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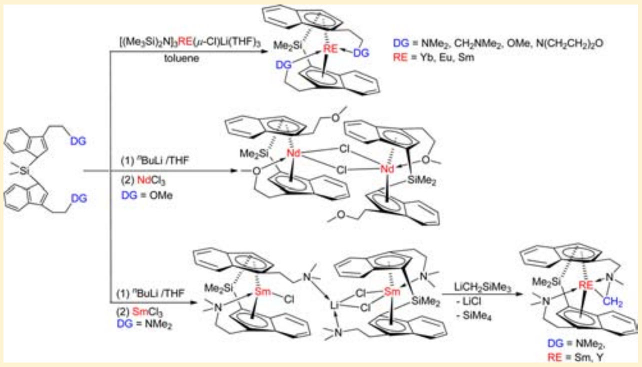
Controlled Synthesis of Racemic Indenyl Rare-Earth Metal Complexes via the Cooperation between the Intramolecular Coordination of Donor Atoms and a Bridge

Shuangliu Zhou,*,[†] Zhangshuan Wu,[†] Lingmin Zhou,[†] Shaowu Wang,*,[†,‡] Lijun Zhang,[†] Xiancui Zhu,[†] Yun Wei,[†] Jinhua Zhai,[†] and Jie Wu[†]

[†]Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China

Ⓢ *Supporting Information*



ABSTRACT: The reactions of $Me_2Si(C_9H_6CH_2CH_2\text{-}DG)_2$ (DG = NMe_2 (**1**), CH_2NMe_2 (**2**), OMe (**3**), and $N(CH_2CH_2)_2O$ (**4**)) with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ in toluene afforded a series of racemic divalent rare-earth metal complexes: $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Me_2Si(C_9H_5CH_2CH_2\text{-}DG)_2\}RE$ (DG = NMe_2, RE = Yb (**6**) and Eu (**7**); DG = CH_2NMe_2, RE = Yb (**8**), Eu (**9**), and Sm (**10**); DG = OMe, RE = Yb (**11**) and Eu (**12**); DG = $N(CH_2CH_2)_2O$, RE = Yb (**13**) and Eu (**14**)). Similarly, the racemic divalent rare-earth metal complexes $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Me_2Si(C_9H_5CH_2CH_2CH_2NMe_2)\text{-}(C_9H_5CH_2CH_2OMe)\}RE$ (RE = Yb (**15**) and Eu (**16**)) were also obtained. The reaction of $Me_2Si(C_9H_5CH_2CH_2OMe)_2Li_2$ with $NdCl_3$ gave a racemic dimeric neodymium chloride $\{\eta^5{:}\eta^1{:}\eta^5\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)_2NdCl\}_2$ (**17**), whereas the reaction of $Me_2Si(C_9H_5CH_2CH_2NMe_2)_2Li_2$ with $SmCl_3$ afforded a racemic dinuclear samarium chloride bridged by lithium chloride $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Me_2Si\text{-}(C_9H_5CH_2CH_2NMe_2)_2SmCl\}_2(\mu\text{-}LiCl)$ (**18**). Further reaction of complex **18** with $LiCH_2SiMe_3$ provided an unexpected rare-earth metal alkyl complex $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)[(C_9H_5CH_2CH_2N(CH_2)Me]\}Sm$ (**19**) through the activation of an sp^3 C−H bond α-adjacent to the nitrogen atom. Complexes **19** and $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)\text{-}[(C_9H_5CH_2CH_2N(CH_2)Me]\}Y$ (**20**) were also obtained by one-pot reactions of $Me_2Si(C_9H_5CH_2CH_2NMe_2)_2Li_2$ with $RECl_3$ followed by treatment with $LiCH_2SiMe_3$. All compounds were fully characterized by spectroscopic methods and elemental analysis. Complexes **6**−**10** and **14**−**20** were further characterized by single-crystal X-ray diffraction analysis. All of the prepared rare-earth metal complexes were racemic, suggesting that racemic organo rare-earth metal complexes could be controllably synthesized by the cooperation between a bridge and the intramolecular coordination of donor atoms.

■ INTRODUCTION

The racemic bis(tetrahydroindenyl) metallocenes have been recognized as a type of privileged catalyst with a wide array of applications, including stereoselective olefin polymerization, the reduction of alkenes and imines, and other organic reactions.[1] However, the metalation of achiral ansa-bis(indenes) could lead to mixtures of meso and racemic bis(indenyl) metal complexes because of epimerization.[2] Since Brintzinger[3] reported the first C_2-symmetrical ansa-metallocene, trimethylenebis[η^5-1-(3-tert-butylcyclopentadienyl)]titanium dichloride, there has been a continuous interest in preparing different racemic group IV ansa-metallocenes.[4] In contrast to a salt metathesis reaction, the amine-elimination reaction of ansa-bis(indenes) with $M(NR_2)_4$ (M = Ti, Zr, and Hf) compounds has provided an efficient route to obtaining C_2-symmetric group IV ansa-metallocenes.[5] However, the efficiency of this method is very substrate-dependent, which has limited the scope of its application. Recently, Jordan and co-workers successfully reported the general controlled synthesis of racemic ansa-bis(indenyl) group IV metallocenes featuring the precoordination of the chelating diamido ligands to the starting materials.[6]

In contrast to group IV metals, the controlled syntheses of racemic rare-earth metallocenes have been rarely studied. Until now, the only documented methods for the syntheses of racemic rare-earth metallocenes were through the introduction of substituents containing coordinative donor atoms or the utilization of bridged cyclopentadienyl/indenyl ligands to restrict the rotation of the normally free ligand.[7] However, these methods have proved to be inefficient for preparing racemic rare-earth metal complexes. The development of a new methodology for the synthesis of racemic rare-earth metal

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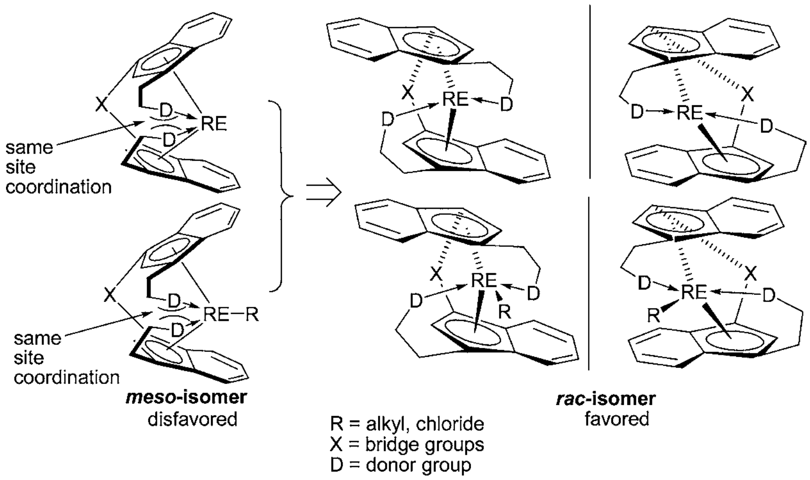
Chart 1. Configuration of the Indenyl Rare-Earth Metal Complexes Containing a Bridge and Coordinative Donor Atoms



complexes is still required. Because rare-earth metal ions have large ionic radii and usually form complexes with large coordination numbers, we envisioned that bridged indenyl ligands bearing coordinative donor atoms would favor the formation of racemic rare-earth metal complexes (Chart 1). In this Article, we report the results of our efforts with this idea.

■ EXPERIMENTAL SECTION

General Remarks. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon in an oxygen-free atmosphere using either standard Schlenk techniques or a glovebox. The solvents were refluxed and distilled over sodium/benzophenone under argon prior to use. $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Eu, Yb, Sm, Nd, and Y),[8] $C_9H_7CH_2CH_2NMe_2$,[7g] $C_9H_7CH_2CH_2CH_2NMe_2$,[9] $C_9H_7CH_2CH_2OMe$,[7h] $Me_2Si(C_9H_6CH_2CH_2OMe)Cl$,[10] and $C_9H_7CH_2CH_2N(CH_2CH_2)_2O$[11] were prepared according to literature methods. The IR spectra were recorded with a Shimadzu FTIR-8400S spectrometer. The ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AV-300 NMR spectrometer using either C_6D_6 or d_8-THF for lanthanide complexes and $CDCl_3$ for organic compounds.

*General Synthesis of $Me_2Si(C_9H_6CH_2CH_2\text{-}DG)_2$ (DG = NMe_2 (**1**), CH_2NMe_2 (**2**), OMe (**3**), and $N(CH_2CH_2)_2O$ (**4**)).* To a solution of $C_9H_6CH_2CH_2$-DG (40.0 mmol) in THF (50.0 mL) was slowly added *n*-BuLi (1.6 M in hexane, 25 mL, 40.0 mmol) at 0 °C. After the reaction mixture was stirred at this temperature for 2 h, Me_2SiCl_2 (20.0 mmol) was added. The resultant mixture was stirred for 1 h at this temperature, followed by stirring at room temperature for another 6 h. The solvent was then evaporated under reduced pressure. The residue was extracted with *n*-hexane (3 × 30.0 mL), and the combined extracts were concentrated to furnish an orange oil that is a meso and racemic mixture according to the ^1H NMR signals of the methyl groups of Me_2Si. They were directly used in the next reaction without further purification. (**1**): Yield: 97%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.46–7.19 (m, 8H), 6.31 (s, 1H), 6.05 (s, 1H), 3.49 (s, 2H), 2.79–2.75 (m, 4H), 2.63–2.53 (m, 4H), 2.34 (s, 12H), −0.001 (s), −0.30 (s), −0.52 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 145.32, 145.27, 144.4, 140.0, 139.8, 129.6, 124.8, 123.82, 123.77, 122.94, 122.88, 118.99, 118.96, 58.8, 58.7, 45.4, 43.4, 43.3, 26.2, 26.1, −4.5, −5.9, −7.2. HRMS (ESI) *m*/*z* calcd for $C_{28}H_{39}N_2Si$ [M + H$^+$]: 431.2883. Found: 431.2880. (**2**): Yield: 98%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.41–7.10 (m, 8H), 6.26 (s, 1H), 6.03 (s, 1H), 3.47–3.44 (m, 2H), 2.63–2.57 (m, 4H), 2.37–2.30 (m, 4H), 2.21 (s, 12H), 1.85–1.75 (m, 4H), −0.16 (s), −0.37 (s), −0.54 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 145.6, 144.7, 142.2, 142.1, 129.1, 127.7, 126.0, 124.9, 123.9, 123.7, 123.0, 119.2, 118.9, 59.7, 45.6, 43.3, 26.8, 26.7, 25.6, −4.5, −5.7, −6.7. HRMS (EI) *m*/*z* calcd for $C_{30}H_{42}N_2Si$ [M$^+$]: 458.3117. Found: 458.3120. (**3**): Yield: 95%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.50–7.18 (m, 8H), 6.39 (s, 1H), 6.13 (s, 1H), 3.74–3.67 (m, 4H), 3.55 (s, 2H), 3.43 (s, 3H), 3.40 (s, 3H), 2.98–2.89 (m, 4H), 0.02 (s), −0.27 (s), −0.48 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 145.3, 144.3, 138.6, 138.4, 130.4, 124.6, 123.8, 123.6, 119.0, 71.5, 58.4, 43.5, 28.0, −4.2, −5.5, −6.8. HRMS (EI) *m*/*z* calcd for $C_{26}H_{32}O_2Si$ [M$^+$]: 404.2172. Found: 404.2170. (**4**): Yield: 97%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.36–7.07 (m, 8H), 6.24 (s, 1H), 5.94 (s, 1H), 3.67–3.64 (m, 8H), 3.44–3.34 (m, 2H), 2.72–2.45 (m, 16H), −0.07 (s), −0.40 (s), −0.60 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 145.4, 144.4, 139.9, 139.8, 129.9, 125.0, 124.0, 123.9, 123.1, 119.0, 67.0, 58.1, 58.0, 43.6, 43.5, 25.1, 25.0, −4.3, −5.9, −7.0. HRMS (EI) *m*/*z* calcd for $C_{32}H_{42}N_2O_2Si$ [M$^+$]: 514.3016. Found: 514.3011.

*Synthesis of $Me_2Si(C_9H_6CH_2CH_2NMe_2)(C_9H_6CH_2CH_2OMe)$ (**5**).* To a solution of $C_9H_6CH_2CH_2CH_2NMe_2$ (40.0 mmol) in THF (50.0 mL) was slowly added *n*-BuLi (1.6 M in hexane, 25 mL, 40.0 mmol) at 0 °C. After the reaction mixture was stirred at this temperature for 2 h, $Me_2Si(C_9H_6CH_2CH_2OMe)Cl$ (40.0 mmol) was added. The mixture was stirred for 1 h at this temperature, followed by stirring at room temperature for another 6 h. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (3 × 30.0 mL), and the combined extracts were concentrated to furnish an orange oil that is a meso and racemic mixture according to the ^1H NMR signals of the methyl groups of Me_2Si. They were directly used in the next reaction without further purification. Yield: 95%. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.48–7.18 (m, 8H), 6.35 (d, *J* = 17.1 Hz, 1H), 6.11 (d, *J* = 17.4 Hz, 1H), 3.70–3.64 (m, 2H), 3.52–3.48 (m, 2H), 3.38 (s, 3H), 2.94–2.90 (m, 2H), 2.67–2.63 (m, 2H), 2.41–2.33 (m, 2H), 2.27 (s, 6H), 1.89–1.84 (m, 2H), 0.01 (s), −0.29 (s), −0.48 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ 145.5, 145.4, 144.6, 144.4, 142.1, 142.0, 138.9, 138.8, 130.5, 129.0, 127.6, 123.8, 122.9, 119.1, 118.9, 71.6, 59.7, 58.5, 45.6, 43.6, 43.2, 28.1, 26.7, 25.4, −4.7, −5.9, −6.0, −6.9. HRMS (EI) *m*/*z* calcd for $C_{28}H_{37}NOSi$ [M$^+$]: 431.2644. Found: 431.2643.

*Synthesis of $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)_2\}RE$ (RE = Yb (**6**) and Eu (**7**)).* To a solution of $Me_2Si(C_9H_6CH_2CH_2NMe_2)_2$ (1.20 mmol) in toluene (10.0 mL) was added a solution of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (1.20 mmol) in toluene (30.0 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was refluxed for 12 h. The solvent was evaporated under reduced pressure, and the residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2 × 15.0 mL), and the extracts were combined and concentrated to about 15.0 mL. The crystals were obtained by storing the concentrated solution at 0 °C for several days. (**6**): Yield: 75%. Mp = 165–167 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 7.44–7.18 (m, 8H), 6.31 (s, 1H), 6.04 (s, 1H), 2.81–2.79 (m, 4H), 2.63–2.60 (m, 4H), 2.35 (s, 12H), 0.07 (s, 6H). IR (Nujol mull, cm^{-1}): ν 2951 (m), 2852 (m), 2779 (s), 2349 (s), 1712 (m), 1519 (m), 1462 (m), 1288 (w), 1259 (m), 1174 (w), 1039 (m), 862 (w), 798 (m), 756 (m). Anal. Calcd for $C_{28}H_{36}N_2SiYb$: C, 55.89; H, 6.03; N, 4.66. Found: C, 56.09; H, 6.47; N, 4.29. (**7**): Yield: 72%. Mp = 204−206 °C. IR (Nujol mull, cm^{-1}): ν 3062 (m), 2941 (m), 2856 (m), 2814 (m), 2763 (m), 2382(m), 2349 (s), 2303 (m), 1712 (m), 1458 (m), 1377 (m), 1247 (s), 1174 (w), 1041(m), 875 (w), 806 (m), 771 (m). Anal. Calcd for $C_{28}H_{36}N_2SiEu$: C, 57.92; H, 6.25; N, 4.82. Found: C, 57.89; H, 6.27; N, 4.59.

Synthesis of {η^5:η^1:η^5:η^1-*Me*$_2$*Si*($C_9H_5CH_2CH_2CH_2NMe_2$)$_2$}*RE (RE = Yb (**8**), Eu (**9**), and Sm (**10**)).* To a solution of $Me_2Si(C_9H_6CH_2CH_2CH_2NMe_2)_2$ (1.20 mmol) in toluene (10.0 mL) was added a solution of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (1.20 mmol) in toluene (10.0 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was refluxed for 12 h. The solvent was evaporated under reduced pressure, and the residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2 × 15.0 mL), and the extracts were combined and concentrated to about 15.0 mL. The crystals were obtained by storing the concentrated solution at 0 °C for several days. (**8**): Yield: 78%. Mp = 250−252 °C. ^{1}H NMR (300 MHz, d_8-THF, 25 °C): δ 7.54−7.25 (m, 8H), 6.47 (s, 1H), 6.25 (s, 1H), 2.79−2.76 (m, 4H), 2.46−2.40 (m, 4H), 2.29 (s, 12H), 1.92−1.84 (m, 4H), 0.20 (s, 6H). IR (Nujol mull, cm^{-1}): ν 3064 (m), 2943 (s), 2856 (m), 2813 (m), 2778 (m), 1714 (m), 1601 (m), 1539 (w), 1457 (m), 1404 (w), 1250 (m), 1150 (w), 1040 (m), 874 (m), 804 (s), 765 (s), 719 (w), 668 (s) 649 (w). Anal. Calcd for $C_{30}H_{40}N_2SiYb$: C, 57.21; H, 6.40; N, 4.45. Found: C, 56.89; H, 6.47; N, 4.19. (**9**): Yield: 71%. Mp = 156−158 °C. IR (Nujol mull, cm^{-1}): ν 3062 (m), 2946 (s), 2857 (m), 2813 (m), 2778 (m) 1712 (m), 1634 (m), 1519 (m), 1455 (s), 1404 (m), 1256 (s), 1152 (w), 1040 (s), 933 (w), 806 (s), 779 (s), 668 (m). Anal. Calcd for $C_{30}H_{40}N_2SiEu$: C, 59.20; H, 6.62; N, 4.60. Found: C, 58.58; H, 6.82; N, 4.70. (**10**): Yield: 64%. Mp = 154−156 °C. IR (Nujol mull, cm^{-1}): ν 3062 (m), 2943 (m), 2854 (m), 2814 (m), 2763 (m), 2349 (s), 2303(m), 1516 (m), 1456 (m), 1247 (m), 1174 (w), 1039 (m), 933 (w), 864 (m), 808 (m), 765(m). Anal. Calcd for $C_{30}H_{40}N_2SiSm$: C, 59.35; H, 6.64; N, 4.61. Found: C, 58.98; H, 6.47; N, 4.29.

Complexes **8**−**10** could also be prepared by the following procedure. To a solution of $Me_2Si(C_9H_6CH_2CH_2CH_2NMe_2)_2$ (1.2 mmol) in THF (30.0 mL) was added *n*-BuLi (1.50 mL, 1.6 M in hexane, 2.4 mmol) at 0 °C. After the reaction mixture was stirred at this temperature for 3 h, the mixture was slowly transferred to a suspension of $RECl_3$ (1.20 mmol) in THF (10.0 mL). The reaction mixture was stirred at room temperature for 12 h before a solution of Me_3SiCH_2Li (1.20 mL, 1.0 M in hexane, 1.20 mmol) was added at 0 °C. The mixture was then stirred for 4 h, and the solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL), and the resulting solid was extracted with toluene (15.0 mL). The crystals of complexes **8**−**10** were obtained by storing the concentrated solution at 0 °C for several days.

Synthesis of {η^5:η^1:η^5:η^1-*Me*$_2$*Si*($C_9H_5CH_2CH_2OMe$)$_2$}*RE (RE = Yb (**11**) and Eu (**12**)).* To a solution of $Me_2Si(C_9H_6CH_2CH_2OMe)_2$ (1.20 mmol) in toluene (10.0 mL) was added a solution of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (1.20 mmol) in toluene (30.0 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, it was refluxed for 12 h. The solvent was evaporated under reduced pressure, and the residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2 × 15.0 mL). The extracts were combined and concentrated to about 15.0 mL. The crystals were obtained by storing the concentrated solution at 0 °C for several days. (**11**): Yield: 75%. Mp = 118−120 °C. ^{1}H NMR (300 MHz, C_5D_5N, 25 °C): δ 7.57−7.20 (m, 8H), 6.54 (s, 1H), 6.23 (s, 1H), 3.62 (m, 4H), 3.26 (s, 6H), 3.09 (m, 4H), 0.13 (s, 6H). IR (Nujol mull, cm^{-1}): ν 3064 (m), 3011 (w), 2921 (s), 2871 (s), 1940 (w), 1710 (m), 1601 (m), 1521 (m), 1457 (s), 1394 (m), 1249 (s), 1193 (w), 1117 (s), 1023 (m), 874 (m), 806 (s), 769 (s), 719 (m), 668 (m). Anal. Calcd for $C_{26}H_{30}O_2SiYb$: C, 54.25; H, 5.28. Found: C, 54.68; H, 5.69. (**12**): Yield: 67%. Mp = 111−113 °C. IR (Nujol mull, cm^{-1}): ν 2921 (s), 1940 (w), 1601 (m), 1458 (s), 1391 (m), 1254 (s), 1193 (m), 1117 (s), 1025 (m), 965 (w), 875 (w), 803 (s), 769 (s), 719 (m), 668 (m), 412 (w). Anal. Calcd for $C_{26}H_{30}O_2SiEu$: C, 56.31; H, 5.45. Found: C, 56.78; H, 5.85.

Synthesis of {η^5:η^1:η^5:η^1-*Me*$_2$*Si*[$C_9H_5CH_2CH_2N(CH_2CH_2)_2O$]$_2$}*RE (RE = Yb (**13**) and Eu (**14**)).* To a solution of $Me_2Si[C_9H_6CH_2CH_2N(CH_2CH_2)_2O]_2$ (1.50 mmol) in toluene (10.0 mL) was added a solution of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (1.50 mmol) in toluene (30.0 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was refluxed for 12 h. The solvent was evaporated under reduced pressure, and the residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2 × 15.0 mL). The extracts were combined and concentrated to about 15.0 mL. The crystals of complexes **13** and **14** were obtained by storing the concentrated solutions at 0 °C for several days. (**13**): Yield: 65%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.37−7.08 (m, 8H), 6.23 (s, 1H), 5.94 (s, 1H), 3.69−3.64 (m, 8H), 2.75−2.46 (s, 16H), −0.38 (s, 6H). IR (Nujol mull, cm^{-1}): ν 2941 (s), 1520 (m), 1452 (s), 1384 (m), 1248 (s), 1179 (w), 1118 (s), 1028 (s), 983 (m), 932 (w), 876 (m), 805 (s), 769 (s), 719 (m), 668 (m), 490 (w), 418 (w). Anal. Calcd for $C_{32}H_{40}N_2O_2SiYb$: C, 56.04; H, 5.88; N, 4.08. Found: C, 56.54; H, 6.28; N, 4.09. (**14**): Yield: 77%. IR (Nujol mull, cm^{-1}): ν 2941 (s), 1520 (m), 1452 (s), 1384 (m), 1248 (s), 1179 (w), 1118 (s), 1028 (s), 983 (m), 932 (w), 876 (m), 805 (s), 769 (s), 719 (m), 668 (m), 490 (w), 418 (w). Anal. Calcd for $C_{32}H_{40}N_2O_2SiEu$: C, 57.82; H, 6.07; N, 4.21. Found: C, 57.64; H, 6.28; N, 4.29.

Synthesis of {η^5:η^1:η^5:η^1-*Me*$_2$*Si*($C_9H_5CH_2CH_2CH_2NMe_2$)($C_9H_5CH_2CH_2OMe$)}*RE (RE = Yb (**15**) and Eu (**16**)).* To a solution of $Me_2Si(C_9H_5CH_2CH_2CH_2NMe_2)(C_9H_5CH_2CH_2OMe)$ (1.20 mmol) in toluene (10.0 mL) was added a solution of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (1.20 mmol) in toluene (30.0 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was refluxed for 12 h. The solvent was evaporated under reduced pressure, and the residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2 × 15.0 mL). The extracts were combined and concentrated to about 15.0 mL. The crystals of complexes **15** and **16** were obtained by storing the concentrated solutions at 0 °C for several days. (**15**): Yield: 58%. Mp = 162−164 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.61−7.28 (m, 8H), 6.38 (s, 1H), 6.16 (s, 1H), 3.66 (m, 2H), 3.28 (s, 3H), 3.17−3.15 (m, 2H), 2.82 (m, 2H), 2.41 (m, 2H), 2.27 (s, 6H), 2.00 (m, 2H), 0.42 (s, 6H). IR (Nujol mull, cm^{-1}): ν 2941 (s), 1520 (m), 1452 (s), 1384 (m), 1248 (s), 1179 (w), 1118 (s), 1028 (s), 983 (m), 932 (w), 876 (m), 805 (s), 769 (s), 719 (m), 668 (m), 490 (w), 418 (w). Anal. Calcd for $C_{28}H_{35}NOSiYb$: C, 55.80; H, 5.85; N, 2.32. Found: C, 55.64; H, 6.28; N, 2.29. (**16**): Yield: 64%. Mp = 159−161 °C. IR (Nujol mull, cm^{-1}): ν 2946 (m), 2859 (m), 2816 (m), 2768 (m), 1609 (w), 1461 (w), 1201 (s), 1126 (s), 1040 (m), 969 (s), 770 (m), 718 (w), 596 (m), 521 (m), 437 (w). Anal. Calcd for $C_{28}H_{35}EuNOSi$: C, 57.82; H, 6.07; N, 2.41. Found: C, 57.49; H, 6.25; N, 2.64.

Synthesis of {η^5:η^1:η^5-*Me*$_2$*Si*($C_9H_5CH_2CH_2OMe$)$_2$*NdCl*}$_2$ *(**17**).* To a solution of $Me_2Si(C_9H_6CH_2CH_2OMe)_2$ (0.81 g, 2.00 mmol) in THF (30.0 mL) was added *n*-BuLi (2.50 mL, 1.6 M in hexane, 4.00 mmol) at 0 °C. After the reaction mixture was stirred at this temperature for 3 h, the mixture was slowly transferred to a suspension of $NdCl_3$ (2.00 mmol) in THF (10.0 mL). The reaction mixture was stirred at room temperature for 12 h, and the solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL), and the resulting solid was extracted with toluene (15.0 mL × 2). The extracts were combined and concentrated to about 15.0 mL. The crystals were obtained by storing the concentrated solution at 0 °C for several days. Yield: 78%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.71−7.28 (m, 8H), 6.51 (s, 1H), 6.11 (s, 1H), 3.55−3.48 (m, 4H), 3.16 (s, 6H), 2.95−2.90 (m, 4H), −0.52 (s, 6H). IR (Nujol mull, cm^{-1}): ν 2972 (m), 2870 (w), 2781 (w), 2360(m), 1647 (m), 1652 (m), 1257 (m), 1087 (m), 1047 (s), 879 (m), 804 (m), 771 (m). Anal. Calcd for $C_{52}H_{60}Cl_2Nd_2O_4Si_2\cdot C_7H_8$: C, 56.39; H, 5.45. Found: C, 56.01; H, 5.22.

Synthesis of {η^5:η^1:η^5:η^1-*Me*$_2$*Si*($C_9H_5CH_2CH_2NMe_2$)$_2$*SmCl*}$_2$(μ-*LiCl*) *(**18**).* Complex **18** was prepared as yellow crystals in a 63% yield from $Me_2Si(C_9H_6CH_2CH_2NMe_2)_2$ by employing procedures similar to those used for the preparation of **17**. Mp = 138−140 °C. ^{1}H NMR

(300 MHz, C_6D_6, 25 °C): δ 7.43−7.22 (m, 16H), 6.12 (s, 2H), 3.13 (s, 2H), 2.76−2.73 (m, 8H), 2.62−2.56 (m, 8H), 2.19 (s, 24H), 0.31 (s, br, 12 H). IR (Nujol mull, cm^{-1}): ν 3064 (m), 2949 (m), 2858 (m), 2816 (m), 2777 (m), 2349 (s), 1656 (w), 1460 (m), 1396 (m), 1249 (m), 1174 (w), 1145(m), 1039(m), 981 (m), 931 (m), 875 (m), 804 (m), 769 (m), 719 (m), 669 (m). Anal. Calcd for $C_{56}H_{72}Cl_3LiN_4Si_2Sm$: C, 52.90; H, 5.71; N, 4.41. Found: C, 52.82; H, 5.53; N, 4.25.

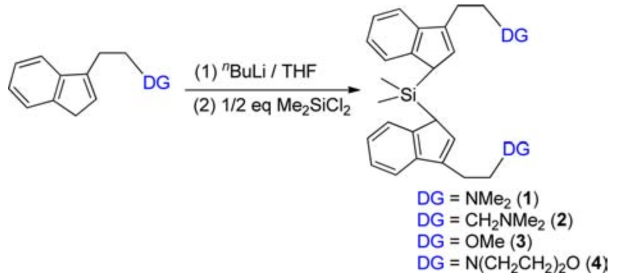
Synthesis of $\{\eta^5:\eta^1:\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)\text{-}[(C_9H_5CH_2CH_2N(CH_2)Me]\}RE$ *(RE = Sm (**19**) and Y (**20**)).* To a solution of $Me_2Si(C_9H_6CH_2CH_2NMe_2)_2$ (0.86 g, 2.00 mmol) in THF (30.0 mL) was added *n*-BuLi (2.50 mL, 1.6 M in hexane, 4.00 mmol) at 0 °C. After being stirred at this temperature for 3 h, the mixture was slowly transferred to a suspension of $RECl_3$ (2.00 mmol) in THF (10.0 mL). The reaction mixture was stirred at room temperature for 12 h and added to a solution of Me_3SiCH_2Li (2.00 mL, 1.0 M in hexane, 2.00 mmol) at 0 °C. The mixture was stirred for 4 h, and the solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (15.0 mL × 2). The extracts were combined and concentrated to about 15.0 mL. The crystals of complexes **19** and **20** were obtained by storing the concentrated solutions at 0 °C for several days. Complex **19** could also be obtained through further reaction of complex **18** with a hexane solution of Me_3SiCH_2Li. (**19**): Yield: 69%. Mp = 208−210 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 7.54−7.22 (s, 8H), 6.36 (s, 1H), 6.13 (s, 1H), 3.55 (s, 1H), 3.13(s, 1H), 2.88−2.60 (m, 8H), 2.25−2.11 (m, 9H), 0.36 (s, 2H), 0.07 (m, 2H), −0.25 (s, 2H). IR (Nujol mull, cm^{-1}): ν 2945 (m), 2816 (m), 2765 (m), 2382 (m), 2349 (s), 2303 (m), 1460 (m), 1396 (m), 1249 (m), 1174 (w), 1039 (m), 862 (m), 806 (m), 769 (m). Anal. Calcd for $C_{28}H_{35}N_2SiSm$: C, 58.18; H, 6.10; N, 4.85. Found: C, 57.91; H, 5.83; N, 4.95. (**20**): Yield: 66%. Mp 236−238 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 7.87−7.85 (m, 2H), 7.23−7.18 (m, 2H), 7.01−6.98 (m, 2H), 6.86−6.83 (m, 2H), 6.53 (s, 1H), 6.24 (s, 1H), 2.72−2.17 (m, 8H), 1.57 (s, 3H), 1.42 (s, 3H), 1.07 (s, 6H), 1.00 (m, 3H), 0.30 (s, 2H). IR (Nujol mull, cm^{-1}): ν 2941 (m), 2860 (m), 2823 (m), 2781 (m), 2349 (s), 2303 (m), 1508 (m), 1462 (s), 1396 (m), 1249 (m), 1178 (w), 1074 (m), 1041(s), 881 (m), 862 (m), 804 (m), 765 (m), 719 (m). Anal. Calcd for $C_{28}H_{35}N_2SiY$: C, 65.10; H, 6.83; N, 5.42. Found: C, 64.82; H, 6.53; N, 5.25.

Crystal Structure Determinations. Suitable crystals of complexes **6**−**10** and **14**−**20** were each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), and an empirical absorption correction was applied using the SADABS program.[12] All structures were solved by direct methods, completed by subsequent difference Fourier synthesis, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[13] All hydrogen atoms were refined using a riding model. See Supporting Information for crystallographic parameters and data collection and refinement information.

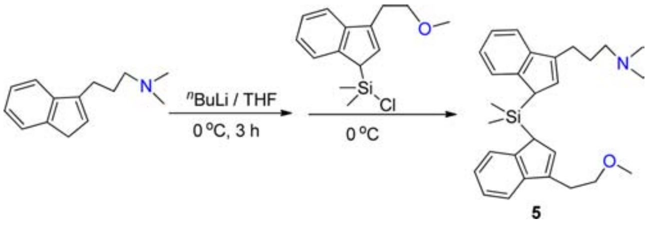
■ RESULTS AND DISCUSSION

Synthesis of Me_2Si-Bridged Substituted Indenyl Compounds. To test our idea that an indenyl ligand bearing coordinative donor atoms and a bridge would favor the formation of racemic rare-earth metal complexes, we first synthesized a series of Me_2Si-linked indenyl proligands with donor groups. The treatment of $C_9H_7CH_2CH_2$-DG with 1 equiv of *n*-BuLi in THF followed by the addition of 0.5 equiv of Me_2SiCl_2 gave $Me_2Si(C_9H_6CH_2CH_2\text{-}DG)_2$ (DG = NMe_2 (**1**), CH_2NMe_2 (**2**), OMe (**3**), and $N(CH_2CH_2)_2O$ (**4**)) in almost quantitative yields (Scheme 1). The treatment of $C_9H_6CH_2CH_2CH_2NMe_2$ with 1 equiv of *n*-BuLi in THF followed by the reaction with 1 equiv of $Me_2Si(C_9H_6CH_2CH_2OMe)Cl$ afforded $Me_2Si(C_9H_6CH_2CH_2CH_2NMe_2)(C_9H_6CH_2CH_2OMe)$ (**5**) in an almost quantitative yield (Scheme 2). Compounds **1**−**5** were a viscous oil and were fully characterized by spectroscopic analysis. The NMR spectra showed that compounds **1**−**5** were mixtures of meso- and racemic- isomers according to the signals

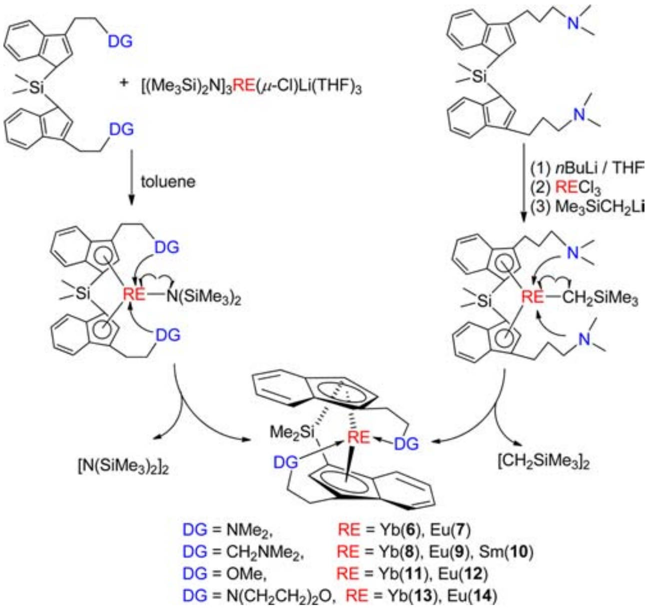
Scheme 1. Synthesis of Me_2Si-Bridged Substituted Indenyl Compounds 1−4



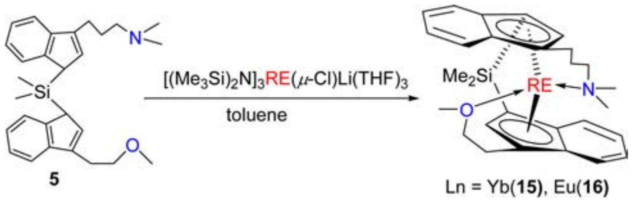
Scheme 2. Synthesis of Me_2Si-Bridged Substituted Indenyl Compound 5



Scheme 3. Formation of Racemic Me_2Si-Bridged Substituted Indenyl Divalent Rare-Earth Metal Complexes



Scheme 4. Racemic Me_2Si-Bridged Substituted Indenyl Divalent Rare-Earth Metal Complexes



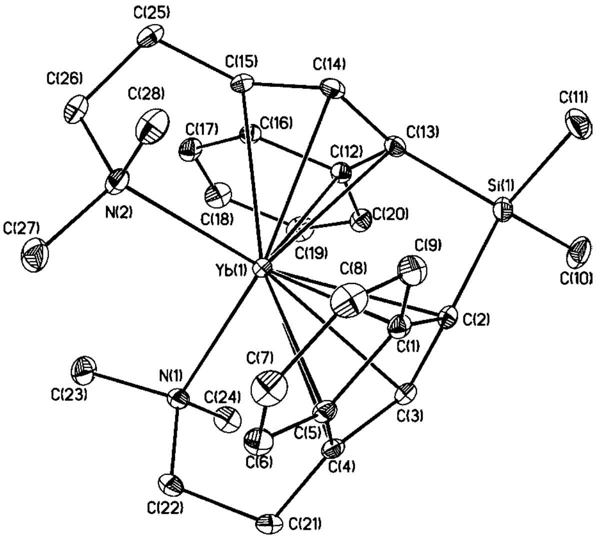


Figure 1. Molecular structure of complex **6**. Hydrogen atoms were omitted for clarity.

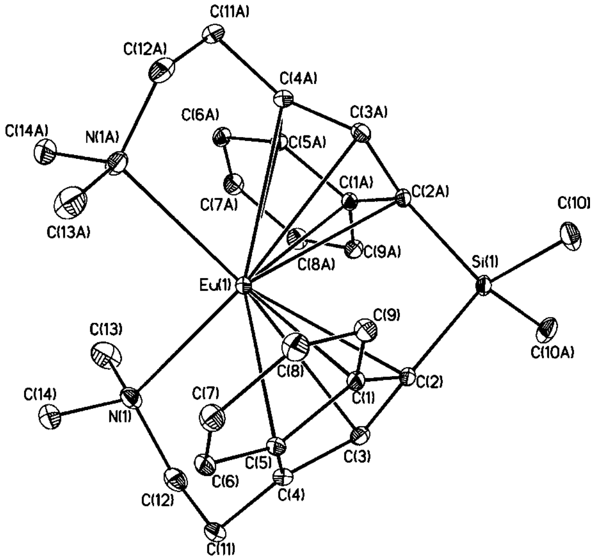


Figure 2. Molecular structure of complex **7**. Hydrogen atoms were omitted for clarity.

of the methyl groups of Me_2Si (as shown in the Experimental Section).[14] These ligands were directly used for further metalation with rare-earth metal starting materials.

Synthesis of Racemic Me_2Si-Bridged Substituted Indenyl Divalent Rare-Earth Metal Complexes through the Homolysis of the RE−N Bond. Much progress has been made in recent years to synthesize divalent, organo rare-earth metal complexes, including the well-known Sm(II), Eu(II), and Yb(II) complexes[15] and other divalent rare-earth metal complexes such as Tm, Dy, Nd, Y, Ho, Er, and La.[16] Most of the divalent lanthanide complexes were prepared from the corresponding lanthanide diiodides (often prepared in situ) or by the reduction of the appropriate Ln^{III} derivatives.[15,16] The sterically induced spontaneous reduction of Sm^{III} to Sm^{II} has also been observed on several occasions.[17] In our previous work, we reported that the reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb and Eu) with indenyl derivatives bearing chelating heteroatoms could afford divalent rare-earth metal complexes through the homolysis of the RE−N bond.[8b,18] Following these results, the base-induced reductions of trivalent rare-earth metal complexes have also been successfully reported by Mitzel[19] and Anwander.[20] This method provided a promising alternative for the synthesis of divalent organo rare-earth metal complexes. Here, we are pleased to find that the reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Yb, Eu, and Sm) with a series of Me_2Si-bridged indenyl proligands having chelating groups also provided the desired divalent rare-earth metal complexes. $Me_2Si(C_9H_6CH_2CH_2\text{-}DG)_2$ (DG = NMe_2 (**1**), CH_2NMe_2 (**2**), OMe (**3**), and $N(CH_2CH_2)_2O$ (**4**)) were reacted with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ in toluene to give a series of racemic divalent rare-earth metal complexes $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Me_2Si(C_9H_6CH_2CH_2\text{-}DG)_2\}RE$ (DG = NMe_2, RE = Yb (**6**) and Eu (**7**); DG = CH_2NMe_2, RE = Yb (**8**), Eu (**9**), and Sm (**10**); DG = OMe, RE = Yb (**11**) and Eu (**12**); DG = $N(CH_2CH_2)_2O$, RE = Yb (**13**) and Eu (**14**)) (Scheme 3). Divalent rare-earth metal complexes **8**−**10** could also be obtained in a one-pot fashion in which

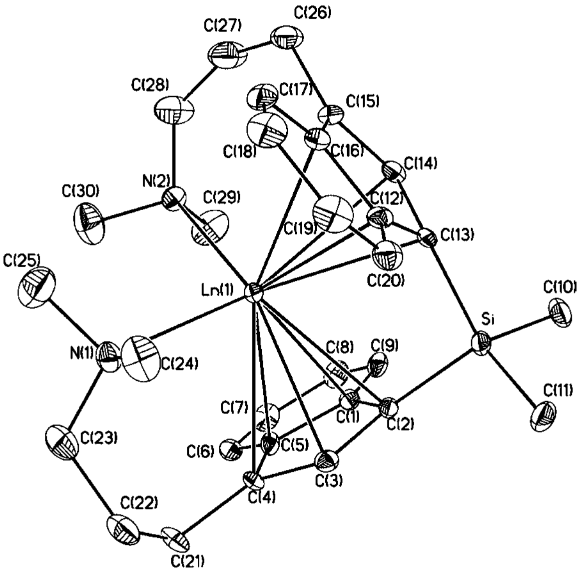


Figure 3. Representative molecular structure of complexes **8**−**10**. Hydrogen atoms were omitted for clarity.

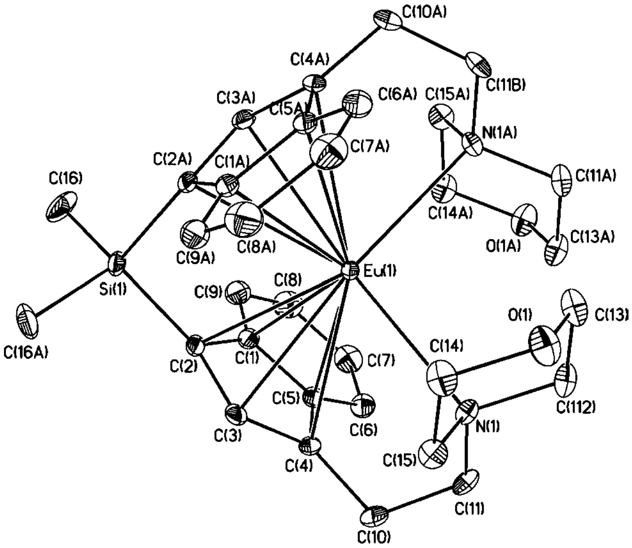


Figure 4. Molecular structure of complex **14**. Hydrogen atoms were omitted for clarity.

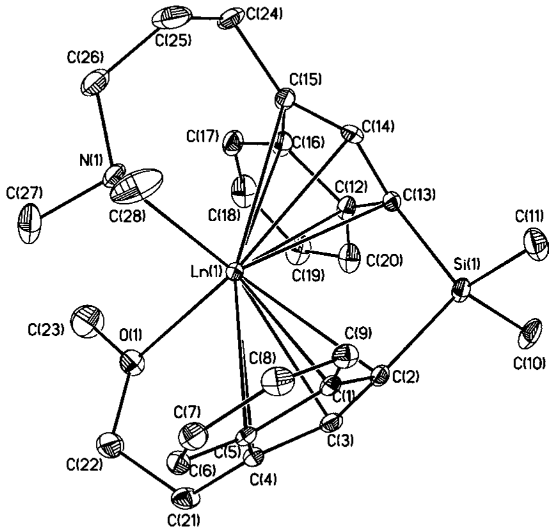


Figure 5. Representative molecular structure of complexes **15** and **16**. Hydrogen atoms were omitted for clarity.

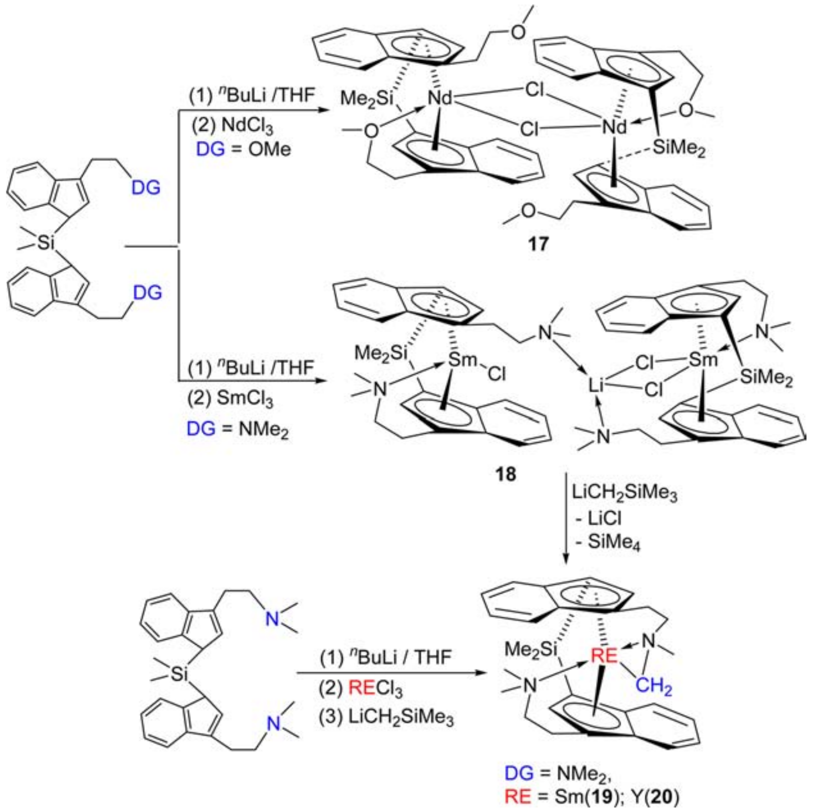
{$Me_2Si(C_9H_5CH_2CH_2CH_2NMe_2)_2$}$Li_2$ was mixed with $RECl_3$ to generate {$Me_2Si(C_9H_5CH_2CH_2CH_2NMe_2)_2$}RECl, which was used in situ to react with Me_3SiCH_2Li. The formation process for the divalent rare-earth metal complexes was revealed by GC-HRMS (EI) analysis of the hydrolysis of the reaction mixtures from the formation of **8−10** and showed an m/z peak at 174.1268 with a relative abundance of about 11.52%, which should be attributed to the fragment of $[(Me_3SiCH_2)_2]^+$ (shown in the Supporting Information). This result suggests that the formation of the divalent rare-earth metal complexes **8−10** probably involves the homolysis of the RE−C bond in a similar manner to that of the homolysis of the RE−N bond reported by us (Scheme 3).[8b,18] Complex **10** represents the first example of a divalent samarium complex obtained by the homolysis of the Sm−N bond or Sm−C bond, indicating that the homolysis of RE−N/C bonds could be extended to samarium chemistry for the preparation of samarium(II) complexes. Under similar reaction conditions, the racemic divalent rare-earth metal complexes {η^5:η^1:η^5:η^1-$Me_2Si(C_9H_5CH_2CH_2CH_2NMe_2)(C_9H_5CH_2CH_2OMe)$}RE (RE = Yb (**15**) and Eu (**16**)) were also obtained from the reactions of $Me_2Si(C_9H_6CH_2CH_2CH_2NMe_2)$-$(C_9H_6CH_2CH_2OMe)$ (**5**) with $[(Me_3Si)_2N]_3RE(\mu$-Cl)Li-$(THF)_3$ in toluene (Scheme 4). Complexes **6−16** are sensitive to air and moisture. They are soluble in polar solvents such as THF, DME, and pyridine, slightly soluble in toluene, and insoluble in n-hexane. All of the complexes were fully characterized by spectroscopic methods and elemental analysis. The structures of complexes **6−10** and **14−16** were further determined by single-crystal X-ray analysis.

In our previous study, we obtained meso-indenyl rare-earth metal complexes by the reaction of $[(Me_3Si)_2N]_3Ln(\mu$-Cl)Li$(THF)_3$ (Ln = Y, Sm, and Yb) with bridged ethylenebis-(indene).[21] Although the use of indenyl ligands containing coordinative donor atoms gave racemic indenyl rare-earth metal complexes in some cases, such results were highly dependent on the specific ligands and the rare-earth metals that were used.[8b,18] For example, although the reaction of $[(Me_3Si)_2N]_3Eu(\mu$-Cl)Li$(THF)_3$ and $C_9H_6CH_2CH_2NMe_2$ provided the racemic indenyl rare-earth metal complexes $(\eta^5$:η^1-$Me_2NCH_2CH_2C_9H_6)_2Eu$,[9] the corresponding reaction with Yb failed to give the racemic indenyl ytterbium complex.[8b] Qian and co-workers reported that the reaction of donor-atom-bridged indenyl potassium salts with rare-earth metal chlorides provided the rac/meso ansa-lanthanocene chlorides with a ratio of up to 6:1 and that the further amination or alkylation of the rac/meso (6:1) mixtures could furnish pure racemic ansa rare-earth metallocene amides and hydrocarbyls.[7e,22] This work indicated that the controlled synthesis of racemic indenyl rare-earth metal complexes could be realized through the cooperation of donor atoms and a bridge; the rare-earth metal complexes containing Me_2Si-linked bisindenyl ligands with various donor groups were all racemic isomers as confirmed by X-ray analysis. The representative structure diagrams are shown in Figure 1 (for complex **6**), Figure 2 (for complex **7**), Figure 3 (for complexes **8−10**), Figure 4 (for complex **14**), and Figure 5 (for complexes **15** and **16**). In these complexes, the rare-earth metal ion adopted a distorted tetrahedral geometry in which the rare-earth metal ion was coordinated by the five-membered rings of two indenyl groups

Table 1. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Complexes 6−10 and 14−16

	6	**7**	**8**	**9**	**10**	**14**	**15**	**16**
Ln(1)−N(1)	2.600(2)	2.732(2)	2.577(9)	2.671(5)	2.661(6)	2.821(5)	2.529(16)	2.617(7)
Ln(1)−N(2)	2.579(3)		2.550(9)	2.715(5)	2.708(7)			
Ln(1)−O(1)							2.446(13)	2.585(6)
Ln(1)−C(1)	2.754(3)	2.773(2)	2.857(10)	2.933(5)	2.888(7)	2.900(4)	2.676(13)	2.886(8)
Ln(1)−C(2)	2.678(3)	2.795(2)	2.672(10)	2.812(5)	2.750(7)	2.786(6)	2.657(18)	2.784(8)
Ln(1)−C(3)	2.633(3)	2.833(3)	2.612(11)	2.798(5)	2.761(7)	2.761(6)	2.740(18)	2.800(10)
Ln(1)−C(4)	2.695(3)	2.873(3)	2.807(10)	2.924(5)	2.923(7)	2.893(5)	2.879(18)	2.864(7)
Ln(1)−C(5)	2.768(3)	2.835(2)	2.980(11)	2.999(5)	3.013(8)	2.979(5)	2.818(18)	2.903(10)
Ln(1)−C(12)	2.715(3)		2.922(9)	2.898(5)	2.927(8)		2.653(16)	2.748(8)
Ln(1)−C(13)	2.676(3)		2.700(10)	2.752(5)	2.807(7)		2.693(18)	2.740(8)
Ln(1)−C(14)	2.658(3)		2.619(10)	2.768(5)	2.801(7)		2.695(17)	2.780(8)
Ln(1)−C(15)	2.695(3)		2.786(10)	2.929(5)	2.926(8)		2.803(18)	2.890(9)
Ln(1)−C(16)	2.740(3)		2.997(10)	3.014(5)	2.982(8)		2.810(18)	2.873(9)
Ln−C_{av}(Ind)	2.701(3)	2.822(3)	2.795(11)	2.883(5)	2.878(8)	2.864(6)	2.742(18)	2.827(10)
N(1)−Ln(1)−N(2)	104.23(9)		100.9(3)	100.99(16)	101.4(2)			
N(1)−Ln(1)−N(1A)		99.75(13)				102.3(2)		
N(1)−Ln(1)−O(1)							95.4(6)	98.5(3)

Scheme 5. Racemic Me_2Si-Bridged Substituted Indenyl Trivalent Rare-Earth Metal Complexes Synthesized by a Salt Metathesis Reaction



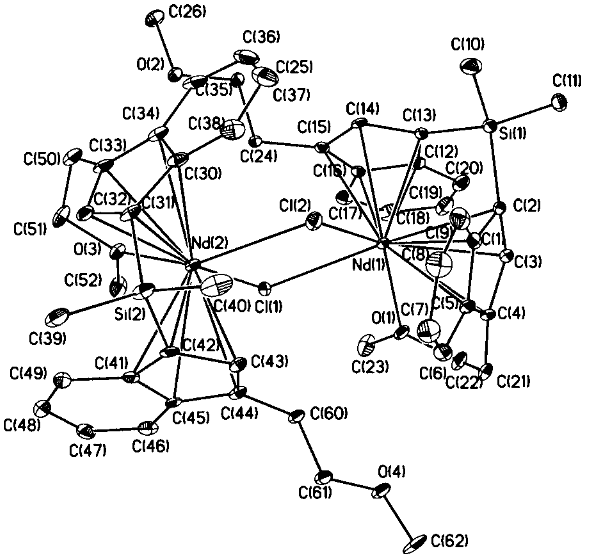


Figure 6. Molecular structure of complex **17**. Hydrogen atoms and solvent were omitted for clarity.

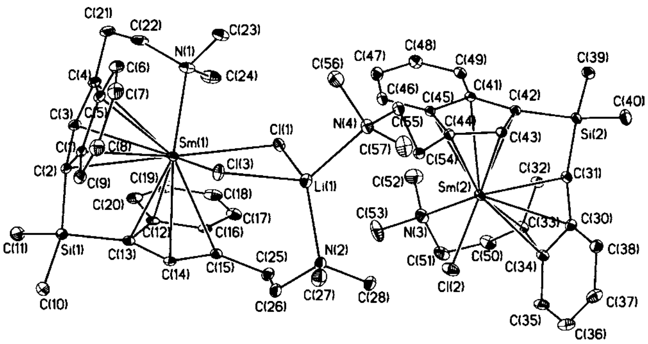


Figure 7. Molecular structure of complex **18**. Hydrogen atoms were omitted for clarity.

in an η^5 fashion and the heteroatoms (N, O), in an η^1 fashion. Selected bond lengths and angles are listed in Table 1.

From Table 1, the average Yb−C distance of 2.701(3) Å in **6** is shorter than the corresponding values for complexes **8** [2.795(11) Å] and **15** [2.742(18) Å], and this distance is slightly different from the corresponding value of 2.722(10) Å found in (η^5:η^1-$Me_2NCH_2CH_2C_9H_6)_2Yb$.[8b] The average Eu−C distance of 2.822(3) Å in complex **7** is comparable to the corresponding value of 2.827(10) Å in complex **16** and is shorter than the corresponding values for complexes **9** [2.883(5) Å], **14** [2.864(6) Å], and (η^5:η^1-$Me_2NCH_2CH_2C_9H_6)_2Eu$ [2.836(7) Å].[9] The varied bond lengths might be due to the steric effects of the ligands for the large substituted $CH_2CH_2CH_2NMe_2$ and $CH_2CH_2N(CH_2CH_2)_2O$ groups in complexes **9** and **14**, respectively. The difference in the average Eu−C distance between complex **7** [2.822(3) Å] and (η^5:η^1-$Me_2NCH_2CH_2C_9H_6)_2Eu$ [2.836(7) Å][9] may be due to the existence of a Me_2Si bridge in **7**, which will favor the interaction of the indenyl ligand and the metal, resulting in a slightly shorter average Eu−C distance in **7** compared to that found in (η^5:η^1-$Me_2NCH_2CH_2C_9H_6)_2Eu$.[9] The average Ln−C distance of 2.883(5) Å in **9** is comparable to the corresponding value of 2.878(8) Å in **10** but is longer than that of 2.795(11) Å in **8**. The different bond lengths in complexes **8**−**10** might be attributed to the different rare-earth ionic radii. The average Yb−N bond length of 2.590(3) Å in **6**

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Complexes 17 and 18

	17	18		17	18
Ln(1)–Cl(1)	2.835(3)	2.839(1)	Ln(2)–Cl(1)	2.829(3)	
Ln(1)–Cl(2)	2.701(4)		Ln(2)–Cl(2)	2.706(4)	2.584(1)
Ln(1)–Cl(3)		2.689(1)			
Ln(1)–O(1)	2.528(9)		Ln(2)–O(3)	2.542(9)	
Ln(1)–N(1)		2.752(3)	Ln(2)–N(3)		2.572(3)
Li(1)–Cl(1)		2.346(7)	Li(1)–N(2)		2.125(7)
Li(1)–Cl(3)		2.361(6)	Li(1)–N(4)		2.140(8)
Ln(1)–C(1)	2.892(13)	2.857(3)	Ln(2)–C(30)	2.860(14)	2.693(4)
Ln(1)–C(2)	2.762(13)	2.781(3)	Ln(2)–C(31)	2.748(11)	2.643(3)
Ln(1)–C(3)	2.675(13)	2.713(3)	Ln(2)–C(32)	2.687(13)	2.651(3)
Ln(1)–C(4)	2.767(13)	2.782(3)	Ln(2)–C(33)	2.758(13)	2.698(3)
Ln(1)–C(5)	2.869(13)	2.855(3)	Ln(2)–C(34)	2.861(14)	2.744(4)
Ln(1)–C(12)	2.749(14)	2.785(3)	Ln(2)–C(41)	2.753(13)	2.765(3)
Ln(1)–C(13)	2.644(13)	2.685(3)	Ln(2)–C(42)	2.642(12)	2.646(3)
Ln(1)–C(14)	2.700(12)	2.738(3)	Ln(2)–C(43)	2.697(12)	2.669(3)
Ln(1)–C(15)	2.835(12)	2.923(3)	Ln(2)–C(44)	2.819(12)	2.807(3)
Ln(1)–C(16)	2.882(13)	2.939(3)	Ln(2)–C(45)	2.889(12)	2.861(3)
Ln(1)–C_{av}(Ind)	2.778(13)	2.806(3)	Ln(2)–C_{av}(Ind)	2.771(14)	2.718(4)
Nd(1)–Cl(1)–Nd(2)	102.34(10)				
Nd(1)–Cl(2)–Nd(2)	109.38(14)				
Sm(1)–Cl(1)–Li(1)		92.72(15)			
Sm(1)–Cl(3)–Li(1)		96.30(16)			
N(2)–Li(1)–N(4)		118.1(3)			

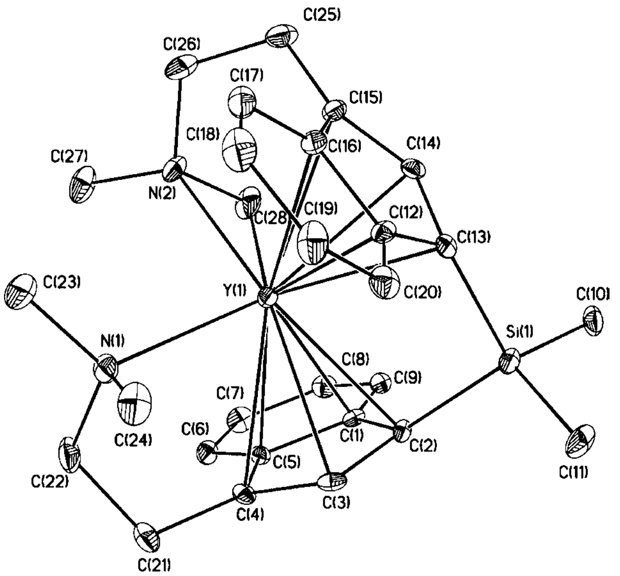


Figure 8. Representative molecular structure of complex **20**. Hydrogen atoms were omitted for clarity.

correlates well with the average Yb–N distances of 2.564(4) Å in **8** and 2.588(7) Å in $(\eta^5:\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Yb$.[8b] The average Eu–N bond length of 2.732(2) Å in **7** is also close to the average Eu–N distance of 2.693(4) Å in **9** and 2.711(6) Å in $(\eta^5:\eta^1\text{-}Me_2NCH_2CH_2C_9H_6)_2Eu$[9] but is shorter than the corresponding value of 2.821(5) Å in **14**, which is probably due to the steric effects of the ligands for bulky substituent $CH_2CH_2N(CH_2CH_2)_2O$ in **14**.

Synthesis of Racemic Me_2Si-Bridged Substituted Indenyl Trivalent Rare-Earth Metal Complexes by a Salt Metathesis Reaction. Encouraged by the above results, we further examined the controlled synthesis of racemic indenyl trivalent rare-earth metal complexes by the cooperation between a Me_2Si bridge and the intramolecular coordination of donor atoms. The reaction of $Me_2Si(C_9H_5CH_2CH_2OMe)_2Li_2$ with $NdCl_3$ gave a racemic dimeric neodymium chloride $\{\eta^5:\eta^1:\eta^5\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)_2NdCl\}_2$ (**17**), whereas the reaction of $Me_2Si(C_9H_5CH_2CH_2NMe_2)_2Li_2$ with $SmCl_3$ gave a racemic dimeric samarium chloride that was bridged by lithium chloride with a formula of $\{\eta^5:\eta^1:\eta^5:\eta^1\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)_2SmCl\}_2(\mu\text{-}LiCl)$ (**18**), which is probably due to the strong coordinating ability of the nitrogen atom. The further reaction of complex **18** with $LiCH_2SiMe_3$ provided an unexpected samarium alkyl complex $\{\eta^5:\eta^1:\eta^5:\eta^1:\sigma\text{-}Me_2Si\text{-}$

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Complexes 19 and 20

	19	20
Ln(1)–N(1)	2.608(13)	2.581(6)
Ln(1)–N(2)	2.504(14)	2.480(6)
Ln(1)–C(28)	2.52(2)	2.448(10)
Ln(1)–C(1)	2.705(16)	2.693(7)
Ln(1)–C(2)	2.704(13)	2.639(6)
Ln(1)–C(3)	2.67(2)	2.641(7)
Ln(1)–C(4)	2.778(13)	2.725(6)
Ln(1)–C(5)	2.812(18)	2.771(7)
Ln(1)–C(12)	2.721(18)	2.714(8)
Ln(1)–C(13)	2.663(14)	2.627(6)
Ln(1)–C(14)	2.654(13)	2.610(6)
Ln(1)–C(15)	2.744(15)	2.682(7)
Ln(1)–C(16)	2.769(19)	2.783(7)
Ln–C_{av}(Ind)	2.722(19)	2.689(10)
N(1)–Ln(1)–C(22)	109.1(9)	110.7(5)
N(1)–Ln(1)–C(23)	108.8(10)	113.7(5)
N(1)–Ln(1)–C(24)	111.4(9)	105.1(5)
N(2)–Ln(1)–C(26)	119.2(10)	118.4(5)
N(2)–Ln(1)–C(27)	122.0(10)	124.4(5)
N(2)–Ln(1)–C(28)	74.3(11)	71.8(5)

$(C_9H_5CH_2CH_2NMe_2)[(C_9H_5CH_2CH_2N(CH_2)Me]\}Sm$ (**19**). The rare-earth metal alkyl complexes **19** and $\{\eta^5:\eta^1:\eta^5:\eta^1:\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)[(C_9H_5CH_2CH_2N(CH_2)Me]\}Y$ (**20**) could also be prepared by one-pot reactions of $Me_2Si(C_9H_5CH_2CH_2NMe_2)_2Li_2$ with $RECl_3$ followed by reaction with $LiCH_2SiMe_3$ through the activation of sp^3 C−H bonds that are α-adjacent to the nitrogen atoms (Scheme 5). This sp^3 C−H bond activation has also been found in crowded pentamethylcyclopentadienyl lanthanide and actinide complexes with the isolation of the "tuck-in" complexes containing the $[\eta^5:\eta^1\text{-}C_5Me_4(CH_2)]^{2-}$ ligand.[23] Complexes **17**−**20** were also fully characterized by spectroscopic methods, elemental analysis, and single-crystal X-ray diffraction analysis.

X-ray diffraction showed that complex **17** (Figure 6) is a dimeric trivalent neodymium chloride with a Nd_2Cl_2 core that is bridged by two chloride atoms. In complex **18** (Figure 7), the two samarium units were bridged by lithium chloride where the lithium ion was coordinated by two chloride atoms and two nitrogen atoms from the two samarium units. In dimeric complexes **17** and **18**, each rare-earth metal ion was coordinated with one Me_2Si-bridged substituted indenyl ligand in a racemic mode. The selected bond lengths and angles are listed in Table 2.

X-ray diffraction also revealed that complexes **19** and **20** (a representative structure diagram of **20** is shown in Figure 8) are isostructural rare-earth metal alkyl complexes in which each rare-earth metal ion is coordinated by the five-membered rings of two indenyl groups in an η^5 fashion, the nitrogen atoms, in an η^1 fashion, and one CH_2 group, in an η^1 fashion that is formed through the sp^3 C−H bond activation of the CH_3 group that is α-adjacent to the nitrogen atoms. The selected bond lengths and angles are listed in Table 3.

The Sm(1)−C(28) distance of 2.52(2) Å in **19** is much shorter than the typical Sm(1)−C(η^5-indenyl) distances that range from 2.654(13) to 2.812(18) Å. The Y(1)−C(28) distance of 2.448(10) Å in **20** is comparable to those of 2.427(19) Å and 2.450(2) Å in $Y(CH_2SiMe_3)_3(THF)_2$[24] and $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2\text{−}C_5Me_4CH_2\text{-}\eta^3)$,[23d] respectively, and is also much shorter than the bridging methyl distances of 2.545(11) and 2.60 (1) Å in $[(C_5H_5)_2Y(\mu\text{-Me})]_2$[25] and $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-Me})]_2$,[26] respectively. Furthermore, the bond angles of N(2)−Ln(1)−C(28) in **19** [74.3(11)°] and **20** [71.8(5)°] are much smaller than the two bond angles of N(2)−Ln(1)−C(26) [119.2(10)° in **19** and 118.4(5)° in **20**] and N(2)−Ln(1)−C(27) [122.0(10)° in **19** and 124.4(5)° in **20**]. These results indicate the formation of rare-earth metal alkyl complexes through the sp^3 C−H bond activation of the CH_3 group that is α-adjacent to the nitrogen atoms.

■ CONCLUSIONS

A series of racemic organo rare-earth metal complexes containing Me_2Si-bridged bisindenyl ligands with various donor groups were controllably synthesized by the cooperation between a bridge and the intramolecular coordination of the donor atoms. This is a general methodology for the synthesis of racemic divalent and trivalent rare-earth metal complexes. In our attempts to transform the racemic rare-earth metal chlorides to their corresponding rare-earth metal alkyl complexes, novel rare-earth metal alkyl complexes resulting from an unexpected sp^3 C−H activation reaction were obtained. Further investigations of the applications of these racemic organo rare-earth metal complexes in organic synthesis are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (CIFs), crystallographic data for complexes, and GC-HRMS analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: slzhou@mail.ahnu.edu.cn (S.Z.), swwang@mail.ahnu.edu.cn (S.W.).

Notes

The authors declare no competing financial interest.

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