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# Samarium(II) Monoalkyl Complex Supported by a β-diketiminato Based Tetradentate Ligand: Synthesis, Structure and Catalytic Hydrosilylation of Internal Alkynes

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**Abstract:** The synthesis and catalytic applications of trivalent rareearth metal alkyl complexes have been well developed, but the chemistry of divalent rare-earth metal alkyl complexes much lagged behind. Here we report the synthesis, structure and catalytic application of a samarium(II) monoalkyl complex supported by a βdiketiminato based tetradentate ligand, [LSmCH(SiMe<sub>3</sub>)<sub>2</sub>] (L = [MeC(NDipp)CHC(Me)NCH<sub>2</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sup>-</sup>, Dipp = 2,6-('Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). This complex is synthesized via the salt metathesis reaction of samarium iodide [LSm( $\mu$ -I)]<sub>2</sub> and KCH(SiMe<sub>3</sub>)<sub>2</sub> in 63% yield. Its structure is characterized by the single-crystal X-ray diffraction, showing a distorted square pyramid coordination geometry. This samarium(II) monoalkyl complex exhibits high catalytic activity in hydrosilylation of aryl and methyl-substituted unsymmetrical internal alkynes with secondary hydrosilanes, selectively providing the  $\alpha$ -(*E*) products in high yields.

#### Introduction

Rare-earth metal alkyl complexes have been of great research interests in the past three decades, such type of complexes exhibit rich reactivity and applications in both stoichiometric and catalytic reactions.<sup>[1]</sup> However, the research was dominated by trivalent rare-earth metal alkyl complexes, the related derivatives of divalent rare-earth metal complexes remain scare and much less explored, owing to their reducibility, strong tendency to undergo ligand redistribution, and β-hydrogen elimination or βhydrogen abstraction.<sup>[2,3]</sup> It is also worth noting that the synthesis of samarium(II) alkyl complexes is even more challenging than that of ytterbium(II) and europium(II) complexes, due to samarium(II) ion's stronger reducibility and larger size. Until 1997, Izod and coworkers reported the first crystallographically characterized samarium(II) alkyl complex [Sm{C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>OMe)}<sub>2</sub>(THF)], which contains two bulky alkyl ligands.[3a] The samarium(II) monoalkyl complexes are of more importance, as their reactivity can be efficiently tuned by an anionic supporting ligand. The first example of such complexes,  $[(C_5Me_5)Sm{CH(SiMe_3)_2}(C_5Me_5)K(THF)_2]_n$ , was reported by Hou and coworkers in 2001.<sup>[3g,h]</sup> This complex can be viewed as a neutral samarium(II) alkyl species " $[(C_5Me_5)Sm{CH(SiMe_3)_2}]$ " stabilized by  $[(C_5Me_5)K]$ . Later, Takats and coworkers used a bulky pyrazolylborate ligand Tp<sup>tBu,Me</sup> to stabilize samarium(II) monoalkyl complex  $[(Tp^{fBu,Me})SmCH(SiMe_3)_2]$ .<sup>[3i]</sup> Overall, to the best of our knowledge, there are only three samarium(II) monoalkyl complexes have been reported up to date,<sup>[3g-i]</sup> and their catalytic applications are little explored.<sup>[3g,h]</sup> It should be noted that for the stabilization of Sm(II)–C bond Trifonov and coworkers recently designed and synthesized several samarium(II) benzyl derivatives<sup>[4]</sup>, and they also used the complexes as the catalysts for the intermolecular hydrophosphination of olefins.<sup>[4b]</sup>

Vinylsilanes have been widely used as important building blocks in organic synthesis.<sup>[5]</sup> Hydrosilylation of alkynes, the addition of a Si-H bond across C-C triple bond, represents the most straightforward method and the most atom-economical reaction for the synthesis of vinylsilanes.<sup>[6]</sup> In contrast to terminal alkynes or symmetrical internal alkynes hydrosilylation, hydrosilylation of unsymmetrical internal alkynes has met with limited success due to the increased difficulty in regiocontrol. Some late transition metals,<sup>[7]</sup> manganese<sup>[8]</sup> and titanium catalysts<sup>[9]</sup> have been reported for this reaction recently. Hydrosilylation of unsymmetrical internal alkynes catalysed by rare-earth metal complexes were little explored, and no successful example of rare-earth metal catalysed stereo- and regio-selective hydrosilylation of aryl and alkyl-substituted unsymmetrical internal alkynes with secondary hydrosilanes has been reported.<sup>[10]</sup> We have developed a β-diketiminato based tetradentate ligand (L) (L  $[MeC(NDipp)CHC(Me)NCH_2CH_2N(Me)CH_2CH_2NMe_2]^-$ , Dipp = 2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which can stabilize a series of highly reactive rareearth metal complexes.[11] Recently, we synthesized a ytterbium(II) monoalkyl complex based on the ligand L, and found

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that the complex can efficiently catalyse the homo- and crosscoupling of primary arylsilanes.<sup>[12]</sup> Interestingly, this ligand can also stabilize the synthetically challenging samarium(II) monoalkyl complex. Herein, we report the synthesis and structure of this samarium monoalkyl complex and its catalytic application for the hydrosilylation of aryl and methyl-substituted unsymmetrical internal alkynes with secondary hydrosilanes.

#### **Results and Discussion**

Reaction of  $SmI_2(THF)_2$  with a potassium salt of ligand KL (L =  $[MeC(NDipp)CHC(Me)NCH_2CH_2N(Me)CH_2CH_2NMe_2]^-, Dipp =$ 2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in THF at room temperature provided a divalent samarium iodide  $[LSm(\mu-I)]_2$  (1) as a green solid in 62% yield (Scheme 1). The complex was characterized by <sup>1</sup>H NMR spectroscopy and elemental analysis, and its structure was further confirmed by single-crystal X-ray crystallography. The molecular structure of 1, shown in Figure 1, is similar to that of  $[LYb(\mu-I)]_2$ .<sup>[12]</sup> In the complex, each samarium(II) ion is coordinated by four nitrogen atoms of the ligand (L) and two bridging iodides, displaying a distorted octahedral geometry. Although N3 and N4 atoms of L both act as the neutral donors, the distance from N4 atom to samarium ion is significantly longer, 2.786(5) Å vs 2.683(4) Å. The two Sm-I bond lengths are not equal, one is 3.324(1) Å while the other is 3.286(1) Å. The shorter Sm–I bond length is comparable with those in  $[(tBu_4Carb)Sm(\mu-$ I)(THF)<sub>2</sub>]<sub>2</sub> (3.2665(4) and 3.2853(4) Å).<sup>[4a]</sup>



Scheme 1. Synthesis of samarium(II) diketiminato iodide complex 1 and alkyl complex 2.



Figure 1. Molecular structure of complex 1 with ellipsoids at 30% probability level. Dipp isopropyl groups and hydrogen atoms were omitted for clarity. Selected bond distances [Å] and angles [°]: Sm–N1 2.521(4), Sm–N2 2.564(4), Sm–N3 2.683(4), Sm–N4 2.786(5), Sm–I 3.324(1), Sm–I(A) 3.286(1), Sm-I Sm(A) 94.31(2), I-Sm-I(A) 85.69(2).

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After the divalent samarium iodide 1 was obtained, the synthesis of the corresponding samarium alkyl complex was carried out. Reaction of 1 with KCH<sub>2</sub>SiMe<sub>3</sub> did not give the divalent samarium alkyl complex, which is possibly due to its low stability. On the other hand, complex 1 reacts with KCH(SiMe<sub>3</sub>)<sub>2</sub> in THF to afford a divalent samarium alkyl complex [LSmCH(SiMe<sub>3</sub>)<sub>2</sub>] (2) as a deep red solid in 63% yield (Scheme 1), the bulky alkyl group is benefit for the stabilization of the complex. Complex 2 was characterized by <sup>1</sup>H NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography (Figure 2). The samarium(II) ion in 2 has a distorted square pyramid coordination geometry, with four nitrogen atoms of L forming the basal plane and a carbon atom of the alkyl ligand occupying the apical position. The Sm-C bond length is 2.707(5) Å, which is slightly longer than that of 2.652(9) Å in [(C5Me5)Sm{CH(SiMe3)2}(C5Me5)K(THF)2]n<sup>[3g]</sup> and 2.667(5) Å in (Tp<sup>fBu,Me</sup>)SmCH(SiMe<sub>3</sub>)<sub>2</sub>.<sup>[3i]</sup> Similar to that observed in 1, the Sm-N4 bond length (2.806(4) Å) is longer than the Sm-N3 bond length (2.693(3) Å).



Figure 1. Molecular structure of complex 2 with ellipsoids at 30% probability level. Dipp isopropyl groups and hydrogen atoms were omitted for clarity. Selected bond distances [Å] and angles [°]: Sm–N1 2.508(3), Sm–N2 2.512(4), Sm–N3 2.693(3), Sm–N4 2.806(4), Sm–C25 2.707(5).

Both divalent ytterbium alkyl complex [LYbCH<sub>2</sub>SiMe<sub>3</sub>] and divalent samarium alkyl complex 2 were tested for catalytic hydrosilylation of phenylmethylacetylene with phenylsilane. Unsurprisingly, when [LYbCH<sub>2</sub>SiMe<sub>3</sub>] was used as catalyst, redistribution of phenylsilane was dominated and no hydrosilylation product was detected. [LYbCH<sub>2</sub>SiMe<sub>3</sub>] has been reported to be a highly efficient catalyst for the redistribution of primary arylsilanes.<sup>[12]</sup> However, by using 2 mol% of 2, 24% yield of vinylsilanes were observed at 30 °C within 1.5 hours (Table 1, entry 1). The reaction is highly stereo- and regio-selective, only syn-addition products are produced and the ratio of  $\alpha$ -(*E*) product (A) to  $\beta$ -(E) product (B) is 11:1. The domination of the  $\alpha$ -(E) product reveals that the electronic effects play the major role in regio-control, as the phenyl group stabilizes partial negative charge on the benzylic carbon of the reaction intermediate when it is located  $\alpha$  to metal ion, this reaction intermediate is formed from an addition of Sm-H bond of the catalytic species to the C-C triple bond of the phenylmethylacetylene. If the steric effects play the major role, the reaction produces the  $\beta$ -(*E*) product, which minimizes the repulsion between the phenyl and silyl groups. When the reaction time was prolonged to 3 hours, the yield of vinylsilanes slightly increased to 31%, indicating a quick decay of

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the catalytic activity. Recently, Cui, Li and their coworkers reported the dihydrosilylation of internal alkynes catalysed by a lanthanum bis(amido) ate complex.<sup>[13]</sup> For the hydrosilylation of phenylmethylacetylene with phenylsilane catalysed by 2, no dihydrosilylation product was observed. Then, we examined the capacity of **2** to perform the hydrosilylation of phenylmethylacetylene with various hydrosilanes (Table 1). The reaction of phenylmethylacetylene with hexylsilane gave the synaddition products in 47% yield in 3 h, the regioselectivity ( $\alpha$ -(E) :  $\beta$ -(E)) is up to 18:1 (Table 1, entry 2). Interestingly, when the secondary hydrosilanes, diphenylsilane and phenylmethylsilane, were used, the vinylsilanes were produced in high yields with excellent stereo- and regio-selectivity (Table 1, entries 3 and 4). Especially, the reaction of phenylmethylacetylene with phenylmethylsilane provided the syn-addition products in 94% yield, and the selectivity for the  $\alpha$ -(E) isomer is up to 95%. It should be noted when phenylmethylsilane was used as the hydrosilvlation reagent, the color of reaction solution kept bark brown during the catalytic reaction. When phenylsilane was used, the color of reaction solution was bark brown at beginning, and then slowly changed into yellow. After the color of reaction solution changed into vellow, the catalytic reaction stopped. resulting in a low product yield when phenylsilane was used. These observations suggested that catalytic active species likely to be a Sm(II) species: the color of the Sm(III) species is generally lighter than that of the Sm(II) species. For the reactions of phenylmethylacetylene with diethylsilane or triphenylsilane, no hydrosilylation product was observed.

complex 2. <sup>[a]</sup>		raneae ny	areen		
	<b>2</b> (2 mol%)	H <sub>3-n</sub> R <sub>n</sub> Si	н	H SiR <sub>n</sub> H <sub>3-n</sub>	
Me + R <sub>n</sub> SiH <sub>4-n</sub>	30 °C C₂D₂	Ph	Me	+ Ph Me	

Table 1 Hydrosilylation of PhCCMe with various hydrosilanes catalyzed by

		30 ºC, C <sub>€</sub>	;D <sub>6</sub> Рһ́	Me Phí A	Me B	
		1.5 h		3	3 h	
entry	R <sub>n</sub> SiH <sub>4-n</sub>	yield (%) <sup>[b]</sup>	ratio (A:B) <sup>[b]</sup>	yield (%) <sup>[b]</sup>	ratio (A:B) <sup>[b]</sup>	
1	PhSiH₃	24	11:1	31	11:1	
2	HexSiH <sub>3</sub>	38	18:1	47	18:1	
3	Ph <sub>2</sub> SiH <sub>2</sub>	78	19:1	87	19:1	
4	PhMeSiH <sub>2</sub>	83	19:1	94	19:1	
5	$Et_2SiH_2$	0	-	0	<u>-</u>	
6	Ph₃SiH	0		0	-	

[a] Reactions were conducted with 2 mol% of complex 2 in C<sub>6</sub>D<sub>6</sub> at 30 °C. [b] Determined by quantitative <sup>1</sup>H NMR spectroscopy using mesitylene as the internal standard.

As we mentioned in the introduction, the stereo- and regioselective hydrosilylation of unsymmetrical internal alkynes with secondary hydrosilanes is of interests. Therefore, the hydrosilylation of various such alkynes with phenylmethylsilane catalysed by complex **2** were studied (Table 2). The reaction of *p*methyl phenylmethylacetylene with phenylmethylsilane gave the *syn*-addition products in 91% yield, and the selectivity for the  $\alpha$ -(*E*) product is 94%, both yield and selectivity are similar to those of the reaction of phenylmethylacetylene. When the methyl

substituent moves to the meta-position, the yield and selectivity are up to 98% and >97%, respectively. Introducing a methyl group to the ortho-position of phenylmethylacetylene causes a decrease of the product yield to 72%, but the selectivity for the  $\alpha$ -(E) product is excellent (>97%). The p-OMe, NMe2 and F substituted phenylmethylacetylene also undergo the hydrosilylation to give the syn-addition products in high yields (84~90%), and the selectivity for the  $\alpha$ -(*E*) products are also high (91~94%). Scheme 2 shows the pathways for the formation of  $\alpha$ -(*E*) (**A**) and  $\beta$ -(*E*) (**B**) products. The reaction of phenylethylacetylene with phenylmethylsilane gave the products in low yield (16%) (Table 2, entry 8), this is possibly due to the steric effect from the ethyl group, which hinders the addition of the Sm-H bond of the catalytic species to the C-C triple bond of the alkyne. Furthermore, Complex 2 can catalyse the hydrosilylation of 3thienylmethylacetylene with phenylmethylsilane, giving the corresponding  $\alpha$ -(E) product in high yield and high selectivity (Table 2, entry 9). This is surprising, we had thought that the coordination of thienvl group with rare-earth metal ion would significantly decrease the catalytic activity. On the hand, the reaction of 2-thienylmethylacetylene gave the product in very low vield and selectivity (Table 2, entry 10). The low vield observed in this reaction can be associated with a 4-member chelating structure formed by sulphur and carbon atoms from the 2thienvlmethylacetylene after the addition of the Sm-H bond of the metal species to the C-C triple bond of the alkyne, which reduces reactivity. When 3-furylmethylacetylene the and 2furylmethylacetylene are used as the substrates, the yields of the products are lower in comparison with the reactions with 3thienylmethylacetylene and 2-thienylmethylacetylene. This is reasonable as the coordination between furyl oxygen atom and rare-earth metal ion is generally stronger than that between thienyl sulphur atom and rare-earth metal ion, and this strong coordination reduces the reactivity. We have also studied the hydrosilylation of unsymmetrical internal alkynes containing two alkyl substituents with phenylmethylsilane, the reactions gave a complicated mixture. In these cases, the hydrosilylation is slow, therefore the redistribution of phenylmethylsilane becomes significant. This redistribution reaction produces new hydrosilanes, such as methylsilane (MeSiH<sub>3</sub>), which participate in the hydrosilylation of alkynes.

Table 2. Hydrosilylation of internal alkynes with $PhMeSiH_2$ catalyzed by complex $2.^{[a]}$				
R <sup>1</sup> R <sup>1</sup> = aryl g R <sup>2</sup> = alkyl g	R <sup>2</sup> + PhMeSiH <sub>2</sub> · roup group	2 (2 mol%) 30 °C, C <sub>6</sub> D <sub>6</sub> 3 h	MePhHSi H R <sup>1</sup> R A	$H + H = SiHPhMe$ $H^{2} + R^{1} = R^{2}$ $B$
entry	alkyne		yield (%) <sup>[b]</sup>	ratio (A:B) <sup>[b]</sup>
1		Me	94	19 : 1
2	~>-=	-Me	91	17 : 1
3		Ме	98	>30 : 1
4		Ле	72	>30 : 1
5	MeO-	≡—Me	90	12 : 1

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6	Me <sub>2</sub> N-	90	16 : 1
7	F-	84	11 : 1
8	EtEt	16	>30: 1
9	SMe	91	13 : 1
10	€Me	19	2:1
11	0Me	44	6 : 1
12	€Me	4.5	-

[a] Reactions were conducted with 2 mol% of complex 2 in C<sub>6</sub>D<sub>6</sub> for 3 h at 30 °C. [b] Determined by quantitative <sup>1</sup>H NMR spectroscopy using mesitylene as the internal standard.



**Scheme 2.** Regioselectivity in the catalytic hydrosilylation of unsymmetrical internal alkynes with phenylmethylsilane.

#### Conclusion

In summary, a samarium(II) monoalkyl complex was synthesized by using a  $\beta$ -diketiminato based tetradentate ligand L (L = [MeC(NDipp)CHC(Me)NCH<sub>2</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sup>-</sup>, Dipp  $2,6-(Pr)_2C_6H_3$ ) as the supporting ligand. The single-crystal X-ray crystallography study showed the complex exits as a monomer with a terminal alkyl ligand, the samarium(II) ion is 5-coordinate and has a distorted square pyramid coordination geometry. This samarium(II) monoalkyl complex can efficiently catalyse the hydrosilylation of various arylmethylacetylenes with secondary hydrosilanes under mild conditions, and the selectivity for the  $\alpha$ -(E) products is high (91~97%). It can also catalyse the hydrosilylation of 3-thienylmethylacetylene with phenylmethylsilane, giving the corresponding  $\alpha$ -(E) product in high yield and high selectivity. But when 2-thienylmethylacetylene, 3-thienylmethylacetylene or 2-thienylmethylacetylene was used as the substrate, the yield and selectivity for the  $\alpha$ -(*E*) products are low. Synthesis of chiral samarium(II) monoalkyl complexes and their applications for the regio- and enantio-selective hydrosilylation of unsymmetrical internal alkynes with aryl and alkyl-substituted secondary hydrosilanes are under investigation.

#### **Experimental Section**

General

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All operations were performed under an atmosphere of argon using Schlenk techniques or in a nitrogen-filled glovebox. Tetrahydrofuran. toluene, hexane, [D6]benzene, and [D8]tetrahydrofuran were dried over Na/K alloy, transferred under vacuum, and stored in the glovebox. KCH(SiMe<sub>3</sub>)<sub>2<sup>[2e]</sup>,</sub> Sml<sub>2</sub>(THF)<sub>2</sub><sup>[14a]</sup>. KL (L [MeC(NDipp)CHC(Me)NCH<sub>2</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]<sup>-</sup>),<sup>[12]</sup> and alkynes<sup>[14b,c]</sup> (except phenylmethylacetylene and phenylethylacetylene) procedures. were synthesized following the literature Phenylmethylacetylene and phenylethylacetylene were purchased from Shanghai Macklin Biochemical Co., Ltd and Shanghai Aladdin Bio-Chem Technology Co., LTD, respectively. Hydrosilanes and alkynes were dried over CaH<sub>2</sub> and distilled under reduced pressure before use. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian 400 MHz, a Bruker 400 MHz or an Agilent 400 MHz spectrometer. Chemical shifts  $\delta$  were reported in ppm with references to the residual resonance of the deuterated solvents for proton and carbon spectroscopies. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

#### Synthesis

**Complex 1**: To a THF (2 mL) solution of Sml<sub>2</sub>(THF)<sub>2</sub> (281 mg, 0.51 mmol) was added a THF (2 mL) solution of KL (216 mg, 0.51 mmol) at room temperature. The reaction was stirred for 2 hours, resulting in a deep green solution with grey precipitates. After filtration, the solvent was removed under vacuum, and the residue was extracted with toluene (25 mL). The solvent of the extraction was removed under vacuum, and the residue was extracted with toluene (25 mL). The solvent of the extraction was removed under vacuum, and the residue was washed with hexane (2 mL × 3) and dried under vacuum to give complex 1 as a green solid (210 mg, 62% yield). The complex was paramagnetic. <sup>1</sup>H NMR (400 MHz,  $d_8$ -THF, 25 °C):  $\delta$  = 14.54, 11.59, 8.94, 8.52, 5.25, 2.70, 1.81, 1.06 ppm; elemental analysis calcd (%) for C4<sub>8</sub>H<sub>82</sub>I<sub>2</sub>N<sub>8</sub>Sm<sub>2</sub>-2toluene: C 49.32, H 6.54, N 7.42; found: C 49.50, H 6.37, N 7.36.

**Complex 2**: To a THF (1.5 mL) of **1** (95 mg, 0.07 mmol) was added a THF (1 mL) of KCH(SiMe<sub>3</sub>)<sub>2</sub> (28 mg, 0.14 mmol) at -35 °C. The reaction was kept at -35 °C for 20 minutes, resulting in a deep red solution with grey precipitates. The solvent was removed under vacuum, and the residue was extracted with hexane (8 mL). The solvent of the extraction was removed under vacuum to afford complex **2** as a deep red solid (63 mg, 63% yield). The complex was paramagnetic. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 18.36, 14.83, 14.14, 13.85, 12.82, 12.18, 11.46, 9.81, 7.04, 6.01, 4.36, 2.88, 1.28, -2.80, -3.15, -3.50, -3.77, -4.64, -8.32, -15.38, -40.49 ppm; elemental analysis calcd (%) for C<sub>31</sub>H<sub>60</sub>N<sub>4</sub>Si<sub>2</sub>Sm: C 53.55, H 8.70, N 8.06; found: C 53.25, H 8.84, N 8.01.

#### Typical procedure for the hydrosilylation of alkynes

In a nitrogen-filled glovebox, a C<sub>6</sub>D<sub>6</sub> (200 mg) solution of alkyne (0.5 mmol) and internal standard mesitylene (0.1 mmol) and a C<sub>6</sub>D<sub>6</sub> (200 mg) solution of hydrosilane (0.5 mmol) were mixed in a J. Young NMR tube, and then a C<sub>6</sub>D<sub>6</sub> (100 mg) solution of complex **2** (0.01 mmol) was added at room temperature. The NMR tube was sealed and immediately taken out of the glovebox, kept in a 30 °C oil bath. The yields of hydrosilylation products were determined by quantitative <sup>1</sup>H NMR spectrum after 1.5 or 3 hours.

#### X-ray crystallography

Single crystals of 1-2toluene suitable for single-crystal X-ray diffraction were grown from a toluene solution, and those of **2** were from a hexane solution.<sup>[15]</sup> The crystals were mounted under a nitrogen atmosphere on a glass fibre at low temperature. Data collection of 1-2toluene was performed on a Bruker APEX-II CCD with graphite-monochromated Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å), that of **2** was performed on a Bruker D8 Venture with Ga<sub>Ka</sub> radiation ( $\lambda = 1.34139$  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 *P*<sup>2</sup> 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

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calculation. Calculations were carried out using the SHELXL-2014 and Olex2 program. The software used is listed in reference.  $^{\rm [16]}$ 

Crystal data for 0.5(1-2toluene): C<sub>31</sub>H<sub>49</sub>IN<sub>4</sub>Sm, green, M<sub>r</sub> = 1509.98, triclinic, space group P-1, a = 11.144(2), b = 11.433(2), c = 15.096(3), a = 69.945(3), \beta = 83.330(3), \gamma = 66.571(2), V = 1657.3(5), Z = 1, Mo<sub>Ka</sub>,  $\lambda$  = 0.71073 Å, T = 130 K, R = 0.0431, wR = 0.1066, for 6117 unique reflections with I > 2 $\sigma$ (I), GOOF = 1.021.

Crystal data for **2**:  $C_{31}H_{60}N_4Si_2Sm$ , red,  $M_r$  = 695.36, monoclinic, space group P2<sub>1</sub>/n, a = 14.9774(4), b = 16.0913(4), c = 15.1412(4), a = 90, \beta = 91.020(2),  $\gamma$  = 90, V = 3648.54(16), Z = 4, GaK<sub>a</sub>,  $\lambda$  = 1.34139 Å, T = 130 K, R = 0.0396, wR = 0.0897, for 5636 unique reflections with I > 2 $\sigma$ (I), GOOF = 1.038.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21602237, 21732007, 21890721 and 21821002), the Program of Shanghai Academic Research Leader, the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB2000000), and Fujian Institute of Innovation, Chinese Academy of Sciences.

**Keywords:** alkyl complex • alkynes • hydrosilylation • homogeneous catalysis • samarium

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A five-coordinate samarium(II) monoalkyl complex is synthesized and structurally characterized. This complex shows high catalytic activity and high stereo- and regio-selectivity in hydrosilylation of various aryl and methyl-substituted unsymmetrical internal alkynes with secondary hydrosilanes under mild conditions.