Account

Synthesis, Structure and Reactivity of Lanthanocene Complexes

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A variety of lanthanocene complexes, *e. g.* chlorides, hydrocarbyls, amides, hydrides and divalent derivatives, were synthesized by using a series of designed cyclopentadienyl, indenyl and fluorenyl ligands with ring bridges or dornor-functionalized sidearms. X-Ray crystallographic analyses reveal the formation of intramolecular coordination bonds between central metals and heteroatoms (O, N) in sidearms or bridging chains. Some applications of these complexes are also discussed in this account.

Keywords   lanthanocene complex, crystal structure, cyclopentadienyl ligand, indenyl ligand, bridging ligand, reduction, polymerization

Introduction

The chemistry of organolanthanides has experienced extremely important developments during the last two decades, and numerous unusual compounds with unprecedented structures and unique reactivity patterns have been prepared.[1] Organolanthanide compounds containing Ln—C, Ln—H and Ln—N bonds have been found to exhibit catalytic activity in various chemical transformations, such as C—H bond activation,[2] hydrogenation,[3] hydrosilylation[4] and hydroamination.[5] Especially, they are very effective single component catalysts for polymerization of polar or nonpolar monomers, and allow the synthesis of high molecular weight polymers with extremely narrow molecular weight distributions.[6] A significant advantage of lanthanocene catalysts lies in high catalytic activity toward olefins polymerization even in the absence of methylaluminoxane (MAO).[7] Moreover studies of lanthanocene complexes have been considered to be valuable for insight into mechanistic aspects of the polymerization of alkenes, since they are isoelectron neutral analogues of the $[Cp_2MR]^+$ d^0 group 4 catalysts, which have been accepted as being key intermediates in the polymerization.[8]

Two important general features of lanthanide metallic ions are their size and electropositivity. Compared with transition metals, the lanthanides are quite large and high coordination numbers of 8—12 are common in lanthanide complexes, which are rather electropositive and quite oxophilic.[9] In view of the radial extension and ionic character of the lanthanides, η^5-cyclopentadienyl, indenyl and fluorenyl ligands and their bridged derivatives are particularly suitable for the stabilization of organolanthanide complexes, because they meet the electronic and steric requirements to form thermally stable, isolable complexes.

In order to find novel structure and synthesize highly active catalysts for organic reactions and olefins polymerization, we have been deeply interested in the synthesis, structure and application of organolanthanocene complexes. This account will outline our efforts to synthesize stable and highly reactive lanthanocene complexes with a series of designed ancillary ligands and some applications of these complexes.

Ansa-lanthanocene complexes

Prior to the early 1980s, no thermally stable bis(cy-

clopentadienyl) lanthanide alkyl complex of large lanthanide metals had been prepared, due to the absence of appropriate starting materials, such as the corresponding bis (cyclopentadienyl) lanthanide chlorides. The introduction of bulky pentamethylcyclopentadiene as an ancillary ligand, which confers stability, solubility and crystallinity on organometallic compounds, made the major breakthrough in lanthanide chemistry. [10] Qian and co-workers developed other stabilization way of lanthanide chlorides, $i.e.$, using the ring-bridged bis(cyclopentadienyl) as ligands preventing the complexes from undergoing intermolecular ligand redistribution.

Five-atom bridges

Bis(cyclopentadienyl) lanthanide chlorides are the most common precursors for synthesis of compounds with Ln—H, Ln—C and Ln—N σ-bonds, and their chemistry has been receiving considerable attention. A series of five-atom bridged bis(cyclopentadienyl) lanthanide chlorides were synthesized as outlined in Scheme 1. They included pentamethylene bridged $(CH_2)_3(CH_2C_5H_4)_2LnCl$-(THF) [Sm (1), Gd (2), Dy (3), Er (4), Lu (5), Y (6)], [11] 3-oxapentamethylene bridged $O(CH_2CH_2C_5H_4)_2$-LnCl [Nd (7), Gd (8), Ho (9), Er (10), Yb (11), Lu (12), Y (13)], [12] furan-skeleton bridged $2,5$-OC_4H_6-$(CH_2C_5H_4)_2LnCl$ [Nd (14), Sm (15), Yb (16), Y (17)], [13] N-containing sidechain bridged $CH_3N(CH_2$-$CH_2C_5H_4)_2LnCl$ [Nd (18), Sm (19), Yb (20), Y (21)], [14] $2,6$-dimethylenepyridyl unit bridged $2,6$-NC_5-$H_3(CH_2C_5H_4)_2LnCl$ [Pr (22), Nd (23), Sm (24), Dy (25), Er (26), Yb (27), Lu (28), Y (29)] [15] and benzene-skeleton bridged m-$C_6H_4(CH_2C_5H_4)_2LnCl(THF)$ [La (30), Nd (31), Dy (32), Er (33), Yb (34), Y (35)]. [16] Bridged biscyclopetadienyl ligands are effective in preventing the complexes from undergoing intermolecular ligand redistribution. Using pentamethylene bridged biscyclopentadienyl as ancillary ligand, samarium and the later rare earth metal chlorides are accessible. But when using oxygen- or nitrogen-containing ring-linked biscyclopentadienyl as ligands, solvent free lanthanocene chlorides are readily accessible for neodymium and the later rare earth metals, implying that heteroatom chelating ligands have similar effects on avoiding intermolecular ligand redistribution. However, efforts to obtain their La- and Pr-congeners under similar conditions failed and a new type of binuclear tricyclopentadienyl lanthanides complex-
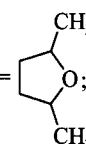
es were obtained. Surprisingly, using rigid pentacarbon chain with a benzene ring, we have succeeded in synthesizing the early lanthanum chloride. Using more rigid trimethylene chain, THF-solvated early lanthanocene chlorides, $CH_2(CH_2C_5H_4)_2LnCl(THF)$ [Ln = Pr (36), Nd (37), Gd (38), Dy (39), Ho (40), Er (41), Yb (42), Lu (43)], were synthesized. [17] We succeeded for the first time in stabilizing Cp_2LnCl by using ring-bridged dicyclopentadienyl ligand.
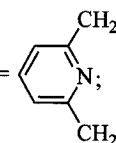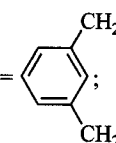
Scheme 1
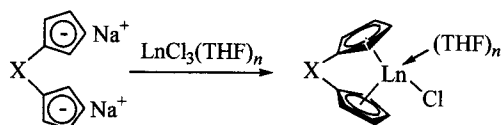
X = $(CH_2)_5$; Ln = Sm (1), Gd (2), Dy (3), Er (4), Lu (5), Y (6);
          $n = 1$

X = $(CH_2)_2O(CH_2)_2$; Ln = Nd (7), Gd (8), Ho (9), Er (10),
                                Yb (11), Lu (12), Y (13); $n = 0$

X = [furan structure with CH₂ groups]; Ln = Nd (14), Sm (15), Yb (16), Y (17);
          $n = 0$

X = $(CH_2)_2N(CH_3)(CH_2)_2$; Ln = Nd (18), Sm (19), Yb (20),
                                Y (21); $n = 0$

X = [pyridyl structure with CH₂ groups]; Ln = Pr (22), Nd (23), Sm (24), Dy (25), Er (26),
                                Yb (27), Lu (28), Y (29); $n = 0$

X = [benzene structure with CH₂ groups]; Ln = La (30), Nd (31), Dy (32), Er (33), Yb (34),
                                Y (35); $n = 1$

X = $(CH_2)_3$; Ln = Pr (36), Nd (37), Gd (38), Dy (39), Ho (40),
          Er (41), Yb (42), Lu (43); $n = 1$

The $\Delta\delta$ value between the α- and β-protons of the Cp ring in an organometallic complex implies the distribution of charge on cyclopentadienyl and torsional mobility of the Cp ring, $i.e.$, an increase in the $\Delta\delta$ value means a decrease in the torsional mobility of the Cp ring. [18] The values for some ring-bridged lanthanocene chlorides are compared and the data are listed in Table 1. From Table 1, it can been seen that when a chain containing nitrogen or oxygen is introduced into the bridged biscyclopentadienyl ligand, because of the formation of an intramolecular coordination bond, the $\Delta\delta$ value obviously increases, as compared with pentamethylene bridged lan-

thanocene chloride. In the case of the chain containing a benzene ring, the rigidity of the chain is strengthened and results in an increase in $\Delta\delta$.

Table 1 Correlation of the bridging chain with ring-proton splitting

Complex	n	$\Delta\delta^a$	Reference
$(CH_2)_5(C_5H_4)_2YCl(THF)$ (**30**)	5	0.07	23
m-$C_6H_4(CH_2C_5H_4)_2YCl(THF)$ (**59**)	5	0.22	24
$O(CH_2CH_2C_5H_4)_2YCl$ (**37**)	4 + O	0.14	25
$CH_3N(CH_2CH_2C_5H_4)_2YCl$ (**45**)	4 + N	0.23	26
$2,5$-$OC_4H_6(CH_2C_5H_4)_2YCl$ (**41**)	4 + N	0.22	27

^{a} $\Delta\delta = \delta_{\alpha\text{-H}} - \delta_{\beta\text{-H}}$

Among these complexes special attention should be given to the compounds having heteroatom-containing bridges. The rigidity of the bridging chain and intramolecular coordination of heteroatom in the bridging chain would decrease the torsional mobility of the cyclopentadienyl ring and open the coordination sphere around the central metal, and therefore might facilitate the availability of coordination sites for other substrates and enhance the possibility of acquiring more stable, and more reactive organolanthanide species. Our studies on the reactivity of those complexes strongly support above statement (*vide infra*).

1, 1'-(3-Oxapentamethylene) biscyclopentadienyl lanthanocene chlorides reacted with equimolar amounts of (3,5-dimethylpyrazoyl)sodium to yield the η^2-dimethylpyrazolyl complexes **44** and **45**. A very small amount of impurity of water in an inert solvent caused partial hydrolysis with formation of **46** and **47** (Scheme 2).[19] Fig. 1 shows the X-ray structure of **47**. Complex **47** is a binuclear complex with both yttrium coordinated by one 1,1'-(3-oxapentamethylene)biscyclopentadienyl ligand and
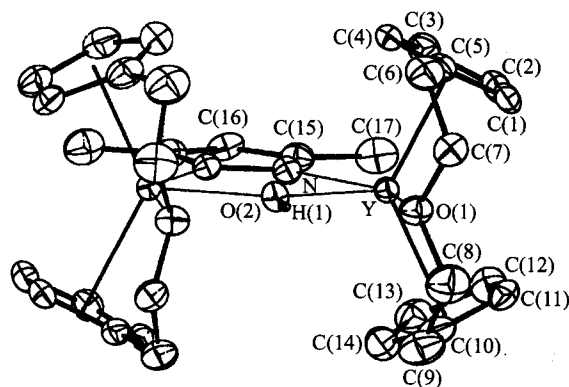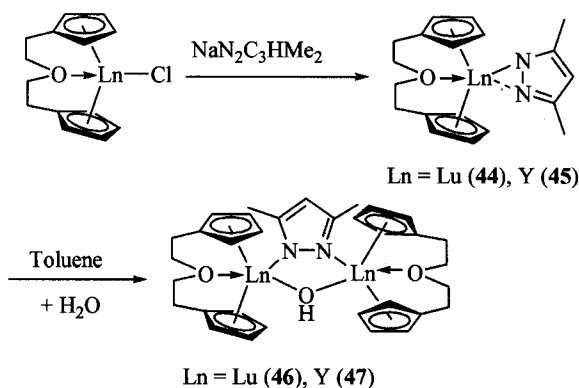
Scheme 2

Ln = Lu (**44**), Y (**45**)

Ln = Lu (**46**), Y (**47**)

Fig. 1　Molecular structure of **47**.

bridged by a pyrazilate via nitrogen and one hydroxyl group with C_2-symmetry. For this type of highly symmetric structure there is no other example known in dimeric organolanthanide complexes containing two different bridging ligands. The most remarkable feature of the structure of **47** is the presence of an intramolecular coordination bond between the oxygen atom of the 1, 1'-(3-oxapentamethylene) bridge and yttrium atom.

Study of the complexes of lanthanide metals that are in the + 2 oxidation state has yielded particularly remarkable and striking results in the case of the organometallic chemistry of rare earth.[20] Oxygen-containing five-atom chain bridged dicyclopentadienyl divalent lanthanide complexes $O(CH_2CH_2C_5H_4)_2Ln(THF)_2$ [Ln = Sm (**48**), Yb (**49**)] have been synthesized by the reduction of lanthanocene chlorides with sodium metal.[20f] Recrystalizing Yb complex **49** from dimethoxyethane (DME) provided single crystals suitable for X-ray diffraction study. Fig. 2 depicts the X-ray structure of $O(CH_2CH_2C_5H_4)_2Yb$-(DME) (**50**). The formal coordination number of the central metal is nine and the coordination geometry around the ytterbium ion can be described as an approximate trigonal bipyramid. The bond length of the bridged oxygen atom and the ytterbium ion is 0.2488 nm.

The poor solubility of some above ansa-matallocene complexes in hydrocarbon solvents, such as toluene, benzene and hexane, prevented us from investigating their feature, and the complexes with early lanthanide chlorides with those ligands could not be isolated. Moreover, a few chiral metallocene chlorides and derivatives have been isolated recently.[21a,21b] For solving these problems and examining the formation of the *meso* and *rac* isomers, bulky t-butyl or trimethylsilyl was introduced to 3-position of the Cp rings of 3-oxo-petamethyene bridged biscyclope-
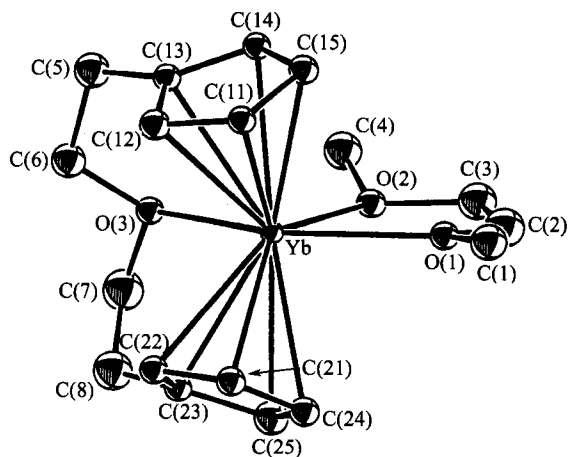
Fig. 2   Molecular structure of **50**.

ntadienyl ligand. The corresponding lanthanocene chloride complexes have been synthesized respectively as shown in Scheme 3.[21c] All these complexes are soluble in hydrocarbon solvents, such as toluene and hexane. Efforts to separate the *rac* isomer from *rac/meso* mixture isomer failed.

Scheme 3

Ln = Nd (**51**), Sm (**52**), Yb (**53**), Y (**54**)

Ln = La (**55**), Nd (**56**), Yb (**57**), Y (**58**)
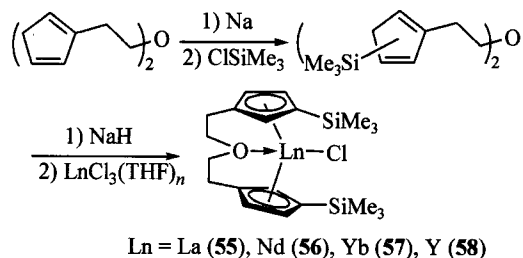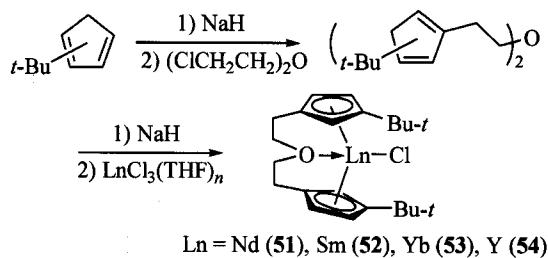
Over recent years, considerable efforts have been devoted to exploring organometallic chemistry of chiral ansa-metallocenes of lanthanides. *Rac/meso* mixtures of 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) ansa-lanthanocene chlorides [Ln = Pr (**59**), Nd (**60**), Gd (**61**), Dy (**62**), Ho (**63**), Lu (**64**), Y (**65**)] have been prepared by the reaction of 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) potassium salt with lanthanide

chlorides in moderate yields with a *rac* : *meso* ratio up to 6 : 1 determined by the integration on the ^{1}H NMR spectra of the five-member portion of indenyl rings.[22] The *rac* isomers of [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnCl(THF) were successfully isolated after recrystallization of a *rac/meso* mixture of [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnCl(THF) in THF. It is surprising that one THF molecule is coordinated in both the light and heavy lanthanoid complexes, considering the corresponding cyclopentadienyl analogues exist as unsolvated complexes. A representative ORTEP drawing of **60** is shown in Fig . 3 . Alkylation of *rac / meso* chlorides
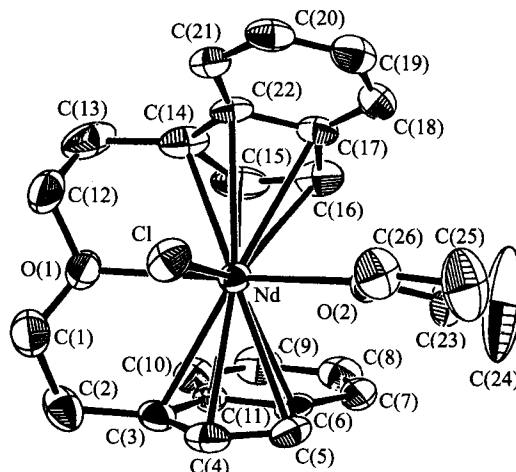

Fig. 3   Molecular structure of **60**.

mixture with LiCH$_2$SiMe$_3$ in toluene afforded the corresponding *rac*-[O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]Ln(CH$_2$SiMe$_3$) [Ln = Y (**66**), Dy (**67**), Yb (**68**), Lu(**69**)] isomers solely in moderate as outlined in Scheme 4.[23,24] No *meso* isomers were observed. An X-ray single crystal structure analysis of complex **66**, which shows two crystallographically molecules with the same configuration in the unit cell, unambiguously confirmed the unsymmetric structure (Fig. 4). Direct amidation of the *rac/meso* lanthanidocene chloride mixtures in toluene also provided solely pure racemic ansa-lanthanidocene amides, [O(CH$_2$CH$_2$C$_9$-H$_6$)$_2$]LnN(SiMe$_3$)$_2$ [Ln = Y (**70**), Pr (**71**), Nd (**72**), Yb (**73**), Lu (**74**)] isomers in moderate yield.[24] The chlorides are soluble in THF, and just slight soluble in toluene, while the hydrocarbyls and amides complexes (**67**—**74**) are very soluble in THF, DME, benzene and sparing soluble in hexane. Elemental analysis and spectroscopic data indicate that the amide and hydrocarbyl-complexes are solvent-free. It is worth to note that pure

racemic hydrocarbyls and amides can be obtained directly from the *rac/meso* lanthanidocene chloride mixtures. Thus, tedious and complicated separation of isomer is avoided.
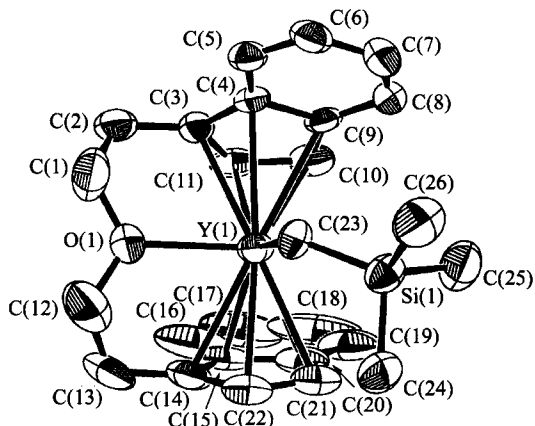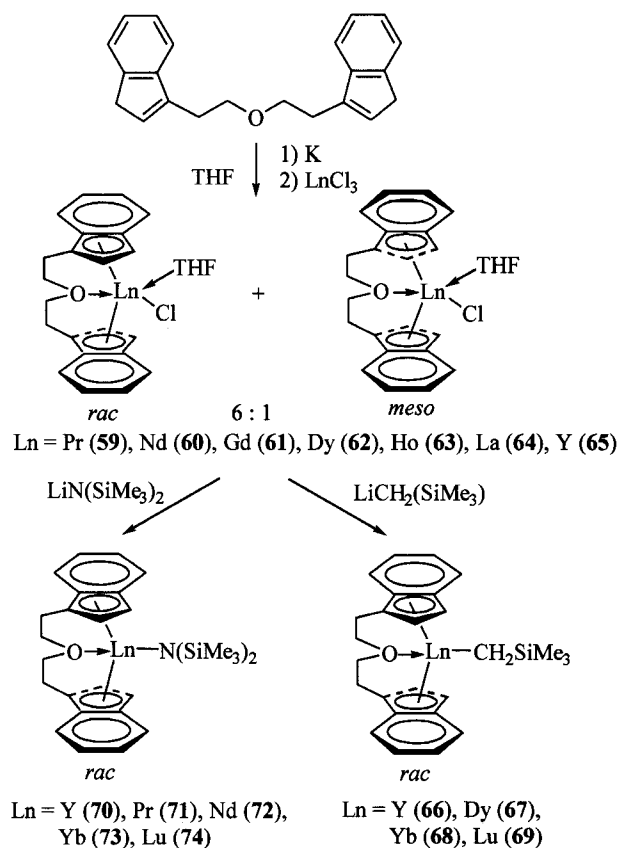
Scheme 4

rac   6 : 1   meso

Ln = Pr (**59**), Nd (**60**), Gd (**61**), Dy (**62**), Ho (**63**), La (**64**), Y (**65**)

LiN(SiMe$_3$)$_2$ LiCH$_2$(SiMe$_3$)

rac   rac

Ln = Y (**70**), Pr (**71**), Nd (**72**),   Ln = Y (**66**), Dy (**67**),
Yb (**73**), Lu (**74**)   Yb (**68**), Lu (**69**)

Fig. 4   Molecular structure of **66**.

Single atom bridges

It was reported that one-atom bridge could result in

further opening of the metal coordination sphere in the vicinity of the σ-ligand equatorial girdle/frontier orbitals and increase the reactivity of organometallic species, while preserving the beneficial properties of the η^5-ligand environment.[25,26] So far, no lanthanocene complexes with ansa-bond fluorenyl ligand were reported. As an extension of the ligand modification for lanthanide complexes, we synthesized these new types of C_s-symmetric methylene- or silyene-bridged fluorenyl cyclopentadienyl organolanthanide chloride, amide and hydrocarbyl complexes to investigate the activities toward MMA and lactone.[27]

Reactions between dilithio salt of diphenylmethylene bridged fluorenyl cyclopentadienyl and anhydrous lanthanide chlorides gave ate-type complexes [Li(THF)$_4$]-[LnCl$_2$ {(C$_{13}$H$_8$)CPh$_2$(C$_5$H$_4$)}] [Ln = Y (**75**), Lu (**76**)] (Scheme 5).[28] We attempted to extend this chemistry to light lanthanide elements, but failed. This can be explained by the steric consideration which determines the stability and structure of lanthanide complexes. The X-ray crystal structure of **76** consists of isolated ion pairs. Fig. 5 shows the anion adopts the pseudotetrahedral, bent metallocene motif commonly observed for Cp$_2$LnX$_2^-$ complexes. The central metal Lu tetrahedrally coordinated with the bridging ligand and the two Cl atoms with the angle of C(1)-Lu-Cl(2) 96.48(7)° and the bond lengths of Lu—Cl(1) 0.2501(2) nm and Lu—Cl(2) 0.2496(2) nm. Organolanthanide tetrahydroborate complexes, [Li-(THF)$_4$][Ln{(μ-H)$_3$BH}$_2${(C$_{13}$H$_8$)CPh$_2$(C$_5$H$_4$)}]] [Ln = La (**77**), Nd (**78**)], were synthesized directly by the reaction of [Ln(BH$_4$)$_3$(THF)$_3$] with (C$_{13}$H$_8$)CPh$_2$-(C$_5$H$_4$)Li$_2$ (Scheme 5). Complexes **77** and **78** have almost identical structures. Fig. 6 shows the ORTEP drawing of **78**. This compound exists as discrete cation and anion pairs, and shows two crystallographically independent molecules in the unit cell. The Nd is bonded to the cyclopentadienyl ring and fluorenyl ring in η^5 fashion, and to two BH$_4$ ligands in a symmetric geometry. The most remarkable structural feature of the complex is the mode of attachment of the tetrahedral BH$_4$ ligands. The two boron atoms have almost the same ligation geometry. Each of them is linked to the metal center via three μ-hydrogens bridging the B and the Nd atoms. The cations [Li-(THF)$_4$]$^+$ which exist in these crystal structures are classical.[29] Since the single atom bridge of the Ph$_2$C linker provides a relatively rigid ansa-metallocene ligand framework and serves to increase the dihedral angle between the cyclopentadienyl and fluorenyl planes, this leads to 'ope-
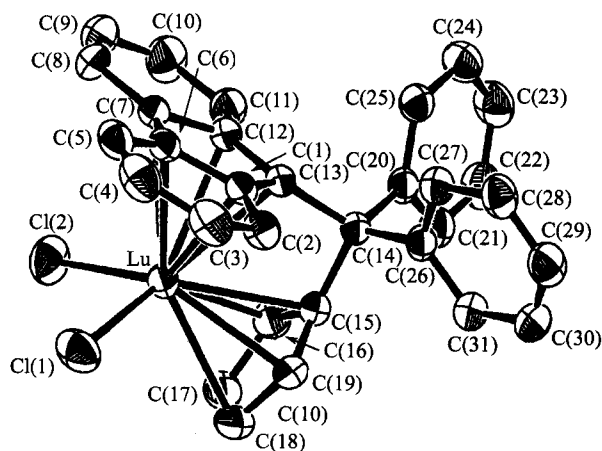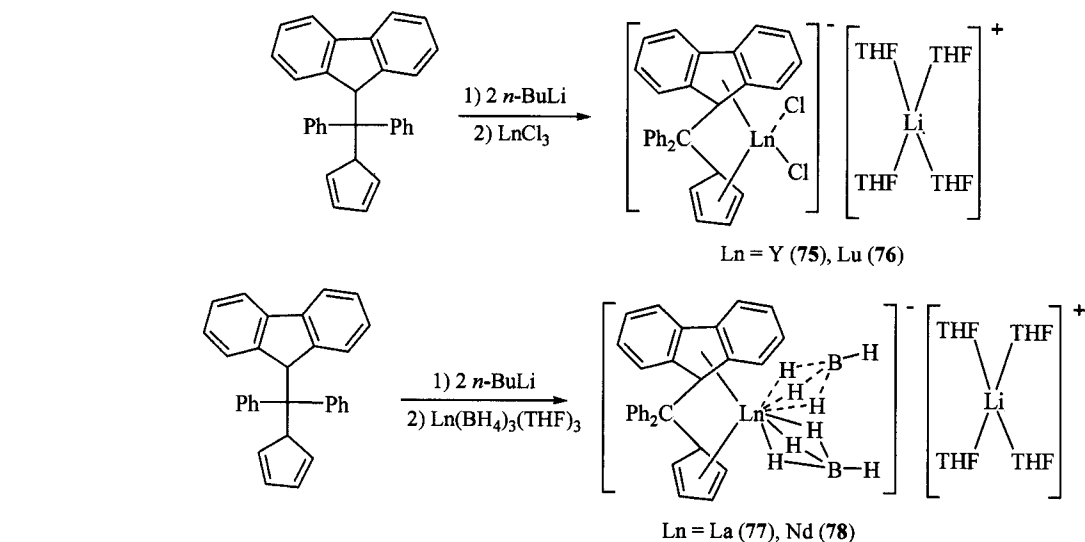
Scheme 5

Ln = Y (**75**), Lu (**76**)

Ln = La (**77**), Nd (**78**)

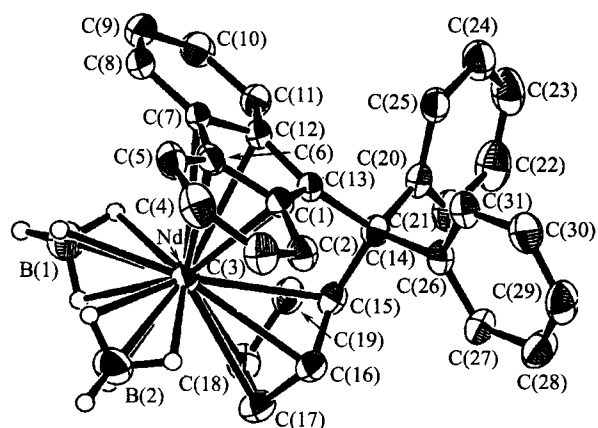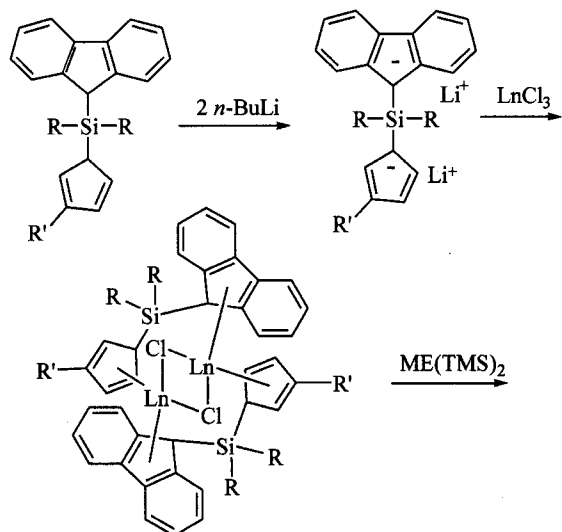**Fig. 5** Molecular structure of **76**.
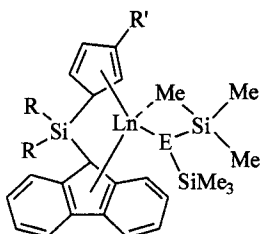

Fig. 6 Molecular structure of **78**.

ning' of the wedge between the two planes where BH_4 or Cl groups can be located on the metal to afford ate-type lanthanide complexes.

C_s-symmetric silyene-bridged fluorenyl cyclopentadienyl organolanthanide halide complexes were synthesized as shown in Scheme 6.[30] The representative X-ray crystal structure (Fig. 7) of those dimeric chlorides $[Me_2Si(C_5H_4)(C_{13}H_8)LnCl]_2$ [Ln = Y (**79**), Dy (**80**), Er (**81**), Lu (**82**)] indicates that all of the complexes assume the Cp-SiMe$_2$-Cp bridging coordination structures instead of the common chelating coordination structures. Organometallic complexes containing two cyclopentadienyl or two tetramethylcyclopentadenyl ligands bridged by silylene units are generally known to assume the metal-chelating structure, although only a few examples of bridging structure has been already reported.[31] It still remains unclear whether dialkylsilyene-linked biscyclopendienyl lanthanide complexes generally would be more stable as the chelating or bridging isomer. To understand the effect of different substituents on the coordination modes, solvent-free dimeric chloride with C_1-symmetric [Ph_2Si (t-BuC_5H_3) ($C_{13}H_8$) LnCl]$_2$ [Ln = Y (**83**), Dy (**84**)] was synthesized. X-Ray diffraction analysis revealed the existence of those C_1-symmetric complexes as a bridging coordination structure. This fact indicated that the bulkier substituents on the Cp ring and the silylene-bridged atom did not hamper the formation of the bridging coordination structure.

Scheme 6

R = Me, R' = H; Ln = Y (**79**), Dy (**80**), Er(**81**), Lu (**82**)
R = Ph, R' = t-Bu; Ln = Y (**83**), Dy (**84**)

E = N; R = Me, R' = H; Ln = Dy (**85**), Er (**86**)
E = CH; R = Me, R' = H; Ln = Dy (**87**), Er (**88**)

Fig. 7　Molecular structure of **79**.

The monomeric salt- and solvent-free amido and hydrocarbyl complexes $Me_2Si(C_5H_4)(C_{13}H_8)LnE(TMS)_2$ [E = N, Ln = Dy (**85**), Er (**86**); E = CH, Ln = Dy (**87**), Er (**88**)] were synthesized by the reaction of anhydrous $LnCl_3$ with the dilithio salt of the silylene-bridged
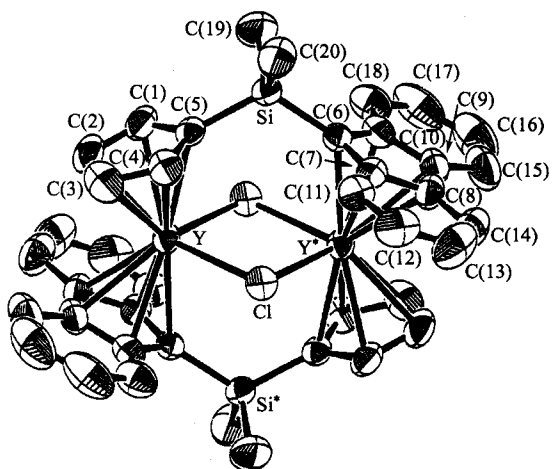
ligand in ether, followed by the treatment with ME-$(TMS)_2$ (M = K or Li; E = N, CH) in toluene in a one-pot procedure. The X-ray crystal structures of **85** and **87**, which are shown in Figs. 8 and 9, display γ-agostic interactions between the metal and methyl group in all of the amido and hydrocarbyl complexes.
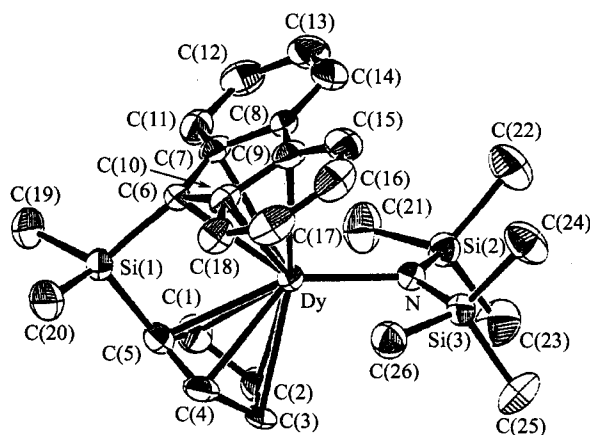
Fig. 8　Molecular structure of **85**.
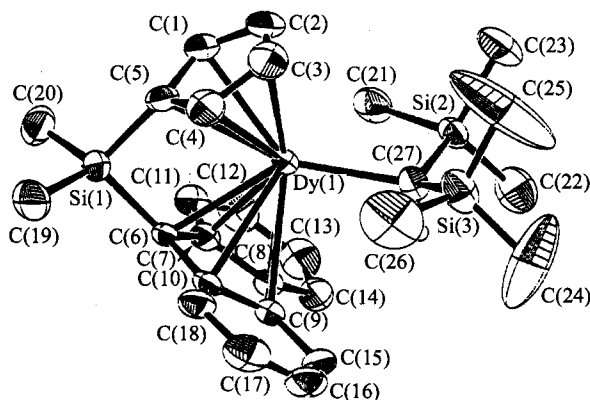
Fig. 9　Molecular structure of **87**.

Lanthanocene complexes with dornor-functionlized sidearm

Donating ability of the terminal functional group in the side chain can stabilize the π-complexes by the additional intramolecular coordination. In addition, sidearm participation may play an important role in catalytic processes. Consequently, the ether- or amine-tethered cyclopentadienyl and indenyl ligands have been used to stabilized lanthanocene complexes.[32] A series of lanthanide complexes containing ether- or amine-substituted cyclopentadienyl and indenyl ligands were prepared in our

group.[1f]

Lanthanocenes with 2-methoxyethylcyclopentadienyl ligand

Triscyclopentadienyl lanthanocenes, (C_5H_5)$_3$Ln, were first synthesized by Birmingham and Wilkinson.[33] The solid-state structures of trivalent lanthanocenes are dependent on the size of both the substituents on the cyclopentadienyl rings and the lanthanide metal.[34] Due to the formation of intramolecular coordination bonds, when $CH_3OCH_2CH_2C_5H_4^-$ was used as a ligand, 11-coordination light and middle lanthanide complexes, ($CH_3OCH_2CH_2C_5H_4$)$_3$Ln [Ln = La (**89**), Pr (**90**), Nd (**91**), Sm (**92**) and Gd (**93**)] were obtained.[35] X-Ray diffraction analyses showed that these complexes are monomers, in which the central metal ions are surrounded by three cyclopentadienyl rings and two oxygen atoms from two substituents, and the third oxygen atom of the other 2-methoxyethyl substituent remains free (Fig. 10). The important bond parameters for those triscyclopentadienyl lanthanocene complexes are listed in Table 2. It can be seen that the bond lengths of Ln—C (Cp ring) and Ln—O(1) follow the trends expected on the basis of ionic radial size. However, the bond length of Ln—O(2) does not follow the trend, but increases as the ionic radii decrease. These facts reveal that the complexes become coordinately over-saturated, as the ionic radii of central metal further decrease, the lanthanide metal would thus tend to form only one intramolecular coordination bond. Therefore, it is possible that 10-coordination complexes may be formed for the heavier lanthanide metals.

Using $CH_3OCH_2CH_2C_5H_4^-$ as a ligand, which can effectively satisfy the need of the largest lanthanide (lanthanum) for coordinate saturation by forming an intramolecular coordination bond, we have succeeded in syn-
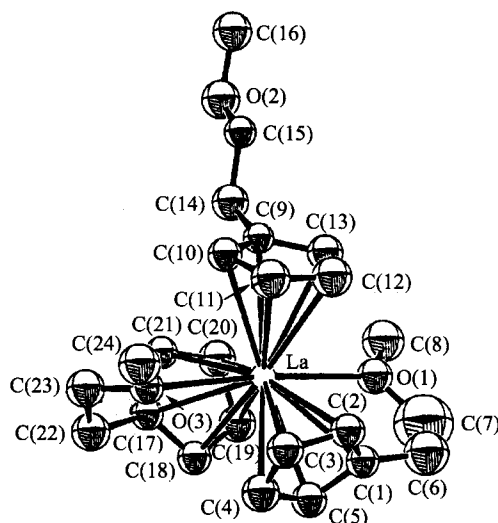

Fig. 10   Molecular structure of **89**.

thesizing biscyclopentadienyl complexes of the lanthanum metal and structurally characterizing the first example of biscyclopentadienyl lanthanum chloride [($CH_3OCH_2CH_2$-C_5H_4)$_2$La(μ-Cl)]$_2$ (**94**).[36] X-Ray structure analyses show that the complex is a chlorine-bridged dimmeric molecule with a symmetry center (Fig. 11). Each lanthanum atom is coordinated by two oxygen atoms from two methoxyethyl substituents, and the formal coordination number of lanthanum is 10. It is noteworthy that when the chlorine ion is replaced by the larger iodine ion, the lanthanum iodide is a monomer and the coordination number of lanthanum ion is 9.[37] This indicates that the size of the anion also affects the coordination number and the geometry of the central metal ion. The complexes ($CH_3OCH_2CH_2C_5H_4$)$_2$LnCl [Ln = Nd (**95**), Dy (**96**), Er (**97**) and Yb (**98**)] are not dimmers, but monomers (Fig. 12). The formal coordination number of the lanthanide metals is nine and the coordination geometry around the lanthanide metals can be described as pseudo-trigonal bipyramid.[38]

Table 2   Important structural data for complexes ($CH_3OCH_2CH_2C_5H_4$)$_3$Ln

Complex	La (**89**)	Pr (**90**)	Nd (**91**)	Sm (**92**)	Gd (**93**)
Ionic radius (nm)	0.1216	0.1179	0.1163	0.1132	0.107
Ln—O(1) (nm)	0.2752	0.2740	0.2731	0.2744	0.2701
Ln—O(2) (nm)	0.2806	0.2836	0.2846	0.2923	0.2985
Ln—C(η^5) (nm)	0.2860	0.2825	0.2807	0.2779	0.2705
O(1)-Ln-O(2) (°)	174.0	174.8	175.0	175.4	175.9
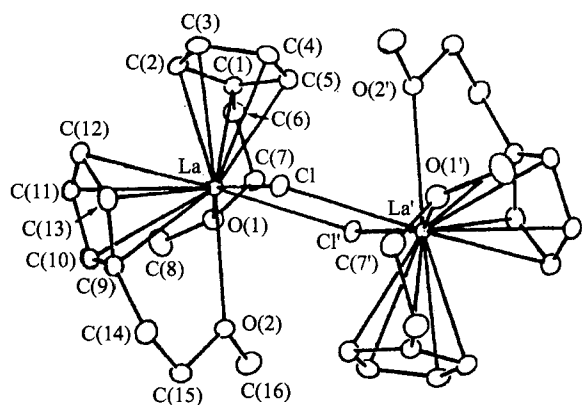
Fig. 11   Molecular structure of **94**.
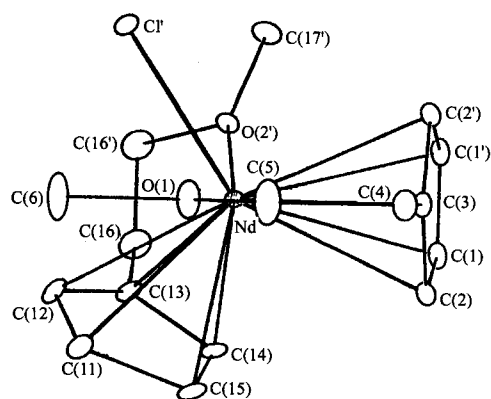
Fig. 12   Molecular structure of **95**.

We have focused on an extension of the reduction method with sodium hydride to synthesis organolanthanide hydrides. Neutral organolanthanide hydrides [(CH_3-$OCH_2CH_2C_5H_4$)$_2$Ln(μ-H)]$_2$ [Ln = La (**99**), Pr (**100**),

Ho (**101**) and Y (**102**)] have been obtained by the direct reduction of corresponding lanthanocene chlorides with excess sodium hydride in THF at 45 ℃.[39] Fig. 13 shows the X-ray crystal structure of [($CH_3OCH_2CH_2C_5$-

(a)

(b)
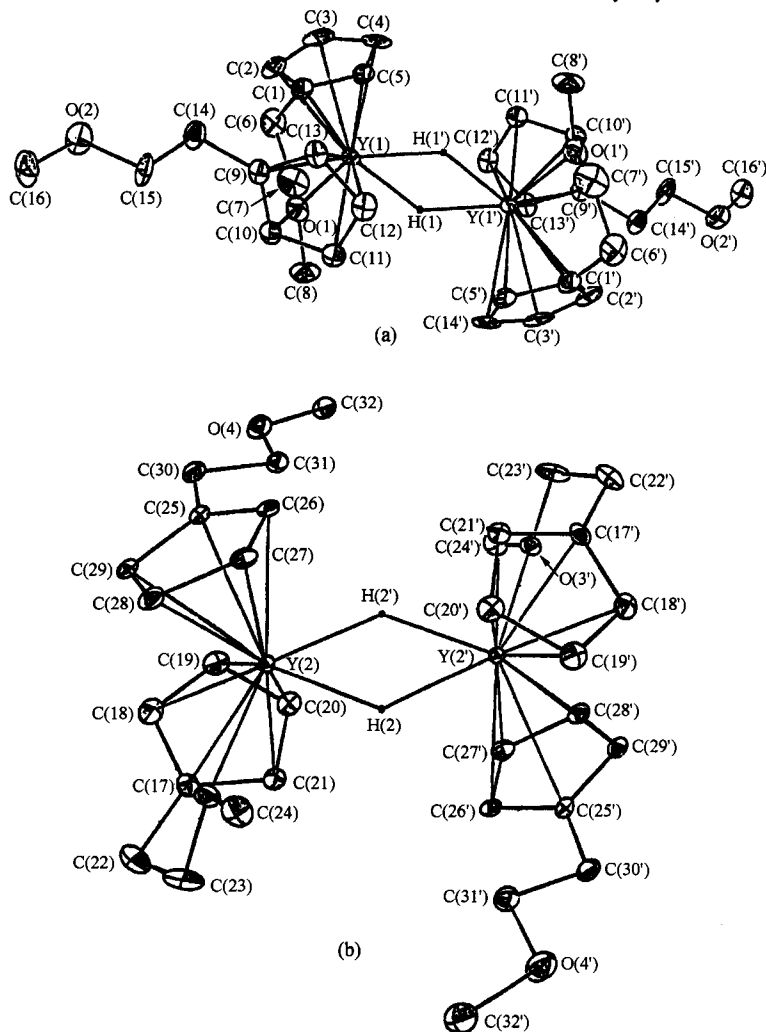
Fig. 13   Molecular structure of **102**.

$H_4)_2Y(\mu\text{-}H)]_2$, which is a hydrogen-bridged dimer with a symmetry center. In the unit cell there are two dimers which are not identical. However, in both dimers, each yttrium atom is coordinated by two Cp rings, two hydrogen atoms and one oxygen from one sidearm.

Lanthanocene chlorides and tetrahydroborates with 1-(2-*methoxyethyl*) *indenyl ligand*

Considering the unique features of indenyl ligand in exploring the chemistry of sandwich organometallic complexes, such as its diversity of bonding modes and the so-called 'indene effect' *etc.*,[40] it was believed that the replacement of cyclopentadienyl with indenyl would help to explore the chemistry of lanthanocene complexes. Moreover, it was envisioned that a properly-enhanced, sterically-demanding ligand could further suppress the flexibility to afford a complex with a defined structure, which in turn would facilitate the formation and isolation with stereoselectivity or even exclusivity, of some diastereoisomers of chiral lanthanocene complexes.

Deprotonation of indene derivative $MeOCH_2CH_2$-C_9H_7, which could be prepared directly from the reaction of methoxyethyl methanesulfonate $MeOCH_2CH_2OMs$ with indenyl lithium, with excess potassium metal suspended in THF provided a clear, slightly yellow solution. Reaction of the solution with a stoichiometric amount of anhydrous lanthanide chlorides provided corresponding chiral complexes $(MeOCH_2CH_2C_9H_6)_2LnCl$ [Ln = Y (**103**), La (**104**), Nd (**105**), Gd (**106**), Ho (**107**) and Lu (**108**)] as crystal in moderate yields (Scheme 7).[41] In the case of diamagnetic complexes, the ^1H NMR spectra indicate that some isomerizations occur when dissolved in THF . For the representative complex **103** , one species

predominates the ^1H NMR spectra with an approximate ratio of 25 : 1 for the major and minor isomers, determined from integration of the corresponding resonances of protons on the five-member portion of the indenyl rings. Examining the possible structure forms (Fig. 14), it is found that the formation of **II** and **III** are geometrically and sterically prohibited since the two coordinated sidearms are in a *cis* arrangement, and the most favorable form is **I** with a *trans* orientation of both the indenyl rings and sidearms. It is clear from the ^1H NMR spectra that the major isomer assumes a symmetrical structure in THF solution. The assignment was made on the basis of chemical shifts, splitting patterns and NOEs. X-Ray diffraction analysis shows that all complexes are *rac*-isomers and have very similar structures in solid state. The representative ORTEP drawing of **103** is depicted in Fig. 15. The coordination geometry is best described as distorted trigonal bipyramidal if an indenyl ring is regarded as occupying a single polyhedral vertex where the basal plane is defined by O(1), O(2) and Cl. All compounds are unsolvated 9-coordinate monomers, although they crystallize from the strongly coordinating solvent THF. It is worth noting that La complex has the monomeric structure considering its Cp analogue is a dimer in solid state.[36] The approximate planar indenyl rings are η^5-bonded to the central metals and both the indenyl rings and sidearms adopt a *trans* configuration as expected, presumably governed by the coordination geometry of the central metals together with steric factors, implying enhanced regularity relative to the Cp analogue.

Scheme 7

Ln = Y (**103**), La (**104**), Nd (**105**), Gd (**106**), Ho (**107**), Lu (**108**)

I (*SR / RS*)   **II** (*SR / RS*)

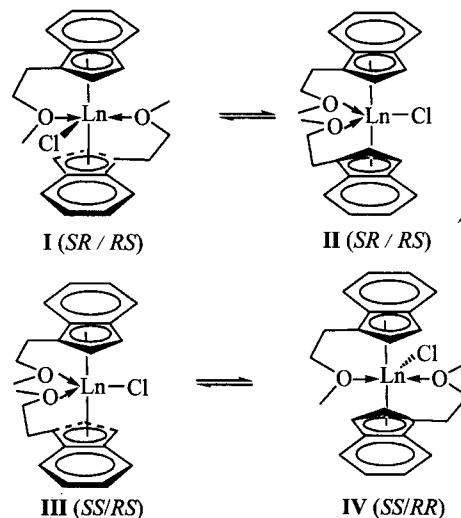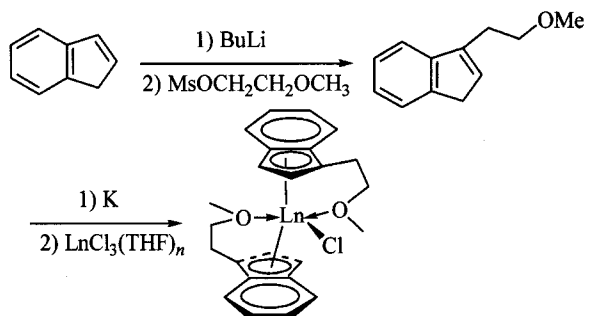**III** (*SS/RS*)   **IV** (*SS/RR*)

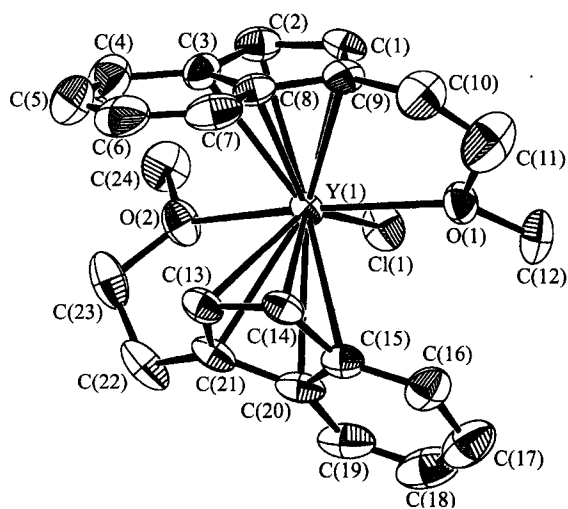**Fig. 14**   Possible structures of bis [1-(2-methoxyethyl) indenyl]lanthanide chlorides.

Fig. 15 Molecular structure of **103**.

Racemic planar chiral metallocenes bis(2-methoxyethylindenyl)yttrium and lanthanum tetrahydroborates ($MeOCH_2CH_2C_9H_6$)$_2$Ln(μ-H)$_n$BH$_{4-n}$ [Ln = Y, $n = 2$ (**109**); Ln = La, $n = 3$ (**110**)] were stereoselectively prepared and isolated in high yields by the reaction of the corresponding lanthanocene chlorides with sodium borohydride in THF at room temperature. The tetrahydroborate ions were identified as slipped bidentate (μ_2-H)$_2$BH$_2$ and tridentate (μ_3-H)$_3$BH in **109** and **110**, respectively.[42]

Lanthanocenes with 1-(2-dimethylaminoethyl) indenyl ligand

Solvent free divalent bis(2-dimethylamino-ethylindenyl)lanthanocene [Ln = Sm (**111**), Yb (**112**)] were synthesized as shown in Scheme 8.[43] The X-ray crystal structure of ($MeNCH_2CH_2C_9H_6$)$_2$Yb is shown in Fig. 16. Nitrogen atoms of both dimethylaminoethyl group are coordinated to the Yb atom to form intramolecular coordination bonds. Only one possible diastereomeric conformation (*rac*) with *trans* arrangement of both indenyl rings and coordinated sidearms was observed. The compound is unsolvated 8-coordinate monomeric complex in solid state.

Reactivity of lanthanocene complexes

A series of lanthanocene complexes with bridging ligands were synthesized in our group. The ultimate aim

Scheme 8

Ln = Sm (**111**), Yb (**112**)
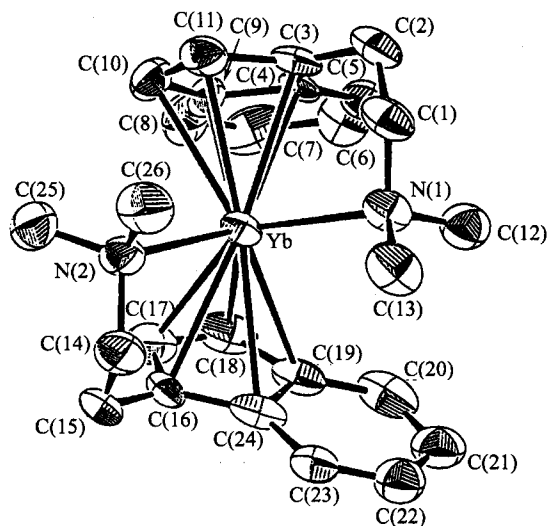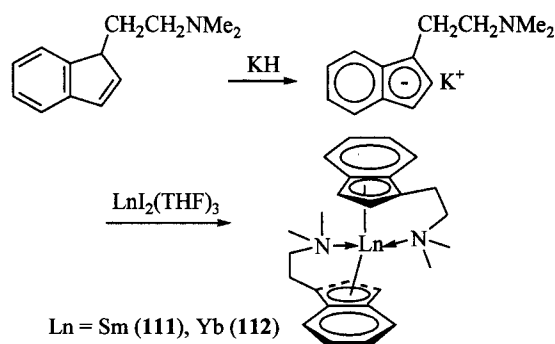
Fig. 16 Molecular structure of **112**.

of this approach is to obtain not only relatively stable but also more reactive organolanthanide catalyst species. How about the reactivity of those lanthanide derivatives? In order to answer this question and acquire more reactive lanthanocene species, the reactivities of some lanthanocene complexes in the following areas were investigated.

Reactivity of organolanthanide hydrides (in situ)

Reduction of 1-octene   Based on our studies on the reactivity of organolanthanide hydrides generated *in situ*,[44] we have investigated the ligand and metal tuning of the reactivity of organolanthanide hydrides, generated *in situ* from the reaction of lanthanocene chlorides with sodium hydride, toward the reduction of 1-octene (Table 3).

From Table 3 it can be seen that the properties of the bridging chains strongly affect the reactivity. The complexes **6** and **35** show no reactivity toward the redu-

Table 3 Effects of the bridging chain and metal on the reduction of 1-octene[a]

$$CH_3(CH_2)_5CH=CH_2 \xrightarrow[\text{NaH, THF, 45 °C}]{\text{Ln complex}} CH_3(CH_2)_5CH_2CH_3$$
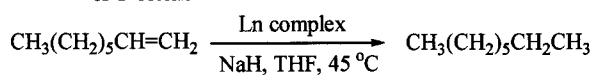
Entry	Complex	Conversion (%)[b]		
		24 h	44 h	72 h
1	$(C_5H_5)_2YCl$	14	20	32
2	$(CH_2)_5(C_5H_4)_2YCl(THF)$ (**6**)	0	0	0
3	$m\text{-}C_6H_4(CH_2C_5H_4)_2YCl(THF)$ (**35**)	0	0	0
4	$2,5\text{-}OC_4H_6(CH_2C_5H_4)_2YCl$ (**17**)	4	4	4
5	$O(CH_2CH_2C_5H_4)_2YCl$ (**13**)	64	84	95
6	$CH_3N(CH_2CH_2C_5H_4)_2YCl$ (**21**)	40	66	94
7	$CH_3N(CH_2CH_2C_5H_4)_2YbCl$ (**20**)	7	11	16
8	$CH_3N(CH_2CH_2C_5H_4)_2SmCl$ (**19**)	60	93	100
9	$CH_3N(CH_2CH_2C_5H_4)_2NdCl$ (**18**)	90	95	100

[a] Complex : NaH : 1-octene = 2 : 8 : 1, in THF at 45 °C. [b] Reduction product octane was determined by GC.

Table 4 Effects of the bridging chain and central metal on the catalytic dechlorination of benzyl chloride[a]

$$C_6H_5CH_2Cl \xrightarrow[\text{NaH, THF, 65 °C}]{\text{Cat. (10% mol)}} C_6H_5CH_3$$

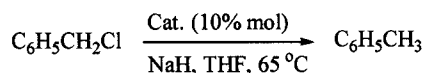| Entry	Complex	Conversion/%[b]			
		12 h	18 h	24 h	36 h
1	none			10	18
2	$(C_5H_5)_2YCl$	39	62	84	100
3	$(CH_2)_5(C_5H_4)_2YCl(THF)$ (**6**)	50	82	100	
4	$m\text{-}C_6H_4(CH_2C_5H_4)_2YCl(THF)$ (**35**)	10		24	41
5	$CH_3N(CH_2CH_2C_5H_4)_2YCl$ (**21**)	26	40	63	100
6	$O(CH_2CH_2C_5H_4)_2YCl$ (**13**)	69	93	100	
7	$2,5\text{-}OC_4H_6(CH_2C_5H_4)_2YCl$ (**17**)	42	72	98	100
8	$2,5\text{-}OC_4H_6(CH_2C_5H_4)_2YbCl$ (**16**)	45	63	85	98
9	$2,5\text{-}OC_4H_6(CH_2C_5H_4)_2SmCl$ (**15**)	57	84	100	
10	$2,5\text{-}OC_4H_6(CH_2C_5H_4)_2NdCl$ (**14**)	61	92	100	

[a] Complex : NaH : 1-octene = 0.1 : 4 : 1, in THF at 65 °C. [b] Determined by GC.

ction. The reason could be that the coordinating THF molecule does not dissociate and just obstructs the "cone angle of reaction", resulting in the olefin being incapable of coordinating to the metal and subsequently inserting into the Ln—H σ-bond. Complexes 13 and 21 show very high reactivity and are much more reactive than [Y-$(C_5H_5)_2Cl$], which might be due to the large "cone angle of reaction" and the change of the orientation of Cp rings arising from the intramolecular coordination between the oxygen or nitrogen atom and the metal, and no external THF coordinating to the metal and obstructing the angle. In addition, the increase of the electron density on the metal by the intramolecular coordination decreases its hardness. According to the hard and soft acid and base principle, the olefins will be easier to coordinate and the reaction readily occurs.

Catalytic dechlorination   Since catalytic dehalogenation of organic halides is one of the most important and fundamental transformation in synthetic organic chemistry and environmental decontamination, we have also examined the tunability of the organolanthanide hydrides (*in situ*) toward the dechlorination of benzyl chloride, by varying the ligands and central metals.[13,45] The results are summarized in Table 4.

From Table 4, it can be seen that all the complexes exhibit high catalytic activity in the order of **13 > 6 > 17 > [(C_5H_5)₂YCl] > 21 > 35**. The activity of early lanthanide metals is a little better than that of late ones.

This is different from the results for the 1-octene reduction, indicating the tunability of these organolanthanide hydride species (*in situ*) varies for the different reactions. Different reaction mechanisms are probably responsible for these results. Nevertheless, the lanthanide metals show the similar tunability trends in both reactions. The goal of acquiring more active organolanthanide hydrides (*in situ*) can be achieved by both 'ligand tuning' and 'metal tuning', *i. e.* selecting the appropriate ligand and the early lanthanide metals.

Polymerization of MMA *and lactone*

Yasuda's and Marks' groups have studied the activity of the C_{2v}- and C_1-symmetric organolanthanocene complexes for the polymerization of methyl methacrylate (MMA).[46,47] As an extension of the ligand modification for lanthanide complexes, we have reported the synthesis of a new type of C_s-symmetric silyene-bridged fluorenyl cyclopentadienyl organolanthanide complexes and their application toward the polymerization of MMA.[30] The polymerization was performed in toluene, and after a fixed time the reaction was quenched with acidified methanol. Results are summarized in Table 5. All of these C_s-symmetric complexes show comparably high initiating activity (60%—100%) and high syndiotacticity (60%—83%). These results are very different from

those reported by Youngkyn and co-workers.[48] They used one of the Si-bridged C_s-symmetric amide complexes $[Me_2Si(C_5Me_4)(Flu)]YN(TMS)_2$ as catalyst, and obtained the iso-rich poly(MMA) in very low yield. It is likely that the stereoregularity varies with subtle difference in steric bulkiness between the complexes. From the results it can be seen that the slight change of R group, which changes from $N(TMS)_2$ to $CH(TMS)_2$, led to obvious difference in activity. When lowing the temperature, the conversion and stereoregulation for the polymerization by amide complexes increased, while those by hydrocarbyls decreased. It can also be seen that Er complexes have higher stereoseletivity than the Dy in this case.

Table 5 Data for the polymerization of methyl methacrylate[a]

Entry	Catal.	tp	Tp (℃)	Conv. (%)	Stereochem. (%) rr	rm	mm
1	85	1	20	80.5	61	31	8
2	85	1	0	81.7	64	27	9
3	85	0.5	− 20	98.2	59	26	4
4	85	0.5	− 78	90.1	73	21	6
5	85	1	− 95	100	80	20	0
6	87	1	20	100	60	33	7
7	87	0.5	0	88.6	59	34	7
8	87	1	− 78	61.4	52	36	12
9	86	2	0	67.5	67	26	7
10	86	0.5	− 78	100	82	12	0
11	86	1	− 95	82.7	83	17	0
12	88	0.5	0	100	56	29	15
13	88	0.5	− 78	48.3	68	26	4
14[b]	86	3	12	56.3	55		
15[c]	86	3	12	28.5	60		

[a] Reaction condition: initiator connection, 0.5 mol% monomer; solvent, toluene; sol./$[M_0]$ = 1 (V/V). [b] Solvent, THF; sol./$[M_0]$ = 2 (V/V). [c] Solvent, DME; sol./$[M_0]$ = 2 (V/V).

We have found that the amides rac-[O-$(CH_2CH_2C_9H_6)_2$] $LnN(SiMe_3)_2$ and hydrocarbyl complexes rac-$[O(CH_2CH_2C_9H_6)_2]LnCH_2SiMe_3$ are efficient single-component catalysts for MMA polymerization (Table 6).[24] The effects of solvent and reaction temperature on the polymerization were studied. Very high molecular weight ($M_n > 10^6$) iso-rich poly(MMA) was obtained at lower temperature, while at high temperature low molecular weight moderately syndiotactic poly(MMA) was obtained. The polymerization behavior was demonstrated to be associated with rac/meso interconversion of

the active center.

Table 6 Data for the polymerization of methyl methacrylate using lanthanocene amides and hydrocarbyls[a]

Catalyst	Solvent	Tp (℃)	Conv. (%)	rr	rm	mm
70	THF	30	6	45	32	23
70	THF	0	26	27	21	52
70	THF	− 25	62	18	19	63
70	THF	− 50	0			
68	DME	30	22	53	30	17
68	DME	0	42	56	28	16
68	DME	− 50	56	18	16	66
68	DME	− 78	0			
68	Toluene	− 25	28	30	20	50
72	THF	5	30	44	28	28
70	THF	5	13	43	28	29
73	THF	5	11	54	32	14
74	THF	5	13	57	31	12
67	DME	0	77	50	28	22
68	DME	0	37	52	27	21

[a] Reaction condition: cat./MMA (mol/mol) = 1:500; polymerization time, 9 h; MMA/solvent (V/V) = 1:1.

The catalytic activity of the amide compounds **85** and **86** was examined toward ring opening polymerization of lactones. Polymerization of lactones was performed in toluene or dichloride methane solution and after a fixed time the reaction was quenched with acidfied methanol. Results of polymerization are summarized in Table 7. All of these complexes show comparably high activity for ring opening polymerization of ε-caprolactone (CL) or δ-valerolactone (VL) in toluene. The polymers formed are of high molecular weight ($M_w > 3 \times 10^4$) and show low polydisperisities ($M_w/M_n < 2.0$).

Summary

For the past decade, our efforts have been devoted to the synthesis, characterization and applications of lanthanocene complexes with a series of designed η^5-ligands. The significant contribution of Qian's group on organolanthanide chemistry is the introduction of heteroatoms, especially oxygen and nitrogen, in ring-bridges and sidearms linked to the cyclopentadienyl and indenyl ligands. Using those ancillary ligands, which are effective in preventing the complexes from undergoing intermolecular ligand redistribution, lanthanocene complexes are readily accessible, but also more reactive.

A series of chiral 1,1'-(3-oxapentamethylene)-

bridged bis(indenyl) ansa-lanthanocenes were highly stereoselectively synthesized. The rac-[O(CH$_2$CH$_2$-C$_9$H$_6$)$_2$]LnCl(THF) complexes were isolated after recrystalization of rac/meso mixture of [O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]-LnCl(THF) in THF. Pure racemic ansa-lanthanocene amides rac-[O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnN(SiMe$_3$)$_2$ and hydrocarbyl complexes rac-[O(CH$_2$CH$_2$C$_9$H$_6$)$_2$]LnCH$_2$-SiMe$_3$ were conveniently synthesized by direct amidation or alkylation of the rac/meso mixture of lanthanocene chlorides in toluene. The amides and hydrocarbyl complexes are active for the polymerization of MMA. Very high molecular weight ($M_n > 10^6$) iso-rich poly(MMA) was obtained at lower temperature.

By using one atom bridged cyclopentadienyl and fluorenyl as ligand, C_s and C_1 symmetric lanthanocene chloride, hydrocarbyl, amide and tetrahydroborate complexes were synthesized. Structure features of silylene bridged lanthanocene chlorides are metal-bridging coordination mode. But the methylene bridged lanthanocene chlorides and tetrahydroborates are ate-type complexes. The C_s-symmetric organolanthanides can be used as efficient catalysts for the the synthesis of syndio rich poly(MMA). All of the amide complexes show comparably high activity for ring opening polymerization of ε-caprolactone or δ-valerolactone in toluene. The polymers formed are of high molecular weight and show low polydisperisities.

Table 7 Data for the ring opening polymerization of lactones[a]

| Entry	Cat.	Solvent	Mon.	[mon.]/[cat.]	Tp (℃)	Yield (%)	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n
1	85	Toluene	CL	180	0	76	3.21	1.76	1.81
2	85	Toluene	CL	225	0	85	4.91	2.70	1.81
3	85	Toluene	CL	450	0	83	8.10	5.00	1.62
4	85	Toluene	CL	675	0	88	9.79	5.85	1.67
5	85	Toluene	CL	675	25	90	2.95	1.36	2.16
6	85	CH$_2$Cl$_2$	CL	675	25	57	0.88	0.51	1.72
7	85	Toluene	VL	600	25	25	2.79	1.93	1.45
8	86	Toluene	CL	130	0	100	3.52	1.98	1.77

[a] Reaction conditions: time, 2 h; solv/[M$_0$] = 2 (V/V).

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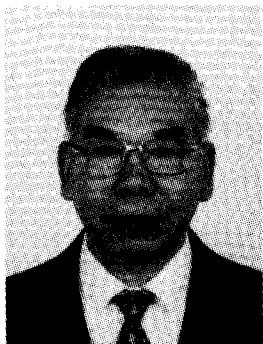
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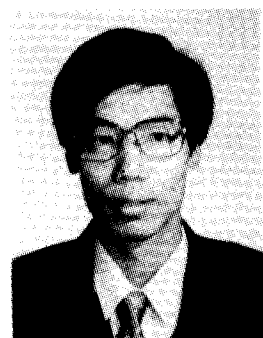
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