Half-Sandwich Indenyl Rare Earth Metal Dialkyl Complexes: Syntheses, Structures, and Catalytic Activities of (1,3-(SiMe$_3$)$_2$C$_9$H$_5$)Ln(CH$_2$SiMe$_3$)$_2$(THF)

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Reactions of 1,3-bis(trimethylsilyl)indene with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ gave half-sandwich rare earth metal complexes (1,3-(SiMe$_3$)$_2$C$_9$H$_5$)Ln(CH$_2$SiMe$_3$)$_2$(THF) (Ln = Y, Lu, Dy). These complexes were characterized by single-crystal X-ray diffraction, which showed the η^5 hapticity of indenyl ligands in all of the complexes. The catalytic behaviors of the complexes for intramolecular hydroamination of aminoalkenes were investigated. The catalytic activity increased with increasing the metal ion size, and the Y and Dy complexes showed excellent activities to a variety of aminoalkenes.

Introduction

Indenyl ligands are close relatives of cyclopentadienyl ligands (Cp). Stimulated by the great success of cyclopentadienyl ligands' utilization in rare earth metal complexes, the indenyl complexes of rare earth metal have received growing interest in the past decade. A number of rare earth metal indenyl complexes have been synthesized,[1−4] some of which showed good catalytic activities, such as ring-opening polymerization of *ε*-caprolactone,[2f,3c] methyl methacrylate polymerization,[3b,4d] addition of the N−H bond to carbodiimides,[3c] and hydroamination of aminoalkenes.[1e] Most of the reported indenyl rare earth metal complexes are bis(indenyl) metal complexes, mono(indenyl) rare earth metal complexes, which have the more open coordination sphere, are rare, and no unfunctionalized mono(indenyl) rare earth metal dialkyl complexes had been reported before our work.[5,6]

The unsubstituted indenyl ligand can be simply viewed as a Cp-type ligand with two substituents in terms of steric contributions, and it is still easy to introduce other substituents on the indenyl ring to form more bulky ligands, which are crucial to the syntheses of the half-sandwich metal complexes. In addition, the indenyl ligands have a property of undergoing haptotropic shifts, which enhances the metal complexes' reactivities in many cases, a phenomenon called the "indenyl effects".[7] Therefore, we considered that indenyl ligands could be one promising ligand set for the half-sandwich rare earth metal dialkyl complexes, which potentially have highly catalytic activities, and carried out our research on this type of metal complexes. Our previous paper reported the syntheses and catalytic activities of Sc dialkyl complexes supported by silyl-substituted indenyl ligands.[8]

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(1) (a) Schumann, H.; Erbstein, F.; Karasiak, D. F.; Fedushkin, I. L.; Demtschuk, J.; Girgsdies, F. *Z. Anorg. Allg. Chem.* **1999**, *625*, 781. (b) Schumann, H.; Karasiak, D. F.; Mühle, S. H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1434. (c) Shen, Q.; Qi, M.; Song, S.; Zhang, L.; Lin, Y. *J. Organomet. Chem.* **1997**, *549*, 95. (d) Cheng, J.; Cui, D.; Chen, W.; Tang, T.; Huang, B. *J. Organomet. Chem.* **2002**, *658*, 153. (e) Vitanova, D. V.; Hampel, F.; Hultzsch, K. C. *J. Organomet. Chem.* **2007**, *692*, 4690.

(2) (a) Klimpel, M. G.; Herrmann, W. A.; Anwander, R. *Organometallics* **2000**, *19*, 4666. (b) Trifonov, A. T.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2003**, 926. (c) Qian, C.; Zou, G.; Jiang, W.; Chen, Y.; Sun, J.; Li, N. *Organometallics* **2004**, *23*, 4980. (d) Trifonov, A. A.; Fedorova, E. A.; Ikorskii, V. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2005**, 2812. (e) Zhang, K.; Zhang, W.; Wang, S.; Sheng, E.; Yang, G.; Xie, M.; Zhou, S.; Feng, Y.; Mao, L.; Huang, Z. *Dalton Trans.* **2004**, 1029. (f) Wang, S.; Wang, S.; Zhou, S.; Yang, G.; Luo, W.; Hu, N.; Zhou, Z.; Song, H. *J. Organomet. Chem.* **2007**, *692*, 2099.

(3) (a) Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080. (b) Sheng, E.; Wang, S.; Yang, G.; Zhou, S.; Cheng, L.; Zhang, K.; Huang, Z. *Organometallics* **2003**, *22*, 684. (c) Zhou, S.; Wang, S.; Yang, G.; Li, Q.; Zhang, L.; Yao, Z.; Zhou, Z.; Song, H. *Organometallics* **2007**, *26*, 3755. (d) Tardif, O.; Kaita, S. *Dalton Trans.* **2008**, 2531.

(4) For the representative bis(indenyl) rare earth metal alkyl complexes, see: (a) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284. (b) Gavenonis, J.; Tilley, T. D. *J. Organomet. Chem.* **2004**, *689*, 870. (c) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1999**, 519. (d) Qian, C.; Zou, G.; Chen, Y.; Sun, J. *Organometallics* **2001**, *20*, 3106. (e) Rodrigues, A. S.; Kirillov, E.; Roisnel, T.; Razavi, A.; Vuillemin, B.; Carpentier, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7240.
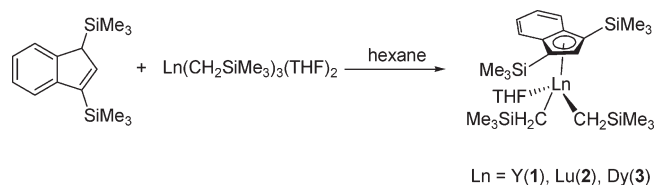
(5) For representative half-sandwich mono(indenyl) rare earth metal halide complexes, see: (a) Tsutsui, M.; Chen, L. B.; Bergbreiter, D. E.; Miyamoto, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 855. (b) Evans, W. J.; Gummersheimer, T. S.; Ziller, J. W. *Appl. Organomet. Chem.* **1995**, *9*, 437. (c) Kong, D.; Wang, S.; Zhu, Q.; Xie, Y.; Huang, X. *Synth. React. Inorg. Met.-Org. Chem.* **1998**, *28*, 1455. (d) Trifonov, A. A.; Kirillov, E. N.; Dechert, S.; Schumann, H.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2001**, 3055.

(6) Recently, there was a report on the N-heterocyclic carbene-functionalized indenyl rare earth metal dialkyl complexes. The N-heterocyclic carbene's coordination to the rare earth metal ion forms a "CGC"-type complex and stabilizes the dialkyl species. Wang, B.; Wang, D.; Cui, D.; Gao, W.; Tang, T.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 3167.

(7) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(8) Xu, X.; Chen, Y.; Sun, J. *Chem.—Eur. J.* **2009**, *15*, 846.
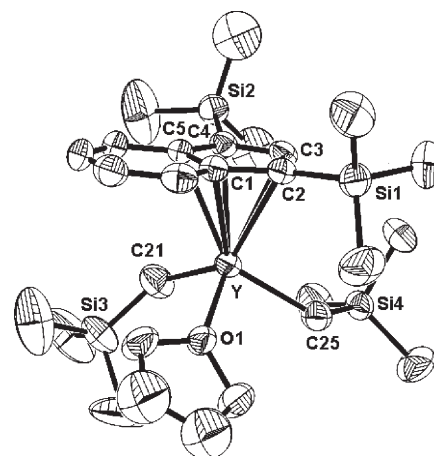
Scheme 1

Ln = Y(**1**), Lu(**2**), Dy(**3**)

The Sc complexes with a bulky 1,3-bis(trimethylsilyl)indenyl ligand showed a good catalytic activity for the highly syndiospecific styrene polymerization upon activation with $[Ph_3C][B(C_6F_5)_4]$. Recently, we found that the 1,3-bis-(trimethylsilyl)indenyl ligand can also stabilize the dialkyl complexes with larger rare earth metal ions, such as Y^{3+}, Lu^{3+}, and Dy^{3+}, and these metal complexes are highly active for intramolecular hydroamination reactions of a variety of aminoalkenes without any activator. Herein we report these results.

Results and Discussion

Synthesis and Characterization. Reactions of 1,3-bis-(trimethylsilyl)indene with $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu, Dy) in hexane gave desired half-sandwich indenyl rare earth metal dialkyl complexes **1**−**3** as crystalline solids in 61−87% yield (Scheme 1). A variable-temperature ¹H NMR study on the diamagnetic complexes **1** and **2** was performed; the variable-temperature ¹H NMR spectra of the complexes are given in the Supporting Information. For the complex **1**, there was nearly no decomposition when the temperature was raised to 60 °C, and when the temperature was raised to 75 °C, the decomposition of the complex was still less than 15%. Complex **2** is more thermally stable; there was nearly no decomposition when the temperature was raised to 75 °C. Reaction of 1,3-bis(trimethylsilyl)indene with Gd-$(CH_2SiMe_3)_3(THF)_2$ gave an oily product; no solid product was obtained after repeated recrystallization of the oily product. NMR analysis could not give useful information on the purity and structure of the product, as the Gd complex is paramagnetic, and the elemental analysis results of the above product did not match well the formula of the desired half-sandwich indenyl Gd dialkyl complex. Attempts to prepare the La and Nd analogues by reactions of

Figure 1. Molecular structure of **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1−3 and $(1,3\text{-}(SiMe_3)_2C_9H_5)Sc(CH_2SiMe_3)_2(THF)$ Complex

	1 (Ln = Y)	**2** (Ln = Lu)	**3** (Ln = Dy)	Sc complex (Ln = Sc)
Ln−C1	2.722(6)	2.687(4)	2.735(7)	2.608(3)
Ln−C2	2.711(6)	2.657(4)	2.724(7)	2.549(3)
Ln−C3	2.695(5)	2.606(4)	2.698(7)	2.493(3)
Ln−C4	2.679(6)	2.642(4)	2.693(7)	2.538(3)
Ln−C5	2.711(6)	2.683(4)	2.734(8)	2.615(3)
Ln−C21	2.371(7)	2.313(5)	2.341(8)	2.191(3)
Ln−C25	2.386(6)	2.319(4)	2.363(8)	2.221(3)
Ln−O1	2.314(4)	2.252(3)	2.332(5)	2.162(2)
C21−Ln−C25	106.3(3)	105.5(2)	105.0(4)	106.1(1)
ΔLn−C	0.021	0.050	0.029	0.085
Ω	3.80	2.70	3.74	3.08

1,3-bis(trimethylsilyl)indene with in situ generated Ln-$(CH_2SiMe_3)_3(THF)_x$ (Ln = La, Nd) failed;[9] only the 1,3-bis-(trimethylsilyl)indenyl lithium salt was isolated.[10] This problem was also observed in the reaction of β-diketimine with the in situ generated $La(CH_2SiMe_3)_3(THF)_x$, where a β-diketiminato lithium salt was produced.[11] We also tried to synthesize the half-sandwich indenyl La dialkyl complex via reaction of 1,3-bis(trimethylsilyl)indenyl lithium salt with $LaI_3(THF)_4$, followed by the addition of 2 equiv of $LiCH_2$-$SiMe_3$, but no desired product was obtained. The synthesis of half-sandwich early lanthanide metal complexes with −CH_2SiMe_3 alkyl is a big challenge. For the Cp′ ligands $[C_5Me_5]^-$ and $[1,3\text{-}(SiMe_3)_2C_5H_3]^-$, to our knowledge, only the Sc and Lu complexes have been reported. Even with the very bulky $[C_5Me_4(SiMe_3)]^-$ ligand, the reported complex with the largest metal ion so far is the Gd complex.[12] The rare earth metal complexes with −$CH(SiMe_3)_2$, −CH_2Ph, or −$N(SiR_3)_2$ generally are more stable. Synthesis of half-sandwich indenyl early lanthanide metal complexes with these ligands is under our consideration.

Single crystals of complexes **1**−**3** were grown from hexane solutions at −35 °C and characterized by X-ray diffraction. An ORTEP figure of **1** is shown in Figure 1, whereas those of **2** and **3** are given in the Supporting Information. Selected bond lengths and angles of **1**−**3** are listed in Table 1. In the

(9) $La(CH_2SiMe_3)_3(THF)_x$ and $Nd(CH_2SiMe_3)_3(THF)_x$ are unstable and have not been isolated so far: Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2422. $La(CH_2SiMe_3)_3$-$(THF)_x$ and $Nd(CH_2SiMe_3)_3(THF)_x$ were in situ prepared as reported in the literature: Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182. Xu, X.; Xu, X.; Chen, Y.; Sun, J. *Organometallics* **2008**, *27*, 758.

(10) For example, the reaction of 1,3-bis(trimethylsilyl)indene with in situ generated $La(CH_2SiMe_3)_3(THF)_x$: A solution of $LiCH_2SiMe_3$ (120 mg, 1.28 mmol in 10 mL of THF) was added to a suspension of $LaI_3(THF)_4$ (349 mg, 0.43 mmol) in 10 mL of THF at room temperature, and a clear colorless solution formed in 10 min. The reaction mixture was stirred for 2 h, and then 1,3-$(SiMe_3)_2C_9H_6$ (102 mg, 0.39 mmol) in 5 mL of hexane was added. After stirring at room temperature for 2 days, the volatiles were removed under vacuum, and the residue was extracted with 25 mL of hexane. Concentration of the extract solution in vacuo to approximately 5 mL and cooling to −35 °C gave 1,3-bis(trimethylsilyl)-indenyl lithium salt as a yellow solid (83 mg, 32% yield based on the 1,3-bis(trimethylsilyl)indene). Anal. Calcd for $C_{27}H_{47}Si_2O_3Li \cdot (LiI)_{1.5}$: C, 47.44; H, 6.93. Found: C, 47.05; H, 7.36. ¹H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.93 (q, 2H, Ind⁴, Ind⁷), 7.11 (s, 1H, Ind²), 7.03 (q, 2H, Ind⁵, Ind⁶), 3.27 (m, 12H, THF), 1.05 (m, 12H, THF), 0.49 (s, 18H, Si*Me₃*). ¹³C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 136.7, 131.3, 122.3, 117.7, 102.3 (Ind), 68.5 (THF), 25.0 (THF), 1.2 (Si*Me₃*).

(11) Bambirra, S.; Perazzolo, F.; Boot, S. J.; Sciarone, T. J. J.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 704.

(12) (a) Cameron, T. M.; Gordon, J. C.; Scott, B. L. *Organometallics* **2004**, *23*, 2995. (b) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114.

complexes, each rare earth metal ion is coordinated by one indenyl ligand, two $-CH_2SiMe_3$ groups, and one THF molecule. The geometry at the metal centers can be described as distorted tetrahedral when the indenyl five-membered ring is regarded as occupying a single polyhedral vertex. The parameters of the slip distortion $(\Delta Ln-C)$ (0.021 Å in **1**, 0.050 Å in **2**, and 0.029 Å in **3**) and the fold angle (Ω) (3.80° in **1**, 2.70° in **2**, and 3.74° in **3**) indicate η^5 hapticity of the indenyl ligands in all of the complexes.[13] The characterization of the solid-state structures of complexes **1−3** and the previously reported Sc complex $(\Delta Sc-C = 0.085$ Å, $\Omega = 3.08°)$, which differ only in the metal ions, provides the direct crystallographic information of the metal size's effect on the indenyl hapticity. The structural data indicate that the slip distortion value of the complex slightly decreases with an increasing of the metal ion radii,[14] from 0.085 Å in the Sc complex to 0.050 Å in the Lu complex, 0.021 Å in the Y complex, and 0.029 Å in the Dy complex. On the other hand, the change in the fold angle is small. Two distinct differences between the structures of these half-sandwich indenyl complexes and their Cp' analogue $1,3\text{-}(SiMe_3)_2C_5H_3Sc\text{-}(CH_2SiMe_3)_2(THF)$[15] were observed. First, the distance from metal ion to indenyl ligand is longer than that to Cp' ligand when the difference in metal ion radii is counted. The average $Ln-C$(five-membered ring) bond lengths in **1−3** and $(1,3\text{-}(SiMe_3)_2C_9H_5)Sc(CH_2SiMe_3)_2(THF)$ are 2.70, 2.66, 2.72, and 2.56 Å, respectively, while that in the Cp' complex $1,3\text{-}(SiMe_3)_2C_5H_3Sc(CH_2SiMe_3)_2(THF)$ it is 2.51 Å. Second, the Sc ion of the Cp' complex is closer to the carbon atoms opposite the $-SiMe_3$ substituents (average 2.49 Å) than to other carbon atoms on the ring (average 2.52 Å) due to the steric effect. In contrast, $Ln-C$ bond lengths in the half-
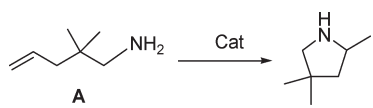
(13) The slip distortion $(\Delta M-C)$ is defined as the difference between the average distance from the metal center to the carbon atoms shared by the five- and six-membered rings and the adjacent carbon atoms unique to the five-membered ring. The fold angle (Ω) is defined as the angle between the plane formed by the carbons unique to the five-membered ring $(C(2)-C(3)-C(4))$ and the plane with $C(1)-C(5)-C(2)-C(4)$. Typically, a slip distortion $(\Delta M-C)$ less than 0.30 Å and a fold angle (Ω) less than 8° indicate an η^5 coordination mode of the indenyl ligand; see: Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332.

(14) Six-coordinate ionic radii: Sc^{3+} (0.745 Å), Lu^{3+} (0.861 Å), Y^{3+} (0.900 Å), Dy^{3+} (0.912 Å). Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(15) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962.

(16) For representative samples of intramolecular hydroamination catalyzed by rare earth metal complexes, see: (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673. (b) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (c) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (d) Yu, X.; Marks, T. J. *Organometallics* **2007**, *26*, 365. (e) Yuen, H. F.; Marks, T. J. *Organometallics* **2008**, *27*, 155. (f) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161. (g) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1998**, *63*, 8983. (h) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1999**, *64*, 6515. (i) Burgstein, M. R.; Berberich, H.; Roesky, P. W. *Organometallics* **1998**, *17*, 1452. (j) Rastatter, M.; Zulys, A.; Roesky, P. W. *Chem.−Eur. J.* **2007**, *13*, 3606. (k) Bambirra, S.; Tsurugi, H.; Leusen, V. D.; Hessen, B. *Dalton Trans.* **2006**, 1157. (l) Ge, S.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 5339. (m) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *Chem.−Eur. J.* **2003**, *9*, 4796. (n) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748. (o) Collin, J.; Daran, J. C.; Schulz, E.; Trifonov, A. A. *Chem. Comm.* **2003**, *24*, 3048. (p) Aillaud, I.; Lyubov, D.; Collin, J.; Guillot, R.; Hannedouhe, J.; Schulz, E.; Trifonov, A. A. *Organometallics* **2008**, *27*, 5929. (q) Lauterwasser, F.; Hayes, P. G.; Bräse, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234. (r) Stanlake, L. J. E.; Schafer, L. L. *Organometallics* **2009**, *28*, 3990. (s) Kim, Y. K.; Livinghouse, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3645. (t) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560. (u) Wang, Q.; Xiang, L.; Song, H.; Zi, G. *Inorg. Chem.* **2008**, *47*, 4319. (v) Xiang, L.; Wang, Q.; Song, H.; Zi, G. *Organometallics* **2007**, *26*, 5323. (w) Yuan, Y.; Chen, Y.; Li, G.; Xia, W. *Organometallics* **2008**, *27*, 6307.

Table 2. Hydroamination of 2,2-Dimethylpent-4-enylamine Catalyzed by 1−3 and $(1,3\text{-}(SiMe_3)_2C_9H_5)Sc(CH_2SiMe_3)_2(THF)$[a]

entry	catalyst	[cat.]/[sub.] (%)	time (h)	yield (%)[b]	TOF (h^{-1})[c]
1	**1(Y)**	1	0.5	98	196
2	**2(Lu)**	1	0.8	98	123
3	**3(Dy)**	1	0.3	98	327
4	**Sc** complex	1	24	67	2.8

[a] 60 °C, C_6D_6 as the solvent (0.50 mL), 0.50 mmol of substrate. [b] NMR yield determined relative to ferrocene internal standard. [c] Turnover frequency.

sandwich indenyl complexes for the carbon atoms shared by the five- and six-membered rings, which are opposite the $-SiMe_3$ substitutents, are longer than those for the adjacent carbon atoms unique to the five-membered ring, due to the indenyl ligand's unique properties.
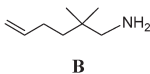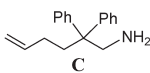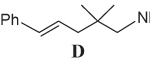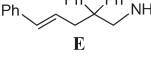
Catalytic Behaviors for Intramolecular Hydroamination of Aminoalkenes. Intramolecular hydroamination of aminoalkenes offers an efficient and atom-economical method to construct nitrogen heterocycles that are important for fine chemicals and pharmaceuticals. Various metal complexes, including those of alkali metals, early transition metals, and late transition metals, have been investigated for this transformation; the rare earth metal complexes are among the most promising.[16] The catalytic behaviors of half-sandwich indenyl rare earth metal dialkyl complexes for intramolecular hydroamination of aminoalkenes were initially tested by employing 2,2-dimethylpent-4-enylamine (**A**) as the substrate (Table 2). A solution of the metal complex, substrate, and standard ferrocene in C_6D_6 was loaded into a NMR tube, and the reaction process was monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum of the mixture showed a rapid protonolysis of the rare earth metal alkyl by amine with a release of $SiMe_4$, and the indenyl ligand remains coordinated to the metal ion. A clean formation of 2,4,4-trimethylpyrrolidine, the Markovnikov-selective product, was observed in several minutes, and no traces of other heterocyclic regioisomers were detected through the proceeding in all cases. Catalytic activity of the metal complex dramatically increased with increasing ionic radii. The indenyl Sc complex gave 67% yield over 24 h with 1.0 mol % catalyst loading. When the Lu complex (**2**) was used, the reaction was much faster and was complete within 0.8 h. For the Y complex (**1**) and Dy complex (**3**), the time for completing the reaction was only 0.5 and 0.3 h, respectively. The activities of **1** and **3** for intramolecular hydroamination are comparable to the most active rare earth metal complexes reported.

1 and **3** were subsequently applied for the intramolecular hydroamination of a series of aminoalkenes (**B−E**) (Table 3). All substrates were converted to the cyclic products in high yield under mild reaction conditions (60 °C) with rather low catalyst loading (1.0−3.0 mol %) and short reaction time (2.5−9 h), and the Dy complex (**3**) showed higher activities than the Y complex (**1**). According to Baldwin's rule for ring closure that the formation of a six-membered ring is less favorable than that of a five-membered ring,[17]

(17) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

Table 3. Hydroamination of Aminoalkenes Catalyzed by 1–3[a]

entry	substrate	product	catalyst	[cat.]/[sub.] (%)	time (h)	yield(%)[b]	TOF(h^{-1})[c]
1			1	2	4	98	12.3
2	**B**		3	2	3.5	98	14.0
3			3	1.5	5	98	13.1
4			1	1	4.5	98	21.8
5	**C**		3	1	4	98	24.5
6			1	3	9	98	3.63
7	**D**		3	3	6.5	98	5.03
8			1	1	3	98	32.7
9	**E**		3	1	2.5	98	39.2

[a] 60 °C, C_6D_6 as the solvent (0.50 mL), 0.50 mmol of substrate. [b] NMR yield determined relative to ferrocene internal standard. [c] Turnover frequency.

higher catalyst loading and longer reaction time were needed for completing the reaction of substrate **B** in comparison to those for substrate **A**, even though the reaction was completed with 2.0 mol % **1** in 4 h, 2.0 mol % **3** in 3.5 h, or 1.5 mol % **3** in 5 h (Table 3, entries 1–3). For substrate **C**, bearing bulky phenyl substituents in the β-position to the amino group, the reaction rate was accelerated. With a very small amount of the metal complex, 1.0 mol % **1** or **3**, the substrate was converted to the cyclic product in 98% yield within 4.5 or 4 h, respectively (Table 3, entries 4 and 5). This observed rate enhancement is consistent with the Thorpe–Ingold effect.[18] One challenge in intramolecular hydroamination of aminoalkenes is the cyclization of internal alkenes. As shown in Table 3, **1** and **3** are also highly active to the internal alkenes **D** and **E**. For the substrate **D**, the cyclic product was formed nearly quantitatively with 3.0 mol % **1** in 9 h or 3.0 mol % **3** in 6.5 h (Table 3, entries 6 and 7). As observed in the cyclization of terminal alkenes, replacing the methyl substituent with a phenyl substituent at the β-position to the amino group caused a much faster cyclization of **E**; the reaction was completed with 1.0 mol % **1** in 3 h or 1.0 mol % **3** in 2.5 h (Table 3, entries 8 and 9).

In summary, with 1,3-bis(trimethylsilyl)indenyl ligand [1,3-(SiMe$_3$)$_2$C$_9$H$_5$]$^-$, half-sandwich indenyl rare earth metal complexes (1,3-(SiMe$_3$)$_2$C$_9$H$_5$)Ln(CH$_2$SiMe$_3$)$_2$(THF) (Ln = Y, Lu, Dy) were accessible. The structural data indicated the η^5 hapticity of indenyl ligands in all of the complexes. These complexes' catalytic activities for intramolecular hydroamination of aminoalkenes increased with increasing metal ion size, and the Y and Dy complexes showed excellent activities to a variety of aminoalkenes. The high activities of the Y and Dy complexes, in addition to the easy preparation and low cost of these complexes and their ligand precursor, make them a type of attractive catalyst for the intramolecular hydroamination of aminoalkenes.

(18) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen gas filled glovebox. Hexane and C_6D_6 were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. Indene and Me$_3$SiCl were purchased from Acros and distilled prior to use. 1,3-Bis(trimethylsilyl)indene[19] and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Y, Lu, Dy, Gd)[20] were synthesized according to literature procedures. (1,3-(SiMe$_3$)$_2$C$_9$H$_5$)-Sc(CH$_2$SiMe$_3$)$_2$(THF) was synthesized as we previously reported.[8] 2,2-Dimethylpent-4-enylamine,[16n] 2,2-dimethyl-5-phenylpent-4-enylamine,[16n] 2,2-diphenyl-5-phenylpent-4-enylamine,[21] 2,2-dimethylhept-5-enylamine,[22] and 2,2-diphenylhept-5-enylamine[23] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or a Varian 400 MHz spectrometer, and the chemical shifts were reported in δ (ppm) units with references to the residual solvent resonance of the deuterated solvents. Elemental analysis was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry. Melting points of the complexes were determined on a SWG X-4 digital melting point apparatus in a sealed capillary and are uncorrected.

(1,3-(SiMe$_3$)$_2$C$_9$H$_5$)Y(CH$_2$SiMe$_3$)$_2$(THF) (1). Y(CH$_2$SiMe$_3$)$_3$-(THF)$_2$ (659 mg, 1.3 mmol) and 1,3-(SiMe$_3$)$_2$C$_9$H$_6$ (347 mg, 1.3 mmol) were mixed in 15 mL of hexane. After stirring at room temperature for 72 h, the reaction mixture was filtered, and evaporation of the resulting solution in vacuo gave a pale yellow oil. Recrystallization of the oily residue from hexane at −35 °C afforded **1** as pale yellow crystals (481 mg, 61% yield), mp 99−101 °C with a small amount of decomposition. Anal. Calcd for C$_{27}$H$_{53}$Si$_4$OY: C, 54.51; H, 8.98. Found: C, 54.52; H, 9.00.

(19) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1996**, *519*, 21.

(20) Estler, F.; Eickerling, G.; Herdtweck, E.; Anwander, R. *Organometallics* **2003**, *22*, 1212.

(21) Kondo, T.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **2002**, *124*, 186.

(22) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

(23) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1988**, *110*, 3994.

Table 4. Crystallographic Data and Refinement for 1−3

	1	2	3
formula	$C_{27}H_{53}OSi_4Y$	$C_{27}H_{53}OSi_4Lu$	$C_{27}H_{53}OSi_4Dy$
fw	594.96	681.02	668.55
color	pale yellow	pale yellow	pale yellow
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
a, Å	14.219(3)	10.2276(7)	14.2015(18)
b, Å	16.076(3)	15.9273(11)	16.031(2)
c, Å	15.857(3)	22.0779(16)	15.788(2)
β, deg	93.051(4)	97.6190(10)	92.893(2)
V, Å^3	3619.4(12)	3564.7(4)	3589.8(8)
Z	4	4	4
D_{calcd}, g/cm^3	1.092	1.269	1.237
$F(000)$	1272	1400	1380
θ range, deg	1.81−25.50	1.58−26.00	1.81−26.50
no. of reflns collected	18 861	19 216	19 904
no. of unique reflns	6722	7004	7406
no. of obsd reflns ($I > 2\sigma(I)$)	2491	4001	4645
no. of params	290	310	270
goodness of fit	0.816	0.831	0.967
final R, R_w ($I > 2\sigma(I)$)	0.0644, 0.1562	0.0333, 0.0662	0.0599, 0.1437
$\Delta\rho_{max,min}$, e Å^{-3}	0.678, −0.548	1.196, −0.541	1.316, −0.993

^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.77 (q, 2H, Ind[4], Ind[7]), 7.58 (s, 1H, Ind[2]), 6.98 (q, 2H, Ind[5], Ind[6]), 3.28 (br s, 4H, THF), 1.05 (br s, 4H, THF), 0.47 (s, 18H, Si*Me*₃), 0.27 (s, 18H, CH_2SiMe₃), −0.57 (br s, 4H, CH_2SiMe₃). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 137.1, 136.1, 124.5, 121.6, 113.4 (Ind), 70.5 (THF), 37.7 (d, [1]J_{YC} = 44 Hz, CH_2SiMe₃), 24.7 (THF), 4.4-(CH₂Si*Me*₃), 0.9 (Si*Me*₃).

(1,3-(SiMe₃)₂C₉H₅)Lu(CH₂SiMe₃)₂(THF) (2). A procedure similar to that for **1** was used. Reaction of Lu(CH₂SiMe₃)₃-(THF)₂ (400 mg, 0.69 mmol) and 1,3-(SiMe₃)₂C₉H₆ (150 mg, 0.58 mmol) at 50 °C for 30 h gave complex **3** as pale yellow crystals (350 mg, 87% yield), mp 114−116 °C with a small amount of decomposition. Anal. Calcd for $C_{27}H_{53}Si_4OLu$: C, 47.62; H, 7.84. Found: C, 47.36; H, 7.77. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.76 (q, 2H, Ind[4], Ind[7]), 7.51 (s, 1H, Ind[2]), 6.99 (q, 2H, Ind[5], Ind[6]), 3.27 (br s, 4H, THF), 1.04 (br s, 4H, THF), 0.48 (s, 18H, Si*Me*₃), 0.26 (s, 18H, CH₂SiMe₃), −0.71 (br s, 2H, CH_2SiMe₃), −0.86 (br s, 2H, CH_2SiMe₃). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 137.2, 136.3, 124.7, 121.6, 112.7 (Ind), 71.0 (THF), 41.6 (br, CH_2SiMe₃), 24.6 (THF), 4.5-(CH₂Si*Me*₃), 1.0 (Si*Me*₃).

(1,3-(SiMe₃)₂C₉H₅)Dy(CH₂SiMe₃)₂(THF) (3). A procedure similar to that for **1** was used. Reaction of Dy(CH₂SiMe₃)₃-(THF)₂ (467 mg, 0.82 mmol) and 1,3-(SiMe₃)₂C₉H₆ (179 mg, 0.69 mmol) at room temperature for 72 h gave complex **3** as a pale yellow crystalline solid (300 mg, 65% yield), mp 104−106 °C. Anal. Calcd for $C_{27}H_{53}Si_4ODy$: C, 48.51; H, 7.99. Found: C, 47.83; H, 7.72. **3** is paramagnetic.

Attempt to Prepare (1,3-(SiMe₃)₂C₉H₅)Gd(CH₂SiMe₃)₂(THF). A procedure similar to that for **1** was used. Reaction of Gd-(CH₂SiMe₃)₃(THF)₂ (155 mg, 0.28 mmol) and 1,3-(SiMe₃)₂C₉H₆ (65 mg, 0.25 mmol) at room temperature for 72 h gave an oily product (88 mg). No solid product was obtained after repeated recrystallization of the oily product. Anal. Calcd for $C_{27}H_{53}$-Si_4OGd: C, 48.89; H, 8.05. Found: C, 51.72; H, 6.94.

General Procedure for Intramolecular Hydroamination of Aminoalkenes. The half-sandwich indenyl dialkyl rare earth metal complex, substrate (0.5 mmol), and standard ferrocene (0.1 mmol) were mixed in C_6D_6 and transferred into a NMR tube. The NMR tube was heated at 60 °C, and the process of the reaction was monitored by ^{1}H NMR.

X-ray Crystallography. Single crystals of **1−3** were sealed in thin-walled glass capillaries, and data collection was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SA-DABS. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. The software used is listed in the references.[24] Crystallographic data and refinement for **1−3** are listed in Table 4.

Supporting Information Available: ORTEP diagrams of molecular structures of **2** and **3**, variable-temperature ^{1}H NMR spectra of **1** and **2**, and CIF files giving X-ray crystallographic data for **1−3**. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) (a) Sheldrick, G. M. *SADABS*, An Empirical Absorption Correction Program for Area Detector Data; University of Goettingen: Germany, 1996. (b) Sheldrick, G. M. *SHELXS-97*; University of Goettingen, Germany, 1997. (c) *SMART*, Version 5.628; Bruker AXS Inc. (d) *SAINT*+, Version 6.22a; Bruker AXS Inc. (e) *SHELXTL* NT/2000, Version 6.1.[1].