinated ions: Ca^{II} 1.00 Å, Yb^{II} 1.02 Å, Sr^{II} 1.18 Å, Eu^{II} 1.17 Å),^[37,62] thus the coordination chemistry of these metals are related and this theory is verified by crystals structures of Ca^{II} and Yb^{II} complexes: they are almost isomorphous and possess very similar unit cell parameters.^[63]

Recent years, there are great advances in the chemistry of rare earth metals. Related compounds found their widely application capability with novel ligands obtained. Reduction chemistry involving low-valent Ln^{II} complexes is one of growing trends of modern rare earth elements chemistry.

1.3 Lanthanide chalcogenide complexes derived from the reduction of chalcogen(ide)s by divalent lanthanide complexes

The reduction of nonmetals by organometallic reagents has recently gained increasing attention in molecular chemistry.^[64-66] Molecular polypnictide Zintl anions such as E₈⁴⁻ (E=P, As, Sb) have been obtained from the elements or other precursors.^[67-70] In the cases of chalcogenides, the reduction of elemental sulfur is functionally significant to rechargeable lithium-sulfur (Li-S) batteries, which have shown promising potential to provide a higher specific energy compared with conventional lithium ion ones.^[71-72] In general, molecular and solid-state chalcogenidometalates have interesting physical properties, including semi- and photoconductivities as well as chemical and catalytic activities and they can even be used for contemporary electronic devices,^[73-77] H₂ large-scale production,^[78] gene expression,^[79] and molecular traps.^[80] Such reduction chemistry involving chalcogenides is of significant interest and focuses mainly on sulfides (*e.g.* chemistry of polysulfide clusters), whilst heavier chalcogen Se and Te related examples are less studied. Such metal chalcogenide compounds have been synthesized generally by the reactions between low-valent lanthanide^[81-84] or transition-metal^[85-86] complex precursors and elemental chalcogens or related

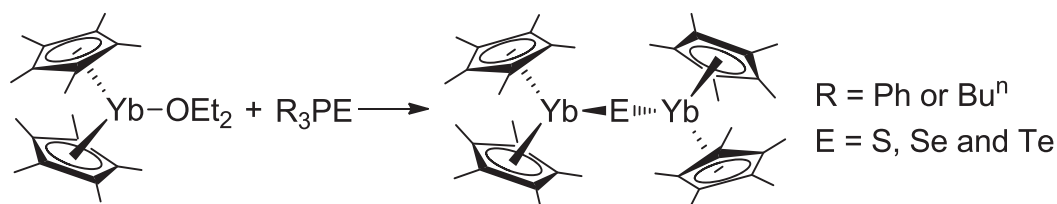


chalcogen-containing substrates such as Ph_3PSe , Ph_2E_2 ($\text{E} = \text{S}, \text{Se}$ and Te) or related species.^[87-93] Different from the normal synthetic routes which require high-temperature and/or high-pressure^[94-95] or toxic reagent,^[96-98] the reduction strategy using low-valent metal complexes, ranging from earlier established metal cyclopentadienyls^[84,99-100] to recently emerged amine-scaffold-supported low-valent metal analogs,^[78,91,101-102] provides a mild alternative to achieve these metal chalcogenide complexes. This field of research offers promising opportunities for the synthesis of metal containing chalcogenides in view of their structural diversity and unusual physical and chemical properties.

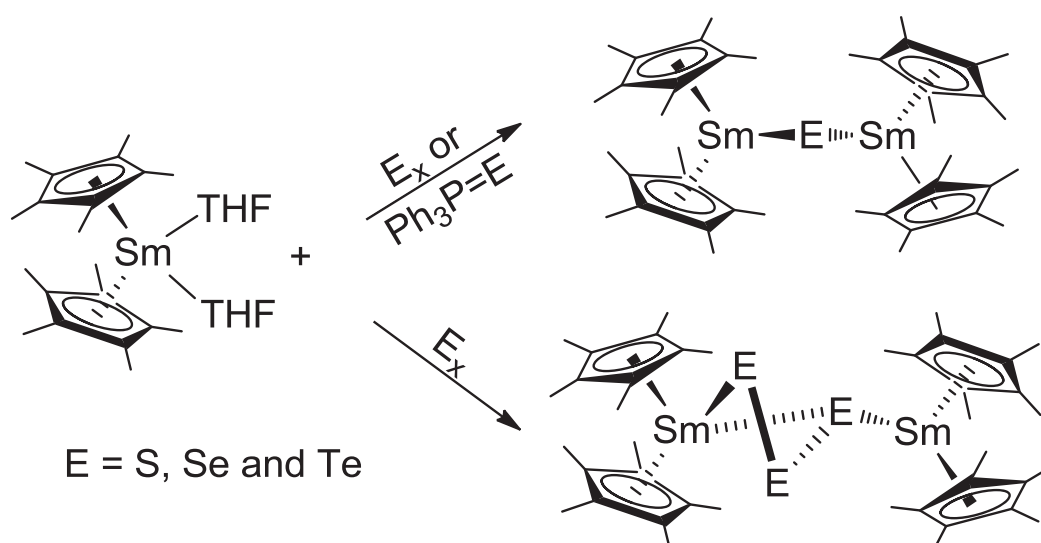
The study of lanthanide metal chalcogenide was limited especially when compared with that of transition metals. Nearly all the chemistry of lanthanide elements was focused on +3 oxidation state. A great number of ligands have been utilized to construct lanthanide complexes. However, most of the ligands were small^[103] until the year of 1965 when the first divalent lanthanide cyclopentadienyl complex, EuCp_2 , was synthesized by Fischer *et al.*^[104] by adopting a non-aqueous procedure. Later in 1978, Evans *et al.* isolated SmCp_2 and YbCp_2 by using a similar method named as metal atomization technique.^[105] However, the compounds are insoluble in common organic solvents.

Since the hydrocarbon-soluble divalent lanthanide metallocene complexes were synthesized,^[106-107] people started to adopt divalent lanthanide complexes as reduction reagents in a variety of reactions towards organic and organometallic compounds.^[108-110] From the reaction of these Ln^{II} complexes with main group elements, scientists achieved numerous results. For example, the treatment of Cp^*_2Sm with group-15-related-compounds N_2 , Ph_3Bi and $n\text{-Bu}_3\text{Sb}$ in organic solutions, could readily give N_2^{2-} ,^[111] Bi_2^{2-} ^[112] and Sb_3^{3-} ^[113] species respectively. There were also related studies on group 16 compounds reported by Andersen *et al.* The treatment of $[\text{Cp}^*_2\text{Yb}(\text{OEt}_2)]$ with R_3PE ($\text{R} = \text{Ph}$ or Bu^n ; $\text{E} = \text{S}, \text{Se}$ and Te) in hydrocarbon solvents resulted a series of lanthanide bridging chalcogenides as shown in Scheme 1.1.^[81] Thus the Ln^{II} ($\text{Ln} = \text{Sm},$

Eu, Yb) reduction chemistry has been extended to group 16 elements and their reagents in order to study the structure and application potential of chalcogenide compounds.



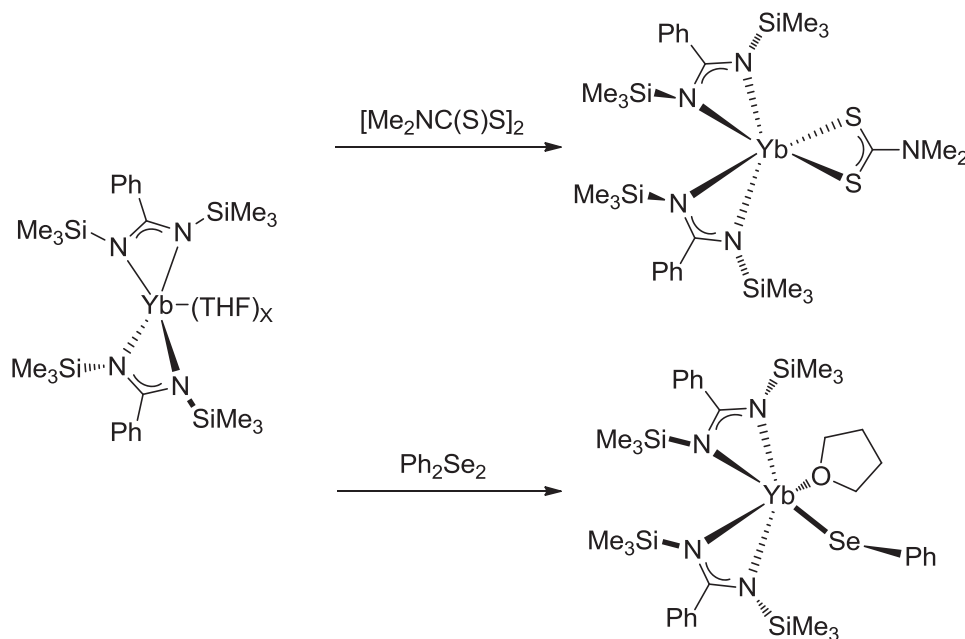
Scheme 1.1 Synthesis of bridging Cp*₂Yb]₂[μ-E].^[81]



Scheme 1.2 Synthesis of the compounds reported by Evans *et al.* in 1994.^[83]

Studies of Evans *et al.* in 1994 (Scheme 1.2) showed that by treating [Cp*₂Sm(THF)₂] with elemental chalcogens or Ph₃P=E (E = S, Se and Te), [Cp*₂Sm]₂[μ-E] can be isolated.^[83] By varying reaction conditions, E₃²⁻ polychalcogenide anions were achieved as well. In addition, a growing number of ancillary ligands have been developed as alternatives for cyclopentadienyl ligands.^[57,114-115] In 1990, Edelmann *et al.* communicated the first example of amidinate supported lanthanide chalcogenides. From the treatment of [{PhC(NSiMe₃)₂]₂Yb(THF)₂] with [{Me₂NC(S)S]₂] or Ph₂Se₂, Edelmann and co-workers isolated [{PhC(NSiMe₃)₂]₂Yb{(S)₂CNMe₂}] and [{PhC(NSiMe₃)₂]₂Yb(SePh)(THF)] respectively (Scheme 1.3).^[116] It worth mentioning that Edelmann and co-workers synthesized

$[\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Yb}(\text{SeMes})(\text{THF})]$ (Mes = mesityl) from similar reaction with Mes_2Se_2 (rather than Ph_2Se_2) in 1992.^[117] To date, the aforementioned $[\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Yb}(\text{SePh})(\text{THF})]$ and $[\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{Yb}(\text{SeMes})(\text{THF})]$ still represent rare examples of mononuclear benzamidinate lanthanide chalcogenide complexes.



Scheme 1.3 The first example of amidinate supported lanthanide chalcogenides reported by Edelmann *et al.*^[116]

Later in 2009, Lam and Lee extended amidinate ligated lanthanide chalcogenides to tellurium for the first time.^[91] The reaction between $[\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3^i\text{Pr}_{2-2,6})\}_2\text{Sm}(\text{THF})_2]$ and Ph_2Te_2 gave binuclear $[\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3^i\text{Pr}_{2-2,6})\}_2\text{Sm}(\text{PhTe})_2]$.

Additionally, polychalcogenides have also gained significant attention aiming to access compounds ligated by novel polyatomic units, rather than species such as E_2^{1-} , E_2^{2-} and E_3^{3-} .^[83,118-130] In 2016, Edelmann and Takats obtained the first molecular lanthanide compounds containing S_4^{2-} and S_4^{3-} (Scheme 1.4).