

Studies on organolanthanide complexes. Part 61¹

Synthesis and characterization of 3-oxa-pentamethylene bridged *ansa*-metallocene chlorides of rare earth elements

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Abstract

Several complexes $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_3\text{H}_3\text{R})_2\text{LnCl}]$ ($\text{R} = \text{t-Bu}$, $\text{Ln} = \text{Y}$, Nd , Sm , Yb ; $\text{R} = \text{SiMe}_3$, $\text{Ln} = \text{La}$, Y , Nd , Yb) were synthesized using chelating ligands and characterized by mass-, IR-, ^1H NMR-spectroscopies and elemental analyses. The spectra indicate that these complexes are unsolvated *ansa*-metallocene chlorides and the two bridged cyclopentadiene rings coordinate to the same metal ion with an intramolecular coordination bond between the oxygen atom of the bridge and the metal ion. These complexes are still sensitive to air and moisture, but they all have good thermal stability under inert gas and excellent solubility in hydrocarbon solvents. The reactivities of the systems of these metallocene chlorides and sodium hydride were investigated. Compared with the solubility of these complexes in a range of solvents, the influences of steric factors arising from the bulky substituents on the cyclopentadiene rings or the radial size of the metal ions are relatively slight.

Keywords: Y; Nd; Sm; Yb; La; Synthesis; Bridged *ansa*-metallocene

1. Introduction

There has been considerable current interest in the studies of *ansa*-metallocene compounds of rare earth elements [1]. It has been reported that metallocene compounds of rare earth elements containing M–H or M–C σ bonds are highly reactive to alkenes, alkynes, and some stable σ bonds including N–H and C–O bonds [2]. Moreover, studies of these sorts of complex have been considered to be valuable for insight into mechanistic aspects of the polymerization of alkenes, since they are isoelectron neutral analogues of the $[\text{Cp}_2\text{MR}]^+ d^0$ Group 4 catalysts which have been accepted as being key intermediates in the polymerization [3]. Metallocene chlorides are most common precursors for the preparation of derivatives with M–H, M–C or M–N bonds. In our laboratory, several ancillary ligands [4] were designed to obtain stable and highly reactive organometallic species of rare earth elements, as shown

in Fig. 1. It was found that the *ansa*-metallocene compounds with the oxygen-containing ligand showed higher reactivities and existed as unsolvated monomers, benefiting from the formation of an intramolecular coordination bond between the oxygen atom of the bridge and the metal ion [5]. However, the poor solubility of these complexes in hydrocarbon solvents, such as toluene, benzene and hexane, prevented us from investigating their features further, and early lanthanide chlorides with these ligands could not be isolated. Moreover, a few chiral metallocene chlorides and derivatives have been isolated recently [6]. The aim of the research is to solve these problems and examine the formation of the *meso* and *race* isomers.

2. Results and discussion

Scheme 1 summarizes the chemistry that led to the preparation of 2,2'-bis (3-*tert*-butylcyclopentadienyl) ethyl ether. The procedure provided a yellow oil originally. The crude product was purified by passage

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¹ For Part 60 see Ref. [1].

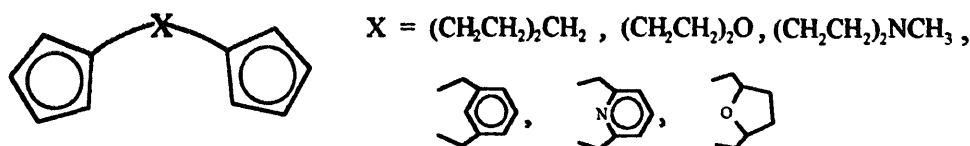


Fig. 1. Previously reported chelating ligands in this series of papers.

through a short pad of silica gel affording a colorless oil. Unfortunately, the polymerization on the supports reduced the yield drastically. Compound **1** exists as a mixture of regioisomers in respect of the position of the double bonds. Initial attempts to prepare **2**, following a procedure similar to that for **1**, met with failure. The poor nucleophilicity of $\text{NaC}_5\text{H}_4\text{SiMe}_3$ is presumably responsible for the inertness. A modified procedure in which the bridge was introduced before SiMe_3 gave **2** in 18% yield. Exposure of **1** or **2** to sodium hydride in THF at 45°C provided a slight yellow solution of the disodium salts of **1** or **2**. The target complexes were synthesized by treatment of LnCl_3 or YCl_3 suspended in THF with equimolar quantities of the disodium salts of **1** or **2** in THF solution at -78°C for 2 h, followed by stirring for 48 h at ambient temperature prior to removal of the solvent in vacuo, as shown in Schemes 1.

The crude products were purified by recrystallization in hexane at -30°C , with the yield exceeding 60%. All the new complexes are soluble in hydrocarbon solvents, such as toluene and hexane, though they are still very sensitive to air and moisture. Efforts to distinguish between the *raceme* and *meso* isomers failed, if they existed as expected. Under the same condition, instead of the desired lanthanum chloride we obtained a bridged binuclear tricyclopentadienyl complex when $\text{R} = \text{CMe}_3$, which presumably resulted from the ionic redistribution reaction, as shown in Scheme 3.

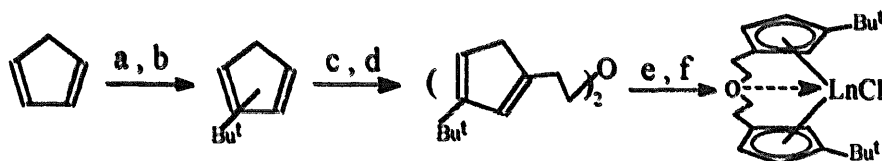
The electron impact (EI) mass spectra of these complexes were measured. Complexes **3–6** give high relative intensity of peaks of parent molecular ions $[\text{M}]^+$ and characteristic fragments including $[\text{M} - \text{Cl}]^+$, $[\text{M} - \text{HCl}]^+$ and $[\text{M} - \text{CH}_3]^+$ (Table 1). The appearance of $[\text{M}]^+$ contributed to the formation of the intramolecular coordination bond [1]. The more favored cleavage of the C–Si bond is probably responsible for the low relative intensity or absence of the parent molecular peaks of **7–10**, considering the m/e of 73 (SiMe_3) being the basic peak in all cases (Table 2). There are two forms, I

and II, of these sorts of complex, as shown in Fig. 2, but the appearance of the $[\text{M}]^+$, $[\text{M} - \text{CH}_3]^+$, as well as the absence of binuclear fragments, leads to the conclusion that these complexes are of type I [7]. The formation of the other isomer may be excluded by the intramolecular coordination bond and the bulky substituents on the cyclopentadiene rings.

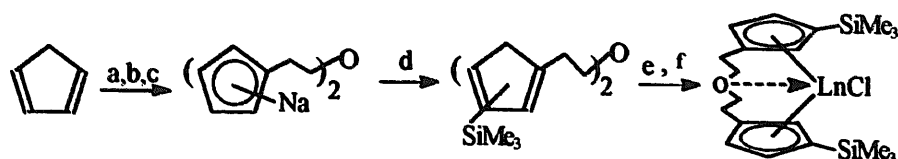
The ^1H NMR spectra of complexes **3**, **7** and **8** in C_6D_6 at 25°C indicate that the molecules are unsymmetrical on the ^1H NMR time scale (300 MHz): for instance, the protons of methyl groups of ^tBu or SiMe_3 consist of multiplets or double-multiplets instead of singlets (Table 3). There are several reasons that could contribute to the results, including: (1) the long bridge or ionic property of the Cp–M bond which allows the rings to rotate to some extent; (2) the effects of the restricted rotation of the C–C and C–Si bonds. The exact reasons are not yet clear.

The IR spectra of all complexes show very similar features from $180\text{--}4000\text{cm}^{-1}$. The absorptions of the cyclopentadiene rings are characteristic of an η^5 -coordination fashion, especially the sharp peak at ca. 3060cm^{-1} [8], while the Cp–H stretching vibration intensity reduces to mild or weak ones in these complexes from strong peaks in unsubstituted cyclopentadienyl lanthanides at around 1000cm^{-1} . It is reasonable that the vibration shifts slightly to low frequency in complexes **7–10**, as SiMe_3 serves as a delocalizing group. The asymmetric C–O–C stretching vibration was assigned at around 1060cm^{-1} , shifting to low frequency with $\Delta\nu = 40\text{--}50\text{cm}^{-1}$, in agreement with the formation of the intramolecular coordination bond [4].

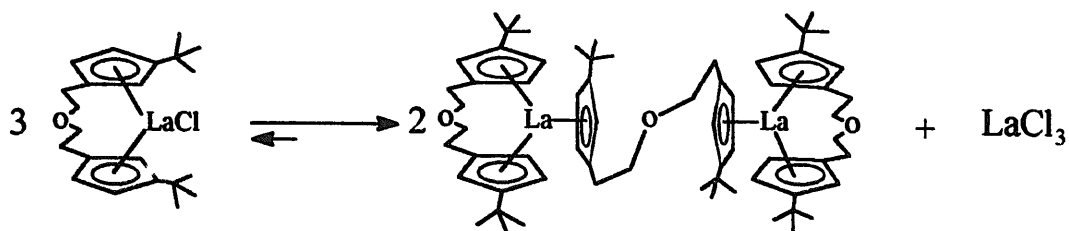
In our previous papers we established that the organolanthanide–sodium hydride systems could dehalogenate organohalides and reduce olefins in THF. It has been known that coordinative solvents depress the activities of the complexes by competitive coordination [9]. It was also reported that the complexes of rare earth elements could react with THF [10]. As the complexes



Scheme 1. (a) EtMgBr , Et_2O , r.t.; (b) $\text{ClC}(\text{CH}_3)_3$, Et_2O , 0°C to r.t. (a–b, 44%); (c) NaH , THF, 40°C ; (d) $(\text{ClCH}_2\text{CH}_2)_2\text{O}$, THF, 0°C to r.t. (c–d, 28%); (e) NaH , THF, 45°C ; (f) $\text{LnCl}_3(\text{thf})_n$, THF, -78°C to r.t. (e–f, 60–70%). Ln = Y (**3**), Nd (**4**), Sm (**5**), Yb (**6**).



Scheme 2. (a) Na (sand), THF, 0°C to r.t.; (b) $(\text{ClCH}_2\text{CH}_2)_2\text{O}$, THF, 0°C to r.t.; (c) Na (sand), THF, 45°C; (d) ClSiMe_3 , THF, -10°C, (a–d, 18%); (e) NaH, THF, 45°C; (f) $\text{LnCl}_3(\text{thf})_n$, THF, -78°C to r.t. (e–f, 60–70%). Ln = La (7), Y (8), Nd (9), Yb (10).



Scheme 3.

Table 1
EI-MS data of $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{Bu}^t)_2\text{LnCl}$ m/e (%RA)^a

| Fragment | Y | Nd | Sm | Yb |
|--|------------|------------|------------|------------|
| $[\text{M}]^+$ | 436(9.39) | 489(—) | 499(6.83) | 521(—) |
| $[\text{M} - \text{CH}_3]^+$ | 421(9.94) | 474(—) | 484(4.18) | 506(1.27) |
| $[\text{M} - \text{Cl}]^+$ | 401(11.10) | 454(12.58) | 464(7.71) | — |
| $[\text{M} - \text{Cl} - \text{CH}_3]^+$ | 386(17.79) | 439(33.04) | 449(10.02) | 471(—) |
| $[\text{M} - \text{Cl} - \text{CH}_4]^+$ | 385(79.05) | 438(49.19) | 448(40.73) | 470(—) |
| $[\text{C}_{10}\text{H}_{13}\text{O}]^+$ | 149(90.91) | 149(63.61) | 149(71.26) | 149(58.92) |
| $[\text{C}_{10}\text{H}_{13}]^+$ | 133(100) | 133(76.26) | 133(76.24) | 133(84.00) |
| $[\text{MCl}]^+$ | 124(3.20) | 177(10.78) | 187(8.39) | 209(1.58) |
| $[\text{C}_7\text{H}_7]^+$ | 91(61.60) | 91(57.26) | 91(99.33) | 91(88.27) |
| $[\text{C}_6\text{H}_7]^+$ | 79(25.26) | 79(25.76) | 79(37.58) | 79(35.52) |
| $[\text{C}_4\text{H}_9]^+$ | 57(94.73) | 57(100) | 57(100) | 57(100) |

^a Data are based on Y(89), Nd(142), Sm(152), Yb(174).

Table 2
EI-MS data of $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{SiMe}_3)_2\text{LnCl}$ m/e (%RA)^a

| Fragment | Y | La | Nd | Yb |
|---|------------|------------|------------|------------|
| $[\text{M}]^+$ | — | 518(2.54) | 521(—) | — |
| $[\text{M} - \text{CH}_3]^+$ | 453(8.91) | 503(31.44) | 506(7.29) | 538(4.35) |
| $[\text{M} - \text{Cl}]^+$ | 433(—) | 483(7.44) | 486(—) | 518(—) |
| $[\text{C}_{16}\text{H}_{21}\text{OSiClM}]^+$ | 381(35.16) | 431(16.7) | 434(3.68) | 466(4.04) |
| $[\text{C}_{14}\text{H}_{16}\text{OM}]^+$ | 289(31.36) | 339(22.40) | 342(3.17) | 374(2.67) |
| $[\text{MCl}]^+$ | 124(3.50) | 174(—) | 177(1.50) | 209(6.11) |
| $[\text{C}_{10}\text{H}_{16}\text{Si}]^+$ | 164(6.95) | 164(11.30) | 164(10.13) | 164(4.78) |
| $[\text{C}_9\text{H}_{13}\text{Si}]^+$ | 149(15.19) | 149(13.47) | 149(10.80) | 149(10.26) |
| $[\text{C}_8\text{H}_{11}\text{Si}]^+$ | 135(10.29) | 135(9.78) | 135(8.05) | 135(3.98) |
| $[\text{C}_7\text{H}_7]^+$ | 91(38.90) | 91(21.32) | 91(22.87) | 91(31.95) |
| $[\text{C}_3\text{H}_9\text{Si}]^+$ | 73(100) | 73(100) | 73(100) | 73(100) |

^a Data are based on La(139), Y(89), Nd(142), Yb(174), Cl(35).

Table 3
¹H NMR data for complexes 3, 7 and 8 (δ , ppm, C_6D_6 , 25°C, SiMe_4)

| Complex | C_5H_3 | OCH_2 | CH_2 | CH_3 |
|---------|------------------------|----------------------------|---------------|-------------------|
| 3 | 5.8–6.4 (m, 6H) | 3.3, 3.6, 3.8, 4.0 (m, 4H) | 2.6(m, 4H) | 1.4, 1.6 (m, 18H) |
| 7 | 6.0–6.8 (m, 6H) | 3.2, 3.6, 3.8, 4.0 (m, 4H) | 2.4(m, 4H) | 0.5 (m, 18H) |
| 8 | 6.0–6.8 (m, 6H) | 3.2, 3.6, 3.8, 4.0 (m, 4H) | 2.4(m, 4H) | 0.4 (m, 18H) |

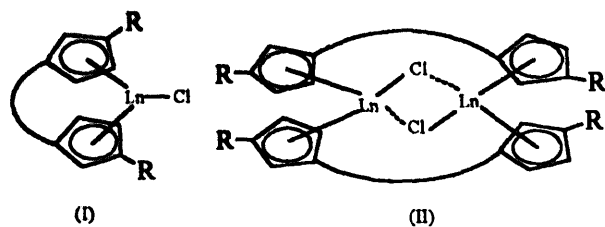


Fig. 2. Two possible forms of the bridged metallocene chloride.

obtained have excellent solubility in hydrocarbon solvents, what will happen if the systems are switched to toluene or hexane? Moreover, we wondered whether the introduction of bulky substituents on the rings, which could block the 'cone angle of reaction' regarded as a crucial factor to activities of metallocene derivatives, would affect the reactivities of the complexes. We investigated the catalytic dehalogenation of aryl halides and the stoichiometric reduction of 1-octene with the systems of the *ansa*-metallocene chlorides and excess sodium hydride. The results are summarized in Tables 4 and 5 respectively. It can be seen that the reactivities of the systems depend on the solvent used in these reactions. The reaction proceeded smoothly in THF, but no reaction took place in toluene or hexane after 60 h (by GC). The requirement of an aprotic dipolar solvent of NaH is presumably responsible for the inertness [11]. The selectivity of the reaction of $O(CH_2CH_2C_5H_3R)_2LnCl=NaH$ with 1-octene was slightly affected by the substituents R on the cyclopentadiene rings. No isomerization product, such as 2-octene, was detected by GC, employing metallocene chlorides with the $SiMe_3$ substituted ligand. If a *tert*-butyl group was substituted for β -H on the rings, 2-octene (15–20%, less than the analogues where $R = H$ [5]) was formed after 12 h, but the sole reduction product octane was given after 48 h. This implied that 2-octene could also be reduced under this condition, which is different from the

Table 4
Reduction dehalogenation of arylhalides catalyzed by $O(CH_2CH_2C_5H_3R)_2LnCl=NaH$ systems^a

| Entry | Sub. | Ln | R | Solvent | Reduction (%) | | |
|-------|------------------|----|-----------------|---------|------------------|-----|-----|
| | | | | | 12h | 24h | 36h |
| 1 | Tol-Br- <i>p</i> | Y | ^t Bu | THF | 28 | 100 | — |
| 2 | Tol-Br- <i>p</i> | Sm | ^t Bu | THF | 17 | 70 | 100 |
| 3 | Tol-Br- <i>p</i> | Nd | ^t Bu | THF | 16 | 70 | 97 |
| 4 | Tol-Br- <i>p</i> | Yb | ^t Bu | THF | 33 | 74 | 100 |
| 5 | Tol-Br- <i>p</i> | Y | $SiMe_3$ | THF | 11 | 57 | 90 |
| 6 | Tol-Cl- <i>p</i> | Yb | ^t Bu | THF | 6 | 12 | 31 |
| 7 | Tol-F- <i>p</i> | Yb | ^t Bu | THF | 0 | 0 | 0 |
| 8 | C_6H_5I | Y | ^t Bu | THF | 100 ^b | — | — |
| 9 | C_6H_5Br | Y | ^t Bu | THF | — | 100 | — |
| 10 | C_6H_5Br | Y | ^t Bu | Tol | — | < 5 | < 7 |
| 11 | Tol-Br- <i>p</i> | Y | ^t Bu | Hex | — | — | < 5 |

^a Sub.:Cat.:NaH = 1:0.1:4 (65°C), conversion by GC. ^b 3h.

Table 5
Reduction of 1-octene by $O(CH_2CH_2C_5H_3R)_2LnCl=NaH$ systems^a

| Entry | R | Ln | Reduction (%) | | |
|-------|-----------------|----|-----------------------|----------------------|-----|
| | | | 12h | 24h | 48h |
| 1 | ^t Bu | Nd | 53 (15 ^b) | 66(23 ^b) | 100 |
| 2 | ^t Bu | Sm | 76 (18 ^b) | 84(16 ^b) | 100 |
| 3 | ^t Bu | Y | 80 (20 ^b) | 90(10 ^b) | 100 |
| 4 | $SiMe_3$ | La | 75 | — | 100 |
| 5 | $SiMe_3$ | Nd | 65 | — | 100 |
| 6 | $SiMe_3$ | Y | 100 | — | — |
| 7 | $SiMe_3$ | Yb | 61 | — | 92 |

^a Sub.:LLnCl:NaH = 1:1:4/THF, no reaction took place in hexane or toluene; conversion by GC. ^b 2-Octene (cis + trans).

$O(CH_2CH_2C_5H_4)_2LnCl=NaH$ and $(C_5H_5)_3Ln=NaH$ systems [12].

To test the idea that the inactivation of the systems in hexane is due to the requirement of an aprotic dipolar solvent of NaH, the complexes were exposed to sodium hydride in THF for 3 days at 60°C, then the solvent was removed and the residue was dried at 40°C for 2 h in vacuo to ensure the complete removal of THF. To the vessel was added the solution of 1-octene or *p*-bromotoluene in hexane, then the mixture was stirred vigorously at 60°C and samples were obtained at given times. The results are given in Table 6. Evidently, the results support the assumption motioned above, despite the decrease of the reactivities. The lower reactivities imply that it may be difficult to convert the chloride into the corresponding hydride completely under this condition. The relatively poor solubility of the corresponding hydrides could also contribute to the decrease of the reactivities. Entries 8 and 9 assured us of the requirement for an aprotic dipolar solvent of NaH, since the conversion rose correspondingly when increasing the quantity of complex from catalytic (10%) to stoichiometric amounts. Evidence also came from two control experiments (entries 4 and 7). The former was conducted in mixed solvents (10% THF + 90% hexane, v/v) and showed no reactivity before 48 h at 60°C, ruling out any effect from traces of residual THF, if any, in the systems. The latter confirmed the importance of solubility of these substituted complexes to the reactivities, since no reaction occurred even after 4 days when the unsubstituted analogue of yttrium was used. Interestingly, the isomerization of the olefin increased and even prevailed over the reduction where $R = ^tBu$ in hexane compared with the reactions in THF. A plausible explanation is absence of the depression of the coordinated THF to β -H elimination of alkyl metal intermediates. Further studies of the complexes are in hand.

In conclusion, several *ansa*-metallocene chlorides of rare earth elements soluble in hydrocarbon solvents were prepared. The reactivities of the systems of these complexes and sodium hydride to aryl halides and

Table 6
Test of reactivities of the $O(CH_2CH_2C_3H_3R)_2LnCl-NaH$ systems^a

| Entry | Sub. | R | Ln | Reduction (%) | | | |
|----------------|------------------|-------------------|----|--------------------------|------------------------|------------------------|------------------------|
| | | | | 12 h | 24 h | 48 h | 96 h |
| 1 | 1-Octene | SiMe ₃ | Y | 37 | 44 | 58 | 70 (< 3 ^b) |
| 2 | 1-Octene | SiMe ₃ | Yb | trace | 5 | 20 (< 3 ^b) | 26 (< 3 ^b) |
| 3 | 1-Octene | SiMe ₃ | Nd | 29 (trace ^b) | 30 (< 3 ^b) | 36 (12 ^b) | 38 (14 ^b) |
| 4 ^c | 1-Octene | SiMe ₃ | Y | no reaction | no reaction | trace | 21 |
| 5 | 1-Octene | ^t Bu | Y | — | 12 (20 ^b) | 14 (24 ^b) | 27 (51 ^b) |
| 6 | 1-Octene | ^t Bu | Nd | — | < 3 (8 ^b) | 12 (16 ^b) | 19 (21 ^b) |
| 7 | 1-Octene | H | Y | — | no reaction | no reaction | no reaction |
| 8 ^d | Tol-Br- <i>p</i> | SiMe ₃ | Yb | 2 | 3 | 3 | 7 |
| 9 ^e | Tol-Br- <i>p</i> | SiMe ₃ | Yb | 25 | 26 | 33 | 34 |

^a Sub.:LLnCl:NaH = 1:1:4, conversion by GC, the mixture of complexes and NaH was stirred 3 days at 60°C. ^b 2-Octene (cis + trans). ^c The reaction was conducted in mixed solvents of hexane and THF (90/10, v/v). ^d Sub.:LLnCl:NaH = 1:0.1:4, the product is toluene. ^e Sub.:LLnCl:NaH = 1:1:4.

1-octene were investigated primarily; the results have demonstrated that the introduction of bulky groups on cyclopentadienes influenced the reactivities far less than solvents used in these reactions.

3. Experimental details

All operations were carried out under purified argon using Schlenk techniques. All solvents were refluxed and distilled either over LiAlH₄ or blue sodium-benzophenone under argon prior to use. Anhydrous lanthanide chlorides [13], *tert*-butyl cyclopentadiene [12] and 1,1'-(3-oxa-pentamethylenedicyclopentadienyl) yttrium chloride [5] were prepared as in literature. Organohalides were dried over anhydrous CaCl₂. Sodium hydride (E. Mark 60% in paraffin oil) was washed with THF or hexane three times and dried in vacuo. Infrared spectra were recorded using a Perkin-Elmer 983 with Nujol and Fluorolube mulls between disc-shaped CsI crystals from 180 to 4000 cm⁻¹; the mulls were prepared in an argon-filled glove-box. Mass spectra were recorded on a Finnigan 4021 spectrometer (*t* = 50–400°C, 1.3 kV); ¹H NMR spectra were recorded on FX-90 Q (90 MHz) or Am-300 (300 MHz) spectrometers referenced to external SiMe₄. Benzene-*d*₆ was dried over an Na-K alloy and degassed by freeze-thaw cycles on a vacuum line. Element analyses were performed by the Analytical Laboratory of Shanghai Institutes of Organic Chemistry.

3.1. Preparation of 2,2'-*tert*-butylcyclopentadienyl ethyl ether 1

A solution of *tert*-butyl-cyclopentadiene (15.0 g, 0.123 mol) in THF (10 ml) was added to sodium sand (4.0 g) suspended in THF (40 ml) at room temperature. The mixture was stirred until no gas gave out, then

centrifuged. The solution was separated from excess sodium sand and cooled to -10°C; 2,2'-dichlorodiethyl ether (8.70 g, 0.061 mol) in THF (10 ml) was then added dropwise with stirring. It took ca. 6 h to finish, monitored by titrating the concentration of base in the solution with standard hydrochloric acid. The mixture was quenched by addition of water (20 ml) and the aqueous phase was separated and extracted with Et₂O (2 × 20 ml). The combined organic phase was dried over MgSO₄ under N₂ at 0°C. Removal of the solvents in vacuo and passage through a short pad of silica gel with petroleum ether (60–90°C) provided spectroscopically pure **1** 4.2 g (28%) (¹H NMR, 90 MHz) which can be stored for weeks without significant polymerization under N₂ at -30°C.

¹H NMR (CCl₄, TMS, 90 MHz), δ, ppm 5.8 (m, 4H); 3.3 (t, 4H); 2.6 (brs, 4H); 2.3 (m, 4H); 1.1 (s), 1.0 (s) 18H.

3.2. Preparation of 2,2'-trimethylsilylcyclopentadienyl ethyl ether 2

Sodium cyclopentadienide C₅H₅Na (0.138 mol) in THF solution (108 ml, 1.286 M) was treated with 2,2'-dichloroethyl ether in THF (20 ml) in an ice bath with stirring. When 90% of base was consumed the mixture was centrifuged, then the precipitate was washed with THF (2 × 20 ml). The combined solution was allowed to react with sodium sand at 40°C for ca. 6 h, before excess sodium sand was separated from the mixture. To the obtained solution was added trimethylchlorosilane (15.0 g, 0.140 mol) in 20 ml THF at -20°C and stirred vigorously for 2 h. The work-up and separation procedure, similar to that for **1**, provided **2** 3.6 g (18%).

¹H NMR (CDCl₃, TMS, 90 MHz), δ, ppm 6.0–6.5 (m, 4H); 3.5 (t, 4H); 2.9 (brs), 3.1 (brs) (4H); 2.6 (m, 4H); 0.1 (s), 0.05 (s) (18).

3.3. Conversion of 1 and 2 into the corresponding disodium salts

To a suspension of sodium hydride (4.0 g) in THF (30 ml) was added 1 (4.0 g, 0.127 mol) in THF (10 ml) at room temperature. The mixture was warmed to 45 °C and stirred for ca. 5 h, then centrifuged. The resulting solution was transferred to another flask.

The procedure described above was followed for the conversion of 2 with 3.0 g, (0.087 mol) 2 in THF (10 ml) and 3.0 g sodium hydride suspended in 30 ml THF. A slightly red solution was obtained.

3.4. Synthesis of 1,1'-[3-oxa-pentamethylene di(3-tert-butylcyclopentadienyl)]yttrium chloride 3

YCl₃ (1.0 g, 0.0051 mol) was suspended in THF (20 ml) and stirred for 6 h at ambient temperature, then cooled to -78 °C, the solution of disodium salt of 1 (17.5 ml, 0.289 M) was added by syringe and stirred for 2 h. The mixture was warmed to ambient temperature and stirred for a further 48 h. The suspension was centrifuged and the solution was transferred to another flask, the residue was washed with THF (2 × 10 ml). Removal of solvent of the combined solution provided crude 3 which was purified by recrystallization in hexane at -30 °C (1.42 g, 64%). The obtained product was white powder.

Anal. Found: C, 60.76; H, 7.33; Cl, 8.21; Y, 19.48. C₂₂H₃₂ClOY (436.5). Calc.: C, 60.48; H, 7.33; Cl, 8.13; Y, 20.39%. IR (cm⁻¹) 3065 (w), 2954 (s), 2860 (s), 2835 (s), 1462 (m), 1440 (m), 1389 (m), 1361 (m), 1204 (m), 1105 (m), 1060 (m), 1025 (s), 1000 (m), 980 (m), 817 (m), 762 (s), 678 (m), 523 (m), 380 (m), 332 (m), 275 (w). The MS and ¹H NMR data are listed in Tables 1 and 3 respectively.

3.5. 1,1'-[3-oxa-pentamethylene di(3-tert-butylcyclopentadienyl)]neodymium chloride 4

NdCl₃ (1.48 g, 0.0059 mol) was suspended in THF and stirred overnight (instead of 6 h) to ensure the powder was converted to NdCl₃(thf)_n completely. The following procedure, similar to that for 3, was adopted with O(CH₂CH₂C₅H₃SiMe₃)₂Na₂-THF 20 ml (0.289 M). It provided analytically pure 4 (1.72 g, 59%) as blue powder.

Anal. Found: C, 52.73; H, 6.86; Cl, 7.32; Nd, 28.74. C₂₂H₃₂ClONd (491.5). Calc.: C, 53.71; H, 6.51; Cl, 7.22; Nd, 29.30%. IR (cm⁻¹) 3065 (m), 2950 (s), 2854 (s), 2835 (s), 1462 (m), 1440 (w), 1391 (s), 1364 (s), 1204 (s), 1106 (s), 1068 (s), 1030 (s), 1000 (m), 982 (m), 897 (m), 807 (s), 759 (s), 682 (m), 463 (m), 326 (m), 250 (w). MS data are in Table 1.

3.6. 1,1'-[3-oxa-pentamethylene di(3-tert-butylcyclopentadienyl)]samarium chloride 5

The procedure for 4 was followed to synthesize 5 with 1.96 g (0.0076 mol) SmCl₃ and O(CH₂CH₂C₅H₃SiMe₃)₂Na₂-THF 52 ml (0.145 M). A yellow powder was obtained (2.47 g, 65%).

Anal. Found: C, 52.71; H, 6.74; Cl, 6.88; Sm, 30.37. C₂₂H₃₂ClOSm (497.9). Calc.: C, 53.02; H, 6.43; Cl, 7.13; Sm, 30.21%. IR (cm⁻¹) 3065 (w), 2964 (s), 2880 (s), 1462 (s), 1445 (m), 1364 (s), 1216 (m), 1203 (m), 1104 (m), 1064 (s), 1040 (s), 1014 (m), 994 (m), 941 (w), 860 (m), 810 (s), 766 (s), 676 (m), 320 (m), 250 (w). MS data are given in Table 1.

3.7. 1,1'-[3-oxa-pentamethylene di(3-tert-butylcyclopentadienyl)]ytterbium chloride 6

The procedure for 3 was adopted with 1.80 g (0.0064 mol) YbCl₃, O(CH₂CH₂C₅H₃SiMe₃)₂Na₂-THF 44 ml (0.145 M). This afforded an orange-red powder 6 (2.40 g, 72%).

Anal. Found: C, 50.76; H, 6.47; Cl, 6.34; Yb, 33.22. C₂₂H₃₂ClOYb (520.5). Calc.: C, 50.72; H, 6.15; Cl, 6.82; Yb, 33.24%. IR (cm⁻¹) 3065 (m), 2960 (s), 2924 (s), 2880 (s), 1462 (m), 1440 (m), 1385 (w), 1365 (m), 1291 (s), 1207 (s), 1167 (m), 1109 (s), 1055 (s), 1005 (m), 981 (s), 941 (m), 868 (m), 821 (s), 760 (s), 690 (s), 655 (m), 576 (m), 510 (w), 380 (m), 340 (m), 258 (m). MS data are in Table 1.

3.8. 1,1'-[3-oxa-pentamethylene di(3-trimethylsilyl-cyclopentadienyl)]yttrium chloride 7

The procedure for 3 was again adopted to obtain 7 with 0.59 g (0.003 mol) YCl₃ and O(CH₂CH₂C₅H₃-SiMe₃)₂Na₂-THF 37 ml (0.082 M). Purification in the same manner provided 7 as white powder (1.08 g, 76%).

Anal. Found: C, 52.05; H, 7.03; Cl, 8.23; Y, 18.69. C₂₀H₃₂ClOSi₂Y (468.5). Calc.: C, 51.23; H, 6.83; Cl, 7.58; Y, 19.00%. IR (cm⁻¹) 3062 (w), 2964 (s), 2880 (s), 1460 (w), 1434 (m), 1400 (m), 1362 (m), 1246 (s), 1100 (s), 1059 (s), 980 (s), 924 (m), 836 (vs), 755 (s), 690 (m), 413 (m), 323 (w), 275 (w). MS and ¹H NMR data are given in Tables 2 and 3 respectively.

3.9. 1,1'-[3-oxa-pentamethylene di(3-trimethylsilyl-cyclopentadienyl)]lanthanum chloride 8

The target product was obtained as white powder (0.70 g, 61%) by a procedure similar to that for 4 with 0.55 g (0.0022 mol) LaCl₃, O(CH₂CH₂C₅H₃SiMe₃)₂Na₂-THF 27 ml (0.082 M).

Anal. Found: C, 46.86; H, 6.36; Cl, 5.96; La, 26.35. C₂₀H₃₂ClOSi₂La (518.5). Calc.: C, 46.29; H, 6.17; Cl,

6.85; La, 26.80%. IR (cm^{-1}) 3065 (w), 2950 (s), 2885 (s), 1440 (m), 1400 (m), 1375 (m), 1250 (s), 1105 (s), 1065 (br,vs), 980 (m), 927 (m), 840 (vs), 757 (s), 690 (m), 297 (w). MS and ^1H NMR data are shown in Tables 2 and 3.

3.10. 1,1'-[3-oxa-pentamethylene di(3-trimethylsilyl-cyclopentadienyl)]neodymium chloride 9

The procedure for 4 was again followed with 0.64 g (0.0026 mol) NdCl_3 and $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{SiMe}_3)_2\text{Na}_2\text{-THF}$ 31 ml (0.082 M) and afforded 9 as blue powder (0.87 g, 65%). Anal. Found: C, 47.36; H, 6.68; Cl, 6.52; Nd, 28.52. $\text{C}_{20}\text{H}_{32}\text{ClOSi}_2\text{Nd}$ (523.5). Calc.: C, 45.85; H, 6.11; Cl, 6.78; Nd, 27.51%. IR (cm^{-1}) 3062 (m), 2950 (s), 2885 (s), 1460 (w), 1439 (m), 1421 (m), 1375 (m), 1250 (s), 1185 (m), 1105 (s), 1065 (s), 978 (m), 926 (m), 838 (br,vs), 758 (s), 690 (m), 649 (m), 630 (m), 439 (w), 413 (w), 306 (m), 250 (w). MS data are shown in Table 2.

3.11. 1,1'-[3-oxa-pentamethylene di(3-trimethylsilyl-cyclopentadienyl)]ytterbium chloride 10

The desired product 10 (1.0 g, 72%) was prepared and purified as described above for the procedure with 3 from 0.71 g (0.0025 mol), YbCl_3 and $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{-SiMe}_3)_2\text{Na}_2\text{-THF}$ 31 ml (0.082 M).

Anal. Found: C, 43.46; H, 6.03; Cl, 6.47; Yb, 31.51. $\text{C}_{20}\text{H}_{32}\text{ClOSi}_2\text{Yb}$ (552.5). Calc.: C, 43.44; H, 5.79; Cl, 6.43; Yb, 31.31%. IR (cm^{-1}) 3062 (w), 2951 (s), 2885 (s), 1440 (m), 1375 (m), 1252 (s), 1107 (s), 1059 (s), 981 (s), 929 (m), 842 (vs), 781 (s), 758 (s), 738 (m), 694 (m), 632 (w), 410 (w), 322 (w). MS data are in Table 2.

3.12. 1,1'-[3-oxa-pentamethylene di(3-tert-butylcyclopentadienyl)] bridged binuclear lanthanum complex

A procedure similar to that for 4 was adopted with $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{Bu})_2\text{Na}_2\text{-THF}$ 14.5 ml (0.2890 M) and LaCl_3 1.05 g (0.0042 mol). It provided a white powder (1.45 g, 85% based on disodium salt).

Anal. Found: C, 65.30; H, 8.41; La, 22.43. $\text{C}_{66}\text{H}_{96}\text{La}_2\text{O}_3$ (1214). Calc.: C, 65.24; H, 7.91; La, 22.90%. ^1H NMR (C_6D_6 , 300 MHz, 25 °C) δ , ppm 6.55–6.10 (m, 18H, C_5H_3); 3.7–3.5 (m, 12H, OCH_2); 2.4 (m, 12H, CH_2); 1.4–1.6 (m, 54H, CH_3). MS (%RA), 506 (2.32, $[\text{M} - \text{L}]/2$), 179 (18.88), 165 (17.72), 149 (73.77), 148 (96.43), 133 (100), 91 (61.06), 57 (86.87). IR (cm^{-1}) 3066 (m), 2964 (s), 2866 (s), 1461 (m), 1440 (m), 1385 (m), 1362 (s), 1204 (m), 1111 (s), 1069 (s), 1015 (m), 979 (m), 898 (m), 797 (s), 746 (s), 679 (m), 577 (m), 320 (br,s), 250 (w).

3.13. Catalytic dehalogenation of aryl halides

The general procedure was as follows (entry 1 in Table 4): a Schlenk tube (10 ml) equipped with a Teflon stopcock was charged with $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{Bu})_2\text{YCl}$ (45 mg, 0.103 mmol), NaH (110 mg, 4.6 mmol) and THF (5 ml), then 1.01 mmol $p\text{-BrC}_6\text{H}_5\text{CH}_3$ (1.0 ml, 1.01 M/THF) was added by syringe. The stopcock was closed and the reaction was carried out with vigorous stirring at 65 °C (bath temperature). At given times, samples were obtained and GC analyses were performed to determine the conversion of $p\text{-BrC}_6\text{H}_5\text{CH}_3$ into methylbenzene.

3.14. Reduction of 1-octene

The procedure described above was followed with 210 mg (0.42 mmol) $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{Bu})_2\text{SmCl}$, 40 mg NaH (1.68 mmol), and 0.42 mmol (0.4 ml, 1.05 M/THF) (entry 2 in Table 5).

3.15. Test of the reactivities of the system in hexane

The general procedure was as follows (entry 1 in Table 6): a Schlenk tube (25 ml) equipped with a Teflon stopcock was charged with $\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_3\text{SiMe}_3)_2\text{YCl}$ (366 mg, 0.78 mmol), NaH (100 mg, 4.2 mmol) and THF (15 ml), the mixture was stirred vigorously at 60 °C for 3 days, then THF was removed in vacuo and the residue was dried at 40 °C for 2 h. To the vessel was added 0.78 mmol 1-octene (7.8 ml, 0.10 M/hexane) by syringe. The stopcock was closed and the reaction was carried out with vigorous stirring at 60 °C (bath temperature). At given times, samples were obtained and GC analyses were performed to determine the conversion.

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