DALTON
PERSPECTIVE

Novel synthesis of lanthanoid complexes starting from metallic lanthanoid sources

Kazushi Mashima *[a] **and Akira Nakamura** [b]

[a] *Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan. E-mail: mashima@chem.es.osaka-u.ac.jp*
[b] *OM Research, 7-2-1308, Minami-ohgimachi, Kita-ku, Osaka 530-0052, Japan*

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This review focuses on a new simple synthetic approach to prepare a series of novel organometallic and coordination compounds of lanthanoids using metallic sources. This method has some advantages: (1) one-pot reaction, (2) purification by simple crystallization, and (3) formation of salt-free compounds. The preparation of COT (cycloocta-1,3,5,7-tetraene), diene, and azo complexes of lanthanoid metals is demonstrated by direct reactions of the corresponding organic compounds with metallic lanthanoids in organic solutions such as THF. Moreover, homoleptic lanthanoid chalcogenolate complexes, $Ln(ER)_n$, were prepared by direct oxidative reaction of metallic lanthanoids with REER (R = aryl or pyridyl, E = S or Se) in organic solution. By controlling the stoichiometry of diaryl disulfides, both lanthanoid-(II) and -(III) compounds can selectively be prepared. Chalcogenolate ligands sometimes bridge two lanthanoid centers to form polymeric compounds, which are transformed to mononuclear compounds upon addition of a strong donor HMPA (= hexamethylphosphoric triamide, $PO(NMe_2)_3$) or introduction of bulkiness on the chalcogenolate ligands. Furthermore, a transannular S–S bond of a hypervalent compound, 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate), reacted with metallic samarium to give a salt-free samarium(II) bis(triflate) compound.

1 Introduction

The importance of lanthanoid coordination compounds containing complex organic ligands has been shown by the recent worldwide research activity on lanthanoid-based homogeneous catalysts and functional materials such as magneto-electronic materials and opto-electronic devices. Preparative routes for the required compounds have been limited mostly to simple metathesis reactions starting from salt-like compounds, *e.g.* oxides, chlorides, and hydrated salts. Although the metal vapor method has been applied for some organolanthanoid(0) compounds[1] and coordination compounds of lanthanoid metals have been prepared by the redox transmetallation of organomercury compounds with metallic lanthanoids followed by protolytic ligand exchange reaction,[2–7] the direct route from the pure metals has not proved attractive. Direct routes would be very convenient and economical for preparation of anhydrous lanthanoid-(II) or -(III) coordination compounds, leading to a great variety of useful lanthanoid complexes.

Since the direct route is redox-driven by suitable combination of metals as reductants, and homo- or hetero-atomic bonds (X–Y) as oxidants, the inherent redox ability of X_2 or XY toward the chosen lanthanoid elements is important. In this perspective we briefly describe the oxidative reactions of REER (where R = aryl or pyridyl; E = S or Se) as well as a hypervalent

Kazushi Mashima received his Doctor degree (1986) from Osaka University under the supervision of Professor A. Nakamura. He became a research associate at Institute for Molecular Science, Okazaki National Institutes in 1983, working with Professor H. Takaya. He moved to Faculty of Engineering, Kyoto University as an Assistant Professor in 1989 with Professor H. Takaya, and then to Faculty of Science, Osaka University in 1991, working with Professor A. Nakamura. He was promoted to an Associate Professor at Faculty of Engineering Science, Osaka University in 1994. He worked with Professor M. A. Bennett, Australian National University in 1992 and Professor W. A. Herrmann, Technisch Universität München in 1993. He received Progress Award in Synthetic Organic Chemistry, Japan in 1994.

Kazushi Mashima

Akira Nakamura

Akira Nakamura obtained a Doctor degree for his study on diene complexes of transition metals under the supervision of Professor N. Hagihara of Osaka University in 1962, and then became a post-doctoral researcher at the Research Division, New York University under Professor Minoru Tsutsui in the period 1962–1963. In 1965 he was promoted to an Associate Professor of Faculty of Engineering Science, Osaka University. In co-operation with Professor Sei Otsuka, he studied various types of homogeneous catalysis. In 1977 he was promoted to Professor at the Department of Macromolecular Science, Faculty of Science, Osaka University. In the period 1993–1995 he was a Director of Coordination Chemistry Laboratory, Institute for Molecular Science at Okazaki. He retired from Osaka University in 1998 and now works at OM Research in Osaka.

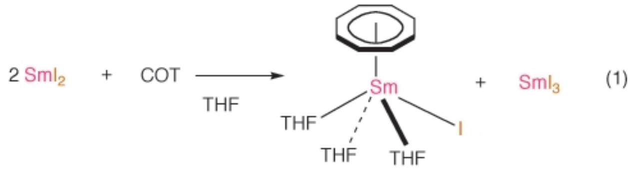
sulfur compound containing a transannular S–S bond with lanthanoid metals. It is of utmost importance that the lanthanoid products obtained this way are anhydrous and thus useful for reagents or catalysts in many cases without any further purification. By considering the difficulty in obtaining anhydrous halides or oxoacid salts of lanthanoids, the remarkable simplicity of the direct reaction opens up a wide possibility for future development of lanthanoid coordination chemistry.

Here we also describe our recent investigations on the chemistry of lanthanoid elements coordinated with various ligands including a conjugated diene, a cyclic tetraene and azo compounds. In these reactions the starting organic molecules are allowed to coordinate to the lanthanoid center as anionic ligands through the redox process. Our synthetic method has thus provided a new way to prepare Cp-free organometallic complexes of lanthanoids.[8,9]

2 Reactions of metallic lanthanoids with unsaturated π-conjugated organic compounds

2.1 Hints and practice: new synthetic method to prepare cyclooctatetraenyl compounds of lanthanoids from metallic sources

Let us first briefly describe the beginning of our synthetic study of lanthanoid complexes from metallic sources. At the CSJ national meeting in 1988, Professor T. Imamoto disclosed that two equivalents of SmI_2, which can readily be prepared by the reaction of samarium metal with alkyl iodides,[10,11] are required to achieve a high chemical yield for the pinacol-type coupling reactions of ketones and, in addition, that SmI_2 can be obtained from the conproportionation (reduction of SmI_3 with samarium metal).[12] This oral presentation led to the question why two equivalents of SmI_2 are essentially required to complete the pinacol-type reactions. One (K. M.) of us anticipated that a disproportionation occurred in these reactions; two moles of SmI_2 are in equilibrium with SmI_3 and a nascent species 'SmI'; the latter may act as a strong reducing reagent like magnesium metal. Alternatively, SmI_2 acts as a one-electron reducing reagent and thus two moles of it are required to achieve the pinacol coupling reactions. Bearing in mind the reaction of magnesium metal with cycloocta-1,3,5,7-tetraene (= COT) giving Mg(η^8-COT),[13] he carried out the reaction in eqn. (1).



1e

On adding a THF solution of COT to a THF solution of two equivalents of SmI_2 the deep purple color of SmI(η^8-COT)(THF)$_3$ **1e** developed and yellow solid SmI_3 precipitated. As mentioned above, SmI_3 can be reduced by samarium metal to regenerate SmI_2.[12] Thus, a stoichiometric mixture of samarium metal, COT, and iodine in THF was found to give highly air- and moisture-sensitive **1e**.[14,15] A related complex, [Sm(μ-Cl)(η^8-COT)(THF)$_2$]$_2$ **2**, had been prepared by the metathesis reaction of anhydrous $SmCl_3$ with K_2(COT).[16] In this reaction, the low solubility of **2** hampered its purification due to the severe contamination with the resulting alkali metal salts.

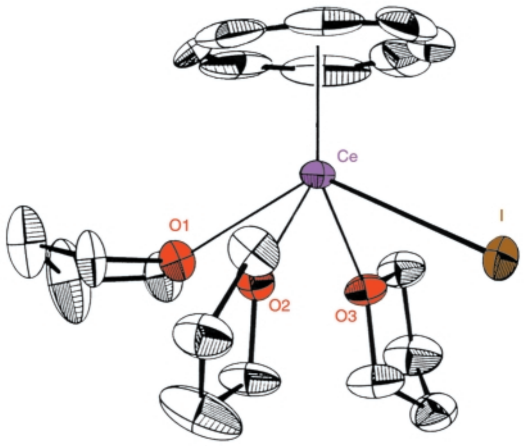
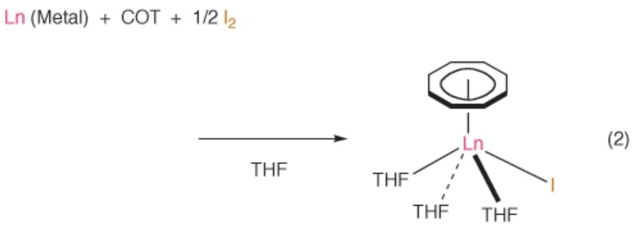


Fig. 1 The molecular structure of CeI(η^8-COT)(THF)$_3$ **1b**.



1a: Ln = La
1b: Ln = Ce
1c: Ln = Pr
1d: Ln = Nd
1e: Ln = Sm

The present synthetic method can be applied for various early lanthanoid metals and thereby complexes having a general formula LnI(η^8-COT)(THF)$_m$ **1a–1e** were isolated in high yield [eqn. (2)].[14,15] Moreover, with Ph_3PCl_2 as a chloride source, the salt-free, one pot reaction produced complex **2** in high yield after a simple crystallization. In contrast to the dimeric structure found for **2**,[17] the newly prepared iodolanthanoid complexes **1** preferred monomeric structures and hence were moderately soluble in THF. Fig. 1 shows the crystal structure of the cerium complex **1b** that adopts a mononuclear four-legged piano stool geometry.[14] The COT of **1b** is coordinated as a capping planar dianion (10 π) ligand, and three THF molecules and one iodine atom represent "legs". A rather long Ce–I bond distance (3.300(1) Å) indicated **1b** to have an ionic character.

When the amount of iodine was reduced to a catalytic amount (less than 5%), polymeric [Sm(η^8-COT)(THF)]$_m$ **3a** was obtained [eqn. (3)].[14,15] In this reaction, iodine acted not only as an activator of metal surface but also as a mediator of the reaction. Similarly, Yb metal reacted with COT to give polymeric [Yb(η^8-COT)]$_m$ **3b**. Our synthetic method in THF is much more convenient compared with the known reaction of Yb in liquid ammonia with COT followed by the addition of pyridine giving an ytterbium(II) complex Yb(η^8-COT)(Py)$_3$ **4**.[18] Reaction of the complex **3a** with iodine gave **1e** quantitatively, while treatment of **3b** with iodine resulted in the formation of YbI_2 with the release of COT.

$$\mathrm{Ln} + \mathrm{COT} \xrightarrow[\mathrm{THF}]{\mathrm{I_2\ (cat.)}} [\mathrm{Ln}(\eta^8\text{-COT})(\mathrm{THF})_n]_m \qquad (3)$$

3a; Ln = Sm, $n = 1$,
3b; Ln = Yb, $n = 0$,

2.2 Cationic cyclooctatetraenyllanthanoid complexes

A variety of neutral and anionic COT complexes of lanthanoids has been prepared; however, no cationic COT complex has been reported so far. Since hexamethylphosphoric triamide, PO(NMe$_2$)$_3$ (= HMPA), is a strong donor ligand to lanthanoid ions, its addition caused cleavage of the Ln–X bond (X = halogen). Such cleavage gave rise to some cationic lanthanoid

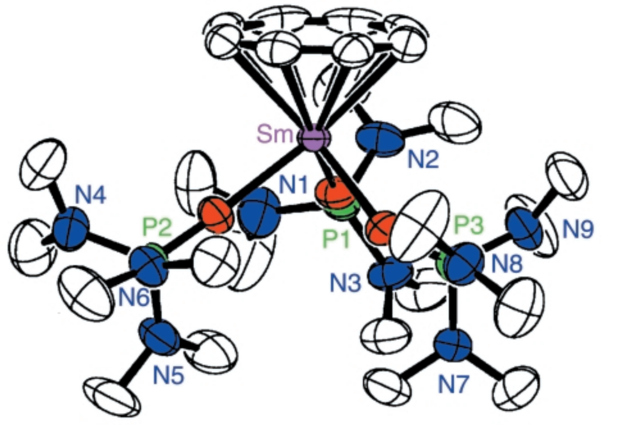


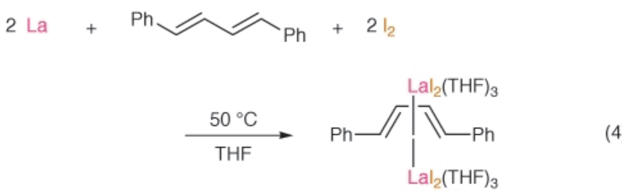
Fig. 2 The molecular structure of the cationic part of [Sm(η^8-COT)(HMPA)$_3$][Sm(η^8-COT)$_2$] **6**.

complexes such as [Yb(HMPA)$_4$(THF)$_2$]I$_2$,[19] [Sm(HMPA)$_6$]I$_2$,[20] and [Ln(SC$_5$H$_4$N)$_2$(HMPA)$_3$]I (see below).[21] On adding a little excess of HMPA to the neutral complex SmI(η^8-COT)(THF)$_3$ **1e** we isolated a cationic samarium complex [Sm(η^8-COT)(HMPA)$_3$]I **5**, which can alternatively be derived from the one-pot reaction of a stoichiometric mixture of metallic samarium, COT, and iodine in the presence of an excess of HMPA.[22]

Furthermore, in sharp contrast to the formation of the samarium(II) complex **3a**, the reaction of samarium metal and COT in the presence of an excess of HMPA resulted in the formation of an ionic complex [Sm(η^8-COT)(HMPA)$_3$][Sm(η^8-COT)$_2$] **6**, in which both anionic and cationic parts have samarium(III) centers.[22] This may be a result of the enhanced redox process by HMPA. Fig. 2 shows the molecular structure of **6**. The complexes **5** and **6** are the first examples of the discrete cationic monocyclooctatetraenyllanthanoids, while a unique COT-bridged dinuclear complex [Nd(η^8-COT)(THF)$_2$]$^+$(μ-η^2:η^8-COT)[Nd(η^8-COT)]$^-$ has previously been reported.[23]

2.3 Diene complexes of lanthanoids

Two approaches for preparing diene complexes from metallic lanthanoid sources have been reported; Evans *et al.*[24] used the metal vapor method for the synthesis of 1,3-butadiene complexes and Saussine *et al.*[25] the solution reaction of metallic samarium or ytterbium with 1,4-diphenyl-1,3-butadiene. However, these diene complexes were not isolated. In the course of our study on diene complexes of Group 4 and 5 metals[26] as well as alkaline earth (Group 2) metals,[27–29] we have maintained an interest in the synthesis of such complexes of Group 3 metals. A reaction of finely divided metallic lanthanum with two equivalents of iodine and half an equivalent of 1,4-diphenyl-1,3-butadiene in THF gave complex **7** [eqn. (4)].[30] Closely



7

(4)

related is the neutral gadolinium complex [(THF)$_3$Cl$_2$Gd(μ-η^4:η^4-*s-cis*-PhCHCHCHCHPh)GdCl$_2$(THF)$_3$] **8**, prepared by reduction of GdCl$_3$ by a potassium salt of 1,4-diphenyl-1,3-butadiene in THF, and the anionic lutetium complex {[K(THF)$_2$][Lu(*s-cis*-PhCHCHCHCHPh)$_2$(THF)$_2$]}$_n$ **9**.[31,32]

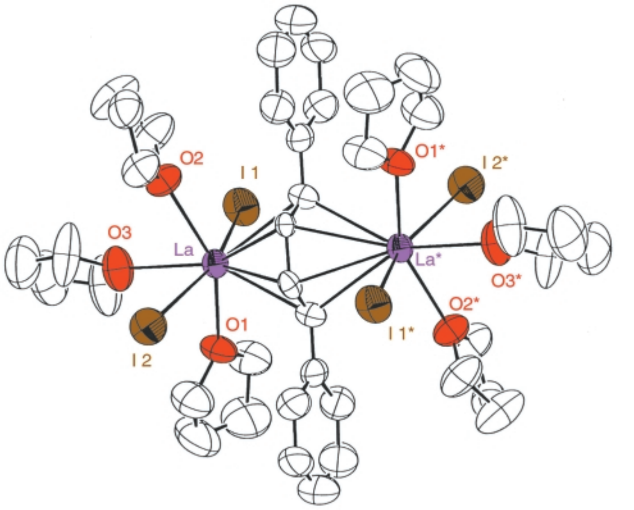
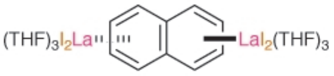


Fig. 3 The molecular structure of [I$_2$La(THF)$_3$(μ-η^4:η^4-*s-cis*-PhCHCHCHCHPh)}LaI$_2$(THF)$_3$] **7**.

The X-ray analysis of a highly air-sensitive crystal of complex **7** clearly revealed its unique inverse sandwich structure where each LaI$_2$(THF)$_3$ moiety is bridged by the diene ligand (Fig. 3). It is of interest that two LaI$_2$(THF)$_3$ moieties are reported to be co-ordinated by another dianionic π-aromatic ligand, to form [LaI$_2$(THF)$_3$][μ-η^4:η^4-C$_{10}$H$_8$][LaI$_2$(THF)$_3$] **10**.[33] The La atoms of **7** and **10** are in the 3+ oxidation state. A noteworthy feature is that the geometry of **7** is similar to that of the compound [(TMEDA)Li(μ-PhCHCHCHCHPh)Li(TMEDA)] **11** (TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine)[34] but different from the dissymmetric bridging structure of [(THF)Cp*$_2$La(μ-η^1:η^3-C$_4$H$_6$)LaCp*$_2$] **12**.[35] On the basis of the structural similarities of **7** and **10** with their lithium analogs, it is reasonably assumed that the 'lanthanoid(II)' moiety acts as alkali metal-like, just like the 'lanthanoid(I)' species acts as alkaline earth metal-like.

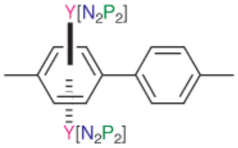


10

It deserves comment that these π-conjugated hydrocarbons interact with two lanthanoid(II) fragments. A representative example is the reaction of a typical samarium(II) organometallic compound SmCp*$_2$ **13** with styrene to give a dinuclear compound, [Cp*$_2$Sm](μ-η^2:η^4-PhCH=CH$_2$)[SmCp*$_2$] **14**.[36] Additionally, unique inverse sandwich complexes **15** and **16** were respectively reported by Lappert and co-workers[37,38] and Fryzuk *et al.*[39]

15

Cp′ = η^5-C$_5$H$_3$(CMe$_3$)$_2$



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[N$_2$P$_2$] = [PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh]

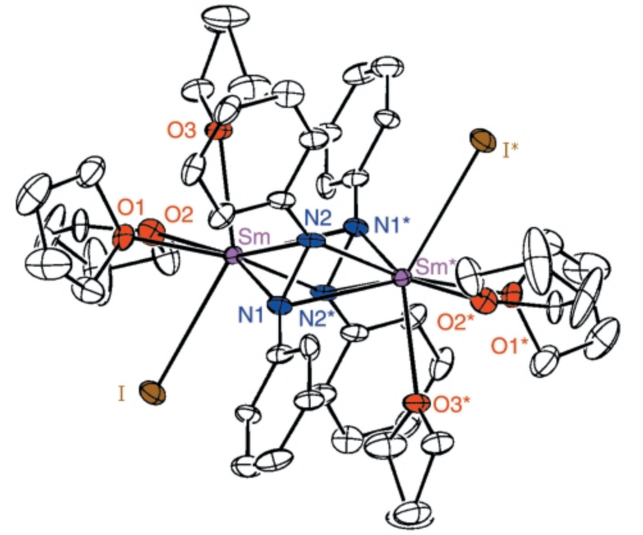
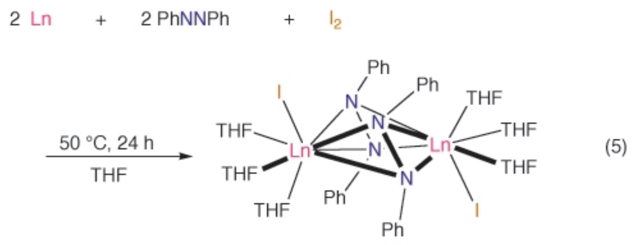


Fig. 4 The molecular structure of [(THF)$_3$ISm(μ-η^2:η^2-*trans*-PhNNPh)$_2$SmI(THF)$_3$] **17**.

2.4 Reactions of metallic lanthanoids with unsaturated organic compounds containing an X=Y bond

Treatment of metallic samarium with azobenzene in the presence of iodine resulted in the formation of a unique binuclear samarium complex of azobenzene, [(THF)$_3$ISm(μ-η^2:η^2-*trans*-PhNNPh)$_2$SmI(THF)$_3$] **17** [eqn. (5)].[40] A similar reaction of ytterbium afforded an analogous ytterbium complex **18**.[40] Fig. 4 shows the crystal structure of **17** in which two *trans*-azobenzene dianion ligands are bridging two 'SmI(THF)$_3$' moieties and each samarium atom adopts distorted doubly capped trigonal prismatic geometry. The structure of **17** was found to be essentially similar to that of a doubly bridged inverse sandwich complex [(THF)Cp*Sm](μ-η^2:η^2-*cis*-PhNNPh)$_2$[SmCp*(THF)] **19**.[41] These complexes have two samarium(I) moieties bridged by two azobenzene dianion ligands, being in sharp contrast to the reported structure where two organosamarium(II), Cp*$_2$Sm, moieties are connected by one bridging azobenzene dianion ligand.[41] In addition, Takats *et al.*[42] and Evans *et al.*[43] respectively reported two monomeric azobenzene complexes, SmTp*$_2$(η^2-PhNNPh) **20** [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate] and SmCp*$_2$(η^2-PhNNPh)(THF) **21**.



17: Ln = Sm
18: Ln = Yb

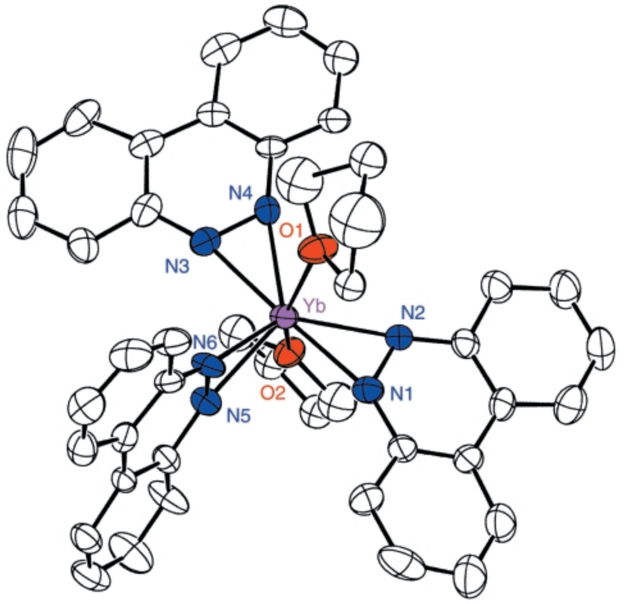
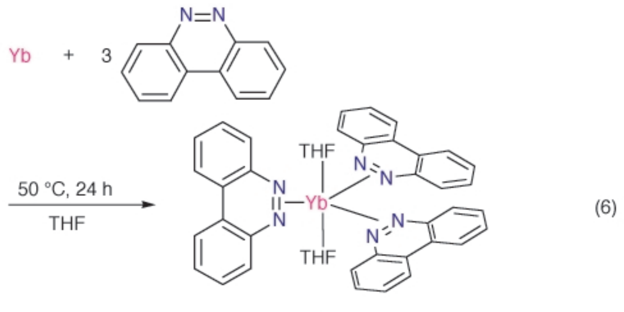
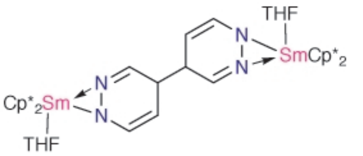


Fig. 5 The molecular structure of Yb(BC)$_3$(THF)$_2$ **22**.



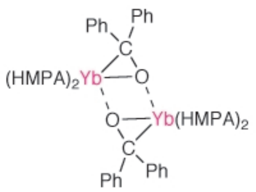
22

Without a stoichiometric amount of iodine, we obtained highly air- and moisture-sensitive azobenzene adducts of samarium and ytterbium; however their structures could not be characterized. With a *cis*-azo compound, benzo[*c*]cinnoline instead of azobenzene, we succeeded in the isolation of an ytterbium compound, Yb(BC)$_3$(THF)$_2$ **22** (BC = benzo[*c*]cinnoline) [eqn. (6)].[40] The structure of **22** was determined by X-ray analysis (Fig. 5), indicating that it has three BC ligands in η^2-*cis*-N–N fashion and the Yb has a distorted dodecahedral geometry. The Yb–N distances of **22** are shorter than typical Yb–N donor bonds, indicating that this is better formulated as a ytterbium(III) complex having three BC radical anions rather than an ytterbium(0) complex with three neutral ones. This is a rare example of a lanthanoid *cis*-azo linkage complex; the other example is complex **23** that has a coupled pyridazine ligand.[44]



23

With respect to lanthanoid compounds with a C=X bond, some ketone[45,46] and imine[47] complexes of lanthanoids (*e.g.* **24** and **25**) have been reported. It is of interest that benzophenone and thiobenzophenone reacted with metallic ytterbium to cleave the C=X double bond.[46,48] Moreover, ketyl radical can be



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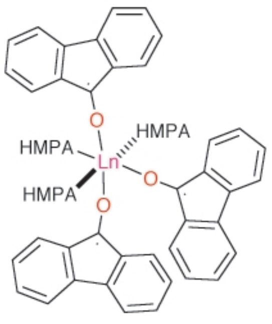
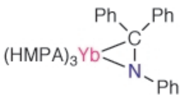


26 Ln = Sm, Yb



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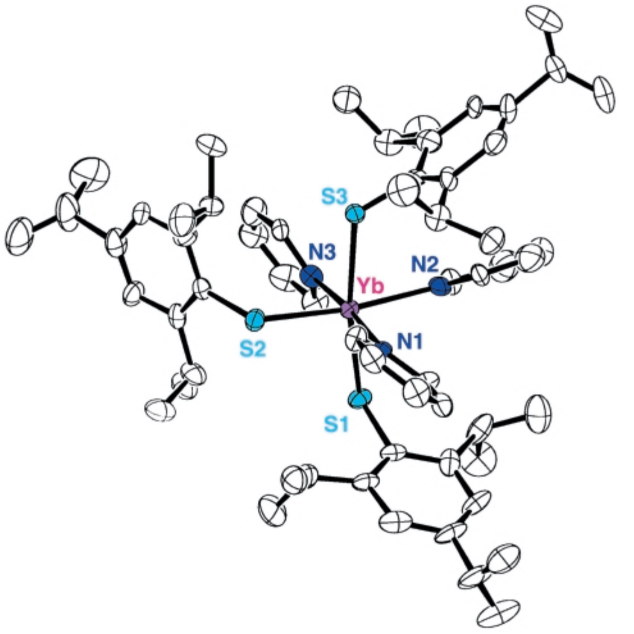


Fig. 6 The molecular structure of *mer*-Yb(SAr)$_3$(Py)$_3$ **28**. The molecular structure of *mer*-Sm(SAr)$_3$(Py)$_3$ **27** is isomorphous to that of **28**.

stabilized by complexation to a lanthanoid metal; reaction of metallic samarium and ytterbium with fluorenone in a mixture of THF and HMPA afforded fluorenone ketyl complexes **26**.[49]

3 Insertion of lanthanoid atom into disulfide bond

Chalcogenolate complexes of lanthanoid elements attract much interest since not only are they precursors for new catalysts and materials but they also provide an insight into the nature of the Ln–E bonds. Most complexes containing such bonds have been prepared by the metathesis reactions of lanthanoid halides with chalcogenolate anions, but the purification of chalcogenolate complexes is in most cases hampered by the strong interaction of the products with alkali and alkaline earth metal salts. The most attractive synthetic method is the salt-free preparation: (1) the oxidative reaction of low-valent organolanthanoid complexes with organic disulfides[50–52] and (2) the reaction of amide and alkyl complexes with bulky thiols.[53–56] As mentioned in the above section, an appropriate synthetic method for preparing lanthanoid chalcogenolate complexes should involve the direct oxidative reaction of metallic lanthanoid with REER in solution.

3.1 Synthesis and characterization of tris(thiolato)lanthanoid(III)

Diaryl disulfides were found to react oxidatively with metallic samarium and ytterbium to give the corresponding tris(thiolato)lanthanoid(III) complexes. Typically, treatment of metallic samarium with 1.5 equivalents of bis(2,4,6-triisopropylphenyl) disulfide in THF followed by pyridine resulted in the formation of *mer*-Sm(SAr)$_3$(Py)$_3$ **27** (Py = pyridine; Ar = 2,4,6-triisopropylphenyl) [eqn. (7)].[57,58] The analogous reaction of ytterbium metal afforded *mer*-Yb(SAr)$_3$(Py)$_3$ **28**. The monomeric structures of **27** and **28** were guaranteed by the bulky isopropyl substituents at *ortho* positions, which prevent the thiolate bridging, leading to oligomeric structures, as shown in Fig. 6. The reaction of europium metal, on the contrary, afforded a europium(II) thiolate complex (see below).

$$\mathrm{Ln} \;+\; 3/2\ \mathrm{ArSSAr} \xrightarrow[\text{ii) Py / THF}]{\text{i) } \mathrm{I_2}\text{ / THF}} \mathrm{Ln(SAr)_3(Py)_3} \qquad (7)$$

Ar = 2,4,6-triisopropylphenyl

27: Ln = Sm
28: Ln = Yb

Metallic samarium dissolves slowly on treating with diphenyl disulfide in THF, but leaves a yellow insoluble powder that is caused by the sterically less demanding thiolate bridging. In order to cleave this bridge we also used HMPA. The same reaction but in the presence of 3 equivalents of HMPA gave a monomeric complex, *mer*-Sm(SPh)$_3$(HMPA)$_3$ **29** [eqn. (8)].[58]

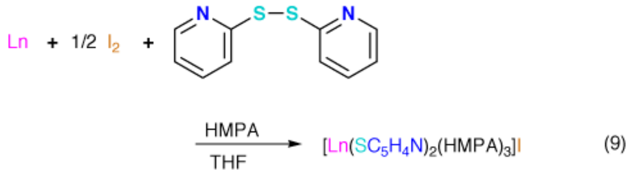
$$\mathrm{Ln} \;+\; 3/2\ \mathrm{PhSSPh} \xrightarrow[\text{THF}]{\mathrm{I_2},\ \text{HMPA}} \mathrm{Ln(SPh)_3(HMPA)_3} \qquad (8)$$

29: Ln = Sm
30: Ln = Eu
31: Ln = Yb

Similarly, the reactions with metallic europium and ytterbium afforded the corresponding lanthanide(III) complexes, *mer*-Ln(SPh)$_3$(HMPA)$_3$ (Ln = Eu **30** or Yb **31**).[58] The reaction rates for the other lanthanide metals such as lanthanum, praseodymium, dysprosium were much slower than those found for Sm, Eu and Yb. The structure of **29** is quite similar to that of **27**, and has mononuclear pseudo octahedral geometry with three thiolate ligands and three HMPA ligands in meridional fashion.

3.2 Synthesis and characterization of pyridine-2-thiolate complexes of lanthanoids

We anticipated the chelate effect to enable the formation of thiolate complexes for the other lanthanoid elements. Thus, we used di-2-pyridyl disulfide as an oxidizing compound. The direct oxidative reactions of metallic lanthanoids in a mixture of THF and HMPA proceeded readily and cationic pyridine-2-thiolate complexes [Ln(SC$_5$H$_4$N)$_2$(HMPA)$_3$]I **32** (SC$_5$H$_4$N = pyridine-2-thiolate) were obtained [eqn. (9)].[21]



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a: Ln = Pr
b: Ln = Nd
c: Ln = Sm
d: Ln = Eu
e: Ln = Er
f: Ln = Yb

Thus, the treatment of metallic samarium with di-2-pyridyl disulfide in the presence of iodine and HMPA afforded brown prisms of [Sm(SC$_5$H$_4$N)$_2$(HMPA)$_3$]I **32c**. This synthetic method can be applied for the preparation of analogous complexes **32a**,**b**,**d**–**f** from metallic Pr, Nd, Eu, Er, and Yb, respectively. These complexes are air- and moisture-stable. This may be attributed to the chelating coordination of the pyridine-2-thiolate ligands combined with the strong π donation from the HMPA ligands. The cationic part of **32c** is shown in Fig. 7. Complex **32c** has pentagonal bipyramidal geometry; two chelating pyridine-2-thiolates and one HMPA ligand lie in the pentagonal plane. Other pyridine-2-thiolate complexes of lanthanoids have been prepared by Brennan and co-workers,[59,60] who reported the transmetallation reactions of Hg(SC$_5$H$_4$N)$_2$ with metallic Ln in pyridine to give complexes Ln(SC$_5$H$_4$N)$_2$(Py)$_4$ **33** (Ln = Eu or Yb), while the reactions of Ln/Hg amalgam with di-2-pyridyl disulfide in the presence of [SC$_5$H$_4$N]$^-$ resulted in the formation of the anionic trivalent complexes [Ln(SC$_5$H$_4$N)$_4$]$^-$ **34** (Ln = Ce, Eu, Tm, or Ho).

3.3 Synthesis and characterization of bis(thiolate) complexes of lanthanoid(II)

As shown in section 3.1, reactions of lanthanoid metals with 1.5 equivalents of disulfides afforded lanthanoid(III) thiolate com-

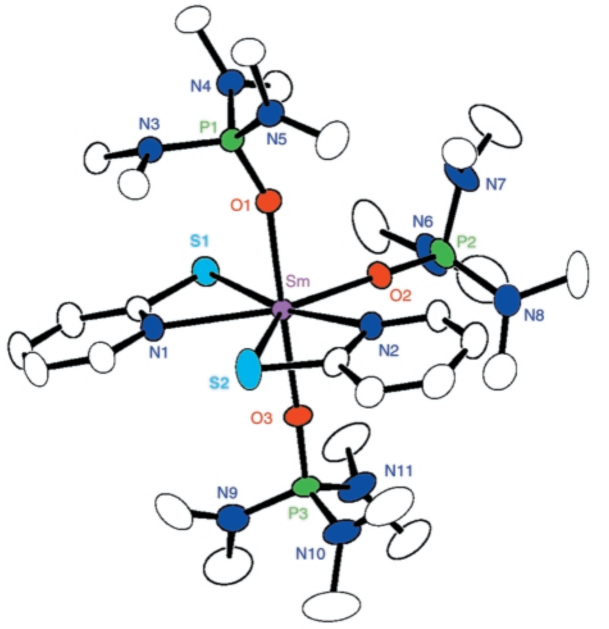


Fig. 7 The molecular structure of the cationic part of [Sm($SC_5H_4N)_2(HMPA)_3$]I **32c**.

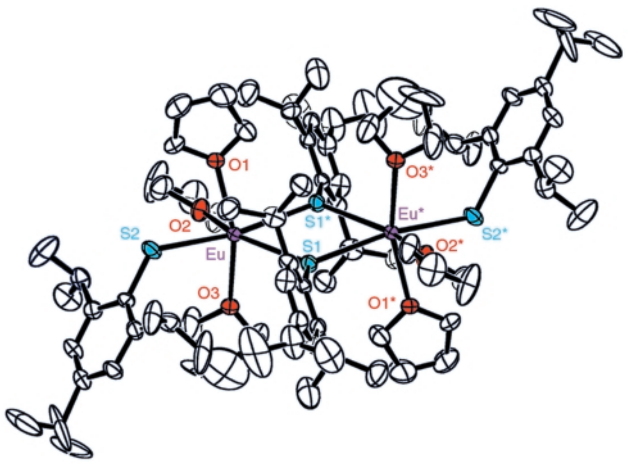


Fig. 8 The molecular structure of [Eu(SAr)(μ-SAr)$(THF)_3]_2$ **36**. The structure of [Sm(SAr)(μ-SAr)$(THF)_3]_2$ **35** is isomorphous to that of **36**.

plexes. On reducing the amount of the disulfides, the corresponding bis(thiolate) complexes of lanthanoid(II), *i.e.* samarium(II), europium(II), and ytterbium(II), can be synthesized. Treatment of bis(2,4,6-triisopropylphenyl) disulfide with a 2-fold excess of metallic samarium in THF afforded a dinuclear bis(2,4,6-triisopropylbenzenethiolate) complex [Sm(SAr)(μ-SAr)$(THF)_3]_2$ **35** (SAr = 2,4,6-triisopropylbenzenethiolate) [eqn. (10)].[57,58] Similar reaction of metallic europium gave a

$$\text{Ln (excess)} \quad + \quad \text{ArSSAr} \xrightarrow[\text{THF}]{I_2\text{ (cat.)}} 1/2\ [\text{Ln(SAr)}(\mu\text{-SAr})(\text{THF})_3]_2 \qquad (10)$$

Ar = 2,4,6-triisopropylphenyl

35: Ln = Sm
36: Ln = Eu

dimeric complex [Eu(SAr)(μ-SAr)$(THF)_3]_2$ **36**. The reaction of metallic Yb with the disulfide in THF gave an orange oily product, from which black crystals of Yb$(SAr)_2(Py)_4$ **37** were obtained after adding pyridine [eqn. (11)].[57,58] Dimeric

$$\text{Yb (excess)} \quad + \quad \text{ArSSAr} \xrightarrow[\text{ii) Py / THF}]{\text{i) } I_2\text{ (cat.)/ THF}} \text{Yb(SAr)}_2(\text{Py})_4 \qquad (11)$$

Ar = 2,4,6-triisopropylphenyl

37

structures of **35** and **36** were confirmed by crystallographic studies (Fig. 8).

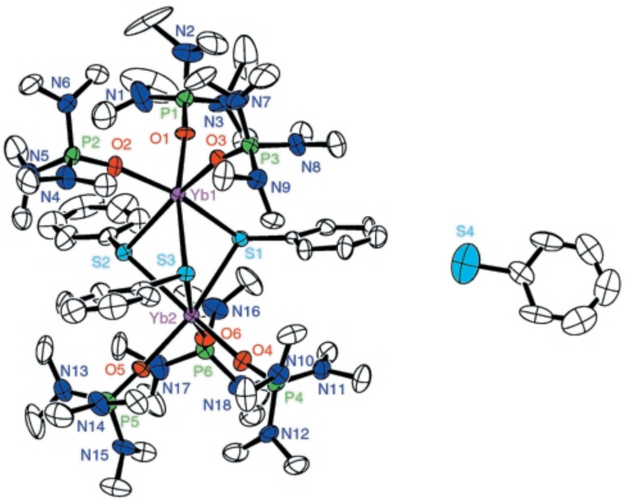


Fig. 9 The molecular structure of [{Yb$(HMPA)_3\}_2$(μ-SPh)$_3$][SPh] **40**.

Since diphenyl disulfide is a non-bulky disulfide, the reaction with ytterbium metal only gave a polymeric compound. The addition of HMPA as a donor ligand to the reaction mixture, however, resulted in crystallization of an ionic HMPA adduct of a triply bridged dinuclear ytterbium(II) complex, [{Yb$(HMPA)_3\}_2$(μ-SPh)$_3$][SPh] **40** [eqn. (12)].[58] Samarium (**38**) and europium (**39**) derivatives were also prepared.

$$\text{Ln (excess)} \quad + \quad \text{PhSSPh} \xrightarrow[\text{ii) HMPA / THF}]{\text{i) } I_2\text{ (cat.)/ THF}} 1/2\ [\{\text{Ln(HMPA)}_3\}_2(\mu\text{-SPh})_3][\text{SPh}] \qquad (12)$$

38: Ln = Sm
39: Ln = Eu
40: Ln = Yb

Fig. 9 shows the molecular structure of complex **40**, which is in sharp contrast to the neutral dimer structure found for **35** and **36**. Each ytterbium atom in the cationic dimer part adopts a distorted octahedral geometry being surrounded by three HMPA ligands and three bridging benzenethiolate ligands in facial mode. The coordination of the polar HMPA ligands to the ytterbium metal caused an elongation of the Yb–S bonds and this effect leads to heterolysis of one of these bonds, releasing a benzenethiolate anion.

Brennan and co-workers[61] recently reported the preparation of Yb$(EPh)_2(Py)_4$ **41** (E = S, Se, or Te), analogous to **37**, by the reaction of PhEEPh with the solvated ytterbium(II) ion in liquid ammonia or Yb/Hg amalgam in THF. In contrast to the dimeric complexes **38**–**40** and the monomeric complex **41**, the benzeneselenolate europium(II) compound, [Eu(μ-SePh)$_2$-$(THF)_3]_n$ **42**, has an infinite 1-D structure.[62] Fujiwara and co-workers[63] reported another synthesis of a bis(thiolate) complex of Yb^{II} by the reaction of metallic Yb and $PhSSiMe_3$ in propionitrile, but the product has not been isolated.

3.4 Chalcogenolate complexes bearing a COT ligand

The observed similarity between the direct reactions using iodine and disulfide as the oxidizing reagent prompted us to prepare thiolate complexes bearing a COT ligand (iodo-derivatives, see above). One-pot reaction of metallic samarium, COT, and diphenyl disulfide afforded a dimeric monocyclooctatetraenyl thiolate complex, [Sm(μ-SPh)(η^8-COT)$(THF)_2]_2$ **43** [eqn. (13)].[64] Similarly, two distinct thiolate complexes **44** and **45**[64] as well as a selenolate complex **46**[15] were prepared.

The thiolate-bridged dinuclear structures of complexes **43** and **45** were determined by X-ray analyses. As shown in Fig. 10, the Sm_2S_2 unit of **43** is planar. Samarium has a pseudo square-pyramidal geometry in **43**, but a pseudo tetrahedral

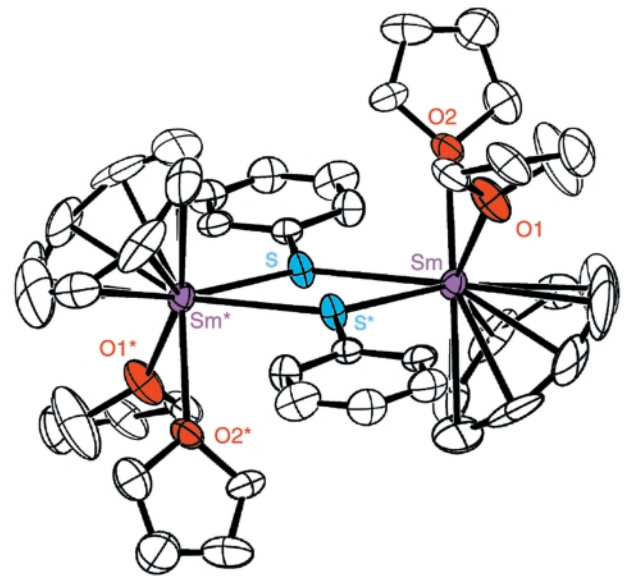


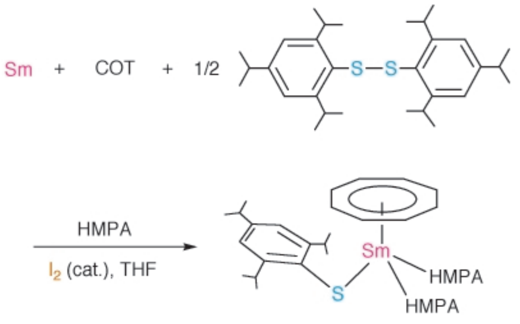
Fig. 10 The molecular structure of $[\mathrm{Sm}(\mu\text{-SPh})(\eta^8\text{-COT})(\mathrm{THF})_2]_2$ **43**.

$$2\,\mathrm{Sm} + 2\,\mathrm{COT} + \mathrm{ArEEAr} \xrightarrow[\mathrm{THF}]{\mathrm{I_2\ (cat.)}} [(\eta^8\text{-COT})\mathrm{Sm}(\mu\text{-EAr})(\mathrm{THF})_n]_2 \qquad (13)$$

43: $\mathrm{EAr} = \mathrm{SC_6H_5}$, $n = 2$
44: $\mathrm{EAr} = \mathrm{SC_6H_2Me_3}$-2,4,6, $n = 2$
45: $\mathrm{EAr} = \mathrm{SC_6H_2Pr^i_3}$-2,4,6, $n = 1$
46: $\mathrm{EAr} = \mathrm{SeC_6H_5}$, $n = 2$

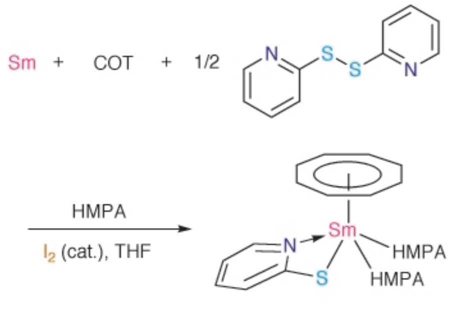
geometry in **45** may be due to the isopropyl groups on the thiolate ligand.

Here again, the addition of HMPA caused cleavage of the bridging structure leading to mononuclear complexes. We thus obtained cyclooctatetraenyl(thiolato)samarium(III) complexes of formula $\mathrm{Sm(SR)}(\eta^8\text{-COT})(\mathrm{HMPA})_2$ (R = 2,4,6-triisopropylphenyl **47** or 2-pyridyl **48**) by one-pot reactions of COT, samarium metal, and the corresponding disulfide [eqns. (14) and (15)].[65] The complex **48** has a pseudo square pyramidal and four-legged piano-stool geometry, while **47** has three-legged piano-stool geometry (Fig. 11).



(14)

47



(15)

48

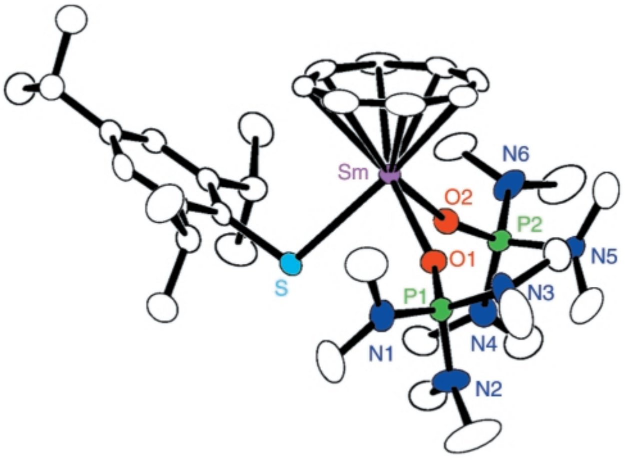
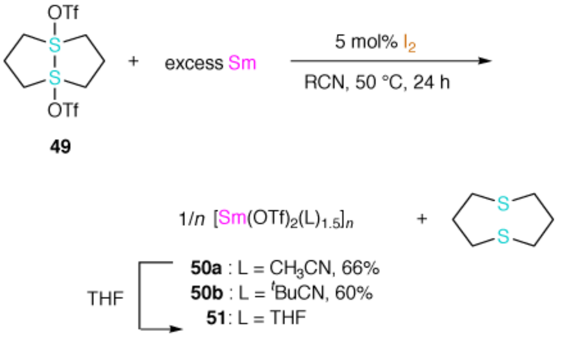


Fig. 11 The molecular structure of $\mathrm{Sm(SC_6H_2Pr^i\text{-}2,4,6)}(\eta^8\text{-COT})(\mathrm{HMPA})_2$ **47**.

3.5 First oxidative addition of hypervalent transannular S–S bond to metallic lanthanoid: synthesis, characterization, and reactivity of bis(triflato)samarium(II)

The hypervalent sulfur compounds have rarely been used for preparing organometallic complexes. 1,5-Dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) **49** is a crystallographically characterized hypervalent compound having a transannular S–S bond.[66] We thus anticipated that the direct reaction of **49** with metallic lanthanoid gives a salt-free triflato complex of lanthanoid metal. The reaction of 1.5 equivalents of **49** with metallic samarium smoothly afforded a tris(triflato)samarium(III) complex, while the reaction of an excess of samarium with **49** led to samarium(II) bis(trifluoromethanesulfonate) complexes of formula $[\mathrm{Sm(OTf)_2(L)_{1.5}}]_n$ (L = MeCN **50a**, *tert*-BuCN **50b** or THF **51**) in modest yield [eqn. (16)].[67]



(16)

Recrystallization of **50a** from THF gave crystals of **51**, which in acetonitrile regenerated **50a** quantitatively. Complex **50a** mediates the intermolecular pinacol coupling reactions of aromatic ketones with high diastereoselectivity (up to 94 : 6 (DL : *meso*) at −40 °C in acetonitrile and −78 °C in propionitrile. Quite recently, Collin *et al.*[68] reported that the combination of $\mathrm{Sm(OTf)_3}$ and Sm metal generates $[\mathrm{Sm(OTf)_2(DME)}]$, which is used as a reagent in organic reactions.

Fig. 12 shows the structure of $[\mathrm{Sm(OTf)_2(THF)_{1.5}}]_n$ **51** elucidated by X-ray analysis. All triflato anions of the complex act as bridging ligands and make infinite 2-D sheets. Fig. 13 shows core structures around the two different samarium atoms of **51**; one samarium atom adopts distorted capped octahedral geometry, while the other has distorted pentagonal bipyramidal geometry.

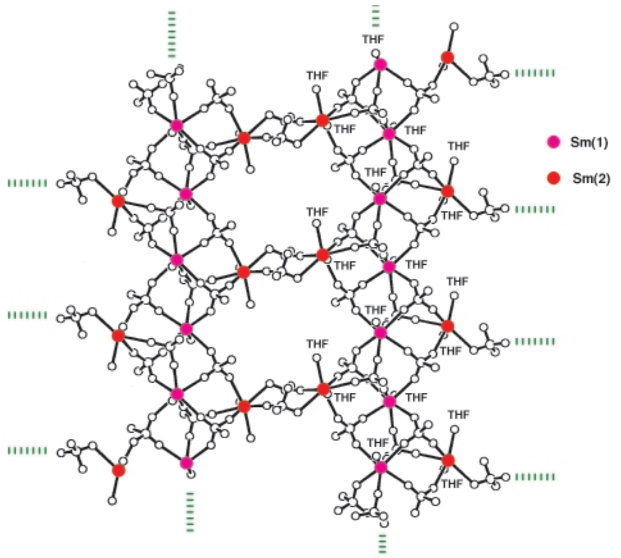


Fig. 12 A drawing of the 2-D sheet structure of [Sm(OTf)$_2$(THF)$_{1.5}$]$_n$ **51**.

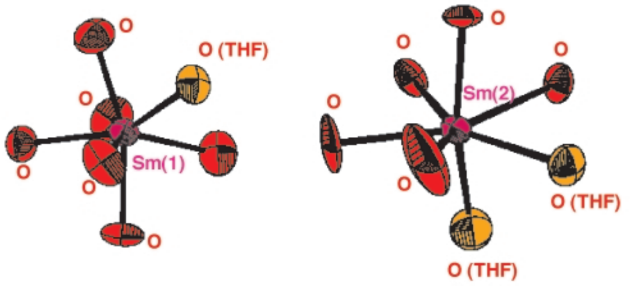


Fig. 13 Drawings of the geometry around the two different samarium atoms of complex **51**.

4 Conclusion

By using simple one-pot reactions, we demonstrated that some organic compounds such as COT, 1,4-diphenyl-1,3-butadiene, and azo compounds reacted with lanthanoid metals to give some interesting, unique organolanthanoid complexes having anionic organic ligands, which are highly air- and moisture-sensitive. The products are readily isolated by simple crystallization. The direct redox reactions of metallic lanthanoids with organic diaryl disulfides were also found to give a variety of highly reactive arenethiolate complexes in the simple one-pot procedure. Further elaboration of the primary thiolate with various donors provides novel coordination compounds with prominent structural features and unique reactivities. It is of interest that both divalent and trivalent lanthanide arenethiolate complexes can be prepared by the direct reactions of some metallic lanthanoids with diaryl disulfides by controlling the stoichiometry of the reactants. We also demonstrated the unique reaction of the transannular S–S bond of the hypervalent compound 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) with metallic samarium, giving the salt-free samarium(II) bis(triflate) compound.

It is a recent trend that some lanthanoid complexes *without* cyclopentadienyl ligands are also used to initiate the polymerization of polar monomers, although Cp*$_2$Ln-type complexes have been utilized as active catalyst precursors.[69,70] The structurally well defined thiolate complexes of lanthanoids were found to be effective initiators for the polymerization of various polar monomers such as methyl methacrylate (MMA),[71] acrylonitrile,[72] and cyclic esters.

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