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# Homolysis of the Eu−N Bond. Synthesis, Structural Characterization, and Catalytic Activity of Novel Europium(II) Complexes

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Two new indene compounds, $C_9H_7CH_2SiMe_2NC_4H_8$ (**1**) and $C_9H_6$-1-Me-3-$CH_2SiMe_2NC_4H_8$ (**2**), were synthesized by the reaction of $C_9H_6RLi$ (R = H, Me) with $ClCH_2SiMe_2Cl$, followed by treatment with lithium pyrrolidinide $C_4H_8NLi$. The interaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of **1** in refluxing toluene produced, after workup, a novel triple-decker sandwich tetranuclear europium(II) compound, $[\{\eta^5{:}\eta^5{:}\eta^1\text{-}(C_9H_5CH_2SiMe_2NC_4H_8)_2\}Eu_2(\mu\text{-}Cl)]_2[\mu\text{-}\eta^3{:}\eta^5{:}\eta^1{:}\eta^3{:}\eta^5{:}\eta^1\text{-}(C_9H_5CH_2SiMe_2NC_4H_8)_2]\cdot C_7H_8\cdot(C_6H_6)_{0.5}$ (**3**), with a coupled indenyl ligand through tandem silylamine elimination, reduction of $Eu^{3+}$ to $Eu^{2+}$, and the C−C coupling reactions. To probe the formation pathway of complex **3**, the interaction of $C_9H_6$-1-Me-3-$CH_2SiMe_2NC_4H_8$ (**3**) with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ was studied. Treatment of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of **2** in refluxing toluene temperature or at 60 °C produced, after workup, a monomeric europium(II) complex, $(\eta^5{:}\eta^1\text{-}C_9H_5\text{-1-Me-3-}CH_2SiMe_2NC_4H_8)_2Eu$ (**4**), via tandem silylamine elimination/homolysis of the Eu−N bond reactions. The formation pathway for complex **3** was proposed. All the compounds were fully characterized by spectroscopic methods and elemental analyses, and the structures of complexes **3** and **4** were additionally determined by single-crystal X-ray diffraction analyses. It was found that complexes **3** and **4** can function as single-component MMA polymerization initiators, which represent the first examples of europium(II) complexes as single-component MMA polymerization catalysts. The solvents and temperature effects' on the activities of the catalysts were also discussed.

## Introduction

The use of lanthanide(II) reagents in organic synthesis has been developed considerably over the last two decades.[1,2] Most of attention has been given to the unique reducing agent lanthanide(II) iodide and other mainly $\pi$-bonded lanthanide species.[3] However, there is a growing interest in searching for the applications of triple-decker sandwich divalent organolanthanide complexes as multielectron reductants in synthetic chemistry. To our knowledge, the structurally characterized triple-decker sandwich divalent lanthanide complexes were only limited to those of dinuclear compounds with cyclooctatetraenyl and cyclopentadienyl mixed ligands. Some of them showed applications as two-electron reductants in synthetic chemistry.[4−6] On the other hand, the catalytic activity of europium(II) organometallics on olefin polymerization catalyst is far less studied compared to the samarium(II) and ytterbium(II) analogoues,[7] and a recent report concluded that the europium(II) complex $[(C_5Me_5Eu(SiH_3)(THF)(C_5Me_5)K(THF)]_n$ must initiate the olefin polymerization through the migration insertion mechanism.[8]

Given the chemistry of the lanthanide complexes with a Ln−N bond having catalytic activity for olefin transformations such as olefin polymerization,[9] hydroamination/cyclyzation reactions,[10] Tishchenko reactions,[11]

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ring-opening polymerization of ϵ-caprolactone and δ-valerolactone,[12] and insertion reactions,[13] the homolysis reaction of the Yb−N bond was recently developed.[14] It was reported that the $Eu^{3+}$ ion can be more easily reduced to $Eu^{2+}$ ion than the $Yb^{3+}$ ion,[3a] and the reduction of $Eu^{3+}$ to $Eu^{2+}$ has been previously observed with $C_5Me_5^-$ and $C_8H_8^{2-}$.[4,15] It is reasonable to extend the chemistry of the homolysis of the Yb−N bond to the europium chemistry. Herein, we report the interaction of heteroatom-functionalized indene compounds with $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$. The reaction results in the synthesis and characterization of novel europium(II) complexes, which showed good catalytic activities on MMA polymerization.

## Experimental Section

**Materials and Methods.** All syntheses and manipulations of air- and moisture-sensitive materials were carried out on flamed Schlenk-type glassware on a Schlenk line. All solvents were distilled over either finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. $CDCl_3$ was dried over activated 4 Å molecular sieves. MMA was dried over finely divided $CaH_2$, distilled before use. $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ was prepared according to literature methods.[16] Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. IR spectra were recorded on a Perkin-Elmer 983(G) spectrometer (CsI crystal plate, Nujol and Fluoroble mulls). GC−MS analyses were carried out on an Agilent 6890/Micromass GCT-MS instrument. $^1H$ NMR and $^{13}C$ NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer in pyridine-$d_5$ for lanthanide complexes and in $CDCl_3$ for polymers and indene compounds, and the chemical shifts for $^1H$ and $^{13}C$ NMR spectra were referenced to internal solvent resonances. Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30 °C using THF as an eluent on a Waters-150C instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 $mL{\cdot}min^{-1}$. Number-average molecular weights and polydispersitites of polymers were given relative to PS standards. The polymers were analyzed according to the literature.[17]

**Preparation of $C_9H_7CH_2SiMe_2NC_4H_8$ (1).** To a THF (80 mL) solution of indene (10.0 mL, 85.2 mmol) at 0 °C was added slowly a 1.57 M solution of *n*-BuLi (54 mL, 85.2 mmol). After the reaction, the mixture was stirred at room temperature for 12 h. The mixture was then cooled to 0 °C, to the mixture was added freshly distilled $ClSiMe_2CH_2Cl$ (11.3 mL, 85.2 mmol) in one portion, and the reaction was stirred at room temperature overnight. The solvent was pumped off under reduced pressure. The residue was extracted with *n*-hexane (2 × 20 mL), the extraction was combined, and the solvent was pumped off. Distillation of the resulting sticky oil gives the product $C_9H_7CH_2SiMe_2Cl$ as a colorless oil (14.9 g, 79% yield). $^1H$ NMR ($CDCl_3$): δ 7.52 (m, 2H), 7.27(m, 2H), 7.01 (d, $J$ = 4.52 Hz, 1H), 6.68 (dd, $J$ = 4.52, 6.99 Hz, 1H), 3.78 (d, $J$ = 6.99, 1H), 2.80, (s, 2H), 0.06(s, 6H). Anal. Calcd for $C_{12}H_{15}ClSi$: C, 64.69; H, 6.79. Found: C, 64.51; H, 7.02. To a freshly prepared THF (50 mL) solution of lithium pyrrolidinide $C_4H_8NLi$ (36.6 mmol) was added slowly the above prepared indene compound $C_9H_7CH_2SiMe_2Cl$ (8.1 g, 36.6 mmol) at 0 °C. The mixture was then stirred at 50 °C for 12 h. The solvent was pumped off under reduced pressure. The residue was extracted with *n*-hexane (3 × 10 mL), the extracts were combined, and the solvent was evaporated under reduced pressure. Distillation of the residue under reduced pressure gave **1** as a colorless oil (6.96 g, 74% yield). $^1H$ NMR ($CDCl_3$): δ 7.34−7.07 (m, 4H, aromatic), 5.92 (m, 1H), 3.20 (d, $J$ = 7.62 Hz, 2H), 2.82 (m, 4H), 1.98 (s, 2H), 1.57 (m, 4H), 0.02 (s, 6H). Anal. Calcd for $C_{16}H_{23}NSi$: C, 74.65; H, 9.00; N, 5.44. Found: C, 74.11; H, 8.86; N, 5.49.

**Preparation of $C_9H_6$-1-Me-3-$CH_2SiMe_2NC_4H_8$ (2).** To a THF (50 mL) solution of 3-methylindene (10.0 mL, 74.7 mmol) at 0 °C was added slowly a 1.57 M solution of *n*-BuLi (47.6 mL, 74.7 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was cooled to 0 °C, and to the solution was added $ClCH_2SiMe_2Cl$ (9.9 mL, 74.7 mmol) in one portion. The reaction was then stirred at room temperature overnight. The solvents was evaporated under vacuum, and the residue was extracted with *n*-hexane (20 mL × 2). The extraction was combined, and the solvent was evaporated under reduced pressure. Distillation under reduced pressure afforded the product $C_9H_6$-1-Me-3-$CH_2SiMe_2Cl$ as a colorless oil (14.3 g, 81% yield). $^1H$ NMR ($CDCl_3$): δ 7.54−7.28 (m, 4H), 6.37 (s, 1H), 3.68 (s, 1H) ($C_9H_6$), 2.83 (s, 2H) ($CH_2$), 2.32 (s, 3H) ($CH_3$), 0.10 (s, 6H) ($Si(CH_3)_2$). $^{13}C$ NMR($CDCl_3$): δ 145.29, 145.02, 138.54, 129.27, 125.24, 122.84, 119.32, 118.46, 41.32 ($C_9H_6$), 29.74 ($CH_3$), 13.15 ($CH_3$), −5.58 ($Si(CH_3)_2$). To a freshly prepared THF solution of $C_4H_8NLi$ (40 mL, 36.6 mmol) at 0 °C was slowly added $C_9H_6$-1-Me-3-$CH_2SiMe_2Cl$ (8.7 g, 36.6 mmol). The temperature of the reaction was gradually raised to room temperature. The mixture was then heated to 50 °C. After the mixture was stirred at that temperature for 12 h the solvent was pumped off, and the residue was extracted with *n*-hexane (10 mL × 3). The extracts were combined, and the solvent was evaporated under reduced pressure. Distillation of the residue under reduced pressure gave the product as a colorless oil (7.17 g, 72%). $^1H$ NMR ($CDCl_3$): δ 7.40−7.18 (m, 4H), 5.97(m, 1H), 3.43 (m, 1H) ($C_9H_6$), 2.94 (m, 4H), 1.70 (m, 4H) ($C_4H_8$), 2.05 (s, 2H) ($CH_2$), 1.29 (s, 3H) ($CH_3$), 0.10(s, 6H) ($Si(CH_3)_2$). Anal. Calcd for $C_{17}H_{25}NSi$: C, 75.21; H, 9.28; N, 5.16. Found: C, 74.93; H, 9.11; N, 5.42.

**Preparation of $[\{\eta^5{:}\eta^5{:}\eta^1\text{-}(C_9H_5CH_2SiMe_2NC_4H_8)_2\}Eu_2(\mu\text{-}Cl)]_2[\mu\text{-}\eta^3{:}\eta^5{:}\eta^1{:}\eta^3{:}\eta^5{:}\eta^1\text{-}(C_9H_5CH_2SiMe_2NC_4H_8)_2]\cdot C_7H_8\cdot(C_6H_6)_{0.5}$ (3).** To a toluene (50 mL) solution of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (1.25 g, 1.40 mmol) was slowly added a toluene solution of **1** (0.72 g, 2.80 mmol). After the reaction mixture was stirred at room temperature for 6 h, the mixture was then refluxed for 12 h and the color of the solution changed from yellow to red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (8.0 mL). The resulting solid was extracted with toluene (2 × 10 mL). The toluene solution was combined and concentrated to 15 mL, and a drop of benzene was added. Orange-red crystals were obtained by cooling the concentrated solution at 0 °C (0.50 g, 61%). NMR (pyridine-$d_5$) analyses gave no information for lack of locking signal due to the strong paramagnetic property of the complex. Anal. Calcd for $C_{106}H_{137}Cl_2Eu_4N_6Si_6$: C, 54.35;

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**Table 1. Crystal and Data Collection Parameters for 3 and 4**

| | 3 | 4 |
|---|---|---|
| empirical formula | $C_{106}H_{137}Cl_2Eu_4N_6Si_6$ | $C_{34}H_{48}EuN_2Si_2$ |
| fw | 2342.50 | 692.88 |
| cryst syst | monoclinic | monoclinic |
| space group | *P*2(1)/*c* | *Cc* |
| *a* (Å) | 16.7799(2) | 15.9779(6) |
| *b* (Å) | 23.2707(3) | 10.2789(4) |
| *c* (Å) | 15.58510(10) | 19.8084(5) |
| $\beta$ (deg) | 109.1290(10) | 92.9960(10) |
| *V* (Å$^3$) | 5749.64(11) | 3248.79(13) |
| *T* (K) | 293(2) | 293(2) |
| $D_{calcd}$ (g cm$^{-3}$) | 1.353 | 1.417 |
| *Z* | 2 | 4 |
| *F*(000) | 2370 | 1428 |
| no. of reflns collected | 18116 | 4492 |
| no. of unique reflns | 9871 ($R_{int} = 0.043$) | 3185 ($R_{int} = 0.016$) |
| no. of params | 554 | 353 |
| $\lambda$, (Å) Mo K$\alpha$ | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 2.304 | 2.029 |
| $2\theta$ range | 3.28 to 50.10 | 4.12 to 50.00 |
| goodness of fit | 0.963 | 1.046 |
| *R* ($I > 2\sigma(I)$) | 0.049 | 0.024 |
| w$R_2$ | 0.086 | 0.052 |

H, 5.89; N, 3.59. Found: C, 54.11; H, 5.92; N, 3.76. IR (Nujol): $\nu$ 1607 (m), 1250 (m), 1080 (m), 1018 (m), 829 (m), 721 (m), 438 (w).

**Preparation of ($\eta^5$:$\eta^1$-$C_9H_5$-1-Me-3-$CH_2SiMe_2NC_4H_8$)$_2$Eu (4).** This compound was prepared as yellow crystals (0.73 g, 75%) from the reaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (1.25 g, 1.40 mmol) with **2** (0.76 g, 2.8 mmol) following procedures similar to those used for the preparation of **3**. NMR (pyridine-$d_5$) analyses gave no information for lack of locking signal due to the strong paramagnetic property of the complex. IR (Nujol): $\nu$ 1604 (m), 1461 (s), 1377 (s), 1249 (m), 962 (m), 831 (m), 752 (m), 734 (m), 439 (w). Anal. Calcd for $C_{34}H_{48}N_2EuSi_2$: C, 58.88; H, 6.98; N, 4.04. Found: C, 58.61; H, 6.90; N, 4.11.

Running the reaction at 60 °C also produced the complex **4** in 67% yield.

**GC−MS Analyses.** A small portion of the reaction mixture for the preparation of **3** and **4** was hydrolyzed and analyzed by GC−MS technology. The corresponding ligands were detected in each component. $HN(SiMe_3)_2$ was detected in the mixture for the preparation of **3**; $HN(SiMe_3)_2$ and a small portion of the coupling product $[N(SiMe_3)_2]_2$ were detected in the mixture for the preparation of **4**.

**X-ray Data Collection and Structure Determination for 3 and 4.** A suitable crystal of the title complexes was mounted in a sealed capillary and used for X-ray diffraction study. Diffraction was performed on a Siemens SMART CCD area-detector diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å), temperature 293(2) K, $\varphi$ and $\omega$ scan technique. SADABS effects and empirical absorption were applied in the data corrections.[18] All structures were solved by directed methods (SHELXS-97),[18] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on $F^2$ (SHELXS-97). The hydrogen atom coordinates were calculated with SHELXS using an appropriate riding model with varied thermal parameters. All the non-hydrogen atoms were refined anisotropically. The residual electron densities were of no chemical significance. The crystal and data collection parameters for **3** and **4** are summarized in Table 1, and key interatomic distances and angles are compiled in Table 2.

**MMA Polymerization.** MMA polymerization reactions were performed in a 50 mL Schlenk flask and an external temperature-controlled bath on a Schlenk line or in a glovebox. In a typical procedure, catalyst (0.030−0.050 g) was loaded into the Schlenk flask and the solvent was added. After the external bath temperature was stabilized, MMA was added through a gastight syringe. The polymerization was terminated by addition of acidic methanol after a measured interval. The polymer product was precipitated into 50 mL of methanol, filtered, washed with methanol, and dried in a vacuum oven at 50 °C to a constant weight.

## Results and Discussion

**Synthesis of $C_9H_7CH_2SiMe_2NC_4H_8$ (1) and $C_9H_6$-1-Me-3-$CH_2SiMe_2NC_4H_8$ (2).** The interactions of $C_9H_6RLi$ (R = H, Me) with 1 equiv of $ClCH_2SiMe_2Cl$, followed by treatment with 1 equiv of lithium pyrrolidinide, produced, after workup, the new indene compounds $C_9H_6$-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H (**1**), Me (**2**)) in good yield (Scheme 1). The compounds were fully characterized by spectroscopic methods and elemental analyses. It was interesting to note that the nucleophilic substitution reactions of $ClCH_2SiMe_2Cl$ with $C_9H_6RLi$ occur at the C−Cl bond, not at the Si−Cl bond on the basis of the NMR analyses of the reaction products. Similar results were observed in the reactions of $C_5Me_4HLi$ or $Ph_2PLi$ with $ClCH_2SiMe_2Cl$, giving the corresponding product $C_5HMe_4CH_2SiMe_2Cl$[19a] or $Ph_2PCH_2SiMe_2Cl$,[19b] indicating the electronic and steric effects on the reactivity of the C−Cl and the Si−Cl bonds.

**Reactions of the Indene Compounds with Europium(III) Amide: Synthesis and Characterization of the Novel Europium(II) Complexes.** The interaction of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$[16] with 2 equiv of $C_9H_7CH_2SiMe_2NC_4H_8$ (**1**) in refluxing toluene produced, after workup, a novel triple-decker sandwich tetranuclear europium(II) compound, $[\{\eta^5:\eta^5:\eta^1\text{-}(C_9H_5\text{-}CH_2SiMe_2NC_4H_8)_2\}Eu_2(\mu\text{-}Cl)]_2[\mu\text{-}\eta^3:\eta^5:\eta^1:\eta^3:\eta^5:\eta^1\text{-}(C_9H_5\text{-}CH_2SiMe_2NC_4H_8)_2]\cdot C_7H_8\cdot(C_6H_6)_{0.5}$ (**3**), as orange-yellow crystals in 61% yield (Scheme 2). The complex is air- and moisture-sensitive and is soluble in polar solvents such as THF, DME, and pyridine. The compound was fully characterized by elemental and spectroscopic analyses, and its structure was determined by single-crystal X-ray analysis (Figure 1).

A key feature of the structure described herein is that it is the first example of a centrosymmetric triple-decker sandwich tetranuclear organolanthanide(II) complex formed by unusual tandem reactions. The two triple-decker sandwich structures are connected side by side due to dimerization of the indenyl ligands, and the chloride bridges connect the metals in the two triple-deckers to form a type of novel ladder structure. The complex represents the first example of structurally characterized organolanthanide complexes with a coupled indenyl ligand to be reported.

The second characteristic feature of the structure is that the coordination chemistry around the two central metal Eu(1) and Eu(2) atoms is different. The bond distances of Eu(1)−C(14) (3.058(6) Å) and Eu(1)−C(15) (3.104(6) Å) (Table 2) are significantly longer than those of others (range from 2.799(6) to 2.979(6) Å), suggesting that the Eu(1) atom is bonded with the five-membered ring (C(8), C(9), C(14), C(15), and C(16)) in an $\eta^3$ fashion. The other Eu(1)−C and Eu(2)−C bond distances fall in

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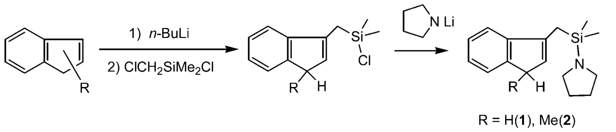
**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3 and 4**[a]

| 3 | | | | 4 | |
|---|---|---|---|---|---|
| Eu(1)−C(24) | 2.852(6) | Eu(2)−C(8a) | 2.894(6) | Eu−N(1) | 2.759(16) |
| Eu(1)−C(25) | 2.906(6) | Eu(2)−C(9a) | 2.931(7) | Eu−N(2) | 2.746(14) |
| Eu(1)−C(30) | 2.876(6) | Eu(2)−C(16a) | 2.885(6) | Eu−C(8) | 2.922(11) |
| Eu(1)−C(31) | 2.815(6) | Eu(2)−C(14a) | 2.962(6) | Eu−C(9) | 2.808(13) |
| Eu(1)−C(32) | 2.799(6) | Eu(2)−C(15a) | 2.950(6) | Eu−C(10) | 2.805(18) |
| Eu(1)−C(8) | 2.886(6) | Eu(2)−C(33) | 2.824(6) | Eu−C(11) | 2.979(16) |
| Eu(1)−C(9) | 2.929(6) | Eu(2)−C(34) | 2.835(6) | Eu−C(12) | 2.999(15) |
| Eu(1)−C(16) | 2.979(6) | Eu(2)−C(39) | 2.880(6) | Eu−C(28) | 2.873(14) |
| Eu(1)−C(14) | 3.058(6) | Eu(2)−C(40) | 2.872(7) | Eu−C(29) | 2.849(11) |
| Eu(1)−C(15) | 3.104(6) | Eu(2)−C(41) | 2.816(6) | Eu−C(30) | 2.942(16) |
| Eu(1)−Cl | 2.7941(17) | Eu(2)−Cl | 2.8034(19) | Eu−C(31) | 2.987(16) |
| Eu(1)−N(2) | 2.732(6) | Eu(2)−N(1a) | 2.761(6) | Eu−C(32) | 2.950(14) |
| Eu(1)−X1a | 2.737 | N(2)−Eu(1)−Cl | 89.2 | Eu−$C_{av}$ | 2.911(18) |
| Eu(1)−X1b | 2.577 | N(1a)−Eu(1)−Cl | 85.6 | N(1)−Eu−N(2) | 110.19(15) |
| Eu(2)−X1c | 2.573 | X1a−Eu(1)−X1b | 128.4 | | |
| Eu(2)−X1d | 2.663 | X1c−Eu(1)−X1d | 130.4 | | |

[a] X1a represents the centroid of C(8), C(9), C(14), C(15), C(16), X1b the centroid of C(24), C(25), C(30), C(31), C(32), X1c the centroid of C(33), C(34), C(39), C(40), C(41), and X1d the centroid of C(8a), C(9a), C(14a), C(15a), C(16a) in the tetranuclear complex.

**Scheme 1**

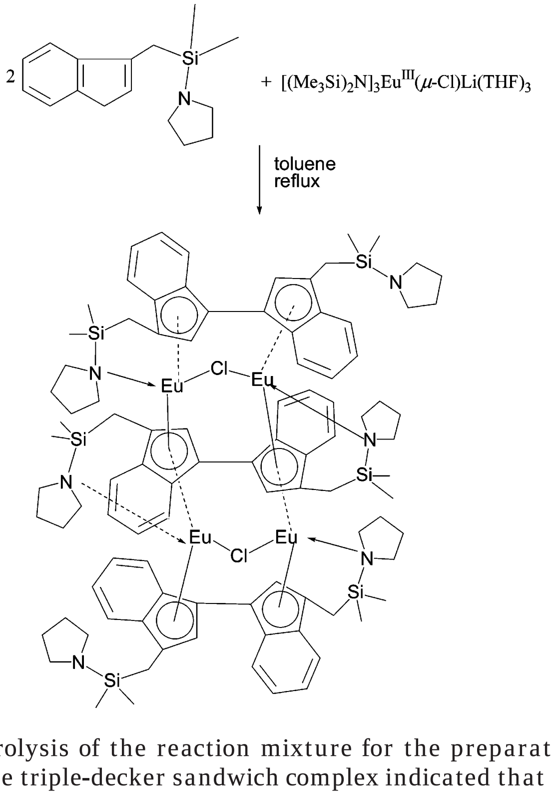


the normal range, and they are comparable to those found in $[(C_5Me_5)(THF)_2Eu]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$.[4] These results indicated that the Eu(1) atom is bonded with the two five-membered rings in $\eta^3$ and $\eta^5$ fashions, respectively, and the Eu(2) atom is bonded with the two five-membered rings in an $\eta^5$ mode.

Another characteristic feature of the structure is that the structural parameters around the two central metals are also different. The Eu(1)−X1a (X represents the centroid of the five-membered ring of the indenyl ligand) distance is 2.737 Å, which is significantly longer than the Eu(1)−X1b distance of 2.577 Å and longer than the Eu(2)−X1c distance of 2.573 Å and the Eu(2)−X1d distance of 2.663 Å. The different bending with the X1a−Eu(1)−X1b and X1c−Eu(2)−X1d angles of 128.4° and 130.4° is smaller than the corresponding values of 139.1° and 137.9° found in $[(C_5Me_5)(THF)_2Eu]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$[4] and is smaller than the values of 137.6° found in $[(C_5Me_5)(diglyme)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$,[5] 148.9° and 149.3° found in $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$,[5] 157.6° found in $[(C_5Me_4Et)Sm]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$,[5] 161.2° and 159.2° found in $[(C_5Me_5)Yb]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$,[6] and 147.2° and 149.5° found in $[(C_5Me_5)Eu]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$.[6] The bending with X1a−Eu(1)−X1b/X1c−Eu(2)−X1d angles of 128.4°/130.4° is also smaller than the corresponding value of 169.5° found in a triple-decker sandwich complex of barium, $[C_5H(CHMe_2)_4Ba]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$.[20] These differences may be due to the coordination difference around the central metal and steric effects.

The formation of the coupled indenyl ligand is also noticeable. The chemistry is somewhat different from the results of our previous work.[14] It has been demonstrated that the interaction of an *N*,*N*-dimethylaminoethyl-functionalized indene compounds with $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ produced the ytterbium(II) compounds via tandem silylamine elimination/homolysis of the Yb−N bond reactions. However, GC−MS analyses of hydrolysis of the reaction mixture for the preparation of the triple-decker sandwich complex indicated that the coupling product $[N(SiMe_3)_2]_2$ was not detected; the amine $HN(SiMe_3)_2$ was detected instead. It should be noted that the homolysis of the Eu−N bond has not been observed by refluxing the compound $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ in toluene for 2 days or sublimation[16] of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ at 100 °C. However, our previous work on studying the ytterbium chemistry showed that the monomeric ytterbium(II) complexes, instead of triple-decker complexes, were isolated, indicating the different reactivity between the europium compounds and the ytterbium compounds, and also the ligands' effect on the reaction chemistry.

**Scheme 2**



To probe whether the reaction for the formation of the title compound involves the homolysis of the Eu−N bond or not, the interaction of $C_9H_6\text{-}1\text{-}Me\text{-}3\text{-}CH_2SiMe_2\text{-}NC_4H_8$ (**2**) with $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(THF)_3$ was studied. The interaction of 2 equiv of $C_9H_6\text{-}1\text{-}Me\text{-}3\text{-}CH_2\text{-}SiMe_2NC_4H_8$ (**2**) with $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(THF)_3$ in

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(20) Sitzmann, H.; Walter, M. D.; Wolmershäuser, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2315.

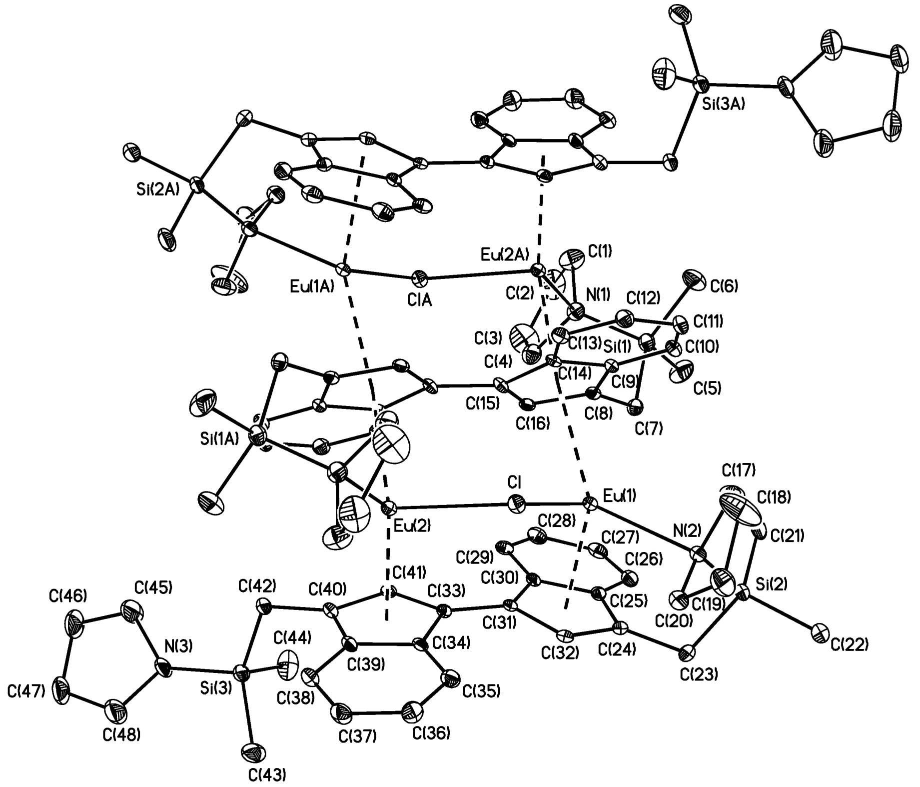
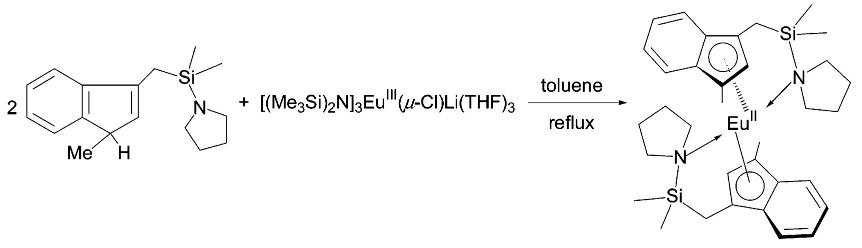


**Figure 1.** Crystal structure of **3**. Hydrogen atoms and the solvated toluene and benzene molecules were omitted for clarity.

**Scheme 3**



refluxing toluene (or at 60 °C) produced, after workup, a monomeric europium(II) complex, ($\eta^5$:$\eta^1$-$C_9H_5$-1-Me-3-$CH_2SiMe_2NC_4H_8$)$_2$Eu (**4**) (Scheme 3). The complex is air- and moisture- sensitive and is soluble in THF, DME, pyridine, and toluene and slightly soluble in *n*-hexane. The complex was fully characterized by elemental and spectroscopic analyses. The NMR study was not informative due to the paramagnetic property of the complex, and its structure was determined by a single-crystal X-ray diffraction study (Figure 2).

X-ray analysis reveals that the central metal is in a +2 oxidative state, and the europium metal is coordinated with two indenyl ligands and two nitrogen atoms of the substituent groups. To the best of our knowledge, it represents the first example of a structurally characterized monomeric europium(II) complex with an indenyl ligand to be reported.

The average Eu$-$C distance of 2.911(18) Å is longer than the corresponding values of 2.806(12) Å found in [$\eta^5$:$\eta^1$-$Me_2Si(Me_2NCH_2CH_2C_9H_5)$(*t*-BuNH)]$_2$Yb, 2.778(14) Å found in [$\eta^5$:$\eta^1$-($Me_2NCH_2CH_2C_9H_5SiMe_3$)]$_2$Yb, and 2.722(10) Å found in ($\eta^5$:$\eta^1$-($Me_2NCH_2CH_2C_9H_6$)$_2$Yb.[14] These results may be due to steric and ionic radii[21] difference of the complexes. Comparison of the 2.808(13) Å Eu$-$C(9) distance to the adjacent Eu$-$C distances in the ring (2.805(18) Å for Eu$-$C(10) and 2.922(11) Å) and the two nonadjacent Eu$-$C distances (2.979(16) Å for Eu$-$C(11) and 2.999(15) Å for Eu$-$C(12)) suggests that this ring is beginning to move toward an $\eta^3$-indenyl orientation. A similar result is observed for the bonding between the other ring and the europium metal. The average Eu$-$N distance of 2.754(16) Å is comparable to the corresponding values of 2.671(11) Å found in [$\eta^5$:$\eta^1$-$Me_2Si(Me_2NCH_2CH_2C_9H_5)$(*t*-BuNH)]$_2$Yb, 2.650(12) Å found in [$\eta^5$:$\eta^1$-($Me_2NCH_2CH_2C_9H_5SiMe_3$)]$_2$Yb, and 2.588(7) Å found in ($\eta^5$:$\eta^1$-($Me_2NCH_2CH_2C_9H_6$)$_2$Yb.[14] The N(1)$-$Eu$-$N(2) angle of 110.19(15)° is larger than the corresponding values found in the ytterbium complexes.[14] Because there are no structural data available for monomeric europium(II) complexes with an indenyl ligand, further structural comparisons are not possible.[3]

The amine $HN(SiMe_3)_2$, indene compound $C_9H_6$-1-Me-3-$CH_2SiMe_2NC_4H_8$, and a small portion of the coupling product $[(Me_3Si)_2N]_2$ were detected from the reaction mixtures by GC$-$high-resolution MS analyses, suggesting that the reaction chemistry for the formation of complex **4** is similar to the ytterbium chemistry through

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(21) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

**Table 3. Data for Polymerization of Methyl Methacrylate (MMA)**

| cat. | solvent | time (min) | temp (°C) | stereochemistry |  |  | $M_n \times 10^{-3}$ | $M_w \times 10^{-3}$ | $M_w/M_n$ | conv (%) | activity ($\times 10^{-6}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | mm | mr | rr |  |  |  |  |  |
| **3**[a] | THF | 30 | 30 | 19 | 34 | 47 | 29.91 | 55.35 | 1.85 | 10 | 0.023 |
|  |  | 30 | 0 | 10 | 32 | 58 | 57.81 | 149.16 | 2.58 | 18 | 0.056 |
|  |  | 2 | −30 | 15 | 28 | 57 | 125.44 | 442.64 | 3.53 | 78 | 2.93 |
|  |  | 2 | −60 | 9 | 33 | 58 | 75.88 | 135.4 | 1.78 | 95 | 3.43 |
| **3** | DME | 30 | 30 | 15 | 39 | 46 | 12.21 | 18.49 | 1.51 | 10 | 0.022 |
|  |  | 30 | 0 | 12 | 33 | 55 | 43.84 | 81.48 | 1.86 | 29 | 0.068 |
|  |  | 2 | −30 | 12 | 30 | 58 | 82.70 | 293.79 | 3.55 | 67 | 2.40 |
|  |  | 2 | −60 | 9 | 29 | 62 | 185.4 | 355.1 | 1.92 | 90 | 3.32 |
| **4**[b] | THF | 30 | 30 | 24 | 30 | 46 | 25.46 | 59.06 | 2.32 | 20 | 0.002 |
|  |  | 1 | 0 | 26 | 32 | 42 | 25.72 | 61.66 | 2.40 | 67 | 2.06 |
|  |  | 1 | −30 | 20 | 33 | 47 | 41.7 | 88.6 | 2.12 | 96 | 2.98 |
|  |  | 8 | −60 | 13 | 35 | 52 | 44.21 | 127.3 | 2.88 | 52 | 0.2 |
| **4** | DME | 30 | −30 | 19 | 35 | 46 | 36.01 | 91.64 | 2.54 | 18 | 0.02 |
|  |  | 2 | −60 | 17 | 29 | 54 | 126.9 | 153.1 | 1.21 | 64 | 1.02 |

[a] Conditions: MMA/solvent (v/v) = 1:3; cat/MMA (mole ratio) 1:1500; activity g PMMA·mol$^{-1}$(cat)·h$^{-1}$; stereoregularity was based on $^1$H NMR analyses. [b] Conditions: cat/MMA (mole ratio) 1:500; other conditions are the same as those in (a).

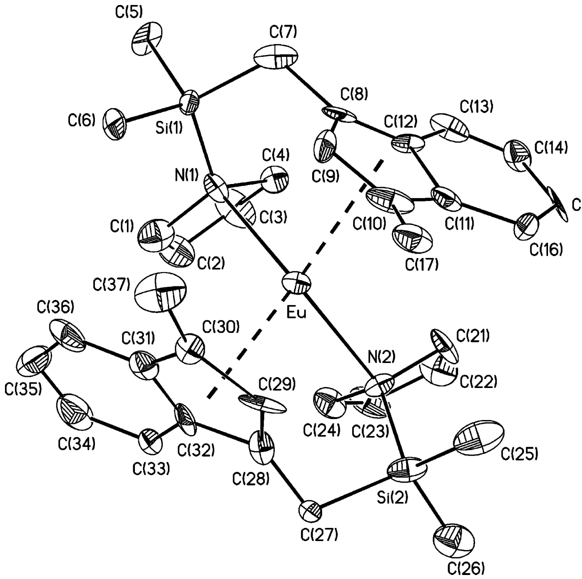

**Figure 2.** Crystal structure of **4**. Hydrogen atoms were omitted for clarity.

silylamine elimination/homolysis of the Yb−N bond reaction.[14] This result also suggested that the substituted methyl group may prevent the radical [(Me$_3$Si)$_2$N] from abstracting hydrogen from the indene compound C$_9$H$_6$-1-Me-3-CH$_2$SiMe$_2$NC$_4$H$_8$.

On the basis of the above evidence, the formation pathway for complex **3** is proposed as follows: the interaction of C$_9$H$_7$CH$_2$SiMe$_2$NC$_4$H$_8$ with europium(III) amide [(Me$_3$Si)$_2$N]$_3$Eu$^{III}$($\mu$-Cl)Li(THF)$_3$ in refluxing toluene produced an unidentified europium(II) compound through the silylamine elimination/homolysis of the Eu−N bond reactions and the radical [(Me$_3$Si)$_2$N] to initiate the reaction. The radical abstracts a hydrogen atom from C$_9$H$_7$CH$_2$SiMe$_2$NC$_4$H$_8$ to produce a new indenyl radical, [C$_9$H$_6$CH$_2$SiMe$_2$NC$_4$H$_8$]$^•$. This radical coupled to form the coupled indene compound [C$_9$H$_6$CH$_2$SiMe$_2$NC$_4$H$_8$]$_2$, which reacted with [(Me$_3$Si)$_2$N]$_3$Eu$^{III}$($\mu$-Cl)Li(THF)$_3$ to produce the novel triple-decker sandwich tetranuclear europium(II) compound [{$\eta^5$:$\eta^5$:$\eta^1$-(C$_9$H$_5$CH$_2$SiMe$_2$NC$_4$H$_8$)$_2$}Eu$_2$($\mu$-Cl)]$_2$[$\mu$-$\eta^3$:$\eta^5$:$\eta^1$:$\eta^3$:$\eta^5$:$\eta^1$-(C$_9$H$_5$CH$_2$SiMe$_2$NC$_4$H$_8$)$_2$]·C$_7$H$_8$·(C$_6$H$_6$)$_{0.5}$ and the radical [(Me$_3$Si)$_2$N] via tandem silylamine elimination/homolysis of the Eu−N bond reactions. The radical [(Me$_3$Si)$_2$N] cycled the reaction to completion. So, the coupling product [N(SiMe$_3$)$_2$]$_2$ has not been detected by GC−MS analyses for the radical (Me$_3$Si)$_2$N abstracting a hydrogen atom from the indene compound C$_9$H$_7$CH$_2$SiMe$_2$NC$_4$H$_8$ to form the amine (Me$_3$Si)$_2$NH.

**MMA Polymerization.** The activities of the europium(II) complexes as single-component catalysts in catalyzing MMA polymerization were examined. The polymerization procedures were carried out in a series of solvents. The polymer product was quenched with acidified methanol after a fixed interval. The microstructure of polymer was analyzed by $^1$H NMR spectra. It was found that these complexes could catalyze MMA polymerization in solvents such as THF and DME. The results are summarized in Table 3.

It was found that the activities of the catalysts are sensitive to temperature and solvents. The complexes showed higher activities in solvents such as THF and DME than in toluene. The catalysts showed poor activities in toluene with only a trace of polymers isolated. The catalytic activity of the complexes is also poor in the temperature range 0−20 °C. It was found that the catalysts' activities increase as the polymerization temperatures decrease. Catalyst **3** showed the highest activity at −60 °C in THF or in DME, and the catalyst **4** had the highest activity at −30 °C in THF and at −60 °C in DME.

GPC analyses showed that the molecular weight of the polymers is dependent on the catalyst and temperature. The molecular weight of the polymers increases as the temperature decreases, indicating that the chain propagation process is favored at low temperatures. Indenyl ligands have not been detected on the polymer chains in all cases based on the $^1$H NMR studies, suggesting that the polymerization may not go through a migration insertion mechanism. The results of the molecular weight studies on the polymers support the supposition that the initiation with the europium(II) complexes occurs through reductive dimerization of MMA via electron transfer from the center Eu(II) metal to form a bis-initiator, comprising two europium(III) enolates joined through their double-bond termini.[22]

A microanalysis of polymers showed that the syndiotactic polymer is the major content of the polymers, and the ratios increase slightly as the polymerization temperatures decrease. These results are similar to those

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(22) Boffa, L. S.; Novak, B. M. *Macromolecules* **1994**, *27*, 6993.

found for the ytterbium(II) catalysts,[14] but different from the results reported by Knjazhanskui.[23] The stereochemistry of the polymers may be due to the empimerization property[14,24] of the active center of the indenyl europium(III) intermediates during the initiation and propagation processes.

## Conclusion

In summary, the homolysis of the Eu−N bond was for the first time developed. The reaction leads to the synthesis and characterization of novel europium(II) complexes. Reactions of different substituted indene compounds with europium(III) amide result in two different types of complexes, an unusual triple-decker sandwich tetranuclear europium(II) complex with a coupled indenyl ligand and the first structurally characterized monomeric europium(II) complex with an indenyl ligand, indicating the ligands' effects on the reactivity and the coordination chemistry. This work indicates that multinuclear sandwich organolanthanide(II) complexes could be constructed with coupled indenyl ligands other than cyclopentadienyl and cyclooctatetraenyl mixed ligands. These kinds of complexes may have potential applications as multielectron reductants in synthetic chemistry. This work also demonstrated that the homolysis of Yb−N bond chemistry can be extended to europium chemistry, which provides a new methodology for the preparation of europium(II) complexes. The catalytic activities of the complexes on MMA polymerization showed the applications of the europium(II) complexes as electron transfer reagents in materials chemistry. An extended study of the electronic and ligand effects on the reaction chemistry is now in progress in our laboratory.

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**Supporting Information Available:** X-ray crystallographic files for the structure determination of complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-207419 (**3**) and CCDC-207420 (**4**) containing this material can also be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB21EZ, UK (fax: (+44) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

OM030306P

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