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ARTICLE TYPE

Reactivity of functionalized indoles with rare-earth metal amides. Synthesis, characterization and catalytic activity of rare-earth metal complexes incorporating indolyl ligands

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The reactivity of several functionalized indoles 2-(RNHCH₂)C₈H₅NH (R = C₆H₅ (**1**), ^tBu (**2**), 2,6-ⁱPr₂C₆H₃ (**3**)) with rare-earth metal amides is described. Reactions of **1** or **2** with [(Me₃Si)₂N]₃RE(μ-Cl)Li(THF)₃ (RE = Eu, Yb) respectively produced the europium
10 complexes [2-(C₆H₅N=CH)C₈H₅N]₂Eu[N(SiMe₃)₂] (**4**), [2-(^tBuN=CH)C₈H₅N]Eu[N(SiMe₃)₂] (**5**), and the ytterbium complex [2-(^tBuN=CH)C₈H₅N]₂Yb[N(SiMe₃)₂] (**6**), containing bidentate anionic indolyl ligands via dehydrogenation of the amine to imine. In contrast, reactions of the more sterically bulky indole **3** with [(Me₃Si)₂N]₃RE(μ-Cl)Li(THF)₃ afforded complexes [2-(2,6-ⁱPr₂C₆H₃NCH₂)C₈H₅N]RE[N(SiMe₃)₂](THF)₂ (RE = Yb (**7**), Y (**8**), Er (**9**), Dy (**10**)) with the deprotonated indolyl ligand. While reactions of **3** with yttrium and ytterbium amides in refluxing toluene respectively gave the complexes [2-(2,6-ⁱPr₂C₆H₃N=CH)C₈H₅N]₃Y (**11**) and
15 [2-(2,6-ⁱPr₂C₆H₃N=CH)C₈H₅N]₂Yb^{II}(THF)₂ (**12**), along with transformation of the amino group to the imino group, and also with a reduction of Yb³⁺ to Yb²⁺ under the formation of **12**. Reactions of **3** with samarium and neodymium amides provided the novel dinuclear complexes {[μ-η⁵:η¹:η¹-2-(2,6-ⁱPr₂C₆H₃NCH₂)C₈H₅N]RE[N(SiMe₃)₂]}₂ (RE = Sm (**13**), Nd (**14**)) having indolyl ligands in μ-η⁵:η¹:η¹ hapticities. The pathway for the transformation of the amino group to the imino group is proposed on the basis of experimental results. The new complexes displayed excellent activity in the intramolecular hydroamination of aminoalkenes.

Introduction

The development of the noncyclopentadienyl ancillary ligands has occupied an important place in the rare-earth metal chemistry.¹ Among them, the nitrogen-containing
25 cyclopentadienyl-like ring systems, due to their easily adjustable steric and electronic properties, are one of the widely investigated ligand families. Given the effects of steric and electronic features of the ligands on reactivity of metal complexes, various modified ring systems such as pyrrolyl,² carbazolyl,³ pyrazolyl⁴ have been
30 developed as ligands.

Similarly, due to their rich and diverse binding abilities through the nitrogen and carbon atoms, electron-rich indole and its derivatives have currently attracted a considerable attention in transition metal chemistry.⁵ However, the rare-earth metal
35 chemistry with indolyl ligands is relatively less developed. After the Yb(II) complexes having the 2-phenylindolide ligand in η¹ and μ-η¹:η¹ bonding modes were respectively reported by Deacon^{3a} and Abrahams *et al.*,^{5c} Evans described the coordination chemistry of yttrium and samarium complexes with 2,3-
40 dimethylindolide ligand^{5d} which is sterically similar to carbazole. In addition, Müller-Buschbaum found that reaction of europium metal with indole produced a bridged indolyl dinuclear

europium(II) complex under harsh conditions,^{5e} in which the indolyl anions are bonded with the europium ions in η¹ and μ-
45 η¹:η⁵ modes. Cui's group prepared the rare-earth metal alkyl complexes incorporating 7-imino-functionalized indolyl ligand, which in combination with appropriate activator could generate efficient homogeneous catalysts for the polymerization of isoprene.^{5f} Our group has recently introduced the amino- or
50 imino-functionalized group at 3-position of indolyl ring, a series of rare-earth metal complexes^{5g,5h} including a unique indolyl-1,2-dianion in η¹:(μ₂-η¹:η¹) bonding modes through C–H activation were isolated. Whilst, reactions of 3-imino-functionalized indole with [RE(CH₂SiMe₃)₃(thf)₂] gave a series of new dinuclear alkyl
55 rare-earth metal complexes in novel μ-η²:η¹:η¹ hapticities with the transformation of the imino to amino group by alkyl CH₂SiMe₃ insertion, and the complexes displayed high catalytic activities and high regio- and stereoselectivities for isoprene *cis*-1,4-polymerization.^{5k} Very recently, we found that reactions of 1-*N*-
60 protected-3-imino-functionalized indoles with [RE(CH₂SiMe₃)₃(thf)₂] produced the carbon σ-bonded indolyl supported rare-earth metal alkyls, which incorporation with Al^{*i*}Bu₃ and borate, displayed high catalytic activities towards isoprene *cis*-1,4-polymerization.^{5l} These results encouraged us to
65 probe the reactivity behavior of the rare-earth metal amides with different 2-amino-functionalized indoles. Fortunately, we

recently found that reaction of 2-(2,6-diisopropylphenylamino)methylene)indole with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ afforded the novel europium(II) complexes possessing indolyl ligands in novel $\mu\text{-}\eta^6\text{:}\eta^1\text{:}\eta^1$, $\mu\text{-}\eta^3\text{:}\eta^1\text{:}\eta^1$, and $\mu\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$ bonding modes with the oxidation of the amino to the imino group.⁵¹ Further investigation of reactivities and coordination chemistry of 2-amino-functionalized indoles with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ needs to be developed. On the other hand, in our previous work, we reported oxidative dehydrogenation of pyrrolyl-functionalized secondary amine to imine, and proposed that the reaction involved the process of the $\beta\text{-H}$ elimination of the corresponding amido complexes.^{2d,2f} On this basis, a better understanding the proposed pathway for the aforementioned transformation of the amino group to the imino group⁵¹ in rare-earth metal chemistry needs to be described.

The intramolecular hydroamination of aminoalkenes is a highly atom-economical synthetic route to the nitrogen containing heterocycles.⁶ Pioneering works using effective rare-earth metal complexes catalysts for hydroamination was accomplished by Marks *et al.*⁷ To date, different kinds of metal-based catalysts, including those of early transition metals,^{6a,6b,8} late transition metals,⁹ alkali earth metals,¹⁰ and group 13 metals,¹¹ have been reported. Despite these advances, catalytic systems affording the desirable reactivity and selectivity for this transformation of unactivated alkenes are still to be developed. Further, the catalytic activity of organo rare-earth metal complexes with electron-rich indolyl ligands for the hydroamination of alkenes has not been reported.⁵

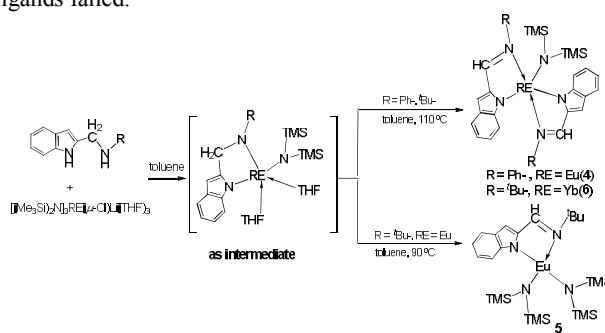
Herein, we wish to report the reactivity of several functionalized indoles 2-(RNHCH_2) $\text{C}_6\text{H}_5\text{NH}$ ($\text{R} = \text{C}_6\text{H}_5$ (**1**), $t\text{Bu}$ (**2**), 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (**3**)) with rare-earth metal amides affording different rare-earth metal complexes containing 2-imino-, and 2-amino-functionalized indolyl ligands, and high catalytic activity of the new complexes in the intramolecular hydroamination of aminoalkenes.

Results and discussion

Reactivities of 2-amino-functionalized indoles with rare-earth metal amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$.

In our previous work,⁵¹ we reported the redox chemistry between $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ and the secondary amine functionalized indole 2-(2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{NHCH}_2$) $\text{C}_6\text{H}_5\text{NH}$ (**3**) giving rise to oxidative dehydrogenation of secondary amine to imine with a reduction of europium(III) to europium(II). On the basis of the result of reaction between the corresponding indole **3** and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Yb}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ which generated the complex $[2\text{-(2,6-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCH}_2\text{)}\text{C}_6\text{H}_5\text{N}]\text{Yb}^{\text{III}}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ (**7**) having deprotonated indolyl ligand, this transformation was proposed through europium(III) amide having imino-functionalized indolyl ligand as intermediate followed by homolysis of the Eu–N bond.⁵¹ However, the corresponding europium(III) amide or ytterbium(III) amide having imino-functionalized indolyl ligand has not been isolated.⁵¹ For better understanding this transformation, we designed new secondary amine-functionalized indolyl compounds 2-($\text{C}_6\text{H}_5\text{NHCH}_2$) $\text{C}_6\text{H}_5\text{NH}$ (**1**) and 2-($t\text{BuNHCH}_2$) $\text{C}_6\text{H}_5\text{NH}$ (**2**), which have different substituents on the nitrogen atoms, and tried to illustrate the aforementioned reaction pathways.

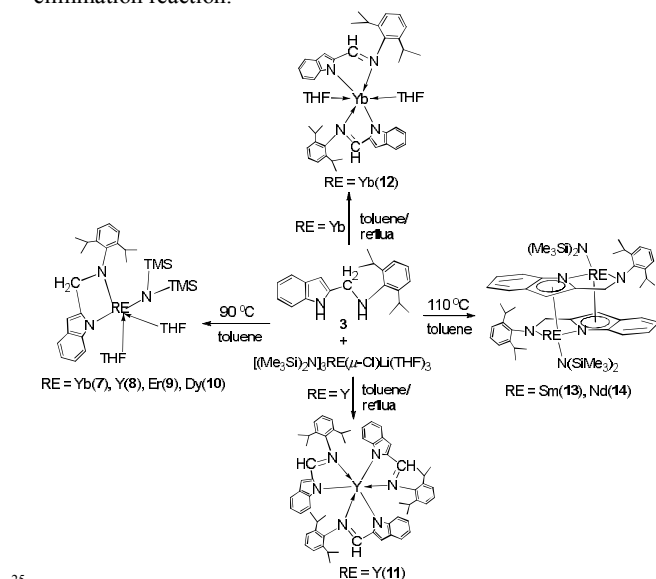
Compounds 2-(RNHCH_2) $\text{C}_6\text{H}_5\text{NH}$ ($\text{R} = \text{C}_6\text{H}_5$ (**1**), $t\text{Bu}$ (**2**)) were prepared according to the similar synthetic procedures as for 2-(2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{NHCH}_2$) $\text{C}_6\text{H}_5\text{NH}$ (**3**).⁵¹ Reaction of 2 equiv. of **1** with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ in toluene at 110 °C afforded the complex $[2\text{-(C}_6\text{H}_5\text{N=CH)}\text{C}_6\text{H}_5\text{N}]\text{Eu}[\text{N}(\text{SiMe}_3)_2]$ (**4**) (Scheme 1), having two indolyl ligands in $\eta^1\text{:}\eta^1$ modes with transformation of the amino group to imino group. The reduction of europium(III) to europium(II) was not observed in this reaction, which is different from our previous findings of the redox chemistry between secondary amine **3** and europium(III) amide.⁵¹ When 2-($t\text{BuNHCH}_2$) $\text{C}_6\text{H}_5\text{NH}$ (**2**) was treated with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{RE} = \text{Eu}$ (1 equiv.), Yb (0.5 equiv.)) in toluene at 90 °C and 110 °C respectively, the corresponding complexes $[2\text{-(}t\text{BuN=CH)}\text{C}_6\text{H}_5\text{N}]\text{Eu}[\text{N}(\text{SiMe}_3)_2]$ (**5**) and $[2\text{-(}t\text{BuN=CH)}\text{C}_6\text{H}_5\text{N}]\text{Yb}[\text{N}(\text{SiMe}_3)_2]$ (**6**) with imino-functionalized indolyl ligands were isolated in good yields (Scheme 1). In the process, the amino groups were transferred into the imino groups, which is similar to the result of reaction of **1** with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$. Again, the reduction process for either europium(III) to europium(II) or ytterbium(III) to ytterbium(II) has not been observed. The results suggested the steric and electronic effects of the ligands on the reactivities of the rare-earth metal amides with secondary amine-functionalized indoles. The formation of complexes **4–6** was proposed to go through the rare-earth metal amido complex containing $[2\text{-(RNCH}_2\text{)}\text{C}_6\text{H}_5\text{N}]^{2-}$ ($\text{R} = \text{C}_6\text{H}_5$ and $t\text{Bu}$) ligand as intermediate through the silylamine elimination reaction, which then undergo the $\beta\text{-H}$ elimination to give the imino-functionalized indolyl rare-earth metal complexes (Scheme 1). The isolation of complexes **4–6** proved our previous proposed intermediate of imino-functionalized indolyl ligand supporting europium(III) amide in the reaction of **3** with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$.⁵¹ However, attempts to isolate the corresponding amido complexes with these ligands failed.



Scheme 1 Reactions of **1** and **2** with europium(III) and ytterbium(III) amides.

To further prove the above proposal of the formation pathway of complexes **4–6**, and to better understand the mechanism of reactions of secondary amine-functionalized indoles **1**, and **2** with rare-earth metal amides, we turned to the reactions of more sterically bulky 2-(2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{NHCH}_2$) $\text{C}_6\text{H}_5\text{NH}$ (**3**) with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$. The complexes $[2\text{-(2,6-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCH}_2\text{)}\text{C}_6\text{H}_5\text{N}]\text{RE}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ ($\text{RE} = \text{Y}$ (**8**), Er (**9**), Dy (**10**)) *via* deprotonation process were isolated in good yields by treatment of 1 equiv. of **3** with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Scheme 2). To prove the amino-functionalized indolyl complexes could undergo $\beta\text{-H}$ elimination reaction to

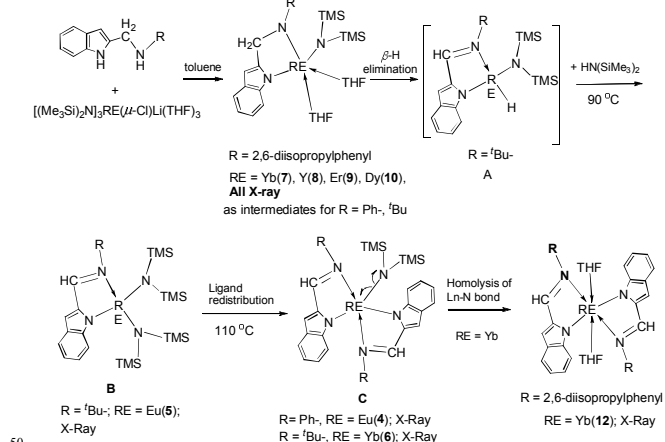
produce the imino-functionalized indolyl complexes, reactions of compound **3** with yttrium and ytterbium amides were further carried out in refluxing toluene for 24 h. It is interesting to find that the corresponding reactions produced the complexes $[2-(2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_8\text{H}_5\text{N}]_3\text{Y}$ (**11**) and $[2-(2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_8\text{H}_5\text{N}]_2\text{Yb}^{\text{II}}(\text{THF})_2$ (**12**) with imino-functionalized indolyl ligands, respectively, and a reduction of ytterbium(III) to ytterbium(II) with formation of **12** was observed (Scheme 2). The formation of complex **11** or **12** is believed *via* β -H elimination of **7** or **8**, which proved our aforementioned proposed pathway for the formation of complexes **4–6**. When the lanthanide having larger ionic radii (Sm^{3+} , Nd^{3+}) was used, reactions of **3** with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{RE} = \text{Sm}$, Nd) afforded the novel dinuclear complexes $\{[\mu\text{-}\eta^5\text{:}\eta^1\text{:}\eta^1\text{-}2-(2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NCH}_2)\text{C}_8\text{H}_5\text{N}]_2\text{RE}[\text{N}(\text{SiMe}_3)_2]\}_2$ ($\text{RE} = \text{Sm}$ (**13**), Nd (**14**)) incorporating amido-appended indolyl ligands in $\mu\text{-}\eta^5\text{:}\eta^1\text{:}\eta^1$ bonding modes different from that in complexes **7–10** (Scheme 2). Obviously, the different bonding modes shown in the above results can be attributed to the effect of metal ionic size. Furthermore, the transformation of the amino group to the imino group has not been observed by running the reactions of **3** with samarium and neodymium amides in refluxing toluene, indicating the effects of the coordination modes or ionic sizes on the β -H elimination reaction.



Scheme 2 Preparation and reactivity of rare-earth metal amido complexes with amido-functionalized indolyl ligands.

The above experimental results gave a clear pathway for the formation of imino-functionalized indolyl complexes (Scheme 3). The silylamine elimination reactions between rare-earth metal amides and secondary amine-functionalized indoles produced the amido-appended indolyl complexes **7–10** which underwent the β -H elimination^{2d,2f} to give the intermediate **A** having the imino-functionalized indolyl ligand. **A** underwent a fast acid-base exchange with $\text{HN}(\text{SiMe}_3)_2$ to afford the intermediate **B** (in this case, complex **5** was isolated when the R group is tertiary butyl). **B** then underwent ligand redistribution to produce the intermediate **C** at elevated temperature (complexes **4**, **6** were respectively isolated in the case of the R groups being phenyl or tertiary butyl). Homolysis of the Yb–N bond¹² of the intermediate

C afforded the ytterbium(II) complex **12** as the final product when the R is the sterically bulky 2,6-diisopropylphenyl group at the elevated temperature. The ytterbium chemistry is similar to our previous report, but in europium case, the $\{[\mu\text{-}\eta^6\text{:}\eta^1\text{:}\eta^1\text{-}2-(2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_8\text{H}_5\text{N}]_2\text{Eu}^{\text{II}}[2-(2,6-{}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{C}_8\text{H}_5\text{N}]\}_2$ with imino-functionalized indolyl ligands in $\mu\text{-}\eta^6\text{:}\eta^1\text{:}\eta^1$ hapticities was isolated due to the coordinated THF and larger ionic radius of europium(II).⁵ⁱ



Scheme 3 Formation pathway for the imino-functionalized indolyl rare-earth metal complexes.

Molecular structures of imino- and amino-functionalized indolyl complexes.

All complexes were characterized by spectroscopic methods and elemental analyses, and their structures were all elucidated by X-ray crystallography.

Complexes **4** (Figure 1) and **6** (Figure 3) adopted a distorted trigonal bipyramid configuration. Differently, **5** adopts a tetrahedral arrangement (Figure 2). The RE–N2 bond lengths of the appendant arm in complexes **4–6** indicate coordination nature of the N2 atom in these complexes (Table 1). The bond lengths of N2–C9 and N4–C24 in **4–6** range from 1.279(3)–1.292(5) Å, in agreement with the corresponding range 1.282(6)–1.296(6) Å observed for C=N double bond in the imino-functionalized pyrrolyl complexes,^{2f} which shows the characteristic of C=N double bond for N2–C9 and N4–C24. The bond angles of N2–C9–C1 and N4–C24–C16 in complexes **4–6** range from 121.5(3)–123.3(3)°, close to the corresponding bond angle of 120° for normal sp^2 carbon. These results have also proved the dehydrogenation of the secondary amine to the imine in the reactions.

Complexes **8–10** are a series of five-coordinate mononuclear complexes and the central metal takes a distorted trigonal bipyramide arrangement (Figure 4 for complex **8**, the molecular structures of complexes **9**, **10** are provided in ESI). These structures are in accordance with that of our previously reported complex **7**.⁵ⁱ The bond lengths of the RE–N bonds (indolyl ligand) (Table 2), varying from 2.159(11) to 2.316(4) Å, are comparable to the range 2.145(4)–2.424(6) Å observed in the indolyl complexes^{5h–j} if the ionic radii difference was taken into account. Furthermore, the N2–C9 bond lengths of 1.474(4), 1.458(16) and 1.467(5) Å in **8–10** are within the range of normal C–N single bond length. So, only the deprotonation of the appended amine

with the formation of the bidentate amido-appended indolyl ligand was observed in the reactions of rare-earth metal amides with 2-(2,6- i Pr₂C₆H₃-NHCH₂)C₈H₅NH (**3**). The results were also supported by the NMR study of the diamagnetic complex **8** in C₆D₆ at 25 °C showing the methylene protons resonances at 4.96 ppm in ¹H NMR spectra, and the methylene carbon resonance at 57.1 ppm in ¹³C NMR spectra. These results are similar to those found in 2-(2,6- i Pr₂C₆H₃NHCH₂)C₈H₅NH (**3**) in CDCl₃,⁵ⁱ where the protons and carbon resonances of the methylene group were observed at 4.22 ppm and 49.3 ppm in ¹H NMR and ¹³C NMR spectra, respectively.

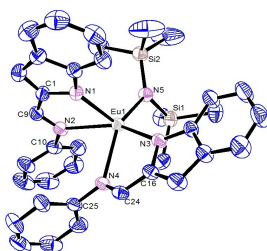


Fig. 1 ORTEP diagram of the molecular structure of complex **4** (ellipsoids at 30% probability level). All hydrogen atoms are omitted for clarity.

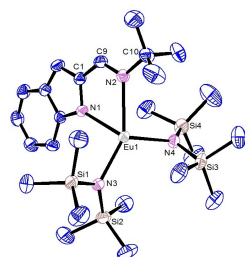


Fig. 2 ORTEP diagram of the molecular structure of complex **5** (ellipsoids at 30% probability level). All hydrogen atoms are omitted for clarity.

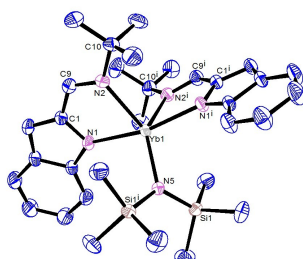


Fig. 3 ORTEP diagram of the molecular structure of complex **6** (ellipsoids at 30% probability level). All hydrogen atoms are omitted for clarity.

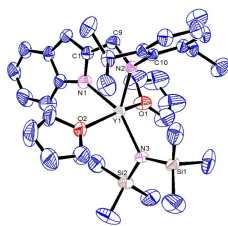


Fig. 4 ORTEP diagram of the molecular structure of complex **8** (ellipsoid at 30% probability level). All hydrogen atoms are omitted for clarity.

An X-ray diffraction revealed that complexes **11** and **12** are six-coordinate imino-functionalized indolyl rare-earth metal complexes (Figures 5 and 6). The bond lengths of N2–C9 of 1.363(3) Å in **11** and 1.381(10) Å in **12** (Table 2) are in the range of a normal C=N double bond length, indicating the formation of imino groups which was proved by the NMR results. The resonance of the proton of the imino group (N=CH) in complex **11** is observed at 7.97 ppm in ¹H NMR spectra, and the resonance of the carbon of imino group (N=CH) is found at 168.7 ppm in ¹³C NMR spectra. Furthermore, the resonances at 4.96 ppm and 57.1 ppm assigned to the methylene protons and carbon of complex **8** in the corresponding ¹H NMR and ¹³C NMR spectra are not observed in corresponding NMR spectra of **11**. These results clearly showed the transformation of the amino group to the imino group in the reaction.

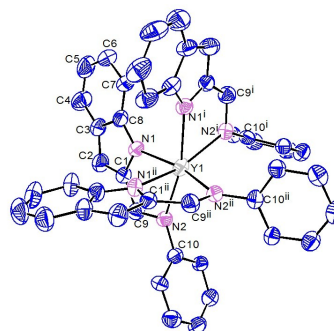


Fig. 5 ORTEP diagram of the molecular structure of complex **11** (ellipsoids at 30% probability level). All hydrogen atoms and the 2,6-diisopropyl groups are omitted for clarity.

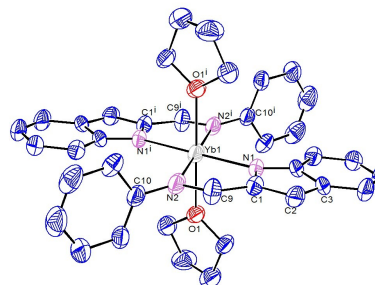


Fig. 6 ORTEP diagram of the molecular structure of complex **12** (ellipsoids at 30% probability level). All hydrogen atoms and the 2,6-diisopropyl groups are omitted for clarity.

X-ray diffraction showed that **13** and **14** are dinuclear complexes, with the amido-appended indolyl dianionic [2-(2,6- i Pr₂C₆H₃NCH₂)C₈H₅N]²⁻ bridging two central metal ions through the two nitrogen atoms of the ligand bonded to one metal and the five-membered ring of the indolyl system bonded to another metal (Figure 7 showed ORTEP diagram of complex **13**. ORTEP diagram of complex **14** is provided in ESI). The bond lengths (Table 3) between the central metal ion and the five-membered ring of indolyl ligand range from 2.780(10) to 2.957(10) Å, 2.772(10) to 2.980(10) Å (with an average of Sm1–Ind of 2.874(10) Å, Sm2–Ind of 2.876(10) Å) (Ind = indolyl) in complex **13**, and from 2.802(2) to 2.965(3) Å (with an average of Nd–Ind of 2.882(3) Å) in complex **14**, respectively. So, the bonding modes of the amido-appended indolyl ligands with the metals in **13**, **14** are best described as the μ - η^5 : η^1 : η^1 fashions.

Complex **14** is a central symmetric structure, while complex **13** is asymmetric due to ionic radii difference on the basis of these structural parameters. The average RE-Ind length in **13** or **14** is comparable to the corresponding value in the dinuclear indolyl complex of $[\text{Eu}_2(\text{Ind})_4(\text{NH}_3)_6]$.^{5e} The coordination geometry of central rare-earth metals in complexes **13** and **14** is similar to the amino-functionalized pyrrolyl complex $\{[(\mu\text{-}\eta^5\text{-}\eta^1)\text{-}\eta^1\text{-}2\text{-}[(2,6\text{-}\textit{i}\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2]\text{C}_4\text{H}_3\text{N}]\text{YbN}(\text{SiMe}_3)_2\}_2$.^{2d} Similarly, the N2–C9 bond length of 1.487(14) Å and the N4–C30 bond length of 1.464(13) Å in **13**, and the N2–C9^{#1} bond length of 1.463(4) Å in **14** show the C–N single bond character, indicating that only deprotonation processes occurred during the reactions, which were also identified by NMR spectroscopic studies. The ¹H NMR resonances of the methylene groups of the side chains at indolyl rings in paramagnetic complexes **13** and **14** were found quite different from those of complex **8** in C₆D₆.

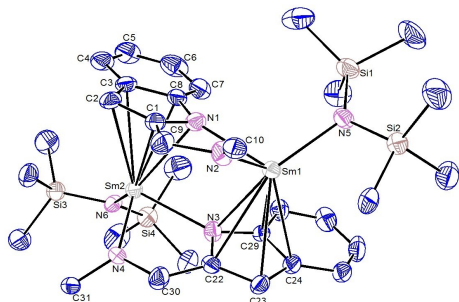


Fig. 7 ORTEP diagram of the molecular structure of complex **13** (ellipsoids at 30% probability level). All hydrogen atoms and the 2,6-diisopropylphenyl groups are omitted for clarity.

Table 1 Selected Bond Lengths (Å) and Bond Angles (°) of Complexes **4–6**.

	4	5	6
RE(1)–N(1)	2.341(3)	2.351(2)	2.2740(16)
RE(1)–N(2)	2.525(3)	2.565(2)	2.4458(16)
RE(1)–N(3)	2.363(3)	2.251(2)	
RE(1)–N(4)	2.517(3)	2.254(2)	
RE(1)–N(5)	2.236(3)		2.165(2)
N(4)–C(24)	1.292(5)		
N(2)–C(9)	1.288(5)	1.279(3)	1.288(3)
N(2)–C(9)–C(1)	121.5(4)	123.3(3)	122.08(18)
N(1)–RE(1)–N(2)	69.35(11)	70.45(7)	72.94(6)
N(2)–RE(1)–N(4)	83.08(10)	100.93(8)	
N(1)–RE(1)–N(5)	113.03(11)		96.53(4)
N(4)–C(24)–C(16)	121.5(3)		

The above results indicated that: (1) the steric effect of substituents at the amino group has a significant influence on the reactivity patterns of rare-earth metal amides with amino-functionalized indoles. Reactions of indole compounds containing less sterically bulky substituents, such as C₆H₅– and ^tBu–, at nitrogen atom with rare-earth metal amides produced the imino-functionalized indolyl complexes **4–6**. Reactions of indole compound having sterically bulky group such as 2,6-diisopropylphenyl with rare-earth metal amides afforded the amido-functionalized indolyl complexes such as **7–10** at given temperature, and the imino-functionalized indolyl ligated complexes could be isolated in refluxing toluene. (2) the sizes of central metal ions have influences on the bonding modes of indolyl ligands with the metal centers.

Table 2 Selected Bond Lengths (Å) and Bond Angles (°) of Complexes **8–12**.

	8	9	10	11	12
RE(1)–N(1)	2.294(3)	2.296(11)	2.316(4)	2.356(2)	2.271(5)
RE(1)–N(2)	2.182(2)	2.159(11)	2.190(3)	2.496(2)	2.420(7)
RE(1)–N(3)	2.275(2)	2.253(11)	2.300(4)		
N(2)–C(9)	1.474(4)	1.458(16)	1.467(5)	1.363(3)	1.381(10)
RE(1)–O(1)	2.361(2)	2.347(11)	2.378(4)		2.297(5)
RE(1)–O(2)	2.357(2)	2.337(11)	2.387(4)		
O(1)–RE(1)–O(2)	155.64(10)	155.7(5)	154.74(16)		
N(2)–C(9)–C(1)	115.2(3)	112.3(13)	113.9(4)	119.0(2)	118.7(7)
O(1)–RE(1)–N(1)	83.49(11)	84.5(5)	83.10(18)		89.99(18)
N(1) ^{#2} –RE(1)–N(2)				163.42(7)	
N(1)–RE(1)–N(1) ^{#1}				92.24(7)	180.0
C(9)–N(2)–C(10)				112.1(2)	111.6(6)
O(1)–RE(1)–O(1) ^{#1}					179.998(1)

Table 3 Selected Bond Lengths (Å) and Bond Angles (°) of Complexes **13** and **14**.

	13	13	14
Sm(1)–N(1)	2.444(8)	Sm(2)–N(3)	2.447(8)
Sm(1)–N(2)	2.238(9)	Sm(2)–N(4)	2.216(8)
		Nd(1)–N(1) ^{#1}	2.519(2)
		Nd(1)–N(2)	2.263(2)

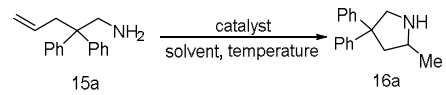
Sm(1)–N(5)	2.276(8)	Sm(2)–N(6)	2.266(8)	Nd(1)–N(3)	2.292(2)
Sm(1)–N(3)	2.813(9)	Sm(2)–N(1)	2.804(9)	Nd(1)–N(1)	2.802(2)
Sm(1)–C(22)	2.949(10)	Sm(2)–C(1)	2.933(11)	Nd(1)–C(1)	2.855(3)
Sm(1)–C(23)	2.957(10)	Sm(2)–C(2)	2.980(10)	Nd(1)–C(2)	2.924(3)
Sm(1)–C(24)	2.873(10)	Sm(2)–C(3)	2.889(10)	Nd(1)–C(3)	2.963(3)
Sm(1)–C(29)	2.780(10)	Sm(2)–C(8)	2.772(10)	Nd(1)–C(4)	2.867(3)
N(4)–C(30)	1.464(13)	N(2)–C(9)	1.487(14)	N(2)–C(9) ^{#1}	1.463(4)
N(1)–Sm(1)–N(5)	109.4(3)	N(3)–Sm(2)–N(6)	110.9(3)	N(2)–Nd(1)–N(3)	112.13(9)
N(4)–C(30)–C(22)	112.1(9)	C(10)–N(2)–C(9)	111.9(9)	C(10)–N(2)–C(9) ^{#1}	114.5(2)
C(31)–N(4)–C(30)	114.4(8)	N(2)–C(9)–C(1)	113.7(9)	N(2) ^{#1} –C(9)–C(1)	111.5(2)

Catalytic activity for the intramolecular hydroamination of aminoalkenes.

The intramolecular hydroamination is one of the most important methods to construct nitrogen containing heterocycles. The catalytic activities of the rare-earth metal complexes **4–10**, **13**, **14** and [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃ for the intramolecular hydroamination have been firstly examined by using 2,2-diphenylpent-4-ene-1-amine (**15a**) as a substrate (Table 4). The reaction process was monitored by the ¹H NMR spectroscopy. The ¹H NMR spectra showed a rapid protonolysis of the rare-earth metal amide by the amine with a release of HN[Si(CH₃)₃]₂.

The conversion of substrate is observed with disappearance of the characteristic alkene protons resonances at 5.03 and 5.40 ppm, and appearance of diagnostic doublet (proton of –CH₂CH(CH₃)NH– signals) at 1.09 ppm. The formation of 2-methyl-4,4-diphenylpyrrolidine, the Markovnikov-selective product, was observed in several minutes, and other heterocyclic regioisomers were not detected through the reaction process in all cases. After full conversion (99%), NMR yields were obtained by comparing the integration of ferrocene standard proton signals (δ_H 4.1 ppm) with the diagnostic proton signals at 3.21 (–CH₂CH(CH₃)NH–) for compound **16a** in the ¹H NMR spectra.

Table 4 Hydroamination of 2,2-Diphenylpent-4-ene-1-amine (**15a**) Catalyzed by Complexes **4–10**, **13**, **14** and [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃.^a

						
Entry	Catalyst	[cat.]/[sub.] (%)	Solvent	Temperature (°C)	Time (h)	Conversion (%) ^b
1	4 (Eu)	2	C ₆ D ₆	50	24	20
2	5 (Eu)	2	C ₆ D ₆	25	5	>97
3	6 (Yb)	3	C ₆ D ₆	50	50	10
4	7 (Yb)	2	C ₆ D ₆	25	12	99
5	8 (Y)	2	C ₆ D ₆	25	0.5	99
6	8 (Y)	1	C ₆ D ₆	25	40	98
7	8 (Y)	1	C ₆ D ₆	50	36	98
8	9 (Er)	2	C ₆ D ₆	25	0.7	99
9	10 (Dy)	2	C ₆ D ₆	25	1	99
10	13 (Sm)	2	Tol- <i>d</i> ₈	25	0.15	99
11	14 (Nd)	2	Tol- <i>d</i> ₈	25	0.15	99
12	[(Me ₃ Si) ₂ N] ₃ Y(μ-Cl)Li(THF) ₃	2	C ₆ D ₆	25	0.65	97

^a Unless otherwise noted, the reactions conducted with 0.32 mmol aminoalkene in 0.6 mL of C₆D₆ at room temperature. ^b Based on ¹H NMR integration relative to ferrocene as the internal standard.

These complexes showed the different catalytic activities for the intramolecular hydroamination of 2,2-diphenylpent-4-ene-1-amine (**15a**). As shown in Table 4, the complexes incorporating bisimino-functionalized indolyl ligands such as **4** and **6** exhibited very poor catalytic activities toward the intramolecular hydroamination, which catalyzed the reaction with less than 20%

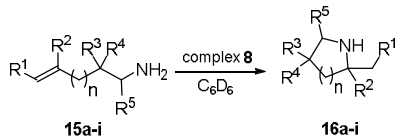
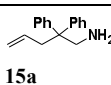
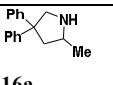
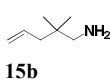
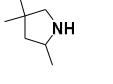
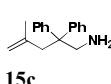
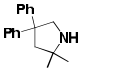
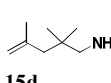
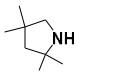
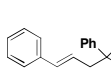
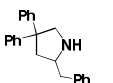
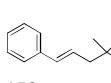
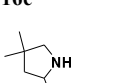
conversion in more than 24 h (Table 4, entries 1 and 3). However, complex **5**, which incorporates monoimino-functionalized indolyl ligand, displayed a very good catalytic activity towards the reaction with a 97% conversion of substrate in the presence of 2 mol % catalyst loading in 5 h. For complexes **7–10**, which incorporate the same mono amido-appended indolyl ligands,

showed very good catalytic activities with an excellent conversion in the presence of 2 mol % catalyst loading (Table 4, entries 4, 5, 8, 9). It is found that the catalytic activities of these complexes with different metal centers (7–10) decreased with the decrease of ionic radii of metal ions. The yttrium complex **8** exhibited the highest catalytic activity among the catalysts 7–10. This observation is in agreement with the results observed in other rare-earth metal complexes catalyzed the intramolecular hydroamination.^{7b} Complex **8** even displayed a very good catalytic activity in the presence of 1 mol % loading (Table 4, entries 6 and 7). To our surprise, the dinuclear complexes **13** and **14**, which incorporate the same mono amido-appended indolyl ligands as those of 7–10, but in different assembly form and coordination modes, exhibited even more higher catalytic activities than that **8** did (Table 4, entries 5, 10 and 11). Complexes **13** and **14** could complete the reaction in only 0.15 h. Finally, a comparison of the catalytic activities between complex **8** and [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃ (Table 4, entries 5 and 12) indicates complex **8** displayed a more high catalytic activity suggesting ligands effects on the catalytic activity.

Next, we used the diamagnetic yttrium complex **8**, which allows convenient NMR monitoring of reactions, to catalyze the intramolecular hydroamination of a series of aminoalkenes (**15a–15i**) (Table 5). All substrates were smoothly converted to the cyclic products with a high conversion under mild conditions with a low catalyst loadings (2–5 mol %), but different substrates shows different activities. For the substrates with terminal

alkenes for the formation different substituted five-membered tetrahydropyrroles rings, only 2 mol % catalyst loading is required to complete the reactions (Table 5, entries 1–4). For the substrates with internal alkenes, the catalytic transformations require a higher catalyst loading (5 mol %) (Table 5, entries 5 and 6) for the corresponding reactions cannot be completed with 2 mol % catalyst loading and prolonged reaction time. For those substrates transformed to the six-membered rings, the catalytic reactions required higher catalyst loading (4 mol %), higher reaction temperature (50 °C) and longer reaction time (Table 5, entries 7 and 8), and these results are in accordance with the Baldwin's rule that the formation of the six-membered ring is less favorable than those of five-membered rings.¹³ For substrates **15a** and **15b** with different substituents at β-position to the amino group, complete conversion of **15a** to final product only required 0.5 h, while complete transformation of **15b** to final product required 3 h under other same conditions (Table 5, entries 1 and 2). This observation is consistent with the Thorpe-Ingold effect¹⁴ that the reaction rate is enhanced for the substrates containing bulky phenyl substituents at the β-position to the amino group. The same effects were observed with substrates **15c**, **15e** and **15g** (Table 5, entries 3, 5 and 7). Finally, it was also of significance that complete conversion of the α-monosubstituted aminoalkene **15i**, having amino group at secondary carbon, required 5.0 mol % loading of **8** in 7.0 h at 60 °C with an albeit moderate diastereoselectivity [*trans:cis* = 6:1] (Table 5, entry 9).

Table 5 Hydroamination of Aminoalkenes (**15a–i**) Catalyzed by Complex **8**^a.

						
Entry	Substrate	Product	[cat.]/[sub.] (%)	Temperature (°C)	Time (h)	Conversion (%) ^b
1	 15a	 16a	2	25	0.5	99(96) ^c
2	 15b	 16b	2	25	3.0	99
3	 15c	 16c	2	25	1.0	99(95) ^c
4	 15d	 16d	2	50	10.0	99
5	 15e	 16e	5	25	1.0	99(96) ^c
6	 15f	 16f	5	50	36.0	97

7			4	50	5.5	98(94) ^c
8			4	50	40.0	98
9			5	60	7.0	99(dr: 16ia/16ib = 6:1) ^d

^a The reactions conducted with 0.32 mmol aminoalkene in 0.6 mL of C₆D₆. ^b Determined by ¹H NMR spectroscopy, using ferrocene as internal standard. ^c The data given in parenthesis are the isolated yields. ^d The *trans*:*cis* ratio was determined using integration techniques on the α -CH resonance of the *trans* at δ 3.15 and the *cis* multiplet at 2.94 ppm.

Conclusions

In summary, studies of reactions of 2-amino-functionalized indoles with [(Me₃Si)₂N]₃RE(μ -Cl)Li(THF)₃ showed that their reactivity patterns and coordination modes were significantly affected by the appended substituents on the nitrogen atom, temperatures and the central metal ions. Treatments of the amino-functionalized indoles with phenyl and *t*-butyl as appended substituents with [(Me₃Si)₂N]₃RE(μ -Cl)Li(THF)₃ afforded the imino-functionalized indolyl complexes with the transformation of amine to imine. Reactions of the bulky 2-(2,6-diisopropylphenylaminomethylene)indole with [(Me₃Si)₂N]₃RE(μ -Cl)Li(THF)₃ (RE = Yb, Er, Dy, and Y) produced the complexes incorporating amido-functionalized indolyl dianion ligand *via* deprotonation process. Furthermore, the corresponding imino-functionalized complexes were isolated by running the reactions of this indole with yttrium and ytterbium amides in refluxing toluene *via* dehydrogenation of secondary amine, and in ytterbium case, reduction of Yb³⁺ to Yb²⁺ was observed as well. When the same indole was treated with [(Me₃Si)₂N]₃RE(μ -Cl)Li(THF)₃ (RE = Sm, Nd), novel dinuclear complexes having the indolyl ligand in μ - η^5 : η^1 : η^1 bonding fashions were obtained. Based on the results, the pathway for the transformation of indolyl-functionalized secondary amine to the imine was proposed. In addition, it is found that the complexes with amido-functionalized indolyl ligand showed high catalytic activities for the intramolecular hydroamination of aminoalkenes, the catalytic activities of mononuclear complexes with different metal centers decreased with the decrease of ionic radii of metal ions. The dinuclear complexes displayed the highest catalytic activity among these catalysts indicating cooperative effects of dinuclear metal ions and coordination modes. Further study on the reactivity and coordination chemistry of the related amido-functionalized indolyl ligands with the rare-earth metal compounds will be reported soon.

Experimental section

General procedure.

All manipulations of air- and moisture-sensitive materials were performed using Schlenk techniques or in a glove box under an atmosphere of purified argon. Toluene, THF, hexane and diethyl ether were refluxed and freshly distilled over sodium benzophenone ketyl under argon prior to use. CDCl₃ was dried over activated 4 Å molecular sieves. Benzene-*d*₆, toluene-*d*₈ and THF-*d*₈ used for the NMR measurements were stored over Na/K alloy and vacuum-transferred immediately prior to use. [(Me₃Si)₂N]₃RE^{III}(μ -Cl)Li(THF)₃ (RE = Y, Eu, Yb, Er, Dy, Sm, Nd)^{12,15} 2-(2,6-*i*-Pr₂C₆H₃NHCH₂)C₈H₅NH,⁵ⁱ 2-(C₆H₅N=CH)C₈H₅NH, 2-(*t*-BuN=CH)C₈H₅NH¹⁶ and complex [2-(2,6-*i*-Pr₂C₆H₃NCH₂)C₈H₅N]Yb[N(SiMe₃)₂](THF)₂ (7)⁵ⁱ were prepared according to the literature methods. The aminoalkene substrates 2,2-diphenylpent-4-en-1-amine (15a), 2,2-dimethylpent-4-en-1-amine (15b), 2,2-diphenyl-4-methylpent-4-en-1-amine (15c), 2,2,4-trimethylpent-4-en-1-amine (15d), (E)-2,2,5-triphenylpent-4-en-1-amine (15e), (E)-2,2-dimethyl-5-phenylpent-4-en-1-amine (15f), 2,2-diphenylhex-5-en-1-amine (15g), 2,2-dimethylhex-5-en-1-amine (15h), 2-amino-2-methylpent-4-en-1-amine (15i),¹⁷ were synthesized according to the literature protocols.^{8k,10a} Their analytical data were in line with those reported ones. These substrates were distilled from Na and stored over 4 Å molecular sieves. Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker NMR spectrometer (500 or 300MHz for ¹H; 125 or 75MHz for ¹³C) in C₆D₆ or toluene-*d*₈ or THF-*d*₈ for rare-earth metals complexes and CDCl₃ for organic compounds at room temperature. Chemical shifts (δ) were reported in ppm. *J* values are reported in Hz. IR spectra were run on a Shimadzu FTIR-8400s spectrometer (KBr pellet). HRMS measurements were conducted with an Agilent 6220 ESI-TOF mass spectrometer. Melting points were determined in sealed capillaries and are uncorrected.

Synthesis of 2-(C₆H₅NHCH₂)C₈H₅NH (1).

LiAlH₄ (3.52 g, 90.0 mmol) was suspended in tetrahydrofuran (30 mL). To the suspension was added a solution of 2-(C₆H₅N=CH)C₈H₅NH (6.60 g, 30.0 mmol) in tetrahydrofuran (30 mL) dropwise at 0 °C. The reaction mixture was stirred overnight at room temperature; then it was hydrolyzed. The organic layer

was separated, and the white residue was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over anhydrous MgSO_4 , followed by filtration. Removal of the solvent under vacuum gave objective compound as a off-white solid (5.99 g) in 90% yield. The product was subsequently recrystallized from a mixture of hexane and ethyl acetate. mp: 83.0–84.0 °C. ν_{max} (KBr)/ cm^{-1} : 3393 s, 1603 s, 1502 m, 1456 s, 1416 m, 1312 m, 1285 m, 798 s, 750 s, 696 m. HRMS (ESI) m/z Calc. for $\text{C}_{15}\text{H}_{13}\text{N}_2^+$: 221.1073. Found: 221.1075. ^1H NMR (300 MHz, CDCl_3): δ_{H} 8.31 (s, 1H, indole-NH-), 7.66–6.74 (m, 9H, Ar-H), 6.50 (s, 1H, indole-CH=C-NH-), 4.52 (s, 2H, $\text{C}_6\text{H}_5\text{NHCH}_2$ -). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 148.4 (aromatic C-NH-), 137.3, 129.8, 100.3 (indole C from 2-pyrrole), 136.3, 129.0, 122.1, 120.7, 120.3, 118.9, 113.7, 111.3 (aromatic C), 42.7 (- CH_2 -NH-).

Synthesis of 2-($^i\text{BuNHCH}_2$) $\text{C}_8\text{H}_5\text{NH}$ (2).

Compound **2** (27 mmol, 90% yield) was prepared in an analogous manner as for **1** using 2-($^i\text{BuN}=\text{CH}$) $\text{C}_8\text{H}_5\text{NH}$ (6.0 g, 30.0 mmol). mp: 79.0–80.0 °C. ν_{max} (KBr)/ cm^{-1} : 3132 s, 1618 w, 1452 s, 1431 s, 1367 s, 1334 s, 1290 s, 1209 s, 1076 m, 1024 m, 796 s, 746 s, 729 s. HRMS (ESI) m/z Calc. for $\text{C}_{13}\text{H}_{17}\text{N}_2^+$: 201.1386. Found: 201.1385. ^1H NMR (300 M, CDCl_3): δ_{H} 8.75 (s, 1H, indole-NH-), 7.53 (d, $J = 7.4$ Hz, 1H, indole-Ar-H), 7.30–7.04 (m, 3H, indole-Ar-H), 6.32 (s, 1H, indole-CH=C-NH-), 3.93 (s, 2H, - CH_2 -NH-), 1.61 (s, 1H, - CH_2 -NH-), 1.18 (s, 9H, - $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (75 M, CDCl_3): δ_{C} 138.8, 136.0, 100.1 (indole C from 2-pyrrole), 128.6, 121.3, 120.0, 119.5, 110.9 (aromatic C), 50.9 (- $\text{C}(\text{CH}_3)_3$), 40.4 (- CH_2 -NH-), 29.0 (- $\text{C}(\text{CH}_3)_3$).

Synthesis of [2-($\text{C}_6\text{H}_5\text{N}=\text{CH}$) $\text{C}_8\text{H}_5\text{N}$] $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_2$ (4).

To a solution of ligand **1** (688 mg, 3.10 mmol) in 15 mL of toluene was added a toluene solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.382 g, 1.55 mmol) (10 mL) at room temperature. After stirred overnight at 110 °C, the solvent was removed from the reaction solution under vacuum, and the orange red residue was extracted with *n*-hexane. The hexane solution was cooled to 5 °C. Dark red crystals **4** that were suitable for X-ray diffraction were obtained from the solution after a few days (498 mg, 43% yield). mp: 211.1–212.0 °C. Found: C, 58.01; H, 5.60; N, 8.87. Calc. for $\text{C}_{36}\text{H}_{40}\text{N}_5\text{Si}_2\text{Eu}$: C, 57.58; H, 5.37; N, 9.33%. ν_{max} (KBr)/ cm^{-1} : 2959 w, 1614 s, 1589 s, 1483 m, 1445 m, 1423 m, 1333 m, 1298 w, 1236 w, 1202 w, 1123 m, 1072 w, 957 w, 907 w, 870 w, 800 m, 766 m, 754 m, 737 m, 694 s.

Synthesis of [2-($^i\text{BuN}=\text{CH}$) $\text{C}_8\text{H}_5\text{N}$] $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_2$ (5).

To a solution of ligand **2** (269 mg, 1.33 mmol) in 10 mL of toluene was added a toluene solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.186 g, 1.33 mmol) (10 mL) at room temperature. After the reaction was stirred overnight at 90 °C, the solvent was removed under vacuum, and the orange red residue was extracted with *n*-hexane. The hexane solution was cooled to 5 °C. Dark red crystals **5** that were suitable for X-ray diffraction were obtained from the solution after a few days (410 mg, 46% yield). mp: 206 °C. Found: C, 44.05; H, 7.68; N, 8.90. Calc. for $\text{C}_{25}\text{H}_{51}\text{N}_4\text{Si}_4\text{Eu}$: C, 44.68; H, 7.65; N, 8.34%. ν_{max} (KBr)/ cm^{-1} : 2967 s, 1634 s, 1614 m, 1452 w, 1364 m, 1333 m, 1294 m, 1253 w, 1211 m, 1157 w, 1036 w, 1011 m, 932 m, 795 m, 754 m, 731 m.

Synthesis of [2-($^i\text{BuN}=\text{CH}$) $\text{C}_8\text{H}_5\text{N}$] $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2$ (6).

Following the procedure described for **5**, reaction of ligand **2** (489 mg, 2.42 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Yb}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.105 g, 1.21 mmol) at 110 °C afforded **6** as yellow crystals (478 mg, 54%). mp: 206.2–207.4 °C. Found: C, 52.33; H, 6.89; N, 9.39. Calc. for $\text{C}_{32}\text{H}_{48}\text{N}_5\text{Si}_2\text{Yb}$: C, 52.51; H, 6.61; N, 9.57%. ν_{max} (KBr)/ cm^{-1} : 2961 w, 1614 s, 1589 s, 1483 m, 1443 m, 1331 m, 1298 w, 1236 w, 1123 m, 1072 w, 957 w, 907 w, 870 w, 800 m, 757 m, 735 m, 694 s, 654 m.

Synthesis of [2-(2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{NCH}_2$) $\text{C}_8\text{H}_5\text{N}$] $\text{RE}[\text{N}(\text{SiMe}_3)_2]_2$ (THF) $_2$ (RE = Y (8), Er (9), Dy (10)).

To a solution of ligand **3** (337 mg, 1.10 mmol) in 10 mL of toluene was added a toluene solution of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (911 mg, 1.10 mmol) (10 mL) at room temperature. After the reaction was stirred overnight at 90 °C, the solvent was removed from the reaction under vacuum, and the yellow residue was extracted with *n*-hexane. The hexane solution was cooled to 5 °C. Light yellow crystals **8** that were suitable for X-ray diffraction were obtained from the solution after a few days (476 mg, 62% yield). mp: 265 °C (Dec.). Found: C, 60.05; H, 8.26; N, 5.83. Calcd. for $\text{C}_{35}\text{H}_{58}\text{N}_3\text{O}_2\text{Si}_2\text{Y}$: C, 60.23; H, 8.38; N 6.02%. ν_{max} (KBr)/ cm^{-1} : 3024 m, 2963 s, 1631 s, 1462 m, 1207 m, 1178 w, 1128 m, 1107 w, 1057 w, 1035 w, 800 w, 737 s. ^1H NMR (300 M, C_6D_6): δ_{H} 8.02–7.92 (m, 2H, Ar-H), 7.49–7.21 (m, 5H, Ar-H), 6.64 (s, 1H, indole-CH=C-NH-), 4.96 (s, 2H, - CH_2 -NH-), 3.72 (s, 10H, - $\text{CH}(\text{CH}_3)_2$ - CH_2 -O- CH_2 -), 1.39–1.29 (m, 12H, - $\text{CH}(\text{CH}_3)_2$), 1.16 (s, 8H, -O- CH_2 - CH_2 -), 0.21 (s, 18H, - $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (75 M, C_6D_6): δ_{C} 153.5 (aromatic C-NH-), 148.7, 144.9, 98.4 (indole C from 2-pyrrole), 128.3, 128.0, 127.7, 123.9, 123.6, 119.5, 118.5, 114.9 (aromatic C), 72.4 (-O- CH_2 - CH_2 -), 57.1 (- CH_2 -NH-), 27.2 (- $\text{CH}(\text{CH}_3)_2$), 26.3 (-O- CH_2 - CH_2 -), 24.7 (- $\text{CH}(\text{CH}_3)_2$), 4.5 (- $\text{Si}(\text{CH}_3)_3$).

Following the procedures described for **8**, reaction of ligand **3** (383 mg, 1.25 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Er}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.134 g, 1.25 mmol) afforded **9** as yellow crystals (553 mg, 57% yield). mp: 279.5 °C (Dec.). Found: C, 54.42; H, 7.39; N, 5.24. Calc. for $\text{C}_{35}\text{H}_{58}\text{N}_3\text{O}_2\text{Si}_2\text{Er}$: C, 54.15; H, 7.53; N, 5.41%. ν_{max} (KBr)/ cm^{-1} : 2955 s, 2868 w, 1456 s, 1413 s, 1383 m, 1362 m, 1319 m, 1303 m, 1286 m, 1248 w, 1196 m, 1064 s, 1051 m, 993 w, 744 s, 634 s. Following the procedures described for **8**, reaction of ligand **3** (370 mg, 1.21 mmol) and $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Dy}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (1.092 g, 1.21 mmol) afforded **10** as light yellow crystals (467 mg, 50% yield). mp: 296 °C (Dec.). Found: C, 54.16; H, 7.52; N, 5.32. Calc. for $\text{C}_{35}\text{H}_{58}\text{N}_3\text{O}_2\text{Si}_2\text{Dy}$: C, 54.49; H, 7.58; N, 5.45%. ν_{max} (KBr)/ cm^{-1} : 2955 s, 2830 s, 1925 vw, 1880 vw, 1456 s, 1413 s, 1382 m, 1362 m, 1319 m, 1286 m, 1246 w, 1196 m, 1051 m, 993 m, 793 s, 744 s, 636 s.

Synthesis of [2-(2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH}$) $\text{C}_8\text{H}_5\text{N}$] Y (11).

A Schlenk flask was charged with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (594 mg, 0.717 mmol), ligand **3** (658 mg, 2.15 mmol) and 25 mL of toluene, and the refluxing solution was stirred for 24 h. Then, the solvent was evaporated under reduced pressure and the yellow residue was extracted with *n*-hexane. Yellow crystals **11** that were suitable for X-ray diffraction were obtained upon crystallization from hexane at 0 °C after a few days (143 mg, 20% yield). mp: 156 °C (Dec.). Found: C, 76.24; H, 7.36; N, 8.43.

Calc. for $C_{63}H_{69}N_6Y$: C, 75.73; H, 6.96; N, 8.41%. ν_{max} (KBr)/ cm^{-1} : 2972 s, 1628 s, 1614 s, 1454 s, 1379 w, 1337 m, 1319 m, 1238 w, 1182 m, 1128 m, 1053 m, 1011 w, 988 w, 806 m, 735 s, 665 m. 1H NMR (500 M, C_6D_6): δ_H 7.91 (s, 1H, -CH=N-), 7.64 (d, 1H, J = 8.0 Hz, Ar-H), 6.97–6.94 (dd, 1H, J = 14.5 Hz, 7.5 Hz, Ar-H), 6.90 (s, 1H, indole-CH=C-N-), 6.89–6.86 (m, 2H, Ar-H), 6.83–6.80 (dd, 1H, J = 14.5, 7.0 Hz, Ar-H), 6.72–6.69 (dd, 1H, J = 15.0, 8.0 Hz, Ar-H), 6.29 (d, 1H, J = 8.5 Hz, Ar-H), 2.56–2.51 (m, 1H, -CH(CH₃)₂), 2.28–2.23 (m, 1H, -CH(CH₃)₂), 0.74–0.72 (d, 3H, J = 6.5 Hz, -CH(CH₃)₂), 0.57–0.53 (m, 6H, -CH(CH₃)₂), 0.48–0.46 (d, J = 7.0 Hz, 3H, -CH(CH₃)₂). ^{13}C NMR (125 M, C_6D_6): δ_C 168.7 (-CH=N-), 150.3 (aromatic C-NH-), 147.8, 142.3, 117.8 (indole C from 2-pyrrole), 141.1, 141.0, 131.0, 124.3, 124.0, 123.5, 121.9, 120.6, 118.3 (aromatic C), 29.0, 28.2 (-CH(CH₃)₂), 23.8, 23.0, 22.3 (-CH(CH₃)₂).

Synthesis of [2-(2,6- $iPr_2C_6H_3N=CH$)C₈H₅N]₂Yb^{II}(THF)₂ (**12**).

Following the procedures described for **11**, reaction of [(Me₃Si)₂N]₃Yb(μ -Cl)Li(THF)₃ (1.095 g, 1.20 mmol) and ligand **3** (734 mg, 2.40 mmol) in refluxing toluene for 30 h gave complex **12** as orange crystals (387 mg, 35 % yield). mp: 229 °C (Dec.). Found: C, 64.64; H, 6.74; N, 6.39. Calc. for C₅₀H₆₂N₄O₂Yb: C, 64.99; H, 6.76; N, 6.06%. ν_{max} (KBr)/ cm^{-1} : 2959 s, 1929 w, 1879 w, 1589 m, 1454 s, 1412 s, 1379 m, 1362 m, 1317 m, 1304 m, 1283 m, 1196 s, 1138 w, 1070 s, 1053 s, 991 m, 926 w, 795 s, 766 s, 745 s, 637 s. 1H NMR (500 M, THF- d_6): δ_H 8.09 (s, 1H, -CH=N-), 7.44 (d, 1H, J = 7.5 Hz, Ar-H), 7.27–7.25 (m, 1H, Ar-H), 7.18–6.98 (m, 3H, Ar-H), 6.86–6.83 (m, 1H, Ar-H), 6.75 (s, 1H, indole-CH=C-NH-), 6.66–6.61 (m, 1H, Ar-H), 3.59 (s, 4H, THF- α -H), 3.20–3.17 (m, 2H, -CH(CH₃)₂), 1.77 (s, 4H, THF- β -H), 1.28 (s, 6H, -CH(CH₃)₂), 1.16 (s, 6H, -CH(CH₃)₂). ^{13}C NMR (125 M, THF- d_6): δ_C 164.2 (-CH=N-), 149.8 (aromatic C-NH-), 145.0, 138.2, 99.7 (indole C from 2-pyrrole), 129.1, 124.3, 123.6, 123.1, 121.1, 119.9, 119.1, 110.8, 108.8 (aromatic C), 67.2 (THF- α -C), 31.9 (-CH(CH₃)₂), 27.8 (THF- β -C), 25.8 (-CH(CH₃)₂), 22.3 (-CH(CH₃)₂).

Synthesis of $\{[\mu-\eta^1:\eta^5-2-(2,6-*iPr_2C_6H_3NCH_2*)C_8H_5N]RE-[N(SiMe_3)_2]\}_2$ (RE = Sm (**13**), Nd (**14**)).

Complex **13** was prepared following the procedures similar to that used for the synthesis of **8** by running the reaction in refluxing toluene, using 404 mg of **3** (1.32 mmol) and 1.175 g of [(Me₃Si)₂N]₃Sm(μ -Cl)Li(THF)₃ (1.32 mmol), yielding light orange crystals of **13** (406 mg, 50% yield). mp: 219 °C (Dec.). Found: C, 52.15; H, 6.86; N, 6.63. Calcd. for C₅₄H₈₄N₆Si₄Sm₂: C, 52.72; H, 6.88; N, 6.83%. ν_{max} (KBr)/ cm^{-1} : 2957 s, 1626 s, 1616 s, 1589 w, 1454 s, 1416 s, 1317 m, 1306 m, 1283 m, 1252 m, 1198 s, 1126 m, 1109 w, 1053 m, 927 m, 802 s, 791 s, 762 s, 748 s, 635 s. 1H NMR (300 M, Tol- d_8): δ_H 14.58 (s, 1H), 12.08 (s, 1H), 11.12 (s, 1H), 10.84 (s, 1H), 8.74 (s, 1H), 7.65 (s, 1H), 7.34 (d, 1H, J = 7.56 Hz), 7.11–6.99 (m, 1H), 6.71 (t, 1H), 5.2 2(d, 1H, J = 7.38 Hz), 3.63 (s, 3H), 3.21 (s, 3H), 2.64 (s, 3H), 0.37 (s, 1H), -2.34 (s, 9H), -2.41 (s, 3H), -5.27 (s, 9H), -10.42 (s, 1H). ^{13}C NMR (125 M, Tol- d_8): δ_C 192.0, 163.9, 143.8, 134.7, 102.9, 128.6, 128.0, 127.1, 111.3, 142.3, 138.4, 132.6, 130.8, 129.7, 40.3, 34.3, 33.8, 32.3, 31.8, 24.3, 7.3, 2.7. Complex **14** was prepared as light blue-green crystals in 55% yield (425 mg) by treatment of [(Me₃Si)₂N]₃Nd(μ -Cl)Li(THF)₃ (1.123 g, 1.27 mmol) with ligand **3** (389 mg, 1.27 mmol)

following the procedures similar to that described above for preparation of complex **13**. mp: 244 °C (Dec.). Found: C, 53.44; H, 6.81; N, 6.88. Calc. for C₅₄H₈₄N₆Si₄Nd₂: C, 53.24; H, 6.95; N, 6.90%. ν_{max} (KBr)/ cm^{-1} : 2960 s, 1616 vw, 1585 vw, 1456 s, 1416 s, 1317 m, 1306 m, 1285 m, 1248 m, 1228 w, 1194 s, 1136 w, 1103 w, 993 m, 976 w, 928 m, 808 s, 793 s, 764 s, 745 s, 637 s. 1H NMR (500 M, C_6D_6): δ_H 10.40 (d, 1H, J = 5.0 Hz), 10.18 (s, 1H), 9.74 (s, 1H), 9.08 (s, 1H), 8.57(d, 1H, J = 6.2 Hz), 7.58 (s, 3H), 6.75 (s, 1H), 6.55 (s, 3H), 6.08 (s, 3H), 5.68 (s, 1H), 5.51 (s, 1H), 5.15 (s, 3H), -1.22 (s, 1H), -2.24 (s, 1H), -3.31 (s, 1H), -6.81 (s, 3H), -8.16 (s, 3H), -10.02 (s, 3H), -10.73 (s, 3H), -11.41 (s, 3H), -12.10 (s, 1H), -13.58 (s, 3H). ^{13}C NMR (125 M, C_6D_6): δ_C 164.7, 161.8, 145.6, 138.3, 108.4, 122.9, 118.0, 116.1, 115.4, 137.1, 135.6, 126.1, 124.8, 124.0, 37.7, 36.8, 35.5, 31.9, 28.2, 24.4, 23.0, 18.9, 16.8, 14.3, 11.6, 6.8, 2.6.

General procedure for intramolecular hydroamination.

In a glove box, the rare-earth metal complex, aminoalkene (0.32 mmol), and the standard ferrocene were mixed in benzene- d_6 (0.6 mL) or toluene- d_8 (0.6 mL) and loaded into a NMR tube. The NMR tube was then sealed, and the reaction was monitored by NMR techniques.

X-ray crystallographic analyses.

Single crystals of complexes **4–6**, **8–14** suitable for X-ray diffraction studies were sealed in thin-walled glass capillaries under argon. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.¹⁸ All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.¹⁹ All hydrogen atoms were refined using a riding model. A summary of the crystallographic data and selected experimental information are listed in Table S1, Table S2 in the Electronic Supplementary Information

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Notes and references

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† Electronic Supplementary Information (ESI) available: Characterization spectra for compounds **1**, **2**, **8**, **11**, **12**, **13**, **14**, substrates and some of products for hydroamination; molecular structures and selected bond lengths and angles of complexes **4–6**, **8–14**; crystallographic data and details of the data collection; spectra of ¹H NMR monitoring of the reactions of all the entries in Table 5. CCDC 1056938 (**4**), 1056939 (**5**), 1056912 (**6**), 1056913 (**8**), 1056941 (**9**), 1056942 (**10**), 1056933 (**11**), 1056934 (**12**), 1056930 (**13**), and 1056931 (**14**). For ESI and crystallographic information files (CIF) or other electronic format see DOI: 10.1039/b000000x/

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Different kinds of rare-earth metal amido complexes were synthesized *via* silylamine elimination or secondary amine dehydrogenation process. The dinuclear complexes displayed the highest catalytic activity for intramolecular hydroamination of aminoalkenes among the catalysts surveyed.

