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A New Heteroatom Coordination Promoted Homolysis of the Yb−N Bond. Synthesis and Structural Characterization of a New Class of Ytterbium(II) and Ytterbium(III) Complexes with Amido and Indenyl Ligands and Catalytic Activities of Ytterbium(II) Complexes

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Reaction of $Me_2Si(Me_2NCH_2CH_2C_9H_6)Cl$ with 1 equiv of *t*-BuNHLi yielded $Me_2Si(Me_2NCH_2CH_2C_9H_6)$(*t*-BuNH) (**1**). Treatment of $Me_2NCH_2CH_2C_9H_7$ with 1 equiv of *n*-BuLi, followed by reaction with an excess of Me_3SiCl, produced $Me_2NCH_2CH_2C_9H_6SiMe_3$ (**2**) in 79% yield. Interaction of $YbCl_3$ with 3 equiv of $(Me_3Si)_2NLi$ in THF, after workup, produced the tetracoordinate ytterbium(III) amide $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-Cl})Li(THF)_3$ (**3**) in 85% yield. Treatment of **3** with 2 equiv of **1** gave the ytterbium(II) complex $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-BuNH})]_2Yb^{II}$ (**4**) in 58% yield via a reductive reaction. To get some insight into the reaction, several reactions were initiated to study the effects of the *t*-BuNH group, silyl group, and *N*,*N*-dimethylaminoethyl group of the indene compounds, effects of coordinate $ClLi(THF)_3$ in **3**, and temperature effect on the reductive reaction. Treatment of **3** with 2 equiv of **2** afforded $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb^{II}$ (**5**) in 52% yield. Interaction of **3** with 2 equiv of $Me_2NCH_2CH_2C_9H_7$ produced a ytterbium(II) complex $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb^{II}$ (**6**) in 63% yield. Treatment of the ytterbium(III) complex $[(Me_3Si)_2N]_3Yb^{III}$ with 2 equiv of $Me_2NCH_2CH_2C_9H_7$ also afforded the ytterbium(II) complex $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb^{II}$ (**6**) in 62% yield, which provides an alternate method for the preparation of **6**. Treatment of **3** with 2 equiv of indene(C_9H_8) produced the ytterbium(III) complex $(\eta^5\text{-}C_9H_7)_2Yb^{III}N(SiMe_3)_2$ (**7**). Treatment of **3** with 1 equiv of 1,2-bis(indenyl)ethane also produced the ytterbium(III) complex *meso*-[ethylenebis(η^5-indenyl)ytterbium^{III} bis(trimethylsily)amide ($(EBI)Yb^{III}N(SiMe_3)_2$) (**8**). All the compounds were fully characterized by spectroscopic methods and elemental analyses. Complexes **3**, **4**, **5**, **6**, and **8** were additionally characterized by a single-crystal X-ray diffraction study. The formation pathway for the ytterbium(II) complexes is proposed. The study showed that ytterbuim(II) complexes **4**, **5**, and **6** can function as single-component MMA polymerization catalysts with good activity.

Introduction

It has been reported that lanthanide complexes with a Ln−N bond show a diverse chemistry, which includes catalytic activity for olefin transformations such as olefin polymerization,[1] hydroamination/cyclyzation reactions,[2] Tishchenko reaction,[3] ring-opening polymerization of ϵ-caprolactone and δ-valerolactone,[4] insertion reaction,[5] and reductive activity.[6]

It has been reported that reaction of dimethylsilyl-bridged indene compounds with $Ln[N(SiMe_3)_2]_3$ or $Ln[N(SiHMe_2)_2]_3$ produced expected C_2-symmetric *ansa*-

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organolanthanide amides via silylamine elimination reaction under refluxing toluene or mesitylene conditions.[7] However, the reactivity of indene compounds containing heteroatom-substituted side chains with lanthanide amides $Ln[N(SiMe_3)_2]_3$ or their analogues is far less elucidated to date. In contrast, ytterbium(II) and samarium(II) complexes showed catalytic activity on olefin polymerization.[8]

We report herein the synthesis and structural characterization of ytterbium(II) complexes by the reaction of ytterbium(III) amides with *N*,*N*-dimethylaminoethyl-substituted indene compounds via heteroatom coordination promoted homolysis of the Yb−N bond. The mechanistic pathway is proposed based on the study of substituent effects of indene compounds, the effect of coordinated $ClLi(THF)_3$ in $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, temperature effects, and reaction product identification. Some of lanthanide(III) complexes were also synthesized and characterized for description of the mechanism. Catalytic activities of ytterbium(II) complexes have been studied.

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 refluxed and 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. $YbCl_3$,[9] $(Me_3Si)_2NLi$,[10] $[(Me_3Si)_2N]_3Yb$,[10] $Me_2Si(Me_2NCH_2CH_2C_9H_6)Cl$,[11] and $Me_2NCH_2CH_2C_9H_7$[12] were prepared according to reported procedures. Elemental analysis 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). Melting points were determined in sealed capillaries. 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 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 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 weight and polydispersities of polymers were given relative to PS standards. The polymers were analyzed according to the literature.[13]

Preparation of $Me_2Si(Me_2NCH_2CH_2C_9H_6)(t\text{-}BuNH)$ (1). To a solution of t-$BuNH_2$ (2.73 g, 37.4 mmol) in 30.0 mL of diethyl ether was slowly added a 1.63 M n-BuLi solution (22.9 mL, 37.4 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 h and was then cooled to 0 °C. To the reaction mixture was slowly added $Me_2Si(Me_2NCH_2CH_2C_9H_6)Cl$ (10.45 g, 37.4 mmol) in 15 mL of diethyl ether. The reaction mixture was stirred at room temperature overnight. The precipitate was filtered off. The solvent was removed under vacuum to give the product as a red oil (9.50 g, 80%). ^1H NMR ($CDCl_3$): δ 7.52 (d, $J = 7.44$ Hz, 1H), 7.40 (d, $J = 7.20$ Hz, 1H), 7.25 (m, 1H), 7.16 (m, 1H), 6.36 (d, $J = 1.8$ Hz, 1H), 3.48 (d, $J = 1.8$ Hz, 1H) (C_9H_6), 2.80 (m, 2H), 2.61 (m, 2H) (CH_2CH_2), 2.33 (s, 6H) ($N(CH_3)_2$), 1.18 (s, 9H) ($C(CH_3)_3$), 0.63 (s, 1H) (NH), −0.06 (s, 3H), −0.12 (s, 3H) ($Si(CH_3)_2$). IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3381 w, 3066 w, 2963 s, 1601 s, 1458 vs, 1379 vs, 1248 vs, 1072 vs, 1021 vs, 850 vs, 780 vs, 721 m, 475 m. Anal. Calcd for $C_{19}H_{32}N_2Si$: C, 72.09; H, 10.19; N, 8.85. Found: C, 71.85; H, 10.15; N, 9.03.

Preparation of $Me_2NCH_2CH_2C_9H_6SiMe_3$ (2). To a solution of $Me_2NCH_2CH_2C_9H_7$ (3.75 g, 20.0 mmol) in 50.0 mL of THF was slowly added a 1.57 M n-BuLi solution (12.7 mL, 20.0 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 6 h. To the reaction mixture was added freshly distilled Me_3SiCl (3.50 g, 32.2 mmol), and the reaction mixture was stirred at room temperature overnight. The solvent was pumped off, and 30 mL of n-hexane was added. The precipitate was filtered off, and the solvent was pumped off, leaving a pale yellow oil (4.08 g, 79%). ^1H NMR ($CDCl_3$): δ 7.42 (m, 2H), 7.26 (m, 2H), 7.16 (m, 1H), 6.34 (s, 1H), 3.39 (s, 1H) (C_9H_6), 2.82 (m, 2H), 2.60 (m, 2H) (CH_2CH_2), 2.33 (s, 6H) ($N(CH_3)_2$), −0.07 (s, 9H) ($Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 146.34, 144.53, 139.82, 130.82, 124.89, 123.98, 123.12, 119.21, 45.02 (C_9H_6), 59.48, 26.69 (CH_2CH_2), 45.89 (($N(CH_3)_2$), −2.13 ($Si(CH_3)_3$). Anal. Calcd for $C_{16}H_{25}NSi$: C, 74.06; H, 9.71; N, 5.40. Found: C, 73.88; H, 9.61; N, 5.45.

Preparation of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (3). To a suspension of $YbCl_3$ (3.9 g, 14.0 mmol) in THF (30.0 mL) was added a freshly prepared solid of $(Me_3Si)_2NLi$ (7.03 g, 42.0 mmol). The reaction mixture was refluxed overnight. The solvent was then pumped off, leaving a pale yellow solid, to which was added 30 mL of toluene. The mixture was heated until all products were dissolved. The precipitate was filtered off, and the solution was concentrated. Yellow crystals were obtained upon standing the solution at room temperature for several days (10.86 g, 85%). Mp: 112−115 °C. Anal. Calcd for $C_{30}H_{78}ClLiN_3O_3Si_6Yb$: C, 39.47; H, 8.61; N, 4.60. Found: C, 39.34; H, 8.37; N, 4.68. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 2959 m, 2927 m, 1250 s, 1203 s, 1178 s, 932 m, 843 m, 721 m, 600 s, 520 s. The ^1H NMR (pyridine-d_5) spectrum provided no chemical information due to the lack of locking signals due to the paramagnetic property of the complex.

Preparation of $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-}BuNH)]_2Yb^{II}$ (4). To a toluene (50.0 mL) solution of **3** (1.39 g, 1.52 mmol) was slowly added a toluene (10.0 mL) solution of $Me_2Si(Me_2NCH_2CH_2C_9H_6)(t\text{-}BuNH)$ (0.96 g, 3.04 mmol). The yellow solution was stirred at room temperature for 3 h. The mixture was then heated to reflux for 3 h. The color of the reaction mixture was gradually changed from yellow to blue to dark red. The solvent was evaporated under vacuum, leaving an oily red residue, which was washed with 10 mL of n-hexane. The solvents were filtered off. The red solid was extracted with toluene (10 mL × 3), and the solution was

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combined and concentrated to about 15 mL. [η^5:η^1-$Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-}BuNH)]_2Yb^{II}$ (**4**) was isolated as orange-red crystals (0.71 g, 58%) by cooling the solution to −10 °C for several days. Mp: 244−246 °C (dec). ^{1}H NMR (pyridine-d_5): δ 7.72 (m, 4H), 7.33 (m, 4H), 6.57 (s, 2H) (C_9H_5), 2.88 (m, 4H), 2.66 (m, 4H) (CH_2CH_2), 2.22 (s, 12H) ($N(CH_3)_2$), 1.19 (s, 18H) ($C(CH_3)_3$), 0.63 (s, 2H) (NH), 0.03 (s, 6H), −0.01 (s, 6H) ($Si(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 146.66, 145.48, 140.04, 132.28, 129.65, 128.91, 126.00, 125.15, 119.58 (C_9H_5), 59.64, 45.76, 26.92 ($CH_2CH_2N(CH_3)_2$), 47.70, 34.10 ($C(CH_3)_3$), 0.29, −0.38 ($Si(CH_3)_2$). IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3393 w, 3065 w, 2965 s, 1603 m, 1459 s, 1379 s, 1249 s, 1072 m, 1020 vs, 849 m, 780 s, 721 m, 435 w. Anal. Calcd for $C_{38}H_{62}N_4Si_2Yb$: C, 56.76; H, 7.77; N, 6.97. Found: C, 56.60; H, 7.54; N, 6.90.

Running the reaction at 50 °C overnight afforded, after workup, a red solid product identified to be complex **4** upon elemental and ^{1}H NMR analyses. Attempts to isolate the blue solution product failed due to instantly conversion to the red product upon recrystallization.

Preparation of [η^5:η^1-($Me_2NCH_2CH_2C_9H_5SiMe_3$)]$_2$Yb^{II} (5). This compound was prepared as red crystals in 52% yield from a reaction of **3** (1.25 g, 1.37 mmol) with **2** (0.71 g, 2.74 mmol) following procedures similar to those used in the preparation of **4**. Mp: 191−193 °C. ^{1}H NMR (pyridine-d_5): δ 7.57 (m, 4H), 7.30 (m, 4H), 7.05 (s, 2H) (C_9H_5), 2.86 (m, 4H), 2.62 (m, 4H) (CH_2CH_2), 2.22 (s, 12H) ($N(CH_3)_2$), 0.38 (s, 12H), −0.036 (s, 6H) ($Si(CH_3)_3$). ^{13}C NMR (pyridine-d_5): δ 146.52, 145.04, 140.33, 134.98, 129.60, 128.85, 125.28, 124.30, 119.65 (C_9H_5), 59.55, 45.68, 26.77 ($CH_2CH_2N(CH_3)_2$), 2.02, −2.30 ($Si(CH_3)_3$). IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3069 m, 2951 s, 1628 m, 1458 s, 1374 m, 1260 m, 1249 vs, 1072 m, 1021 m, 839 vs, 764 m, 720 m, 433 w, 387 w. Anal. Calcd for $C_{32}H_{48}N_2Si_2Yb$: C, 55.71; H, 7.01; N, 4.06. Found: C, 55.36; H, 6.88; N, 3.92.

All attempts to isolate the blue solution product in the temperature range from 30 to 70 °C failed. Compound **5** was isolated upon recrystallization.

Preparation of (η^5:η^1-$Me_2NCH_2CH_2C_9H_6$)$_2$Yb^{II} (6). This complex was prepared as dark red crystals in 63% yield from a reaction of **3** (1.37 g, 1.50 mmol) with $Me_2NCH_2CH_2C_9H_7$ (0.56 g, 3.0 mmol) following procedures similar to those used in preparation of **4**. Mp: 1184−186 °C. ^{1}H NMR (pyridine-d_5): δ 7.45 (m, 4H), 7.38 (m, 4H), 7.00 (m, 2H), 6.21 (m, 2H) (C_9H_6), 2.72 (m, 4H), 2.56 (m, 4H) (CH_2CH_2), 2.19 (s, 12H) ($N(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 146.16, 144.96, 143.28, 129.08, 126.72, 125.24, 119.65, 119.37, 117.06 (C_9H_6), 58.78, 45.73, 26.69 ($CH_2CH_2N(CH_3)_2$). IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3183 m, 2922 vs, 1609 m, 1457 vs, 1375 s, 1265 m, 1073 m, 1018 m, 769 s, 718 m, 410 w, 387 w. Anal. Calcd for $C_{26}H_{32}N_2Yb$: C, 57.24; H, 5.91; N, 5.13. Found: C, 57.01; H, 5.94; N, 5.36.

Running the reaction at 60 °C also produced a red solid product identified as complex **6** by spectroscopic methods.

Reaction of $Me_2NCH_2CH_2C_9H_7$ with [$(Me_3Si)_2N]_3Yb^{III}$. To a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}$ (0.78 g, 1.19 mmol) was slowly added a toluene (10.0 mL) solution of $Me_2NCH_2CH_2C_9H_7$ (0.44 g, 2.38 mmol). The yellow solution was stirred at room temperature overnight. The mixture was then refluxed for 6 h. The color of the reaction mixture was gradually changed from yellow to dark red. The solvent was evaporated under vacuum, leaving an oily red residue, which was washed with 10 mL of *n*-hexane. The solvents were filtered off. The red solid was extracted with toluene (10 mL × 2), and the solution was combined and concentrated to about 15 mL. The complex was isolated as orange-red crystals (0.51 g, 62%) by cooling the solution to −15 °C for several days. The complex was identified as (η^5:η^1-$Me_2NCH_2CH_2C_9H_6)_2Yb^{II}$ (**6**) upon spectroscopic analyses and single-crystal structure determination. ^{1}H NMR (pyridine-d_5): δ 7.45 (m, 4H), 7.38 (m, 4H), 7.00 (m, 2H), 6.21 (m, 2H) (C_9H_6), 2.72 (m, 4H), 2.56 (m, 4H) (CH_2CH_2), 2.19 (s, 12H) ($N(CH_3)_2$). ^{13}C NMR (pyridine-d_5): δ 146.16, 144.96, 143.28, 129.08, 126.72, 125.24, 119.65, 119.37, 117.06 (C_9H_6), 58.78, 45.73, 26.69 ($CH_2CH_2N(CH_3)_2$).

GC−MS and MS Analyses. A small portion of the reaction mixtures for the preparation of **4**, **5**, and **6** was hydrolyzed and analyzed by GC−MS technology; indene compounds **1** or **2** or $Me_2NCH_2CH_2C_9H_7$, $HN(SiMe_3)_2$, and $[N(SiMe_3)_2]_2$ were detected in each component. MS analyses of the reaction mixtures for the preparation of **4**, **5**, and **6** showed a fragment with $m/z = 319$ with relative abundance about 7%, which can be attributed to the fragment of $\{[N(SiMe_3)_2]_2 - H\}^+$. No indene coupling product was detected.

Preparation of (η^5-$C_9H_7)_2Yb^{III}N(SiMe_3)_2$ (7). To a toluene (30.0 mL) solution of **3** (1.59 g, 1.75 mmol) was added slowly a toluene (10.0 mL) solution of C_9H_8 (0.41 g, 3.50 mmol). The mixture was stirred at room temperature for 3 h. The mixture was then refluxed overnight. The color of the reaction mixture gradually changed from yellow to dark blue. The solvent was evaporated to dryness under vacuum, leaving a dark blue solid. The dark blue solid was extracted with *n*-hexane (10 mL × 2), and the solution was combined and concentrated to about 15.0 mL. The complex (η^5-$C_9H_7)_2Yb^{III}N(SiMe_3)_2$ was isolated as a dark blue crystalline solid (0.60 g, 61%) by cooling the solution to −15 °C for several days. The ^{1}H NMR (pyridine-d_5) spectrum gave several very broad unresolved resonances due to the paramagnetic property of the complex. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3067 w, 2959 m, 1609 m, 1457 m, 1397 m, 1250m, 1225 m, 1172 m, 1121 m, 1019 m, 969 m, 945 m, 845 m, 765 s, 717 s, 690 s, 550 m, 417 m. Anal. Calcd for $C_{24}H_{32}NSi_2Yb$: C, 51.13; H, 5.72; N, 2.48. Found: C, 50.84; H, 5.49; N, 2.60.

Preparation of *meso*-(EBI)Yb^{III}N(SiMe$_3$)$_2$ (8). This complex was prepared as dark blue crystals in 68% yield from reaction of **3** (1.21 g, 1.33 mmol) with 1,2-bis(indenyl)ethane (0.34 g, 1.33 mmol) following procedures similar to those used in the preparation of **7**. The ^{1}H NMR (pyridine-d_5) spectrum was not informative due to the lack of locking signals due to the paramagnetic property of the complex. IR (Nujol and Fluoroble mulls, cm^{-1}): ν 3059 w, 2952 m, 2927 m, 1248 m, 1203 m, 1085 m, 929 m, 767 s, 737 m, 720 m. Anal. Calcd for $C_{26}H_{34}NSi_2Yb$: C, 52.95; H, 5.81; N, 2.37. Found: C, 52.69; H, 5.81; N, 2.58. Refluxing the reaction or refluxing **8** in toluene for 3 days did not lead to reduction of Yb(III) to Yb(II); complex **8** was isolated.

X-ray Data Collection and Structure Determination for 3, 4, 5, 6, and 8. 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 Kα radiation (λ = 0.71073 Å), temperature 293(2) K, φ and ω scan technique. SADABS effects and empirical absorption were applied in the data corrections.[14] All structures were solved by direct methods (SHELXS-97),[14] 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**, **4**, **5**, **6**, and **8** 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 (0.020 g to 0.045 g) was loaded into the Schlenk flask and solvent was added. After the external bath temperature was stabilized, MMA was added

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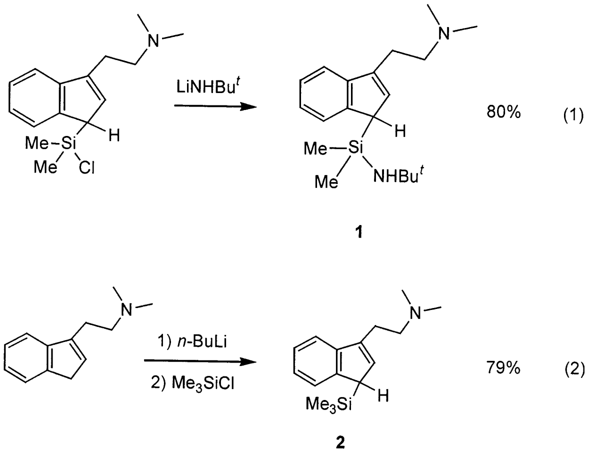
[14] Sheldrick, G. M. *SHELXTL*, version 5.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

Table 1. Crystal and Data Collection Parameters for 3, 4, 5, 6, and 8

	3	4	5	6	8
empirical formula	$C_{30}H_{78}N_3ClLiO_3Si_6Yb$	$C_{38}H_{62}N_4Si_2Yb$	$C_{32}H_{48}N_2Si_2Yb$	$C_{26}H_{32}N_2Yb$	$C_{52}H_{66}N_2Si_4Yb_2$
fw	912.92	804.14	689.94	545.58	1177.51
cryst syst	monoclinic	tetragonal	tetragonal	monoclinic	monoclinic
space group	*I*2/*a*	*I*(−4)2*d*	*I*(−4)	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	25.0333(8)	23.296(7)	21.2358(10)	17.32110(10)	10.62030(10)
b (Å)	16.3725(6)	23.296(7)	21.2358(10)	8.53030(10)	21.2833(2)
c (Å)	27.4177(15)	14.964(4)	15.8285(11)	17.29840(10)	23.1279(2)
β (deg)	90.8290(10)			118.67(10)	91.9080
V (Å^3)	11236.2(8)	8121(4)	7142.5(7)	2242.51(3)	5224.82(8)
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
D_{calcd} (g cm^{-3})	1.079	1.315	1.283	1.616	1.497
Z	8	8	8	4	4
F(000)	3816	3328	2816	1088	2352
no. of reflns collected	20 327	4240	8672	4524	16 691
no. of unique reflns	9726 (R_{int} = 0.030)	2160 (R_{int} = 0.130)	5300 (R_{int} = 0.035)	4377 (R_{int} = 0.050)	9126 (R_{int} = 0.026)
no. of params	406	199	334	262	541
λ (Å), Mo Kα	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	1.865	2.391	2.706	4.184	3.684
2θ range	4.34 to 50.22	3.24 to 51.90	5.82 to 50.04	5.48 to 52.04	2.60 to 50.10
goodness of fit	1.089	1.003	1.138	1.061	1.128
R ($I > 2\sigma(I)$)	0.046	0.060	0.053	0.052	0.040
wR_2	0.106	0.118	0.104	0.123	0.084

Scheme 1



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 overnight to a constant weight.

Results and Discussion

Synthesis of $Me_2Si(Me_2NCH_2CH_2C_9H_6)$(*t*-BuNH) (1) and $Me_2NCH_2CH_2C_9H_6SiMe_3$ (2). Treatment of $Me_2Si(Me_2NCH_2CH_2C_9H_6)Cl$ with 1 equiv of *t*-BuNHLi in diethyl ether yielded, after workup, $Me_2Si(Me_2NCH_2CH_2C_9H_6)$(*t*-BuNH) (**1**) in 80% yield (Scheme 1, eq 1). Reaction of $Me_2NCH_2CH_2C_9H_7$ with 1 equiv of *n*-BuLi, followed by reaction with excess Me_3SiCl, produced **2** in 79% yield (Scheme 1, eq 2). **1** and **2** were characterized by spectroscopic and elemental analyses. ^{1}H NMR spectra show that **1** and **2** are pure compounds in which the *N*,*N*-dimethylaminoethyl group bonds to the sp^2 carbon of the five-membered ring of the indenyl group and the silyl group connects to the sp^3 carbon atom of the five-membered ring of the indenyl group.

Synthesis and Characterization of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (3). Interaction of anhydrous $YbCl_3$ with 3 equiv of $(Me_3Si)_2NLi$ gave, after recrystallization from hot toluene, $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (**3**) in 85% yield (Scheme 2). **3** is soluble in THF and toluene and slightly soluble in *n*-hexane. Complex **3** was fully characterized by spectroscopic and elemental analyses. Its structure was determined by a single-crystal X-ray diffraction study.

Scheme 2

$$YbCl_3 + 3\ LiN(SiMe_3)_2 \xrightarrow{THF} [(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$$

3 85%

Reactions of Indene Compounds with Ytterbium(III) Amides: Homolysis of the Yb−N Bond. Interaction between $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (**3**) and 2 equiv of $Me_2Si(Me_2NCH_2CH_2C_9H_6)$(*t*-BuNH) (**1**) in refluxing toluene gave, after recrystallization from toluene, the ytterbium(II) complex $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-}BuNH)]_2Yb^{II}$ (**4**) (Scheme 3, eq 1), instead of the ytterbium(III) amide $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-}BuNH)]_2YbN(SiMe_3)_2$, as orange-red crystals in 58% yield. Complex **4** is air- and moisture-sensitive and is soluble in THF, pyridine, and toluene and slightly soluble in *n*-hexane. The complex was fully characterized by spectroscopic methods and elemental analyses. NMR spectroscopic analyses showed a diamagnetic property of the complex, suggesting it is a ytterbium(II) complex. Its structure was confirmed by single-crystal X-ray diffraction.

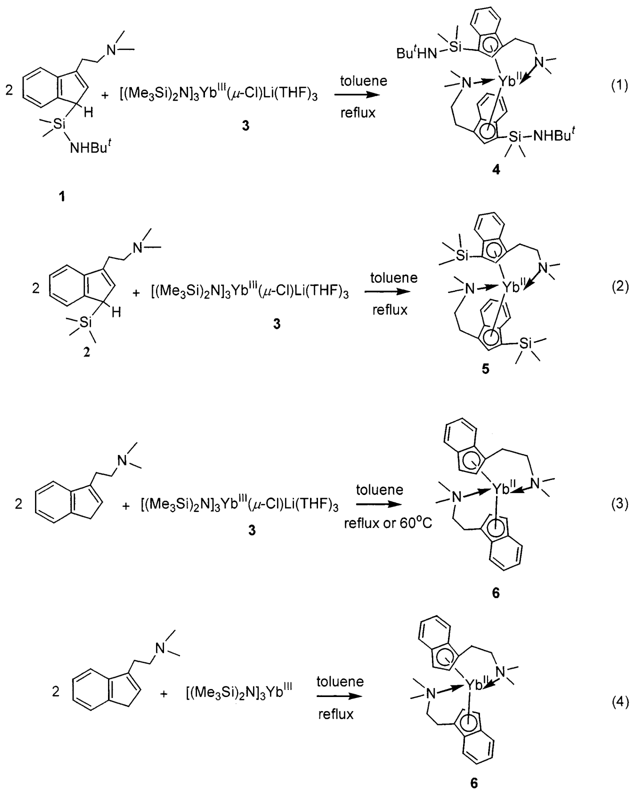
The formation of complex **4** clearly indicated that the reaction goes through a reductive process. To get some insight into the reaction mechanism, several reactions were initiated to study the effects of the *t*-BuNH, silyl, and *N*,*N*-dimethylaminoethyl groups of indene compounds, the effect of coordinated $ClLi(THF)_3$ in **3**, and the temperature effects on the reductive reaction.

Reaction of **3** with 2 equiv of $Me_2NCH_2CH_2C_9H_6SiMe_3$ (**2**) produced, after workup, $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Yb^{II}$ (**5**) as red crystals in 52% yield (Scheme 3, eq 2). Complex **5** is air- and moisture-sensitive and is soluble in THF, pyridine, and toluene and slightly soluble in *n*-hexane. The complex was fully characterized by spectroscopic methods and elemental analyses, and its structure was determined by single-crystal X-ray diffraction. NMR spectroscopic analyses showed a dia-

Table 2. Selected Bond Lengths (Å) and Angles (deg)

3		**4**		**5**		**6**		**8**			
Yb−N(1)	2.219(5)	Yb−N(1)	2.673(11)	Yb−N(1)	2.655(12)	Yb−N(1)	2.575(7)	Yb(1)−N(1)	2.160(5)	Yb(2)−N(2)	2.163(5)
Yb−N(2)	2.199(4)	Yb−C(1)	2.827(11)	Yb−C(4)	2.849(13)	Yb−C(1)	2.744(8)	Yb(1)−C(1)	2.580(8)	Yb(2)−C(31)	2.574(9)
Yb−N(3)	2.214(5)	Yb−C(6)	2.890(10)	Yb−C(5)	2.845(13)	Yb−C(2)	2.677(8)	Yb(1)−C(2)	2.597(7)	Yb(2)−C(32)	2.596(8)
Yb−N_{av}.	2.211(5)	Yb−C(7)	2.813(12)	Yb−C(10)	2.755(13)	Yb−C(3)	2.688(9)	Yb(1)−C(3)	2.684(7)	Yb(2)−C(33)	2.672(6)
Yb−Cl	2.5519(16)	Yb−C(8)	2.753(11)	Yb−C(11)	2.724(14)	Yb−C(4)	2.740(9)	Yb(1)−C(8)	2.686(7)	Yb(2)−C(38)	2.662(7)
Li−Cl	2.353(14)	Yb−C(9)	2.749(12)	Yb−C(12)	2.756(14)	Yb−C(5)	2.783(8)	Yb(1)−C(9)	2.612(8)	Yb(2)−C(39)	2.610(8)
N(2)−Yb−N(3)	117.2(2)	Yb−C(av)	2.806(12)	Yb−N(2)	2.645(11)	Yb−N(2)	2.601(7)	Yb(1)−C(12)	2.627(7)	Yb(2)−C(42)	2.613(8)
N(2)−Yb−N(1)	114.83(18)	N(1)#−Yb−N(1)	95.1(4)	Yb−C(24)	2.823(12)	Yb−C(14)	2.791(7)	Yb(1)−C(13)	2.596(7)	Yb(2)−C(43)	2.579(7)
N(3)−Yb−N(1)	117.88(18)			Yb−C(25)	2.828(10)	Yb−C(15)	2.695(8)	Yb(1)−C(14)	2.592(8)	Yb(2)−C(44)	2.606(7)
N(2)−Yb−Cl	100.71(14)			Yb−C(30)	2.754(11)	Yb−C(16)	2.642(9)	Yb(1)−C(15)	2.666(7)	Yb(2)−C(45)	2.693(7)
N(3)−Yb−Cl	100.59(13)			Yb−C(31)	2.729(14)	Yb−C(17)	2.678(10)	Yb(1)−C(16)	2.658(7)	Yb(2)−C(46)	2.671(7)
N(1)−Yb−Cl	100.77(13)			Yb−C(32)	2.722(12)	Yb−C(18)	2.786(9)				
				Yb−C(av.)	2.778(14)	Yb−C(av)	2.722(10)				
				N(1)−Yb−N(2)	92.8(5)	N(1)−Yb−N(2)	103.7(2)				

Scheme 3



magnetic property of the complex, suggesting it is a ytterbium(II) complex.

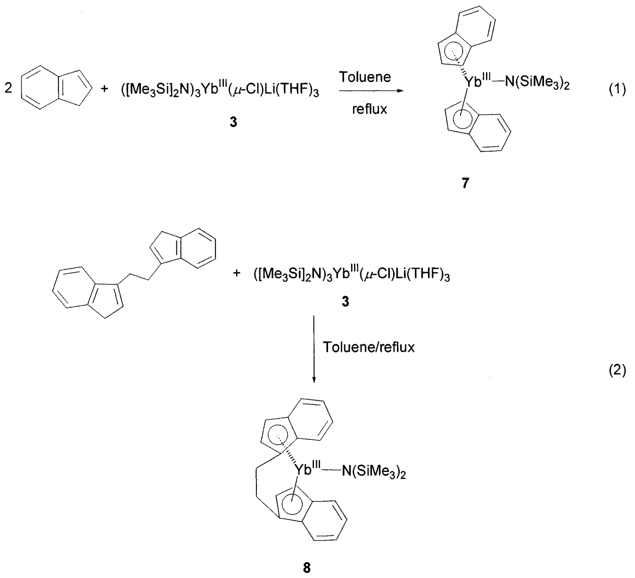
The above results suggested that the *t*-BuNH group of indene compounds has no influence on the reductive reaction. To get further information about the reaction, the following reaction was studied.

Treatment of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of $Me_2NCH_2CH_2C_9H_7$ in refluxing toluene produced, after recrystallization from toluene, $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb^{II}$ (**6**) as dark red crystals in 63% yield (Scheme 3, eq 3). Complex **6** is air- and moisture-sensitive and is soluble in THF, pyridine, and toluene and insoluble in *n*-hexane. The complex was fully characterized by spectroscopic methods and elemental analyses, and NMR analyses showed a diamagnetic property of the complex, indicating that it is a ytterbium(II) compound. Its structure was determined by single-crystal X-ray diffraction study. Running the reaction at 60 °C also produced the complex **6**.

The above results suggested that the reductive reaction does not involve the homolytic cleavage of the Si−C bond of the indene compound. To probe the effect of the coordinate $ClLi(THF)_3$ in $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ (**3**) on the reductive reaction, the interaction of $[(Me_3Si)_2N]_3Yb^{III}$ with $Me_2NCH_2CH_2C_9H_7$ was studied.

Treatment of $[(Me_3Si)_2N]_3Yb^{III}$ with 2 equiv of $Me_2NCH_2CH_2C_9H_7$ in refluxing toluene produced, after recrystallization from hot toluene, dark red crystals in 62% yield (Scheme 3, eq 4). The compound was identified as $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb^{II}$ (**6**) upon spectroscopic and single-crystal structure determination; this reaction also provides an alternate method for the preparation of **6**. This result suggested that coordinate $ClLi(THF)_3$ in **3** has no influence on the one-electron reductive reaction.

Scheme 4



The above results show that the interaction of tetracoordinate ytterbium(III) amide (**3**) and triscoordinate ytterbium(III) amide with either silyl-substituted or non-silyl-substituted *N*,*N*-dimethylaminoethyl-functionalized indene compounds goes through a reductive reaction. To get some information about the function of *N*,*N*-dimethylaminoethyl groups of the indene compounds on the reaction, the following reactions were studied.

Interaction of **3** with 2 equiv of indene (C_9H_8) in refluxing toluene gave (Scheme 4, eq 1), after recrystallization from *n*-hexane, $(\eta^5\text{-}C_9H_7)_2Yb^{III}N(SiMe_3)_2$ (**7**) as a dark blue air- and moisture-sensitive crystalline solid. Compound **7** is soluble in THF, pyridine, and toluene and slightly soluble in *n*-hexane. Complex **7** was fully characterized by spectroscopic and elemental analyses. NMR spectral analyses showed a paramagnetic property of the complex, indicating the +3 oxidation state of Yb metal. All attempts to grow single crystals suitable for X-ray analyses to confirm the ytterbium(III) complex failed due to severe twinning problems. To overcome this difficulty, the interaction of 1,2-bis(indenyl)ethane with **3** was studied.

Treatment of **3** with 1 equiv of 1,2-bis(indenyl)ethane in refluxing toluene (Scheme 4, eq 2) afforded, after recrystallization from *n*-hexane, *meso*-(EBI)$Yb^{III}N(SiMe_3)_2$ (**8**) as dark blue crystals in 68% yield. The complex is soluble in THF, pyridine, toluene, and *n*-hexane. It was characterized by spectroscopic and elemental analyses. NMR spectral study showed a paramagnetic property of the complex, suggesting the +3 oxidation state of the Yb metal. Its structure was determined by single-crystal X-ray diffraction study.

These results not only suggested that the *N*,*N*-dimethylaminoethyl group in the indene compounds might be responsible for the reductive reaction in the formation of **4**, **5**, and **6** but also suggested that the formation of **4**, **5**, and **6** might involve ytterbium(III) amides $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-}BuNH)]_2Yb^{III}N(SiMe_3)_2$, $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Yb^{III}N(SiMe_3)_2$, and $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb^{III}N(SiMe_3)_2$ as intermediates. All the attempts to isolate the intermediates failed, due to quick conversion of the intermediates to the final ytterbium(II) complexes upon purification. The color change during the reaction processes indicated that the reaction may involve ytterbium(III) intermediates. These results also indicated that the intermediates do not involve the coordination of $ClLi(THF)_3$.

Although ytterbium(III) amides **7** and **8** were synthesized at the same temperature reaction conditions for the preparation of **4**, **5**, and **6**, refluxing ytterbium(III) amide **8** in toluene for 3 days did not lead to the reduction of ytterbium(III) to ytterbium(II) complex, suggesting that the temperature may not be the major effect for the reductive reaction. Silylamine elimination reaction sometimes requires higher temperature,[7] which makes it difficult for us to further study the temperature effects on the reaction.

Indene compounds **1** or **2** or $Me_2NCH_2CH_2C_9H_7$, $HN(SiMe_3)_2$, and coupling product $[N(SiMe_3)_2]_2$ have been detected by GC−MS analyses of the hydrolysis of reaction mixtures of the corresponding reactions in the formation of **4**, **5**, and **6**. MS analyses of the reaction mixture for the preparation of **4**, **5**, and **6** showed an *m*/*z* peak at 319 with relative abundance about 7%, which can be attributed to the fragment of $\{[N(SiMe_3)_2]_2 - H\}^+$. No indene coupling product was detected in all the components. These results suggested that the reductive reaction does not go through a tris(indenyl′)ytterbium(III) complex pathway.[15b] It should be noted that the ratio of $HN(SiMe_3)_2$ and coupling product $[N(SiMe_3)_2]_2$ should be 4:1 according to calculations, but only a very small amount of coupling product $[N(SiMe_3)_2]_2$ was detected in all experiments, possibly due to the stability of $[N(SiMe_3)_2]_2$ or the abstraction of a hydrogen atom of the $N(SiMe_3)_2$ radical from the solvent under the reaction conditions.

Evans and co-workers reported that thermal conversion of $[(MeC_5H_4)_2Yb^{III}Me]_2$ to $(MeC_5H_4)_2Yb^{II}$ requires several months at 80 °C in toluene. The presence of diethyl ether facilitates the reaction, however, and conversion of 50% can be achieved in 8 h using a mixed pentane−ether solvent at 80 °C in a pressure vessel.[15a] They have also observed the tendency of $\eta^5\text{-}C_5Me_5$ to form $\eta^1\text{-}C_5Me_5$ by addition of 3 equiv of pyridine to $(\eta^5\text{-}C_5Me_5)_3Sm$ toulene-d_8 solution with the formation of $(\eta^5\text{-}C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)(Pyr)$,[15b] indicating the donor ligand's effects on the conversions.

On the basis of the above results, the pathway for the formation of the ytterbium(II) complexes is proposed as follows: interaction of $Me_2Si(Me_2NCH_2CH_2C_9H_6)(t\text{-}BuNH)$ (**1**), or $Me_2NCH_2CH_2C_9H_6SiMe_3$, or $Me_2NCH_2CH_2C_9H_7$ with $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ (**3**) or $[(Me_3Si)_2N]_3Yb^{III}$ produced $(indenyl')_2Yb^{III}N(SiMe_3)_2$ as intermediates and $HN(SiMe_3)_2$ via silylamine elimination reaction[6,7] and coordination of the nitrogen atom of *N*,*N*-dimethylaminoethyl groups of indenyl ligands to ytterbium metal promoted homolysis of the Yb−N bond to afford the final ytterbium(II) complexes and coupling product $[N(SiMe_3)_2]_2$ at the reaction conditions (Scheme 5).

Molecular Structures. Structures of complexes **3**, **4**, **5**, **6**, and **8** were determined by X-ray diffraction analyses.

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(15) (a) Zinnen, H. A.; Pluth, J.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810. (b) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.***1998**, *120*, 9273.

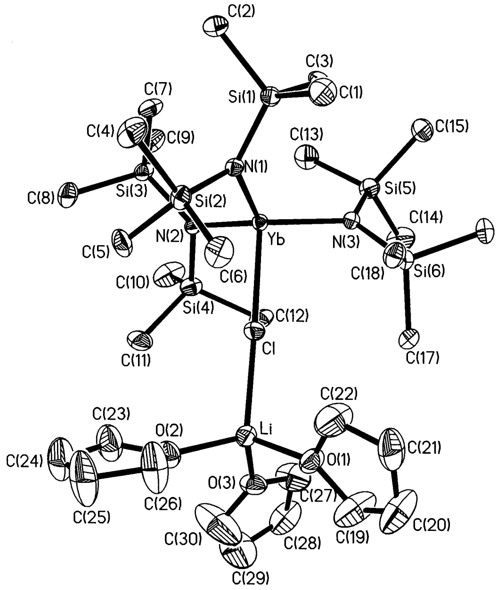
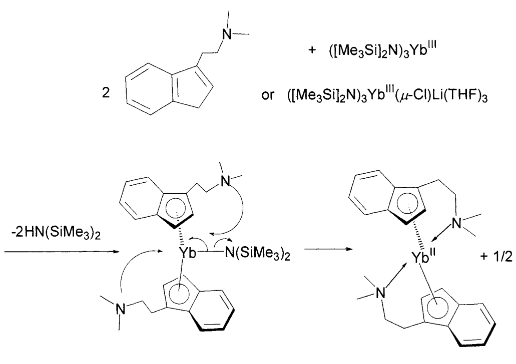


Figure 1. Molecular structure and atom-numbering scheme for $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (**3**). Hydrogen atoms are omitted for clarity.

Scheme 5



Proposed mechanism for the reductive reaction

X-ray analysis reveals that the central metal in complex **3** (Figure 1) coordinated with three nitrogen atoms and a chlorine atom in a distorted tetrahedral form. The angles formed around the metal center Cl−Yb−N(1), Cl−Yb−N(2), and Cl−Yb−N(3) of about 100° (Table 2), and the angles N(1)−Yb−N(2), N(1)−Yb−N(3), and N(2)−Yb−N(3) in the range 114.83(18)−117.88(18)° (Table 2) in compound **3** differ slightly from those found in $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3{\cdot}OC_4H_8$,[16] but largely deviate from an ideal tetrahedral angle. The N−Yb−N angles of 114.83(18)−117.88(18)° found in the complex are close to the corresponding average values of 116.6° and 117.8° found in three-coordinate pyramidal complexes $[(Me_3Si)_2N]_3Ln$ (Ln = Nd,[17] Eu[18]). These results may be due to steric effects.

The chlorine atom bridged lithium and ytterbium metals are almost linear (175.5(4)°, Table 2), which is larger than those (170 ± 2°) found in $Ln\{N[Si(Me_2)_2CH_2CH_2Si(Me_2)]\}_3(\mu\text{-}Cl)Li(L)_3$ (L = THF or Et_2O).[19]

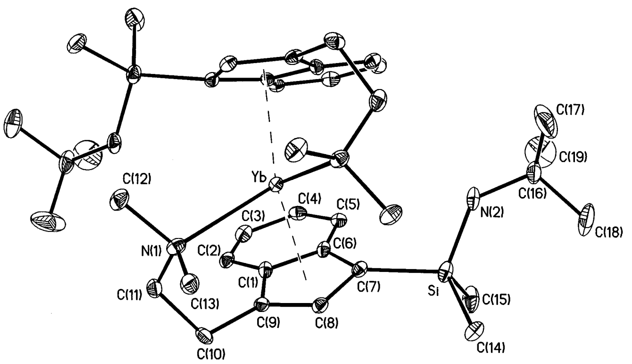


Figure 2. Molecular structure and atom-numbering scheme for $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(t\text{-}BuNH)]_2Yb^{II}$ (**4**). Hydrogen atoms are omitted for clarity.

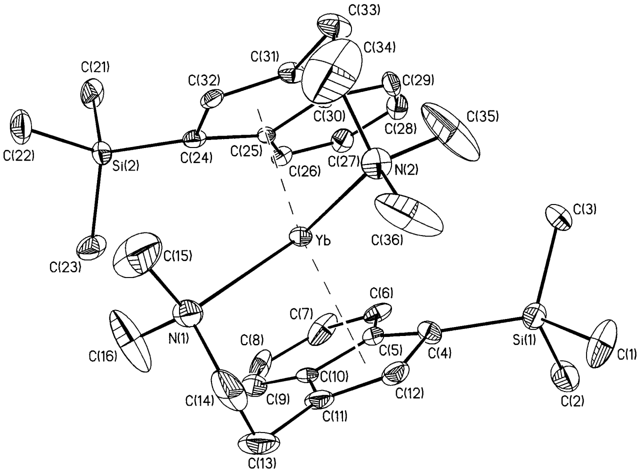


Figure 3. Molecular structure and atom-numbering scheme for $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb^{II}$ (**5**). Hydrogen atoms are omitted for clarity.

These deviation may be due to steric effects. The Ln−Cl and Li−Cl bond distances are comparable to those found in $Ln\{N[Si(Me_2)_2CH_2CH_2Si(Me_2)]\}_3(\mu\text{-}Cl)Li(L)_3$ (L = THF or Et_2O).[19]

The Yb−N bond lengths range from 2.199(4) to 2.219(5) Å, an average of 2.211(5) Å, which is shorter than the corresponding values of 2.29(2) and 2.259(9) Å in the three-coordinate complexes $[(Me_3Si)_2N]_3Ln$ (Ln = Nd,[17] Eu[18]) and is longer than that of 2.158 Å in $[(Me_3Si)_2N]_3Yb$[20] due to the ionic radii difference and steric effects. The Yb−Cl bond length is 2.5519(16) Å, which is slightly shorter than that of 2.572 (2) Å in $[\eta^5\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{11})]YbCl_2(THF)_3$;[21a] this difference is attributed to the ionic radii difference of the different coordinate Yb^{3+} ion.[22]

X-ray analyses confirm the +2 oxidation of ytterbium metal in complexes **4** (Figure 2), **5** (Figure 3), and **6** (Figure 4). The central ytterbium atom in all three complexes lies in a distorted pseudo-tetrahedral coordination sphere and is η^5-bond to each of two indenyl ligands and η^1-bond to the two nitrogen atoms of the

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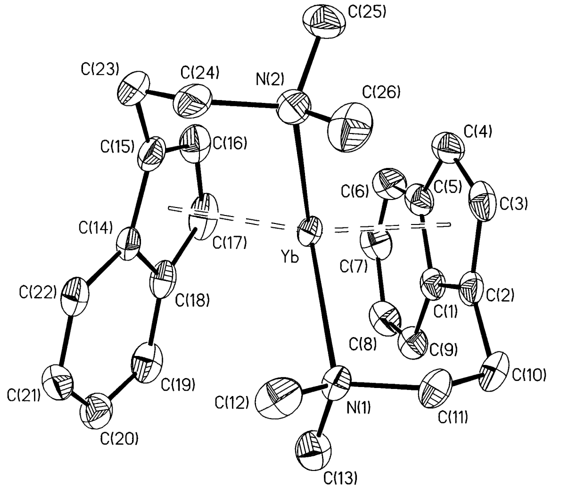

Figure 4. Molecular structure and atom-numbering scheme for $(\eta^5{:}\eta^1\text{-Me}_2NCH_2CH_2C_9H_6)_2Yb^{II}$ (**6**). Hydrogen atoms are omitted for clarity.

Table 3. Comparison of the Selected Geometric Parameters in Distorted Tetrahedral Ytterbium(II) Complexes

complex	$(Yb{-}C)_{av}$ (Å)	$(Yb{-}N)_{av}$ (Å)	N−Yb−N (deg)	ref
4	2.806(12)	2.673(11)	95.1(4)	this work
5	2.778(14)	2.650(12)	92.8(5)	this work
6	2.722(10)	2.588(7)	103.7(2)	this work and 12
$[Yb(Cp^{py})_2]$	2.68(1)	2.48(1)	100.8(2)	24
$[Yb(Cp^{tpy}(s))_2]$	2.68(2)	2.48(1)	84.04(4)	24
$[YbCp^*_2(py)_2]$	2.74(4)	2.56(1)	82.5(2)	25

N,*N*-dimethylaminoethyl groups. A comparison of selected geometric parameters in some of the distorted tetrahedral ytterbium(II) complexes is listed in Table 3. It was found that the more bulky the substitute groups in the five-membered rings are, the longer the average Yb−C and Yb−N bond distances are, indicating steric effects. These results suggested that the smaller substitute groups on the five-membered rings would favor the bonding of the five-membered rings with the metal. The N−Yb−N angles varied with different substitute groups in the five-membered ring.

The average value of the Yb−C distance 2.806(12) Å in **4** is shorter than the corresponding value of 2.818(3) Å in $[\eta^5\text{-Me}_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-Me}_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$,[21b] but is longer than the corresponding value of 2.789(8) Å in $[\eta^5\text{-Me}_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$[23] and is significantly longer than the values of 2.68(1) Å in $[Yb(Cp^{py})_2]$,[24] 2.68(2) Å in $[Yb(Cp^{tpy(s)})_2]$,[24] and 2.74(4) Å in $[YbCp^*_2(Py)_2]$,[25] indicating steric effects. The average Yb−C distance of 2.778(14) Å in **5** is shorter than the corresponding average values of 2.818(3) Å found in $[\eta^5\text{-Me}_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-Me}_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$[21b] and 2.789(8) Å in $[\eta^5\text{-Me}_2C(C_9H_6)(C_2B_{10}H_{10})]Yb(DME)_2$,[23] due to steric effects. The average Yb−N distances 2.673(11) Å in **4**, 2.650(12) Å in **5**, and 2.588(7) Å in **6** are longer than the values of 2.48(1) Å in $[Yb(Cp^{py})_2]$[24] and

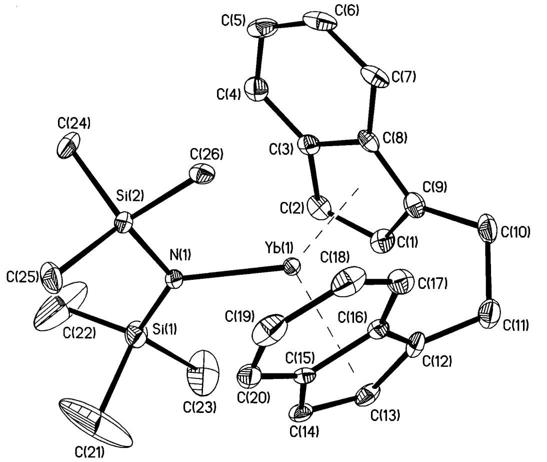

Figure 5. Molecular structure and atom-numbering scheme for $(EBI)Yb^{III}N(SiMe_3)_2$ (**8**). Hydrogen atoms are omitted for clarity.

$[Yb(Cp^{tpy(s)})_2]$[24] and 2.56(1) Å in $[YbCp^*_2(Py)_2]$.[25] The Yb−N distance of 2.588(7) Å in **6** is shorter than that of 2.603(4) Å in $[Yb\{S)\text{-}\eta^5{:}\eta^1\text{-}C_5H_4(CH_2CH(Me)NMe_2)\}_2]$,[26] indicating steric effects.

It is interesting to note that the two Yb−C distances of each five-membered ring in either **4** or **5** are longer than those of others, suggesting that the coordination mode of the indenyl ligands is beginning to bond to the metal in a η^3-fashion.[21b]

X-ray diffraction study reveals that the ytterbium(III) metal in **8** (Figure 5) is η^5-bond to each of the two indenyl groups and σ-bond to the nitrogen atom of the $N(SiMe_3)_2$ ligand. The crystal data and structural parameters of the compound are almost identical to the reported *meso*-$(EBI)Yb^{III}N(SiMe_3)_2$ prepared by the metathesis reaction of *rac*- or *meso*-$(EBI)YbCl_2Li(THF)_2$ with $LiN(SiMe_3)_2$.[27]

MMA Polymerization. The activities of complexes **4**, **5**, and **6** as single-component catalysts in catalyzing MMA polymerization were examined. The polymerization procedures were carried out in a series of solvents. The product was quenched with acidified methanol after a fixed time. Thriad microstructure analysis of polymers was carried out using ^1H NMR or ^{13}C NMR spectra. It was found that these complexes could function as single-component catalysts in catalyzing MMA polymerization in DME, but not in toluene and THF. It is found that some polymers cannot be dissolved in THF or passed through the GPC columns. The results are summarized in Table 4.

It was found that activities of catalysts are temperature dependent. They showed a poor activity in the temperature range 20 to 0 °C. The catalysts' activities increase as the polymerization temperatures decrease, and all the catalysts showed the highest activities (as high as 485.7 kg polymer/mol·cat·h) at low temperature. The activity of catalysts decrease when the polymerization temperatures were below −45 °C. These results are very similar to those of lanthanide(III) complexes.[1b]

It was found that substitute groups on the indenyl ligands also have influence on the activities of the

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Table 4. Data for the Polymerization of Methyl Methacrylate (MMA)[a]

									stereochem(%)		
entry	cat.	t_p (min)	T_p (°C)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	conv (%)	activity	rr	rm	mm
1	**4**	5	20				7	32.2	55	34	11
2	**4**	5	0				27	130.9	60	32	8
3	**4**	5	−15	117.7	68.4	1.72	61	289.4	64	29	7
4	**4**	5	−30	66.0	39.5	1.67	83	399.4	65	27	8
5	**4**	5	−45	132.1	80.7	1.64	100	485.7	73	23	4
6	**4**	5	−60	131.0	71.9	1.82	100	465.7	70	24	6
7	**5**	5	0	31.9	23.3	1.37	16	74.5	58	34	8
8	**5**	5	−15	65.8	41.1	1.60	37	170.2	61	32	7
9	**5**	5	−30				41	195.5	46	30	24
10	**5**	5	−45	93.5	54.0	1.73	90	409.1	64	30	6
11	**5**	5	−60	205.7	117.5	1.75	9	39.7	75	21	4
12	**6**	240	20				4	<0.1	49	38	13
13	**6**	240	0				6	0.55	53	32	15
14	**6**	10	−15	104.8	45.4	2.31	51	121.4	62	28	10
15	**6**	10	−30				77	185.8	56	29	15
16	**6**	10	−45	158.6	91.7	1.73	85	206.8	66	26	8

[a] Conditions: solvent, DME; solvent/monomer, 2.5 (v/v); MMA/catalyst initial ratio, 400:1; activity, kg PolyMMA/mol·catalyst·h; t_p, time for polymerization; T_p, temperature for polymerization.

catalysts. It was found that the larger the substitute group of the indenyl ligand is, the higher the catalytic activity of the catalyst.

GPC analyses showed that the molecular weight of polymers is dependent on the catalyst and the polymerization temperature. The results of molecular weight studies on the polymers support the supposition that initiation with divalent lanthanidocene complexes occurs through reductive dimerization of MMA to form a bis-initiator, comprising two lanthanide(III) enolates joined through their double-bond termini.[28]

A microstructure analysis of polymers showed that the syndiotactic polymer is the major content of the polymer, which is different from the results reported by Knjazhanskui,[29] suggesting that the active center of indenyl ytterbium(III) intermediates may have *meso*-geometry for the empimerization property[1b,30] during initiation and propagation processes. The fact that the value of M_w/M_n (range from 1.37 to 2.31) is far from 1.0 may be explained by partial chain termination caused by deactivation of catalysts with a trace amount of impurities included in the system.

Conclusion

In summary, heteroatom coordination promoted homolysis of the Yb−N bond is developed for the first time. The mechanistic pathway is proposed on the basis of a study of substituent effects of indene compounds, the effect of coordinated $ClLi(THF)_3$ in $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, temperature effects, and reaction product identification. Some of the lanthanide(III) complexes were also synthesized and characterized for a description of the chemistry. This work demonstrates that homolysis of the Yb−N bond provides a new route to obtain ytterbium(II) metallocenes, which showed applications in olefin polymerization. Extension of the chemistry is now in progress in our laboratory.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for structure determination of complexes **3**, **4**, **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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