This article is published as part of the *Dalton Transactions* themed issue entitled:

New Talent Asia

Highlighting the excellent work being carried out by younger members of the inorganic academic community in Asia

Guest Editor Masahiro Yamashita
Tohoku University, Japan

Published in issue 10, 2011 of *Dalton Transactions*

Image reproduced with permission of Kenneth Kam-Wing Lo

Articles in the issue include:

PERSPECTIVES:

ARTICLES:

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research
www.rsc.org/dalton

Dalton Transactions

Dynamic Article Links

Cite this: *Dalton Trans.*, 2011, **40**, 2366

www.rsc.org/dalton

PAPER

Monoalkyl and monoanilide yttrium complexes containing tridentate pyridyl-1-azaallyl dianionic ligands†

Erli Lu,[a] Wei Gan[a,b] and Yaofeng Chen*[a]

Received 4th November 2010, Accepted 29th November 2010
DOI: 10.1039/c0dt01539c

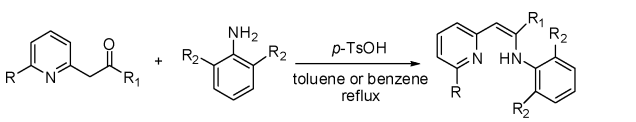
A series of pyridyl-1-azaallyl ligand precursors (**HL1–HL5**) were synthesized *via* condensation of pyridine ketones with anilines. The alkane elimination reactions between $Y(CH_2SiMe_3)_3(THF)_2$ and **HL4** or **HL5** gave the monoalkyl complexes (**L4–H**)$YCH_2SiMe_3(THF)$ (**1**) and (**L5–H**)YCH_2SiMe_3-(THF) (**2**) supported by new tridentate pyridyl-1-azaallyl dianionic ligands. The reactions of monoalkyl complexes, **1** and **2**, with one equivalent of 2,6-diisopropylaniline produced the corresponding monoanilide complexes, (**L4–H**)YNHAr(THF) (**3**) and (**L5–H**)YNHAr(THF) (**4**) (Ar = 2,6-(^{i}Pr)$_2$C$_6$H$_3$), *via* highly selective protonolysis of the terminal alkyl Y–CH_2SiMe_3 bond. Complexes **1–4** are active for intramolecular hydroamination of aminoalkenes.

Introduction

Due to their rich and diversified coordinating properties and reactivities, organometallic complexes of rare-earth metals have received growing attention.[1,2,3] The most widely investigated organometallic complexes of rare-earth metals are those bearing Cp-type ligands. Recently, there is a tendency to explore "non-Cp" ligands and their application in rare-earth organometallic chemistry.[4] Among the "non-Cp" ligands, β-diketiminato ligands are one of the most promising ligand families.[5] Numerous β-diketiminato rare-earth organometallic complexes have been prepared, and some have shown interesting structural features and good catalytic activities.[6,7,8,9,10,11] Pyridyl-1-azaallyl ligands are close relatives of the β-diketiminato ligands, which introduce a neighboring fused six-membered nitrogen heterocyclic ring into the backbone of the primitive β-diketiminato.[5,12] The pyridine ring, with its electronic delocalization and steric rigidity, may introduce some special structural features and interesting catalytic activities into the primitive β-diketiminato based metal complexes. Pyridyl-1-azaallyl ligands have been used in early transition metal,[13] late transition metal[14] as well as main-group metal[15] chemistry. However, the pyridyl-1-azaallyl ligands have not been introduced into rare-earth metal chemistry. From another aspect, in contrast with the diversified synthetic pathways to β-diketiminato ligands, the method reported for the synthesis of pyridyl-1-azaallyl ligands is the insertion reaction between lithiated 2-alkyl substituted pyridines and cyanides, such as phenyl cyanide and trimethylsilyl cyanide.[13,14,15] Recently, rare-earth metal complexes supported by aminopyridinate ligands have received considerable attention.[16] Herein we report the synthesis of pyridyl-1-azaallyl ligand precursors by condensation of pyridine ketones with anilines, the monoalkyl and monoanilide yttrium complexes supported by exceptional pyridyl-1-azaallyl dianionic ligands and their catalytic behavior for intramolecular hydroamination of aminoalkenes.

Results and discussion

A series of pyridyl-1-azaallyl ligand precursors (**HL1–HL5**) were readily synthesized *via* condensation of pyridine ketones with anilines in the presence of *p*-toluenesulfonic acid in toluene (or benzene) with removal of water by azeotropic distillation (Scheme 1). These compounds were characterized by NMR (^{1}H and ^{13}C) and HRMS spectroscopy.



HL1: R = R_1 = R_2 = CH_3
HL2: R = CH_3, R_1 = C_6H_5, R_2 = CH_3
HL3: R = CH_3, R_1 = C_6H_5, R_2 = $CH(CH_3)_2$
HL4: R = $SiMe_3$, R_1 = CH_3, R_2 = $CH(CH_3)_2$
HL5: R = C_6H_5, R_1 = CH_3, R_2 = $CH(CH_3)_2$

Scheme 1 Synthesis of **HL1–HL5**.

The ^{1}H NMR spectral monitoring of reactions between the ligand precursors (**HL1–HL3**) and one equivalent of $Y(CH_2SiMe_3)_3(THF)_2$ in C_6D_6 showed that all the reactions led to complicated mixtures within several hours at room temperature. We then turned to the ligand precursors (**HL4** and **HL5**), which have more sterically demanding trimethylsilyl (for **HL4**) or phenyl (for **HL5**) substituents on the pyridine ring. The ^{1}H NMR spectral monitoring showed that **HL4** and **HL5** were nearly

[a]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai, 200032, China. E-mail: yaofchen@mail.sioc.ac.cn; Fax: 86-21-64166128*
[b]*Department of Chemistry, Northwest University, 229 Taibai North Avenue, Xi'an, 710069, China*

† CCDC reference numbers 789698–789700. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01539c

completely converted into new complexes **1** and **2**, respectively, at room temperature in 24 h, with concomitant disappearance of $Y(CH_2SiMe_3)_3(THF)_2$ and formation of two equivalents of Me_4Si. The reactions were then scaled up in hexane, **1** and **2** were isolated as yellow crystalline solids (77% and 71% yield, respectively).

^{1}H NMR spectra of **1** and **2** in C_6D_6 show the existence of a pyridyl-1-azaallyl ligand fragment, a $-CH_2SiMe_3$ alkyl group (–0.42 and 0.17 ppm for **1**, –0.43 and 0.09 ppm for **2**) and a THF molecule in each complex. For **1**, a broad signal is observed at 0.61 ppm with an area of 6 H, which can be assigned as two methyls on the Si atom of the ligand. However, the signal of the third methyl on the Si atom is absent, while a broad peak with an area of 2 H at –0.36 ppm is observed, which is suspected to be the signal of YCH_2. For **2**, in its ^{1}H NMR spectrum, the signals in the aromatic region are too complicated to allow an unambiguous assignment, while the ^{13}C NMR spectrum is more informative. A doublet is observed at 187.5 ppm with a $^2J_{YC}$ coupling constant of 46.4 Hz, which is suspected to be the signal of YC^{Ar}.

To obtain an unambiguous characterization of the structures of **1** and **2**, single crystals of the complexes were grown from the toluene solutions and characterized by X-ray diffraction studies (Fig. 1 and 2). Complexes **1** and **2** are the monoalkyl yttrium complexes with new tridentate pyridyl-1-azaallyl dianionic ligands, as shown in Scheme 2. Therefore, the reactions of $Y(CH_2SiMe_3)_3(THF)_2$ with **HL4** or **HL5** not only lead to

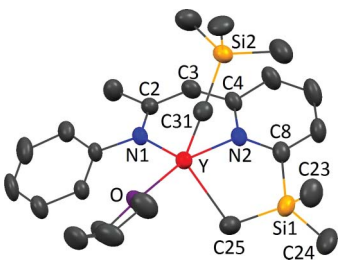


Fig. 1 Molecular structure of **1** with thermal ellipsoids at 30% probability level. Isopropyl groups on the Ar substituents and hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Y–C31 2.371(4), Y–C25 2.403(4), Y–N1 2.285(3), Y–N2 2.385 (3), Y–O 2.367(3), N1–C2 1.362(5), N2–C4 1.364(5), C2–C3 1.366(5), C3–C4 1.416(6), C31–Y–C25 114.20(14).

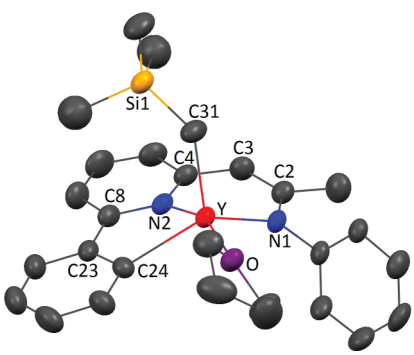
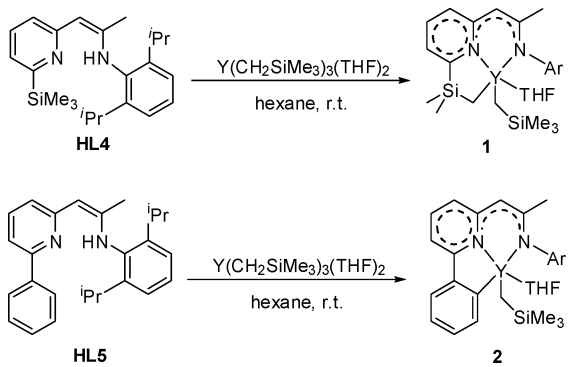


Fig. 2 Molecular structure of **2** with thermal ellipsoids at 30% probability level. Isopropyl groups on the Ar substituents and hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Y–C31 2.360(3), Y–C24 2.396(3), Y–N1 2.273(3), Y–N2 2.371(3), Y–O 2.355(2), N1–C2 1.344(4), N2–C4 1.367(4), C2–C3 1.362(4), C3–C4 1.426(4), C31–Y–C24 112.40(12).



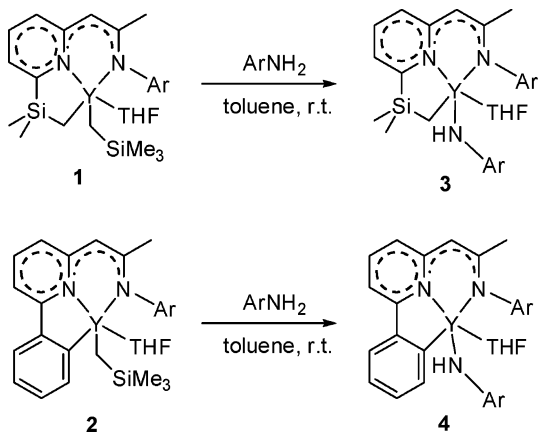
Scheme 2 Reactions of **HL4** and **HL5** with one equivalent of $Y(CH_2SiMe_3)_3(THF)_2$.

the deprotonation of the *β*-diketimine backbone but also the activation of a sp^3 C–H bond of a trimethylsilyl substituent (for **HL4**) or a sp^2 C–H bond of a phenyl substituent (for **HL5**) on the pyridine ring of the ligand precursors. Both **1** and **2** are five-coordinate monomers. In **1**, the Y(III) center adopts a distorted trigonal bipyramidal geometry with a nitrogen atom of the imine group, a carbon atom of the $-CH_2SiMe_2$ group, and a carbon atom of the $-CH_2SiMe_3$ alkyl ligand forming the equatorial plane, and a nitrogen atom on the pyridine ring and an oxygen atom of the THF occupying the axial positions. The Y–N2 distance of 2.385(3) Å is significantly longer than the Y–N1 distance (2.285(3) Å). Although the C2–N1 and C4–N2 distances (1.362(5) and 1.364(5) Å, respectively) are almost the same, the C2–C3 distance (1.366(5) Å) is shorter than the C3–C4 distance (1.416(6) Å), and the N1, C2, C3, C4 and N4 atoms are not well fit in a plane. Therefore, the *β*-diketiminato backbone is better described as the partially delocalized electronic structure. The pyridine ring's plane forms a dihedral angle of 8.27° with the N1–C2–C3–C4–N2 plane. The yttrium ion sits above the N1–C2–C3–C4–N2 ligand plane by 0.743 Å; the distances from the yttrium ion to the atoms C2, C3 and C4 (>3.31 Å) are too long for effective interaction. The Y–C25 distance (2.403(4) Å) is close to the Y–C31 distance (2.371(4) Å). For the Y–N2–C8–Si1–C25 five-membered ring, the atoms N2, C8, Si1 and C25 are nearly coplanar with the yttrium ion 1.117 Å out of the plane to adopt a folded-like conformation. The THF is bonded to the metal ion with a reasonable Y–O separation of 2.367(3) Å.

The structural features of **2** are very similar to those of **1**, and the distances from the yttrium ion to the coordinated atoms in these two complexes are nearly the same. For **2**, it's worthy noting that the η^1 coordinated phenyl ring is nearly coplanar with the pyridine ring. It's also interesting to do a brief structural comparison between **2** and a yttrium hydrido complex supported by a tridentate phenyl substituted amidopyridinate dianionic ligand reported by Trifonov *et al.*, where a sp^2 C–H bond of a phenyl substituent on the pyridine ring is also activated and the phenyl ring is η^1 coordinated to the metal center.[16f] In **2**, the dianionic ligand forms one six-membered ring and one five-membered ring with the metal center, while in Trifonov's complex, the dianionic ligand forms two five-membered rings with the metal center. The $Y–C^{Ar}$ and $Y–N^{Py}$ distances in **2** (2.396(3) and 2.371(3) Å, respectively) are shorter than those in Trifonov's complex (2.469(2) and 2.4252(17) Å, respectively), while the other Y–N distance is longer in **2** (2.273(3) Å *vs.* 2.2205(18) Å). The

yttrium ion in **2** sits more out of the N–N–C plane than that in Trifonov's complex (0.977 Å *vs.* 0.696 Å). Alkyl complexes **1** and **2** are stable at room temperature for several days. When the temperature is elevated to 60 °C, the decomposition of **1** is less than 20% in C_6D_6 in 5.5 h; **2** is more stable and show less than 10% decomposition in C_6D_6 in 12 h.

As shown in Scheme 2, besides a terminal Y–CH_2SiMe_3 bond, **1** and **2** have a metallacyclic Y–C^{sp^3} (Y–CH_2SiMe_2) or Y–C^{sp^2} (Y–C^{Ar}) bond, respectively. How the terminal and metallacyclic Y–C bonds differentiate in reactivity should be an intriguing question. To answer the question, protonolysis reactions of **1** and **2** with one equivalent of a Brønsted acid 2,6-diisopropylaniline were carried out. ^{1}H NMR spectral monitoring of the reactions in C_6D_6 showed that **1** and **2** were nearly completely converted into anilide complexes **3** and **4** with concomitant disappearance of the terminal –YCH_2SiMe_3 functional group in the metal complexes and formation of one equivalent of Me_4Si in 6 h (for **1**) and 3 h (for **2**) at room temperature. The experiments demonstrated that the terminal Y–CH_2SiMe_3 bond is more reactive than the metallacyclic Y–C bond. The reactions were then scaled up in toluene, **3** and **4** were isolated as yellow crystalline solids in 55% and 64% yield, respectively (Scheme 3).



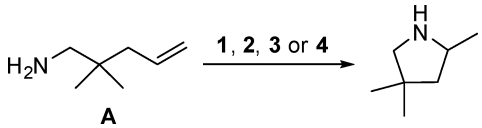
Scheme 3 Protonolysis reactions of **3** and **4** with one equivalent of 2,6-diisopropylaniline.

Single crystals of **4** were grown from the toluene solution and characterized by X-ray diffraction studies (Fig. 3). The structure of **4** takes great resemblance to its alkyl precursor **2**, while the terminal alkyl functional group in **2** is replaced by the anilide functional group in **4**. The Y–$N^{anilide}$ distance is 2.197(5) Å, and the ∠Y–$N^{anilide}$–C29 is 154.9(4)°. The anilide complexes **3** and **4** are stable at room temperature for several days. When the temperature is elevated to 60 °C, the decomposition of **3** is less than 15% in C_6D_6 in 5.5 h; **4** is more stable and shows less than 5% decomposition in C_6D_6 in 12 h.

Catalytic behavior for intramolecular hydroamination of aminoalkenes

Intramolecular hydroamination of aminoalkenes offers an efficient and atom-economical method to construct nitrogen heterocycles that are important for the fine chemicals and pharmaceuticals. Rare-earth metal complexes have been employed as one of the most promising catalysts for this transformation.[2,17,18] The catalytic

Table 1 Hydroamination of **A** catalyzed by **1–4**[a]



A

Entry	Catalyst	[Cat.]/[Sub.] (%)	Time (min)	Conv. (%)[b]	TOF (h^{-1})[c]
1	**1**	2.5	60	96	38.4
2	**2**	2.5	35	97	66.5
3	**3**	2.5	120	97	19.4
4	**4**	2.5	70	98	33.6

[a] 15.3 mmol L^{-1} [cat.], 0.0613 mol L^{-1} [Cp_2Fe], 0.613 mol L^{-1} [sub.], 60 °C, 0.46 mL of C_6D_6 as solvent. [b] NMR conv. determined relative to ferrocene internal standard. [c] Turnover frequency.

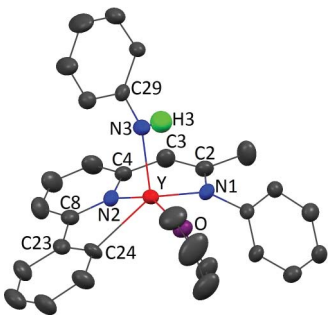


Fig. 3 Molecular structure of **4** with thermal ellipsoids at 30% probability level. Isopropyl groups on the Ar substituents and hydrogen atoms (except anilide hydrogen atom) have been removed for clarity. Selected bond lengths (Å) and angles (°): Y–N3 2.197(5), Y–N1 2.281(4), Y–N2 2.361(4), Y–C24 2.424(6), Y–O 2.355(3), N1–C2 1.342(6), N2–C4 1.371(7), C2–C3 1.383(8), C3–C4 1.397(7), Y–N3–C29 154.9(4).

behavior of complexes **1–4** for intramolecular hydroamination were initially tested by employing 2,2-dimethyl-1-aminopent-4-ene (**A**) as substrate (Table 1). A solution of the yttrium complex, the standard ferrocene and substrate in C_6D_6 was loaded into an NMR tube, and the reaction process was monitored by ^{1}H NMR spectroscopy.

When alkyl complexes **1** and **2** were used as catalysts, the ^{1}H NMR spectrum showed a rapid protonolysis of the terminal alkyl by amine with a release of Me_4Si. A clean formation of 2,4,4-trimethylpyrrolidine, the Markovnikov-selective product, was observed in several minutes. No traces of other heterocyclic regioisomers were detected through the proceeding. Intriguingly, anilide complexes **3** and **4** also exhibited good catalytic activities for the intramolecular hydroamination, and the regioselectivity was identical with that catalyzed by the alkyl complexes. The hydroaminations of **A** catalyzed by **1–4** could be completed within 2 h at 60 °C, with a catalyst loading of 2.5 mol% (Table 1). The alkyl complexes **1** and **2** are more active than the corresponding anilide complexes **3** and **4**; the complexes with the phenyl substituted ligand **L5–H**, **2** and **4**, are more active than the corresponding ones with the silyl substituted ligand **L4–H**, **1** and **3**. The catalytic activity order is as the following: **2** > **1** > **4** > **3**.

To investigate the initiation of catalytic reaction in detail, experiments with a high [cat.]/[sub.] mole ratio of 1/5 were performed in C_6D_6 at room temperature and monitored by ^{1}H NMR spectroscopy. In the case of alkyl complex **1**, the protonolysis

of the terminal alkyl with concomitant appearance of one equivalent of Me_4Si was observed immediately. The protonolysis of metallacyclic Y–CH_2SiMe_2 bond was observed immediately, which was evidenced by the disappearance of the Y–CH_2SiMe_2 signal. For anilide complex **3**, there was no observation of 2,6-diisopropylanilide throughout the reaction; but, similar to that of the alkyl complex **1**, the protonolysis of the metallacyclic Y–CH_2SiMe_2 bond was observed immediately. The foregoing observations suggested that in the hydroamination catalyzed by alkyl complex **1**, both the terminal Y–CH_2SiMe_3 bond and the metallacyclic Y–CH_2SiMe_2 bond initiated the reaction; while in the hydroamination catalyzed by anilide complex **3**, the metallacyclic Y–CH_2SiMe_2 bond initiated the reaction solely, and the Y–$N^{anilide}$ bond was retained. Complexes **2** and **4**, which bear the phenyl substituted ligand, showed similar behavior to complexes **1** and **3**. In the case of alkyl complex **2**, the protonolysis of the terminal alkyl with concomitant appearance of one equivalent of Me_4Si and dramatic changes of the proton signals for the aromatic rings were observed immediately. For anilide complex **4**, 2,6-diisopropylanilide was not observed throughout the reaction, while the proton signals for the aromatic rings immediately changed dramatically. Thus in the hydroamination catalyzed by alkyl complex **2**, both the terminal Y–CH_2SiMe_3 bond and the metallacyclic Y–C^{Ar} bond initiated the reaction; while in the hydroamination catalyzed by the anilide complex **4**, the metallacyclic Y–C^{Ar} bond initiated the reaction solely. These observations indicated that the alkyl complexes (**1** and **2**) and the anilide complexes (**3** and **4**) have a different number of active sites, which is responsible for the difference in activity between the alkyl complexes and the anilide complexes.

Kinetic studies of **1–4** catalyzed intramolecular hydroamination of **A** were carried out at 60 °C by *in situ* ^{1}H NMR spectroscopy. Fig. 4 presents substrate concentration decay curves for the reactions catalyzed by **1–4**. All of the four substrate decay curves deviate from the typical zero-order dependence on substrate concentration and show a decrease in rate at low substrate concentrations. Actually, the reactions catalyzed by complexes **1** and **3** were about first-order dependent on substrate concentration (Fig. 5), suggesting the protonation of the insertion product by the substrate is rate limiting (although a preceding intramolecular

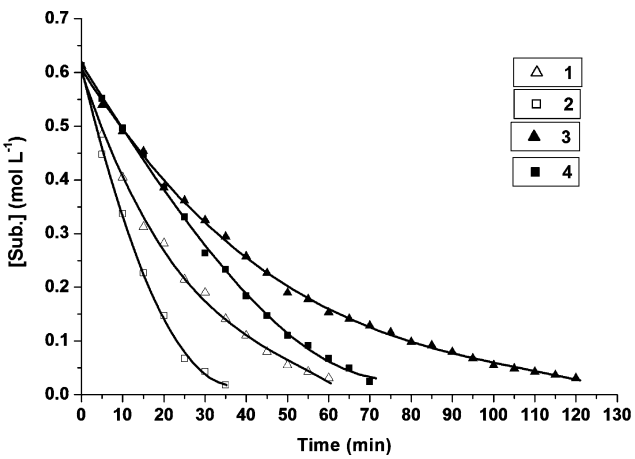


Fig. 4 Substrate concentration decay curves for hydroamination reactions of **A** catalyzed by **1–4** ([cat.] = 15.3 mmol L^{-1}) at 60 °C.

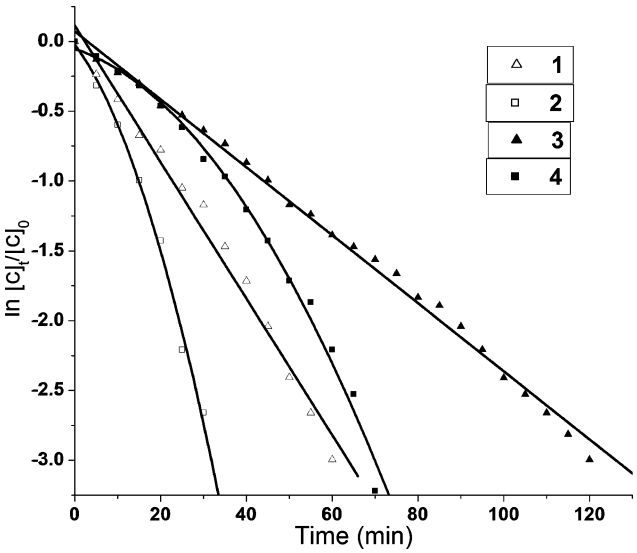


Fig. 5 Plots showing $\ln[c]_t/[c]_0$ *versus* time of hydroamination reactions of **A** catalyzed by **1–4** ([cat.] = 15.3 mmol L^{-1}) at 60 °C.

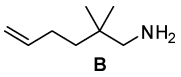
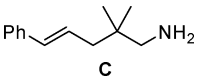
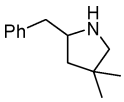
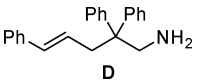
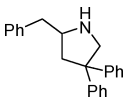
rearrangement of the insertion product to the secondary amide cannot be rule out *a priori*).[18g,19]

Complexes **1** and **2**, which have higher catalytic activity, were subsequently applied for the intramolecular hydroamination of a series of aminoalkenes (**B–D**) (Table 2). As observed in the intramolecular hydroamination of substrate **A**, **2** showed higher catalytic activity than **1**. Under mild conditions (60 °C) with a rather low catalyst loading (2.5 mol% **2**), all substrates were converted to the cyclic products in high conversions within short reaction times (0.5 to 7 h). According to Baldwin's rule for ring closure[20] that the formation of a six-membered ring is less favorable than that of a five-membered ring, a longer reaction time was needed for completing the reaction of substrate **B** in comparison to that for substrate **A** (Table 2, entries 1 and 2 *vs.* Table 1, entries 1 and 2). The internal alkene's intramolecular hydroamination is still challenging. As shown in Table 2, **2** is also highly active to the internal alkenes **C** and **D**. For substrate **C**, the cyclic product was formed nearly quantitatively with 2.5 mol% **2** in 7 h (Table 2, entry 4). For substrate **D**, bearing bulky phenyl substituents in the β-position to the amino group, the reaction rate was accelerated. The substrate was converted to the cyclic product in 98% yield within 0.5 h (Table 2, entry 6), this observed rate enhancement is consistent with the Thorpe–Ingold effect.[21]

Conclusions

A variety of pyridyl-1-azaallyl ligand precursors (**HL1–HL5**) can be readily synthesized *via* condensation of pyridine ketones with anilines in the presence of *p*-toluenesulfonic acid. The alkane elimination reactions of $Y(CH_2SiMe_3)_3(THF)_2$ with **HL1–HL3** gave complicated mixtures, while that with the more sterically demanding **HL4** or **HL5** afforded the monoalkyl complexes **1** and **2** supported by new tridentate pyridyl-1-azaallyl dianionic ligands. Thus not only the deprotonation of the β-diketimine backbone but also the activation of a sp^3 C–H bond of trimethylsilyl substituent (for **HL4**) or a sp^2 C–H bond of phenyl substituent (for **HL5**) on the pyridine ring of the ligand precursors were involved in

Table 2 Hydroamination of aminoalkenes catalyzed by **1** and **2**[a]

Entry	Substrate	Product	Catalyst	[Cat.]/[Sub.] (%)	Time (h)	Conv. (%)[b]	TOF (h^{-1})[c]
1	 B		**1**	2.5	36	60	0.67
2			**2**	2.5	3	97	12.9
3	 C		**1**	2.5	24	85	1.42
4			**2**	2.5	7	98	5.60
5	 D		**1**	2.5	0.75	97	51.7
6			**2**	2.5	0.5	98	78.4

[a] 15.3 mmol L^{-1} [cat.], 0.0613 mol L^{-1} [Cp_2Fe], 0.613 mol L^{-1} [sub.], 60 °C, 0.46 mL of C_6D_6 as solvent. [b] NMR conv. determined relative to ferrocene internal standard. [c] Turnover frequency.

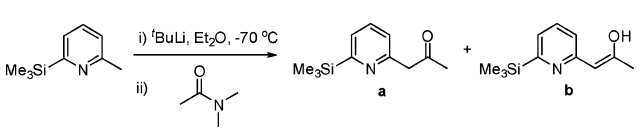
the reactions. The protonolysis reactions of **1** and **2** with one equivalent of 2,6-diisopropylaniline were highly selective and gave the corresponding monoanilide complexes (**L4–H**)YNHAr(THF) (**3**) and (**L5–H**)YNHAr(THF) (**4**). Complexes **1–4** showed moderate to good catalytic activities for intramolecular hydroamination of a series of aminoalkenes to give the Markovnikov-selective product. In the hydroamination catalyzed by the alkyl complexes, both the terminal Y–CH_2SiMe_3 bond and the metallacyclic Y–CH_2SiMe_2 (or Y–C^{Ar}) bond of the complexes initiated the reaction; while in the hydroamination catalyzed by the anilide complexes, the metallacyclic Y–CH_2SiMe_2 (or Y–C^{Ar}) bond of the complexes initiated the reaction solely, and the Y–$N^{anilide}$ bond was retained.

Experimental

General procedures

All operations were carried out under an atmosphere of argon 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, followed by vacuum transfer and stored in the glovebox. 2,6-Diisopropylaniline for the protonolysis reaction was purchased from Aldrich, dried over 4 Å molecular sieves, distilled under vacuum, and degassed by freeze–thaw–vacuum prior to use. 2-Methyl-6-aminopyridine, trimethylchlorosilane and phenylboronic acid were purchased from Acros and used without further purification. 1-(6-Methyl-pyridin-2-yl)-propan-2-one, 2-(6-methyl-pyridin-2-yl)-1-phenyl-ethanone,[22] 2-methyl-6-trimethylsilanyl-pyridine [23] and 2-methyl-6-phenyl-pyridine [24] were synthesized according to literature procedures. $Y(CH_2SiMe_3)_3(THF)_2$ was synthesized as reported.[25] ^1H 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.

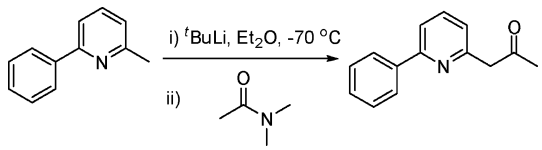
(1-(6-Trimethylsilyl-pyridin-2-yl)propan-2-one). 2-Methyl-6-trimethylsilanyl-pyridine (4.01 g, 24.0 mmol) was dissolved in 30 mL of dry Et_2O, and was then cooled to −70 °C. The pentane solution of ^{t}BuLi (1.6 M, 15 mL, 24.0 mmol) was added dropwise into the ether solution at −70 °C. After the addition, the reaction mixture was kept at −70 °C for an additional 30 min, then *N*,*N*-dimethyl-acetamide (2.10 g, 2.25 mL, 24.0 mmol) was added dropwise at −70 °C. The slurry brown mixture was warmed to room temperature, stirred for 2 h, and quenched by 10 mL of water. The mixture was extracted by dichloromethane (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4 overnight. The solvent was removed under vacuum, and the residues was purified by flash column chromatography to give the desired product as a yellow oil (1.83 g, 37% yield) (Scheme 4). The product existed as a mixture of two isomers, **a** (1-(6-trimethylsilyl-pyridin-2-yl)propan-2-one) and **b** (1-(6-trimethylsilyl-pyridin-2-yl)prop-1-en-2-ol), at room temperature. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.45 (t, $^3J_{HH}$ = 7.5 Hz, 0.6 H, Ar*H* of **a**), 7.28 (t, $^3J_{HH}$ = 7.2 Hz, 0.6 H, Ar*H* of **a**), 7.26 (t, $^3J_{HH}$ = 6.9 Hz, 1H, Ar*H* of **b**), 7.01 (d, $^3J_{HH}$ = 7.8 Hz, 0.6 H, Ar*H* of **a**), 6.72 (d, $^3J_{HH}$ = 6.6 Hz, 1H, Ar*H* of **b**), 6.61 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ar*H* of **b**), 5.20 (s, 1H, CC*H*=C(OH)(CH_3) of **b**), 3.85 (s, 1.2H, CH_2C=O(CH_3) of **a**), 2.16 (s, 1.8 H, CH_2C=O(CH_3) of **a**), 2.02 (s, 3H, CCH=C(OH)(CH_3) of **b**), 0.30 (s, 9H, SiMe_3 of **b**), 0.24 (s, 5.5 H, SiMe_3 of **a**). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 206.1 (CH_2C=O(CH_3)), 181.1 (CH=*C*(OH)CH_3), 168.1, 156.3, 154.8, 154.6, 135.7, 134.2, 126.5, 122.6, 120.1, 120.0 (Ar*C*), 91.1 (*C*H=C(OH)CH_3), 53.5 (CH_2C=O(CH_3)), 29.6 (CH_2C=O(*C*H_3)), 25.6 (CH=C(OH)*C*H_3), −2.0, −2.5 (SiMe_3). HRMS (EI) calcd for $C_{11}H_{17}NOSi$ (M^+) 207.1079; found 207.1074.



Scheme 4 Synthesis of 1-(6-trimethylsilyl-pyridin-2-yl)propan-2-one.

1-(6-Phenyl-pyridin-2-yl)propan-2-one. The procedure described for (1-(6-trimethylsilyl-pyridin-2-yl)propan-2-one) was used, but with 2-methyl-6-phenyl-pyridine (2.04 g, 12.0 mmol)

and ^{t}BuLi (1.6 M, 7.5 mL, 12.0 mmol), and the reaction time was extended to 6 h. 1-(6-Phenyl-pyridin-2-yl)propan-2-one was obtained as a yellow oil (1.31 g, 52% yield) (Scheme 5). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.64 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar*H*), 7.57–7.54 (m, 1H, Ar*H*), 7.44–7.35 (m, 3H, Ar*H*), 7.09 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 3.93 (s, 2H, $CH_2C{=}O(CH_3)$), 2.22 (s, 3H, $CH_2C{=}O(CH_3)$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 205.6 ($CH_2C{=}O(CH_3)$), 156.9, 154.5, 139.0, 137.2, 128.8, 128.7, 126.8, 122.2, 118.5 (Ar*C*), 53.2 ($CH_2C{=}O(CH_3)$), 29.9 ($CH_2C{=}O(CH_3)$). HRMS (EI) calcd for $C_{14}H_{13}NO$ (M^+) 211.0997; found 211.1000.



Scheme 5 Synthesis of 1-(6-phenyl-pyridin-2-yl)propan-2-one.

HL1. 1-(6-Methyl-pyridin-2-yl)-propan-2-one (6.01 g, 40.2 mmol), 2,6-diisopropylaniline (4.87 g, 40.2 mmol), *p*-toluenesulfonic acid (6.92 g, 36.4 mmol) and toluene (60 mL) were introduced into a 150 mL flask equipped with Dean–Stark apparatus. After refluxing for 15 h, the solvent was removed under vacuum. The orange viscous residue was dissolved in 100 mL of dichloromethane, washed by saturated aqueous Na_2CO_3 (100 mL), and dried over anhydrous Na_2SO_4 overnight. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to give **HL1** as a yellow oil (6.24 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 11.34 (s, 1H, MeC(N*H*)CH), 7.52 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar*H*), 6.88 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar*H*), 6.81 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 5.31 (s, 1H, C*H*), 2.58 (s, 3H, Py-CH_3), 2.45 (s, 6H, ArCH_3), 1.86 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 159.6 (imine *C*), 155.3, 150.0, 139.3, 137.2, 135.7, 127.9, 126.1, 117.7, 115.5 (Ar*C*), 93.7(*C*H), 24.6, 20.0, 18.6 (Ar*Me*, Py*Me* and *Me*C). HRMS (EI) calcd for $C_{17}H_{20}N_2$ (M^+) 252.1626; found 252.1630.

HL2. The procedure described for **HL1** was used, but with 2-(6-methyl-pyridin-2-yl)-1-phenyl-ethanone (4.20 g, 19.9 mmol), 2,6-dimethylaniline (2.41 g, 19.9 mmol), *p*-toluenesulfonic acid (3.42 g, 18.0 mmol) in toluene (60 mL), and the reaction time was extended to 22 h. **HL2** was obtained as a yellow solid (5.08 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 11.58 (s, 1H, PhC(N*H*)CH), 7.43 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 7.26–7.28 (m, 1H, Ar*H*), 7.24–7.26 (m, 1H, Ar*H*), 7.12–7.20 (m, 3H, Ar*H*), 6.90–6.96 (m, 3H, Ar*H*), 6.88 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar*H*), 6.75 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar*H*), 5.43 (s, 1H, C*H*), 2.49 (s, 3H, Py-CH_3), 2.22 (s, 6H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 159.0 (imine *C*), 155.5, 152.2, 139.7, 138.6, 135.9, 134.6, 128.2, 128.0, 127.9, 127.8, 127.6, 124.7, 119.2, 116.7 (Ar*C*), 97.8 (MeC(NH)*C*H), 24.6, 19.1 (Ar*Me* and Py*Me*). HRMS (EI) calcd for $C_{22}H_{22}N_2$ (M^+) 314.1783; found 314.1784.

HL3. The procedure described for **HL1** was used, but with 2-(6-methyl-pyridin-2-yl)-1-phenyl-ethanone (6.01 g, 28.4 mmol), 2,6-diisopropylaniline (5.47 g, 28.4 mmol), *p*-toluenesulfonic acid (4.90 g, 25.8 mmol) in toluene (100 mL), and the reaction time was extended to 20 h. **HL3** was obtained as a yellow solid (9.16 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 11.62 (s, 1H, N*H*), 7.44 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Py-*H*), 7.19–7.23 (m, 2H, Ar*H*), 7.11–7.17 (m, 4H, Ar*H*), 7.05 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.89 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Py-*H*), 6.75 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Py-*H*), 5.40 (s, 1H, C*H*), 3.41 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*Me$_2$), 2.46(s, 3H, Py-CH_3), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 159.3 (imine *C*), 155.4, 152.8, 145.8, 137.8, 136.1, 135.9, 128.2, 127.7, 127.5, 126.1, 122.9, 119.0, 116.4 (Py*C* and Ar*C*), 96.6 (MeC(NH)*C*H), 28.3, 25.6, 24.5, 21.8 (Ar*Me*$_2$ and Py*Me*). HRMS (EI) calcd for $C_{26}H_{30}N_2$ (M^+) 370.2409; found 370.2413.

HL4. The procedure described for **HL1** was used, but with 2,6-diisopropylaniline (1.56 g, 8.84 mmol), a mixture of 1-(6-trimethylsilyl-pyridin-2-yl)propan-2-one and 1-(6-trimethylsilyl-pyridin-2-yl)prop-1-en-2-ol (1.83 g, 8.84 mmol), a catalytic amount of *p*-toluenesulfonic acid (300 mg) in benzene (30 mL), and the reaction time was extended to 24 h. **HL4** was obtained as a yellow oil (1.50 g, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 11.51 (s, 1H, MeC(N*H*)CH), 7.41–7.37 (m, 1H, Ar*H*), 7.28–7.26 (m, 1H, Ar*H*), 7.19–7.17 (m, 2H, Ar*H*), 7.02 (d, $^3J_{HH}$ = 6.8 Hz, 1H, Ar*H*), 6.85 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar*H*), 5.15 (s, 1H, MeC(NH)C*H*), 3.31 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 1.68 (s, 3H, *Me*C(NH)CH), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$), 0.21 (s, 9H, Si*Me*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 164.3 (imine *C*), 160.3, 150.8, 147.6, 135.6, 133.5, 127.2, 122.8, 121.5, 120.3 (Ar*C*), 93.1 (MeC(NH)*C*H), 28.2 (*Me*C(NH)CH), 24.8, 22.9, 20.1 (Ar^i*Pr*), −1.7 (Si*Me*$_3$). HRMS (ESI) calcd for $C_{23}H_{35}N_2Si$ (M^+) 367.2564; found 367.2561.

HL5. The procedure described for **HL1** was used, but with 2,6-diisopropylaniline (1.16 g, 6.55 mmol), 1-(6-phenyl-pyridin-2-yl)propan-2-one (1.38 g, 6.55 mmol), *p*-toluenesulfonic acid (0.997 g, 5.24 mmol) and benzene (30 mL), and the reaction time was extended to 24 h. **HL5** was obtained as a yellow solid (0.70 g, 29% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 11.34 (s, 1H, MeC(N*H*)CH), 7.82 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ar*H*), 7.50 (t, $^3J_{HH}$ = 8.1 Hz, 1H, Ar*H*), 7.32–7.14 (m, 6H, Ar*H*), 6.86 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar*H*), 5.20 (s, 1H, MeC(NH)C*H*), 3.28 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 1.68 (s, 3H, *Me*C(NH)CH), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 159.9 (imine *C*), 154.9, 151.0, 147.6, 136.1, 135.6, 128.5, 128.3, 127.2, 126.4, 123.1, 119.4, 113.4 (Ar*C*), 93.2 (MeC(NH)*C*H), 28.3 (*Me*C(NH)CH), 25.0, 22.5, 20.2 (Ar^i*Pr*). HRMS (ESI) calcd for $C_{26}H_{31}N_2$ (MH^+) 371.2482; found 371.2495.

(L4-H)YCH$_2$SiMe$_3$(THF) (1). **HL4** (270 mg, 0.738 mmol) and $Y(CH_2SiMe_3)_3(THF)_2$ (400 mg, 0.811 mmol) were dissolved in 5 mL of hexane at room temperature. The reaction mixture was allowed to stand at room temperature for 24 h. The volatiles were removed under vacuum, and the residue was extracted by hexane (3 mL × 3). The extract was concentrated to approximately 1 mL, stored at −35 °C for 24 h to afford **1** as a pale yellow crystalline solid (348 mg, 77% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 7.07–7.03 (m, 1H, Ar*H*), 7.00 (s, 3H, Ar*H*), 6.93 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar*H*), 6.80 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar*H*), 5.36 (s, 1H, MeC(N)C*H*), 3.50–3.05 (br, 6H, THF-H^α and C*H*Me$_2$), 1.73 (s,

3H, *Me*C(N)CH), 1.21–1.09 (m, br, 16H, THF-H^{β} and CHMe_2), 0.61 (br, 6H, Si(CH_3)$_2$), 0.17 (s, 9H, $CH_2Si$$Me_3$), –0.36 (s, br, 2H, Me_2SiCH_2Y), –0.42 (d, $^2J_{YH}$ = 2.8 Hz, 2H, YCH_2SiMe_3). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 171.3 (imine *C*), 158.0, 157.4, 143.8, 135.5, 125.4, 124.0, 123.1, 121.3 (Ar*C*), 96.0 (MeC(N)*C*H), 69.5 (THF-C^{α}), 38.4 (d, $^1J_{YC}$ = 43.2 Hz, YCH_2SiMe_3), 28.1 (Ar^i*Pr*), 25.1 (br, YCH_2SiMe_2), 24.9, 23.7, 23.4, 23.0 (Ar^i*Pr*, C*Me* and THF-C^{β}). 3.6 (SiMe_3 and SiMe_2). Elemental analysis (%) calcd for $C_{31}H_{51}N_2OSi_2Y$: C 60.76, H 8.39, N 4.57; found: C 60.32, H 8.50, N 4.41.

(L5-H)YCH$_2$SiMe$_3$(THF) (2). **HL5** (217 mg, 0.587 mmol) and $Y(CH_2SiMe_3)_3(THF)_2$ (289 mg, 0.587 mmol) were dissolved in 5 mL of hexane at room temperature. The reaction mixture was allowed to stand at room temperature for 24 h. The volatiles were removed under vacuum, and the residue was washed by hexane (1.5 mL × 4) to afford **2** as a yellow solid (258 mg, 71% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.96–7.93 (m, 1H, Ar*H*), 7.60–7.58 (m, 1H, Ar*H*), 7.38–7.27 (m, 3H, Ar*H*), 7.20–7.15 (m, 1H, Ar*H*), 6.97 (s, 3H, Ar*H*), 6.85 (d, $^3J_{HH}$ = 8.1 Hz, Ar*H*), 5.51 (s, 1H, MeC(N)C*H*), 3.33 (br, 4H, THF-H^{α}), 3.27 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 1.79 (s, 3H, *Me*C(N)CH), 1.13 (br, 4H, THF-H^{β}), 1.06 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CHMe_2), 0.98 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CHMe_2), 0.09 (s, 9H, $YCH_2Si$$Me_3$), –0.43 (d, $^1J_{YH}$ = 3.3 Hz, 2H, YCH_2SiMe_3). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 187.5 (YC^{Ar}, $^2J_{YC}$ = 46.4 Hz), 161.2 (imine *C*), 157.7, 157.2, 148.7, 145.9, 142.8, 137.7, 135.9, 126.8, 126.7, 125.5, 124.8, 124.0, 121.9, 109.9 (Ar*C*), 96.3 (MeC(N)*C*H), 70.1 (THF-C^{α}), 38.0 (d, $^1J_{YC}$ = 43.0 Hz, YCH_2SiMe_3), 27.9 (Ar^i*Pr*), 25.5, 25.2, 24.0, 23.8 (Ar^i*Pr*, C*Me* and THF-C^{β}), 3.6 ($CH_2Si$$Me_3$). Elemental analysis (%) calcd for $C_{34}H_{47}N_2OSiY$: C 66.21, H 7.68, N 4.54; found: C 65.74, H 7.48, N 4.32.

(L4-H)Y[NH(2,6-^{i}Pr$_2$–C$_6$H$_3$)](THF) (3). A toluene solution of **1** (150 mg, 0.245 mmol, 1 mL) was added to 2,6-diisopropylaniline (43.4 mg, 0.245 mmol) at room temperature. The reaction mixture was allowed to stand at room temperature for 6 h. The volatiles were removed under vacuum, the residue was extracted by 2 mL of toluene. The volatiles were removed under vacuum, and the residues was washed by hexane (0.5 mL × 3) to afford **3** as a yellow crystalline solid (95.0 mg, 55% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 7.12 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 7.00 (s, 3H, Ar*H*), 6.96–6.94 (m, 1H, Ar*H*), 6.85–6.83 (m, 2H, Ar*H*), 6.72–6.69 (m, 1H, Ar*H*), 5.32 (s, MeC(N)C*H*), 4.75 (s, br, 1H, YN*H*Ar), 3.35 (br, 2H, C*H*Me$_2$), 3.21 (br, 4H, THF-H^{α}), 2.98 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 1.76 (s, 3H, *Me*C(N)CH), 1.40–0.90 (m, br, 24H, CHMe_2), 1.05 (m, 4H, THF-H^{β}), 0.68 (br, 3H, $YCH_2Si$$Me_2$), 0.49 (br, 3H, $YCH_2Si$$Me_2$), –0.20 – –0.28 (br, 2H, YCH_2SiMe_2). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 171.3 (imine *C*), 158.1, 158.0, 151.8, 144.5, 135.1, 132.9, 125.3, 124.9–123.9 (br), 122.9, 122.7, 121.0, 115.5 (Ar*C*), 96.3 (MeC(N)*C*H), 70.4 (THF-C^{α}), 30.7, 28.3, 24.8, 24.7, 24.3, 23.4 (Ar^i*Pr*, C*Me* and THF-C^{β}), 20.9 (d, $^1J_{YC}$ = 37.7 Hz, YCH_2SiMe_2), 4.6–4.4 (br, $YCH_2Si$$Me_2$), 2.0–1.8 (br, $YCH_2Si$$Me_2$). Elemental analysis (%) calcd for $C_{39}H_{58}N_3OSiY$: C 66.74, H 8.33, N 5.99; found: C 67.47, H 8.43, N 6.11.

(L5-H)Y[NH(2,6-^{i}Pr$_2$–C$_6$H$_3$)](THF) (4). Following the procedure described for **3**, but with **2** (100 mg, 0.162 mmol) and 2,6-diisopropylaniline (29.0 mg, 0.162 mmol), and the reaction time was 3 h. **4** was obtained as a yellow crystalline solid (74.0 mg, 64% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 7.91–7.89 (m, 1H, Ar*H*), 7.61–7.58 (m, 1H, Ar*H*), 7.33–7.31 (m, 2H, Ar*H*), 7.20–7.18 (m, 1H, Ar*H*), 7.09–7.05 (m, 3H, Ar*H*), 6.99 (s, 3H, Ar*H*), 6.79 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 6.73 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar*H*), 5.48 (s, 1H, MeC(N)C*H*), 4.96 (s, br, 1H, YN*H*Ar), 3.33 (br, 6H, THF-H^{α} and C*H*Me$_2$), 2.93 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, C*H*Me$_2$), 1.84 (s, 3H, *Me*C(N)CH), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CHMe_2), 1.25–0.95 (m, br, 16H, CHMe_2 and THF-H^{β}). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ (ppm) 186.0 (YC^{Ar}, $^2J_{YC}$ = 48.4 Hz), 161.1 (imine *C*), 161.0, 158.4, 156.8, 152.5, 152.4, 149.0, 145.5, 143.8, 137.6, 136.3, 132.4, 127.0, 126.5, 125.3, 124.4, 123.9, 122.8, 121.3, 115.4, 109.9 (Ar*C*), 96.1 (MeC(N)*C*H), 70.6 (THF-C^{α}), 31.2, 28.3, 25.5, 25.3, 24.3, 24.0, 23.0 (Ar^{i}Pr, C*Me* and THF-C^{β}). Elemental analysis (%) calcd for $C_{42}H_{54}N_3OY$: C 71.47, H 7.71, N 5.95; found: C 71.31, H 7.76, N 5.91.

Table 3 Crystallographic data and refinement for complexes **1**, **2**, and **4**

Complex	**1**	**2**	**4**
Empirical formula	$C_{31}H_{51}N_2OSi_2Y$	$C_{34}H_{47}N_2OSiY$	$C_{42}H_{54}N_3OY$
Formula weight	612.83	616.74	705.79
Colour	Yellow	Yellow	Yellow
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1$
a/Å	9.2709(11)	12.1821(11)	9.6805(11)
b/Å	17.719(2)	13.4126(12)	17.3700(19)
c/Å	21.296(2)	20.8185(18)	11.7004(13)
α/°	90	90	90
β/°	90	95.134(2)	98.877(2)
γ/°	90	90	90
Volume/Å^3	3498.2(7)	3388.0(5)	1943.9(4)
Z	4	4	2
Density (calculated)/ g cm^{-3}	1.164	1.209	1.206
F(000)	1304	1304	748
θ range/°	1.50–27.50	1.96–27.00	1.76–25.50
Reflections collected	21215	19537	10141
Unique reflections	7892	7358	6841
Unique reflections ($I > 2\sigma(I)$)	3954	3157	4156
Parameters	344	401	448
Goodness of fit	0.863	0.835	0.821
Final R indices [$I > 2\sigma(I)$]	0.0420, 0.0722	0.0453, 0.0712	0.0503, 0.0996
$\Delta\rho_{max,min}$/e Å^{-3}	0.506, –0.320	0.618, –0.337	0.487, –0.388

General procedure for intramolecular hydroamination. The yttrium complex, aminoalkene and the standard ferrocene were mixed in C_6D_6 and transferred into an 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 yttrium complex, aminoalkene and the standard ferrocene were mixed in C_6D_6 and transferred into an NMR tube The tube was immediately inserted into the probe of the Varian 400 MHz spectrometer, which had been previously set to 60 ± 0.1 °C. Data were corrected using four scans per time interval with a 5 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†. Suitable single crystals of **1**, **2** and **4** 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 ($\lambda = 0.71073$ 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 excepted for the hydrogen atom of anilide functional group in **4**, which was located in Fourier map. All calculations were carried out using the SHELXL-97 program. The software used is listed in the references.[26,27,28,29] Crystallographic data and refinement for **1**, **2** and **4** are listed in Table 3.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20872164, 20821002 and 21072209), Chinese Academy of Sciences, and Shanghai Municipal Committee of Science and Technology (10DJ1400104).

Notes and references

1 (*a*) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865; (*b*) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953; (*c*) W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119; (*d*) W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435.

2 (*a*) G. A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161; (*b*) S. Hong and T. J. Marks, *Acc. Chem. Res.*, 2004, **37**, 673.

3 (*a*) H. Yasuda, *J. Organomet. Chem.*, 2002, **647**, 128; (*b*) Z. M. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1; (*c*) J. Gromada, J. F. Carpentier and A. Mortreux, *Coord. Chem. Rev.*, 2004, **248**, 397.

4 (*a*) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (*b*) W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233–234**, 131; (*c*) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.

5 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.

6 (*a*) P. B. Hitchcock, M. F. Lappert and S. Tian, *J. Chem. Soc., Dalton Trans.*, 1997, 1945; (*b*) O. Eisenstein, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, L. Maron, L. Perrin and A. V. Protchenko, *J. Am. Chem. Soc.*, 2003, **125**, 10790; (*c*) A. Avent, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, *Dalton Trans.*, 2003, 1070; (*d*) A. G. Avent, C. F. Caro, P. B. Hitchcock, M. F. Lappert, Z. Li and X. H. Wei, *Dalton Trans.*, 2004, 1567; (*e*) A. G. Avent, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, *Dalton Trans.*, 2004, 2272; (*f*) P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, *Chem. Commun.*, 2005, 951.

7 (*a*) L. W. M. Lee, W. E. Piers, M. R. J. Elsegood, W. Clegg and M. Parvez, *Organometallics*, 1999, **18**, 2947; (*b*) P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2001, **20**, 2533; (*c*) P. G. Hayes, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 2132; (*d*) P. G. Hayes, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2003, **125**, 5622; (*e*) L. K. Knight, W. E. Piers, P. Fleurat-Lessard, M. Parvez and R. McDonald, *Organometallics*, 2004, **23**, 2087; (*f*) F. Lauterwasser, P. G. Hayes, S. Bräse, W. E. Piers and L. L. Schafer, *Organometallics*, 2004, **23**, 2234; (*g*) P. G. Hayes, W. E. Piers and M. Parvez, *Organometallics*, 2005, **24**, 1173.

8 (*a*) D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, H. G. Schmidt and M. Noltemeyer, *J. Organomet. Chem.*, 2002, **643–644**, 47; (*b*) D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, R. Herbst-Irmer, B. Walfort and D. Stalke, *Organometallics*, 2003, **22**, 2279; (*c*) G. B. Nikiforov, H. W. Roesky, T. Labalm, D. Vidovic and D. Neculai, *Eur. J. Inorg. Chem.*, 2003, 433; (*d*) A. M. Neculai, D. Neculai, H. W. Roesky, J. Magull, M. Baldus, O. Andronesi and M. Jansen, *Organometallics*, 2002, **21**, 2590; (*e*) A. M. Neculai, D. Neculai, H. W. Roesky and J. Magull, *Polyhedron*, 2004, **23**, 183.

9 (*a*) C. M. Cui, A. Shafir, J. A. R. Schmidt, A. G. Oliver and J. Arnold, *Dalton Trans.*, 2005, 1387; (*b*) L. F. Sa'nchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2005, **24**, 3792; (*c*) D. V. Vitanova, F. Hampel and K. C. Hultzsch, *Dalton Trans.*, 2005, 1565; (*d*) X. L. Liu, X. M. Shang, T. Tang, N. H. Hu, F. K. Pei, D. M. Cui, X. S. Chen and X. B. Jing, *Organometallics*, 2007, **26**, 2747.

10 (*a*) Y. M. Yao, Y. Zhang, Q. Shen and K. B. Yu, *Organometallics*, 2002, **21**, 819; (*b*) Y. M. Yao, Y. Zhang, Z. Q. Zhang, Q. Shen and K. B. Yu, *Organometallics*, 2003, **22**, 2876; (*c*) Z. Q. Zhang, Y. M. Yao, Y. Zhang, Q. Shen and W. T. Wong, *Inorg. Chim. Acta*, 2004, **357**, 3173; (*d*) M. Q. Xue, Y. M. Yao, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2005, **690**, 4685; (*e*) Y. M. Yao, Z. Q. Zhang, H. M. Peng, Y. Zhang, Q. Shen and J. Lin, *Inorg. Chem.*, 2006, **45**, 2175; (*f*) R. Jiao, X. D. Shen, M. Q. Xue, Y. Zhang, Y. M. Yao and Q. Shen, *Chem. Commun.*, 2010, **46**, 4118; (*g*) R. Jiao, M. Q. Xue, X. D. Shen, Y. Zhang, Y. M. Yao and Q. Shen, *Eur. J. Inorg. Chem.*, 2010, 2523.

11 (*a*) X. Xu, X. Y. Xu, Y. F. Chen and J. Sun, *Organometallics*, 2008, **27**, 758; (*b*) E. L. Lu, W. Gan and Y. F. Chen, *Organometallics*, 2009, **28**, 2318; (*c*) X. Xu, Y. F. Chen, G. Zou and J. Sun, *Dalton Trans.*, 2010, **39**, 3952; (*d*) E. L. Lu, Y. X. Li and Y. F. Chen, *Chem. Commun.*, 2010, **46**, 4469.

12 C. F. Caro, M. F. Lappert and P. G. Merle, *Coord. Chem. Rev.*, 2001, **605**, 219–221.

13 (*a*) A. S. Guram, R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, 1991, **113**, 1833; (*b*) B. J. Deelman, P. B. Hitchcock, M. F. Lappert, H. K. Lee and W. P. Leung, *J. Organomet. Chem.*, 1996, **513**, 281; (*c*) B. J. Deelman, P. B. Hitchcock, M. F. Lappert, W. P. Leung, H. K. Lee and T. C. W. Mak, *Organometallics*, 1999, **18**, 1444.

14 (*a*) R. J. Bowen, F. A. Fernandes and M. Layh, *J. Organomet. Chem.*, 2004, **689**, 1230; (*b*) L. Wang, C. Zhang and Z. X. Wang, *Eur. J. Inorg. Chem.*, 2007, 2477.

15 (*a*) B. J. Deelman, M. F. Lappert, H. K. Lee, T. C. W. Mak, W. P. Leung and P. R. Wei, *Organometallics*, 1997, **16**, 1247; (*b*) W. P. Leung, H Cheng, D. S. Liu, Q. G. Wang and T. C. W. Mak, *Organometallics*, 2000, **19**, 3001; (*c*) W. P. Leung, H. Cheng, H. L. Hou, Q. C. Yang, Q. G. Wang and T. C. W. Mak, *Organometallics*, 2000, **19**, 5431; (*d*) P. B. Hitchcock, M. F. Lappert, M Layh, D. S. Liu, R. Sablong and T. Shun, *J. Chem. Soc., Dalton Trans.*, 2000, 2301; (*e*) P. B. Hitchcock, M. F. Lappert and M. Layh, *J. Chem. Soc., Dalton Trans.*, 2001, 2409; (*f*) W. P. Leung, Q. W. Y. Ip, T. W. Lam and T. C. W. Mak, *Organometallics*, 2004, **23**, 1284; (*g*) W. P. Leung, C. W. So, Y. S. Wu, H. W. Li and T. C. W. Mak, *Eur. J. Inorg. Chem.*, 2005, 513; (*h*) C. Jin and Z. X. Wang, *New J. Chem.*, 2009, **33**, 659; (*i*) X. Chen, L. L. Guan, M. S. Eisen, H. F. Li, H. B. Tong, L. P. Zhang and D. S. Liu, *Eur. J. Inorg. Chem.*, 2009, 3488; (*j*) W. P. Leung, W. K. Chiu, K. H. Chong and T. C. W. Mak, *Chem. Commun.*, 2009, 6822.

16 (*a*) R. Kempe, *Eur. J. Inorg. Chem.*, 2003, 791; (*b*) R. Kempe, H. Noss and T. Irrgang, *J. Organomet. Chem.*, 2002, **647**, 12; (*c*) N. M. Scott and R. Kempe, *Eur. J. Inorg. Chem.*, 2005, 1319; (*d*) W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum and R. Kempe, *Chem.–Eur. J.*, 2006, **12**, 8969; (*e*) D. M. Lyubov, C. Döring, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, R. Kempe and A. A. Trifonov, *Organometallics*, 2008, **27**, 2905; (*f*) D. M. Lyubov, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, A. A. Trifonov, L. Luconi, C. Bianchini, A. Meli and G. Giambastiani, *Organometallics*, 2009, **28**, 1227; (*g*) L. Luconi, D. M. Lyubov, C. Bianchini, A. Rossin, C. Faggi, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, A. A. Trifonov and G. Giambastiani, *Eur. J. Inorg. Chem.*, 2010, 608.

17 (*a*) T. E. Müller, K. C. Hultzsch, M. Yus, F Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795; (*b*) G. F. Zi, *Dalton Trans.*, 2009, 9101.

18 (*a*) X. Yu and T. J. Marks, *Organometallics*, 2007, **26**, 365; (*b*) H. F. Yuen and T. J. Marks, *Organometallics*, 2008, **27**, 155; (*c*) G. A. Molander and E. D. Dowdy, *J. Org. Chem.*, 1998, **63**, 8983; (*d*) G. A. Molander and E. D. Dowdy, *J. Org. Chem.*, 1999, **64**, 6515; (*e*) M. R. Burgstein, H. Berberich and P. W. Roesky, *Organometallics*, 1998, **17**, 1452; (*f*) M. Rastatter, A. Zulys and P. W. Roesky, *Chem.–Eur. J.*, 2007, **13**, 3606; (*g*) S. Bambirra, H. Tsurugi, V. D. Leusen and B. Hessen, *Dalton Trans.*, 2006, 1157; (*h*) S. Ge, A. Meetsma and B. Hessen, *Organometallics*, 2008, **27**, 5339; (*i*) D. V. Gribkov, K. C. Hultzsch and F. Hampel, *Chem.–Eur. J.*, 2003, **9**, 4796; (*j*) D. V. Gribkov, K. C. Hultzsch and F. Hampel, *J. Am. Chem. Soc.*, 2006, **128**, 3748; (*k*) J. Collin, J. C. Daran, E. Schulz and A. A. Trifonov, *Chem. Commun.*, 2003, 3048; (*l*) I. Aillaud, D. Lyubov, J. Collin, R. Guillot, J. Hannedouhe, E. Schulz and A. A. Trifonov, *Organometallics*, 2008, **27**, 5929; (*m*) F. Lauterwasser, P. G. Hayes, S. Brase, W. E. Piers and L. L. Schafer, *Organometallics*, 2004, **23**, 2234; (*n*) L. J. E. Stanlake and L. L. Schafer, *Organometallics*, 2009, **28**, 3990; (*o*) Y. K. Kim and T. Livinghouse, *Angew. Chem., Int.*

Ed., 2002, **41**, 3645; (*p*) Y. K. Kim, T. Livinghouse and Y. Horino, *J. Am. Chem. Soc.*, 2003, **125**, 9560; (*q*) Q. Wang, L. Xiang, H. Song and G. Zi, *Inorg. Chem.*, 2008, **47**, 4319; (*r*) L. Xiang, Q. Wang, H. Song and G. Zi, *Organometallics*, 2007, **26**, 5323; (*s*) Y. Y. Yuan, Y. F. Chen, G. Y. Li and W. Xia, *Organometallics*, 2008, **27**, 6307; (*t*) X. Xu, Y. F. Chen, J. Feng, G. Zou and J. Sun, *Organometallics*, 2010, **29**, 549.
19 A. Motta, G. Lanza, I. L. Fragalà and T. J. Marks, *Organometallics*, 2004, **23**, 4097.
20 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
21 M. E. Jung and G. Piizzi, *Chem. Rev.*, 2005, **105**, 1735.
22 R. P. Cassity, L. T. Taylor and J. F. Wolfe, *J. Org. Chem.*, 1978, **43**, 2286.
23 S. G. Davies and M. R. Shipton, *J. Chem. Soc., Perkin Trans. 1*, 1991, 501.
24 H. Huang, H. Chen, X. Hu, C. Bai and Z. Zheng, *Tetrahedron: Asymmetry*, 2003, **14**, 297 .
25 M. F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.*, 1973, 126.
26 G. M. Sheldrick, *SADABS, An Empirical Absorption Correction Program for Area Detector Data*. University of Goettingen, Germany, 1996.
27 G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, University of Goettingen, Germany, 1997.
28 *SMART Version 5.628, Bruker Axs Inc*.
29 *SAINT + Version 6.22a, Bruker Axs Inc.*.

