Monoalkyllanthanide Complexes with New β-Diketiminato Derivative Dianionic Ligands

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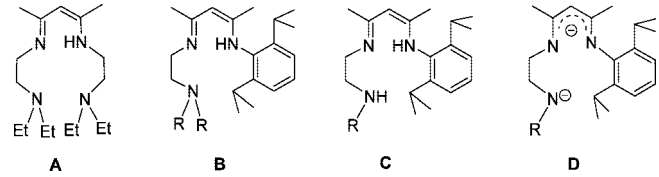
A new class of β-diketiminato derivative dianionic ligands was designed, and three ligand precursors [$CH_3C(ArNH)CHC(CH_3)(NCH_2CH_2$-$NHR)$] (Ar = 2,6-(^{i}Pr)$_2C_6H_3$; R = ^{t}Bu (**$H_2$L1**), 2,6-$(CH_3)_2C_6H_3$ (**H_2L2**), 2,6-(^{i}Pr)$_2C_6H_3$ (**H_2L3**)) were synthesized. The alkane elimination reactions between these ligand precursors and $Ln(CH_2SiMe_3)_3(THF)_n$ provided eight five-coordinate monoalkyllanthanide complexes, in which the ligand serves as a tridentate dianionic donor, with one $-CH_2SiMe_3$ and one THF molecule completing the five-coordinate center. These monoalkyl complexes exhibited low to very high catalytic activities for intramolecular hydroamination of 2,2-dimethyl-1-aminopent-4-ene. The catalytic activity increased with increasing metal ion size. For the Nd complex, 98% yield was obtained in 1 h at 60 °C with 0.5 mol % catalyst loading.

Introduction

Due to their rich and diversified coordinating properties and reactivities, organolanthanide complexes have received growing attention.[1−3] The most widely investigated organolanthanide complexes are those bearing Cp-type ligands. Recently, there is a tendency to explore "non-Cp" organolanthanide complexes.[4] Among the "non-Cp" type ligands, β-diketiminato ligands are one of the most promising ligand families. The precursors for these ligands can be readily prepared by condensation of β-diketones with amines. The steric and electronic properties of these ligands can be easily tuned by an appropriate choice of β-diketone and amine, and coordination to a lanthanide ion can range from purely σ to a combination of σ and π donation.[5] Numerous β-diketiminato lanthanide complexes have been prepared, and some of them show good catalytic activities in organic and polymer synthesis.[6−9]

Chart 1



For the purpose of stabilizing the reactive complexes with larger size lanthanide ions, some modifications on β-diketiminato ligands were made. Roesky and co-workers developed a β-diketiminato derivative **A** (Chart 1), which contains two dangling arms with nitrogen donors incorporated. With the tetradentate monoanionic ligand derived from **A**, they prepared a series of lanthanide complexes.[10] On considering both steric and electronic features of the ligand, we had designed tridentate monoanionic NNN ligands derived from **B** and successfully prepared highly reactive organolanthanide dialkyl complexes.[11] For the organolanthanide complexes, the chelating dianionic ligands are of great importance, as they are capable of creating

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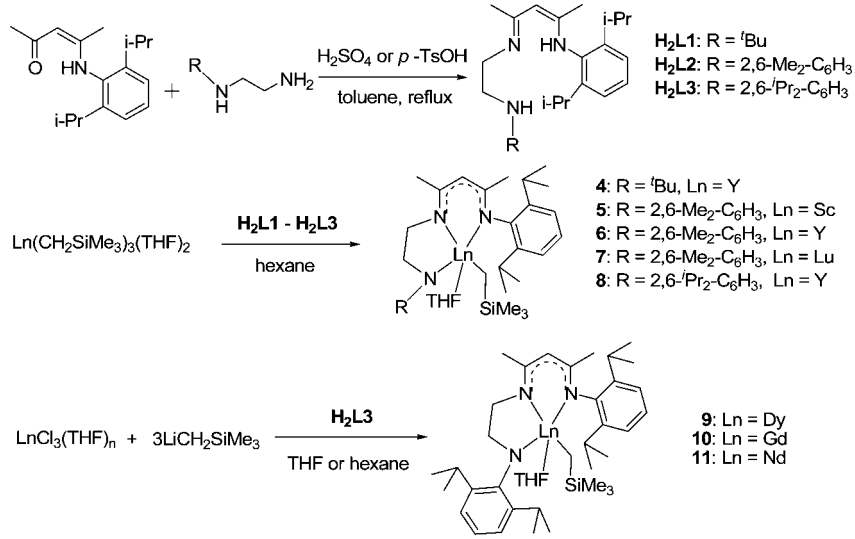
Scheme 1



rigid supporting environments for steric control during the catalytic reactions, and the corresponding monoalkyl complexes can provide the sole initiating group. Therefore, our rationale began with our previous ligand precursors **B**; replacing the tertiary amino groups by the secondary amino groups resulted in ligand precursors **C**, which, upon deprotonation, are anticipated to yield dianionic ligands **D**. Herein we report the preparation of ligand precursors **C**, the preparation and structures of monoalkyllanthanide complexes containing dianionic ligands **D**, and their catalytic activities in the intramolecular hydroamination of 2,2-dimethyl-1-aminopent-4-ene.

Results and Discussion

Synthesis and Characterization. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one was prepared by condensation of acetylacetone with 2,6-diisopropylaniline.[12] This product was subsequently treated with diamines (N^1-tetrabutylethane-1,2-diamine,[13] N^1-(2,6-dimethylphenyl)ethane-1,2-diamine, and N^1-(2,6-diisopropylphenyl)ethane-1,2-diamine[14]) in toluene, with the presence of a catalytic amount of sulfuric acid or *p*-toluenesulfonic acid, to provide the desired ligand precursors **H$_2$L1** (**1**), **H$_2$L2** (**2**), and **H$_2$L3** (**3**) in 62%−74% yield (Scheme 1). These compounds were characterized by NMR (^{1}H and ^{13}C) and HRMS spectroscopy.

The alkane elimination method was applied for the synthesis of desired monoalkyllanthanide complexes. The reaction between **H$_2$L1** and Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ in hexane under ambient temperature gave a complicated mixture. Thus, the reaction was carried out at −35 °C, from which some colorless crystals covered by red viscous oil were obtained. The crystals and the oil were both readily soluble in hexane and toluene, and attempts to obtain pure product from the mixture failed. Finally, the oil was carefully removed by grease, and the crystal structure was determined by single-crystal X-ray diffraction. It was found that the product is the monoalkyl complex **4** (Figure 1). As the reaction between **H$_2$L1** and Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ was complicated, we turned to **H$_2$L2**, which has a bulky aryl substituent on the nitrogen atom of the pendant arm. The reactions between **H$_2$L2** and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) in hexane proceeded well and gave the desired monoalkyl complexes **L2**Ln(CH$_2$SiMe$_3$)(THF) (Ln = Sc (**5**), Y (**6**), Lu (**7**)) in 71%−90% yields (Scheme 1). When large lanthanide ions (Dy^{3+}, Gd^{3+}, Nd^{3+}) were introduced, some modifications to the previous procedure were adopted. Ln(CH$_2$SiMe$_3$)$_3$(THF)$_n$ (Ln = Gd, Dy, Nd) were produced by reactions of LnCl$_3$(THF)$_n$ with LiCH$_2$SiMe$_3$,[15] and the in situ generated trialkyl complexes

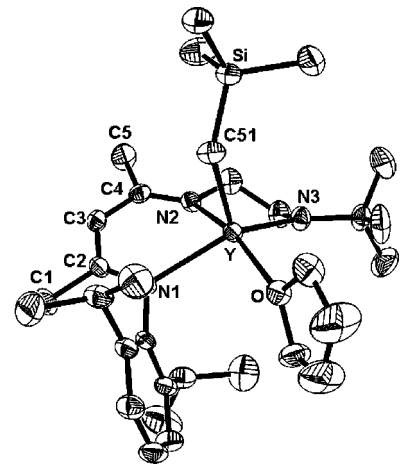


Figure 1. Molecular structure of **4** with thermal ellipsoids at the 30% probability level.

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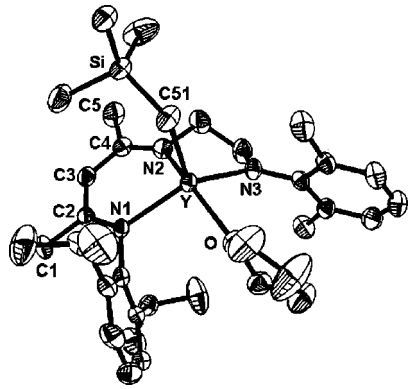


Figure 2. Molecular structure of **6** with thermal ellipsoids at the 30% probability level.

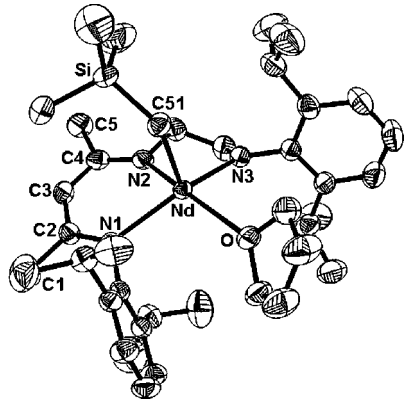


Figure 3. Molecular structure of **11** with thermal ellipsoids at the 30% probability level.

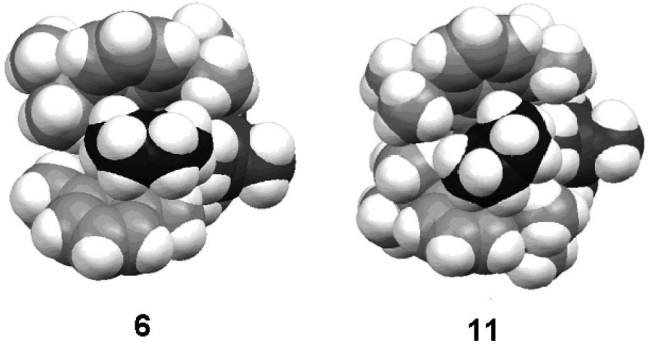


Figure 4. Space-filling views of **6** and **11**.

in hexane or THF were subsequently added to the ligand. However, repeated attempts to synthesize monoalkyl complexes with Dy^{3+}, Gd^{3+}, and Nd^{3+} ions gave only complicated mixtures either at room temperature or at −35 °C. When $\mathbf{H_2L3}$, which has the more bulky 2,6-diisopropylphenyl on the pendant arm, was introduced, first $\mathbf{L3}Y(CH_2SiMe_3)(THF)$ (**8**) was synthesized in 59% yield by the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ with $\mathbf{H_2L3}$ in hexane. In addition, $\mathbf{L3}Ln(CH_2SiMe_3)(THF)$ (Ln = Dy (**9**), Gd (**10**), Nd (**11**)) were obtained by reactions between $LnCl_3(THF)_n$, $LiCH_2SiMe_3$, and $\mathbf{H_2L3}$ in hexane or THF at 0 °C (Scheme 1).

Single crystals of complexes **6** and **11** were grown from hexane solutions at −35 °C and characterized by X-ray diffraction. ORTEP diagrams are shown in Figures 2 and 3, and selected bond lengths and angles are given in Table 1. Complexes **4**, **6**, and **11** all are five-coordinate monomers. **L1**, **L2**, and **L3** serve as tridentate ligands, and the five-coordinate

Table 1. Selected Bonds Lengths (Å) and Angles (deg) for 4, 6, and 11

	4 (Ln = Y)	**6** (Ln = Y)	**11** (Ln = Nd)
Ln−N1	2.377(3)	2.350(4)	2.397(3)
Ln−N2	2.317(3)	2.309(4)	2.451(3)
Ln−N3	2.212(3)	2.258(4)	2.274(3)
Ln−C51	2.377(3)	2.411(5)	2.474(4)
Ln−O	2.444(2)	2.379(3)	2.497(3)
N1−C2	1.338(4)	1.323(6)	1.343(5)
C2−C3	1.385(4)	1.399(7)	1.377(5)
C3−C4	1.402(5)	1.407(7)	1.400(6)
C4−N2	1.310(4)	1.318(6)	1.312(5)
N_2C_3 plane−Ln	0.911(4)	0.645(8)	0.792(8)
N1−Ln−N2	76.07(9)	76.93(15)	72.98(11)
N1−Ln−N3	133.51(10)	128.67(14)	133.66(12)
N2−Ln−N3	74.96(10)	74.65(15)	71.72(12)
C51−Ln−O1	92.69(11)	100.93(15)	95.18(12)
N1−C2−C3	124.4(3)	123.4(5)	122.2(4)
C2−C3−C4	128.0(3)	130.0(5)	129.4(4)
C3−C4−N2	123.0(3)	121.4(5)	123.6(4)
Ln−N1−C2	126.3(2)	129.4(3)	132.7(3)
Ln−N2−C4	127.9(2)	131.7(3)	128.7(3)

center is completed by one $-CH_2SiMe_3$ and one THF molecule. The geometry at the metal center is best described as a distorted square pyramid, with $-CH_2SiMe_3$ taking the apical position. The β-diketiminato backbone is bonded to the metal ion through two Ln−N bonds, the length of which varies from 2.31 to 2.45 Å, falling in the range 2.04−2.49 Å observed for Ln−N bonds in other β-diketiminato lanthanide complexes.[6−9] The Ln−N3 bond lengths of the pendant arm in complexes **4**, **6**, and **11** (2.21−2.27 Å) are significantly shorter than their counterparts in our previously reported dialkyl complexes (2.50 to 2.65 Å);[11] this is in accordance with the anionic nature of N3 in **4**, **6**, and **11**. The C−N and C−C bond lengths of the β-diketiminato backbone are between those of typical single and double bonds, and N1, C2, C3, C4, and N2 atoms are coplanar, indicating that there is a delocalized electronic structure. The metal ions sit above the C_3N_2 plane (C_3N_2 plane−Ln = 0.65 to 0.91 Å); the Ln−C2, Ln−C3, and Ln−C4 distances (>3.3 Å) are too long for effective interaction. Thus, the bonding mode of the β-diketiminato backbone is best described as a 2σ electron donor. The alkyl ligand ($-CH_2SiMe_3$) is coordinated with Ln−C bond lengths of 2.377(3) Å (**4**), 2.411(5) Å (**6**), and 2.474(4) Å (**11**). The spatial arrangement of the two aromatic rings and the THF molecule in **6** and **11** is interesting (Figure 4). The THF is bound by two phenyl rings, to adopt a sandwich-like arrangement. In the Nd complex **11**, the THF between the two phenyl rings has a larger inclination than that in **6**; this can be attributed to the larger radii of the Nd^{3+} ion.

The ^{1}H NMR spectra of the diamagnetic complexes **5**, **6**, **7**, and **8** in C_6D_6 at 25 °C showed AB systems for the Ln-CH_2 methylene protons, which indicated a C_s-symmetric structure in solution. In complex **5**, the two methyl groups on the phenyl ring are diastereotopic and display two distinct singlets (Figure 5, a), revealing a large rotation barrier of the N3−C_{Ar} bond. Increasing the temperature from 25 to 80 °C results in broadening and coalescence of the ArCH_3 resonances followed by sharpening of the resulting coalesced signal (Figure 5). The coalescence temperature (ca. 335 K) and the $\Delta\delta$ for the individual ^{1}H NMR resonances due to ArCH_3 groups (ca. 160 Hz) have been used to estimate a $\Delta G^{\ddagger}$ value of ca. 66.0 kJ/mol for the rotation of the N−C_{Ar} bond.[16] The THF of **5** has some interesting ^{1}H NMR features: the α-H's appeared as four multiplets in the range 3.05 to 4.25 ppm,[17] and the β-H's appeared as two significantly upfield shifted broad peaks at 0.68 and 0.58 ppm, respectively (Figure 5, a). Therefore, the THF is strongly bonded and the rotation restricted. Upon increasing the

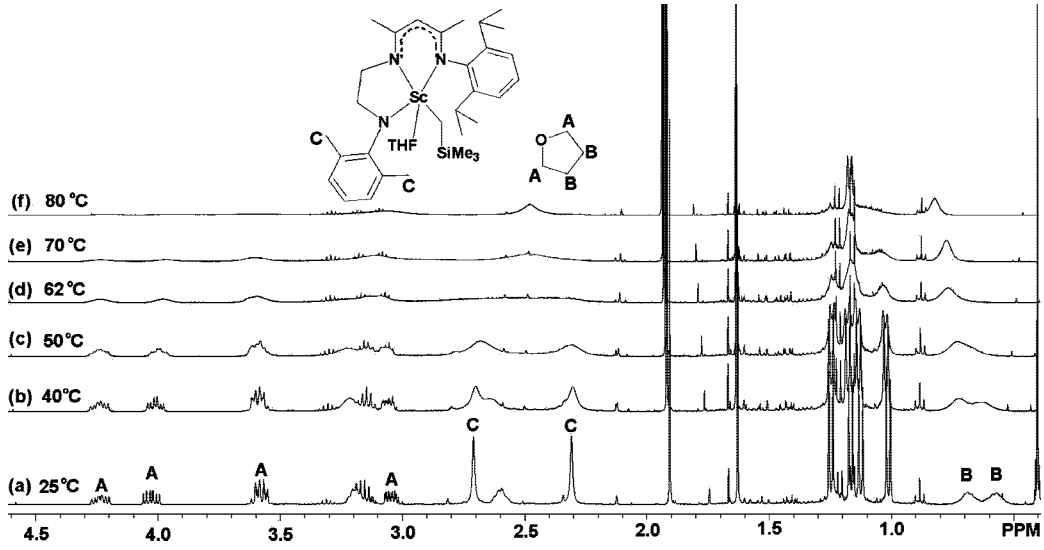


Figure 5. Variable-temperature ^{1}H NMR spectra for **5** (400 MHz, C_6D_6).

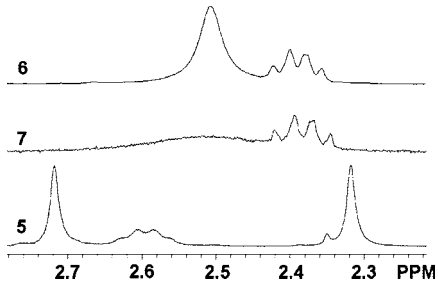
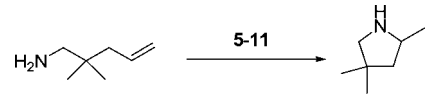


Figure 6. Comparison of ArC*H*$_3$ signals between **5**(**L2**Sc), **6**(**L2**Y), and **7**(**L2**Lu) (300 MHz, C_6D_6, 25 °C).

temperature, the resonances due to α-H's broaden, and those for β-H's coalesced and shifted downfield. The ^{1}H NMR spectra of other diamagnetic complexes (**6**, **7**, and **8**) at 25 °C showed similar behavior for the THF. The restricted rotation of THF observed in solution is in agreement with the arrangement of THF in the solid state, where the THF is bound by two phenyl rings. It is noteworthy that the size of the central metal ion[18] has a significant influence on the rotation barrier of the N−C_{Ar} bond; ^{1}H NMR resonances for the methyl groups on the phenyl ring at 25 °C varied from two singlets in the Sc complex **5** to one broad singlet near coalescence in the Lu complex **7** and to one singlet in the Y complex **6** (Figure 6).

Catalytic Behaviors for Intramolecular Hydroamination. Intramolecular hydroamination 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 lanthanide complexes are among the most promising.[2,7f,19] The catalytic behaviors of lanthanide complexes **5**−**11** for intramolecular hydroamination were briefly tested by employing 2,2-dimethyl-1- aminopent-4-ene as substrate (Table 2). A solution of the lanthanide complex and substrate in C_6D_6 was loaded into a NMR tube, and the reaction process was monitored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the mixture showed a rapid protonolysis of the lanthanide alkyl by amine with a release of $SiMe_4$, and the pendant group remains coordinated to the metal. 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 increased with increasing ionic radii, as observed in other lanthanide complex-catalyzed intramolecular hydroaminations.[20] Complex **5**, which with the smallest Sc^{3+} ion, gave less than 5% yield in 24 h. When Lu complex **7** was used, the reaction was nearly complete

Table 2. Hydroamination of 2,2-Dimethylpent-4-ene-1-amine Catalyzed by 5−11[a]



entry	catalyst	[cat.]/[sub.] (%)	time (h)	yield (%)[b]
1	**5**	1	24.0	<5
2	**6**	1	4.0	98
3	**7**	1	12.0	96
4	**8**	1	2.0	97
5	**9**	1	1.0	97
6	**10**	1	1.0	98
7	**11**	1	0.5	98
8	**11**	0.5	1.0	98

[a] 10 mmol L^{-1} [cat.], 60 °C, C_6D_6 as the solvent. [b] NMR yield determined relative to *p*-xylene internal standard.

(16) $\Delta G^{\ddagger} = aT_c(9.972 + \log(T_c/\Delta\delta))$, a is a constant of 1.914×10^{-2} kJ/mol, T_c (K) is the coalescence temperature, and $\Delta\delta$ (Hz) is the frequency difference of the coalescing signals. Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press Inc.: London, 1982; Chapter 7.

(17) 4.24 (1H), 4.04 (1H), 3.60 (1H, overlapped with $ArCHMe_2$), 3.06 (1H).

(18) Six-coordinate ionic radii: Sc^{3+} (0.745 Å), Lu^{3+} (0.861 Å), Y^{3+} (0.900 Å), Dy^{3+} (0.912 Å), Gd^{3+} (0.938 Å), Nd^{3+} (0.983 Å). Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

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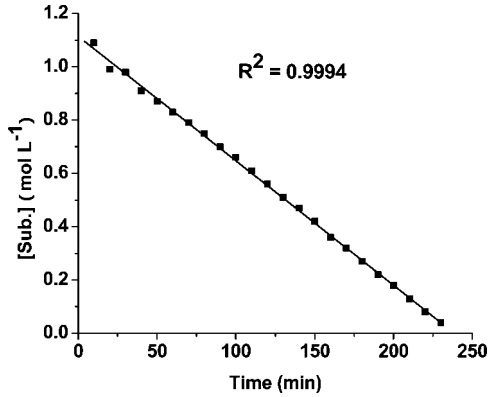

Figure 7. Concentration of substrate versus time for the intramolecular hydroamination catalyzed by **8** ([cat.] = 40 mmol L^{-1}) at 25 °C.

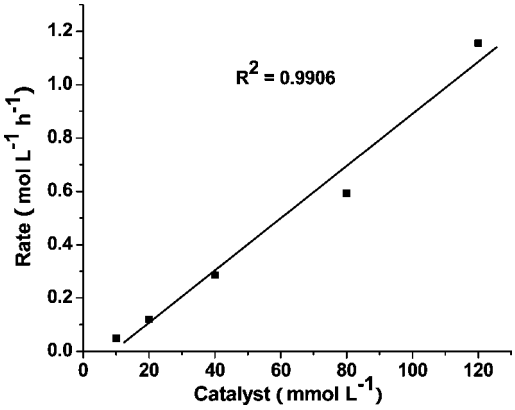

Figure 8. Observed reaction rate versus concentration of catalyst for the intramolecular hydroamination catalyzed by **8** at 1.0 mol L^{-1} [sub.]$_0$ and 25 °C.

in 12 h. For the Y complexes (**6** and **8**), the Dy complex (**9**), and the Gd complex (**10**), the time for completing the reaction was 4, 2, 1, and 1 h, respectively. When complex **11**, which has the largest, Nd^{3+}, ion, was introduced, the reaction was completed in only 30 min. Even with a very small amount of **11**, 0.5 mol % catalyst loading, the reaction could be completed in 1 h.

Kinetic studies of this class of lanthanide complex-catalyzed intramolecular hydroamination of 2,2-dimethyl-1-aminopent-4-ene were carried out at 25 °C by in situ ^{1}H NMR spectroscopy. The diamagnetic yttrium complex **8**, which allows convenient NMR monitoring of reactions, was used as the catalyst. The concentration of substrate was held constant (1.0 mol/L), and the catalyst concentration was varied over a 12-fold range from 120 to 10 mmol/L. Figure 7 presents the typical relevance of the substrate concentration versus time, and Figure 8 shows rate dependence on catalyst concentration. The in situ ^{1}H NMR studies indicated the rate to be zero-order in substrate and first-order in catalyst, which is in accordance with the generally accepted mechanism of intramolecular hydroamination catalyzed by organolanthanide complex, in which the alkyl complex undergoes a rapid protonolysis by amine, and the olefin insertion is rate-determining.[20]

Conclusions

A new class of β-diketiminato derivative dianionic ligands was designed, which provided versatile tridentate ligand sets for organolanthanide complexes. The precursors for these ligands can be readily prepared by condensation of ketoaryliminato with diamines, and the alkane elimination reactions between these ligand precursors and $Ln(CH_2SiMe_3)_3(THF)_n$ gave five-coordinate monoalkyllanthanide complexes. The substituent on the nitrogen atom of the pendant arm has a significant influence on the synthesis of monoalkyllanthanide complexes. With a bulky 2,6-^{i}Pr$_2$-C$_6$H$_3$ substituent, complexes of larger size lanthanide ions, such as Nd^{3+} and Gd^{3+}, were accessible. These monoalkyl complexes are active for intramolecular hydroamination of 2,2-dimethyl-1-aminopent-4-ene, and the catalytic activity increases with increasing size of the metal ion. Kinetic studies of the reaction showed the rate to be zero-order in substrate and first-order in catalyst. Future studies will strive to prepare the related ligand precusors with chiral pendent arms and corresponding metal complexes.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox. THF was distilled from Na-benzophenoneketyl and degassed by freeze−thaw−vacuum prior to use. Toluene, hexane, and C_6D_6 were dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. 2,6-Diisopropylaniline, 2,6-dimethylaniline, 2-aminoethyl chloride hydrochloride, and 2,4-pentanedione were purchased from Aldrich and used without further purification. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one,[12] N^1-tetrabutylethane-1,2-diamine,[13] N^1-(2,6-dimethylphenyl)ethane-1,2-diamine, and N^1-(2,6-diisopropylphenyl)ethane-1,2-diamine[14] were synthesized according to literature procedures. $LiCH_2SiMe_3$[21] and $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y, Lu)[22] were synthesized following the standard procedures. 2,2-Dimethyl-1-aminopent-4-ene was synthesized following the literature procedure,[20,23] dried over CaH_2, and distilled under vacuum prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or a Varian 400 MHz spectrometer. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry. Melting points of the compounds were determined on a SWG X-4 digital melting point apparatus in a sealed capillary and are uncorrected.

H_2L1 (1). 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one (11.06 g, 42.6 mmol), N^1-tetrabutylethane-1,2-diamine (5.00 g, 43.0 mmol), 10 drops of concentrated sulfuric acid, and toluene (100 mL) were introduced into a 250 mL flask equipped with a Dean−Stark apparatus. After refluxing for 24 h, the solvent was removed under vacuum. Distillation of the crude product under reduced pressure (bp 135−137 °C, 5 Pa) gave **1** as a yellow viscous oil (9.51 g, 62% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 11.03 (br, 1H, MeC(N*H*)CH), 7.06−7.18 (m, 3H, Ar*H*), 4.67 (s, 1H, MeC(N)C*H*), 3.14 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, ArC*H*Me$_2$), 2.97 (q, 2H, NCH_2), 2.45 (t, $^3J_{HH}$ = 6.3 Hz, 2H, NCH_2), 1.68 (s, 3H, *Me*C), 1.64 (s, 3H, *Me*C), 1.24 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.88 (s, 9H, NC*Me*$_3$), 0.45 (br, 1H, ^{t}Bu-N*H*). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 10.83 (br, 1H, MeC(N*H*)CH), 6.99−7.12 (m, 3H, Ar*H*), 4.65 (s, 1H, MeC(N)C*H*), 3.34 (br, 2H, NCH_2), 2.87 (sp, 2H, ArC*H*Me$_2$), 2.68 (br, 2H, NCH_2), 2.02 (s, 3H, *Me*C), 1.62 (s, 3H, *Me*C), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 6H,

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ArCH*Me*$_2$), 1.03 (s, 9H, C*Me*$_3$), 0.82 (br, 1H, ^{t}Bu-N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 165.8, 155.5 (imine *C*), 146.6, 137.7, 122.4, 122.3(Ar*C*), 93.1 (MeC(N)*C*H), 49.9, 44.2, 43.1(N*C*H$_2$ and N*C*Me$_3$), 28.8, 27.8, 23.6, 22.6, 21.4, 19.4 (Ar^i*Pr*, *Me*C and NC*Me*$_3$). HRMS (EI): calcd for $C_{23}H_{39}N_3$ (M^+) 357.3144; found 357.3145.

H_2L2 (2). 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one (13.01 g, 50.2 mmol), N^1-(2,6-dimethylphenyl)ethane-1,2-diamine (8.24 g, 50.2 mmol), a catalytic amount of *p*-toluenesulfonic acid (250 mg), and toluene (100 mL) were introduced into a 250 mL flask equipped with a Dean−Stark apparatus. After refluxing for 24 h, the solvent was removed under vacuum. Recrystallization of the crude product from methanol gave **2** as a pale yellow solid (13.01 g, 64% yield). Mp: 58−60 °C without decomposition. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 11.18 (br, 1H, MeC(N*H*)CH), 7.13−7.22 (m, 3H, Ar*H*), 6.87−6.96 (m, 3H, Ar*H*), 4.71 (s, 1H, MeC(NH)C*H*), 3.17 (sp, $^3J_{HH}$ = 7.2 Hz, 2H, ArC*H*Me$_2$), 3.15 (br, 1H, N*H*), 2.92 (br, 2H, NC*H*$_2$), 2.86 (br, 2H, NC*H*$_2$), 2.14 (s, 6H, Ar*Me*), 1.67 (s, 3H, *Me*C), 1.58 (s, 3H, *Me*C), 1.22 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 10.99 (br, 1H, MeC(N*H*)CH), 7.00−7.12 (m, 3H, Ar*H*), 6.97 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar*H*^{3or5}), 6.81 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*^{4}), 4.69 (s, 1H, MeC(N)C*H*), 3.37 (br, 2H, NC*H*$_2$), 3.27 (br, 1H, N*H*), 3.12 (br, 2H, NC*H*$_2$), 2.89 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.22 (s, 6H, Ar*Me*), 1.94 (s, 3H, *Me*C), 1.65 (s, 3H, *Me*C), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 166.3, 155.8 (imine *C*), 146.6, 145.2, 138.0, 129.5, 128.8, 122.7, 122.6, 121.9 (Ar*C*), 93.7 (MeC(N)*C*H), 48.6, 43.5 (N*C*H$_2$), 28.0, 23.8, 22.8, 21.7, 19.4, 18.3 (Ar*Me*, Ar^i*Pr* and *Me*C). HRMS (EI): calcd for $C_{27}H_{39}N_3$ (M^+) 405.3144; found 405.3146.

H_2L3 (3). The procedure described for **2** was followed, but with 2-((2,6-diisopropylphenyl)imido)-2-penten-4-one (6.32 g, 24.4 mmol) and N^1-(2,6-diisopropylphenyl)ethane-1,2-diamine (5.37 g, 24.4 mmol). Recrystallization of the crude product from methanol gave **3** as a pale yellow solid (7.32 g, 74% yield). Mp: 72−74 °C without decomposition. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 11.29 (br, s, 1H, MeC(N*H*)CH), 7.24−7.25 (br, m, 6H, Ar*H*), 4.80 (s, 1H, MeC(NH)C*H*), 3.36 (sp, $^3J_{HH}$ = 7.2 Hz, 2H, ArC*H*Me$_2$), 3.23 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 3.15 (br, 2H, NC*H*$_2$), 2.98 (br, 2H, NC*H*$_2$), 1.75 (s, 3H, *Me*C), 1.74 (s, 3H, *Me*C), 1.29 (d, $^3J_{HH}$ = 7.2 Hz, 12H, ArCH*Me*$_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 12H, ArCH*Me*$_2$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 10.99 (br, 1H, MeC(N*H*)CH), 7.01−7.11 (m, 6H, Ar*H*), 4.70 (s, 1H, MeC(N)C*H*), 3.46 (br, 2H, NC*H*$_2$), 3.20 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, ArC*H*Me$_2$), 3.06 (br, 1H, N*H*), 3.00 (br, 2H, NC*H*$_2$), 2.87 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, ArC*H*Me$_2$), 2.04 (s, 3H, *Me*C), 1.65 (s, 3H, *Me*C), 1.14−1.18 (m, 18H, ArCH*Me*$_2$), 1.09 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 166.2, 155.6 (imine *C*), 146.6, 142.6, 142.5, 137.9, 123.9, 123.5, 122.7, 122.6 (Ar*C*), 93.7 (MeC(N)*C*H), 52.1, 43.8 (N*C*H$_2$), 28.1, 28.0, 27.6, 24.2, 23.7, 22.8, 21.6, 19.3 (Ar^i*Pr* and *Me*C). HRMS (EI): calcd for $C_{31}H_{47}N_3$ (M^+) 461.3770; found 461.3768.

L1YCH$_2$SiMe$_3$(THF) (4). A solution of **H_2L1** (166 mg, 0.464 mmol in 5 mL of hexane) was added to Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (252 mg, 0.511 mmol) in 5 mL of hexane at −35 °C. The color of the solution turned from colorless to red immediately. After standing at −35 °C for 2 h, the reaction solution was concentrated to approximately 2.5 mL, and the residue was cooled to −35 °C to give some colorless crystals, which were surrounded by a red, viscous oil. The crystals and the oil were both readily soluble in hexane and toluene; attempts to obtain pure product from the mixture failed. Therefore, the single crystals covered by the red oil were put into grease, and the red oil was carefully wiped using grease and a needle. The single crystals with grease were sealed in thin-walled glass capillaries and monitored on a single-crystal X-ray diffractometer. The X-ray analysis showed the complex is **4**.

L2ScCH$_2$SiMe$_3$(THF) (5). **H_2L2** (260 mg, 0.641 mmol) and Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (288 mg, 0.642 mmol) were mixed in 5 mL of hexane at −35 °C. The reaction mixture was gradually warmed to room temperature and stirred for 1 h. The volatiles were removed under vacuum, and the residue was extracted by 5 mL of hexane. The extract was concentrated to approximately 2 mL, and the residue was cooled to −35 °C to afford **5** as a white solid (276 mg, 71% yield). Mp: 76−78 °C without decomposition. Anal. Calcd for $C_{35}H_{55}N_3OSiSc$: C, 69.27; H, 9.13; N, 6.92. Found: C, 69.29; H, 9.07; N, 7.05. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.12 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar*H*^{3or5}), 7.03−6.96 (m, 4H, Ar*H*), 6.85 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*^{4}), 5.05 (s, 1H, MeC(N)C*H*), 4.24 (m, 1H, THF-*H*^{α}), 4.04 (m, 1H, THF-*H*^{α}), 3.64−3.55 (m, 2H, THF-*H*^{α} and ArC*H*Me$_2$), 3.21−3.12 (m, 3H, NC*H*$_2$ and ArC*H*Me$_2$), 3.06 (m, 1H, THF-*H*^{α}), 2.72 (s, 3H, Ar*Me*), 2.58 (br, 2H, NC*H*$_2$), 2.32 (s, 3H, Ar*Me*), 1.91 (s, 3H, *Me*C), 1.63 (s, 3H, *Me*C), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.01 (d, $^3J_{HH}$ = 6.6 Hz, 3H, ArCH*Me*$_2$), 0.67 (br, 2H, THF-*H*^{β}), 0.58 (br, 2H, THF-*H*^{β}), 0.42 (s, 9H, CH$_2$Si*Me*$_3$), 0.19 (d, $^2J_{HH}$ = 11.1 Hz, 1H, C*H*$_2$SiMe$_3$), −0.42 (d, $^2J_{HH}$ = 11.1 Hz, 1H, C*H*$_2$SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 166.1, 164.8 (imine *C*), 157.9, 147.0, 145.7, 143.7, 136.0, 134.0, 126.2, 125.0, 124.2, 122.4 (Ar*C*), 99.7 (MeC(N)*C*H), 71.0 (THF-*C*^{α}), 56.9, 54.7 (N*C*H$_2$), 32.6 (*C*H$_2$SiMe$_3$), 29.3, 28.0, 25.9, 25.6, 25.3, 25.2, 25.1, 24.9, 22.6, 21.0, 20.5 (Ar*Me*, Ar^i*Pr*, THF-*C*^{β} and *Me*C), 4.7 (CH$_2$Si*Me*$_3$).

L2YCH$_2$SiMe$_3$(THF) (6). Following the procedure described for **5**, reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (277 mg, 0.562 mmol) and **H_2L2** (228 mg, 0.562 mmol) gave **6** as a white crystalline solid (275 mg, 75% yield). Mp: 118−120 °C without decomposition. Anal. Calcd for $C_{35}H_{55}N_3OSiY$: C, 64.59; H, 8.52; N, 6.46. Found: C, 64.17; H, 8.02; N, 6.22. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.08 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*^{3or5}), 6.99−6.94 (m, 3H, Ar*H*), 6.83 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ar*H*^{4}), 5.00 (s, 1H, MeC(N)C*H*), 4.24 (m, 2H, THF-*H*^{α}), 3.63−3.55 (m, 2H, THF-*H*^{α} and ArC*H*Me$_2$), 3.16−3.08 (m, 2H, THF-*H*^{α} and ArC*H*Me$_2$), 2.95 (q, 2H, NC*H*$_2$), 2.54 (br, 6H, Ar*Me*), 2.43 (q, 2H, NC*H*$_2$), 1.92 (s, 3H, *Me*C), 1.64 (s, 3H, *Me*C), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 0.73 (m, 2H, THF-*H*^{β}), 0.65 (m, 2H, THF-*H*^{β}), 0.45 (s, 9H, CH$_2$Si*Me*$_3$), −0.21 (dd, $^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.3 Hz, 1H, C*H*$_2$SiMe$_3$), −0.66 (dd, $^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.3 Hz, 1H, C*H*$_2$SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 166.3, 162.6 (imine *C*), 156.9, 145.1, 144.0, 143.8, 134.1, 125.4, 124.2, 123.9, 120.7 (Ar*C*), 98.5 (MeC(N)*C*H), 69.4 (THF-*C*^{α}), 56.7, 55.5 (N*C*H$_2$), 32.1 (d, $^1J_{YC}$ = 45.9 Hz, *C*H$_2$SiMe$_3$), 28.2, 27.8, 25.4, 25.1, 24.5, 23.9, 23.8, 22.4, 20.6 (Ar*Me*, Ar^i*Pr*, THF-*C*^{β} and *Me*C), 4.3 (CH$_2$Si*Me*$_3$).

L2LuCH$_2$SiMe$_3$(THF) (7). Following the procedure described for **5**, reaction of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (150 mg, 0.258 mmol) and **H_2L2** (104 mg, 0.258 mmol) gave **7** as a white crystalline solid (175 mg, 90% yield). Mp: 125−127 °C without decomposition. Anal. Calcd for $C_{35}H_{55}N_3OSiLu$: C, 57.05; H, 7.52; N, 5.70. Found: C, 56.58; H, 6.75; N, 5.65. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.08 (br, 2H, Ar*H*$^{3\ or\ 5}$), 6.98 (m, 3H, Ar*H*), 6.83 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar*H*^{4}), 4.98 (s, 1H, MeC(N)C*H*), 4.15 (m, 2H, THF-*H*^{α}), 3.63−3.55 (m, 2H, THF-*H*^{α} and ArC*H*Me$_2$), 3.22−3.14 (m, 2H, THF-*H*^{α} and ArC*H*Me$_2$), 3.00 (q, 2H, NC*H*$_2$), 2.57 (br, 6H, Ar*Me*), 2.45 (q, 2H, NC*H*$_2$), 1.89 (s, 3H, *Me*C), 1.63 (s, 3H, *Me*C), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, 3H, ArCH*Me*$_2$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 3H, ArCH*Me*$_2$), 0.72 (m, 2H, THF-*H*^{β}), 0.59 (m, 2H, THF-*H*^{β}), 0.46 (s, 9H, CH$_2$Si*Me*$_3$), −0.36 (d, $^2J_{HH}$ = 11.1 Hz, 1H, C*H*$_2$SiMe$_3$), −0.80 (d, $^2J_{HH}$ = 11.1 Hz, 1H, C*H*$_2$SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 166.7, 163.7 (imine *C*),

157.9, 145.0, 144.9, 143.6, 125.4, 124.2, 123.9, 120.9 (Ar*C*), 99.0 (MeC(N)*C*H), 69.8 (THF-C^{α}), 56.4, 55.0 (NCH_2), 38.0 (CH_2SiMe_3), 28.4, 27.6, 25.3, 25.0, 24.8, 24.4, 24.3, 24.1, 22.3, 20.5 (Ar*Me*, Ar^i*Pr*, THF-C^{β} and *Me*C), 4.4 (CH_2Si*Me*$_3$).

L3YCH$_2$SiMe$_3$(THF) (8). Following the procedure described for **5**, reaction of $Y(CH_2SiMe_3)_3(THF)_2$ (150 mg, 0.305 mmol) and **H$_2$L3** (142 mg, 0.306 mmol) gave **8** as a white crystalline solid (127 mg, 59% yield). Mp: 148−150 °C without decomposition. Anal. Calcd for $C_{39}H_{63}N_3OSiY$: C, 66.26; H, 8.98; N, 5.94. Found: C, 66.15; H, 9.22; N, 5.59. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.23 (t, $^3J_{HH}$ = 4.8 Hz, 1H, ArH^4), 7.06 (d, $^3J_{HH}$ = 4.5 Hz, 2H, Ar$H^{3\ or\ 5}$), 6.96 (m, 3H, Ar*H*), 5.03 (s, 1H, MeC(N)C*H*), 4.79 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, ArC*H*Me$_2$), 4.38 (m, 2H, THF-H^{α}), 3.67−2.57 (m, 3H, THF-H^{α} and ArC*H*Me$_2$), 3.12−2.99 (m, 4H, THF-H^{α}, ArC*H*Me$_2$ and N-CH_2), 2.40 (q, 2H, N-CH_2), 1.94 (s, 3H, *Me*C), 1.61 (s, 3H, *Me*C), 1.55 (d, $^3J_{HH}$ = 7.2 Hz, 3H, ArCHMe_2), 1.40 (d, $^3J_{HH}$ = 6.6 Hz, 3H, ArCHMe_2), 1.39 (d, $^3J_{HH}$ = 6.6 Hz, 3H, ArCHMe_2), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCHMe_2), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCHMe_2), 1.16 (d, $^3J_{HH}$ = 6.6 Hz, 3H, ArCHMe_2), 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCHMe_2), 1.04 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCHMe_2), 0.77 (m, 2H, THF- H^{β}), 0.64 (m, 2H, THF- H^{β}), 0.46 (s, 9H, CH_2Si*Me*$_3$), −0.13 (dd, $^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.3 Hz, 1H, CH_2SiMe$_3$), −0.68 (dd, $^2J_{HH}$ = 10.8 Hz, $^2J_{YH}$ = 3.3 Hz, 1H, CH_2SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 167.1, 163.3 (imine *C*), 155.8, 146.7, 145.9, 145.8, 144.6, 144.5, 126.2, 124.9, 124.6, 124.1, 123.7, 122.9 (Ar*C*), 99.3 (MeC(N)*C*H), 70.2 (THF-C^{α}), 61.0, 56.4 (NCH_2), 32.5 (d, $^1J_{YC}$ = 47.4 Hz, CH_2SiMe_3), 28.9, 28.6, 28.5, 28.4, 28.0, 26.2, 25.9, 25.8, 25.3, 24.7, 24.4, 24.1, 23.5, 23.2 (Ar^i*Pr*, THF-C^{β} and *Me*C), 4.8 (CH_2Si*Me*$_3$).

L3DyCH$_2$SiMe$_3$(THF) (9). $DyCl_3$ (225 mg, 0.837 mmol) was suspended in 10 mL of THF and stirred overnight. The THF solvent was removed under vacuum, and 5 mL of hexane was added. To the above suspension was added a solution of $LiCH_2SiMe_3$ (232 mg, 2.47 mmol in 5 mL of hexane) at room temperature and stirred for 1 h. The precipitate was separated by centrifugation, and the clear solution was added to a solution of **H$_2$L3** (318 mg, 0.689 mmol in 10 mL of hexane) at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was gradually warmed to room temperature. The precipitate was removed by centrifugation, and the clear solution was concentrated to approximately 5 mL and cooled to −35 °C to afford **9** as a pale yellow crystalline solid (485 mg, 90% yield). Mp: 149−151 °C without decomposition. Anal. Calcd for $C_{39}H_{63}N_3OSiDy$: C, 60.01; H, 8.14; N, 5.38. Found: C, 60.20; H, 8.07; N, 5.21. **9** is paramagnetic.

L3GdCH$_2$SiMe$_3$(THF) (10). Following the procedure described for **9**, reaction of $GdCl_3$ (187 mg, 0.709 mmol), $LiCH_2SiMe_3$ (197 mg, 2.09 mmol), and **H$_2$L3** (278 mg, 0.602 mmol) afforded **10** as a white crystalline solid (251 mg, 54% yield). Mp: 131−133 °C without decomposition. Anal. Calcd for $C_{39}H_{63}N_3OSiGd$: C, 60.42; H, 8.19; N, 5.42. Found: C, 61.48; H, 8.72; N, 5.18. **10** is paramagnetic.

L3NdCH$_2$SiMe$_3$(THF) (11). $NdCl_3$ (230 mg, 0.918 mmol) was suspended in 10 mL of THF and stirred overnight. To the above suspension was added a solution of $LiCH_2SiMe_3$ (255 mg, 2.708 mmol in 10 mL of THF) at room temperature and stirred for 2 h. The reaction mixture was cooled to 0 °C, and **H$_2$L3** (305 mg, 0.661 mmol) in 5 mL of THF was added. After stirring at 0 °C for 2 h, the volatiles were removed under vacuum. The residue was extracted by 20 mL of hexane. The extract was concentrated to approximately 5 mL and cooled to −35 °C to afford **11** as a green crystalline solid (393 mg, 78% yield). Mp: 137−139 °C without decomposition. Anal. Calcd for $C_{39}H_{63}N_3OSiNd$: C, 61.45; H, 8.33; N, 5.51. Found: C, 61.30; H, 8.88; N, 5.22. **11** is paramagnetic.

General Procedure for Intramolecular Hydroamination. The lanthanide complex, 2,2-dimethyl-1-aminopent-4-ene, and the standard *p*-xylene 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.

Kinetic Studies of Intramolecular Hydroamination. The Y complex **8**, 2,2-dimethyl-1-aminopent-4-ene, the standard ferrocene, and C_6D_6 were loaded into a NMR tube. The tube was immediately inserted into the probe of the Varian 400 MHz spectrometer, which had been previously set to 25 ± 0.2 °C. Data were corrected using four scans per time interval with a 10 s delay to ensure accurate integration. The substrate concentration was measured from the olefin peak area standardized to the area of Cp_2Fe (4.00 ppm in C_6D_6).

X-ray Crystallography. Single crystals of **4**, **6**, and **11** 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 SADABS. 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 ref 24. Crystallographic data and refinement for **4**, **6**, and **11** are listed in Table S-1 (Supporting Information).

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Supporting Information Available: Crystallographic data and refinement for **4**, **6**, and **11**, and CIF files giving X-ray crystallographic data for **4**, **6**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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