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Synthesis of Divalent Ytterbium Terphenylamide and Catalytic Application for Regioselective Hydrosilylation of Alkenes

The dimeric heteroleptic ytterbium amido complex $[(2,6-(3,5-Me_2C_6H_3)_2C_6H_3NH)Yb(N(SiMe_3)_2)]_2$ (1) have been prepared and characterized. This divalent terphenylamido complex enabled highly regioselective hydrosilylation of various terminal alkenes with very low catalyst loading. Reaction of 1 with phenylsilane at high temperature led to the dehydrogenative coupling of the silane with terphenylamide ligand and redistributions of amide ligands via a hypervalent silane intermediate, which has been spectroscopically characterized.

Introduction

Hydrosilylation is an important and indispensable chemical reaction for the production of organosilanes, which are important intermediates in silicon industry, synthetic chemistry and material science.¹ Transition metal-catalyzed hydrosilylation of alkenes have been widely employed due to their high efficiency, chemoselectivity and broad substrate scopes. Lanthanide catalysts supported by various ligand frameworks for alkene hydrosilylation have also attracted much attention for several decades.²⁻⁴ Compared with transition metal catalysts, lanthanide alkyls and amides generally offer clean reaction in the hydrosilylation of alkenes and side reactions such as isomerization and dehydrogentaive silulation have been rarely observed. In addition, the interaction between highly electropositive lanthanide ions with alkenes is unique, leading to different selectivity and reaction modes from transition metal catalysts. As such, the development of highly regioselective and efficient lanthanide catalysts is highly desirable.

Lanthanide amides have shown interesting features for silane transformation. For example, La[N(SiMe₃)₂]₃ has been reported as a highly regioselective catalyst for hydrosilylation of alkene by Livinghouse.⁵ Roesky reported the bis(phosphinimino)methanide lanthanide amides for the highly efficient hydrosilylation.⁶ However, the divalent lanthanide amides have rarely been explored for the hydrosilylation of alkenes. Bulky terphenylamido ligand is important ligand to stabilize highly active organometallic complexes with low coordination number.⁷ Our group previously reported the dehydrosilylation reaction of Yb[N(SiMe₃)₂]₂(THF)₂ with the bulky terphenylaminosilane ArNHSiH₃ (Ar = 2,6-(3,5-Me₂C₆H₃)₂C₆H₃), leading to the formation of the first solvent-free monomeric

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ytterbium amide with the significant agostic interactions between ytterbium center and Si–H bonds.⁸ Herein we report the synthesis and characterization of a divalent ytterbium amide with the terphenylamido ligand (1). 1 can catalyze hydrosilylation of alkenes with high regioselectivity and high yields.

Results and discussion

Synthesis and molecular structure of [(ArNH)Yb(N(SiMe₃)₂)]₂ (1)

The reaction of terphenylamine ArNH₂ (Ar = 2,6-(3,5-Me₂C₆H₃)₂C₆H₃) with Yb[N(SiMe₃)₂]₂(THF)₂ yielded the divalent ytterbium amide (**1**, [(ArNH)Yb(N(SiMe₃)₂)]₂) in 79 % yield as dark purple crystals in toluene at room temperature (Scheme 1). Complex **1** is air- and moisture-sensitive, but significantly thermal-stable. For example, **1** persisted for several hours in refluxing toluene. Complex **1** is well soluble in THF and toluene and has been characterized by ¹H, ¹³C ²⁹Si NMR and IR spectroscopy. In the ¹³C NMR spectrum of **1**, the resonances at δ 152.19 and 147.56 ppm were assigned to the C(ispo) atom, indicating the Yb…arene interactions. The molecular structure of **1** has been determined by single-crystal X-ray analysis.





Single crystals of **1** suitable for X-ray diffraction studies were obtained by recrystallization from toluene solution at -40 °C. The molecular structure of **1** is depicted in Figure 1 together with selected bond lengths and angles. The X-ray single crystal analysis of **1** disclosed a dimeric structure with ArNH bridged the two Yb atoms, leading to a planar Yb₂N₂ ring. The average length (2.458(3) Å) of bridging Yb–N bonds is similar to those reported in the literature, for example, the complex [Yb{NPhSiMe₃}₂(THF)₂] (2.497

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Å), $[NaYb{N(SiMe_3)_2}_3]$ (2.46(2) Å) and the dimeric complexes $[Yb_2{N(SiMe_3)_2}_4]$ (2.502(3) Å).⁹ The Yb…arene interactions are also proved by the short Yb—C contacts of 2.804(5) Å and 2.805(5) Å.



Figure 1. ORTEP drawing of **1** with 50% probability ellipsoids. Hydrogen atoms and methyl groups on SiMe₃ have been omitted for clarity except the hydrogen atoms on N of terphenylamine. Selected bond lengths (Å) and angles (deg): Yb1–N2 2.434(3), Yb1–N1 2.486(3), Yb2–N2 2.477(3), Yb2–N1 2.436(3), Yb1–N3 2.293(3), Yb2–N4 2.305(3), Yb1–C34 2.804(5), Yb2–C16 2.805(5), N1–Yb1–N2 92.23(11), Yb1–N1–Yb2 87.54(10), N1–Yb2–N2 92.43(11), Yb1–N2–Yb2 87.78(10).

The reaction of complex 1 with phenylsilane

The reaction of 1 and phenylsilane has been investigated, which gave A as a dark green solid at room temperature after 6 hours (Scheme 2). Attempts to grow single crystals of A under various conditions were unsuccessful. However, the compound A can be spectroscopically characterized. The absorption for the Si-H bonds appeared at 2124 cm⁻¹ in IR spectrum of **A** which is similar to the normal Si-H absorption (2152 cm⁻¹).⁸ The resonance of hydrogen atoms on silicon was observed at 5.18 ppm with integration of two in ¹H NMR of **A**. This chemical shift is similar to those in f-element scandium and thorium complexes with (aryl)N(SiH₂Ph) ligands (5.53 and 5.59 ppm).¹⁰ The silane resonance of **A** displayed a triplet at -36.5 ppm with ${}^{1}J_{SiH}$ of 205.3 Hz in the pronton-coupled ${}^{29}Si$ NMR spectrum, which indicated the one-bond coupling of Si nucleus with two magnetic equivalent H nuclei. Based on these spectroscopic data and experimental phenomena,¹¹ it was proposed that PhSiH₃ attacked the bridging nitrogen atoms, leading to the dissociation and dehydrogenative Si-N coupling with the formation of A ArN(SiH₂Ph)YbN(SiMe₃)₂ without Si–H agostic interactions with Yb. Hill also suggested the similar complex in the reaction between magnesium amide and phenylsilane.¹²

Heating a solution of **A** in 1,2-dimethoxyethane (DME) at 80 °C for 3 hours yielded a black solution, from which the divalent ytterbium silylamido complex [ArNSiH(Ph)NAr]Yb(DME) (**2**) was isolated. In addition, NMR analysis of the crude mixture indicated the formation of solvated Yb[N(SiMe₃)₂]₂. These results indicated the ligand redistribution took place upon heating. The proposed mechanism for the formation of **2** is shown in Scheme 2. The ligand redistribution of Yb[N(SiMe₃)₂]₂. This type of redistribution is very common for lanthanide complexes. The next step may involve the desilylative cyclization via a hypervalent silicon intermediate in DME

solvent, leading to the final product 2.





Complex **2** has been structurally characterized by ¹H, ¹³C and ²⁹Si NMR and IR spectroscopy, elemental analysis and X-ray crystallographic study. The molecular structure of **2** is depicted in Figure 2 together with selected bond lengths and angles. Complex **2** featured the rare N–Yb–N–Si four-membered ring. The Yb—arene interactions were suggested by the short Yb–C29 and Yb–C30 distances of 2.868(3)Å and 2.818(3)Å.¹³ The Yb–N bond lengths (2.350(2) and 2.380(2)Å) are within the known range for ytterbium amides in the literature.¹⁴ In addition, the two Yb–N–Si angles 97.77(9)° and 96.64(10)° are very close to right angles. Hill reported the isolation of the similar magnesium bis(amido)silane complexe by the reaction between magnesium amide and phenylsilane.¹²



Figure 2. ORTEP drawing of **2** with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity except the hydrogen atoms on Si. Selected bond lengths (Å) and angles (deg): Yb1–N1 2.350(2), Yb1–N2 2.380(2), Si1–N1 1.713(2), Si1–N2 1.714(2), Yb–C29 2.868(3), Yb–C30 2.818(3), Yb1–Si1 3.0896(8), N1–Yb1–N2 66.74(7), Yb1–N1–Si1 97.77(9), Yb1–N2–Si1 96.64(10), N1–Si1–N2 98.78(11).

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Catalytic hydrosilylation of alkene

We investigated the catalytic behavior of 1 (0.5–1 mol % catalyst loading) for alkene hydrosilylation. Among these catalysis, we find that vinylarenes react with silanes can selectively (>95%) afford the Markovnikov products in more than 95% GC yields (Table 1). Due to the aryl-directed effect, 1, like the most of lanthanide catalysts, led to different regioselectivity from transition metal catalysts in the hydrosilylation of aryl-substituted alkenes.^{1a} The aliphatic alkenes react with silanes can selectively (>95%) afford the anti-Markovnikov products in more than 95% GC yields (Table 2). The heteroleptic amide 1 was found to be aslo active in the reaction of olefins with bulky groups (3d, 3e) in high yields and regioselectivity. Furthermore, the hydrosilylation of nonconjugated 4-vinylcyclohexene (3j) occurred chemoselectively at the terminal C=C double bond to afford the anti-Markovnikov products in 99% GC yields. Complex 1 also showed good activity in the hydrosilylation of the nonconjugated double bond in 1,5-hexadiene (3m), the reaction with two equivalents of silane yielded anti-Markovnikov products in high regioselectivity (95%).

We used three primary hydrosilanes: phenylsilane, n-hexylsilane and cyclohexylsilane as the silane sources in this transformation. n-Hexylsilane and cyclohexylsilane have not been employed in the hydrosilylation of alkenes with lanthanide catalysts previously. It was found that the activities of the hydrosilylation reactions in the order: phenylsilane > n-hexylsilane > cyclohexylsilane. The hydrosilylation reactions of vinylarenes and aliphatic alkenes with secondary silanes (Ph₂SiH₂, PhMeSiH₂ and Et₂SiH₂) and tertiary silanes (Ph₃SiH, PhMe₂SiH, Et₃SiH, and (EtO)₃SiH) did not occur in the presence of 1 mol % of 1 at 70 °C.

Table 2. Hydrosilylation of aliphatic alkenes^a

$RSiH_3 + Alkyl \xrightarrow{\frown} 0.5-1 \text{ mol\% 1} \xrightarrow{\bullet} Alkyl \xrightarrow{\bullet} SiH_2R$ $3g-m toluene, 70-90^{\circ}C, 6-8h 4g-m, 5g-m, 6g-m$						
product	R	т (°С)	time (h)	yield (%)	regiosel. (%)	
SiH ₂ R	4g Ph⁵	70	6	90	97	
	5g C ₆ H ₁₃ ^b	70	8	95	97.5	
	6g Cy ^c	90	8	90	97	
SiH ₂ R	4h Ph⁵	70	6	90	99	
	5h C ₆ H ₁₃ ^b	70	8	95	98	
	6h Cy ^c	90	8	90	97	
SiH ₂ R	4i Ph ^c	70	6	70	98	
	5i C ₆ H ₁₃ ^c	70	8	92	98	
	6i Cy ^c	90	8	93	99	
SiH ₂ R	4j Ph⁰	70	6	90	99	
	5j C ₆ H ₁₃ ^c	70	8	95	98	
	6j Cy ^c	90	8	93	99	
C ₄ H ₉ SiH ₂ R	4k Ph [℃]	70	6	75	97	
	5k C ₆ H ₁₃ ^c	70	8	95	98.5	
	6k Cy ^c	90	8	95	98	
C ₆ H ₁₃ SiH ₂ R	4l Ph⁰	70	6	80	97	
	5I C ₆ H ₁₃ ^c	70	8	95	98	
	6l Cγ ^ε	90	8	95	98	
C ₂ H ₄ SiH ₂ R ^d	4m Ph ^ւ	70	6	70	95	
	5m C ₆ H ₁₃ ^c	70	8	80	97	
C ₂ H ₄ SiH ₂ R	6m Cv ^c	90	8	80	95	

^a Conditions: alkene (1.0 mmol), silane (1.0 mmol), 0.2 ml toluene. The yields were isolated yields. The regioselectivity was determined by GC-MS analysis. ^b0.5 mol % 1. ^c 1 mol % 1. ^d silane (2.0 mmol)

Complex 1 exhibited high regioselectivity (>95%) and high activity (0.5-1 mol % catalyst loading) for these alkenes compared to the known trivalent lanthanide catalysts.² In general, lanthanidecatalyzed hydrosilylation of alkenes requires ca 5 mol% loadings of catalysts for high conversions. The comparable catalytic activity has

Table 1. Hydrosilylation of vinylarenes^a

	0.5-1 mol% 1			SiH₂R ↓		
RSiH₃ + Aryl	3a-f ^{tolue}	ene, 60-90°	, 60-90°C, 4-8h		Aryl Aryl 4a-f, 5a-f, 6a-f	
product	R	т (°С)	time (h)	yield (%)	regiosel. (%)	
SiH ₂ R	4a Ph⁵	60	4	95	99.9	
	5a C ₆ H ₁₃ ^b	60	4	97	99.9	
	6a Cy ^c	70	5	95	99.9	
SiH ₂ R	4b Ph⁵	60	4	95	98	
	5b C ₆ H ₁₃ ^b	60	4	97	98	
	6b Cy ^c	70	5	95	98	
SiH ₂ R MeO	4c Ph⁵	60	6	95	99.9	
	5c C ₆ H ₁₃ ^b	60	6	95	99	
	6c Cy ^c	80	6	95	99.5	
SIH ₂ R	4d Ph⁰	70	6	92	96	
	5d C ₆ H ₁₃ ^c	70	6	92	98	
	6d Cy ^c	90	8	90	98	
SiH ₂ R	4e Ph⁰	70	8	93	99	
	5e C ₆ H ₁₃ ^c	70	8	93	99	
	6e Cy ^c	90	8	90	99.8	
SiH ₂ R	4f Ph⁵	70	6	90	99	
	5f C ₆ H ₁₃ ^b	70	8	90	99	
	6f Cv ^c	90	8	90	99	

^a Conditions: alkene (1.0 mmol), silane (1.0 mmol), 0.2 ml toluene. The yields were isolated vields. The regioselectivity was determined by GC-MS analysis. ^b 0.5 mol % **1**.^c 1 mol % **1**.

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only been reported with lanthanocene catalysts by Marks and coworkers.^{2b} The hydrosilylation of alkene catalyzed by divalent lanthanide complexes is rare. Harder has reported the highly regioselective hydrosilylation of 1,1-diphenylethylene catalyzed by 5 mol % Yb(II) hydride complex with nacnac ligand (nacnac = CH{(CMe)(2,6-*i*Pr₂C₆H₃N)}₂).¹⁵ Takaki reported the hydrosilylation of aryl-substituted alkene in moderate activity by 10 mol % Yb(II) imine complex.¹⁶ However, the anti-Markovnikov products were obtained in these catalysis reported by Takaki, which were opposite to the Markovnikov products generated by the most of lanthanide catalysts.²

The catalytic behaviors of **1** have been compared with those of the simple divant ytterbium amide Yb[N(SiMe₃)₂]₂(THF)₂. **1** and Yb[N(SiMe₃)₂]₂(THF)₂ have the similar activity and regioselectivity for the hydroslilylation of less bulky aryl-substituted alkenes. However, **1** has much higher activity than Yb[N(SiMe₃)₂]₂(THF)₂ for the alkyl-substituted alkenes or bulky alkenes. For example, 95% GC yield and 98% regioselectivity **4i** can be produced by 1 mol % of **1** at 70 °C after 6 hours, but 60 % GC yield and 98% regioselectivity same produt was affored by 1% of Yb[N(SiMe₃)₂]₂(THF)₂ in the same catalytic conditions. And 96% GC yield and 99% regioselectivity **4e** can be produced by 1 mol % of **1** at 70 °C after 8 hours, but 33 % GC yield and 98% regioselectivity same product was affored by 1% of Yb[N(SiMe₃)₂]₂(THF)₂ in the same catalytic conditions. Furthermore, complex **2** displayed very low activity for all the alkenes in Table 1 and 2 in the optimized catalytic conditions of **1**.

The mechanism of the hydrosilylation reaction has be investigated. The byproduct PhSiH₂N(SiMe₃)₂ can be observed in the stoichiometric reaction of compound **1** with phenylsilane and styrene in the ¹H NMR spectrum and GC-MS analyses of the reaction mixtures. Based on preliminary results, it is postulated that the complex **A** underwent σ -bond metathesis in the presence of an excess of RSiH₃ to a hydride intermediate with the elimination of RSiH₂N(SiMe₃)₂ followed by alkene insertion into the Yb–H bond. Unfortunately, attempts to isolate these postulated intermediates were unsuccessful so far.

Conclusions

In summary, we have disclosed that the divalent ytterbium amide **1** is capable of catalyzing regioselective hydrosilylation (>95%) of vinylarenes and aliphatic alkenes. Complex **1** exhibited high regioselectivity and activity compared to known lanthanide amide catalysts probably due to the unique bonding of the terphenylamido ligand.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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Experimental section

General Considerations. All operations on air- and moisturesensitive materials were carried out under an atmosphere of dry argon by using modified Schlenk line and glove box techniques. All solvents were freshly distilled from sodium and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ¹H, ¹³C and ²⁹Si NMR spectroscopic data were recorded on a Bruker Mercury Plus AV400 spectrometer. Chemical shifts are referenced against external Me₄Si (¹H, ¹³C, ²⁹Si). Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br s = broad singlet, m = multiplet. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer and a Bruker Alpha infrared spectrometer with ATR operator station. GC-MS data were obtained with a Thermo Scientific TRACE 1300 & ISQ QD system, equipped with a TG-5MS column. Injection temperature 250 °C, helium flow 1.0 mL/min, temperature program 100 °C for 2 min to 280 °C, rate 10 °C/min. GC-MS data are reported as m/z (M^+) for characteristic peaks. Alkenes and dienes were vacuum-distilled over CaH₂ and then were degassed prior to use. The complexes Yb[N(SiMe₃)₂]₂(THF)₂¹⁷ and the terphenyl amine ArNH₂ (Ar = 2,6-(3,5-Me₂C₆H₃)₂C₆H₃)¹⁸ were prepared according to literature procedures. Phenylsilane, nhexylsilane and cyclohexylsilane were purchased from Aldrich and dried over CaH₂ prior to use. Other reagents and solvents were purchased from chemical vendors and used as received unless otherwise noted.

Crystal structure determinations: CCDC 1545003 (2) and 1545004 (1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Preparation of [(ArNH)Yb(N(SiMe₃)₂)]₂(1). ArNH₂ (1.5 g, 5.0 mmol) in toluene (10 mL) was added to a mixture of $Yb[N(SiMe_3)_2]_2(THF)_2$ (3.2 g, 5 mmol) in toluene (10 mL) at room temperature. The color immediately changed from orange red to atropurpureus. The mixture was stirred for 6 h to yield a purple black solution. The solvents were removed under vacuum, and the remaining residue was washed by hexane (10 mL) and dried under vacuum to give 1 as a atropurpureus powder solid (2.5 g, 79%). M. P.: 190-192 °C. IR (KBr cm⁻¹): v (N–H): 3383. ¹H NMR (C_6D_6 , 400 MHz, 298K): δ (ppm) 0-0.31 (m, 36H, Si(CH₃)₃), 1.84-2.30 (m, 24H, Ar-CH₃), 4.57 (br, 2H, NH), 6.20–7.42 (m, 18H, Ar-H). ¹³C NMR (C₆D₆, 101 MHz, 298K): δ (ppm) 5.7 (Si(CH₃)₃), 21.6 (Ar-CH₃), 115.6, 125.0, 131.6, 132.5, 138.3, 142.3, 147.6, 152.2 (Ar-C). ²⁹Si NMR (C₆D₆, 79 MHz, 298K): δ (ppm) – 12.72. Anal. Calcd. for $C_{56}H_{80}N_4Si_4Yb_2$ (1268): C, 53.06; H, 6.36; N, 4.42. Found: C, 52.10; H, 6.05; N, 4.96. The solution of 1 in dilute toluene stored at -40 °C for 48 h afforded atropurpureus crystals.

Preparation of [ArNSiH(Ph)NAr]Yb(DME) (2). PhSiH₃ (0.22 g, 2.0 mmol) in toluene (5 mL) was added to a stirred solution of **1** (1.3 g, 1.0 mmol) in toluene (10 mL) at room temperature, and stirred for 6 h to yield a dark green solution. The solvents were removed under vacuum, and the remaining oily residue was extracted with *n*-hexane (50 mL). The exact was concentrated (ca.10 mL) and stored at -40 °C for 24 h to give **A** (1.0 g, 70%) as a dark green solid. M. P.: 140 °C (decomp.). IR (KBr, cm⁻¹): v (Si-H): 2124. ¹H NMR (C₆D₆, 400 MHz, 298K): δ (ppm) 0.16 (s, 18H, Si(CH₃)₃), 2.05 (br, 12H, Ar-CH₃), 5.18 (br, 2H, SiH₂), 6.58–7.62 (m, 14H, Ar-H). ¹³C NMR (C₆D₆, 101

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MHz, 298K): δ (ppm) 3.5 (Si(CH₃)₃), 21.3 (Ar-CH₃), 114.2, 129.3, 129.8, 130.0, 131.6, 133.8, 134.0, 135.9, 138.0, 139.4, 143.9, 153.0 (Ar-C). Proton-coupled 29 Si NMR (C₆D₆, 79 MHz, 298K): δ (ppm) – 36.3 (t, ${}^{1}J_{SiH}$ = 205.3 Hz, PhSiH₂), 5.7 (m, Si(CH₃)₃). A (0.74 g, 1.0 mmol) dissolved in DME (10 mL) and then the mixture was heated to 80 $^{\circ}\text{C}$ and stirred for 3 h to yield a black solution. The solvents were removed under vacuum, and the remaining purple black oily residue was extracted with toluene (10 mL). The exact was concentrated (ca. 2 mL) and stored at -40 °C for 24 h to give 2 (0.24 g, 25%) as a black solid. M.P.: 167–172 °C. IR (KBr, cm⁻¹): v (Si-H): 1798. ¹H NMR (C₆D₆, 400 MHz, 298K): δ (ppm) 2.12 (s, 24H, Ar-CH₃), 2.92 (br, 10H, DME-H), 4.10(s, 1H, SiH), 6.61-7.41(m, 23H, Ar-H). ¹³C NMR (C₆D₆, 101 MHz, 298K): δ (ppm) 21.7 (Ar-CH₃), 59.5, 73.5 (DME-C), 116.8, 124.6, 130.6, 133.5, 137.8, 139.0, 145.2, 148.4, 151.3 (Ar-C). ²⁹Si NMR (C₆D₆, 79 MHz, 298K): δ (ppm) –49.65. Anal. Calcd. For C₅₄H₅₈N₂O₂SiYb(968.18): C, 66.99; H, 6.04; N, 2.89; Found: C, 65.34; H, 6.50; N, 2.06. The solution of 2 in dilute toluene stored at –40 °C for 24 h afforded black crystals.

General Procedures for the Catalytic Hydrosilylation Reactions. In an Ar glove box, a Schlenk tube (10 ml) was charged with catalyst **1** (0.005–0.01 mmol) and toluene (0.2 mL). And then silane (1.0 mmol) and the appropriate alkene or diene (1.0 mmol) were added by microsyringe. The Schlenk tube was quickly removed from the glovebox. The reaction mixture was stirred 4–8 h at 60–90 °C using oil bath, and then the resulting solution was concentrated in vacuum. The crude product was purified by column chromatography on silica gel with hexane as eluent.

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ARTICLE

Synthesis of Divalent Ytterbium Terphenylamide and Catalytic Application for Regioselective Hydrosilylation of Alkenes

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Divalent ytterbium terphenylamide exhibited high regioselectivity and activity in hydrosilylation of alkenes with low catalyst loading.