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TRANSITION METAL COMPOUNDS**

A Doctoral Thesis
by
Yuushou Nakayama

Submitted to
the Faculty of Science, Osaka University
February, 1995

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Approval

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This thesis is approved as to
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February, 1995

中山祐正
Yuushou Nakayama

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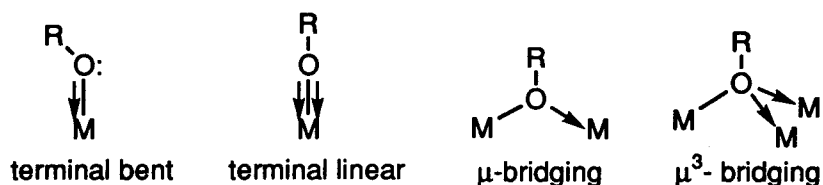
Chapter 1

General Introduction

Since the discovery of Ziegler-Natta catalyst, heterogeneous catalyst systems comprised of transition metals and alkyl aluminum compounds have attracted much interest. The discovery of Kaminsky catalyst¹ prompted us to study the homogeneous single-site catalysts bearing cyclopentadienyl ligands. During 1980's, the early transition metal complexes have taken a special place in the field of the polymerization of α -olefins. The stereoregular polymerization of α -olefins has been accomplished by using *ansa*-type metallocene complexes of group 4 metals, where *ansa*-type denotes two cyclopentadienyl ligands bridged. At present, the research on polymerization is not only by trial-and-error but by the modern theoretical methods where the design of the catalyst precursor is the most important factor on the stereoselectivity and activity of the polymerization of α -olefins.²⁻⁴ Thus, the mechanism for the polymerization of α -olefins is now well-established and the design of the catalyst precursor for the desired polymerization of α -olefins is based on the advanced theoretical chemistry.

In the field of homogeneous polymerization catalysts for α -olefins, cyclopentadienyl or substituted cyclopentadienyl ligands have played specially important role. Cyclopentadienyl ligands are highly electron-donating (5 electron donor), sterically bulky, and therefore ideal ligands for electrically positive early transition metal ions. These ligands stabilize highly reactive metal fragments such as metal alkyl and metal hydride and suppress association of these organometallic complexes. The use of such ligands enabled us to control the selectivity and activity of the catalyst by designing the catalyst precursor.

On the other hand, alkoxo ligands are attracting much attention as a new kind of ancillary ligand for early transition metal complexes. Alkoxo ligands have many unique features including: (1) they can be regarded as 5 electron donors like cyclopentadienyl ligands considering donation of four lone pair electrons; (2) consequently, strong metal—oxygen bonds are formed, the bond which are more resistant to alkylation than halide ligands; (3) alkyl (aryl) group on oxo ligands can be extensively varied to modulate the solubility and steric effect of the whole complex; (4) such ligands have a variety of bonding mode to the metal such as terminal, μ -bridging, and μ^3 -bridging (see, Scheme I). When the steric bulkiness of the ligands is relatively small, the complex often associates each other and becomes hardly soluble due to the bridging. This problem can generally be solved by the use of sterically crowded alkoxo ligands.



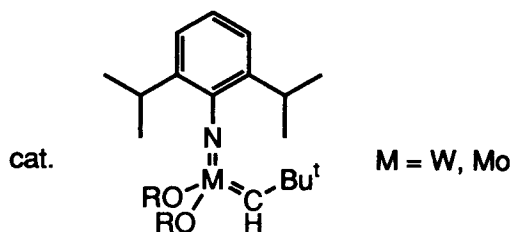
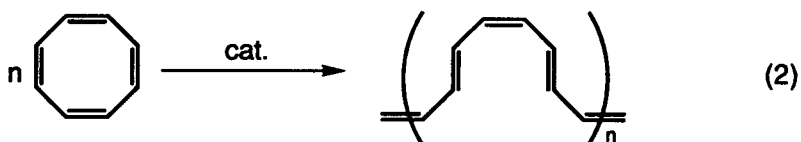
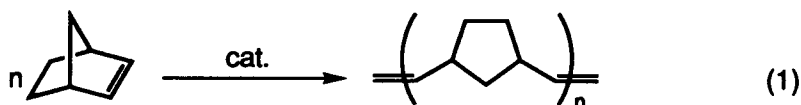
Scheme I

The number of the catalytic activity of the complexes bearing alkoxo ligands have been reported hitherto in literature. The polymerization activity toward ethylene of the catalyst system, (TBP)TiCl₂/MAO (TBP = 2,2'-thiobis(6-*tert*-butyl-4-methylphenoxo); MAO = methylaluminoxane; amount of Ti = 1.1×10^{-3} mmol: of Al = 5.17 mmol: of solvent (toluene) = 10 mL), has been reported to be 821 kg/g of Ti·h, comparable to that of Cp₂ZrCl₂ system (958 kg/g of Zr·h). In the propylene polymerization, the TBP-Ti complex system also shows very high activity: the activity of (TBP)TiCl₂ is 180 kg/g of Ti·h and gave polypropylenes having extremely high molecular weight ($M_w > 800 \times 10^4$).⁵

Enantioselective cyclopolymerization of 1,5-hexadiene catalyzed by chiral zirconocenes, (+)-(S,S)-(EBTHI)Zr(BINOL)/MAO (EBTHI = ethylene-1,2-bis(4,5,6,7-

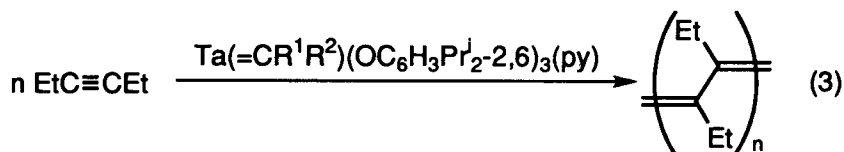
tetrahydro-1-indenyl); BINOL = 1,1'-bi-2-naphtholate), was reported by Waymouth *et al.* where BINOL was used as resolving chiral source and a leaving group to generate active species⁶

Especially, alkoxide ligands are frequently used as ancillary ligands to stabilize metal-carbene complexes which catalyze ring-opening metathesis polymerizations (ROMP) of cycloolefins.⁷⁻⁹ Schrock *et al.* have isolated carbene complexes of tungsten and molybdenum, $M(=CHBu^t)(=NC_6H_3Pr^i_{2-2,6})(OR)_2$ ($M = W, Mo$; $OR = OBU^t, OMe_2(CF_3), OMe(CF_3)_2, OC(CF_3)_3$),^{10,11} whose structures were characterized by spectroscopic measurements as well as by X-ray studies, and these were found to catalyze the living ring opening metathesis polymerization of norbornene derivatives (eqn. 1).⁷ The well-characterized carbene complexes, some of them are now commercially available, are used for block copolymerization of functionalized norbornenes^{12,13} and triblock copolymerization composed of norbornene—acetylene—norbornene.¹⁴ The most interesting application is the polymerization of cyclooctatetraene and its derivatives, affording conducting materials of conjugated polyene structures (eqn. 2).^{15,16}



For group 5 metals, carbene complexes of tantalum, $Ta(=CHBu^t)(EAr)_3(thf)$ ($EAr = OC_6H_3Me_2-2,6, OC_6H_3Pr^i_{2-2,6}, SC_6H_2Pr^i_{3-2,4,6}$),¹⁷ have been prepared and

found to be active catalysts for the living polymerization of norbornene. It is noteworthy that carbene complexes of tantalum can also polymerize 2-butyne in a living fashion (eqn 3).¹⁸ Therefore, carbene complexes are now quite well accepted as active species in the polymerization of cyclic olefins and alkynes.



In the studies described above, the effects of ligand on the polymerizations of cycloolefins were investigated in detail, but the effects on the polymerizations of acetylenes have been less defined until now. In *Part I* of this thesis, the author studied the polymerization of substituted acetylenes by group 5 and 6 aryloxide based catalysts.

Polymer of acetylene without a substituent consist of alternating double bonds along the main chain and show the following unique properties:

- i) electrical conductivity
- ii) paramagnetism
- iii) chain stiffness

Moreover, polymers of substituted acetylenes with exhibit the additional properties:

- iv) thermal stability¹⁹
- v) high solubility
- vi) gas permeability²⁰
- vii) liquid mixture separation²¹
- viii) non-linear optical property²²
- ix) radiation degradation²³

These physical properties are highly affected by the molecular weight, molecular weight distribution and microstructures of the polymers, *e.g.*, undoped *trans*-polyacetylene ($\sigma = 4 \times 10^{-5} \text{ Scm}^{-1}$) shows higher electrical conductivity than undoped *cis*-polyacetylene ($\sigma = 2 \times 10^{-9} \text{ Scm}^{-1}$).²⁴ In order to find a desired physical property for a polyalkyne, we should exploit a new synthetic method controlling the molecular

weight, molecular weight distribution and microstructures. Thus, we started to make a new catalyst system for the polymerization of substituted acetylenes. The background in this field is briefly reviewed as follows.

Unsubstituted acetylene can be polymerized by the typical Ziegler-Natta Catalysts. The first successful polymerization of unsubstituted acetylene to make the polyacetylene films was carried out by using Ziegler-Natta type catalyst such as $\text{Ti}(\text{O}-n\text{-Bu})_4/\text{Et}_3\text{Al}$.^{25,26} However, the polymerization of substituted acetylenes has been difficult by using the typical Ziegler-Natta type catalysts except the polymerization of isopropylacetylene and *sec*-butylacetylene by $\text{Fe}(\text{acac})_3/\text{Et}_3\text{Al}$ affording soluble high polymers.^{27,28} For the polymerization of monosubstituted acetylenes including *n*-alkyl, aromatic, and heteroatom-containing substituents, mixtures of mostly insoluble polymers and soluble oligomers are obtained. Furthermore, no disubstituted acetylenes are polymerized with Ziegler-Natta type catalysts.

In 1974, Masuda and coworkers found that phenylacetylene was polymerized in the presence of WCl_6 and MoCl_5 as catalyst precursors. Since then, various complexes of group 5 and 6 metals have been exploited as new effective catalysts for the polymerization of substituted acetylenes.²⁹ Group 5 and 6 transition metal catalyst systems developed so far are classified and their catalytic merits are summarized as class (1) — (5).

1) MoCl_5 and WCl_6 .

Effective only for the polymerization of monosubstituted acetylenes.

2) MoCl_5 -cocatalyst and WCl_6 -cocatalyst.

Effective for the polymerization of monosubstituted acetylenes and some disubstituted acetylenes where main group metal compounds such as Ph_4Sn , Et_3SiH , Ph_3Bi are acting as effective cocatalysts.

3) $\text{Mo}(\text{CO})_6\text{-CCl}_4\text{-h}\nu$ and $\text{W}(\text{CO})_6\text{-CCl}_4\text{-h}\nu$.

These catalyst systems polymerize monosubstituted acetylenes and disubstituted acetylenes with at least one chloro substituent.

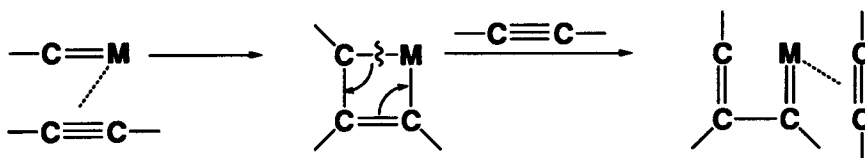
4) NbX₅ and TaX₅ (X = Cl, Br).

Effective for sterically crowded disubstituted acetylenes.

5) NbCl₅-cocatalyst and TaCl₅-cocatalyst.

Addition of a cocatalyst such as Ph₄Sn accelerates the polymerization, increases the molecular weight, and inhibits polymer degradation.

The metal carbene mechanism shown in Scheme II has been proposed by Masuda *et al.* for the present polymerization of substituted acetylenes based on the following evidence: (i) There are many catalysts effective to both olefin metathesis (including metathesis polymerization) and polymerization of acetylenes; (ii) acetylenes can be regarded as extreme members of cycloolefins, *i.e.*, two membered rings in which the aliphatic chains of cycloolefins are replaced by carbon-carbon single bonds; (iii) the random copolymerization of cycloolefins with mono- and di-substituted acetylenes was reported as well as the chain transfer reaction to vinylsilane compounds in the polymerization of acetylenes by WCl₆-Ph₄Sn.^{30,31} Moreover, the metal carbene mechanism is also supported by the fact that the carbene complexes such as Ph(CH₃O)C=W(CO)₅ and Ph₂C=W(CO)₅ were found to be active catalysts for the polymerization of acetylenes.³²

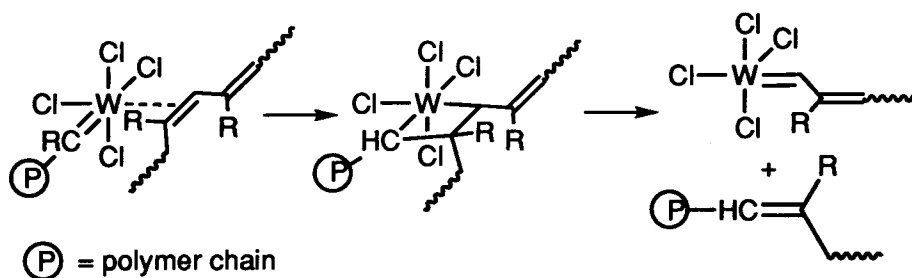


Scheme II

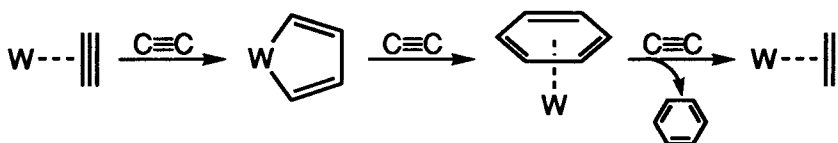
The catalyst system comprised of MoOCl₄, *n*-Bu₄Sn, and EtOH, is known to catalyze the living polymerization of ClC≡CR (R = *n*-C₄H₉, *n*-C₆H₁₃, *n*-C₈H₁₇, and *n*-C₁₄H₂₉),³³ HC≡C[C₆H₄(SiMe₃)-*o*],³⁴ HC≡C[C₆H₄(CF₃)-*o*],³⁵ HC≡C[C₆F₄(*n*-Bu)-*p*],³⁶ and HC≡C-*t*-Bu.³⁷ The addition of EtOH as a third component is essentially important to accomplish a living polymerization, where ethanol replaces one of the chloro ligands by an ethoxo ligand and stabilize a metal carbene intermediate. In the

polymerization of *tert*-butylacetylene, this catalyst system also controls microstructure of double bond in the main chain (up to 97% of *cis*), and thus this system is the first example of stereospecific living polymerization of alkynes.

In the polymerization of alkyne, steric bulkiness of the substituents on monomer is important to obtain high polymer. The bulkiness accelerates the cleavage of the M—C bond on metallacyclobutene (Scheme II) at the propagating reaction and prevents the side reactions such as chain transfer reaction and cyclotrimerization giving benzene derivatives. As shown in Scheme III, the chain transfer reaction in this system is mainly caused by the metathesis of the polymer. Cyclotrimerization reaction of alkynes proceeds via η^6 -arene intermediates (Scheme IV). For less bulky substituted acetylenes such as *n*-alkylacetylenes, high polymers are not obtained by these catalysts but cyclotrimerization and/or oligomerization occur. Therefore, the polymerization of less bulky substituted acetylenes has been still one of the challenging target of synthetic polymer chemists.

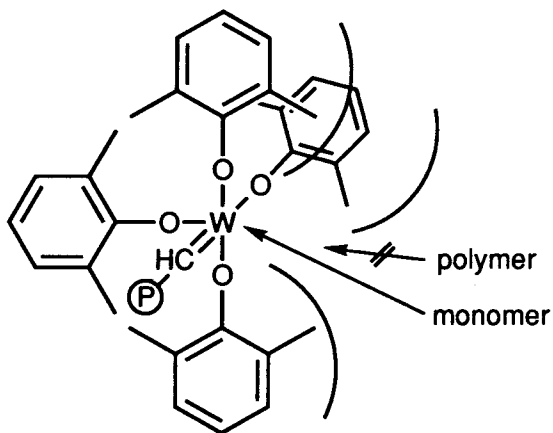


Scheme III



Scheme IV

The author proposed that "*the bulkiness on the metal center by bulky phenoxo ligands compensates the deficient steric effect of monomers and prevents the side reactions to afford high polymer of less bulky substituted acetylenes such as n-alkylacetylenes*" as shown in Scheme V.



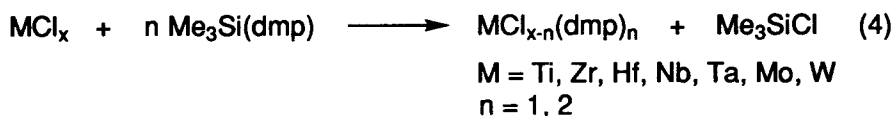
Scheme V

Thus, a systematic synthetic study for early transition metal complexes bearing bulky ancillary phenoxo ligands is described in this thesis. The author used 2,6-dimethylphenoxo as a bulky phenoxo ligand and many different kinds of 2,6-dimethylphenoxo complexes of group 4, 5 and 6 metals are prepared to determine the most favorable number of the aryloxo ligands for the polymerization of substituted alkynes.

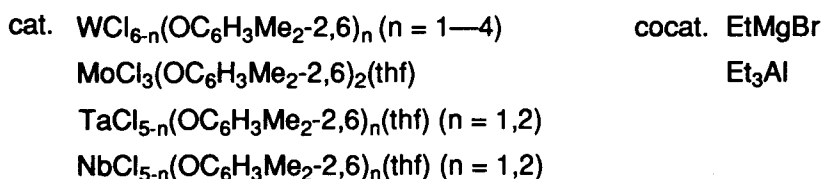
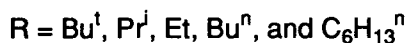
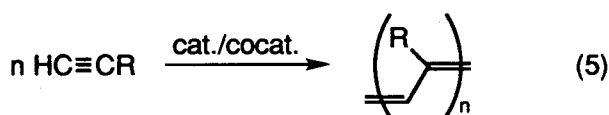
The selective synthesis of mono(2,6-dimethylphenoxo) complexes of group 4—6 metals had never been reported due to the concomitant formation of higher substituted derivatives, *e.g.*, mixtures of complexes, $M(O-C_6H_3-2,6-Me_2)_nCl_{m-n}$ ($M =$ group 4—6 metals; $n \geq 2$), have been prepared so far by the reactions of early transition metal halides with alkali metal alkoxides or alcohols.

In **Chapter 2**, the author successfully used 2,6-dimethylphenyl trimethylsilyl ether as a reagent to give aryloxo complexes in high purity and in moderate yield. Thus, the 1:1 and 1:2 reactions of metal chlorides with the trimethylsilyl ether selectively afforded mono- and bis(aryloxide) complexes, respectively. In this manner, mono- and

bis(aryloxo) complexes of group 4—6 transition metals, $MCl_{4-n}(dmp)_n(thf)_2$ ($M = Ti, Zr, Hf$), $MCl_{5-n}(dmp)_n(thf)$ ($M = Nb, Ta$), $MoCl_3(dmp)_2(thf)$, and $WCl_{6-n}(dmp)_n$ ($n = 1, 2$; $dmp = 2,6$ -dimethylphenoxide) were prepared (eqn. 4). Crystal structures of those complexes were determined by X-ray analyses.



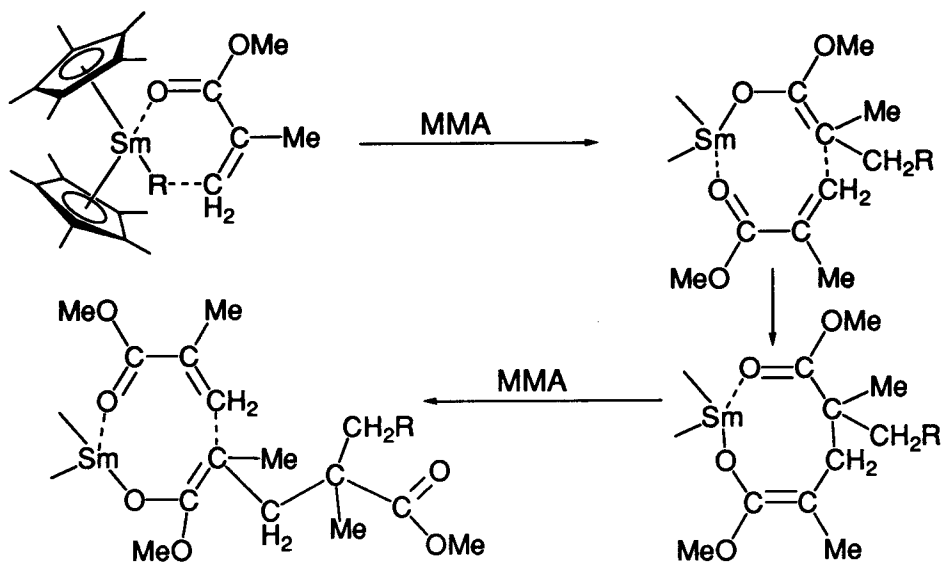
In **Chapter 3**, the polymerization of substituted acetylenes catalyzed by a series of 2,6-dimethylphenoxo complexes of group 5 and 6 transition metals is investigated (eqn. 5). The catalyst system, $WCl_4(dmp)_2/Et_3Al$, was found to polymerize t -BuC \equiv CH to a very high molecular weight polymer ($M_n > 2 \times 10^6$) with relatively narrow molecular weight distribution ($M_w/M_n \sim 1.2$) and with high stereoregularity ($cis = 88\%$). By increasing the number of aryloxo ligands on W(VI) species, less bulky 1-alkynes could be polymerized to get high molecular weight polymers. For instance, the polymerization of 1-butyne gave an orange polymer with $M_n = 9.4 \times 10^4$, $M_w/M_n = 3.5$ in contrast to the previous researches that such high polymers have never been obtained. Similarly, poly(1-hexyne) and poly(1-octyne) with high molecular weights ($M_n > 10^5$) were also obtained.



In **Part II** of this thesis, the author studied the polymerization of polar monomers such as vinyl monomers having electron withdrawing groups and cyclic esters.

Methyl methacrylate (MMA) is one of the most common monomers for industrial use. MMA can be polymerized by radical and anionic initiators, giving poly(methyl methacrylate) (abbreviated to PMMA). Radical polymerization of MMA at $-40\text{ }^{\circ}\text{C}$ affords syndiotactic PMMA with $rr \sim 75\%$, while the anionic polymerization by organo alkali metal compounds afforded isotactic PMMA (toluene) and syndiotactic PMMA (THF), depending on the polarity of the solvent.³⁸

Well-characterized organolanthanide complexes such as Cp^*_2LnR ($\text{Ln} = \text{Sm}, \text{Yb}, \text{Lu}, \text{Y}; \text{R} = \text{H}, \text{Me}$) has been used as the catalyst for the living polymerization of MMA to produce highly syndiotactic PMMA with high molecular weight and narrow molecular weight distribution.^{39,40} In this system, the growing end group is metal enolate (Scheme VI), whose structure was revealed by a single crystal X-ray analysis. This breakthrough prompted many polymer chemists to study the polymerization of polar monomers by using lanthanide catalysts. Thus the polymerization of MMA, Bu^tA ($\text{Bu}^t\text{A} = t\text{-butyl acrylate}$), and DPAA (DPAA = *N,N*-diphenylacrylamide) has been reported to be catalyzed by $\text{Ln}(\text{OPr}^i)_3$ ($\text{Ln} = \text{La}, \text{Ce}$) and $\text{La}(\text{btsa})_3$ [$\text{btsa} = \text{bis}(\text{trimethylsilyl})\text{amide}$].^{41,42}



Scheme VI

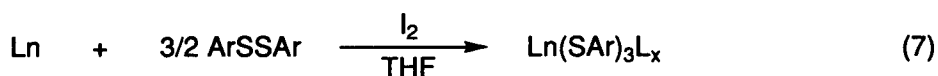
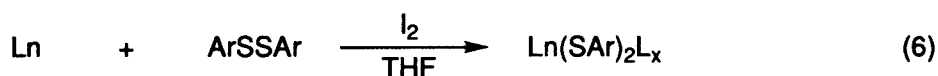
These organolanthanide complexes are also found to cause the living polymerization of cyclic lactones such as ϵ -caprolactone and δ -valerolactone. In this case, the living chain end is a lanthanide alkoxide compound. Thus alkoxide complexes such as $\text{Cp}^*_2\text{Sm}(\text{OEt})(\text{OEt}_2)$, $[\text{Cp}^*_2\text{Y}(\text{OMe})_2]$, and $\text{Cp}^*_2\text{Y}(\text{OMe})(\text{thf})$ are able to catalyze the living polymerization of ϵ -caprolactone and δ -valerolactone. It is noteworthy that the alkoxide complexes catalyze the polymerization of β -propiolactone, whose polymerization has been difficult so far by usual lanthanide alkyl complexes.⁴³ The lanthanide alkoxide complexes such as $\text{M}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ ($\text{M} = \text{Y}$, Lanthanides) are the catalysts for the living ring-opening polymerization of ϵ -caprolactone⁴⁴ and lactide,⁴⁵ whose polymers are of great interest for medical applications due to their biodegradability.

Thus, lanthanide alkoxide species have highly catalytic activities for the polymerization of these kinds of monomers. Generally, the bond strength between lanthanide metal ions and chalcogen atom can be evaluated by comparing with the bond disruption enthalpy values of $\text{Cp}^*_2\text{Sm}-\text{OBu}^t$ (82.4 kcal/mol) and $\text{Cp}^*_2\text{Sm}-\text{SPr}^n$ (73.4 kcal/mol).⁴⁶ Since the lanthanide-sulfur bond is weaker than the lanthanide-oxygen bond, thiolate complexes of lanthanide elements might exhibit higher catalytic activity than the corresponding alkoxide complexes. Therefore the author investigated the polymerization of polar monomers by lanthanide thiolate complexes.

The systematic synthetic study for thiolate complexes of lanthanide metals is described in **Chapter 4**. Lanthanide thiolate complexes have been prepared by metathesis reactions of lanthanide halides with alkali metal thiolates.⁴⁷⁻⁴⁹ In these preparations, the rather strong interaction of lanthanide cations with the alkali metal halides often disturbs the isolation and purification of the product. In order to prepare the salt free complexes, the reaction of bis(trimethylsilyl)amide and bis(trimethylsilyl)methyl complexes of lanthanide with bulky thiols⁵⁰ and the oxidative reaction of low valent organolanthanide complexes with organic disulfide^{51-53,46} have been applied. However,

usually a mixture of Ln(II) and Ln(III) complexes results and the purification by recrystallization has been precluded by the instability to air and atmospheric moisture.

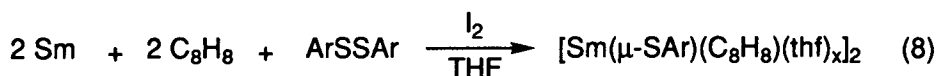
In order to develop a facile preparation of lanthanide thiolates, the author studied a novel synthetic route to divalent and trivalent lanthanide thiolate complexes from metallic lanthanides. The reaction of an excess of Sm, Eu and Yb metals with diaryl disulfides, ArSSAr (Ar = C₆H₂Prⁱ_{3-2,4,6}, Ph), selectively afforded bis(thiolato) complexes of divalent lanthanides (eqn. 6). On the other hand, the reaction of lanthanides with 3 equiv. of the diaryl disulfides cleanly gave tris(thiolato) complexes of trivalent lanthanides (eqn. 7). When the reaction was performed in the presence of cyclooctatetraene, cyclooctatetraenyl(arenethiolate)samarium(III) complexes could be obtained in one step (eqn. 8).



Ln = Sm, Eu, Yb

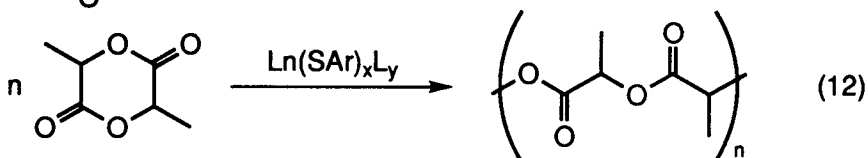
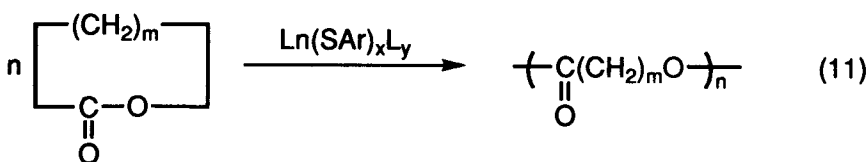
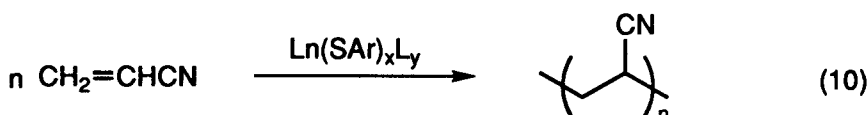
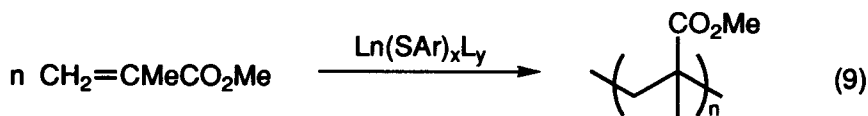
Ar = Ph, C₆H₂Prⁱ_{3-2,4,6}

L = thf, pyridine, hmpa



In **Chapter 5**, these complexes were found to catalyze the polymerization of polar monomers such as MMA, acrylonitrile, lactones, and lactide. The polymerization of MMA with samarium benzenethiolates bearing HMPA (hexamethylphosphoric triamide) ligands, Sm(SPh)_n(hmpa)₃ (n = 2, 3), afforded syndiotactic PMMA with narrow molecular weight distribution ($M_n = 16000$, $M_w/M_n = 1.34$, $rr = 80\%$). Acrylonitrile (AN) can be polymerized not only by radical initiators but also anionic initiators to give polyacrylonitrile (PAN), which has occupied an industrially important position, particularly, as fibers. Alkyl, ketyl, amide and alkoxide compounds of alkali metals and alkaline earth metals are mainly used as initiator for anionic polymerization of

AN. To our knowledge, however, polymerization of acrylonitrile by lanthanide compounds has not been reported yet. The polymerization of AN by lanthanide thiolate complexes was neither living nor stereospecific, although these complexes were highly active for polymerization of the monomers. In the case of lactones, ϵ -caprolactone and δ -valerolactone could be polymerized by these complexes to produce polymers with relatively narrow molecular weight distributions ($M_w/M_n \sim 1.5$). β -Lactones comprised of 4-membered ring are rather difficult to be polymerized with early transition metal initiators.^{54,43} β -Butyrolactone could be polymerized by $\text{Sm}(\text{SAr})_3(\text{py})_3$ at 100 °C for 24 h without solvent to afford poly(β -butyrolactone) with bimodal molecular weight distribution ($M_n = 6400$, $M_w/M_n = 1.04$ and $M_n = 1200$, $M_w/M_n = 1.23$) in 23% yield. Lactide were polymerized only by $[\text{Sm}(\text{SAr})_2(\text{thf})_3]_2$ to afford a polymer with relatively narrow molecular weight distribution ($M_w/M_n \sim 1.2$).



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Part I

Polymerization of Substituted Acetylenes

Chapter 2

Selective Synthesis of Mono- and Bis(2,6-dimethylphenoxy) Complexes of Group 4—6 Transition Metals

Introduction

Early transition metal alkoxide complexes are attracting much interest in the field of catalysis in organic synthesis¹⁻¹¹ and polymerization.¹²⁻³¹ Especially, bulky aryloxy complexes have an advantage to provide soluble mononuclear complexes.^{4,5,16,32-54}

The previous synthetic methods for such compounds are summarized as follows.

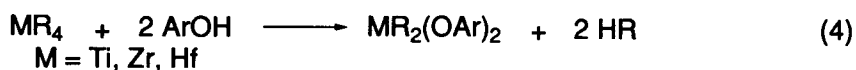
1) The reaction of metal halides with alkali metal alkoxides is used for the synthesis of alkoxide complexes. This reaction proceeds rapidly even at low temperature. The number of introduced alkoxy ligands depends on the bulkiness of the ligands (eqn. 1).^{53,43,51,34}

2) Highly Lewis acidic early transition metal halides react with alcohols releasing HCl as shown in eqn. 2. In this reaction, both of the starting materials are commercially available. However, this reaction sometimes yields a mixture of alkoxide complexes bearing the different numbers of alkoxy ligands.^{51,32,47}

3) The reaction of early transition metal amides with alcohols proceeds only at high temperature (>80 °C). The remaining amido ligands can be replaced by chloro ligands with Me₃SiCl (eqn. 3).^{55,53,49}

4) In the case of group 4 metals, the reaction of tetraalkyl complexes, MR₄ (M = Ti, Zr; R = CH₂Ph, CH₂SiMe₃), with 2,6-di-*tert*-butylphenol are used to give

bis(phenoxide) complexes (eqn. 4).⁴¹ The tetraalkyl compounds must be prepared just before use and reacted *in situ* because of their high air- and moisture-sensitivity.



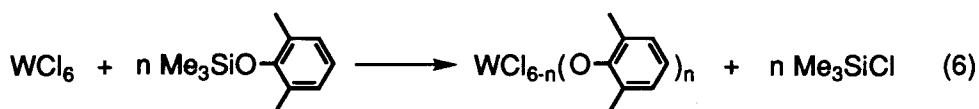
The catalytic property of those complexes is expected to be influenced by the coordination environments. However, any systematic study about the effects of the number of alkoxo ligands on the activities has not been performed except for a tungsten oxytetrachloride system.⁵⁶ One reason for the difficulty of such studies is that the selective synthesis of mono(alkoxide) complexes has been hindered by the serious contamination of further substituted derivatives in the reactions noted above. Thus, the author tried to find better synthetic methods. Up to now only one example was reported for the synthesis of niobium mono(alkoxide) compounds, NbCl₄(OR) (R = Me, Et, SiMe₃), from the reaction of NbCl₅ with Me₃SiOR.⁴⁷ The author applied this reaction for the systematic synthesis of a series of early transition metal complexes bearing bulky aryloxo ligands (eqn. 5).



Results and Discussion

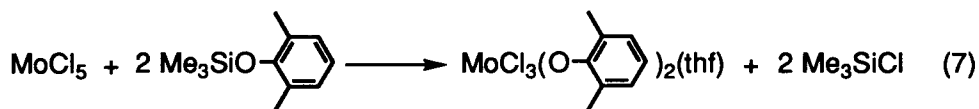
The Formation of Mono- and Bis(2,6-dimethylphenoxo) Complexes of Tungsten and Molybdenum. The author has selected a bulkyphenoxo ligand, 2,6-dimethylphenoxo (dmp), as an ancillary ligand in order to suppress aggregation of the products and to obtain monomeric complexes. A 1 : 1 reaction of anhydrous WCl₆ with 2,6-dimethylphenoxy(trimethyl)silane in toluene at -78 °C followed by heating to ambient

temperature resulted in the formation of $WCl_5(dmp)$ (**1a**) as purple crystals in 73% yield. Similarly, the 1 : 2 reaction of WCl_6 with the phenoxysilane in refluxing toluene for 2 h gave $WCl_4(dmp)_2$ (**1b**) as dark blue crystals in 60% yield (eqn. 6). Further addition of 2,6-dimethylphenoxy(trimethyl)silane to WCl_6 or $WCl_4(dmp)_2$ did not afford the tris- or the tetrakis(phenoxide) complexes. However we have failed to isolate $MoCl_4(dmp)(thf)$ because of the predominant formation of the complex mixture. $MoCl_3(dmp)_2(thf)$ (**2**) was successfully isolated as purple crystals in 15% yield from the 1 : 2 reaction of $MoCl_5$ with $Me_3SiOC_6H_3Me_{2-2,6}$ followed by recrystallization from THF / hexane (eqn. 7).



1a: $n = 1$

1b: $n = 2$



recrystallized from THF-hexane
2

In order to elucidate the exact geometries of these complexes, the X-ray structure analyses of **1a** and **1b** have been performed. An ORTEP drawing of **1a** is shown in Fig. 1(a) and the molecular structure of **1b** is shown in Fig. 1(b) together with partial atomic labeling. Selected bond distances and angles for complexes **1a** and **1b** are listed in Table 1. The compound **1a** is six-coordinated on the tungsten atom and the $W-O-C(11)$ angle is exactly 180° . The $W-O(1)-C(11)$ and $W-O(2)-C(22)$ angles of **1b** are again 179° due to strong $p\pi(\text{oxygen})-d\pi(\text{metal})$ interaction. Consequently, the $W-O$ distances of 1.79–1.82 Å in **1a** and **1b** are shortest in the tungsten phenoxide hitherto reported, *i. e.*, $WCl_3(OC_6H_3Pr^i_{2-2,6})_3$ (1.832, 1.836, and 1.848 Å),⁵¹ $WCl_4(OC_6H_3Ph_{2-2,6})_2$ (1.840(3) and 1.851(3) Å),⁴⁸ $W(OC_6H_3Pr^i_{2-2,6})_4$ (1.849, 1.851, 1.851, and 1.866 Å)³³ and $W(dmp)_4$ (1.843 Å).³³

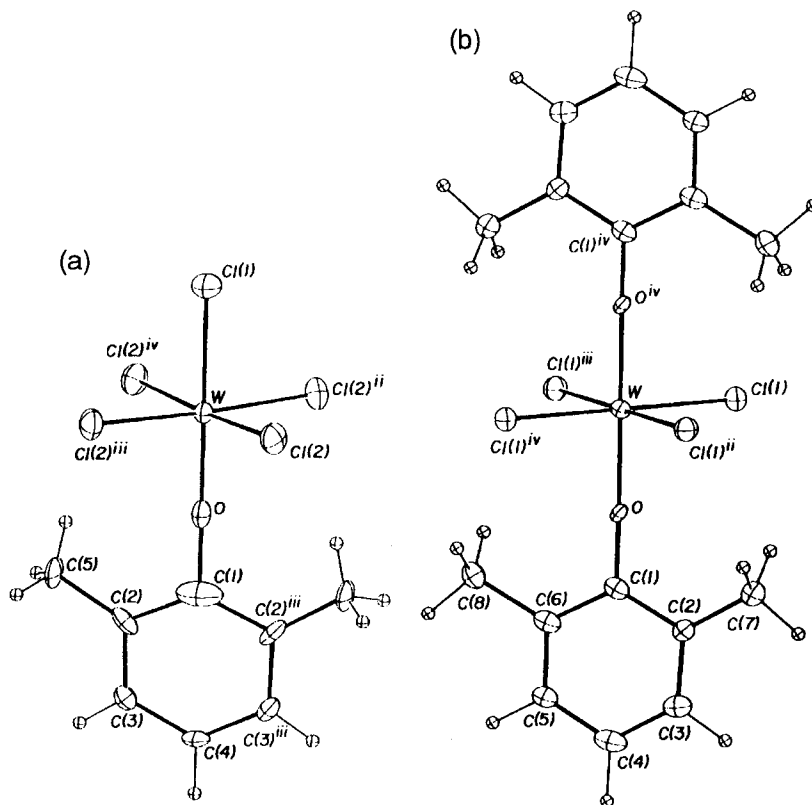


Figure 1. Molecular structures of **1a** (a) and **1b** (b).

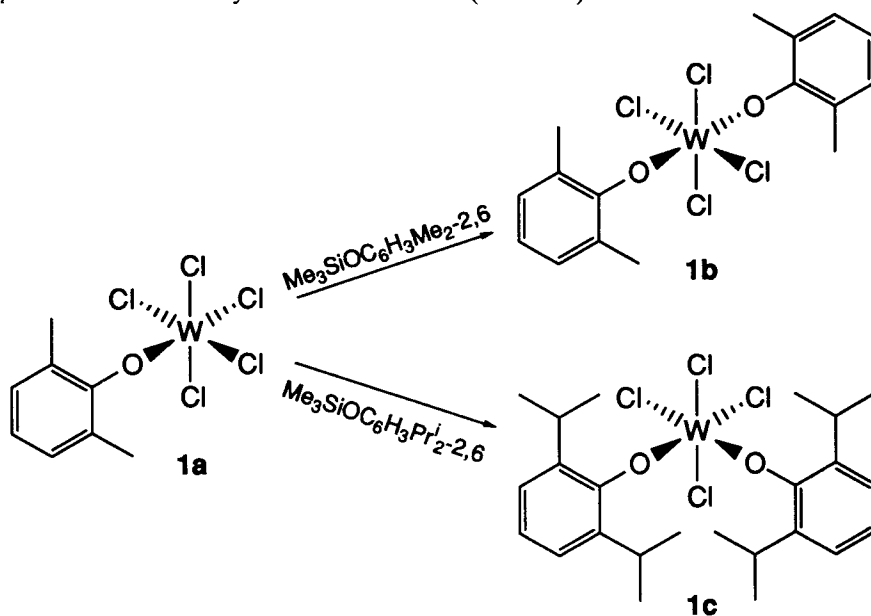
Table 1. Interatomic bond distances (Å) and bond angles (°) in complex **1a**.

Bond distances			
W—Cl(1)	2.299(9)	W—Cl(2)	2.307(3)
W—O	1.82(2)	O—C(1)	1.41(4)
C(1)—C(2)	1.45(2)	C(2)—C(3)	1.38(2)
C(2)—C(5)	1.49(2)	C(3)—C(4)	1.41(2)
Bond angles			
Cl(1)—W—Cl(2)	88.4(1)	Cl(2)—W—Cl(2) ⁱⁱ	89.5(3)
Cl(2)—W—Cl(2) ⁱⁱⁱ	90.4(3)	Cl(2)—W—Cl(2) ^{iv}	176.9(3)
Cl(1)—W—O	180.0	Cl(2)—W—O	91.6(1)
W—O—C(1)	180.0	O—C(1)—C(2)	169.8(9)

Table 2. Interatomic bond distances (Å) and bond angles (°) in complex **1b**.

Bond distances			
W—Cl(1)	2.333(3)	W—O(1)	1.860(7)
O—Cl(1)	1.34(1)		
Bond angles			
Cl(1)—W—Cl(1) ⁱⁱ	90.4(1)	Cl(1)—W—Cl(1) ⁱⁱⁱ	89.6(1)
Cl(1)—W—Cl(1) ^{iv}	180.0	Cl(1)—W—O	90.2(3)
Cl(1) ⁱⁱⁱ —W—O	89.8(1)	W—O—C(1)	179(1)

The molecular structure of **1b** includes phenoxide groups in the *trans* position (O(1)—W—O(2) angle, 180°) in sharp contrast to the *cis* position in an analogous complex, WCl₄(OC₆H₃Ph_{2-2,6})₂.⁴⁸ This conflict may arise from the steric bulkiness of the 2,6-substituents. To examine this situation, we used 2,6-diisopropylphenoxy(trimethyl)silane in place of the 2,6-dimethyl substituted phenyl silane. The reaction was carried out under essentially the same conditions as described for **1b** and WCl₄(OC₆H₃Prⁱ_{2-2,6})₂ (**1c**) was obtained in high yield. The X-ray structure of this molecule revealed the location of bis(phenoxide) in *cis* position (Fig. 2(a)). Therefore, we can estimate that the arrangement of two phenoxo ligands in tungsten complexes is controlled by the steric bulkiness (scheme I).



During the course of synthesizing a carbene complex, we have found that treatment of **1b** with LiCH_2Bu^t in hexane produced $\text{WCl}(\text{dmp})_4$ (**1d**) in 18% yield as dark red crystals. This complex is presumably formed by the reduction of **1b** followed by the disproportionation of the resulting $\text{WCl}_3(\text{dmp})_2$. The X-ray analysis revealed a novel square-pyramidal structure where the Cl atom locates at the apical position and phenoxide groups locate at the basal position (Fig. 2(b)). Similar W(V) phenoxide complexes are known in cases of $\text{WCl}_3(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2(\text{thf})$,⁴⁸ $\text{WCl}_3(\text{OC}_6\text{H}_3\text{Ph}_{2-2,6})_2(\text{PMe}_2\text{Ph})$ ⁴⁸ and $\text{WCl}(\text{OC}_6\text{H}_3\text{Cl}_{2-2,6})_4(\text{OEt}_2)$,³² but these complexes assume a six-coordinated octahedral structure. Similar tungsten tetra(phenoxide), $\text{W}(\text{dmp})_4$ and $\text{W}(\text{OC}_6\text{H}_3\text{Pr}^i_{2-2,6})_4$ are reported to exhibit square planar structure.³³

Table 3. Interatomic bond distances (Å) and bond angles (°) in complex **1c**.

Bond distances			
W—Cl(1)	2.318(4)	W—Cl(2)	2.319(4)
W—Cl(3)	2.327(4)	W—Cl(4)	2.325(5)
W—O(1)	1.814(8)	W—O(2)	1.796(9)
O(1)—C(11)	1.39(1)	O(2)—C(21)	1.40(2)
Bond angles			
Cl(1)—W—Cl(2)	171.1(2)	Cl(1)—W—Cl(3)	89.9(2)
Cl(1)—W—Cl(4)	86.5(2)	Cl(1)—W—O(1)	93.4(3)
Cl(1)—W—O(2)	92.5(3)	Cl(2)—W—Cl(3)	87.3(2)
Cl(2)—W—Cl(4)	86.6(2)	Cl(2)—W—O(1)	92.4(3)
Cl(2)—W—O(2)	94.1(3)	Cl(3)—W—Cl(4)	89.5(2)
Cl(3)—W—O(1)	179.7(3)	Cl(3)—W—O(2)	88.6(3)
Cl(4)—W—O(1)	90.6(3)	Cl(4)—W—O(2)	177.9(3)
O(1)—W—O(2)	91.4(4)	W—O(1)—C(11)	169.8(9)
W—O(2)—C(21)	177.7(9)		

Table 4. Interatomic bond distances (Å) and bond angles (°) in complex **1d**.

Bond distances			
W—Cl(1)	2.427(6)	W—O(1)	1.844(7)
O(1)—C(11)	1.37(1)		
Bond angles			
O(1)—W—O(1)'	90.0	O(1)—W—O(1)''	180(2)
Cl(1)—W—O(1)	90.1(8)	W—O(1)—C(11)	176(3)

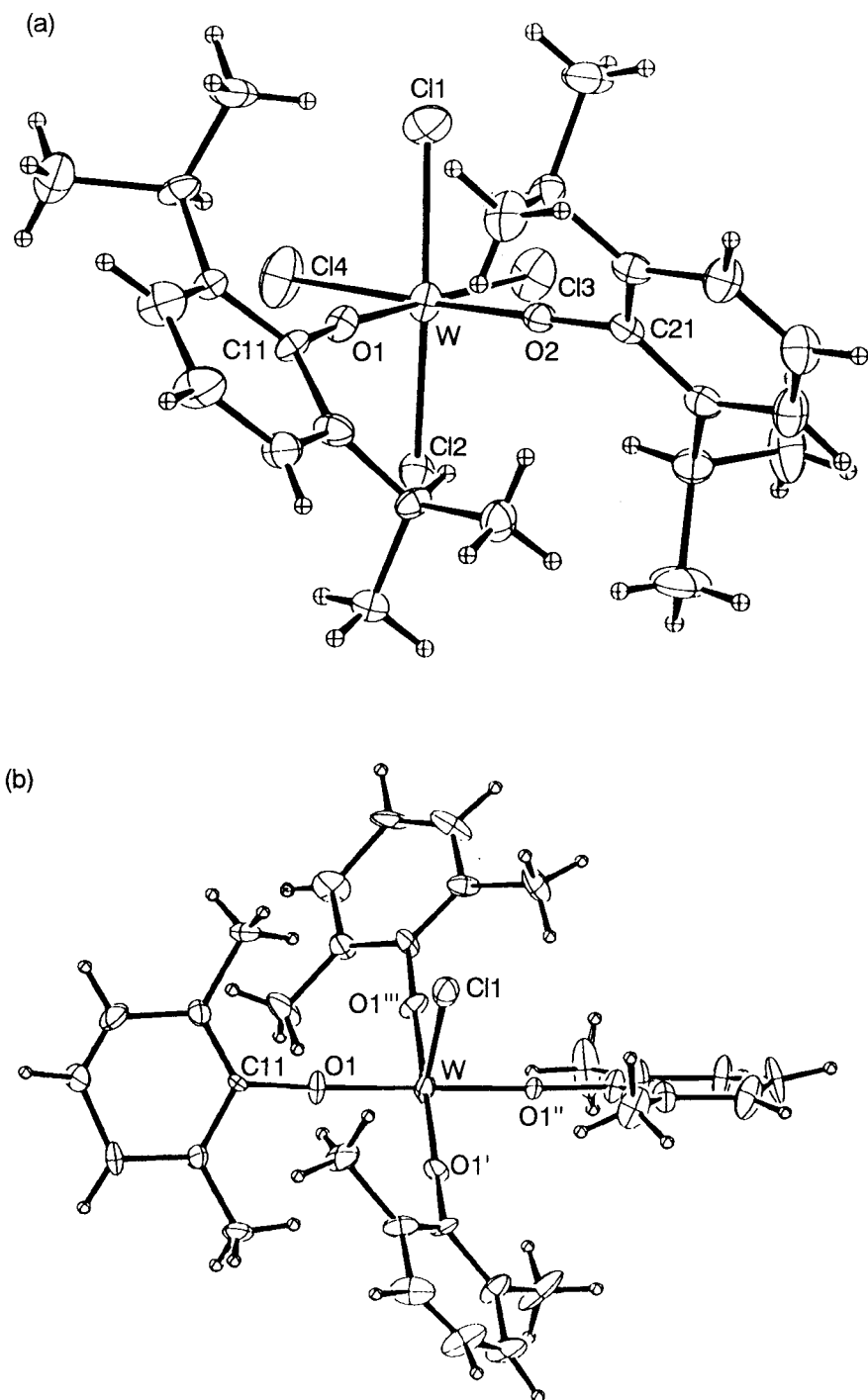
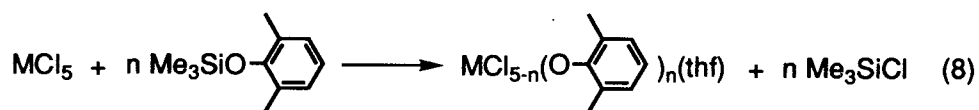


Figure 2. Molecular structures of **1c** (a) and **1d** (b).

The Formation of Mono- and Bis(2,6-dimethylphenoxy) Complexes of Niobium and Tantalum. The present method is also useful for the synthesis of Group 5 niobium- and tantalum-phenoxide. The 1 : 1 reaction of anhydrous NbCl₅ with 2,6-dimethylphenoxy(trimethyl)silane in toluene at 80 °C for 2 h followed by the addition of 20 equivalents of THF gave NbCl₄(dmp)(thf) (**3a**) in quantitative yield. Direct addition of NbCl₅ to THF must be avoided since cationic ring opening polymerization of THF occurs promptly. Recrystallization of the product from THF/hexane provides **3a** as red crystals in 66% yield. Using essentially the same method, the 1 : 2 reaction of anhydrous NbCl₅ with 2,6-dimethylphenoxy(trimethyl)silane in toluene at 80 °C for 2 h followed by the addition of THF gave NbCl₃(dmp)₂(thf) (**3b**) as red crystals in 75% yield. Direct reaction of **3a** with 2,6-dimethylphenoxy(trimethyl)silane (1.5 : 1 ratio) in THF also provides **3b** as revealed by the NMR measurements. However, further addition of 2,6-dimethylphenoxy(trimethyl)silane to **3b** did not form higher analogues such as NbCl₂(dmp)₃(thf), since **3b** was completely inert to 2,6-dimethylphenoxy(trimethyl)silane. In a similar way, TaCl₄(dmp)(thf) (**4a**) and TaCl₃(dmp)₂(thf) (**4b**) were prepared as yellow crystals.



recrystallized from THF-hexane

3a: M = Nb, n = 1

3b: n = 2

4a: M = Ta, n = 1

4b: n = 2

The exact structures were determined by the X-ray analysis of **3a** and **3b**. The Nb atom in **3a** has six-coordinated geometry with the THF molecule in the *trans* position to the phenoxy group (Fig. 3(a)). Four chlorine atoms locate in the meridional position. The selected bond distances and angles of **3a** and **3b** are summarized in Table 5. The Nb—O(1)—C(11) angle of **3a** is exactly 180°. This is ascribable to the strong $p\pi(\text{oxygen})-\text{d}\pi(\text{metal})$ interaction existing in the compounds. The Nb—O(1) distance

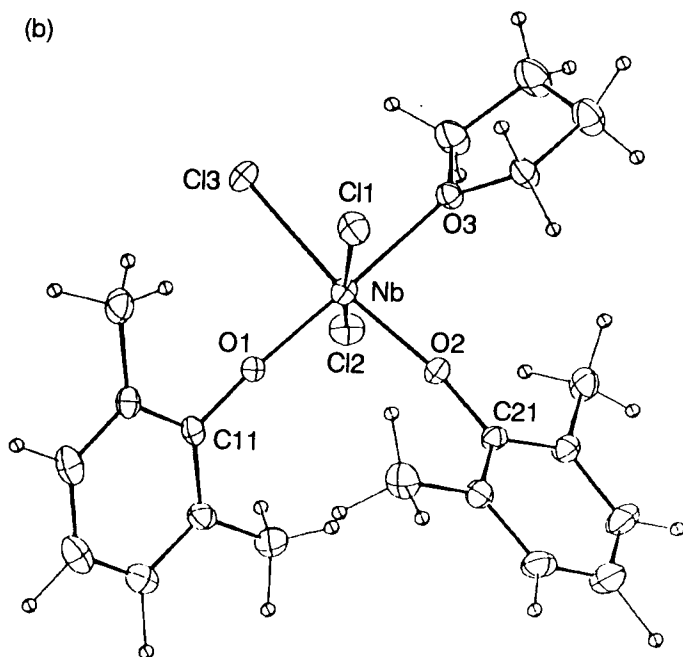
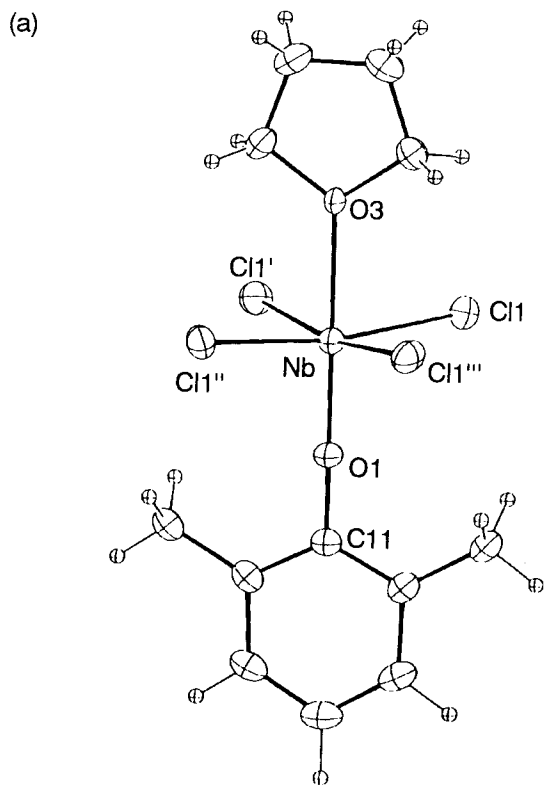


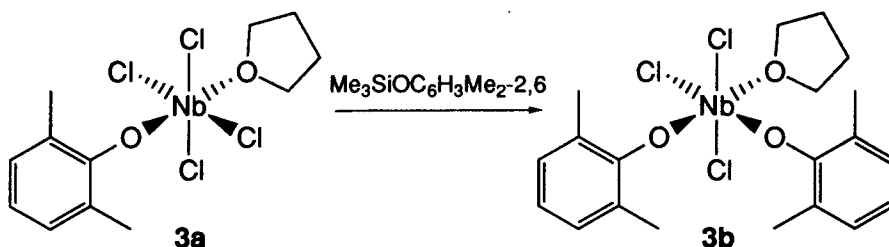
Figure 3. Molecular structures of **3a** (a) and **3b** (b).

Table 5. Selected bond distances (Å) and bond angles (°) of complex **3a** and **3b**.

	3a	3b
Bond distances		
Nb—Cl(1)	2.351(2)	2.366(3)
Nb—Cl(2)		2.391(3)
Nb—Cl(3)		2.388(3)
Nb—O(1)	1.819(8)	1.829(6)
Nb—O(2)		1.854(6)
Nb—O(3)	2.207(7)	2.194(6)
O(1)—C(13)	1.40(1)	1.360(11)
O(3)—C(31)	1.465(9)	1.483(13)
Bond angles		
Cl(1)—Nb—Cl(1) ^{(Cl(3))}	89.6(1)	88.7(1)
Cl(1)—Nb—Cl(1) ^{'''}	89.5(1)	
Cl(1)—Nb—Cl(1) ^{''(Cl(2))}	169.8(1)	168.8(1)
Cl(1)—Nb—O(1)	95.1(1)	95.0(2)
Cl(1)—Nb—O(2)		92.5(2)
Cl(1)—Nb—O(3)	84.9(1)	84.5(2)
O(1)—Nb—O(3)	180.0	177.4
O(1)—Nb—O(2)		96.3(3)
Nb—O(1)—C(11)	180.0	173.2(6)
Nb—O(2)—C(21)		170.2(5)
Nb—O(3)—C(31)	124.8(4)	122.6(6)

(1.819 Å) is significantly shorter than the sum of the covalent radii. Actually, the Nb—O(1)—C(11) angle decreases with increasing the number of phenoxide groups attached. The Nb—O(1)—C(11) angle of NbCl₄[O-2,6-(CH₃)₂C₆H₃](thf) decreases to 173.2° in the case of NbCl₃[O-2,6-(CH₃)₂C₆H₃]₂(thf) (**3b**) (Fig. 3(b)). Nb—O bond distances in complexes **3a** and **3b** (1.819 Å and 1.829 Å, respectively) are shorter than those in complexes, Nb(OC₆H₃Prⁱ-2,6)₂(OC₆H₃Prⁱ-η²-CMe=CH₂)(thf) (1.875(2), 1.949(2) and 1.967(2) Å) and Nb(OC₆H₃Prⁱ-2,6)₂(OC₆H₃PrⁱCMcCH₂CPh=CPh) (1.943(4), 1.873(4) and 1.882(4) Å).⁴⁶

The 1 : 2 addition of **3a** with 2,6-dimethylphenoxy(trimethyl)silane again provides the compound **3b** with six-coordinated geometry around the Nb atom (Fig. 3(b)). In this case, one of the meridional chlorine atoms of **3a** reacted with the phenoxysilane to afford *cis*-bis(phenoxide) type compound and a THF molecule is coordinated in the *trans* position of the phenoxide group. If the coordination site of THF does not change during the reaction, we can readily conclude that Nb-mono(phenoxide) changes to Nb-bis(phenoxide) by the attack on a chloro ligand with the phenoxysilane as illustrated in Scheme II.

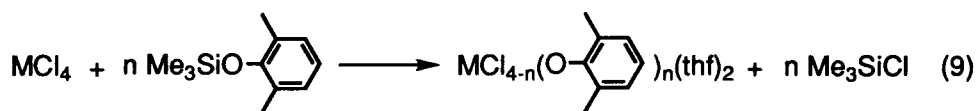


Scheme II

The Formation of Mono- and Bis(2,6-dimethylphenoxy) Complexes of Titanium, Zirconium, and Hafnium. The 1 : 1 reaction of TiCl₄(thf)₂ with 2,6-dimethylphenoxy(trimethyl)silane in THF at ambient temperature for 2 h was found to afford a pure sample of a new compound, TiCl₃(dmp)(thf)₂ (**5a**) in 90% yield releasing Me₃SiCl as monitored by the NMR spectra. After the usual workup, the resulting

product was purified by recrystallization from THF / hexane to give red crystals of **5a** in 73% yield. A bis(phenoxo) derivative, $\text{TiCl}_2(\text{dmp})_2(\text{thf})_2$ (**5b**) was also available by refluxing a mixture of $\text{TiCl}_4(\text{thf})_2$ and $\text{Me}_3\text{SiOC}_6\text{H}_3\text{Me}_{2,6}$ (1 : 2.5 ratio) in THF for 8 h. Recrystallization of the product from THF / hexane gave a titanium compound **5b** as dark-red crystals in 70% yield.

Analogously, the corresponding zirconium and hafnium mono(phenoxide) complexes, $\text{MCl}_3(\text{dmp})(\text{thf})_2$ (**6a**: M = Zr; **7a**: M = Hf) were obtained in high purity by stirring the 1 : 1 mixture in THF for 3 h, and were isolated as colorless crystals in 72% and 91% yield, respectively. Bis(phenoxo) derivatives of zirconium (**6b**) and hafnium (**7b**) were also available by refluxing the 1 : 6 mixture in THF for 8 h. Further addition of 2,6-dimethylphenoxy(trimethyl)silane to MCl_4 (M = Ti, Zr, Hf) or $\text{MCl}_2(\text{dmp})_2(\text{thf})_2$ did not form the tris- or tetrakis(phenoxide) of these metals.



5a: M = Ti, n = 1

5b: n = 2

6a: M = Zr, n = 1

6b: n = 2

7a: M = Hf, n = 1

7b: n = 2

In order to elucidate the exact geometries of $\text{TiCl}_3(\text{dmp})(\text{thf})_2$ (**5a**), $\text{TiCl}_2(\text{dmp})_2(\text{thf})_2$ (**5b**) and $\text{ZrCl}_2(\text{dmp})_2(\text{thf})_2$ (**6b**), the X-ray structure analyses have been performed. An ORTEP drawing illustrated in Fig. 4(a) shows the molecular structure of **5a** and Fig. 4(b) shows the molecular structure of **5b** together with partial atomic labeling. In both complexes, the central Ti atoms have six-coordinated geometries and two phenoxo groups of **5b** are located in the *cis* position. As the remaining two chlorine atoms occupy the *trans* position in both complexes, two coordinated THF molecules assume the *cis* position. The ORTEP drawing of **6b** showed geometry similar to complex **5b** (Fig. 5). Selected bond distances and angles for complexes **5a**, **5b** and

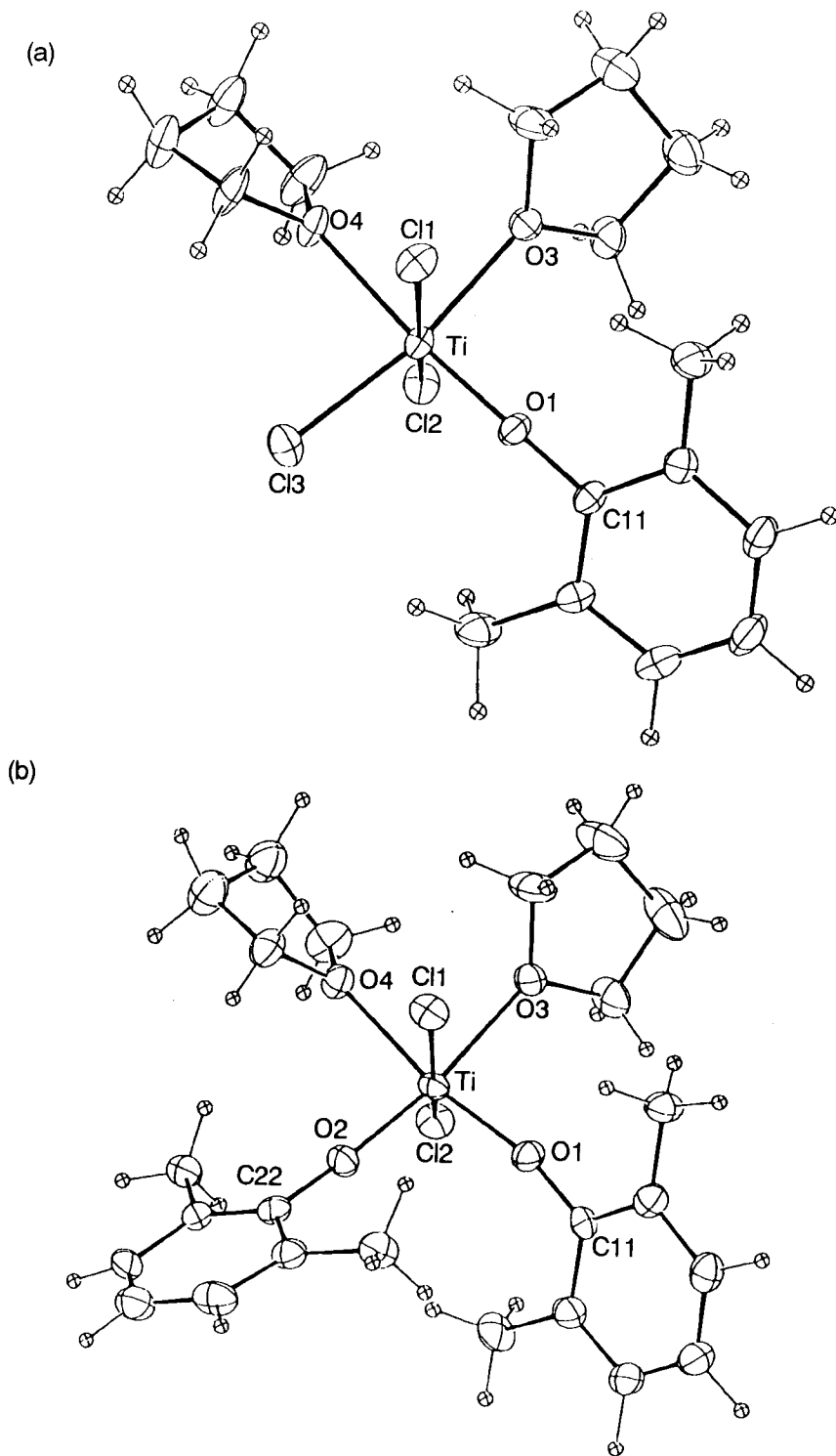


Table 6. Selected bond distances (Å) and bond angles (°) of complex **5a**, **5b** and **6b**.

	5a	5b	6b
Bond distances			
M—Cl(1)	2.327(3)	2.374(4)	2.476(5)
M—Cl(2)	2.330(3)	2.374(4)	2.456(5)
M—Cl(3)	2.277(3)		
M—O(1)	1.752(5)	1.788(9)	1.906(9)
M—O(2)		1.788(9)	1.904(8)
M—O(3)	2.168(5)	2.202(9)	2.275(9)
M—O(4)	2.171(6)	2.197(9)	2.288(10)
Bond angles			
Cl(1)—M—Cl(2)	166.9(1)	165.0(2)	163.3(2)
Cl(1)—M—Cl(3)	92.7(1)		
Cl(1)—M—O(1)	95.9(2)	96.0(3)	96.0(3)
Cl(1)—M—O(2)		93.3(3)	93.3(3)
Cl(1)—M—O(3)	85.0(1)	83.8(3)	82.9(3)
Cl(1)—M—O(4)	84.7(2)	83.4(2)	83.5(3)
Cl(2)—Nb—Cl(3)	95.6(1)		
Cl(2)—M—O(1)	93.1(2)	94.3(3)	95.2(3)
Cl(2)—M—O(2)		95.8(3)	96.9(3)
Cl(2)—M—O(3)	85.0(1)	85.6(3)	84.9(3)
Cl(2)—M—O(4)	85.3(2)	84.4(2)	83.1(3)
Cl(3)—M—O(1)	97.4(2)		
Cl(3)—M—O(3)	169.7(2)		
Cl(3)—M—O(4)	88.4(2)		
O(1)—M—O(2)		99.2(4)	100.3(4)
O(1)—M—O(3)	92.8(2)	88.8(4)	88.9(3)
O(1)—M—O(4)	174.2(2)	169.3	168.7(4)
O(2)—M—O(3)		171.7(4)	170.4(3)
O(2)—M—O(4)		169.3(4)	168.7(4)
O(3)—M—O(4)	81.4(2)	80.6(3)	79.9(3)
M—O(1)—C(11)	173.4(5)	165.7(8)	166.6(8)
M—O(2)—C(21)		170.0(9)	170.8(8)

6b are listed in Table 6. The Cl(1)—Ti—Cl(2) angles show slight deformations of two chloride ligands from the exact *trans* position. The central atoms lie on the basal plane defined by O(1), O(3), O(4) atoms for complexes **5a**, **5b** and **6b**. In the complexes **5b** and **6b**, the O(phenoxy)—M—O(phenoxy) angles are much larger than the right angle while the O(thf)—M—O(thf) angles are smaller than 90°. These characteristics are also found in other six-coordinated Ti complex bearing a bis-phenoxy group in the *cis* position, Ti(OC₆H₃Prⁱ_{2-2,6})₂(bipy)₂.³⁸ The Ti—O(phenoxy) distances (1.788(11) and 1.789(10) Å) in **5b** are comparable or shorter compared with those of Ti(OC₆H₃Prⁱ_{2-2,6})₂(bipy)₂ (1.882 and 1.896 Å),³⁸ TiI(OC₆H₃Bu^t_{2-2,6})₃ (1.79(2) Å)⁴⁰ and Ti(OC₆H₃Prⁱ_{2-2,6})₄ (1.78(1) Å)³⁹ but is longer than that of **5a** (1.762(5) Å). However, the Zr—O bonds (1.904 and 1.906 Å) are little shorter than those in Zr(OAr)₂{C₈H₉NC(CH₃)C(CH₃)NC₈H₉} (2.009 and 1.950 Å).³⁷

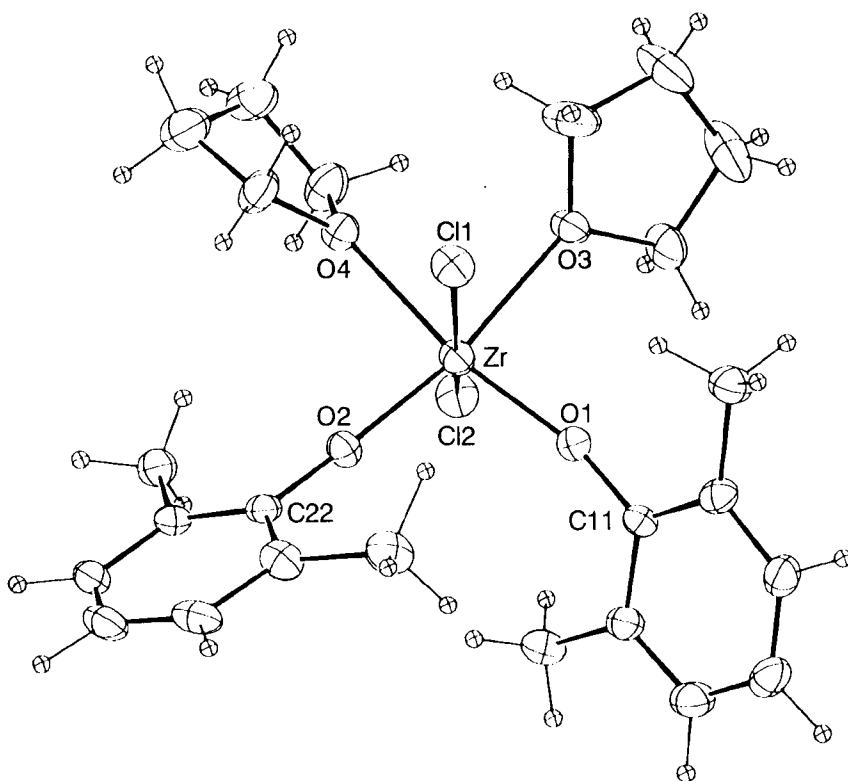
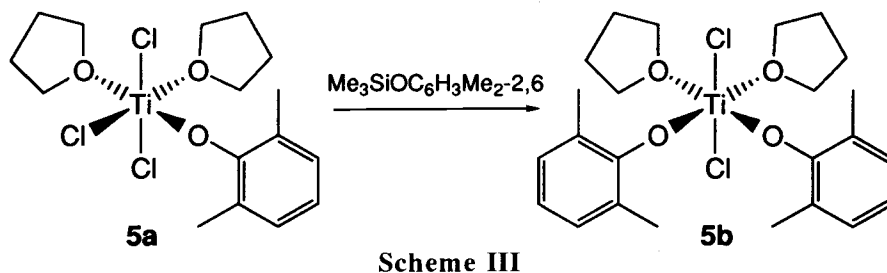


Figure 5. Molecular structures of **6b**.

These results indicate that complex **5a** changes to **5b** by the attack of 2,6-dimethylphenoxy(trimethyl)silane to the Cl(3) atom of **5a**, nevertheless the Cl(3)—Ti bond distance [2.277(3) Å] in **5a** is significantly shorter than the Cl(1)—Ti (2.327(3) Å) and Cl(2)—Ti (2.330(3) Å) bond lengths due to the *trans* effect of the THF molecule (Scheme III).



Experimental Section

General. All manipulations for air- and moisture-sensitive compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl.

Nuclear magnetic resonance (^1H NMR) spectra were measured on a JEOL JNM-FX90Q and JEOL JNM-GSX-270 spectrometers. Mass spectra were recorded on a JEOL SX-102 spectrometer. Elemental analyses were performed at Elemental Analysis Center of Osaka University. All melting points were measured in sealed tubes and were not corrected.

Preparation of $\text{Me}_3\text{Si}(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)$. A solution of *n*-BuLi (210 mmol) in hexane (130 mL) was dropwise added to a solution of 2,6-dimethylphenol (25.1 g, 206 mmol) in THF (100 mL) at 0 °C. The reaction mixture was warmed up to ambient temperature and stirred for 1 h. To the resulting solution of 2,6-dimethylphenoxolithium was dropwise added Me_3SiCl (27.4 g, 252 mmol) at 0 °C. After stirring the reaction mixture for 1 h at ambient temperature, the precipitated salt was

removed by filtration. Distillation under reduced pressure (110 °C, 24 mmHg) afforded Me₃Si(OC₆H₃-2,6-Me₂) (36.6 g, 92%) as colorless oil. ¹H NMR (CDCl₃, 30 °C): δ 6.8—7.0 (m, 3H, aromatic protons), 2.20 (s, 6H, CH₃), 0.40 (s, 9H, SiMe₃). Mass spectrum *m/z*, 194 (M⁺). Spectral data was superimposable to that of literature.⁵

Synthesis of WCl₅(OC₆H₃-2,6-Me₂) (1a). To a solution of WCl₆ (3.49 g, 8.80 mmol) in toluene (100 mL) at -78 °C was added Me₃Si(OC₆H₃-2,6-Me₂) (1.75 g, 8.99 mmol). The reaction mixture was allowed to warm to ambient temperature. During this period, deep purple powdery product was precipitated. The powder was dissolved in toluene by heating to 80 °C. The deep purple crystals of WCl₅(OC₆H₃-2,6-Me₂) (3.12 g, 73%), which contained a small amount of the bisphenoxo complex as an impurity (ca. 6%), were obtained upon cooling the solution to -20 °C. Repeated recrystallization afforded an analytically pure complex, m.p. 244—248 °C. Anal. Calcd for C₈H₉Cl₅O₂W: C, 19.92; H, 1.88. Found: C, 20.13; H, 1.99. ¹H NMR (CDCl₃, 30 °C): δ 7.38 (d, 2H, *m*-H), 6.28 (t, 1H, *p*-H), 3.58 (s, 6H, CH₃). Mass spectrum for ¹⁸⁴W *m/z*, 305 (M⁺ - C₆H₃Me₂Cl₂).

Synthesis of WCl₄(OC₆H₃-2,6-Me₂)₂ (1b). A reaction mixture of WCl₆ (2.25 g, 5.67 mmol) and Me₃Si(OC₆H₃-2,6-Me₂) (2.41 g, 12.41 mmol) in toluene (100 mL) was refluxed with stirring for 2 h, and then this solution was cooled to 0 °C to afford the titled complex as deep purple crystals (1.08 g, 39%). Concentration of the supernatant solution gave 2nd and 3rd crops. Total yield was 60%. M.p. 162—170 °C. Anal. Calcd for C₁₆H₁₈Cl₄O₂W: C, 33.84; H, 3.19. Found: C, 34.00; H, 3.25. ¹H NMR (CDCl₃, 30 °C): δ 7.21 (d, 4H, *m*-H), 6.76 (t, 2H, *p*-H), 2.91 (s, 12H, CH₃). Mass spectrum for ¹⁸⁴W *m/z*, 566 (M⁺).

Synthesis of WCl₄(OC₆H₃-2,6-Pr^{*i*}₂)₂ (1c). A reaction mixture of WCl₆ (0.74 g, 1.87 mmol) and Me₃Si(OC₆H₃-2,6-Pr^{*i*}₂) (0.99 g, 3.96 mmol) in toluene (40 mL) was refluxed with stirring for 2 h, and then this solution was cooled to 0 °C to afford the titled complex as deep purple crystals (0.64 g, 5%). Concentration of the supernatant solution gave 2nd and 3rd crops. Total yield was 50%. M.p. 162—170 °C. Anal. Calcd for C₁₆H₁₈Cl₄O₂W: C, 33.84; H, 3.19. Found: C, 34.00; H, 3.25. ¹H NMR

(CDCl₃, 30 °C): δ 7.35 (d, 4H, *m*-H), 6.92 (t, 2H, *p*-H), 3.99 (m, 4H, CHMe₂), 1.22 (d, 24H, CHMe₂).

Synthesis of WCl(OC₆H₃-2,6-Me₂)₄ (1d). To a solution of WCl₄(OC₆H₃-2,6-Me₂)₂ (1.15 g, 2.03 mmol) in THF (150 mL) at -78 °C was added 0.38 M solution of LiCH₂Bu^t in hexane (11.0 mL, 4.16 mmol). The reaction mixture was allowed to warm to ambient temperature. The color of the solution turned to red brown from deep purple. Then the solvent was removed in vacuo. The extraction from the residue by toluene and cooling the extract to -20 °C gave dark red brown crystals of WCl(OC₆H₃-2,6-Me₂)₄. The yield was 18%. M.p. >300 °C. FAB Mass spectrum for ¹⁸⁴W *m/z*, 703 (M⁺).

Synthesis of MoCl₃(OC₆H₃-2,6-Me₂)₂(thf) (2). The 1:2 reaction of anhydrous MoCl₅ (0.56 g, 2.06 mmol) with Me₃Si(OC₆H₃-2,6-Me₂) (0.81 g, 4.19 mmol) in toluene (30 mL) under reflux for 7 h followed by recrystallization from a mixture of THF and hexane gave MoCl₃(OC₆H₃-2,6-Me₂)₂(thf) (0.16 g, 15%) as purple black crystals. Anal. Calcd for C₂₀H₂₆Cl₃MoO₃: C, 46.49; H, 5.07. Found: C, 46.39; H, 5.27.

Synthesis of NbCl₄(OC₆H₃-2,6-Me₂)(thf) (3a). To a suspension of NbCl₅ (350 mg, 1.30 mmol) in toluene (40 mL) at -78 °C was added Me₃Si(OC₆H₃-2,6-Me₂) (250 mg, 1.30 mmol). The reaction mixture was allowed to stir at ambient temperature for 12 h. After the solvents were removed, the resulting powdery product was recrystallized from a mixture of THF and hexane to give NbCl₄(OC₆H₃-2,6-Me₂)(thf) (369 mg, 66%) as red crystals. M.p. 141—145 °C. Anal. Calcd for C₁₂H₁₇Cl₄NbO₂: C, 33.68; H, 4.00. Found: C, 34.00; H, 4.05. ¹H NMR (CDCl₃, 30 °C): δ 6.9—7.1 (m, 3H, aromatic protons), 4.92 (m, 4H, thf), 2.83 (s, 6H, CH₃), 2.24 (m, 4H, thf). Mass spectrum for ⁹³Nb *m/z*, 354 (M⁺ - C₄H₈O).

Synthesis of NbCl₃(OC₆H₃-2,6-Me₂)₂(thf) (3b). The 1:2 reaction of anhydrous NbCl₅ (3.34 g, 12.4 mmol) with Me₃Si(OC₆H₃-2,6-Me₂) (4.93 g, 25.4 mmol) in toluene (100 mL) at 80 °C for 2 h followed by recrystallization from a mixture of THF and hexane gave NbCl₃(OC₆H₃-2,6-Me₂)₂(thf) (4.17 g, 66%) as red crystals.

M.p. 173—176 °C. Anal. Calcd for C₂₀H₂₆Cl₃NbO₃: C, 46.76; H, 5.10. Found: C, 46.43; H, 5.29. ¹H NMR (CDCl₃, 30 °C): δ 6.7—7.0 (m, 6H, aromatic protons), 4.66 (m, 4H, thf), 3.80 (m, 2H, thf), 2.54 (s, 6H, CH₃), 2.45 (s, 6H, CH₃), 2.14 (m, 4H, thf), 1.89 (m, 2H, thf). Mass spectrum for ⁹³Nb *m/z*, 440 (M⁺ - C₄H₈O).

Synthesis of TaCl₄(OC₆H₃-2,6-Me₂)(thf) (4a). To a suspension of TaCl₅ (1.56 g, 4.35 mmol) in toluene (40 mL) at -78 °C was added Me₃Si(OC₆H₃-2,6-Me₂) (0.86 g, 4.42 mmol). The reaction mixture was allowed to stir at ambient temperature for 3 h. The color of the reaction mixture turned from yellow to orange. At this time, 1 mL (0.89 g, 12 mmol) of THF was added at room temperature. The precipitates were dissolved, yielding a clear yellow solution. Filtration and cooling to -20 °C afforded TaCl₄(OC₆H₃-2,6-Me₂)(thf) (1.67 g, 74%) as yellow crystals. Concentration of the supernatant solution gave 2nd crop. Total yield was 84%. M.p. 163—164 °C. Anal. Calcd for C₁₂H₁₇Cl₄O₂Ta: C, 27.93; H, 3.32. Found: C, 28.05; H, 3.51. ¹H NMR (C₆D₆, 30 °C): δ 6.75 (d, 2H, *m*-H), 6.60 (t, 1H, *p*-H), 4.47 (m, 4H, thf), 2.86 (s, 6H, CH₃), 1.11 (m, 4H, thf). Mass spectrum for ¹⁸¹Ta *m/z*, 442 (M⁺ - C₄H₈O).

Synthesis of TaCl₃(OC₆H₃-2,6-Me₂)₂(thf) (4b). The 1:2 reaction of anhydrous TaCl₅ (1.09 g, 3.04 mmol) with Me₃Si(OC₆H₃-2,6-Me₂) (1.27 g, 6.52 mmol) in toluene (30 mL) at room temperature for 3 h followed by recrystallization from a mixture of THF and hexane gave yellow crystals of TaCl₃(OC₆H₃-2,6-Me₂)₂(thf) (0.77 g, 42%). M.p. 170—172 °C. Anal. Calcd for C₂₂H₃₀Cl₃O_{3.5}Ta (1.5thf / Ta): C, 41.43; H, 4.74. Found: C, 41.87; H, 4.78. ¹H NMR (C₆D₆, 30 °C): δ 6.6—7.2 (m, 6H, aromatic protons), 4.30 (m, 4H, thf), 2.70 (s, 6H, CH₃), 2.49 (s, 6H, CH₃), 1.11 (m, 4H, thf). Mass spectrum for ¹⁸¹Ta *m/z*, 528 (M⁺ - C₄H₈O).

Synthesis of TiCl₃(OC₆H₃-2,6-Me₂)(thf)₂ (5a). To a solution of TiCl₄(THF)₂ (1.82 g, 5.46 mmol) in THF (80 mL) at -78 °C was added Me₃Si(OC₆H₃-2,6-Me₂) (1.10 g, 5.66 mmol). The reaction mixture was allowed to warm to ambient temperature. After THF was removed, the resulting powdery product was recrystallized from a mixture of THF and hexane to give red crystals of TiCl₃(OC₆H₃-2,6-Me₂)(thf)₂

(1.81 g, 73%). M.p. 122 — 27 °C. Anal. Calcd for C₁₆H₂₅Cl₃O₃Ti: C, 45.80; H, 6.01. Found: C, 43.35; H, 5.92. ¹H NMR (CDCl₃, 30 °C): δ 6.7—7.1 (m, 3H, aromatic protons), 4.30(m, 8H, thf), 2.70 (s, 6H, CH₃), 2.03(m, 8H, thf). Mass spectrum for ⁴⁸Ti *m/z*, 274 (M⁺ - 2C₄H₈O).

Synthesis of TiCl₂(OC₆H₃-2,6-Me₂)₂(thf)₂ (5b). A reaction mixture of TiCl₄ (4.67 g, 24.6 mmol) and Me₃Si(OC₆H₃-2,6-Me₂) (9.54 g, 49.2 mmol) in hexane (80 mL) was refluxed with stirring for 2 h. After hexane was removed, the resulting powdery product was recrystallized from a mixture of THF and hexane to give red crystals of TiCl₂(OC₆H₃-2,6-Me₂)₂(thf)₂ (0.51 g, 4%). Concentration of the supernatant solution gave 2nd and 3rd crops. Total yield was 70%. M.p. 122 — 127 °C. Anal. Calcd for C₂₄H₃₄Cl₂O₄Ti: C, 57.05; H, 6.78. Found: C, 54.56; H, 6.79. ¹H NMR (CDCl₃, 30 °C): δ 6.8—7.0 (m, 3H, aromatic protons), 4.08(m, 8H, thf), 2.33 (s, 6H, CH₃), 1.97(m, 8H, thf). Mass spectrum for ⁴⁸Ti *m/z*, 360 (M⁺ - 2C₄H₈O).

Synthesis of ZrCl₃(OC₆H₃-2,6-Me₂)(thf)₂ (6a). To a suspension of ZrCl₄ (0.44 g, 1.90 mmol) in toluene (3 mL) at 0 °C was added THF (20 mL, 25 mmol). Stirring at ambient temperature made the precipitate dissolved. To the resulting solution of ZrCl₄(thf)₂ was dropwise added Me₃Si(OC₆H₃-2,6-Me₂) (0.38 g, 1.97 mmol) at - 78 °C. The reaction mixture was stirred at ambient temperature for 3 h. The solvents were removed under reduced pressure to give colorless powdery product. Recrystallization of the product from a mixture of THF and hexane gave colorless crystals of ZrCl₃(OC₆H₃-2,6-Me₂)(thf)₂ (0.58 g, 67%). Concentration of the supernatant solution gave 2nd crop. Total yield was 72%. M.p. 138 — 147 °C (dec.). Anal. Calcd for C₁₆H₂₅Cl₃O₃Zr: C, 41.51; H, 5.44. Found: C, 40.35; H, 5.68. ¹H NMR (CDCl₃, 30 °C): δ 6.6—7.0 (m, 3H, aromatic protons), 4.46(m, 8H, thf), 2.53 (s, 6H, CH₃), 2.09(m, 8H, thf). Mass spectrum for ⁹⁰Zr *m/z*, 316 (M⁺ - 2C₄H₈O).

Synthesis of ZrCl₂(OC₆H₃-2,6-Me₂)₂(thf)₂ (6b). ZrCl₄ (2.15 g, 9.24 mmol) was dissolved in a mixture of benzene (10 mL) and THF (100 mL, 1.23 mol). To the resulting solution of ZrCl₄(thf)₂ was dropwise added Me₃Si(OC₆H₃-2,6-Me₂) (10.65

g, 54.92 mmol) at 0 °C and then the reaction mixture was refluxed for 6 h. The product was recrystallized from a mixture of THF and hexane to afford colorless crystals of $\text{ZrCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)_2(\text{thf})_2$ (1.94 g, 67%). Concentration of the supernatant solution gave 2nd and 3rd crops. Total yield was 84%. M.p. 140—176 °C (dec.). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{O}_4\text{Zr}$: C, 52.54; H, 6.25. Found: C, 50.98; H, 6.33. $^1\text{H NMR}$ (CDCl_3 , 30 °C): δ 6.6—7.0 (m, 3H, aromatic protons), 4.39(m, 8H, thf), 2.36 (s, 6H, CH_3), 2.06(m, 8H, thf). Mass spectrum for ^{90}Zr m/z , 402 ($\text{M}^+ - 2\text{C}_4\text{H}_8\text{O}$).

Synthesis of $\text{HfCl}_3(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)(\text{thf})_2$ (7a). To HfCl_4 (0.49 g, 1.52 mmol) dissolved in a mixture of toluene (5 mL) and THF (20 mL, 25 mmol) was dropwise added $\text{Me}_3\text{Si}(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)$ (0.31 g, 1.58 mmol) at - 78 °C. The reaction mixture was allowed to stir at ambient temperature for 24 h. Colorless powdery product of $\text{HfCl}_3(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)(\text{thf})_2$ (0.76 g, 91%) was obtained by removing the volatiles, washing the resulting powder with a minimal volume of hexane, and drying the sample *in vacuo*. Recrystallization from a mixture of THF and hexane gave colorless crystals. M.p. 154 — 168 °C (dec.). Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{Cl}_3\text{HfO}_3$: C, 34.93; H, 4.58. Found: C, 32.76; H, 5.05. $^1\text{H NMR}$ (CDCl_3 , 30 °C): δ 6.5—7.0 (m, 3H, aromatic protons), 4.48(m, 8H, thf), 2.50 (s, 6H, CH_3), 2.10(m, 8H, thf). Mass spectrum for ^{180}Hf m/z , 406 ($\text{M}^+ - 2\text{C}_4\text{H}_8\text{O}$).

Synthesis of $\text{HfCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)_2(\text{thf})_2$ (7b). To a solution of HfCl_4 (0.39 g, 1.23 mmol) in toluene (5 mL) and THF (20 mL, 25 mmol) was dropwise added $\text{Me}_3\text{Si}(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)$ (0.66 g, 3.42 mmol) at 0 °C. The reaction mixture was refluxed for 30 h. The product was recrystallized from a mixture of THF and hexane yielding $\text{HfCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Me}_2)_2(\text{thf})_2$ (0.66 g, 84%) as colorless crystals. M.p. 160 — 188 °C (dec.). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{HfO}_4$: C, 45.33; H, 5.39. Found: C, 42.28; H, 5.79. $^1\text{H NMR}$ (CDCl_3 , 30 °C): δ 6.5—7.0 (m, 3H, aromatic protons), 4.38 (m, 8H, thf), 2.33 (s, 6H, CH_3), 2.06 (m, 8H, thf). Mass spectrum for ^{180}Hf m/z , 492 ($\text{M}^+ - 2\text{C}_4\text{H}_8\text{O}$).

Crystallographic Data Collections and Structure Determination of 1a, 1b, 1c, 1d, 3a, 3b, 5a, 5b and 6b. The crystals of 1a suitable for X-ray

diffraction sealed in glass capillaries under argon atmosphere, were mounted on a Rigaku AFC-5R four-circle diffractometer for data collection using MoK α radiation. Three standard reflections were chosen and monitored every 150 reflections. Measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. Empirical absorption correction was carried out based on an azimuthal scan. The crystal structure of **1a** was solved by a heavy-atom method. Successive Fourier synthesis phased by the tungsten atom found in Patterson maps clearly revealed the remaining nonhydrogen atoms. The structures were refined anisotropically by a full-matrix least-squares method. In the final refinement cycle, hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were given the same temperature factor as that of the carbon atom to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package.

The crystallographic studies for **1b**, **1c**, **1d**, **3a**, **3b**, **5a**, **5b** and **6b** are carried out similarly. Crystal data of these complexes are summarized in Tables 7—10 and atomic coordinates are listed in Table 11—19, respectively.

Table 7. Crystal Data and Data Collection Parameters.

complex	1a	1b
formula	WCl ₅ OC ₈ H ₉	WCl ₄ O ₂ C ₁₆ H ₁₈
formula weight	482.3	568.4
crystal system	orthorhombic	monoclinic
space group	<i>Cmcm</i>	<i>C2₁/m</i>
<i>a</i> , Å	12.952(5)	17.615(4)
<i>b</i> , Å	12.386(3)	7.188(2)
<i>c</i> , Å	8.279(3)	8.396(2)
β, deg.		119.93(2)
<i>V</i> , Å ³	1328.0(10)	921.3(4)
<i>Z</i>	4	4
<i>D</i> _{calcd}	2.412	2.047
<i>F</i> (000)	896	544
radiation	Mo Kα	Mo Kα
abs. coeff, cm ⁻¹	98.7	72.2
scan mode	θ—2θ	θ—2θ
temp, °C	23	20
scan speed, deg/min	8—16	4
scan width, deg	1.0 + 0.30tanθ	1.0 + 0.35tanθ
2θ _{max} , deg	60	60
unique data	895	912
unique data (<i>I</i> > 3σ(<i>I</i>))	576	908
no. of variables	48	101
<i>R</i>	0.046	0.032
<i>R</i> _w	0.036	0.016
GOF	1.84	1.969

Table 8. Crystal Data and Data Collection Parameters.

complex	1c	1d
formula	WCl ₄ O ₂ C ₂₄ H ₂₈	WClO ₄ C ₃₂ H ₃₆
formula weight	674.15	703.94
crystal system	monoclinic	tetragonal
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> 4
<i>a</i> , Å	9.697(2)	12.328(1)
<i>b</i> , Å	17.115(2)	
<i>c</i> , Å	16.799(2)	10.287(4)
β, deg.	91.80(1)	
<i>V</i> , Å ³	2786.7(8)	1563.5(7)
<i>Z</i>	4	2
<i>D</i> _{calcd}	1.607	1.495
<i>F</i> (000)	1320	702
radiation	Mo Kα	Mo Kα
abs. coeff, cm ⁻¹	46.37	38.89
temp, °C	25	25
scan speed, deg/min	10	10
scan width, deg	1.73 + 0.35 tanθ	1.21 + 0.35 tanθ
2θ _{max} , deg	55	55
unique data	7008	1038
unique data (<i>I</i> > 3σ(<i>I</i>))	6625	952
no. of variables	280	87
<i>R</i>	0.079	0.049
<i>R</i> _w	0.056	0.063
GOF	3.97	5.77

Table 9. Crystal Data and Data Collection Parameters.

complex	3a	3b
formula	NbCl ₄ O ₂ C ₁₂ H ₁₇	NbCl ₃ O ₃ C ₂₀ H ₂₆
formula weight	482.0	513.7
crystal system	orthorhombic	triclinic
space group	<i>Cmcm</i>	<i>P1</i>
<i>a</i> , Å	7.979(3)	9.639(9)
<i>b</i> , Å	17.094(4)	15.396(6)
<i>c</i> , Å	12.536(2)	8.763(4)
α , deg.		98.68(4)
β , deg.		98.61(9)
γ , deg.		75.45(6)
<i>V</i> , Å ³	1709.7(8)	1235.8(15)
<i>Z</i>	4	2
<i>D</i> _{calcd}	1.663	1.379
<i>F</i> (000)	856	524
radiation	Mo K α	Mo K α
abs. coeff, cm ⁻¹	13.0	8.1
scan mode	θ — 2θ	θ — 2θ
temp, °C	23	20
scan speed, deg/min	8—16	8—16
scan width, deg	1.63 + 0.30tan θ	0.84 + 0.35tan θ
2θ _{max} , deg	55	60
unique data	1146	7218
unique data (<i>I</i> > 3 σ (<i>I</i>))	702	4483
no. of variables	60	349
<i>R</i>	0.053	0.080
<i>R</i> _w	0.038	0.130
GOF	2.27	4.937

Table 10. Crystal Data and Data Collection Parameters.

complex	5a	5b	6b
formula	C ₁₆ H ₂₅ Cl ₃ O ₃ Ti	C ₂₄ H ₃₄ Cl ₂ O ₄ Ti	C ₂₄ H ₃₄ Cl ₂ O ₄ Zr
formula weight	419.7	505.3	548.7
crystal system	orthorhombic	monoclinic	monoclinic
space group	<i>Pna</i> 2 ₁	<i>Cc</i>	<i>Cc</i>
<i>a</i> , Å	17.389(3)	16.794(4)	16.660(9)
<i>b</i> , Å	10.610(1)	13.498(2)	13.647(2)
<i>c</i> , Å	10.8358(2)	11.421(1)	11.589(2)
β, deg.		90.72(1)	91.11(2)
<i>V</i> , Å ³	1998.9(5)	2588.8(7)	2634.0(8)
<i>Z</i>	4	4	4
<i>D</i> _{calcd}	1.394	1.296	1.383
<i>F</i> (000)	872	1064	1136
radiation	Mo Kα	Mo Kα	Mo Kα
abs. coeff, cm ⁻¹	8.5	2.9	6.4
scan mode	θ—2θ	θ—2θ	θ—2θ
temp, °C	20	20	20
scan speed, deg/min	4	4	8—16
scan width, deg	1.0 + 0.35tanθ	1.0 + 0.35tanθ	1.103 + 0.35 tanθ
2θ _{max} , deg	60	60	60
unique data	3058	3771	3997
unique data (<i>I</i> >3σ(<i>I</i>))	2345	1948	2266
no. of variables	308	415	415
<i>R</i>	0.053	0.084	0.060
<i>R</i> _w	0.074	0.092	0.086
GOF	2.793	3.040	4.579

Table 11. Atomic coordinates for non-hydrogen atoms in complex **1a**.

Atom	x	y	z	B _{eq}
W	0	0.1828(1)	1/4	2.82
Cl(1)	0	-0.0028(7)	1/4	5.4
Cl(2)	0.1264(2)	0.1777(4)	0.0538(4)	5.0
O	0	0.329(2)	1/4	4
C(1)	0	0.443(3)	1/4	7
C(2)	-0.100(1)	0.495(2)	1/4	4
C(3)	-0.096(1)	0.607(2)	1/4	4
C(4)	0	0.659(2)	1/4	4
C(5)	-0.199(1)	0.432(2)	1/4	7

Table 12. Atomic coordinates for non-hydrogen atoms in complex **1b**.

Atom	x	y	z	B _{eq}
W	0	0	0	2.77
Cl(1)	-0.04868(13)	0.2303(3)	0.1237(4)	3.63
O	0.1090(5)	0	0.2132(14)	2.9
C(1)	0.1878(7)	0	0.366(3)	3.2
C(2)	0.1915(7)	0	0.537(3)	3.1
C(3)	0.2746(8)	0	0.687(4)	3.9
C(4)	0.3509(8)	0	0.675(4)	4.6
C(5)	0.3441(7)	0	0.502(4)	3.5
C(6)	0.2638(7)	0	0.347(3)	3.5
C(7)	0.1122(9)	0	0.547(3)	3.7
C(8)	0.2600(9)	0	0.160(4)	5.0

Table 13. Atomic coordinates for non-hydrogen atoms in complex **1c**.

Atom	x	y	z	B _{eq}
W	0.47807(7)	0.21657(4)	0.30644(4)	3.77(3)
Cl(1)	0.2391(4)	0.2124(3)	0.2986(2)	6.1(2)
Cl(2)	0.7129(4)	0.2294(3)	0.3335(2)	5.5(2)
Cl(3)	0.4629(5)	0.1584(3)	0.4310(2)	6.7(3)
Cl(4)	0.4543(6)	0.3386(3)	0.3654(3)	7.9(3)
O(1)	0.4908(9)	0.2619(5)	0.2093(5)	3.6(5)
O(2)	0.4934(8)	0.1208(5)	0.2640(5)	3.1(5)
C(11)	0.5060(13)	0.2833(9)	0.1304(7)	3.1(6)
C(12)	0.4176(14)	0.3396(8)	0.0981(8)	3.7(8)
C(13)	0.4332(19)	0.3572(11)	0.0181(9)	6(1)
C(14)	0.535(2)	0.3228(13)	-0.0248(9)	7(1)
C(15)	0.6214(16)	0.2698(11)	0.0086(9)	5(1)
C(16)	0.6096(15)	0.2445(9)	0.0874(8)	4.2(8)
C(21)	0.5024(15)	0.0470(9)	0.2281(8)	3.4(7)
C(22)	0.4109(15)	0.0295(9)	0.1644(8)	3.8(8)
C(23)	0.424(2)	-0.0443(11)	0.1323(9)	6(1)
C(24)	0.521(2)	-0.0969(10)	0.1606(10)	6(1)
C(25)	0.6110(18)	-0.0766(10)	0.2213(10)	5(1)
C(26)	0.6033(15)	-0.0042(9)	0.2590(8)	3.8(8)
C(51)	0.3012(16)	0.3720(10)	0.1456(8)	4.3(9)
C(52)	0.1704(17)	0.3291(12)	0.1286(10)	7(1)
C(53)	0.277(2)	0.4595(11)	0.1308(11)	7(1)
C(61)	0.7136(14)	0.1913(8)	0.1224(8)	3.8(8)
C(62)	0.8525(16)	0.2255(10)	0.1382(10)	6(1)
C(63)	0.7313(16)	0.1166(9)	0.0724(9)	5(1)
C(71)	0.3026(17)	0.0850(9)	0.1321(10)	4.6(9)
C(72)	0.315(2)	0.1000(10)	0.0429(10)	7(1)
C(73)	0.1571(18)	0.0599(12)	0.1500(12)	9(1)
C(81)	0.7008(16)	0.0158(9)	0.3270(10)	4.7(9)
C(82)	0.848(2)	0.0220(13)	0.2993(13)	9(1)
C(83)	0.693(2)	-0.0398(11)	0.3952(11)	9(1)

Table 14. Atomic coordinates for non-hydrogen atoms in complex **1d**.

Atom	x	y	z	B _{eq}
W(1)	0	0	0	3.64(4)
Cl(1)	0	0	0.2359(5)	4.8(2)
O(1)	0.1059(6)	0.1069(6)	-0.000(3)	3.6(4)
C(1)	0.185(1)	0.184(1)	0.008(3)	3.3(6)
C(2)	0.169(2)	0.275(1)	-0.073(2)	4.8(9)
C(3)	0.246(2)	0.358(2)	-0.075(2)	6(1)
C(4)	0.337(2)	0.343(1)	0.020(4)	6(1)
C(5)	0.354(2)	0.256(2)	0.074(2)	6(1)
C(6)	0.275(1)	0.171(1)	0.080(2)	4.0(8)
C(7)	0.073(2)	0.290(2)	-0.152(3)	9(1)
C(8)	0.292(2)	0.067(2)	0.166(2)	6(1)

Table 15. Atomic coordinates for non-hydrogen atoms in complex **3a**.

Atom	x	y	z	B _{eq}
Nb	0	0.10268(7)	1/4	3.73
Cl(1)	0.2075(2)	0.0905(1)	0.1179(1)	5.3
O(1)	0	0.2091(4)	1/4	4.2
O(3)	0	-0.0264(4)	1/4	3.7
C(11)	0	0.2907(7)	1/4	3.7
C(12)	0	0.3277(5)	0.3492(7)	4.3
C(13)	0	0.4102(6)	0.3446(8)	5.3
C(14)	0	0.4501(8)	1/4	6.0
C(15)	0	0.2843(5)	0.4519(7)	5.4
C(31)	0	-0.0753(5)	0.3460(7)	6.4
C(32)	0	-0.1555(6)	0.3081(7)	7.4

Table 16. Atomic coordinates for non-hydrogen atoms in complex **3b**.

Atom	x	y	z	B _{eq}
Nb	0.72962(8)	0.31630(5)	0.14411(9)	3.31
Cl(1)	0.7812(4)	0.44889(17)	0.0846(3)	4.42
Cl(2)	0.6400(3)	0.18751(17)	0.1640(4)	4.40
Cl(3)	0.5030(3)	0.4054(2)	0.2165(4)	4.90
O(1)	0.8168(7)	0.3248(4)	0.3443(7)	3.3
O(2)	0.8891(6)	0.2426(4)	0.0575(7)	3.0
O(3)	0.6164(6)	0.3107(5)	-0.0925(7)	3.3
C(11)	0.8966(9)	0.3294(7)	0.4858(9)	3.3
C(12)	0.8839(10)	0.4145(7)	0.5707(11)	3.6
C(13)	0.9699(13)	0.4202(9)	0.7126(12)	4.7
C(14)	1.0637(13)	0.3414(10)	0.7673(12)	5.2
C(15)	1.0707(11)	0.2586(9)	0.6789(13)	4.7
C(16)	0.9855(10)	0.2509(7)	0.5360(11)	3.7
C(17)	0.7807(13)	0.4979(8)	0.5153(13)	4.9
C(18)	0.9886(13)	0.1607(8)	0.4426(14)	5.2
C(21)	1.0127(8)	0.1835(6)	0.0183(10)	2.9
C(22)	1.1447(10)	0.2034(7)	0.0849(11)	3.3
C(23)	1.2727(11)	0.1419(9)	0.0438(14)	4.9
C(24)	1.2673(14)	0.0660(9)	-0.0572(16)	5.8
C(25)	1.1321(13)	0.0486(8)	-0.1243(15)	5.1
C(26)	1.0063(10)	0.1087(6)	-0.0889(11)	3.6
C(27)	1.1536(12)	0.2869(8)	0.1969(13)	5.0
C(28)	0.8612(12)	0.0915(7)	-0.1670(12)	4.5
C(31)	0.6733(11)	0.3338(8)	-0.2255(11)	4.2
C(32)	0.5766(13)	0.3022(10)	-0.3688(13)	5.7
C(33)	0.4419(13)	0.3069(12)	-0.3116(14)	6.7
C(34)	0.4732(12)	0.2938(12)	-0.1402(14)	5.7

Table 17. Atomic coordinates for non-hydrogen atoms in complex **5a**.

Atom	x	y	z	B _{eq}
Ti	0.17659(5)	0.05375(9)	0	3.25
Cl(1)	0.12358(9)	-0.13336(14)	0.0729(3)	4.76
Cl(2)	0.21494(10)	0.26119(15)	-0.0346(3)	4.72
Cl(3)	0.13359(12)	0.0188(3)	-0.1956(3)	5.66
O(1)	0.2703(2)	-0.0058(4)	-0.0204(5)	4.0
O(3)	0.1963(3)	0.0963(5)	0.1931(5)	4.1
O(4)	0.0650(2)	0.1342(4)	0.0432(6)	4.5
C(11)	0.3450(3)	-0.0375(5)	-0.0360(7)	3.5
C(12)	0.3807(4)	-0.1093(6)	0.0559(7)	4.0
C(13)	0.4579(4)	-0.1430(8)	0.0382(9)	5.4
C(14)	0.4975(5)	-0.1006(9)	-0.0667(10)	6.3
C(15)	0.4614(5)	-0.0302(8)	-0.1540(9)	5.5
C(16)	0.3832(4)	0.0029(6)	-0.1437(7)	4.3
C(17)	0.3374(5)	-0.1546(9)	0.1665(8)	5.6
C(18)	0.3423(6)	0.0725(8)	-0.2437(9)	5.9
C(31)	0.1516(6)	0.0483(13)	0.2980(9)	8.0
C(32)	0.1857(7)	0.1021(12)	0.4095(10)	7.2
C(33)	0.2672(6)	0.1393(10)	0.3735(9)	6.6
C(34)	0.2613(5)	0.1717(8)	0.2382(8)	5.3
C(41)	-0.0090(4)	0.0720(7)	0.0190(12)	6.5
C(42)	-0.0673(5)	0.1744(8)	0.0208(12)	6.9
C(43)	-0.0343(5)	0.2665(9)	0.1095(13)	7.2
C(44)	0.0502(5)	0.2613(7)	0.0856(14)	7.2

Table 18. Atomic coordinates for non-hydrogen atoms in complex **5b**.

Atom	x	y	z	B _{eq}
Ti	0.25	0.28505(15)	0.25	3.70
Cl(1)	0.2163(3)	0.2787(3)	0.4511(3)	5.48
Cl(2)	0.2493(3)	0.3073(3)	0.0462(4)	5.51
O(1)	0.3451(5)	0.3423(7)	0.2717(8)	4.7
O(2)	0.2806(5)	0.1582(7)	0.2468(8)	4.8
O(3)	0.1948(5)	0.4329(6)	0.2570(8)	4.8
O(4)	0.1247(5)	0.2431(7)	0.2233(8)	4.8
C(11)	0.4233(7)	0.3622(9)	0.2931(10)	4.0
C(12)	0.4808(9)	0.3189(10)	0.2196(13)	5.5
C(13)	0.5602(9)	0.3411(11)	0.2421(16)	6.4
C(14)	0.5815(9)	0.4027(13)	0.3377(16)	6.5
C(15)	0.5245(9)	0.4418(10)	0.4085(12)	5.8
C(16)	0.4427(8)	0.4245(11)	0.3852(12)	5.2
C(17)	0.4571(10)	0.2557(12)	0.1162(13)	6.7
C(18)	0.3806(9)	0.4676(12)	0.4648(12)	5.9
C(21)	0.2997(8)	0.0606(11)	0.2643(11)	4.3
C(22)	0.2662(8)	-0.0087(10)	0.1927(13)	4.8
C(23)	0.2837(10)	-0.1093(11)	0.2147(15)	6.5
C(24)	0.3336(10)	-0.1364(13)	0.3054(17)	7.0
C(25)	0.3682(10)	-0.0629(14)	0.3736(15)	6.8
C(26)	0.3552(8)	0.0389(10)	0.3544(12)	5.0
C(27)	0.2103(9)	0.0181(11)	0.0951(14)	5.8
C(28)	0.3940(9)	0.1171(12)	0.4284(13)	6.1
C(31)	0.2300(11)	0.5177(11)	0.1973(14)	7.0
C(32)	0.1858(16)	0.6056(13)	0.2382(16)	9.7
C(33)	0.1112(14)	0.5658(16)	0.292(2)	9.8
C(34)	0.1298(10)	0.4611(14)	0.3301(15)	7.8
C(41)	0.0727(10)	0.2731(14)	0.1225(14)	7.5
C(42)	-0.0107(10)	0.2397(14)	0.1551(19)	8.0
C(43)	0.0053(10)	0.1511(14)	0.2339(16)	8.0
C(44)	0.0819(9)	0.1742(12)	0.2946(15)	6.8

Table 19. Atomic coordinates for non-hydrogen atoms in complex **6b**.

Atom	x	y	z	B _{eq}
Zr	0.25	0.28577(7)	0.25	4.25
Cl(1)	0.2107(3)	0.2825(3)	0.4549(3)	5.39
Cl(2)	0.2493(3)	0.3084(4)	0.0397(4)	5.47
O(1)	0.3513(5)	0.3476(7)	0.2763(8)	4.2
O(2)	0.2819(5)	0.1518(6)	0.2506(8)	4.2
O(3)	0.1908(6)	0.4359(7)	0.2536(8)	4.5
O(4)	0.1189(6)	0.2424(8)	0.2168(8)	4.5
C(11)	0.4302(7)	0.3702(9)	0.2991(11)	4.1
C(12)	0.4892(8)	0.3285(10)	0.2293(13)	4.9
C(13)	0.5679(9)	0.3515(13)	0.2540(16)	6.0
C(14)	0.5887(9)	0.4115(13)	0.3482(16)	6.3
C(15)	0.5286(9)	0.4511(11)	0.4150(14)	5.4
C(16)	0.4491(8)	0.4313(10)	0.3912(11)	4.5
C(17)	0.4677(10)	0.2667(12)	0.1272(15)	6.1
C(18)	0.3827(10)	0.4737(13)	0.4650(14)	6.1
C(21)	0.3025(7)	0.0522(9)	0.2698(10)	3.7
C(22)	0.2725(8)	-0.0153(10)	0.1990(12)	4.5
C(23)	0.2915(9)	-0.1128(10)	0.2226(15)	5.8
C(24)	0.3406(11)	-0.1352(12)	0.3133(17)	6.6
C(25)	0.3738(10)	-0.0648(13)	0.3801(15)	6.1
C(26)	0.3568(10)	0.0343(11)	0.3593(12)	5.2
C(27)	0.2170(9)	0.0104(12)	0.0972(15)	5.4
C(28)	0.3941(10)	0.1171(13)	0.4329(13)	6.2
C(31)	0.2270(11)	0.5210(11)	0.1948(14)	6.2
C(32)	0.1830(19)	0.6051(13)	0.2384(18)	9.5
C(33)	0.1119(18)	0.5744(16)	0.293(3)	10.0
C(34)	0.1226(13)	0.4678(15)	0.323(2)	8.6
C(41)	0.0688(11)	0.2665(14)	0.1157(18)	6.7
C(42)	-0.0129(11)	0.2322(16)	0.1435(19)	7.2
C(43)	-0.0013(10)	0.1483(16)	0.2256(18)	7.3
C(44)	0.0747(10)	0.1746(13)	0.2924(17)	6.3

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Chapter 3

Polymerization of Monosubstituted Acetylenes Catalyzed by 2,6-Dimethylphenoxo Complexes of Group 5 and 6 Metals

Introduction

The polymerization of alkynes has attracted much interest in view of new organic materials, *e.g.*, as conducting or gas permeable polymers.^{1,2} In the case of the simplest alkyne, acetylene, Ziegler type catalysts such as $\text{Ti}(\text{O}-n\text{-Bu})_4/\text{Et}_3\text{Al}$ are most useful as polymerization catalyst.³ On the other hand, group 5 and 6 transition-metal halides have been reported as polymerization catalysts for bulky substituted acetylenes by Masuda *et al.*⁴ However, high polymers of less bulky substituted acetylenes such as *n*-alkylacetylenes have not been obtained by the reported catalysts. Recently, the living polymerization of 1-chloro-1-alkynes has been achieved by the catalyst system based on a mixture of MoOCl_4 , tetrabutyltin, and ethanol.⁵ The ethanol might be a source of alkoxide ligand which is important for the activity and selectivity of catalyst.

Alkoxide and aryloxy groups have been used as ligands stabilizing the carbene species, which has been regarded as the key intermediate of the polymerization of 1-alkyne.⁶ Although various carbene complexes with aryloxy ligands have been prepared and were applied to the living ring-opening polymerization of cyclic olefins,⁷⁻⁹ only a little examples of such complexes have been found useful for the polymerization of acetylenes.¹⁰

We have systematically prepared a series of 2,6-dimethylphenoxo complexes of group 5 and 6 transition metals (**1**, **2**, **3**, and **4**, dmp = 2,6-dimethylphenoxo) which have been revealed to have monomeric structures by crystallographic studies.^{11,12} In a course of our research on the reactivity of these complexes, we found that they became effective catalyst precursors for polymerization of 1-alkynes upon treating them with a reducing reagent such as Grignard reagent or alkyl aluminums.¹³ The catalyst system based on well-characterized 2,6-dimethylphenoxo complexes (**1—4**) affords some important insights into the mechanism of alkyne polymerization, and thus we can tune the catalyst to a highly active and selective one. The catalyst activity and selectivity for the polymerization of 1-alkynes were found to be delicately affected by the number of bulky aryloxo ligand and the geometry at metal center. Thus, an extra high molecular weight polymer with narrow molecular distribution was obtained as the result of our investigation. Moreover, we report here that the tungsten complexes bearing three or four 2,6-dimethylphenoxo ligands catalyzed the polymerization of less bulky substituted acetylenes such as 1-butyne, 1-hexyne, and 1-octyne to give high molecular weight polymers for the first time.

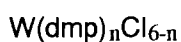
Results and Discussion

Preparation of 2,6-Dimethylphenoxo Complexes of Tungsten, Molybdenum, Tantalum, and Niobium. A series of bulky aryloxo complexes of group 5 and 6 metals have already been reported.¹⁴ Some of them have been prepared by the reaction of metal halides with phenol derivatives or alkali metal phenolate in suitable solvents or without solvent.^{14(a)–(c)} However it is difficult to control the number of aryloxo ligands to be introduced on metal by such methods. It is especially difficult to prepare mono(aryloxo) complexes.

The author have synthesized mono- and bis(2,6-dimethylphenoxo) complexes of group 5 and 6 metals by the reaction of metal halides with 2,6-

dimethylphenyltrimethylsilyl ether.^{11,12} This method was used to prepare complexes **1a**, **1b**, **2**, **3a**, **3b**, **4a**, and **4b** as described in Chapter 2. Some of them have already been characterized by our crystallographic studies, which provide information on the catalytic mechanism (*vide infra*).

Complex **1c** was prepared according with the literature method.^{14(a)} **1d** has already been reported by Schrock and coworkers.^{14(b)} According to their paper, **1d** was prepared by the reaction of WCl_6 in melt 2,6-dimethylphenol at 80 °C. We modified the reaction condition for the ease of separation of **1d** from excess 2,6-dimethylphenol. Thus **1d** was obtained by refluxing a mixture of WCl_6 and 2,6-dimethylphenol in toluene. Only the pure above-mentioned complexes were used as catalyst precursors in the present investigation to limit the structure of active species.



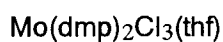
1

a: $n = 1$

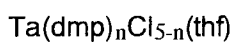
b: $n = 2$

c: $n = 3$

d: $n = 4$



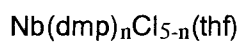
2



3

a: $n = 1$

b: $n = 2$



4

a: $n = 1$

b: $n = 2$

dmp = 2,6-Dimethylphenoxo

Polymerization of 3,3-Dimethyl-1-butyne. Bulky monosubstituted acetylene, *e.g.* 3,3-dimethyl-1-butyne, has been generally known to give higher polymers by catalysis of $MoCl_5$ - and WCl_6 -based catalysts.¹⁵ Since 3,3-dimethyl-1-butyne is reported to form stable high molecular weight polymers, we chose 3,3-dimethyl-1-butyne as a monomer to investigate the catalytic feature of complexes **1—4** for the polymerization. In general, the stepwise replacement of chloride by aryloxide in

$WCl_n(OAr)_{6-n}$ or $WOCl_n(OAr)_{4-n}$ complexes makes the species harder to be reduced. Therefore, we selected a stronger reducing agent such as a Grignard agent or trialkylaluminum as a cocatalyst rather than alkyltin compounds which were usually used as a cocatalyst for WCl_6 , $MoCl_5$, and $MoOCl_4$.

The polymerization of 3,3-dimethyl-1-butyne was carried out in the presence of **1b** with various molar equivalents of EtMgBr. The results are shown in Figure 1, which

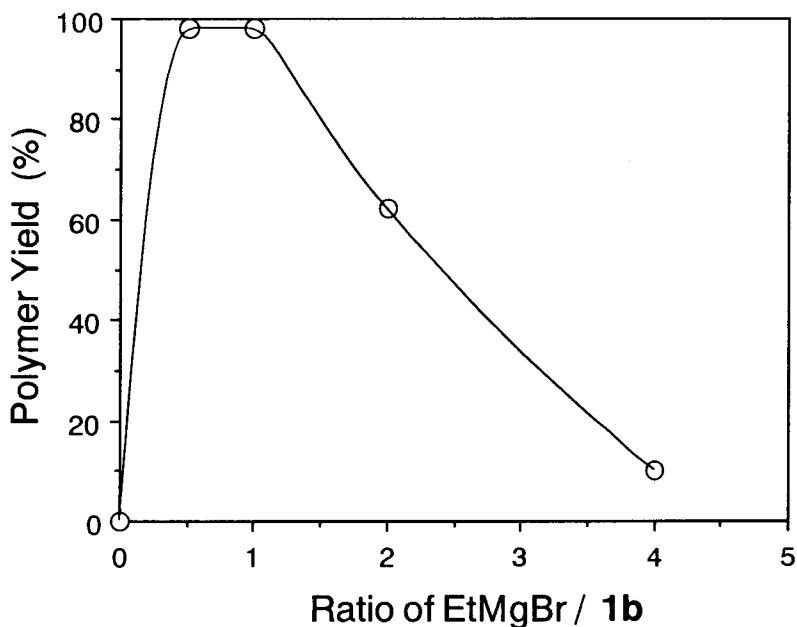


Figure 1. The yield of poly(3,3-dimethyl-1-butyene) depending on the molar ratio of complex **1b** and cocatalyst ethyl Grignard reagent. Polymerization was carried out in toluene at 30 °C for 24 h. $[monomer]_0 = 1M$; $[1b] = 10\text{ mM}$.

shows clearly that the more reduced tungsten species are less active as the catalyst for polymerization. Thus, tungsten species in the high oxidation state may be a catalytic species because 0.5:1 and 1:1 ratios for the mixture of reducing reagent/**1b** gave the maximum yield of the polymerization. Such a tendency is consistent with the reported fact that a tungsten complex, $W(CHCMe_3)(NC_6H_3Pr^{1-2,6})(OBu^t)_2$, is the catalyst for polymerization of C_2H_2 .^{10(a)} This carbene complex is in a formal oxidation state 6+,

which is in accord with the formal oxidation states (5+ or 6+) estimated for the present catalyst species. Thus, the 1:1 ratio for catalyst/cocatalyst was used consistently for the following polymerization.

The nature of cocatalyst sometimes caused difference in the catalyst activity. In the series of tungsten complexes when complexes **1a** or **1b** was used above 30 °C as a catalyst for the polymerization, both of the cocatalysts, EtMgBr and Et₃Al exhibit essentially the same activity. When complex **1b**/EtMgBr was used at -20 °C as a catalyst for the polymerization, the yield of the polymer is only 3%. When EtMgBr was replaced by AlEt₃, the polymer yield increased to 28% at the same condition. Such a tendency can speculatively be attributed to Lewis acidity of the metal center. Complex **1b** seems to interact with magnesium salt such as MgCl₂ to block the active site. On the other hand, a system, **1d**/EtMgBr is the good catalyst at 60 °C to give high polymer in 88% yield, while the low yield (5%) was observed for the catalyst system **1d**/AlEt₃. This probably resulted from the decreased reactivity of the chlorotungsten moiety of **1d** to MgCl₂ or MgBr₂.

Bis(2,6-dimethylphenoxy)—metal complexes with AlEt₃, were examined as catalyst for polymerization of 3,3-dimethyl-1-butyne and results are summarized in Table I. Generally, group 6 metals showed higher catalyst activity than group 5 metals. In the case of tantalum, the activity for the polymerization of 3,3-dimethyl-1-butyne is very low. It is interesting that the ligation of 2,6-dimethylphenoxy on niobium enabled polymerization of monosubstituted acetylenes instead of cyclotrimerization (*vide infra*). When mono- or bis(aryloxy)niobium complexes (**4a** and **4b**)/Grignard reagents or triethylaluminium, were used as catalyst precursors for 3,3-dimethyl-1-butyne, high polymers formed in modest yields with M_n values of $>2 \times 10^6$ and 3.7×10^5 , respectively.

This is in sharp contrast to the fact that most niobium complexes such as NbCl₅,¹⁶ [CpNb(diene)Cl]₂,¹⁷ CpNbCl₄/Mg,¹⁸ [NbCl₃(THT)]₂ (THT = tetrahydrothiophene)¹⁹ and NbCl₃(DME) (DME = 1,2-dimethoxyethane)²⁰ have been used as catalysts for the cyclotrimerization of 1-alkynes.^{4, 16–20} The previous exception

is the polymerization of $\text{HC}\equiv\text{CCH}(\text{SiMe}_3)\text{R}$ ($\text{R} = n\text{-C}_5\text{H}_{11}$ and $n\text{-C}_7\text{H}_{15}$)²¹ and $\text{HC}\equiv\text{CCH}(\text{SiMe}_2\text{R})\text{-}n\text{-Pr}$ ($\text{R} = n\text{-C}_6\text{H}_{13}$ and Ph),²² which was catalyzed by NbCl_5 based catalysts. The bulkiness of the substituent on acetylene prevents the cyclotrimerization and linear oligomerization.

Activity of our catalyst system might be attributed to the presence of a bulky aryloxo group which has the same effect as the bulkiness on monomer. A catalyst system **4a**/*tert*-BuMgCl is also applied for the polymerization of phenylacetylene to find the polymer with $M_n = 1.9 \times 10^4$, $M_w/M_n = 2.7$. In the case of less bulky acetylene 1-butyne, however, only cyclotrimers were produced by **4a**/EtMgBr and **4b**/EtMgBr (monitored by GLC).

Table I. Polymerization of 3,3-Dimethyl-1-butyne by Various Catalysts.^a

run	catalyst	cocatalyst	temp	yield ^b	$M_n/10^5$ ^c	M_w/M_n ^c
			°C	%		
1	1b	AlEt ₃	60	83	7.8	2.1
2		AlEt ₃	-20	28	>20	1.2
3	2	AlEt ₃	60	64	6.1	2.5
4		AlEt ₃	-20	82	7.5	1.8
5	3a	AlEt ₃	60	9	bimodal	—
6	3b	AlEt ₃	60	5	—	—
7	4a	<i>tert</i> -BuMgCl	60	92	>20	1.6
8	4b	AlEt ₃	60	69	3.7	2.2

^a Polymerization was carried out in toluene for 24 h; $[\text{monomer}]_0 = 1 \text{ M}$, $[\text{catalyst}] = [\text{cocatalyst}] = 10 \text{ mM}$. ^b Insoluble part in methanol. ^c Determined by GPC analysis.

Molybdenum complex **2** in the presence of AlEt₃ is the most active catalyst precursor, and high polymers were obtained. As the number of aryloxo ligand coordinated to tungsten can easily be controlled, we investigated the tungsten system more precisely. Results are shown in Table II. Tungsten complexes such as WCl₆, **1a** and **1b** became the catalyst precursor for polymerization of 3,3-dimethyl-1-butyne, but higher temperature (60 °C) was required for **1a** and **1b**. While WCl₆ could be used as a

catalyst even at 0 °C without cocatalysts, complex **1** showed no catalyst activity below 30 °C. On the other hand, the addition of cocatalyst activated the catalyst. At 60 °C, catalyst activity of complex **1** in the presence of cocatalyst increased and higher number-averaged molecular weight M_n values (5.4×10^5 to $>20 \times 10^5$) are obtained for resulting polymers. The M_n values of the obtained polymers are increased with increasing the number of the aryloxo ligands. Thus, active species seems to be stabilized by increasing the number of the bulky aryloxo ligands.

Table II. Polymerization of 3,3-Dimethyl-1-butyne Catalyzed by Tungsten Complexes.^a

run	catalyst	cocatalyst	temp °C	yield ^b %	$M_n/10^5$ ^c	M_w/M_n ^c
1	WCl ₆	—	60	76	1.4	2.0
2		—	0	55	2.3	2.6
3	1a	—	60	76	2.6	1.7
4		—	30	<1	—	—
5		AlEt ₃	60	86	5.4	2.5
6		AlEt ₃	0	99	14	1.7
7		AlEt ₃	-20	72	>20	1.5
8	1b	—	60	82	4.3	2.3
9		—	30	<1	—	—
10		AlEt ₃	60	83	7.8	2.1
11		AlEt ₃	0	79	6.1	2.0
12		AlEt ₃	-20	28	>20	1.2
13	1c	—	60	<1	—	—
14		AlEt ₃	60	80	18	1.5
15		AlEt ₃	0	66	>20	1.2
16	1d	—	60	7	15	1.5
17		EtMgBr	60	88	>20	1.4
18		EtMgBr	0	<1	—	—

^a Polymerization was carried out in toluene for 24 h; [monomer]₀ = 1 M, [catalyst] = [cocatalyst] = 10 mM. ^b Insoluble part in methanol. ^c Determined by GPC analysis.

At lower temperature (0 °C or -20 °C), complexes **1d** showed low catalyst activity with or without cocatalyst. Complexes **1a**, **1b** and **1c** still have catalyst activity for the polymerization to afford extra high molecular weight polymers ($M_n \geq 2 \times 10^6$) with narrow molecular weight distribution. The best system is the combination of **1b** with AlEt₃ at -20 °C and **1c** with AlEt₃ at 0 °C. In the case of these catalyst systems, the polydispersity index (M_w/M_n) reached to 1.2. It is very interesting that such an extra high polymer can be a result of a kind of living polymerization.

Conversion of 3,3-dimethyl-1-butyne was monitored by GLC analysis and the molecular weight M_n of polymer at each stage was quantitatively estimated by GPC analysis. The results were shown in Figure 2. The obtained good linear relationship indicates that the reaction is considered to be almost living polymerization ($M_w/M_n = 1.5\text{—}1.8$) and thus active species are rather stable and long living. Although the initiator efficiency is very low (<1 %), it is interesting that such extra high polymers can be obtained in a somewhat living fashion. This is attributed to the stabilization effect of bulky aryloxy ligand on active species.

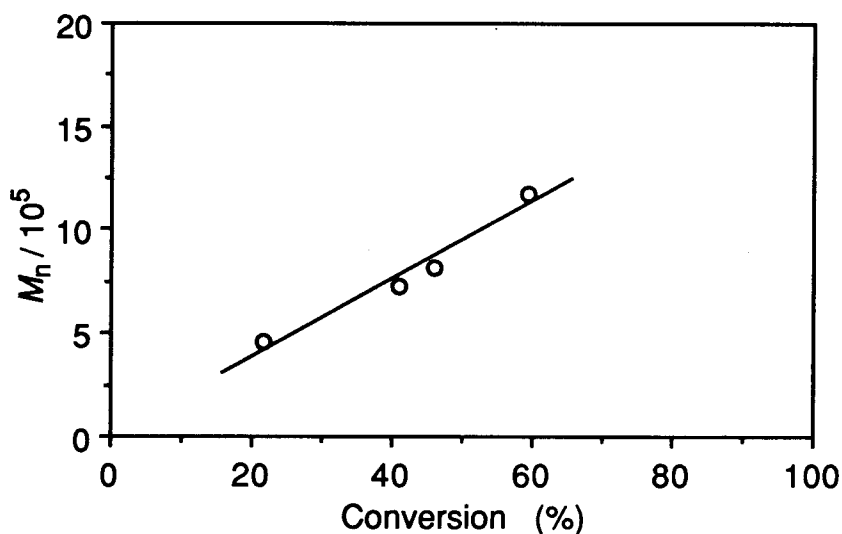


Figure 2. A plot for the number averaged molecular weight M_n vs. consumption of monomer for the polymerization of 3,3-dimethyl-1-butyne. Polymerization was carried out in toluene at 0 °C by using catalyst system **1a**/AlEt₃.

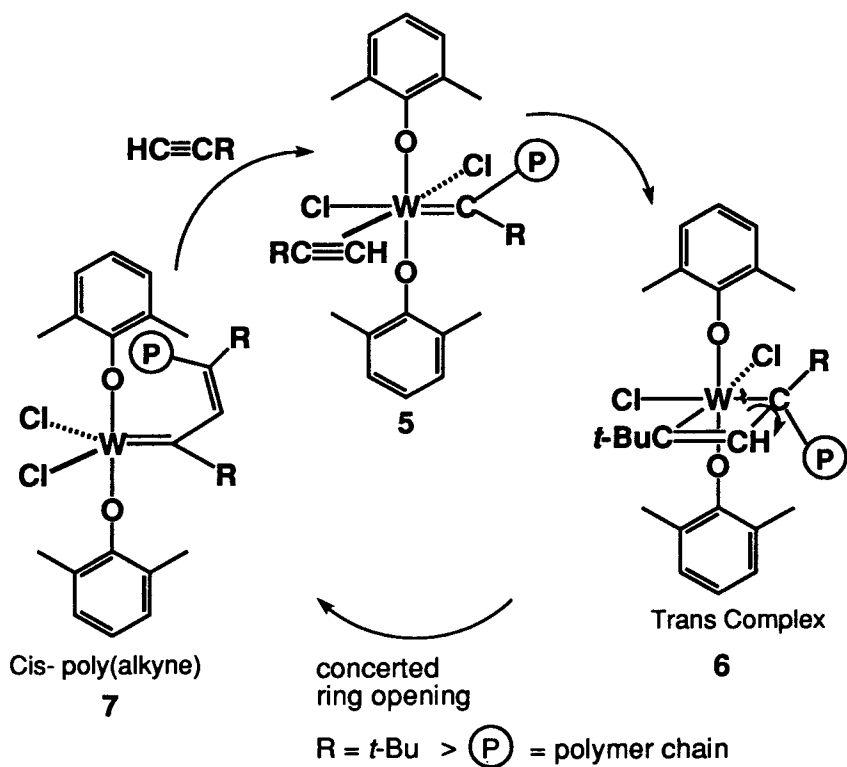
Cis Content of poly(3,3-dimethyl-1-butyne) can be estimated by ^{13}C NMR spectroscopy²³ and is shown in Table III. The increase of the bulkiness around tungsten increased the content of *cis* geometry of the polyene chain. As shown in scheme I, alkylating reagents produce carbene species and there must be an open site available for the following alkyne coordination.^{24,25} Thus, carbene—alkyne species **5** is assumed as one of the intermediates, where *trans* geometry for two aryloxo groups are based on the structure of **1b** determined by X-ray crystallography. In the next stage, the propagation reaction is the cleavage of W—C(sp³) bond in the key intermediate, metallacyclobutene **6**, with rotating C(sp³)—C(sp²) bonds around its axis to form a double bond. During this rotation the steric repulsion between the aryloxo ligands on tungsten and *t*-butyl group on C(sp³) can drive the *t*-butyl group away. The resulting polymer chain may predominantly have *cis* geometry. Thus, the bulkiness both on monomer and on catalyst are essentially important factors to produce high polymers with high *cis* content.

Table III. *Cis*-contents of Poly(3,3-dimethyl-1-butyne) Catalyzed by Various Catalysts.^a

run	catalyst	cocatalyst	$M_n/10^3$ ^b	<i>cis</i> -content ^c %
1	4a	<i>tert</i> -BuMgCl	>2000	50
2	4b	<i>tert</i> -BuMgCl	>2000	47
3	WCl ₆	-	140	63
4	2	-	590	70
5	1a	-	260	71
6	1b	-	430	80
7	1b	AlEt ₃ ^d	>2000	88

^a Polymerization was carried out in toluene at 60 °C for 24 h unless otherwise noted; [monomer]₀ = 1 M, [catalyst] = [cocatalyst] = 10 mM. ^b Determined by GPC analysis. ^c Determined by ^{13}C NMR spectra.²³ ^d Polymerization was carried out at -20 °C.

Scheme I



The cis contents of polymers obtained by using niobium complexes **4a** and **4b** are 50 and 47%, respectively. These values can be rationalized by assuming the intermediate **8**, whose stereochemistry is based on the crystal structure of **4b** as shown in Figure 3. The intermediate **6** has two aryloxo ligands at *trans* position and catalyzes formation of *cis*-polyene as described above. On the other hand, niobium in **8** has two aryloxo ligands in *cis*-fashion and one coordination site is open to be coordinated by a solvent molecule. Therefore, the propagation step through **8** is not effectively restricted and no selection was observed.

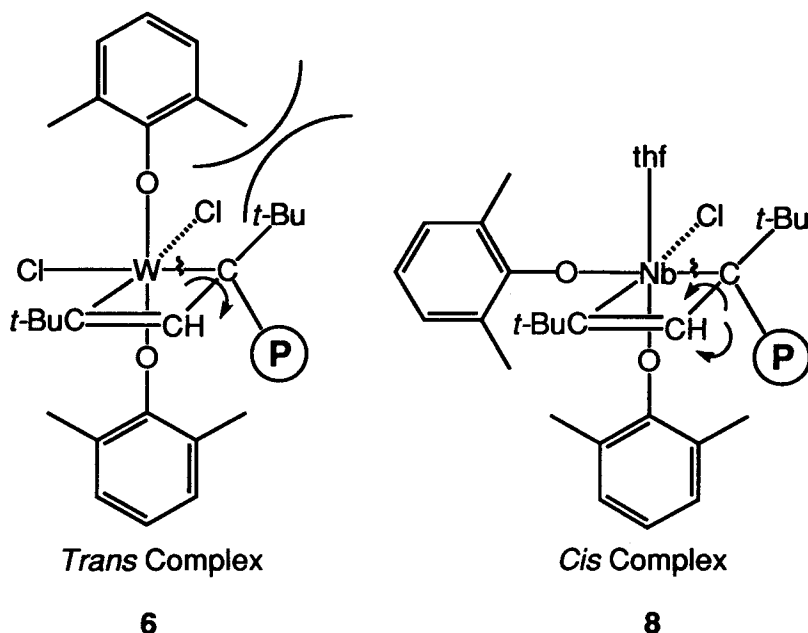


Figure 3. Schematic drawings for the metallacyclic intermediates responsible for the stereoselectivity of polymerization catalyzed by **1b** and **4b**.

Polymerization of 1-Alkynes with Less Bulky Substituents. We investigated steric influence in the polymerization by a systematic variation of substituent R on acetylene; thus, ethyl-, *i*-propyl-, *t*-butylacetylenes were examined for polymerization. The polymerization of 3-methyl-1-butyne was carried out by using tungsten complexes. As shown in Table IV, the catalyst system based on **1c** gave a polymer with higher M_n value (7.3×10^5) than that (4.5×10^4) obtained by using WCl_6 . Bulkiness on tungsten also increased the value of M_n .

We have also examined polymerization of *n*-alkyl substituted acetylenes. Previous reports on the polymers from *n*-alkylacetylene have shown that the molecular weight is rather low ($M_n = \sim 10^4$).^{25,26} 1-Butyne has been reported to be polymerized by

Table IV. Polymerization of 1-Alkynes by Tungsten Catalysts.^a

run	monomer	catalyst	cocatalyst	yield ^b		M_w/M_n ^c
				%	$M_n/10^3$ ^c	
1	3-methyl-1-butyne	WCl ₆	—	71	45	1.6
2		1a	AlEt ₃	88	130	1.5
3		1b	AlEt ₃	7	110	1.8
4		1c	EtMgBr	7	730	1.7
5	1-butyne	WCl ₆	—	41	5	1.6
6		1a	AlEt ₃	89	bimodal ^d	—
7		1b	AlEt ₃	59	4	1.3
8		1c	EtMgBr	69	94	3.5
9	1-hexyne	1d	EtMgBr	92	50	2.0
10		WCl ₆	—	50	8	1.7
11		1c	EtMgBr	63	92	2.7
12	1-octyne	1d	EtMgBr	92	170	2.9
13		WCl ₆	—	67	10	1.7
14		1c	EtMgBr	98	220	2.6
15		1d	EtMgBr	17	350	2.2

^a Polymerization was carried out in toluene at 0 °C for 24 h; [monomer]₀ = 1 M, [catalyst] = [cocatalyst] = 10 mM. ^b Insoluble part in methanol. ^c Determined by GPC analysis. ^d $M_n = 2.4 \times 10^4$ and 2.2×10^3 .

catalysis of WCl₆, but the molecular weight of the obtained polymer is rather low ($M_n = 5 \times 10^3$). The catalyst systems based on **1a** or **1b** exhibited comparable reactivity with WCl₆. On the other hand, the system **1c**/EtMgBr is the best catalyst precursor of polymerization of 1-butyne to give high polymer, $M_n = 9.4 \times 10^4$. The obtained polymer is an orange elastomer.

Similarly, the polymerization of 1-hexyne and 1-octyne by using WCl₆ as a catalyst afforded a yellow viscous oil, while the catalyst system **1d**/EtMgBr afforded red elastomers ($M_n = 1.7 \times 10^5$ and 3.5×10^5 , respectively). These values of M_n were about 10 times larger than those previously reported.^{25,26(a),(c)} This remarkable feature can presumably be attributed to the bulkiness around the active metal center in these

catalyst systems. The bulky phenoxo group may prevent the side reactions such as chain transfer reaction²⁷ or cyclotrimerization.^{26(a)}

UV-visible spectra (Figure 4) of the high polymer of 1-hexyne show a new peak at λ_{\max} of 305 nm. Compared with the low molecular weight conjugated polyenes,²⁸ the λ_{\max} values of the poly(*n*-alkylacetylene)s obtained by **1d**/EtMgBr were close to those of H(-CH=CH-)_{*n*}H whose *n* values are 4 to 5 as shown in table V. Considering that the λ_{\max} values of the polymers obtained by WCl₆ were close to those of H(-CH=CH-)_{*n*}H whose *n* are 3, the present result indicates the extension of conjugated segments in the polymers produced by aryloxo complex-based catalysts.

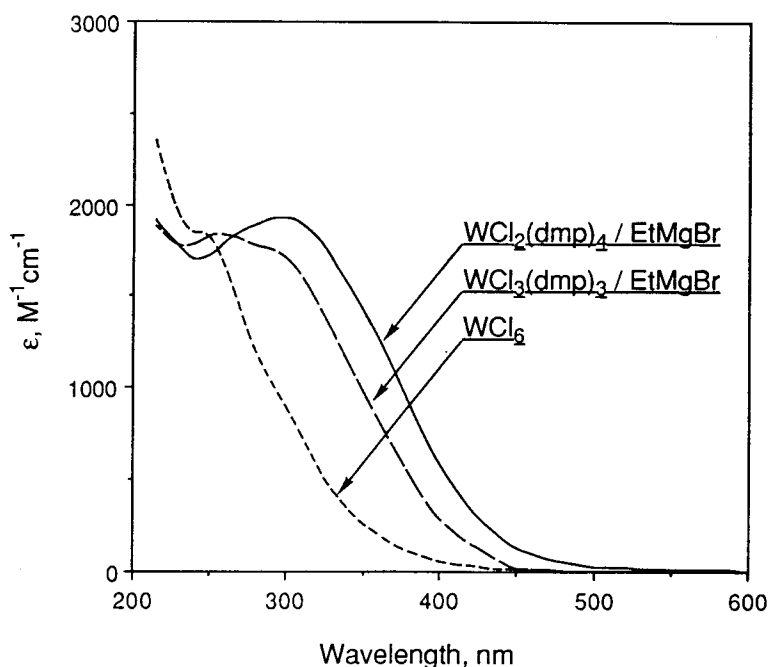


Figure 4. UV-visible spectra of poly(1-hexyne) in hexane. ϵ_{\max} values of the polymers were calculated per monomer unit.

Structural regularity of poly(1-butyne) can be estimated by ¹³C NMR spectroscopy. *Cis* content of the poly(1-butyne) obtained by WCl₆ and **1d**/EtMgBr was similar, *i.e.* 84% and 86%, respectively. Thus, the extension of conjugated segments is

mainly due to the increase of the molecular weight. Preparation of high polymers of 1-butyne enabled us to prepare a firm pellet. The specific conductivity of poly(1-butyne) measured with the two-probe method was less than 10^{-9} S/cm. After doping with iodine vapor, the iodine uptake was 66 wt% and the specific conductivity increased to 3.3×10^{-4} S/cm. The iodine-doped poly(1-butyne) was a black brittle solid. The conductivities of poly(1-hexyne) and poly(1-octyne) were also less than 10^{-9} S/cm, while iodine-doped poly(1-hexyne) (including 62 wt % iodine) and poly(1-octyne) (including 42 wt % iodine) showed conductivities of 3.1×10^{-5} S/cm and 8.9×10^{-5} S/cm, respectively, and both were black gummy materials. These values were comparable to the conductivities of iodine-doped poly(phenylacetylene) (10^{-4} — 10^{-3} S/cm)²⁹ or polypropyne (10^{-3} S/cm).³⁰

Table V. UV-visible spectral data of low molecular weight conjugated polyenes and poly(1-alkyne)s.

compounds	λ_{\max}	ϵ_{\max}^a
H(-CH=CH-) _n H ^b		
n = 2	217	11000
3	268	11000
4	304	16000
5	334	24000
6	364	23000
poly(1-butyne) ^c		
catalyzed by WCl ₆	240	2100
WCl ₂ (dmp) ₄ / EtMgBr	291	1900
poly(1-hexyne) ^c		
catalyzed by WCl ₆	248	1900
WCl ₂ (dmp) ₄ / EtMgBr	305	1900
poly(1-octyne) ^c		
catalyzed by WCl ₆	255	1200
WCl ₂ (dmp) ₄ / EtMgBr	330	1900

^a Calculated per one double bond. ^b Measured in isoctane.²⁸ ^c Measured in hexane.

Thus we have found that the ligation of the bulky aryloxo group on the active metal center dramatically enhances the molecular weight of the resulting polymer with higher conjugated structure.

Experimental Section

General. Nuclear magnetic resonance (^1H , and ^{13}C NMR) spectra were measured on a JEOL JNM-FX90Q and a JEOL GX-270 spectrometers. Elemental analyses were performed at the Elemental Analysis Center of Osaka University. All melting points were measured in sealed tubes and were not corrected.

All manipulations involving air- and moisture-sensitive compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl. Phenylacetylene, 1-butyne, 1-hexyne, and 1-octyne were purchased from Tokyo Chemical Industry Co., Ltd. 3-Methyl-1-butyne and 3,3-dimethyl-1-butyne were obtained from Lancaster. These monomers were dried by calcium hydride and distilled under argon atmosphere before use.

Complexes **1a**, **1b**, **2**, **4a** and **4b** were prepared as described in Chapter 2. Complexes **1c**, ^{14(a)}**3a**^{14(e)} and **3b**^{14(e)} were prepared according to literature method, but THF was used instead of ether for **3a** and **3b**.

Preparation of 1d. To a solution of WCl_6 (1.61 g, 4.06 mmol) in toluene (40 mL) at $0\text{ }^\circ\text{C}$ was added a solution of $\text{HOC}_6\text{H}_3\text{-2,6-Me}_2$ (2.64 g, 21.61 mmol) in toluene. The color of the solution immediately changed from deep blue to deep purple. The reaction mixture was refluxed for 5 h and then this solution was cooled to $0\text{ }^\circ\text{C}$ to afford the titled complex as deep purple microcrystals (2.45 g, 82 %). Spectral data were superimposable to those in literature ^{14(b)}.

Polymerization of 1-butyne. General Procedures: To a suspension of $\text{WCl}_2(\text{dmp})_4$ (15 mg, 0.02 mmol) in toluene (0.9 mL) was added an 0.2 M ethereal solution of EtMgBr (0.1 mL, 0.02 mmol) at $0\text{ }^\circ\text{C}$. The color of the suspension scarcely

changed from deep purple. After stirring for 10 minutes at room temperature, the reaction mixture was cooled to -78°C and then a solution of 1-butyne (0.24 mL, 0.16 g, 2 mmol) in toluene (0.76 mL) was added to the mixture. The reaction tube was sealed in argon and kept for 24 h at 0 °C with stirring. A large excess (ca. 20 mL) of methanol was added to the reaction mixture under argon atmosphere to precipitate the polymer. The resulting orange rubbery solid polymer was collected by centrifugation and dried *in vacuo*. The yield was 92 %.

GPC Analyses. Gel permeation chromatographic (GPC) analyses were carried out using TOSOH TSKgel HXL-H and L columns connected to a TOSOH RI-8021 differential refractometer and a TOSOH UV-8010 absorbance detector. Samples were prepared in THF (0.1—0.3%w/v) and were filtered through a Toyo Roshi DISMIC-25JP filter in order to remove particulates before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) which ranged from 500 to 1.11×10^6 MW.

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Part II

Polymerization of Polar Monomers

Chapter 4

A Novel Convenient Preparation of Arenethiolate Complexes of Divalent and Trivalent Lanthanides from Metallic Lanthanides and Diaryl Disulfides

Introduction

Lanthanide compounds are of current interest as highly active catalysts for the polymerization of ethylene,¹ MMA,²⁻⁶ lactones,⁷⁻¹⁰ lactide^{11,12} and isocyanate¹³ to yield polymers with narrow molecular weight distribution, and in some case, high stereoregularity. In the polymerizations of these monomers except for ethylene, lanthanide alkoxide species are active initiators or propagating end groups. The author expected the lanthanide thiolate compounds to be also active because Ln—S bond is weaker than Ln—O bond.¹⁴ Such compounds are also of current interest in the field of organic synthesis¹⁵ and precursors of materials.¹⁶⁻²⁴

However, the synthesis of lanthanide thiolate complexes has remained to be rare. Metathesis reactions of lanthanide halides with alkali metal thiolates have been reported for the syntheses of lanthanide thiolates.²⁵⁻²⁷ In these preparations, the isolation and purification of the product is often hindered by the rather strong interaction of lanthanide cations with the alkali metal halides. The salt free complexes have been successfully prepared by the reaction of alkyl or amido complexes of lanthanide with thiols²⁸⁻³¹ and the oxidative reaction of low valent organosamarium or ytterbium complexes with

organic disulfides.^{14,32-35} The author tried the direct reaction of lanthanide metals with diaryl disulfides to prepare such compounds, since lanthanide metals are highly reactive.

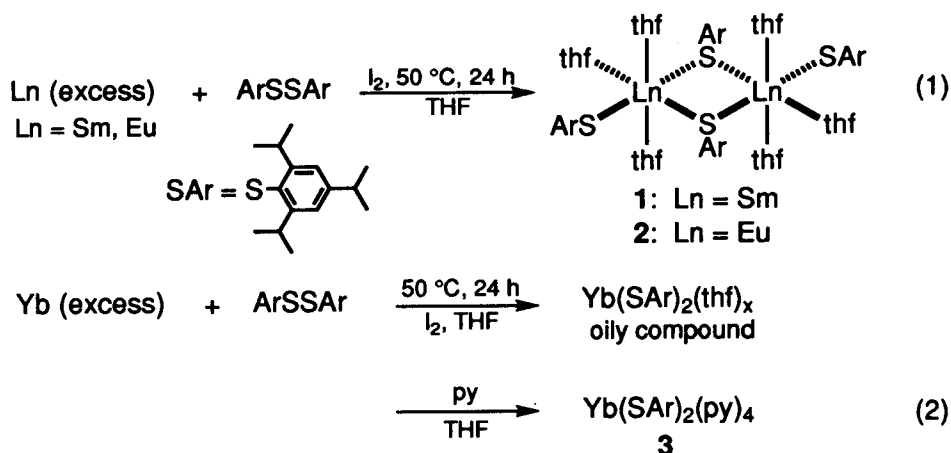
Lanthanides are significantly electropositive elements, whose electronegativities (1.0—1.2) are comparable to those of alkali metals and alkaline earth metals such as lithium (1.0), sodium (1.0), magnesium (1.2), calcium (1.1) and strontium (1.0). They have high reactivities even in their metallic states compared to the other transition metals. Such high reactivities have been utilized to prepare a variety of lanthanide complexes, *e.g.*, halides,³⁶⁻³⁸ alkoxides,³⁹⁻⁴¹ amides⁴² and organolanthanides.⁴³⁻⁵⁰ Due to the higher availability of pure lanthanide metals than anhydrous lanthanide halides, such a synthetic route from metallic lanthanides is practically useful. However, the synthesis of lanthanide thiolate complexes from lanthanide metals have not yet been reported.

The author found a new synthetic method of Ln(II) and Ln(III) arenethiolates by the direct reaction of lanthanide metals with diaryl disulfides. Thus, the convenient one-pot reaction of metallic samarium, europium, and ytterbium with diaryl disulfides cleanly gives the thiolate complexes in the two or three oxidation states by controlling the stoichiometry of metallic lanthanide and the disulfide.

Results and Discussion

Synthesis and structures of bis(thiolato)lanthanide(II). The binuclear bis(2,4,6-triisopropylbenzenethiolate) complexes of samarium(II) and europium(II), [Ln(SC₆H₂Prⁱ_{3-2,4,6})₂(thf)₃]₂ (**1**: Ln = Sm; **2**: Ln = Eu), were prepared by a direct reaction of an 2-fold excess of metallic lanthanide with bis(2,4,6-triisopropylphenyl) disulfide in THF in the presence of a catalytic amount (ca. 3 mol%) of iodine (eqn. 1). This reaction did not proceed at all without iodine. The lanthanide metal was quantitatively consumed within 24 h at 50 °C. Dimeric structures bearing bridging thiolate and terminal thiolate ligands for **1** and **2** have been revealed by the crystallographic study.⁵¹ In the case of dialkyl disulfide, such as di(*t*-butyl) disulfide or dimethyl disulfide, no reaction was observed in the same condition. Once isolated as

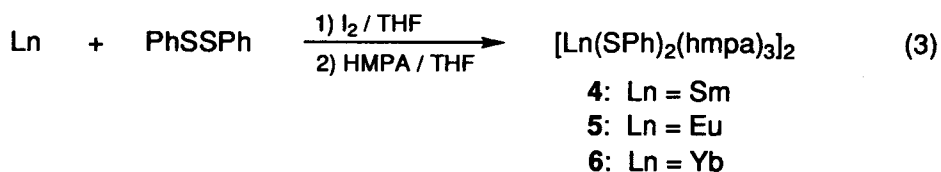
crystals, complexes **1** and **2** gradually became opaque due to the loss of THF ligands, resulting in the formation of $[\text{Ln}(\text{SC}_6\text{H}_2\text{Pr}^{i3-2,4,6})_2(\text{thf})_n]_2$ ($\text{Ln} = \text{Sm}$, $n = 1$; $\text{Ln} = \text{Eu}$, $n = 2$). The similar reaction of metallic Yb with bis(2,4,6-triisopropylphenyl) disulfide in THF gave an orange oily product, from which black crystals of $\text{Yb}(\text{SC}_6\text{H}_2\text{Pr}^{i3-2,4,6})_2(\text{py})_4$ (**3**) were obtained on the addition of an excess amount of pyridine to the solution (eqn. 2). Recently, Brennan *et al.* reported the preparation of $\text{Yb}(\text{SPh})_2(\text{py})_4$ by the reaction of diphenyl disulfide with the solvated Yb metal ion in liquid ammonia or Yb/Hg amalgam in THF.²⁰ Nief *et al.* reported the preparation of $[\text{Yb}(\mu\text{-X})(\eta^5\text{-C}_4\text{Me}_4\text{P})(\text{thf})_2]_2$ ($\text{X} = \text{Cl}$, SPh) from metallic Yb and $\text{C}_4\text{Me}_4\text{PX}$ in THF.⁵²



The samarium(II) complex **1** has high reactivity. Reaction of **1** with one equiv. of cyclooctatetraene afforded $[\text{Sm}(\mu\text{-SC}_6\text{H}_2\text{Pr}^{i3-2,4,6})(\eta\text{-C}_8\text{H}_8)(\text{thf})]_2$ and $[\text{Sm}(\text{SC}_6\text{H}_2\text{Pr}^{i3-2,4,6})_3(\text{thf})_x]_n$. When **1** was treated with two equiv. of cyclooctatetraene and one equiv. of metallic samarium, $[\text{Sm}(\mu\text{-SC}_6\text{H}_2\text{Pr}^{i3-2,4,6})(\eta\text{-C}_8\text{H}_8)(\text{thf})]_2$ was isolated as purple crystals in 69% yield. Reaction of benzyl bromide with two equiv. of **1** afforded bibenzyl in 58% yield.

When diphenyl disulfide was used instead of the bulky substituted diaryl disulfide, the separation of the product from the unreacted metal was hampered by their low solubility. This was solved by the use of HMPA (hexamethylphosphoric triamide) as a ligand. The reaction of excess samarium metal and diphenyl disulfide in the same condition afforded a suspension of hardly soluble dark green powder. The addition of 4

equiv. of HMPA gave a dark green solution. Removal of the unreacted metal followed by concentration and cooling of the supernatant solution gave the HMPA adduct of samarium(II) bis(benzenethiolate), $[\text{Sm}(\text{SPh})_2(\text{hmpa})_3]_2$ (**4**), as black crystals. Elemental analysis of **4** indicated the composition of tris(hmpa) adduct instead of monomeric tetrakis(hmpa) adduct similar to complexes **1** and **2**. Europium (**5**) and ytterbium (**6**) derivatives were prepared by the same method (eqn. 3). When the reaction of excess samarium metal and diphenyl disulfide was carried out in the presence of HMPA, tris(benzenethiolate) complexes such as $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$ are contaminated in the product. Thus, the reactivity of Sm(II) thiolate complexes is affected by the coordination of HMPA on samarium, forming mononuclear Sm(III) complex.



The molecular structures of lanthanide(II) complexes **1** and **2** are shown in Figure 1 and the selected bond distances and angles are given in Table 1. Both compounds have binuclear structure with one bridging thiolate and one terminal thiolate, in which each monomer moiety is related by a center of symmetry. The Ln_2S_2 units are planar in both complexes. The metal centers in **1** and **2** have a distorted octahedral geometry with three thiolate and three thf ligands in meridional fashion.

The Sm—S distance [2.908(6) Å] of terminal thiolate in **1** is longer than those of the trivalent complexes, $\text{Sm}(\text{SAr})_3(\text{py})_2(\text{thf})$ [*av.* 2.740(3) Å, *vide infra*], $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$ [*av.* 2.821(2) Å, *vide infra*], $[\text{Li}(\text{tmeda})]_3[\text{Sm}(\text{SBu}^1)_6]$ [*av.* 2.827(3) Å]²⁶ and $[\text{Sm}(\text{SC}_6\text{H}_2\text{Bu}^1_{3-2,4,6})_3]$ [*av.* 2.644(8) Å].²⁸ The Sm—S distance [*av.* 3.017(5) Å] of bridging thiolate in **1** is significantly longer by 0.136 Å than that of the trivalent samarium complex $[\text{Sm}(\mu\text{-SAr})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]$ [*av.* 2.881(5) Å, *vide infra*]. These differences of Sm—S distances can be attributed to the size of metal ions, *i.e.* Sm(II) (1.11 Å) and Sm(III) (1.00 Å), as well as the coordination geometry. Complex **2**

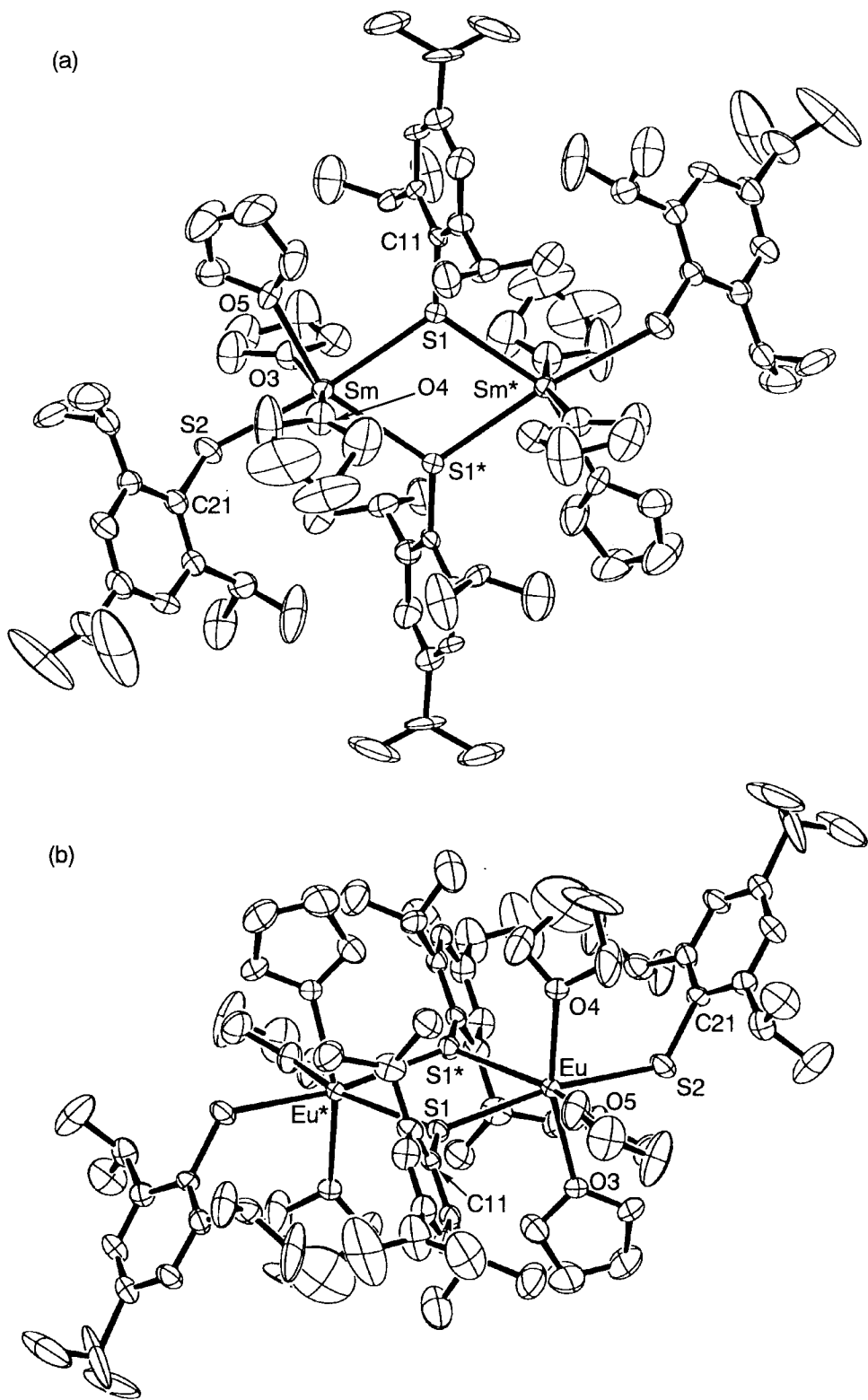


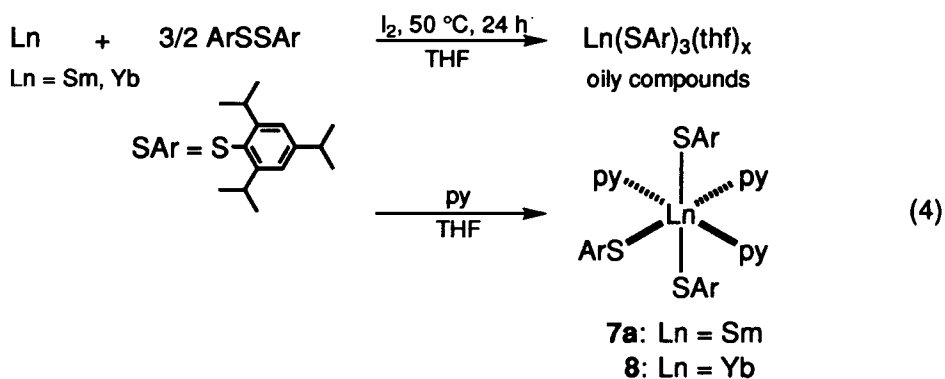
Figure 1. Molecular structures of **1** (a) and **2** (b).

Table 1. Selected bond distances (Å) and bond angles (°) of complex **1** and **2**.

	1	2
Bond distances		
Ln—S(11)	3.035(5)	3.030(3)
Ln—S(11)*	2.999(6)	3.001(3)
Ln—S(21)	2.908(6)	2.898(4)
Ln—O(31)	2.62(2)	2.593(9)
Ln—O(41)	2.59(2)	2.583(9)
Ln—O(51)	2.62(2)	2.557(10)
S(11)—C(11)	1.80(2)	1.74(1)
S(21)—C(21)	1.78(2)	1.76(1)
Bond angles		
S(11)—Ln—S(11)*	68.8(2)	69.0(1)
Ln—S(11)—Ln*	111.2(2)	111.0(1)
S(11)—Ln—S(21)	170.6(2)	170.82(9)
S(11)—Ln—O(31)	94.0(4)	93.5(2)
S(11)—Ln—O(41)	97.9(5)	97.9(2)
S(11)—Ln—O(51)	85.0(4)	85.6(2)
S(11)*—Ln—S(21)	115.9(2)	115.3(1)
S(11)*—Ln—O(31)	103.7(4)	103.5(2)
S(11)*—Ln—O(41)	92.2(5)	92.0(3)
S(11)*—Ln—O(51)	151.2(4)	152.0(3)
S(21)—Ln—O(31)	77.1(4)	77.7(2)
S(21)—Ln—O(41)	90.2(5)	90.2(2)
S(21)—Ln—O(51)	91.9(4)	91.7(3)
O(31)—Ln—O(41)	162.8(6)	163.3(3)
O(31)—Ln—O(51)	89.3(6)	88.9(4)
O(41)—Ln—O(51)	79.4(6)	79.9(4)
Ln—S(11)—C(11)	124.0(6)	124.8(4)
Ln*—S(11)—C(11)	123.4(7)	122.7(5)
Ln—S(21)—C(21)	124.0(8)	124.6(5)

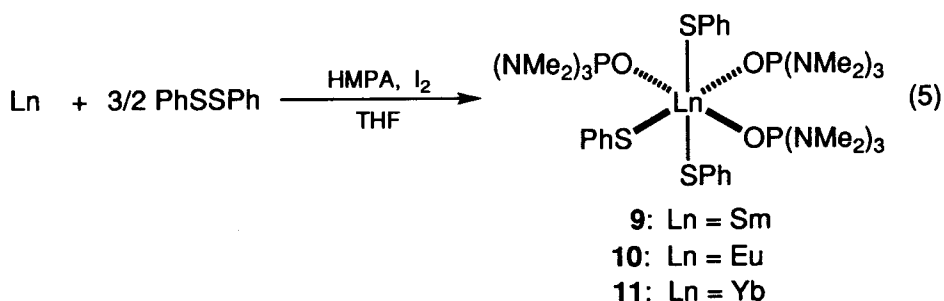
has the similar Eu—S distances to those of **1**, which is reasonable considering the similar atom size of Eu(II) to that of Sm(II).

Synthesis and structures of tris(thiolato)lanthanide(III). The reaction of metallic lanthanide with three equiv. of bis(2,4,6-triisopropylphenyl) disulfide in THF in the presence of a catalytic amount of iodine gave oily compounds of the formula of $\text{Ln}(\text{SAr})_3(\text{thf})_x$. Addition of pyridine to the reaction mixture resulted in the formation of $\text{Ln}(\text{SAr})_3(\text{py})_3$ (**7a**: Ln = Sm; **8**: Ln = Yb) as orange and red crystals in 39% and 30% yield, respectively (eqn. 4). When the crude crystals of **7a** was recrystallized from THF, one of the pyridine ligands on **7a** was replaced by THF ligand to afford $\text{Sm}(\text{SAr})_3(\text{py})_2(\text{thf})$ (**7b**), whose formula was revealed by X-ray crystallography.⁵¹ The reaction of the isolated Sm(II) complex **1** with bis(2,4,6-triisopropylphenyl) disulfide in THF also resulted in the formation of Sm(III) complex **7a** after treatment with pyridine. The reaction of metallic europium did not give tris(thiolate) complexes but afforded complex **2**. The smaller negative value of normal redox potential of Eu than Sm and Yb rationalizes the above finding.



The direct reaction of metallic samarium and diphenyl disulfide in THF gave hardly soluble yellow powder. When the reaction was carried out in the presence of 3 equiv. of HMPA, $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$ (**9**) was obtained as THF soluble colorless crystals in 77% yield. Similarly, europium (**10**) and ytterbium (**11**) derivatives were prepared in moderate yield (eqn. 5). This is in sharp contrast to the fact that the

reaction of metallic europium with more than 3 equiv. of bis(2,4,6-triisopropylphenyl) disulfide in THF without HMPA did not give europium(III) tris(thiolate). This is consistent with the fact that the addition of HMPA to the solution of LnI₂ (Ln = Sm and Yb) in THF greatly accelerates the electron transfer reactions.⁵³ Elemental analysis of these complexes indicated that they have one THF as a solvent molecule, which was further confirmed by crystallographic studies (*vide infra*).



In the case of other lanthanide metals such as lanthanum, praseodymium, dysprosium, and neodymium, the rate of the reaction of metal were slower than Sm, Eu and Yb. The reaction of lanthanum metals with PhSSPh in the presence of HMPA consumed 80% of lanthanum, although crystallization of the product has been unsuccessful yet.

Figure 2 shows the molecular structures of tris(thiolato)lanthanides **7b** and **8** which are isostructural except that one of the coordinated pyridine in **8** was replaced by one thf ligand in **7b**. The selected bond length and angles are listed in Table 2. Complexes **7b** and **8** also have a distorted octahedral geometry with three thiolate ligands in meridional fashion.

The average Sm—S distance (2.740(3) Å) of the six coordinated complex **7b** is shorter by 0.17 Å than terminal Sm—S bond in the six coordinated divalent samarium complex **1** and 0.10 Å longer than the three coordinated samarium(III) complex, Sm(SC₆H₂Bu^t_{3-2,4,6})₃.²⁸ In the comparison of three intramolecular Sm—S bonds, Sm—S₂ bond, which is trans to nitrogen, is shorter by 0.03 Å than the other Sm—S bonds trans to sulfur due to the trans effects. Similarly, Yb—S₂ distance is the smallest of the three Yb—S bonds in **8**. The average Yb—S distance (av. 2.648(7) Å) is

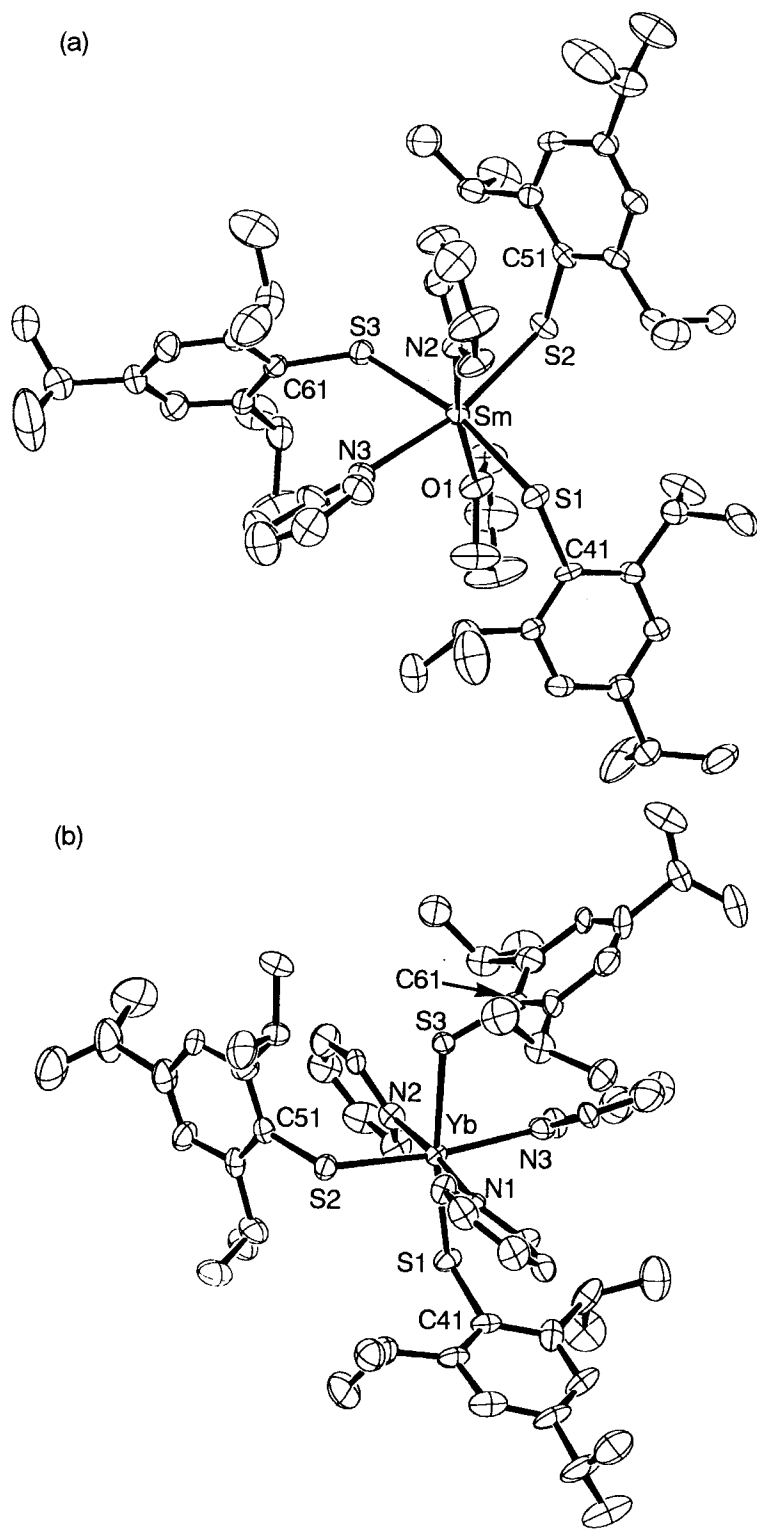


Figure 2. Molecular structures of **7b** (a) and **8** (b).

Table 2. Selected bond distances (Å) and bond angles (°) of complex **7b** and **8**.

	7b	8
Bond distances		
Ln—S(1)	2.751(3)	2.665(6)
Ln—S(2)	2.720(3)	2.622(7)
Ln—S(3)	2.749(3)	2.656(6)
Ln—[O(1)/N(1)]	2.422(7)	2.38(2)
Ln—N(2)	2.533(9)	2.42(2)
Ln—N(3)	2.543(9)	2.43(2)
S(1)—C(41)	1.792(10)	1.80(3)
S(2)—C(51)	1.78(1)	1.77(3)
S(3)—C(61)	1.77(1)	1.77(3)
Bond angles		
S(1)—Ln—S(2)	104.6(1)	102.7(2)
S(1)—Ln—S(3)	168.41(9)	169.2(2)
S(1)—Ln—[O(1)/N(1)]	89.6(2)	93.2(4)
S(1)—Ln—N(2)	82.5(3)	82.4(5)
S(1)—Ln—N(3)	84.3(2)	87.0(5)
S(2)—Ln—S(3)	86.41(10)	87.9(2)
S(2)—Ln—[O(1)/N(1)]	88.4(2)	85.6(5)
S(2)—Ln—N(2)	88.9(2)	91.7(5)
S(2)—Ln—N(3)	167.5(2)	169.9(5)
S(3)—Ln—[O(1)/N(1)]	87.2(2)	89.7(4)
S(3)—Ln—N(2)	101.5(3)	95.3(5)
S(3)—Ln—N(3)	85.4(2)	82.5(5)
[O(1)/N(1)]—Ln—N(2)	170.7(3)	174.2(7)
[O(1)/N(1)]—Ln—N(3)	100.6(3)	91.1(8)
N(2)—Ln—N(3)	83.6(3)	92.4(8)
Ln—S(1)—C(41)	122.2(3)	114.4(8)
Ln—S(2)—C(51)	116.4(3)	115.6(8)
Ln—S(3)—C(61)	126.9(4)	120.4(7)

comparable to those of the Yb(III) complex having terminal thiolate, $(C_5Me_5)_2Yb(SPh)(NH_3)$ (*av.* 2.675(3) Å; two molecules in an asymmetric unit),³³ and shorter than those of the Yb(III) complex bearing thiolate ligands bridging between Yb and Li, $[Li(tmeda)]_3[Yb(SBu^t)_6]$ (*av.* 2.737(2) Å),²⁶ and the divalent complex, $[Yb(SC_6H_2Bu^t_{3-2,4,6})_2(dme)_2]$ (2.756(8) Å).²⁸

Molecular structures of **9** and **11** are shown in Figure 3. The selected bond distances and angles in **9** and **11** are summarized in Table 3. Both complexes **9** and **11** have essentially the same mononuclear octahedral geometry with three benzene thiolato ligands and three HMPA ligands in meridional fashion as observed for complexes **7b** and **8**.

The Ln—S distances (*av.* 2.821(2) Å) of **9** are significantly longer than other samarium(III) complexes bearing terminal thiolato ligands, *e.g.*, $Sm(SC_6H_2Bu^t_{3-2,4,6})_3$ (*av.* 2.645(9) Å)²⁸ and **7b** (2.740(3) Å). The Yb—S bonds of **11** (*av.* 2.728(3) Å) are also longest among the ytterbium(III) complexes bearing terminal-thiolates, *e.g.*, $(\eta-C_5Me_5)_2Yb(SPh)(NH_3)$ (*av.* 2.675(3) Å)³³ and **8** (*av.* 2.648(6) Å).⁵¹ The similar elongation of Sm—I bond caused by the coordination of hmpa has been reported in the system of SmI_2 , *e.g.* Sm—I bond lengths are 3.260(1) and 3.225(1) Å in $[Sm(\mu-I)_2(NCCMe_3)_2]_\infty$,⁵⁴ 3.265(1) Å in *trans*- $SmI_2\{O(CH_2CH_2OCH_3)_2\}_2$,⁵⁴ 3.332(1) and 3.333(1) Å in *cis*- $SmI_2\{O(CH_2CH_2OCH_3)_2\}_2$,⁵⁵ 3.3414(9) and 3.3553(9) Å in $[{(Me_3Si)_2N}Sm(\mu-I)(dme)(thf)]_2$ ⁵⁶ while 3.390(2) Å in $SmI_2(hmpa)_4$.⁵⁷

In comparison among the three Sm—S distances in complex **9**, the Sm—S3 bond, which is trans to oxygen, is shorter by 0.015 Å than the *av.* distances of Sm—S1 and Sm—S2 which are trans to sulfur. In this complex, the other two Sm—S bonds are significantly different each other. In the case of **11**, Yb—S3 is also shorter by 0.015 Å than Yb—S1 and Yb—S2. The stronger trans effects have been observed in **7b** and **8**, Ln—S bonds, which are trans to nitrogen, are ca. 0.03 Å shorter than Ln—S bonds trans to sulfur.⁵¹

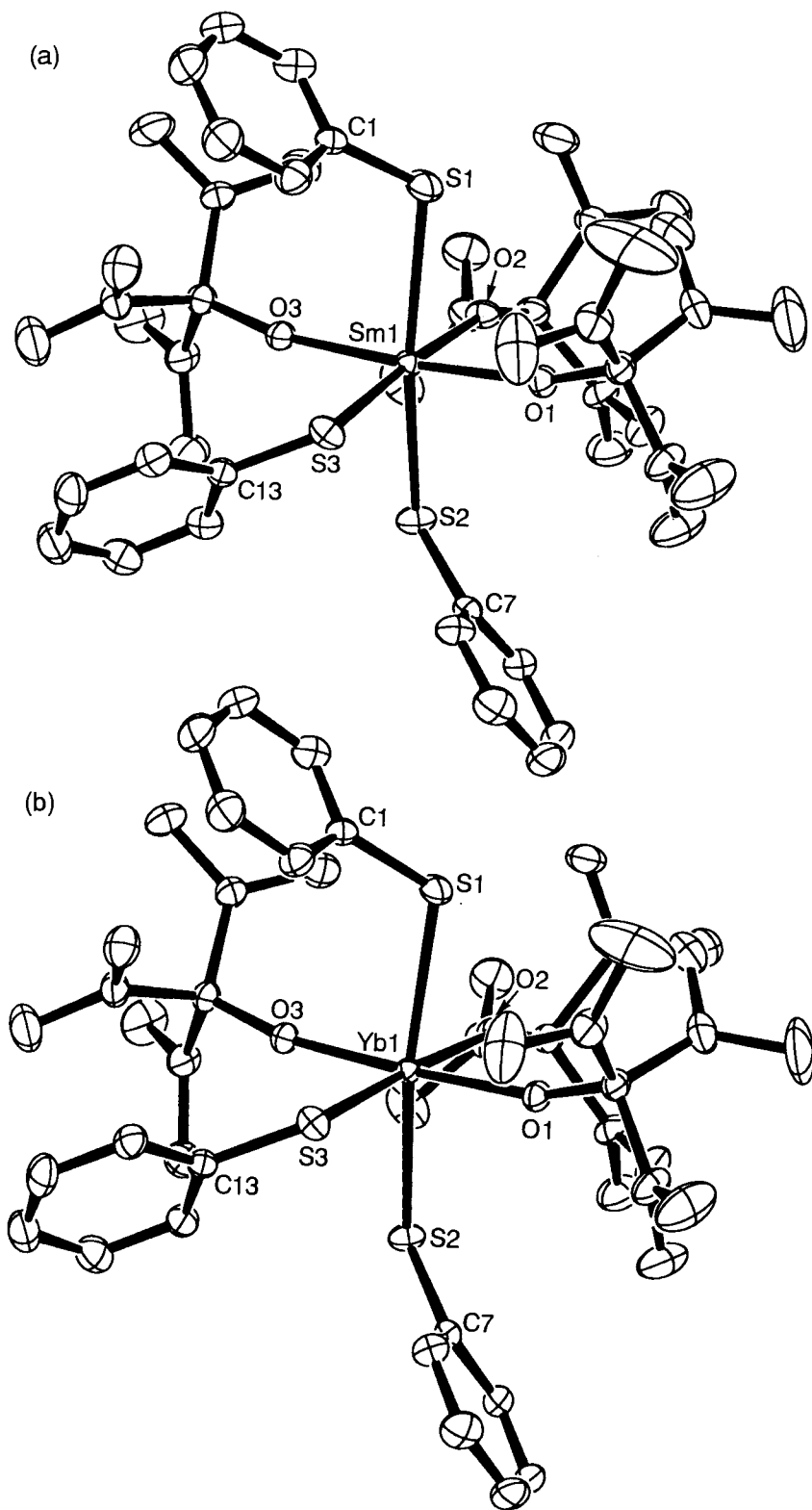


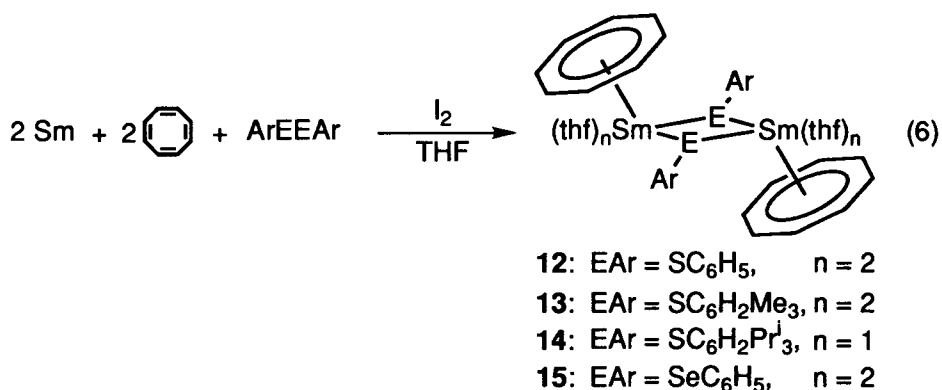
Figure 3. Molecular structures of **9** (a) and **11** (b).

Table 3. The selected bond distances (Å) and angles (°) in **9** and **11**.

	9	11
bond distances		
Ln—S(1)	2.815(2)	2.740(1)
Ln—S(2)	2.837(2)	2.727(1)
Ln—S(3)	2.811(2)	2.718(1)
Ln—O(1)	2.307(4)	2.181(3)
Ln—O(2)	2.318(4)	2.232(2)
Ln—O(3)	2.271(4)	2.212(3)
S(1)—C(1)	1.756(8)	1.752(4)
S(2)—C(7)	1.734(7)	1.756(4)
S(3)—C(13)	1.770(7)	1.768(4)
bond angles		
S(1)—Ln—S(2)	162.87(7)	164.33(4)
S(1)—Ln—S(3)	99.87(7)	97.42(3)
S(1)—Ln—O(1)	85.2(1)	86.98(7)
S(1)—Ln—O(2)	83.0(1)	80.93(7)
S(1)—Ln—O(3)	91.2(1)	95.41(7)
S(2)—Ln—S(3)	97.25(6)	98.25(4)
S(2)—Ln—O(1)	95.8(1)	91.99(7)
S(2)—Ln—O(2)	80.0(1)	83.42(7)
S(2)—Ln—O(3)	87.0(1)	85.30(7)
S(3)—Ln—O(1)	88.6(1)	93.14(7)
S(3)—Ln—O(2)	175.8(1)	176.85(7)
S(3)—Ln—O(3)	94.2(1)	88.04(7)
O(1)—Ln—O(2)	88.6(2)	89.46(10)
O(1)—Ln—O(3)	175.8(2)	177.18(9)
O(2)—Ln—O(3)	88.8(2)	89.44(10)
Ln—S(1)—C(1)	115.6(3)	117.7(1)
Ln—S(2)—C(7)	116.8(2)	117.2(1)
Ln—S(3)—C(13)	111.5(2)	113.2(1)

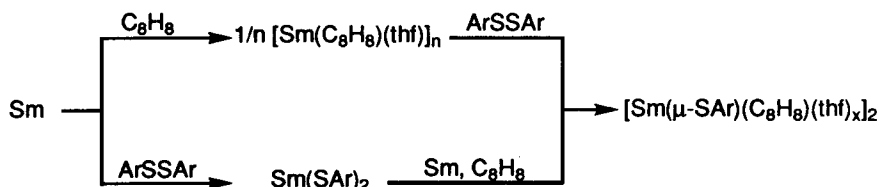
On the other hand, Sm—O(hmpa) (*av.* 2.299(4) Å) and Yb—O(hmpa) (*av.* 2.208(3) Å) distances in **9** and **11** are much shorter than other O-donor ligands such as THF, *e.g.*, Sm—O(thf) (2.422(7) Å) in **7b**,⁵¹ Sm—O(thf) (*av.* 2.56(1) Å) in [Sm(μ -SPh)(η -C₈H₈)(thf)₂]₂⁵⁸ and Yb—O(thf) in [YbCl₃(thf)₂]₂ (*av.* 2.265(8) Å),³⁸ and (η -C₅H₅)₂YbMe(thf) (2.311(6) Å).⁵⁹ Compared to the divalent lanthanide complexes, SmI₂(hmpa)₄ (*av.* Sm—O = 2.500(6) Å) and [Yb(hmpa)₄(thf)₂]₂ (*av.* Yb—O = 2.357(6) Å),⁵⁷ The Ln—O(hmpa) distances of **9** and **11** are comparable to those found in the divalent lanthanide complexes such as SmI₂(hmpa)₄ (*av.* Sm—O = 2.500(6) Å) and [Yb(hmpa)₄(thf)₂]₂ (*av.* Yb—O = 2.357(6) Å).⁵⁷

Synthesis and structures of cyclooctatetraenyl(thiolato)-samarium(III). When the metallic samarium was reacted with diaryl disulfides in the presence of cyclooctatetraene, cyclooctatetraenyl(arenethiolato)samarium complexes were obtained. Reaction among Sm, COT, and diphenyl disulfide in THF afforded [Sm(μ -SPh)(cot)(thf)₂]₂ (**12**) in 76% yield (eqn. 6). Similarly, [Sm(μ -SC₆H₂Me₃-2,4,6)(cot)(thf)₂]₂ (**13**) and [Sm(μ -SC₆H₂Prⁱ₃-2,4,6)(cot)(thf)₂]₂ (**14**) were prepared in 34% and 25% yields, respectively. A benzeneselenolate complex [Sm(μ -SePh)(cot)(thf)₂]₂ (**15**) was also prepared in 46% yield by the same procedure.



Two plausible pathways of the formation of these complexes have been found by the careful search for the possible intermediates (Scheme 1). The reaction of Sm with cyclooctatetraene without diaryl disulfides have been reported to form [Sm(η^8 -cot)(thf)_n]

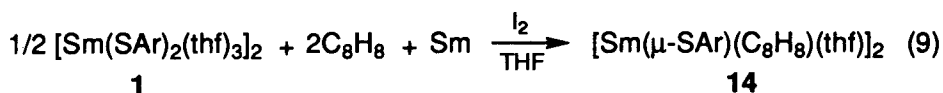
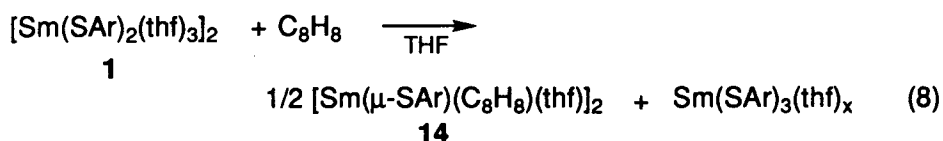
(**16**) in modest yield.⁴⁶ It is important to observe that complex **16** does not dissolve in common organic solvents. In the reaction course of **12**—**15**, the brown compound **16** was precipitated initially and then gradually disappeared by the reaction with diaryl disulfides. Actually, the reaction of **16** with diphenyl disulfide afforded **12** in 49% yield (eqn. 7).



Scheme I



On the other hand, the reaction of **1** with one equiv. of cyclooctatetraene afforded **14** and $\text{Sm}(\text{SC}_6\text{H}_2\text{Pr}^{i3-2,4,6})_3(\text{thf})_x$ in quantitative yield as evidenced by ¹H NMR (eqn. 8). When **1** was treated with two equiv. of cyclooctatetraene and one equiv. of metallic samarium, **14** was isolated as purple crystals in 69% yield (eqn. 9). Such an oxidative reaction of Sm(II) complexes with cyclooctatetraene has already been reported; *i.e.* two moles of $\text{Sm}^{\text{II}}\text{Cp}^*2$ with C_8H_8 give $\text{Sm}^{\text{III}}\text{Cp}^*3$ and $\text{Sm}^{\text{III}}\text{Cp}^*(\eta^8\text{-C}_8\text{H}_8)$.⁶⁰ Thus, both of these two pathways are possible for the formation of cyclooctatetraenyl(thiolato)samarium(III) complexes.



The molecular structures of compound **12** and **14** are shown in Figure 4 and their selected bond distances are listed in Table 4. Both compounds have thiolate-bridged

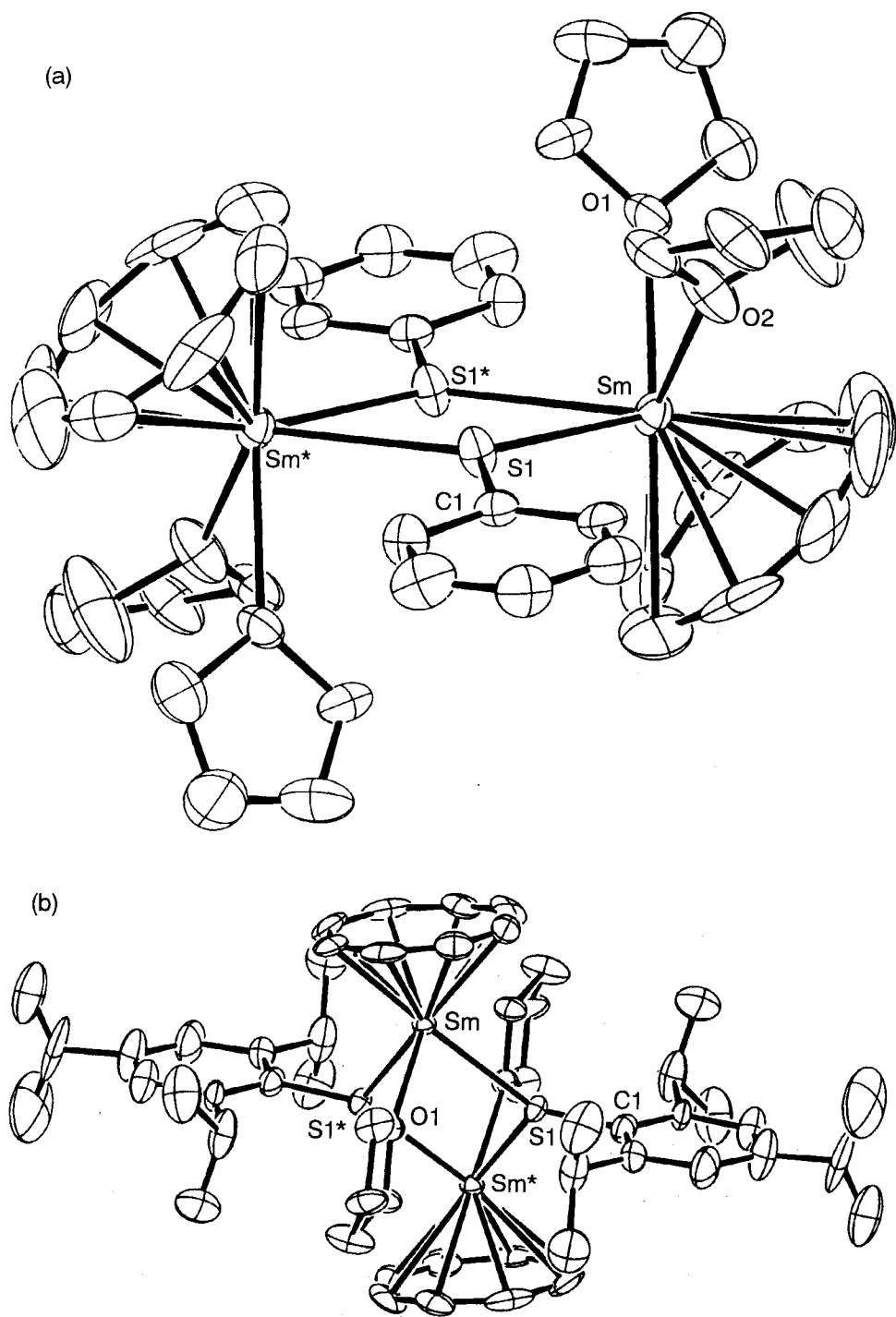


Figure 4. Molecular structures of 12 (a) and 14 (b).

Table 4. Selected bond distances (Å) and bond angles (°) of complex **12**, **14** and **15**.^a

	12	14	15
Bond distances			
Sm—[S(1)/Se(1)]	2.914(8)	2.889(5)	3.015(2)
Sm—[S(1)*/Se(1)*]	2.934(8)	2.873(5)	3.174(2)
Sm—O(1)	2.55(1)	2.53(1)	2.581(9)
Sm—O(2)	2.58(2)		2.503(9)
Sm—C(11)	2.65(2)	2.61(3)	2.67(1)
Sm—C(12)	2.63(4)	2.65(3)	2.68(1)
Sm—C(13)	2.72(4)	2.68(3)	2.70(1)
Sm—C(14)	2.65(3)	2.61(3)	2.70(1)
Sm—C(15)	2.68(4)	2.61(3)	2.68(1)
Sm—C(16)	2.70(7)	2.60(3)	2.69(1)
Sm—C(17)	2.70(5)	2.61(3)	2.66(1)
Sm—C(18)	2.65(3)	2.63(3)	2.66(1)
Sm—C ₈ H ₈	1.97	1.90	1.94
[S(1)/Se(1)]—C(1)	1.79(2)	1.79(2)	1.92(1)
Bond angles			
C ₈ H ₈ —Sm—[S(1)/Se(1)]	127.3	130.8	138.2
C ₈ H ₈ —Sm—[S(1)*/Se(1)*]	127.8	131.8	118.2
C ₈ H ₈ —Sm—O(1)	124.5	126.8	115.7
C ₈ H ₈ —Sm—O(2)	114.0		128.4
[S(1)/Se(1)]—Sm—[S(1)*/Se(1)*]	63.6(1)	74.6(2)	61.52(5)
[S(1)/Se(1)]—Sm—O(1)	108.0(4)	87.0(4)	79.7(2)
[S(1)/Se(1)]—Sm—O(2)	79.1(4)		93.1(2)
[S(1)*/Se(1)*]—Sm—O(1)	77.3(4)	88.3(3)	126.0(2)
[S(1)*/Se(1)*]—Sm—O(2)	118.0(5)		75.7(2)
O(1)—Sm—O(2)	69.3(6)		70.2(3)
Sm—[S(1)/Se(1)]—Sm*	116.4(1)	105.4(2)	118.48(5)
Sm—[S(1)/Se(1)]—C(1)	122.8(7)	121.0(8)	116.4(4)
Sm*—[S(1)/Se(1)]—C(1)	119.9(7)	132.9(8)	119.1(4)

^a C₈H₈ denotes the center of gravity in the cyclooctatetraenyl ring.

binuclear structure in which each monomer moiety is related by the center of symmetry. The Sm₂S₂ units are strictly planar, and the sulfur atoms of thiolates are surrounded by two samarium atoms and a carbon atom of the phenyl group, and these four atoms are in a plane because the summation of angles around sulfur atom is 359.1° for **12** and 359.3° for **14**, respectively. The samarium atom has a pseudo square-pyramidal geometry in **12**, while it has pseudo tetrahedral geometry in **14**. Thus, the geometry of samarium atom depends on the steric effect of thiolate ligand.

The C₈H₈ coordinates to samarium in η⁸-fashion and is planar. The bond distances between Sm and carbons of C₈H₈ [2.63(2) to 2.72(4) Å for **12** and from 2.61(3) to 2.70(3) Å for **14**] are normal.⁶¹ The bond distances (2.892(6) and 2.874(5) Å) of Sm—S of **14** are somewhat shorter than those (2.899(8) and 2.949(8) Å) of **12**. These Sm-S bond distances of dimeric complexes **12** and **14** are longer than those of monomeric samarium complexes, Sm(SC₆H₂Bu^t_{3-2,4,6})₃ (2.646(7), 2.652(9) and 2.634(9) Å)²⁸ and [Li(tmeda)]₃[Sm(S-Bu^t)₆] (2.838(3), 2.821(3), and 2.821(3) Å),²⁶ and shorter than those in divalent complex **1** (av. 3.017(6) Å). The S-Sm-S' bond angle of **3** (75.6(3)°) is larger than that of **1** (63.6(1)°), depending on the geometry.

An ORTEP drawing of **15** is shown in Figure 5 with pertinent bond distances and angles in Table 4. The dimeric structure of **15** is essentially the same as that of **12**. The comparable data for **12** and **15** are summarized in Table 5. The samarium atom has a pseudo square pyramidal and four-legged piano-stool geometry coordinated by one planar η⁸-C₈H₈ ring, two bridging selenium atoms, and two oxygen atoms of THF. Each unit of the binuclear structure is related by the center of symmetry. The bond distances and angles of Sm(η⁸-cot)(thf)₂ fragment is quite normal and is similar to that found in **12**.

The Sm₂Se₂ unit of **15** is exactly planar and two bridging selenium ligands are in a distorted trigonal-planar geometry; the angle sum for selenium atom is 354.0°, which is slightly deviated from the angle sum for sulfur atom (359.1°) of **12**. Sm₂E₂ and phenyl planes are not parallel in **15**, while almost coplanar in **12**. The Sm—Se bond distances of 3.015(2) and 3.174(2) Å in **15** are longer than that of monomeric selenolate

complexes, $\text{Cp}^*_2\text{Sm}(\text{SeC}_6\text{H}_2(\text{CF}_3)_3)(\text{thf})$ (2.919(1) Å)³⁴ and $\text{L}_2\text{Yb}(\text{SePh})(\text{thf})$ (L = *N,N'*-di-(trimethylsilyl)benzamidinate) (2.793(2) Å),⁶² taking into account the difference in ionic radii. The selenium bridges are distinctly asymmetric. The difference between two Sm—Se bonds is 0.159(2) Å and is larger than that (0.020(8) Å) found in **12**.

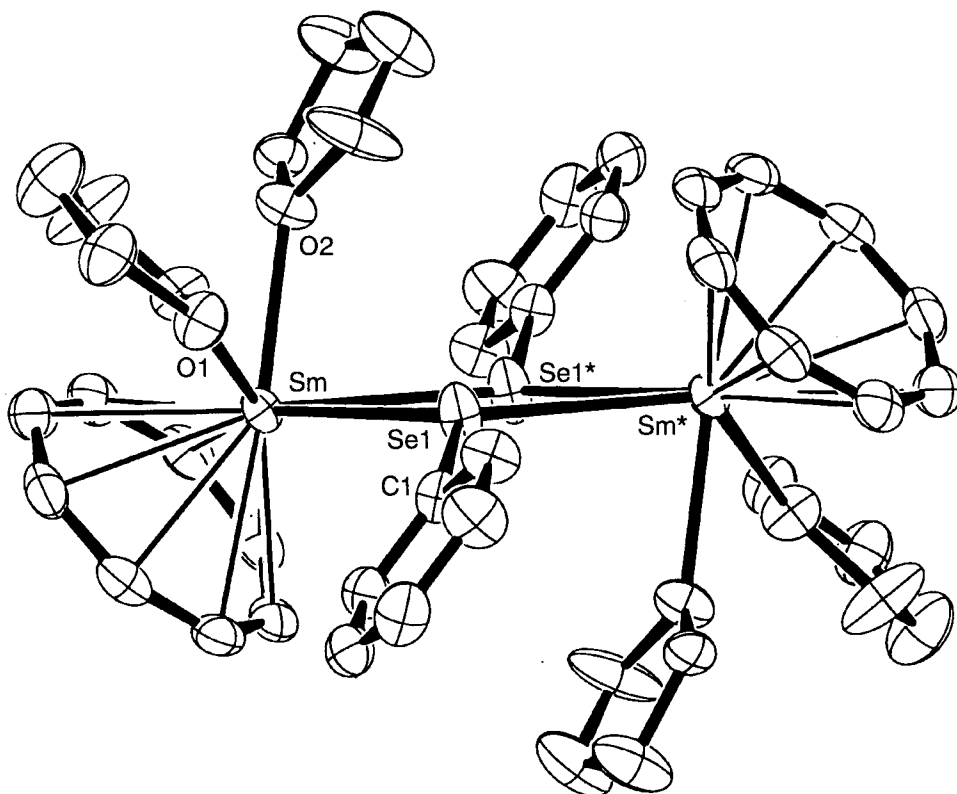


Figure 5. Molecular structure of **15**.

Such a $\text{Ln}^{\text{II}}_2\text{Se}_2$ fragment has been found in the extended one-dimensional network of $[\text{Eu}(\mu\text{-SePh})_2(\text{THF})_3]_n$, in which the averaged Eu—Se distance is 3.14(1) Å.¹⁷ This bond distance indicates that the bonding character is ionic. The complexes $\text{Cp}^*_2\text{Lu}(\mu\text{-SePh})_2\text{Li}(\text{THF})_2$ ³⁰ and $(\text{py})_2\text{Yb}(\text{SePh})_2(\mu\text{-SePh})_2\text{Li}(\text{Py})_2$ ¹⁸ have the bridging selenolate ligands. The Lu—Se bond distance is 2.80(1) Å and Yb—Se bond distances are 2.813(2) and 2.833(2) Å, which are rather shorter than that of **15**, even though taking account of the difference of metal radii. This difference is attributed to the bridging lithium atoms.

Table 5. Comparison of structural data of **12** and **15**.

	12	15
$d(\text{Sm-E})$ (Å)	2.914(8), 2.934(8)	3.015(2), 3.174(2)
average	2.924	3.095
difference	0.020	0.159
$\angle(\text{Sm-E-C})$ (°)	122.8(7), 119.9(7)	116.4(4), 119.1(4)
average	121.4	117.8
difference	2.9	2.7
$\angle(\text{Sm-E-Sm})$ (°)	116.4(1)	118.48(5)
sum of angle (°) around E	359.1	354.0
$\angle(\text{E-Sm-E})$ (°)	63.6(1)	61.52(5)
dihedral angle (°) between Sm_2E_2 and Ph planes	8.5	50.6

Comparative Ln—S bond distances and Ln—S—C bond angles for these complexes and previously X-ray characterized lanthanide metal thiolates are summarized in Table 6. The Ln—S bond distances of Table 6 are plotted vs. the atomic number of the lanthanide metal in Figure 6.

Among the 6-coordinated divalent complexes with terminal thiolate ligand, **1** (2.908(6) Å), **2** (2.898(4) Å), **23** (2.756(8) Å)²⁸ and **24** (2.827(3) Å),²⁰ Ln—S bond distance decreases according to the increase of the atomic number in accord with the ionic radii.⁶³ The differences of Ln—S bond length between the 6-coordinated Sm(III) and Yb(III) complexes, e.g., 0.092 Å between **7b** and **8**, 0.093 Å between **9** and **11** and 0.090 Å between **19** and **22**, are in agreement with the difference of 6-coordinated ionic radii between Sm^{III} and Yb^{III}, 0.09 Å.⁶³ For the 6-coordinated trivalent complexes bearing terminal thiolate ligand, the Ln—S distances of **7b** (2.740(3) Å), **8** (2.648(6) Å), **9** (2.821(2) Å) and **11** (2.728(3) Å) are apparently shorter than those of the divalent complexes such as **1**, **2**, **23**, and **24**, indicating that the distance of Ln—S bond is a

simple summation of ionic radii of Ln^{2+} and Ln^{3+} with S^{2-} . As a result, these complexes have the ionic $\text{Ln}-\text{S}$ bond rather than covalent one.

Table 6. Comparative structural data of lanthanide thiolate complexes

Complexes ^a	$d(\text{Ln}-\text{S})/\text{\AA}^b$	$\angle(\text{LnSC})^\circ$ ^b	CN^c	ref.
$[(\eta\text{-C}_5\text{H}_4\text{Bu}^1)_2\text{Ce}(\mu\text{-SPr}^i)]_2$ (17)	2.882(2)		8	31
$[\text{Sm}(\text{SAr})(\mu\text{-SAr})(\text{thf})_3]_2$ (1)	terminal 2.908(6) bridging 3.017(6)	124.0(8) 123.7(7)	6	this work
$\text{Sm}(\text{SAr})_3(\text{py})_2(\text{thf})$ (7b)	2.740(3)	121.8(3)	6	this work
$\text{Sm}(\text{SPh})_3(\text{hmpa})_3 \cdot \text{THF}$ (9)	2.821(2)	114.6(2)	6	this work
$\text{Sm}(\text{SC}_6\text{H}_2\text{Bu}^1_{3-2,4,6})_3$ (18)	2.645(9)	82.9(8)	3	28
$[\text{Sm}(\mu\text{-SPh})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]_2$ (12)	2.924(8)	121.4(7)	8	this work
$[\text{Sm}(\mu\text{-SAr})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]$ (14)	2.883(6)	127.0(8)	7	this work
$[\text{Li}(\text{tmeda})]_3[\text{Sm}(\mu\text{-SBu}^1)_6]$ (19)	2.827(3)		6	26
$[\text{Eu}(\text{SAr})(\mu\text{-SAr})(\text{thf})_3]_2$ (2)	terminal 2.898(4) bridging 3.016(3)	124.6(5) 123.8(5)	6	this work
$[\text{Gd}\{\text{N}(\text{SiMe}_3)_2\}_2(\mu\text{-SBu}^1)]_2$ (20)	2.791(5)		4	25
$\text{Yb}(\text{SAr})_3(\text{py})_3$ (8)	2.648(6)	116.8(8)	6	this work
$\text{Yb}(\text{SPh})_3(\text{hmpa})_3 \cdot \text{THF}$ (11)	2.728(3)	116.0(1)	6	this work
$(\eta\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{SPh})(\text{NH}_3)$ (21)	2.675(3)	118.5(3)	8	33
$[\text{Li}(\text{tmeda})]_3[\text{Yb}(\mu\text{-SBu}^1)_6]$ (22)	2.737(2)		6	26
$\text{Yb}(\text{SC}_6\text{H}_2\text{Bu}^1_{3-2,4,6})_2(\text{dme})_2$ (23)	2.756(8)	125.0(8)	6	28
$\text{Yb}(\text{SPh})_2(\text{py})_4$ (24)	2.827(3)	101.6(3)	6	20
$[\text{Yb}(\mu\text{-X})(\eta^5\text{-C}_4\text{Me}_4\text{P})(\text{thf})_2]_2$ (25)	2.817(3)		7	52
$(\eta\text{-C}_5\text{Me}_5)_2\text{Lu}(\mu\text{-SBu}^1)_2\text{Li}(\text{thf})_2$ (26)	2.766(2)	136.6(4)	8	30

^a Ar = 2,4,6-triisopropylphenyl.

^b Averaged value in each complex.

^c CN = coordination number. η -Cyclopentadienyl and η -cyclooctatetraenyl may be taken as occupying three and four coordination sites around the metal, respectively.

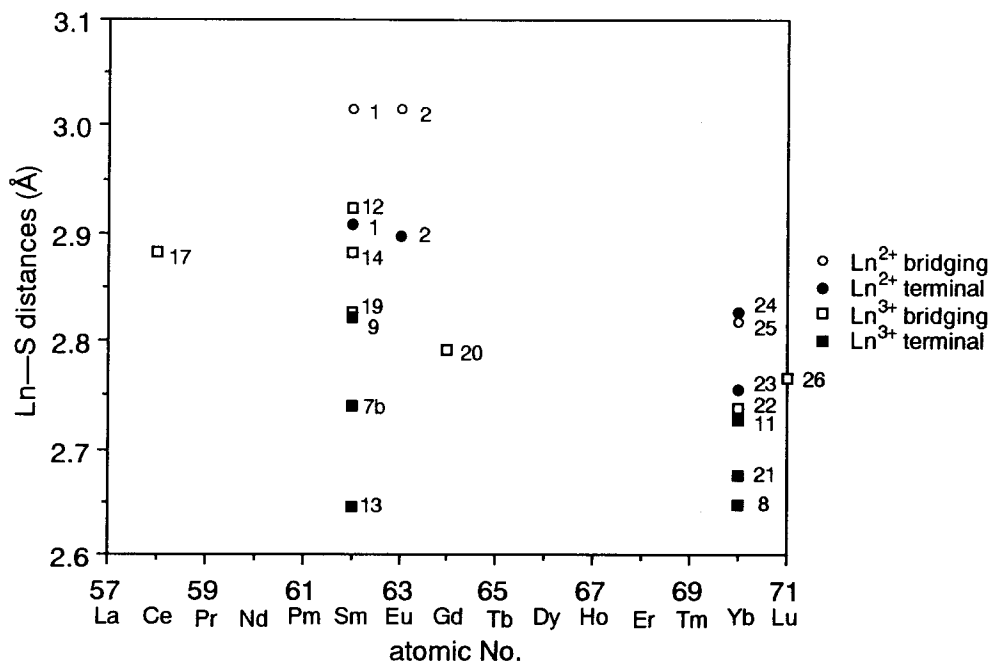


Figure 6. Ln—S distances vs. atomic number plot.

Experimental Section

General. All manipulations involving air- and moisture-sensitive lanthanide compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. THF and hexane were dried over sodium benzophenone ketyl and then distilled before use.

¹H NMR (270 MHz) spectra were measured on a JEOL GSX-270 spectrometer. Elemental analyses were performed at Elemental Analysis Center of Faculty of Science, Osaka University. All melting points were measured in sealed tubes and were not corrected.

Synthesis of [Sm(SC₆H₂Prⁱ₃-2,4,6)₂(thf)₃]₂ (1). To a mixture of samarium metal powder (453 mg, 3.01 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (712 mg, 1.51 mmol) in THF (40 mL) was added a catalytic amount of iodine (12 mg, 0.05 mmol). The reaction mixture was stirred at 50 °C for 24 h. A dark green

solution was separated from the unreacted metal. Concentration of the solution, addition of hexane, and cooling to $-20\text{ }^{\circ}\text{C}$ afforded dark green prisms of **1** (351 mg, 28% yield). Further concentration and cooling the mother liquor gave 2nd, 3rd, and 4th crops. The total yield was 74%. Mp $160\text{--}178\text{ }^{\circ}\text{C}$ (dec.). Anal. Calcd. for $\text{C}_{34}\text{H}_{54}\text{OS}_2\text{Sm}$: C, 58.90; H, 7.85. Found: C, 58.94; H, 8.25.

Synthesis of $[\text{Eu}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{thf})_3]_2$ (2**).** The mixture of europium metal (300 mg, 1.97 mmol), bis(2,4,6-triisopropylphenyl) disulfide (430 mg, 0.91 mmol) and iodine (6 mg, 0.02 mmol) in THF (30 mL) was stirred at $50\text{ }^{\circ}\text{C}$ overnight to give yellow solution. Removal of unreacted metal followed by concentration, addition of hexane and cooling the solution afforded yellow crystals (286 mg, 37% yield). Further concentration and cooling the mother liquor gave the 2nd crop. The total yield was 56%. Mp $>300\text{ }^{\circ}\text{C}$ (dec.). Anal. Calcd. for $\text{C}_{38}\text{H}_{62}\text{O}_2\text{S}_2\text{Eu}$: C, 59.51; H, 8.15. Found: C, 59.10; H, 8.51.

Synthesis of $\text{Yb}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{py})_4$ (3**).** To a mixture of ytterbium metal (172 mg, 0.99 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (435 mg, 0.92 mmol) in THF (40 mL) was added a catalytic amount of iodine (5 mg, 0.02 mmol). The reaction mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 24 h. After removal of an excess of ytterbium metal, the addition of pyridine (1 mL) to the solution caused immediate the change of the color from orange yellow to black. Recrystallization afforded black micro crystals of **3** (407 mg, 46% yield). Mp $170\text{--}215\text{ }^{\circ}\text{C}$ (dec.). Anal. Calcd. for $\text{C}_{50}\text{H}_{66}\text{N}_4\text{S}_2\text{Yb}$: C, 62.54; H, 6.93; N, 5.83. Found: C, 61.85; H, 6.85; N, 6.25. ^1H NMR (270 MHz, THF-*d*₈, $30\text{ }^{\circ}\text{C}$) δ 8.56 (s, 8H, py), 7.67 (t, 4H, py), 7.26 (m, 8H, py), 6.73 (s, 4H, *m*-H), 4.23 (brs, 4H, *o*-CHMe₂), 2.75 (brs, 2H, *p*-CHMe₂), 1.18 (m, 36H, *o*- and *p*-CHMe₂).

Synthesis of $[\text{Sm}(\text{SPh})_2(\text{hmpa})_3]_2$ (4**).** To a mixture of samarium metal (912 mg, 6.07 mmol) and diphenyl disulfide (684 mg, 3.13 mmol) in THF (30 mL) was added a catalytic amount of iodine (20 mg, 0.08 mmol). The reaction mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 24 h to give a mixture of dark green powder and the unreacted metal. When the HMPA (2,20 mL, 12.6 mmol) was added to the reaction mixture, the dark green

powder gradually disappeared within 1 h. Removal of the metal followed by recrystallization afforded dark green prisms of **4** (241 mg, 8% yield) yield. Further concentration and cooling the mother liquor gave 2nd crop. The total yield was 29%. Mp 87—93 °C (dec.). Anal. Calcd for C₃₀H₆₄N₉O₃P₃S₂Sm: C, 39.76; H, 7.12; N, 13.91. Found: C, 37.65; H, 7.20; N, 13.45.

Synthesis of [Eu(SPh)₂(hmpa)₃]₂ (5). The mixture of europium metal (197 mg, 1.30 mmol), diphenyl disulfide (142 mg, 0.67 mmol) and iodine (6 mg, 0.02 mmol) in THF (10 mL) was stirred at 50 °C for 24 h to give yellow suspension. To the reaction mixture, HMPA (2,20 mL, 12.6 mmol) was added to afford a red orange solution. Removal of unreacted metal followed by recrystallization afforded yellow crystals (79 mg, 13% yield). Mp 162—164 °C (dec.). Anal. Calcd for C₃₀H₆₄EuN₉O₃P₃S₂: C, 39.69; H, 7.11; N, 13.88. Found: C, 37.16; H, 7.07; N, 13.38.

Synthesis of [Yb(SPh)₂(hmpa)₃]₂ (6). To a mixture of ytterbium metal (663 mg, 3.83 mmol) and diphenyl disulfide (429 mg, 1.97 mmol) in THF (30 mL) was added a catalytic amount of iodine (11 mg, 0.04 mmol). The reaction mixture was stirred at 50 °C for 24 h to give a mixture of a red powder and the unreacted metal. When HMPA (1.40 mL, 8.05 mmol) was added to the mixture, the powder gradually disappeared. Removal of an excess of ytterbium metal followed by concentration and cooling to -20 °C afforded dark red crystals of **6** (846 mg, 46% yield). Mp 135—137 °C (dec.). Anal. Calcd for C₃₀H₆₄N₉O₃P₃S₂Yb: C, 38.79; H, 6.94; N, 13.57. Found: C, 38.65; H, 7.01; N, 13.33. ¹H NMR (270 MHz, THF-*d*₈, 30 °C) δ 7.48 (d, 4H, *o*-H), 6.74 (m, 4H, *m*-H), 6.55 (t, 2H, *p*-H), 2.95 (d, 54H, Me(hmpa)).

Synthesis of Sm(SC₆H₂Pr^{*i*}-2,4,6)₃(py)₃ (7a). To a mixture of samarium metal powder (151 mg, 1.00 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (727 mg, 1.54 mmol) in THF (40 mL) was added a catalytic amount of iodine (6 mg, 0.02 mmol). Stirring the mixture at 50 °C for 24 h afforded a red orange solution. After removal of a small amount of insoluble impurities, pyridine (1 mL) was added. Concentration, addition of hexane, and cooling to -20 °C afforded orange micro

crystals of **7a** (305 mg, 28% yield). Further concentration and cooling the mother liquor gave the 2nd crop. The total yield was 39%. Mp 160—164 °C. Anal. Calcd. for C₆₀H₈₄N₃S₃Sm: C, 65.88; H, 7.74; N, 3.84. Found: C, 65.12; H, 7.62; N, 3.76. ¹H NMR (270 MHz, THF-*d*₈, 30 °C) δ 8.45 (d, 6H, py), 7.64 (t, 3H, py), 7.22 (m, 6H, py), 6.70 (s, 6H, *m*-H), 4.76 (m, 6H, *o*-CHMe₂), 2.67 (m, 3H, *p*-CHMe₂), 1.28 (d, 36H, *o*-CHMe₂), 1.15 (d, 18H, *p*-CHMe₂).

Synthesis of Sm(SC₆H₂Prⁱ₃-2,4,6)₃(py)₂(thf) (7b**).** Complex **7a** (348 mg) was redissolved in THF followed by addition of hexane, concentration and cooling the mixture to -20 °C gave orange crystals (5 mg) of **7b**. Further concentration to ca. 1.5 mL and cooling the mother liquor to -20 °C gave the 2nd crop (83 mg). The total yield was 24%. Mp 163—167 °C. Anal. Calcd. for C₅₉H₈₇N₂OS₃Sm: C, 65.20; H, 8.07; N, 2.58. Found: C, 63.86; H, 8.09; N, 2.54. ¹H NMR (270 MHz, THF-*d*₈, 30 °C) δ 8.45 (d, 4H, py), 7.64 (t, 2H, py), 7.21 (m, 4H, py), 6.71 (s, 6H, *m*-H), 4.77 (m, 6H, *o*-CHMe₂), 2.68 (m, 3H, *p*-CHMe₂), 1.29 (d, 36H, *o*-CHMe₂), 1.15 (d, 18H, *p*-CHMe₂).

Synthesis of Yb(SC₆H₂Prⁱ₃-2,4,6)₃(py)₃ (8**).** To a mixture of ytterbium metal powder (201 mg, 1.16 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (820 mg, 1.74 mmol) in THF (30 mL) was added a catalytic amount of iodine (11 mg, 0.04 mmol). The reaction mixture was stirred at 50 °C for 24 h. After removal of insoluble impurities, the addition of pyridine (1 mL) caused immediate color change of the solution from red orange to dark red. Concentration, addition of hexane, and cooling to -20 °C afforded black micro crystals of **8** (217 mg, 17% yield). Further concentration and cooling the mother liquor gave the 2nd crop. The total yield was 30%. Mp 198—201 °C. Anal. Calcd. for C₆₀H₈₄N₃S₃Yb: C, 64.54; H, 7.58; N, 3.76. Found: C, 63.70; H, 7.77; N, 3.34.

Synthesis of Sm(SPh)₃(hmpa)₃·THF (9**).** To a mixture of samarium metal (402 mg, 2.67 mmol), diphenyl disulfide (883 mg, 4.05 mmol) and HMPA (1.40 mL, 8.05 mmol) in THF (30 mL) was added a catalytic amount of iodine (21 mg, 0.08 mmol). The reaction mixture was stirred at 50 °C in 24 h to give a brown solution.

Removal of a small amount of insoluble impurities followed by cooling to $-20\text{ }^{\circ}\text{C}$ afforded colorless crystals of **9** in (2.10 g, 77% yield) yield. Mp $142\text{--}146\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{40}\text{H}_{77}\text{N}_9\text{O}_4\text{P}_3\text{S}_3\text{Sm}$: C, 44.17; H, 7.14; N, 11.59. Found: C, 43.96; H, 7.28; N, 11.69. ^1H NMR (270 MHz, THF-*d*₈, $30\text{ }^{\circ}\text{C}$) δ 7.01 (m, 3H, *p*-H), 6.76 (d, 6H, *o*-H), 6.35 (brs, 6H, *m*-H), 2.58 (d, 54H, hmpa).

Synthesis of Eu(SPh)₃(hmpa)₃·THF (10). To a mixture of europium metal (499 mg, 3.28 mmol), diphenyl disulfide (1133 mg, 5.19 mmol) and HMPA (1.80 mL, 10.35 mmol) in THF (30 mL) was added a catalytic amount of iodine (16 mg, 0.06 mmol). The reaction mixture was stirred at $50\text{ }^{\circ}\text{C}$ in 24 h to give a dark red solution. Removal of a small amount of insoluble impurities followed by concentration and cooling to $-20\text{ }^{\circ}\text{C}$ afforded dark red crystals of **10** (2.53 g, 70% yield). Mp $128\text{--}131\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{40}\text{H}_{77}\text{EuN}_9\text{O}_4\text{P}_3\text{S}_3$: C, 44.11; H, 7.13; Eu, 13.95; N, 11.57. Found: C, 43.96; H, 7.14; N, 11.81. ^1H NMR (270 MHz, THF-*d*₈, $30\text{ }^{\circ}\text{C}$) δ 11.63 (brs, 6H, *m*- or *o*-H), 8.81 (brs, 3H, *p*-H), 6.66 (brs, 6H, *m*- or *o*-H), 1.90 (d, 54H, Me(hmpa)).

Synthesis of Yb(SPh)₃(hmpa)₃·THF (11). To a mixture of ytterbium metal (492 mg, 2.84 mmol), diphenyl disulfide (954 mg, 4.37 mmol) and HMPA (1.50 mL, 8.62 mmol) in THF (30 mL) was added a catalytic amount of iodine (18 mg, 0.07 mmol). The reaction mixture was stirred at $50\text{ }^{\circ}\text{C}$ in 24 h to give a light yellow powder in a brown solution. 30 mL of THF was added to the suspension followed by removal of a small amount of insoluble impurities and cooling to $-20\text{ }^{\circ}\text{C}$ afforded yellow crystals of **11** (2.48 g, 79% yield). Mp $187\text{--}190\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{40}\text{H}_{77}\text{N}_9\text{O}_4\text{P}_3\text{S}_3\text{Yb}$: C, 43.27; H, 6.99; N, 11.35. Found: C, 43.27; H, 7.11; N, 11.39.

Synthesis of [Sm(μ -SPh)(η^8 -cot)(thf)₂]₂ (12). To the mixture of samarium metal (0.36 g, 2.43 mmol), COT (0.30 mL, 2.66 mmol) and diphenyl disulfide (0.28 g, 1.27 mmol) in THF (40 mL) was added a catalytic amount of iodine (19 mg, 0.15 mmol) and then this mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 24 h. **12** was obtained by recrystallization from THF in 76% yield as deep purple crystals. Mp. $>300\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (270 MHz, THF-*d*₈, $30\text{ }^{\circ}\text{C}$) δ 11.24 (s, 16H, C₈H₈), 10.41 (s, 4H, *o*-H), 7.99 (s, 4H, *m*-H), 7.83 (s, 2H, *p*-H).

Synthesis of [Sm(μ -SC₆H₂Me₃-2,4,6)(η^8 -cot)(thf)₂]₂ (13). The reaction mixture of samarium metal (0.50 g, 3.32 mmol), COT (0.40 mL, 3.55 mmol), bis(2,4,6-trimethylphenyl) disulfide (0.51 g, 1.70 mmol) and a catalytic amount of iodine in THF (40 mL) was stirred for a period of 48 h to give a deep violet THF solution and brown powder of [Sm(cot)(thf)]_n as a by-product. The brown powder was filtered off, and then THF was removed from the filtrate *in vacuo*. The resulting residue was extracted with toluene. Cooling the saturated toluene solution gave **13** in 34% yield as deep purple crystals. Mp. >300 °C (dec.). ¹H NMR (270 MHz, THF-*d*₈, 30 °C) δ 11.19 (s, 16H, C₈H₈), 8.07 (s, 4H, *m*-H), 4.66 (s, 12H, *o*-Me), 2.65 (s, 6H, *p*-Me).

Synthesis of [Sm(μ -SC₆H₂Pr^{*i*}₃-2,4,6)(η^8 -cot)(thf)₂]₂ (14). To a mixture of samarium metal (0.24 g, 1.58 mmol), COT (0.20 mL, 1.77 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (0.40 g, 0.86 mmol) in THF (40 mL) was added a catalytic amount of iodine. The color of the solution changed to deep violet after 5 d and brown powder [Sm(cot)(thf)]_n was precipitated in 49% yield. The brown powder was filtered out, and then THF was removed from the filtrate under reduced pressure. The residue was extracted with toluene, and cooling the saturated toluene solution gave **14** in 32% yield as deep purple crystals. Mp. >300 °C (dec.). ¹H NMR (270 MHz, THF-*d*₈, 30 °C) δ 11.27 (s, 16H, C₈H₈), 7.95 (s, 4H, *m*-H), 7.08 (m, 4H, *o*-CHMe₂), 3.33 (m, 2H, *p*-CHMe₂), 2.25 (d, 24H, *o*-CHMe₂), 1.21 (d, 12H, *p*-CHMe₂).

Synthesis of [Sm(μ -SePh)(η^8 -cot)(thf)₂]₂ (15). To a mixture of samarium metal (0.57 g, 3.78 mmol), COT (0.50 mL, 4.44 mmol) and diphenyl diselenide (0.61 g, 1.96 mmol) in THF (40 mL) was added a catalytic amount of iodine (21 mg, 0.16 mmol) and then the reaction mixture was stirred at 50 °C for a period of 5 d. Recrystallization from the deep violet THF solution afforded **15** in 46% yield as deep purple crystals. Mp. >300 °C (dec.). ¹H NMR (270 MHz, THF-*d*₈, 30 °C) δ 11.49 (s, 16H, C₈H₈), 9.74 (s, 4H, *o*-H), 7.71 (s, 6H, *m*- and *p*-H).

Crystallographic Data Collections and Structure Determination of 1, 2, 7b, 8, 9, 11, 12, 14 and 15. The crystals of these complexes suitable for X-ray diffraction sealed in glass capillaries under argon atmosphere, were mounted on a Rigaku

AFC-5R four-circle diffractometer for data collection using MoK α radiation. Measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. Empirical absorption correction was carried out based on an azimuthal scan.

The structures of complexes **1**, **2**, **7b**, **8**, **9**, **11** and **14** were solved by heavy-atom Patterson methods⁶⁴⁻⁶⁶ and expanded using Fourier techniques.⁶⁷ The structures of complexes **12** and **15** were solved by direct methods.^{68,69} Complexes **9** and **11** have one THF as a solvent molecule which showed disordered form, and the occupancy of the disordered atoms were fixed at 0.5. All the other non-hydrogen atoms were refined anisotropically. In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were given the same temperature factor as that of the carbon atom to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package.

Crystal data of these complexes are summarized in Tables 7—10 and atomic coordinates are listed in Table 11—19, respectively.

Table 7. Crystal Data and Data Collection Parameters.

complex	1	2
formula	C ₈₄ H ₁₄₀ O ₆ S ₄ Sm ₂	C ₈₄ H ₁₄₀ O ₆ S ₄ Eu ₂
formula weight	1675.06	1678.19
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	12.715(7)	12.685(5)
<i>b</i> , Å	20.802(4)	20.799(4)
<i>c</i> , Å	18.137(3)	18.130(3)
β, deg.	108.92(2)	108.88(2)
<i>V</i> , Å ³	4538(2)	4526(1)
<i>Z</i>	2	2
<i>D</i> _{calcd}	1.226	1.231
F(000)	1760	3528
radiation	Mo Kα	Mo Kα
abs. coeff., cm ⁻¹	14.2	30.1
scan mode	ω—2θ	ω—2θ
temp, °C	23	23
scan speed, deg/min	10	10
scan width, deg	1.15 + 0.35tanθ	0.79 + 0.35tanθ
2θ _{max} , deg	55	55
unique data	10737	10690
unique data (<i>I</i> >3σ(<i>I</i>))	3319	3777
no. of variables	433	433
<i>R</i>	0.068	0.071
<i>R</i> _w	0.079	0.043
GOF	1.87	1.80
Δ, eÅ ⁻³	0.79, -0.53	1.10, -1.16

Table 8. Crystal Data and Data Collection Parameters.

complex	7b	8
formula	C ₅₉ H ₈₇ N ₂ S ₃ SmO	C ₆₀ H ₈₄ N ₃ S ₃ Yb
formula weight	1086.93	1116.56
crystal system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	14.580(3)	20.402(3)
<i>b</i> , Å	18.627(4)	16.654(3)
<i>c</i> , Å	12.383(4)	22.258(3)
α , deg.	104.67(2)	—
β , deg.	96.44(2)	117.10(1)
γ , deg.	69.45(2)	—
<i>V</i> , Å ³	3045(1)	6731(1)
<i>Z</i>	2	4
<i>D</i> _{calcd}	1.185	1.102
<i>F</i> (000)	1146	2332
radiation	Mo K α	Mo K α
reflections measd.	+ <i>h</i> , \pm <i>k</i> , \pm <i>l</i>	+ <i>h</i> , + <i>k</i> , \pm <i>l</i>
crystal size, mm	0.30 \times 0.30 \times 0.10	0.50 \times 0.50 \times 0.10
abs. coeff., cm ⁻¹	11.1	15.1
scan mode	ω —2 θ	ω —2 θ
temp, °C	23	23
scan speed, deg/min	10	10
scan width, deg	1.47 + 0.35tan θ	1.63 + 0.35tan θ
2 θ _{max} , deg	55	55
unique data	14004	16050
unique data (<i>I</i> > 3 σ (<i>I</i>))	5269	4928
no. of variables	595	604
<i>R</i>	0.067	0.081
<i>R</i> _w	0.063	0.106
GOF	1.30	2.88
Δ , eÅ ⁻³	1.03, -0.63	1.37, -0.84

Table 9. Crystal Data and Data Collection Parameters.

complex	9	11
formula	C ₄₀ H ₇₇ O ₄ N ₉ P ₃ S ₃ Sm	C ₄₀ H ₇₇ O ₄ N ₉ P ₃ S ₃ Yb
formula weight	1087.61	1110.25
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	14.719(3)	14.565(2)
<i>b</i> , Å	17.989(2)	17.961(2)
<i>c</i> , Å	11.344(2)	11.302(1)
α, deg.	97.91(1)	97.72(1)
β, deg.	110.30(2)	110.49(1)
γ, deg.	78.40(1)	78.37(1)
<i>V</i> , Å ³	2751.9(9)	2706.0(7)
<i>Z</i>	2	2
D _{calcd}	1.312	1.363
F(000)	1134	1150
radiation	Mo Kα	Mo Kα
abs. coeff., cm ⁻¹	13.1	19.8
scan mode	ω—2θ	ω—2θ
temp, °C	23	23
scan speed, deg/min	16	16
scan width, deg	0.73 + 0.30tanθ	0.84 + 0.30tanθ
2θ _{max} , deg	55	55
unique data	12631	12410
unique data (<i>I</i> >3σ(<i>I</i>))	7111	9837
no. of variables	536	536
<i>R</i>	0.045	0.031
<i>R</i> _w	0.041	0.035
GOF	1.99	1.48
Δ, eÅ ⁻³	0.75, -1.09	1.05, -0.68

Table 10. Crystal Data and Data Collection Parameters.

complex	12	14	15
formula	C ₄₄ H ₅₈ O ₄ S ₂ Sm ₂	C ₅₄ H ₇₈ O ₂ S ₂ Sm ₂	C ₄₄ H ₅₈ O ₄ Se ₂ Sm ₂
formula weight	1015.86	1124.13	1109.66
crystal system	orthorhombic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>C2/c</i>	<i>P2₁/n</i>
<i>a</i> , Å	18.762(5)	26.820(3)	8.500(5)
<i>b</i> , Å	15.383(5)	10.793(3)	21.805(6)
<i>c</i> , Å	14.775(4)	21.122(2)	12.042(5)
β, deg.	—	98.424(8)	105.98(4)
<i>V</i> , Å ³	4264(4)	6048(2)	2145(1)
<i>Z</i>	4	4	2
<i>D</i> _{calcd}	1.582	1.234	1.717
<i>F</i> (000)	2040	2296	1092
radiation	Mo Kα	Mo Kα	Mo Kα
crystal size, mm	0.30 × 0.25 × 0.25	0.60 × 0.40 × 0.10	0.25 × 0.30 × 0.50
abs. coeff., cm ⁻¹	28.7	20.3	28.7
scan mode	ω—2θ	ω—2θ	ω—2θ
temp, °C	23	23	23
scan speed, deg/min	10	10	10
scan width, deg	1.68 + 0.35tanθ	0.73 + 0.35tanθ	1.73 + 0.35tanθ
2θ _{max} , deg	55	55	55
unique data (<i>I</i> >3σ(<i>I</i>))	2061	2942	2061
no. of variables	235	271	235
<i>R</i>	0.050	0.073	0.055
<i>R</i> _w	0.071	0.098	0.062
GOF	9.31	6.50	2.29
Δ, eÅ ⁻³	0.91, -0.86	1.20, -0.84	1.12, -0.78

Table 11. Atomic Coordinates of Complex 1.

Atom	x	y	z	B _{eq}
Sm	0.12947(10)	0.08834(6)	0.06404(7)	4.37(2)
S(11)	0.0271(5)	0.0124(3)	-0.0850(3)	5.0(1)
S(21)	0.2115(6)	0.1794(3)	0.1915(3)	6.8(2)
O(31)	0.002(2)	0.1889(9)	0.014(1)	7.4(5)
O(41)	0.301(1)	0.0155(10)	0.125(1)	8.1(5)
O(51)	0.266(2)	0.1325(9)	-0.006(1)	7.4(5)
C(11)	0.077(2)	0.015(1)	-0.167(1)	4.3(5)
C(12)	0.052(2)	0.068(1)	-0.218(1)	4.6(6)
C(13)	0.094(2)	0.068(1)	-0.280(1)	6.7(8)
C(14)	0.156(3)	0.022(2)	-0.295(2)	7.7(9)
C(15)	0.180(2)	-0.029(1)	-0.245(2)	8.1(9)
C(16)	0.142(2)	-0.035(1)	-0.181(1)	6.0(7)
C(21)	0.317(2)	0.161(1)	0.281(1)	5.2(6)
C(22)	0.292(2)	0.130(1)	0.342(1)	6.3(7)
C(23)	0.377(2)	0.119(1)	0.413(1)	6.8(7)
C(24)	0.483(2)	0.139(1)	0.425(2)	7.5(8)
C(25)	0.505(2)	0.168(1)	0.365(2)	6.6(7)
C(26)	0.426(2)	0.182(1)	0.293(1)	5.7(6)
C(31)	-0.110(3)	0.183(2)	-0.037(2)	8(1)
C(32)	-0.154(4)	0.245(2)	-0.055(3)	17(1)
C(33)	-0.079(3)	0.287(2)	-0.001(3)	11(1)
C(34)	-0.021(3)	0.255(2)	0.037(2)	10(1)
C(41)	0.305(4)	-0.045(2)	0.138(3)	16(1)
C(42)	0.381(8)	-0.046(5)	0.227(6)	25(4)
C(43)	0.457(6)	-0.015(5)	0.214(5)	29(3)
C(44)	0.412(2)	0.035(2)	0.173(4)	18(1)
C(51)	0.302(3)	0.196(2)	-0.005(2)	9(1)
C(52)	0.373(5)	0.195(2)	-0.051(3)	15(1)
C(53)	0.380(4)	0.134(3)	-0.082(3)	13(1)
C(54)	0.320(3)	0.093(2)	-0.046(2)	11(1)
C(121)	-0.019(2)	0.122(1)	-0.208(1)	6.4(7)
C(122)	-0.127(3)	0.128(2)	-0.268(3)	15(1)
C(123)	0.035(3)	0.184(2)	-0.200(3)	13(1)
C(141)	0.199(4)	0.020(2)	-0.365(2)	12(1)
C(142)	0.259(4)	0.077(3)	-0.371(2)	16(1)
C(143)	0.139(5)	-0.011(4)	-0.424(2)	25(2)
C(161)	0.174(2)	-0.092(2)	-0.130(1)	7.0(7)
C(162)	0.141(3)	-0.155(2)	-0.172(2)	10(1)
C(163)	0.298(3)	-0.096(2)	-0.085(2)	10(1)
C(221)	0.175(2)	0.107(2)	0.331(2)	8.0(9)
C(222)	0.119(3)	0.144(2)	0.377(3)	13(1)
C(223)	0.160(3)	0.040(2)	0.344(3)	16(1)
C(241)	0.574(3)	0.127(2)	0.502(2)	11(1)
C(242)	0.588(5)	0.171(3)	0.558(2)	25(2)
C(243)	0.609(7)	0.076(3)	0.520(4)	38(3)
C(261)	0.460(2)	0.217(2)	0.234(2)	7.6(9)
C(262)	0.452(4)	0.287(2)	0.244(2)	15(1)
C(263)	0.571(3)	0.204(2)	0.229(2)	12(2)

Table 12. Atomic Coordinates of Complex 2.

Atom	x	y	z	B _{eq}
Eu	0.12966(6)	0.08826(4)	0.06368(4)	4.66(1)
S(11)	0.0274(3)	0.0124(2)	-0.0851(2)	5.23(9)
S(21)	0.2105(3)	0.1785(2)	0.1914(2)	7.3(1)
O(31)	0.0019(8)	0.1871(5)	0.0135(5)	6.8(3)
O(41)	0.3007(9)	0.0155(5)	0.1253(6)	8.1(3)
O(51)	0.2631(8)	0.1327(6)	-0.0035(6)	7.5(3)
C(11)	0.074(1)	0.0139(7)	-0.1653(7)	4.5(4)
C(12)	0.054(1)	0.0666(7)	-0.2166(8)	5.6(4)
C(13)	0.093(1)	0.0690(7)	-0.2815(8)	6.5(5)
C(14)	0.156(1)	0.0211(9)	-0.2950(10)	7.7(6)
C(15)	0.179(1)	-0.0305(8)	-0.245(1)	7.7(5)
C(16)	0.141(1)	-0.0336(8)	-0.1810(9)	6.0(5)
C(21)	0.314(1)	0.1611(6)	0.2809(6)	5.1(4)
C(22)	0.292(1)	0.1306(7)	0.3405(9)	6.4(5)
C(23)	0.374(1)	0.1192(7)	0.4138(8)	7.1(5)
C(24)	0.483(1)	0.1379(7)	0.4247(9)	6.7(5)
C(25)	0.506(1)	0.1682(8)	0.3649(9)	7.2(5)
C(26)	0.428(1)	0.1816(7)	0.2936(9)	6.0(4)
C(31)	-0.109(1)	0.1840(8)	-0.0383(9)	8.8(6)
C(32)	-0.148(2)	0.247(1)	-0.051(2)	18(1)
C(33)	-0.075(2)	0.2892(9)	0.006(1)	13.2(9)
C(34)	0.024(1)	0.2518(9)	0.0372(10)	10.8(6)
C(41)	0.311(3)	-0.047(1)	0.138(2)	16(1)
C(42)	0.370(4)	-0.032(4)	0.226(3)	34(3)
C(43)	0.455(3)	-0.018(3)	0.217(2)	28(1)
C(44)	0.414(2)	0.037(1)	0.165(2)	20(1)
C(51)	0.301(2)	0.196(1)	-0.0052(10)	10.5(7)
C(52)	0.375(2)	0.196(1)	-0.050(2)	17(1)
C(53)	0.376(2)	0.134(1)	-0.081(1)	14(1)
C(54)	0.317(1)	0.0967(10)	-0.044(1)	11.5(7)
C(121)	-0.017(2)	0.1217(8)	-0.2080(9)	7.2(5)
C(122)	-0.127(1)	0.1288(9)	-0.268(1)	16.1(8)
C(123)	0.034(1)	0.1860(9)	-0.201(1)	14.4(8)
C(141)	0.191(2)	0.022(1)	-0.367(1)	13.1(9)
C(142)	0.259(2)	0.071(1)	-0.370(1)	17.2(10)
C(143)	0.143(2)	-0.014(2)	-0.424(1)	27(1)
C(161)	0.174(1)	-0.092(1)	-0.1295(9)	7.8(5)
C(162)	0.141(1)	-0.1554(8)	-0.171(1)	10.4(7)
C(163)	0.297(1)	-0.0965(9)	-0.0860(9)	11.2(6)
C(221)	0.174(2)	0.1069(10)	0.3322(9)	8.7(7)
C(222)	0.123(1)	0.1411(9)	0.379(1)	13.8(8)
C(223)	0.164(2)	0.040(1)	0.343(2)	19(1)
C(241)	0.560(2)	0.121(1)	0.519(2)	29(1)
C(242)	0.588(2)	0.171(1)	0.553(1)	22(1)
C(243)	0.619(2)	0.083(2)	0.507(1)	26(1)
C(261)	0.459(1)	0.2166(9)	0.2326(8)	7.3(5)
C(262)	0.451(2)	0.2878(9)	0.241(1)	16.0(9)
C(263)	0.572(1)	0.2039(9)	0.2283(10)	12.9(7)

Table 13. Atomic Coordinates of Complex **7b**.

Atom	x	y	z	B _{eq}
Sm(1)	0.05227(5)	-0.25124(4)	0.05950(5)	3.90(1)
S(1)	-0.0929(2)	-0.3144(2)	0.0554(3)	5.37(9)
S(2)	0.0632(3)	-0.2458(2)	-0.1560(2)	5.72(9)
S(3)	0.1909(2)	-0.1780(2)	0.1091(2)	4.95(8)
O(1)	-0.0701(6)	-0.1210(4)	0.0878(8)	6.4(2)
N(2)	0.1586(8)	-0.3951(6)	0.0119(8)	5.4(3)
N(3)	0.0823(7)	-0.2684(6)	0.2592(8)	5.1(3)
C(11)	-0.066(1)	-0.0627(9)	0.033(1)	8.4(5)
C(12)	-0.144(2)	0.0098(10)	0.075(2)	12.9(7)
C(13)	-0.207(1)	-0.008(1)	0.137(2)	16.3(9)
C(14)	-0.152(1)	0.085(1)	-0.161(2)	11.4(6)
C(21)	0.246(1)	-0.4107(8)	-0.031(1)	6.6(4)
C(22)	0.308(1)	-0.485(1)	-0.062(1)	10.0(5)
C(23)	0.283(2)	-0.5441(9)	-0.050(2)	11.4(7)
C(24)	0.196(1)	-0.529(1)	-0.010(2)	12.3(7)
C(25)	0.1365(10)	-0.4567(10)	0.017(1)	8.1(5)
C(31)	0.084(1)	-0.3327(10)	0.292(1)	7.8(5)
C(32)	0.092(1)	-0.338(1)	0.400(2)	10.0(7)
C(33)	0.106(2)	-0.279(1)	0.471(2)	11.9(8)
C(34)	0.106(1)	-0.215(1)	0.451(1)	10.7(7)
C(35)	0.087(1)	-0.2081(9)	0.342(1)	8.2(5)
C(41)	-0.2181(7)	-0.2541(6)	0.082(1)	4.2(3)
C(42)	-0.2824(9)	-0.2332(6)	-0.0065(9)	4.7(3)
C(43)	-0.3782(9)	-0.1853(7)	0.0154(10)	5.6(3)
C(44)	-0.4133(9)	-0.1589(7)	0.123(1)	5.8(3)
C(45)	-0.3490(10)	-0.1833(8)	0.208(1)	6.5(4)
C(46)	-0.2517(9)	-0.2298(7)	0.1912(10)	5.3(3)
C(51)	0.1384(9)	-0.3334(6)	-0.2445(8)	4.5(3)
C(52)	0.2369(10)	-0.3417(7)	-0.2636(10)	5.5(4)
C(53)	0.2902(9)	-0.4087(8)	-0.342(1)	6.0(4)
C(54)	0.2508(10)	-0.4652(7)	-0.4002(10)	5.1(3)
C(55)	0.1593(10)	-0.4575(6)	-0.3768(9)	4.9(3)

C(56)	0.1007(9)	-0.3931(6)	-0.3005(8)	4.6(3)
C(61)	0.2535(8)	-0.1603(6)	0.2389(9)	4.5(3)
C(62)	0.3338(9)	-0.2214(7)	0.272(1)	5.4(3)
C(63)	0.3852(10)	-0.2031(8)	0.372(1)	7.0(4)
C(64)	0.363(1)	-0.1280(9)	0.438(1)	6.6(4)
C(65)	0.286(1)	-0.0715(8)	0.403(1)	7.1(4)
C(66)	0.2285(9)	-0.0845(7)	0.307(1)	5.7(4)
C(421)	-0.2511(9)	-0.2609(8)	-0.125(1)	6.3(4)
C(422)	-0.250(1)	-0.1943(10)	-0.173(1)	11.3(6)
C(423)	-0.311(1)	-0.304(1)	-0.197(1)	12.5(6)
C(441)	-0.519(1)	-0.1050(9)	0.149(1)	7.8(4)
C(442)	-0.591(1)	-0.1135(9)	0.061(2)	10.5(6)
C(443)	-0.522(1)	-0.022(1)	0.177(2)	17.5(8)
C(461)	-0.1887(10)	-0.2518(9)	0.289(1)	7.4(4)
C(462)	-0.198(1)	-0.186(1)	0.393(1)	11.0(6)
C(463)	-0.205(2)	-0.319(1)	0.321(2)	13.8(7)
C(521)	0.282(1)	-0.281(1)	-0.203(1)	8.1(5)
C(522)	0.390(2)	-0.314(1)	-0.186(2)	13.8(8)
C(523)	0.259(2)	-0.217(1)	-0.266(2)	12.6(7)
C(541)	0.313(1)	-0.5357(9)	-0.485(1)	8.3(5)
C(542)	0.383(2)	-0.592(1)	-0.445(2)	18.6(3)
C(543)	0.338(2)	-0.5124(10)	-0.579(1)	13.3(7)
C(561)	-0.0022(10)	-0.3875(7)	-0.2842(9)	5.9(4)
C(562)	-0.0681(10)	-0.3551(9)	-0.379(1)	8.6(5)
C(563)	-0.014(1)	-0.4636(9)	-0.277(1)	9.2(5)
C(621)	0.361(1)	-0.3034(8)	0.202(1)	8.5(5)
C(622)	0.457(2)	-0.3267(9)	0.148(2)	13.7(7)
C(623)	0.365(1)	-0.363(1)	0.264(2)	12.7(7)
C(641)	0.424(1)	-0.109(1)	0.541(1)	9.8(6)
C(642)	0.521(2)	-0.122(2)	0.521(2)	19(1)
C(643)	0.420(2)	-0.137(2)	0.625(2)	24(1)
C(661)	0.145(1)	-0.0150(8)	0.280(1)	7.5(4)
C(662)	0.174(1)	0.0531(10)	0.277(1)	11.2(6)
C(663)	0.064(1)	0.0143(10)	0.363(2)	13.8(7)

Table 14. Atomic Coordinates of Complex **8**.

Atom	x	y	z	B _{eq}
Yb(1)	0.36040(6)	0.01824(6)	0.12821(5)	3.92(2)
S(1)	0.3891(2)	0.1120(4)	0.0460(4)	5.5(2)
S(2)	0.4753(4)	0.0413(4)	0.2454(3)	5.5(2)
S(3)	0.3117(4)	-0.0863(4)	0.1888(3)	4.6(2)
N(1)	0.305(1)	0.124(4)	0.1606(10)	4.1(5)
N(2)	0.426(1)	-0.080(1)	0.096(1)	5.4(6)
N(3)	0.244(1)	-0.013(2)	0.031(1)	6.1(6)
C(11)	0.321(1)	0.132(2)	0.226(1)	5.3(7)
C(12)	0.290(2)	0.190(2)	0.250(2)	8(1)
C(13)	0.244(2)	0.243(2)	0.206(2)	8(1)
C(14)	0.228(2)	0.238(2)	0.141(2)	6.8(9)
C(15)	0.255(2)	0.179(2)	0.119(1)	5.6(8)
C(21)	0.454(1)	-0.147(2)	0.136(1)	5.8(8)
C(22)	0.494(2)	-0.199(2)	0.126(2)	9(1)
C(23)	0.514(2)	-0.193(2)	0.083(3)	10(1)
C(24)	0.486(3)	-0.134(2)	0.036(2)	10(1)
C(25)	0.444(2)	-0.074(2)	0.045(2)	7.4(10)
C(31)	0.242(2)	-0.046(2)	-0.024(2)	8(1)
C(32)	0.174(3)	-0.067(3)	-0.077(2)	12(1)
C(33)	0.113(3)	-0.056(4)	-0.066(4)	14(2)
C(34)	0.116(3)	-0.026(4)	-0.019(2)	11(1)
C(35)	0.179(2)	-0.005(2)	0.029(1)	7.6(9)
C(41)	0.349(2)	0.211(2)	0.034(2)	5.3(8)
C(42)	0.383(2)	0.268(2)	0.082(2)	6.5(9)
C(43)	0.346(3)	0.343(2)	0.070(2)	9(1)
C(44)	0.282(3)	0.365(2)	0.015(2)	9(1)
C(45)	0.252(2)	0.307(3)	-0.032(2)	9(1)
C(46)	0.282(2)	0.230(2)	-0.026(1)	6.9(9)
C(51)	0.547(1)	-0.030(2)	0.268(1)	5.0(6)
C(52)	0.550(2)	-0.099(2)	0.306(1)	6.6(8)
C(53)	0.609(2)	-0.152(2)	0.324(2)	7.5(9)
C(54)	0.662(2)	-0.140(2)	0.304(2)	7(1)
C(55)	0.658(2)	-0.078(2)	0.262(2)	7.3(10)

C(56)	0.600(1)	-0.023(2)	0.244(1)	5.0(6)
C(61)	0.222(1)	-0.126(2)	0.146(1)	4.7(7)
C(62)	0.206(2)	-0.197(2)	0.107(1)	7.1(10)
C(63)	0.137(2)	-0.235(2)	0.077(1)	7.1(8)
C(64)	0.082(2)	-0.206(3)	0.084(2)	11(1)
C(65)	0.095(2)	-0.137(3)	0.126(2)	8(1)
C(66)	0.166(1)	-0.094(2)	0.157(1)	6.3(8)
C(421)	0.457(2)	0.258(2)	0.144(2)	7(1)
C(422)	0.456(2)	0.294(2)	0.210(2)	9(1)
C(423)	0.519(2)	0.279(3)	0.135(2)	12(1)
C(441)	0.250(3)	0.444(2)	0.007(3)	13(1)
C(442)	0.241(3)	0.484(3)	-0.043(3)	15(1)
C(443)	0.197(3)	0.454(3)	0.032(3)	13(1)
C(461)	0.247(2)	0.165(2)	-0.082(2)	8(1)
C(462)	0.165(3)	0.160(3)	-0.112(2)	14(1)
C(463)	0.273(3)	0.172(3)	-0.133(2)	13(1)
C(521)	0.494(2)	-0.109(2)	0.335(2)	6.9(9)
C(522)	0.479(2)	-0.198(3)	0.341(2)	12(1)
C(523)	0.518(2)	-0.067(3)	0.401(2)	10(1)
C(541)	0.722(2)	-0.203(3)	0.325(3)	13(1)
C(542)	0.699(3)	-0.271(3)	0.287(3)	17(2)
C(543)	0.792(3)	-0.180(3)	0.360(3)	15(2)
C(561)	0.599(2)	0.051(2)	0.206(2)	6.9(9)
C(562)	0.640(2)	0.116(2)	0.253(2)	10(1)
C(563)	0.631(2)	0.037(2)	0.158(2)	9(1)
C(621)	0.272(2)	-0.232(2)	0.093(1)	7.3(10)
C(622)	0.313(2)	-0.292(3)	0.145(2)	10(1)
C(623)	0.244(3)	-0.269(3)	0.023(2)	12(1)
C(641)	0.007(2)	-0.250(3)	0.060(2)	12(1)
C(642)	0.005(3)	-0.315(4)	0.093(4)	19(2)
C(643)	-0.044(2)	-0.210(3)	0.008(3)	15(1)
C(661)	0.175(2)	-0.019(2)	0.196(1)	6.9(8)
C(662)	0.201(2)	-0.035(3)	0.270(2)	12(1)
C(663)	0.107(2)	0.038(2)	0.168(2)	10(1)

Table 15. Atomic Coordinates of Complex **9**.

Atom	x	y	z	B _{eq}
Sm(1)	0.25566(3)	0.23309(2)	0.03776(4)	3.251(8)
S(1)	0.2191(2)	0.3835(1)	0.1393(3)	6.95(7)
S(2)	0.2848(2)	0.0720(1)	0.0019(2)	4.89(5)
S(3)	0.2886(2)	0.2611(1)	-0.1806(2)	4.94(5)
P(1)	-0.0136(1)	0.2883(1)	-0.1361(2)	4.83(5)
P(2)	0.1996(2)	0.1620(1)	0.2991(2)	4.37(5)
P(3)	0.5170(1)	0.2272(1)	0.2501(2)	4.25(5)
O(1)	0.0894(3)	0.2510(2)	-0.0724(4)	4.4(1)
O(2)	0.2209(3)	0.2040(2)	0.2088(4)	4.3(1)
O(3)	0.4167(3)	0.2214(2)	0.1578(4)	4.2(1)
N(1)	-0.0194(5)	0.3670(4)	-0.1932(7)	6.7(2)
N(2)	-0.0749(5)	0.3035(4)	-0.0374(8)	7.2(2)
N(3)	-0.0684(5)	0.2328(4)	-0.2573(7)	6.7(2)
N(4)	0.1315(5)	0.0979(3)	0.2246(6)	4.8(2)
N(5)	0.2986(5)	0.1189(4)	0.3994(6)	5.3(2)
N(6)	0.1376(5)	0.2226(3)	0.3756(6)	5.2(2)
N(7)	0.5090(5)	0.2850(4)	0.3713(6)	5.1(2)
N(8)	0.5701(4)	0.1429(3)	0.2988(6)	5.1(2)
N(9)	0.5855(4)	0.2590(4)	0.1904(6)	5.0(2)
C(1)	0.2990(6)	0.4433(4)	0.1367(8)	4.7(2)
C(2)	0.3130(6)	0.4557(5)	0.0272(9)	6.1(3)
C(3)	0.3740(8)	0.5039(6)	0.026(1)	8.3(4)
C(4)	0.4225(8)	0.5411(6)	0.135(1)	8.9(4)
C(5)	0.4122(9)	0.5299(6)	0.246(1)	9.2(4)
C(6)	0.3499(8)	0.4801(5)	0.2476(10)	7.4(3)
C(7)	0.2136(5)	0.0325(4)	-0.1401(7)	3.9(2)
C(8)	0.1951(6)	0.0616(4)	-0.2548(8)	5.4(2)
C(9)	0.1416(7)	0.0247(6)	-0.3665(8)	7.0(3)
C(10)	0.1066(7)	-0.0406(6)	-0.3644(9)	7.0(3)
C(11)	0.1252(6)	-0.0684(5)	-0.2524(10)	6.2(3)
C(12)	0.1773(6)	-0.0333(4)	-0.1420(8)	4.9(2)
C(13)	0.4102(5)	0.2232(4)	-0.1766(6)	4.1(2)
C(14)	0.4562(6)	0.1506(4)	-0.1369(7)	5.0(2)
C(15)	0.4621(6)	0.2632(4)	-0.2197(7)	5.4(2)
C(16)	0.5553(7)	0.2329(6)	-0.2221(9)	6.8(3)
C(17)	0.5495(7)	0.1218(5)	-0.1396(8)	6.2(3)
C(18)	0.5992(6)	0.1618(6)	-0.1821(9)	7.1(3)
C(19)	0.0451(8)	0.3735(7)	-0.258(1)	13.7(5)
C(20)	-0.072(1)	0.4372(6)	-0.170(2)	22.3(8)
C(21)	-0.0333(7)	0.3330(6)	0.089(1)	9.1(4)
C(22)	-0.1786(8)	0.3012(9)	-0.076(1)	16.7(6)
C(23)	-0.1387(9)	0.2583(7)	-0.376(1)	14.3(5)
C(24)	-0.0568(8)	0.1536(5)	-0.2437(10)	10.0(3)
C(25)	0.1624(7)	0.2984(5)	0.4175(9)	7.8(3)
C(26)	0.0739(7)	0.2016(5)	0.4340(9)	7.6(3)
C(27)	0.3264(7)	0.1270(5)	0.5350(8)	7.4(3)
C(28)	0.3709(7)	0.0695(5)	0.3514(8)	7.9(3)
C(29)	0.1506(7)	0.0202(5)	0.2564(9)	7.9(3)
C(30)	0.0582(6)	0.1118(5)	0.1034(8)	6.7(3)
C(31)	0.6805(7)	0.2237(5)	0.187(1)	9.8(4)
C(32)	0.4321(7)	0.2858(5)	0.4231(8)	7.3(3)
C(33)	0.5777(7)	0.3352(5)	0.4379(8)	8.2(3)
C(34)	0.6430(7)	0.1307(5)	0.4222(9)	8.7(3)
C(35)	0.5631(6)	0.0755(5)	0.2104(9)	7.1(3)
C(36)	0.5467(6)	0.3274(5)	0.1218(9)	7.3(3)

Table 16. Atomic Coordinates of Complex 11.

Atom	x	y	z	B _{eq}
Yb(1)	0.25488(1)	0.232904(9)	0.04246(2)	2.718(3)
S(1)	0.2182(1)	0.37976(6)	0.1359(1)	5.69(3)
S(2)	0.28294(8)	0.07713(6)	0.00651(9)	3.96(2)
S(3)	0.28911(8)	0.26152(6)	-0.1673(1)	4.16(2)
P(1)	-0.00970(8)	0.28745(6)	-0.1335(1)	4.09(2)
P(2)	0.19817(9)	0.16421(6)	0.29791(10)	3.63(2)
P(3)	0.51323(8)	0.22664(6)	0.24896(10)	3.56(2)
O(1)	0.0943(2)	0.2500(1)	-0.0682(2)	3.67(6)
O(2)	0.2200(2)	0.2061(1)	0.2077(2)	3.75(6)
O(3)	0.4118(2)	0.2210(1)	0.1575(2)	3.72(6)
N(1)	-0.0158(3)	0.3670(2)	-0.1899(4)	5.8(1)
N(2)	-0.0731(3)	0.3019(3)	-0.0370(4)	6.2(1)
N(3)	-0.0634(3)	0.2320(2)	-0.2558(4)	5.53(10)
N(4)	0.1307(3)	0.0991(2)	0.2253(3)	4.24(9)
N(5)	0.2984(3)	0.1226(2)	0.4006(3)	4.61(9)
N(6)	0.1346(3)	0.2257(2)	0.3729(3)	4.62(9)
N(7)	0.5066(3)	0.2851(2)	0.3700(3)	4.57(9)
N(8)	0.5682(3)	0.1426(2)	0.2997(3)	4.46(8)
N(9)	0.5812(2)	0.2588(2)	0.1874(3)	4.41(9)
C(1)	0.2980(3)	0.4410(2)	0.1353(4)	4.2(1)
C(2)	0.3118(4)	0.4543(3)	0.0263(5)	5.3(1)
C(3)	0.3726(5)	0.5053(3)	0.0277(6)	7.0(2)
C(4)	0.4212(5)	0.5430(3)	0.1372(8)	7.9(2)
C(5)	0.4102(5)	0.5307(4)	0.2452(7)	7.8(2)
C(6)	0.3490(4)	0.4794(3)	0.2461(5)	6.2(1)
C(7)	0.2133(3)	0.0367(2)	-0.1390(4)	3.25(8)
C(8)	0.1944(3)	0.0660(3)	-0.2538(4)	4.6(1)
C(9)	0.1433(4)	0.0290(3)	-0.3654(5)	6.2(1)
C(10)	0.1093(4)	-0.0369(3)	-0.3656(5)	6.1(1)
C(11)	0.1266(4)	-0.0666(3)	-0.2539(6)	5.6(1)
C(12)	0.1781(3)	-0.0302(2)	-0.1414(4)	4.4(1)
C(13)	0.4100(3)	0.2214(2)	-0.1688(3)	3.54(9)
C(14)	0.4605(4)	0.2625(3)	-0.2157(4)	4.6(1)
C(15)	0.5530(4)	0.2320(3)	-0.2235(5)	6.0(1)
C(16)	0.5977(4)	0.1606(4)	-0.1851(5)	6.1(1)
C(17)	0.5493(4)	0.1187(3)	-0.1390(5)	5.7(1)
C(18)	0.4565(3)	0.1492(2)	-0.1304(4)	4.2(1)
C(19)	0.0491(5)	0.3734(4)	-0.2553(9)	11.9(3)
C(20)	-0.0668(9)	0.4380(4)	-0.1595(9)	17.0(4)
C(21)	-0.0320(5)	0.3314(4)	0.0919(6)	7.7(2)
C(22)	-0.1802(5)	0.2999(6)	-0.0790(9)	14.6(3)
C(23)	-0.1341(6)	0.2585(4)	-0.3740(7)	10.8(2)
C(24)	-0.0527(5)	0.1518(3)	-0.2433(6)	7.9(2)
C(25)	0.1592(4)	0.3012(3)	0.4148(5)	6.6(2)
C(26)	0.0694(4)	0.2035(3)	0.4307(5)	6.6(2)
C(27)	0.3238(4)	0.1299(3)	0.5367(4)	6.6(2)
C(28)	0.3740(4)	0.0720(3)	0.3569(5)	6.7(2)
C(29)	0.1505(4)	0.0217(3)	0.2594(5)	6.7(2)
C(30)	0.0550(4)	0.1120(3)	0.1016(5)	5.5(1)
C(31)	0.6768(4)	0.2220(3)	0.1823(7)	8.1(2)
C(32)	0.4294(4)	0.2862(3)	0.4241(4)	6.0(1)
C(33)	0.5783(4)	0.3346(3)	0.4374(5)	6.8(2)
C(34)	0.6427(4)	0.1317(3)	0.4248(5)	7.4(2)
C(35)	0.5617(4)	0.0754(3)	0.2113(5)	5.8(1)
C(36)	0.5408(4)	0.3282(3)	0.1202(5)	6.0(1)

Table 17. Atomic Coordinates of Complex 12.

Atom	x	y	z	B _{eq}
Sm(1)	0.12922(4)	0.0021(1)	0.03679(6)	3.66(3)
S(1)	0.0026(2)	-0.1000(3)	-0.0049(1)	4.3(2)
O(1)	0.1089(9)	0.078(1)	0.188(1)	5.1(8)
O(2)	0.131(1)	-0.109(1)	0.167(1)	7(1)
C(1)	0.006(1)	-0.214(1)	-0.030(1)	3.6(8)
C(2)	-0.054(1)	-0.257(1)	-0.062(2)	5(1)
C(3)	-0.050(1)	-0.346(2)	-0.078(2)	6(1)
C(4)	0.009(1)	-0.392(1)	-0.062(2)	6(1)
C(5)	0.068(1)	-0.352(1)	-0.030(2)	6(1)
C(6)	0.068(1)	-0.264(1)	-0.015(1)	5(1)
C(11)	0.199(2)	0.132(2)	-0.041(4)	9(2)
C(12)	0.161(2)	0.071(4)	-0.121(3)	12(4)
C(13)	0.165(2)	-0.019(5)	-0.140(2)	14(4)
C(14)	0.201(2)	-0.087(3)	-0.088(3)	9(3)
C(15)	0.244(3)	-0.089(5)	-0.016(4)	13(4)
C(16)	0.261(4)	-0.066(9)	0.053(7)	21(8)
C(17)	0.272(3)	0.017(6)	0.056(4)	15(5)
C(18)	0.246(2)	0.100(4)	0.034(3)	10(3)
C(21)	0.157(2)	0.125(3)	0.245(3)	10(2)
C(22)	0.122(2)	0.141(4)	0.331(3)	20(4)
C(23)	0.055(2)	0.131(3)	0.317(2)	12(3)
C(24)	0.044(1)	0.079(2)	0.239(2)	7(1)
C(31)	0.184(2)	-0.116(3)	0.234(4)	20(4)
C(32)	0.188(2)	-0.203(2)	0.263(2)	8(2)
C(33)	0.119(2)	-0.243(2)	0.239(2)	8(2)
C(34)	0.079(1)	-0.170(2)	0.200(1)	7(1)

Table 18. Atomic Coordinates of Complex 14.

Atom	x	y	z	Beq
Sm(1)	0.74352(4)	0.2406(1)	0.10688(4)	3.69(4)
S(1)	0.8133(2)	0.2926(5)	0.0183(2)	4.2(2)
O(1)	0.7202(6)	0.468(1)	0.0993(7)	4.8(7)
C(1)	0.879(1)	0.315(3)	0.046(1)	6(1)
C(2)	0.915(1)	0.227(3)	0.028(1)	7(1)
C(3)	0.966(1)	0.253(4)	0.049(2)	11(2)
C(4)	0.982(1)	0.354(4)	0.088(2)	12(3)
C(5)	0.947(1)	0.434(4)	0.106(1)	9(2)
C(6)	0.894(1)	0.419(3)	0.087(1)	7(1)
C(11)	0.698(2)	0.210(4)	0.207(2)	9(2)
C(12)	0.686(1)	0.105(5)	0.171(2)	11(3)
C(13)	0.713(2)	0.016(4)	0.140(2)	10(3)
C(14)	0.760(2)	0.006(3)	0.132(1)	7(2)
C(15)	0.804(2)	0.063(5)	0.153(2)	10(2)
C(16)	0.818(1)	0.178(6)	0.194(2)	11(3)
C(17)	0.787(2)	0.268(4)	0.225(2)	10(2)
C(18)	0.738(2)	0.276(3)	0.229(1)	9(2)
C(21)	0.902(1)	0.114(4)	-0.017(2)	10(2)
C(22)	0.916(2)	-0.010(4)	0.020(2)	13(3)
C(23)	0.924(2)	0.117(5)	-0.075(2)	14(3)
C(31)	0.704(1)	0.545(3)	0.150(1)	8(2)
C(32)	0.690(2)	0.664(3)	0.115(1)	9(2)
C(33)	0.716(1)	0.673(2)	0.064(2)	9(2)
C(34)	0.723(1)	0.545(2)	0.044(1)	5(1)
C(41)	1.042(2)	0.381(8)	0.099(4)	20(5)
C(42)	1.060(3)	0.44(1)	0.051(4)	11(1)
C(43)	1.055(2)	0.357(9)	0.159(4)	26(7)
C(61)	0.858(1)	0.524(4)	0.101(2)	9(2)
C(62)	0.867(2)	0.554(5)	0.170(2)	15(3)
C(63)	0.863(2)	0.633(4)	0.063(2)	12(3)

Table 19. Atomic Coordinates of Complex 15.

Atom	x	y	z	B _{eq}
Sm(1)	0.11619(7)	0.11332(3)	0.04404(6)	3.32(1)
Se(1)	-0.1473(2)	0.02963(6)	-0.0952(1)	4.93(3)
O(1)	-0.139(1)	0.1799(5)	0.0304(8)	5.0(2)
O(2)	0.025(1)	0.1006(5)	0.2234(7)	4.9(2)
C(1)	-0.262(1)	0.0573(6)	-0.247(1)	3.8(3)
C(2)	-0.182(2)	0.0932(6)	-0.312(1)	4.6(3)
C(3)	-0.268(2)	0.1137(7)	-0.423(1)	5.3(4)
C(4)	-0.429(2)	0.0995(8)	-0.468(1)	6.0(4)
C(5)	-0.511(2)	0.0634(9)	-0.403(1)	6.7(5)
C(6)	-0.428(2)	0.0433(7)	-0.290(1)	5.1(3)
C(11)	0.429(1)	0.1234(7)	0.164(1)	4.8(3)
C(12)	0.359(2)	0.1799(8)	0.179(1)	5.1(4)
C(13)	0.258(2)	0.2237(8)	0.105(1)	5.5(4)
C(14)	0.187(2)	0.2273(7)	-0.016(2)	5.3(4)
C(15)	0.182(2)	0.1886(8)	-0.114(1)	4.9(4)
C(16)	0.253(2)	0.1320(7)	-0.129(1)	4.8(4)
C(17)	0.355(2)	0.0902(6)	-0.054(2)	5.1(4)
C(18)	0.429(1)	0.0875(7)	0.067(2)	5.0(4)
C(21)	-0.130(2)	0.049(1)	0.323(2)	8.8(6)
C(22)	0.034(2)	0.064(1)	0.408(1)	8.0(5)
C(23)	0.135(2)	0.0902(7)	0.337(1)	4.4(3)
C(24)	-0.138(2)	0.076(1)	0.217(2)	9.6(6)
C(31)	-0.151(2)	0.228(1)	0.113(2)	9.2(6)
C(32)	-0.294(3)	0.2617(9)	0.066(2)	8.3(6)
C(33)	-0.370(2)	0.2415(8)	-0.055(2)	6.4(5)
C(34)	-0.275(2)	0.1836(7)	-0.072(1)	5.2(4)

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Chapter 5

Polymerization of MMA, Acrylonitrile, Lactones, and Lactide Initiated by Lanthanide Thiolate Complexes

Introduction

Recently polymerization of vinyl as well as heterocyclic monomers has been a focus of interest. Lanthanide compounds are expected to initiate the coordinated anionic polymerizations of such kinds of monomers because lanthanide elements are generally highly electropositive comparable to alkali metals and alkaline earth metals. Especially, alkyl and alkoxide compounds of lanthanides have been reported to give polymers with narrow molecular weight distribution, and in some cases, with high stereoregularity.¹⁻¹¹

Lanthanide hydride complexes, $(Cp^*_2LnH)_2$ ($Ln = La, Nd$ and Lu), has been reported to polymerize ethylene. The lutetium complex yielded polyethylene with narrow molecular weight distribution ($M_w/M_n = 1.37$).¹ *ansa*-Metallocene type complexes can polymerize not only ethylene but also α -olefins such as 1-hexene.⁵

Recently Prof. H. Yasuda and Prof. A. Nakamura have reported new finding that metallocene alkyl or hydride complexes of lanthanides, Cp^*_2LnR ($Ln = Sm, Yb, Lu, Y$; $R = H, Me$), also catalyze the living polymerization of MMA to produce highly syndiotactic PMMA with high molecular weight and narrow molecular weight distribution, which open new era for the organolanthanide-assisted polymerization of polar monomers.^{3,4} These metallocene complexes of lanthanides also cause the living

polymerization of ϵ -caprolactone and δ -valerolactone. For ring opening polymerization, metal alkoxide is the living chain end. Actually, the corresponding alkoxide complexes such as $\text{Cp}^*_2\text{Sm}(\text{OEt})(\text{OEt}_2)$, $[\text{Cp}^*_2\text{Y}(\text{OMe})]_2$, and $\text{Cp}^*_2\text{Y}(\text{OMe})(\text{thf})$ are able to conduct the living polymerization of ϵ -caprolactone and δ -valerolactone.² In addition, these alkoxide complexes catalyze the living polymerization of β -propiolactone which is not polymerized by the alkyl complexes of lanthanides.²

Simpler examples of lanthanide tris(alkoxide) complexes can also initiate the polymerization of polar monomers and cyclic esters. Trialkoxides such as $\text{M}(\text{OPr}^i)_3$ (M = yttrium and lanthanide) have recently been found to initiate the polymerization of ϵ -caprolactone,⁷ lactide,⁸ MMA,¹⁰ Bu^tA (Bu^tA = *t*-butyl acrylate),⁹ DPAA (DPAA = *N,N*-diphenylacrylamide),⁹ and *n*-hexyl isocyanate.¹¹

Thus, lanthanide alkoxide species have high catalytic activities for the polymerization of these kinds of monomers. Generally, the bond strength between lanthanide metal ions and chalcogen atom can be evaluated by comparing with the bond disruption enthalpy values, *e.g.* $\text{Cp}^*_2\text{Sm}-\text{OBu}^t$ (82.4 kcal/mol) and $\text{Cp}^*_2\text{Sm}-\text{SPr}^n$ (73.4 kcal/mol).¹² Since the lanthanide-sulfur bond is weaker than the lanthanide-oxygen bond, thiolate complexes of lanthanide elements might also exhibit catalytic activity superior to the corresponding alkoxide complexes. Therefore, the author investigated the polymerization of polar monomers using the lanthanide thiolate complexes to contribute this rapidly developing field of the polymerization.

Results and Discussion.

Polymerization of MMA. Methyl methacrylate (MMA) is one of the most common monomers for industrial use. MMA can be polymerized by both radical and anionic initiators, yielding poly(methyl methacrylate) (PMMA). Radical polymerization of MMA at -40 °C affords syndiotactic PMMA with $r_1 \sim 75\%$, while the anionic polymerization by organo alkali metal compounds afforded isotactic PMMA (toluene) and syndiotactic PMMA (THF), depending on the polarity of the solvent.^{13,14}

The polymerization of MMA by lanthanide thiolate complexes was carried out in THF at 0 °C for 24 h and the results are summarized in Table 1. The catalytic activities of these lanthanide arenethiolate complexes were lower than other lanthanide catalysts such as Cp*₂LnR (Ln = Sm, Yb, Lu and Y; R = H, Me)⁴ and Ln(OPrⁱ)₃ (Ln = La, Ce),¹⁰ which are reported to give PMMA in ~90% yield at 0 °C within 1 h.¹⁰ The less activity of thiolate complexes might be attributed to the bulkiness of aryl group of sulfur ligand. As shown in Table 1, the activity of tris(thiolate) complexes of trivalent lanthanides was higher than that of divalent lanthanide thiolates, indicating that the oxidation state of active species should be three. The cyclooctatetraenyl complex, [Sm(SPh)(C₈H₈)(thf)₂]₂, was inactive in this condition. Cyclooctatetraenyl ligand might prevent the coordination of the monomer to the metal center to some extent.

The HMPA adduct of samarium benzenethiolates, Sm(SPh)_n(hmpa)₃ (n = 2, 3), gave PMMA with relatively narrow unimodal molecular weight distribution, while GPC analysis of the PMMA obtained by the other lanthanide thiolate catalysts showed broad or bimodal pattern. As described in Chapter 4, HMPA ligand strongly coordinated to the metal and weakened the Ln—S bonds, and kept the complexes monomeric. Such a ligand effect might accelerate the initiation step and slow down the rate of the propagation reaction, resulting the polymers with narrow molecular weight distribution. Moreover, these hmpa complexes afforded syndiotactic PMMA (rr = 80%). These values of tacticity for the resulting polymers were comparable to those reported in the polymerization of MMA by Cp*₂LnR (Ln = Sm, Yb, Lu and Y; R = H, Me) in toluene at 0 °C (rr = 82—84%),⁴ although catalytic activities of Sm(SPh)_n(hmpa)₃ (n = 2, 3) were far lower. The catalytic properties of these two HMPA adducts of divalent and trivalent samarium were quite similar to each other. Thus, the same active species should be regarded to be generated in these systems.

The tacticity of PMMA obtained by the other lanthanide thiolate complexes showed no simple tendency and the polymers were not stereoregular. The polymers obtained by Sm(II) and Yb(II) complexes were syndio-rich, while that obtained by Eu(II) complex was iso-rich. A toluene-soluble tris(thiolate) complex of samarium

Sm(SAr)₃(py)₃ afforded iso-rich PMMA in toluene and syndio-rich PMMA in THF. Such a solvent effect have already been observed in the polymerization of MMA catalyzed by alkyl lithium.¹³ Tacticities and molecular weight distributions of the resulting PMMA by the catalysts without HMPA show that at least two different kinds of active species catalyzed the polymerization of MMA.

Table 1. Polymerization of MMA with lanthanide thiolate complexes.^a

complex ^b	solvent	yield ^c (%)	$M_n/10^3$ ^d	M_w/M_n ^d	tacticity (%)		
					mm	mr	rr
[Sm(SPh) ₂ (hmpa) ₃] ₂	THF	14	16	1.34	1	19	80
[Sm(SAr) ₂ (thf) ₃] ₂	THF	41	21	1.87	30	26	44
Sm(SPh) ₃ (hmpa) ₃	THF	24	17	1.41	1	19	80
Sm(SAr) ₃ (py) ₃	THF	44	bimodal	—	34	27	39
Sm(SAr) ₃ (py) ₃	toluene	73	bimodal	—	56	24	20
[Sm(SPh)(C ₈ H ₈)(thf) ₂] ₂	THF	<1	—	—	—	—	—
[Eu(SAr) ₂ (thf) ₃] ₂	THF	85	29	3.58	68	21	11
Yb(SAr) ₂ (py) ₄	THF	38	21	2.10	16	28	56
Yb(SAr) ₃ (py) ₃	THF	52	bimodal	—	21	32	47

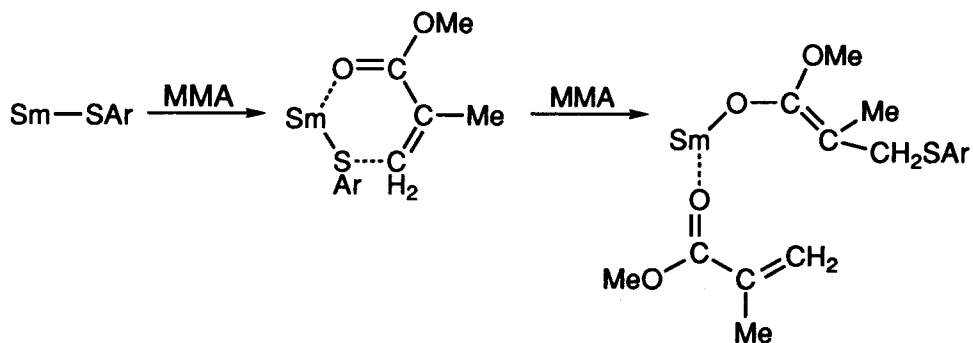
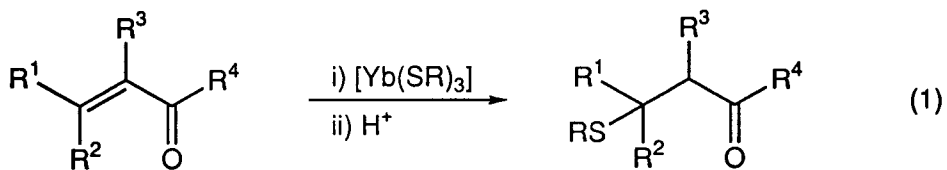
^a Polymerization was carried out at 0 °C for 24 h; [monomer]₀ = 1 M, [Ln] = 20 mM.

^b Ar = 2,4,6-triisopropylphenyl.

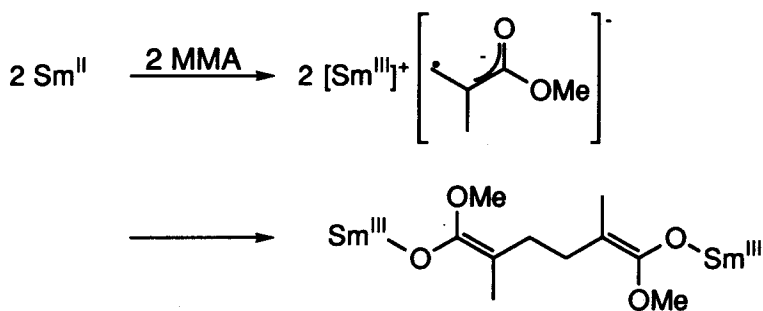
^c Insoluble part in methanol.

^d Determined by GPC analysis, calibrated to a polystyrene standard.

Considering that lanthanide thiolate compounds react with α,β -unsaturated ketones and aldehydes to give Michael adducts (eqn. 1),¹⁵ it is plausible that the initiation reaction in these systems were the insertion of MMA to the Ln—S bonds to generate lanthanide enolate species (Scheme I). In the case of Sm(II) system, the reductive coupling of the monomer by divalent lanthanides might also be possible to initiate the polymerization of MMA as proposed in the systems of SmI₂¹⁶ and Cp*₂Sm¹⁷ (Scheme II). Such lanthanide enolate species have been reported to catalyze the polymerization of MMA.⁴



Scheme I



Scheme II

Polymerization of acrylonitrile. The author further investigated the polymerization of acrylonitrile as another polar vinyl monomer bearing electron withdrawing group.

Acrylonitrile (AN) can be polymerized not only by radical initiators but also anionic initiators to give polyacrylonitrile (PAN), which has occupied an industrially important position, particularly, as fibers. It is recently reported that highly stereoregular PAN (mm content 87%) can be synthesized by γ -ray irradiation on AN-urea canal complex through a radical polymerization mechanism,¹⁸ since the tacticity of PAN can be estimated by ¹³C NMR spectroscopy.¹⁹ However, stereoregular anionic polymerization

of AN in solution has been found to be difficult.²⁰ Recently, Kamide *et al.* reported isospecific (mm content ~70%) polymerization of AN by R_2Be and $Mg(n-C_6H_{13})_2$ /cocatalyst (cocatalyst = R_3Al and R_3B).^{21,22}

Alkyl,^{23,24} arene,^{25,26} amide²⁷ and alkoxide²⁸ compounds of alkali metals and alkali earth metals are mainly used as initiator for anionic polymerization of AN. In the case of polymerization of AN, side reactions based on the attack of propagating carbanion on cyano group result in loss of the living nature of the system. Thus, in order to obtain high molecular weight PAN in high yield, it is necessary to polymerize under strictly limited conditions, *e.g.*, at very low temperature.²⁴ The author expected that the polymerization of AN by lanthanide compounds afforded high polymer because of the rather low activity of $Ln-C$ and $Ln-S$ bonds on cyano group.

The author found that the lanthanide thiolate complexes have high catalytic activity for the polymerization of acrylonitrile. The polymerization was carried out in THF at -78 °C to obtain high polymer and the results are shown in Table 2. Divalent samarium and europium bis(thiolate) complexes, $[Ln(SAr)_2(thf)_3]_2$ ($Ln = Sm, Eu$; $Ar = 2,4,6$ -triisopropylphenyl), showed high catalytic activity for polymerization of acrylonitrile. In contrast, the pyridine adduct of divalent ytterbium, $Yb(SAr)_2(py)_4$, showed lower activity. The tris(thiolate) complexes of lanthanide(III) have a tendency to show higher activities than the corresponding divalent complexes. This result might indicate that the active species in this catalyst system are lanthanide(III) species. Unlike in the polymerization of MMA, the coordination of HMPA showed no significant influence on activity and stereospecificity. Catalytic activities of these complexes were comparable to that of potassium alkoxides²⁸ and butyl lithium,²³ and higher than those of sodium alkoxides²⁸ and dialkyl magnesium.²⁰ On the other hand, the coordination of a cyclooctatetraenyl ligand to samarium dramatically lowered its catalytic activity as observed in the case of the polymerization of MMA. All of the polymers obtained by these catalysts were essentially atactic.

Table 2. Polymerization of acrylonitrile with lanthanide thiolate complexes.^a

complex ^b	temp. (°C)	solvent	yield ^c (%)	$M_n/10^3$ ^d	M_w/M_n ^d	tacticity (%)		
						mm	mr	rr
[Sm(SAr) ₂ (thf) ₃] ₂	-78	THF	52	71	2.2	32	45	23
[Sm(SPh) ₂ (hmpa) ₃] ₂	-78	THF	56			32	43	25
Sm(SAr) ₃ (py) ₃	-78	THF	81	68	2.6	31	45	24
Sm(SPh) ₃ (hmpa) ₃	-78	THF	66			31	41	28
[Sm(SPh)(C ₈ H ₈)(thf) ₂] ₂	50 ^e	THF	9	4	2.3	30	41	29
[Eu(SAr) ₂ (thf) ₃] ₂	-78	THF	83	32	2.8	27	47	26
Yb(SAr) ₂ (py) ₄	-78	THF	15	65	3.3	30	45	25
Yb(SAr) ₃ (py) ₃	-78	THF	85	77	3.4	34	42	24

^a Polymerization was carried out for 1 h; [monomer]₀ = 2 M, [Ln] = 20 mM.

^b Ar = 2,4,6-triisopropylphenyl.

^c Insoluble part in methanol.

^d Determined by GPC analysis, calibrated to a polystyrene standard.

^e Polymerized for 24 h.

Polymerization of cyclic esters. Polymerization of cyclic esters such as lactones and lactide are known to be catalyzed by compounds containing alkali metals,^{29,30} lanthanides,^{2,6-8,31,32} transition metals,^{33,34} aluminum,³⁵⁻³⁹ zinc⁴⁰⁻⁴² and tin.⁴³⁻⁴⁷ Such polymers are attracting great interest for their biodegradability.^{48,42} Recently, yttrium and lanthanide alkoxide complexes has been reported to catalyze the living polymerization of ϵ -caprolactone and lactide.^{7,8} Evans and his coworkers have reported the polymerization of ϵ -caprolactone by a variety of samarium(II) compounds.³¹

The author tried the polymerization of lactones and lactide with samarium thiolate complexes. As summarized in Table 3, ϵ -caprolactone and δ -valerolactone could be polymerized by a variety of samarium thiolate complexes. Both of the thiolate complexes of divalent and trivalent lanthanides were active for the polymerization of ϵ -caprolactone. Tris(thiolate) complexes of lanthanide(III) also have a tendency to show higher activities than the corresponding divalent complexes as observed in the polymerization of MMA and AN.

Poly(ϵ -caprolactone) with relatively narrow molecular weight distribution was obtained by a system of $\text{Sm}(\text{SAr})_3(\text{py})_3$ in toluene. HMPA adducts of benzenethiolate complexes, $[\text{Sm}(\text{SPh})_2(\text{hmpa})_3]_2$ and $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$, exhibited higher activity for the polymerization of ϵ -caprolactone than other complexes, although the resulting polymers had a tailing and broad molecular weight distribution. In the polymerization of lactones, the cyclooctatetraenyl complex, $[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$, showed also high activity.

In the case of the polymerization of δ -valerolactone, $[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$ yielded the polymer with relatively narrow molecular weight distribution. Generally, the polymer yields of δ -valerolactone were less than those of ϵ -caprolactone in accord with smaller ring-distortion in the 6-membered ring.

Table 3. Polymerization of lactones with lanthanide thiolate complexes.^a

monomer	complex ^b	solvent	yield ^c (%)	$M_n/10^3$ ^d	M_w/M_n ^d
ϵ -caprolactone	$[\text{Sm}(\text{SAr})_2(\text{thf})_3]_2$	THF	53	8.1	1.5
	$[\text{Sm}(\text{SPh})_2(\text{hmpa})_3]_2$	THF	98	14	4.3
	$\text{Sm}(\text{SAr})_3(\text{py})_3$	THF	78	9.9	1.8
	$\text{Sm}(\text{SAr})_3(\text{py})_3$	toluene	57	14	1.4
	$\text{Sm}(\text{SPh})_3(\text{hmpa})_3$	THF	97	16	11
	$[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$	THF	97	34	2.1
δ -valerolactone	$[\text{Sm}(\text{SAr})_2(\text{thf})_3]_2$	THF	33	9.7	3.4
	$[\text{Sm}(\text{SPh})_2(\text{hmpa})_3]_2$	THF	51	15	4.0
	$\text{Sm}(\text{SAr})_3(\text{py})_3$	THF	55	13	2.1
	$\text{Sm}(\text{SAr})_3(\text{py})_3$	toluene	75	16	2.0
	$\text{Sm}(\text{SPh})_3(\text{hmpa})_3$	THF	50	9.8	4.3
	$[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$	THF	61	10	1.5

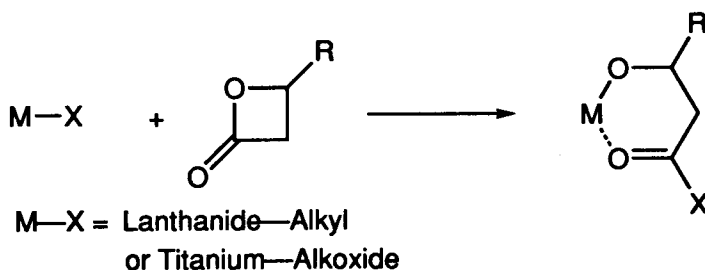
^a Polymerization was carried out at 30 °C for 24 h; $[\text{monomer}]_0 = 1 \text{ M}$, $[\text{Ln}] = 20 \text{ mM}$.

^b Ar = 2,4,6-triisopropylphenyl.

^c Insoluble part in methanol.

^d Determined by GPC analysis, calibrated to a polystyrene standard.

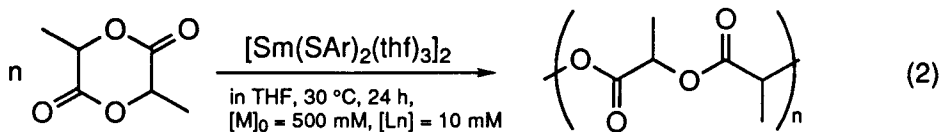
β -Lactones comprised of 4-membered ring are rather difficult to be polymerized with early transition metal initiators compared to δ - and ϵ -lactones due to the formation of the stable 6-membered chelate ring compounds as intermediate (Scheme III).^{2,33} β -Butyrolactone could be polymerized by $\text{Sm}(\text{SAr})_3(\text{py})_3$ at 100 °C for 24 h without solvent to afford poly(β -butyrolactone) with bimodal molecular weight distribution ($M_n = 6400$, $M_w/M_n = 1.04$ and $M_n = 1200$, $M_w/M_n = 1.23$) in 23% yield.



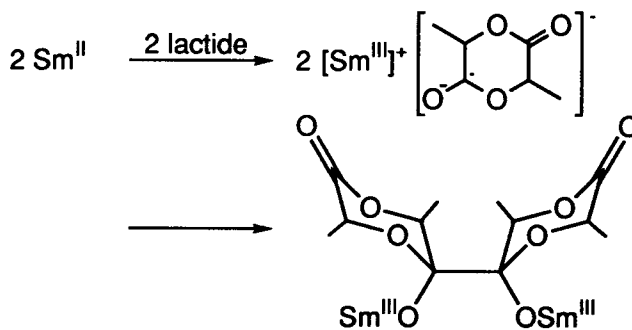
Scheme III

It is reported that the active species in the polymerization of lactones with Cp^*_2LnR ($\text{Ln} = \text{Sm}, \text{Yb}, \text{Lu}$ and Y ; $\text{R} = \text{H}, \text{Me}$) are lanthanide alkoxides and the cleavage of the lactone ring occur at $\text{O}-\text{C}(\text{carbonyl})$ bond. The author inferred that the polymerization of lactones with lanthanide thiolate may proceed in a similar manner.

In the case of polymerization of lactide by lanthanide thiolates, DL-lactide could be polymerized only by the divalent samarium complex, $[\text{Sm}(\text{SAr})_2(\text{thf})_3]_2$, and was not polymerized by $\text{Sm}(\text{SAr})_3(\text{py})_3$ and $[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$ (eqn. 2). Polymerization was carried out in THF at 30 °C for 24 h to afford poly(lactide) with narrow molecular weight distribution. At the present stage of this study, the author speculates that the initiation step might include the reduction of monomer by the samarium(II) compound as proposed in the polymerization of MMA by SmI_2 ¹⁶ and $\text{Cp}^*_2\text{Sm}^{17}$ (Scheme IV).



43% yield, $M_n = 8.3 \times 10^3$, $M_w/M_n = 1.25$



Scheme IV

Thus, the author found that the lanthanide thiolate complexes have high catalytic activity for the polymerization of polar monomers depending on the coordination environment and oxidation state of the metal center.

Experimental Section.

General. Thiolate complexes of lanthanide(II) and (III), $[\text{Ln}(\text{SAr})_2(\text{thf})_3]_2$ ($\text{Ln} = \text{Sm}, \text{Eu}$; $\text{Ar} = 2,4,6\text{-triisopropylphenyl}$), $\text{Yb}(\text{SAr})_2(\text{py})_4$, $\text{Ln}(\text{SAr})_3(\text{py})_3$ ($\text{Ln} = \text{Sm}, \text{Yb}$), $[\text{Sm}(\text{SPh})_2(\text{hmpa})_3]_2$, $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$ and $[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$ were prepared as described in Chapter 4. Acrylonitrile was dried by P_2O_5 and distilled under argon atmosphere. MMA and lactones were distilled from CaH_2 under argon atmosphere and dried over molecular sieves. DL-Lactide was used as purchased. All polymerizations were carried out under argon atmosphere using the standard Schlenk tube technique. Nuclear magnetic resonance (^1H , and ^{13}C -NMR) spectra were measured on a JEOL GX-270 spectrometer.

Polymerization of MMA. To a solution of $\text{Sm}(\text{SAr})_3(\text{py})_3$ (22 mg, 20 μmol) in THF (0.89 mL) was added MMA (0.11 mL, 0.10 g, 1.0 mmol) at -78°C . The reaction tube was sealed in argon and kept for 24 h at 0°C with stirring. An excess of methanol was added to the reaction mixture. The resulting colorless polymer was collected by centrifugation and dried *in vacuo*. The yield was 44%.

Polymerization of acrylonitrile. To an orange solution of $\text{Sm}(\text{SAr})_3(\text{py})_3$ (25 mg, 23 μmol) in THF (0.58 mL) was added a solution of acrylonitrile (0.15 mL, 0.12 g, 2.3 mmol) in THF (0.43 mL) at -78°C . The polymer immediately began to precipitate. The reaction tube was sealed in argon and kept for 1 h at -78°C with stirring. An excess (ca. 20 mL) of methanol was added to the reaction mixture. The resulting pale yellow polymer was collected by centrifugation and dried *in vacuo*. The yield was 81%.

Polymerization of lactones. To a solution of $\text{Sm}(\text{SAr})_3(\text{py})_3$ (22 mg, 20 μmol) in toluene (0.89 mL) was added ϵ -caprolactone (0.11 mL, 0.11 g, 1.0 mmol) at -78°C . The reaction tube was sealed in argon and kept for 24 h at 30°C with stirring. An excess of methanol was added to the reaction mixture. The resulting colorless polymer was collected by centrifugation and dried *in vacuo*. The yield was 57%.

Polymerization of lactide. To a solution of $[\text{Sm}(\text{SAr})_2(\text{thf})_3]_2$ (17 mg, 10 μmol) in THF (0.50 mL) was added a solution of lactide (0.15 g, 1.0 mmol) in THF (1.5 mL) at -78°C . The reaction tube was sealed in argon and kept for 24 h at 30°C with stirring. An excess of methanol was added to the reaction mixture. The resulting colorless polymer was collected by centrifugation and dried *in vacuo*. The yield was 43%.

GPC Analyses. For PMMA, poly(lactone)s and poly(lactide), gel permeation chromatographic (GPC) analyses were carried out using TOSOH TSKgel HXL-H and L columns connected to a TOSOH RI-8021 differential refractometer and a TOSOH UV-8010 absorbance detector. Samples were prepared in THF (1 mg/mL) and were filtered through a Toyo Roshi DISMIC-25JP filter in order to remove particulates before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.). For polyacrylonitrile GPC data were recorded on a Waters ALC/GPC Model 242 with Hitachi GL-W500MT column using NMP (N-methylpyrrolidone) as an eluent at Central Research Laboratories, Idemitsu Kosan Co., Ltd.

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Summary and Conclusions

In *Part I* of this thesis, the author studied the polymerization of substituted acetylenes by group 5 and 6 aryloxo based catalysts.

For this study, the novel synthetic method of early transition metal complexes having one or two aryloxo ligands has been developed. A series of mono- and bis(2,6-dimethylphenoxo) complexes of group 4—6 transition metals, $MCl_{4-n}(dmp)_n(thf)_2$ ($M = Ti, Zr, Hf$), $MCl_{5-n}(dmp)_n(thf)$ ($M = Nb, Ta$), $MoCl_3(dmp)_2(thf)$, and $WCl_{6-n}(dmp)_n$ ($n = 1, 2$; $dmp = 2,6$ -dimethylphenoxide), were selectively prepared by the 1:1 and 1:2 reactions of metal chlorides with the (2,6-dimethylphenyl)trimethylsilyl ether. The molecular structures of these complexes were characterized by the single crystal X-ray analyses.

The polymerization of substituted acetylenes catalyzed by a series of 2,6-dimethylphenoxo complexes of group 5 and 6 transition metals is precisely investigated. The catalyst system, $WCl_4(dmp)_2/Et_3Al$, was found to polymerize $t\text{-BuC}\equiv\text{CH}$ to a extremely high molecular weight polymer ($M_n > 2 \times 10^6$) with relatively narrow molecular weight distribution ($M_w/M_n \sim 1.2$) and with high stereoregularity ($cis = 88\%$). By increasing the number of aryloxo ligands on W(VI) species, less bulky 1-alkynes could be polymerized to get high molecular weight polymers. For instance, the polymerization of 1-butyne gave an orange polymer with $M_n = 9.4 \times 10^4$, $M_w/M_n = 3.5$, and poly(1-hexyne) and poly(1-octyne) with high molecular weights ($M_n > 10^5$) were obtained. Such high polymers of 1-alkynes with less bulky substituents were obtained at the first example.

In *Part II* of this thesis, the author investigated the polymerization of polar monomers such as vinyl monomers having electron withdrawing groups and cyclic esters by using lanthanide thiolate complexes as the polymerization initiator.

The author developed a novel synthetic route for divalent and trivalent lanthanide thiolate complexes from metallic lanthanides. The reaction of an excess of Sm, Eu and

Yb metals with diaryl disulfides, ArSSAr (Ar = C₆H₂Pr¹_{3-2,4,6}, Ph), selectively afforded bis(thiolato) complexes of divalent lanthanides. On the other hand, the reaction of metallic lanthanides with 3 equiv. of the diaryl disulfides gave tris(thiolato) complexes of trivalent lanthanides. Thus, the convenient one-pot reaction of metallic samarium, europium, and ytterbium with diaryl disulfide cleanly gives the thiolate complexes in the two and three oxidation states by controlling the stoichiometry of metallic lanthanide and the disulfide. When the reaction was performed in the presence of cyclooctatetraene, cyclooctatetraenyl(arenethiolate)samarium(III) complexes could be obtained in one step. These complexes were structurally characterized by X-ray crystallography.

These complexes were found to catalyze the polymerization of polar monomers such as MMA, acrylonitrile, lactones and lactide. The polymerization of MMA by the use of samarium benzenethiolates bearing HMPA (hexamethylphosphoric triamide) ligands, Sm(SPh)_n(hmpa)₃ (n = 2,3), as initiators afforded syndiotactic PMMA with narrow molecular weight distribution ($M_n = 16000$, $M_w/M_n = 1.34$, $\pi = 80\%$). These thiolate complexes were highly active for polymerization of acrylonitrile, although this polymerization was neither living nor stereospecific. In the case of lactones, ϵ -caprolactone and δ -valerolactone were polymerized by these complexes to produce polymers with relatively narrow molecular weight distributions ($M_w/M_n \sim 1.5$). Lactide were polymerized only by [Sm(SAr)₂(thf)₃]₂ to afford a polymer with narrow molecular weight distribution ($M_n = 8300$, $M_w/M_n = 1.25$). Thus the thiolate complexes of lanthanides proved to be versatile catalyst precursors for a wide variety of the polymerizations of polar monomers.

List of Publications

1. Facile Synthesis of Group 4—6 Transition Metal Phenoxides and X-Ray Structures of $\text{TiCl}_2[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})_2$ and $\text{NbCl}_3[\text{O}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3]_2(\text{THF})$
Kanehisa, N.; Kai, Y.; Kasai, N.; Yasuda, H.; Nakayama, Y.; Takei, K.; Nakamura, A. *Chem. Lett.* **1990**, 2167—2170.
2. Reaction Courses for Formation of Early Transition Metal Phenoxides
Yasuda, H.; Nakayama, Y.; Takei, K.; Nakamura, A.; Kai, Y.; Kanehisa, N. *J. Organomet. Chem.* **1994**, 473, 105—116.
3. Bulky Aryloxo Complexes of Tungsten and Niobium as Catalyst Precursors for High Polymerizations of Alk-1-yne
Nakayama, Y.; Mashima, K.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1496—1498.
4. Polymerization of Monosubstituted Acetylenes Catalyzed by 2,6-Dimethylphenoxo Complexes of Group 5 and 6 Metals
Nakayama, Y.; Mashima, K.; Nakamura, A. *Macromolecules* **1993**, 26, 6267—6272.
5. Monocyclooctatetraenyl(thiolato)samarium(III) Complexes from the Reaction of Metallic Samarium with Cyclooctatetraene and Diaryldisulfide: Crystal Structures of $[\text{Sm}(\mu\text{-SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$ and $[\{\text{Sm}[\mu\text{-S}(2,4,6\text{-triisopropylphenyl})](\text{C}_8\text{H}_8)(\text{thf})\}_2]$
Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1847—1848.
6. Formation of Lanthanoid(II) and Lanthanoid(III) Thiolate Complexes Derived from Metals and Organic Disulfides: Crystal Structures of $[\{\text{Ln}(\text{SAr})(\mu\text{-SAr})(\text{thf})_3\}_2]$ (Ln = Sm, Eu), $[\text{Sm}(\text{SAr})_3(\text{py})_2(\text{thf})]$ and $[\text{Yb}(\text{SAr})_3(\text{py})_3]$ (Ar = 2,4,6-triisopropylphenyl; py = pyridine)
Mashima, K.; Nakayama, Y.; Fukumoto, H.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2523—2524.
7. Convenient Synthesis of Arenethiolate Complexes of Divalent and Trivalent Lanthanides from Metallic Lanthanides and Diaryl Disulfides: Crystal Structures of $\text{Ln}(\text{SPh})_3(\text{hmpa})_3$ (Ln = Sm, Yb; hmpa = hexamethylphosphoric triamide)
Mashima, K.; Nakayama, Y.; Shibahara, T.; Nakamura, A. submitted for publication.

8. Syndiospecific Polymerization of MMA Catalyzed by Lanthanide Thiolate Complexes bearing HMPA Ligands

Nakayama, Y.; Mashima, K.; Shibahara, T.; Nakamura, A. to be published.

Related Papers

1. Unique Molecular Structures of Tungsten Phenoxides

Kanehisa, N.; Kai, Y.; Kasai, N.; Yasuda, H.; Nakayama, Y.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1197—1202.

2. A New Convenient Preparation of Monocyclooctatetraenyl-lanthanide Complexes from Metallic Lanthanides and Oxidants

Mashima, K.; Nakayama, Y.; Nakamura, A. ; Kanehisa, N.; Kai, Y.; Takaya, H. *J. Organomet. Chem.* **1994**, *473*, 85—91.

