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Coordination of allenyl/propargyl group to samarium(III): the first crystal structures of η^3-allenyl and η^1-propargyl lanthanide complexes

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Abstract

The synthesis and crystal structures of samarium complexes incorporating bridged Cp′–SiMe$_2$–allenyl/propargyl ligands [Cp′ = $\mathrm{(Me_3Si)_2(C_5H_2)}$] are described. The reaction of a dilithium salt of $\mathrm{[(Me_3Si)_2(C_5H_3)]SiMe_2CH_2C{\equiv}CSiMe_3}$ (**1a**) with $\mathrm{SmCl_3}$ yielded an η^3-allenyl complex $\{\mathrm{[(Me_3Si)_2(C_5H_2)]SiMe_2(\eta^3\text{-}C{=}C{=}C[\mathit{H}]SiMe_3)\}SmCl_3Li_2(TMEDA)_2}$ (**2a**) (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). On the other hand, the reaction of a dilithium salt of a $\mathrm{Ph_3Si}$ substituted ligand $\mathrm{[(Me_3Si)_2(C_5H_3)]SiMe_2CH_2C{\equiv}CSiPh_3}$ (**1b**) with $\mathrm{SmCl_3}$ yielded an η^1-propargyl complex $\{\mathrm{[(Me_3Si)_2(C_5H_2)]SiMe_2(\eta^1\text{-}CHC{\equiv}CSiPh_3)\}\text{-}Sm(TMEDA)[Cl_2Li(TMEDA)]}$ (**2b**). A conversion of bonding mode from η^1-propargyl to η^3-allenyl was observed when **2b** was treated with $\mathrm{(Me_3Si)_3CLi/LiI}$ to give an η^3-allenyl complex $\{\mathrm{[(Me_3Si)_2(C_5H_2)]SiMe_2(\eta^3\text{-}CH{=}C{=}CSiPh_3)\}SmI_2Li(TMEDA)}$ (**3b**). The same structural conversion was also observed when **2b** was treated with $\mathrm{(Me_3Si)_2CHLi}$ to give an anionic ate complex $(\{\mathrm{[(Me_3Si)_2(C_5H_2)]SiMe_2(\eta^3\text{-}CH{=}C{=}CSiPh_3)\}SmCl[CH(SiMe_3)_2]})\mathrm{[Li(TMEDA)_2]}$ (**4b**), which had the η^3-allenyl bonding structure. The structures of these four complexes (**2a**, **2b**, **3b**, and **4b**) were revealed by X-ray crystallography. These are the first examples of the structural characterization of η^3-allenyl and η^1-propargyl lanthanide complexes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Samarium; η^3-Allenyl; η^1-Propargyl; η^5-Cyclopentadienyl; Crystal structure

1. Introduction

Much attention has been paid to the chemistry of transition metal allenyl/propargyl complexes because of the intriguing structural features and unusual reactivities of these complexes [1]. However, in contrast to the extensive studies on late transition metal allenyl/propargyl complexes [1], much less has been reported on early transition metal complexes of this type. $\mathrm{Cp_2Zr(CH_3)[\eta^3\text{-}C(Ph){=}C{=}CH_2]}$ [2] and $\mathrm{Cp^*(TBM)Zr[\eta^3\text{-}C(Me){=}C{=}CH_2]}$ (TBM = tribenzylidenemethane) [3] are the rare examples of structurally characterized η^3-allenyl complexes of Group IV elements. Although Teuben reported the synthesis and spectroscopic characterization of 2-butynyl lanthanide complexes [$\mathrm{Cp_2^*LnCH_2C{\equiv}CCH_3}$, Ln = La, Ce] [4], no crystal structure has been reported on lanthanide allenyl/propargyl complexes to date [5]. On the other hand, Takaki and Fujiwara reported in situ generation of the allenic Sm species and its use for synthetic reactions [6]. In this article, we report the syntheses and the first structure analyses of allenyl/propargyl samarium complexes with two coordination modes (η^3-allenyl and η^1-propargyl), which we discovered in the course of applying our new bridged Cp′–SiMe$_2$–allenyl/propargyl ligands [Cp′ = $\mathrm{(Me_3Si)_2(C_5H_2)}$] for complexation with lanthanide metals.

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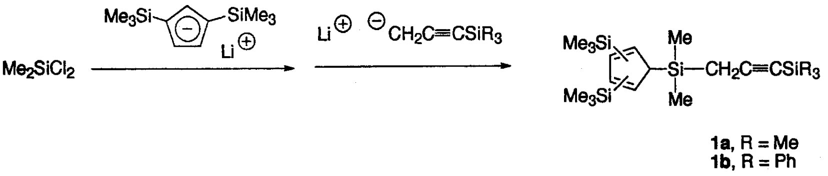
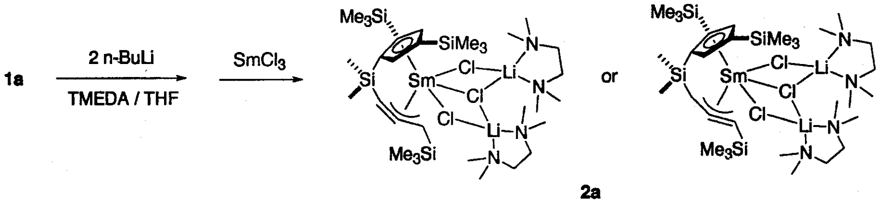


Scheme 1.



Scheme 2.

2. Results and discussion

As bridged Cp′–SiMe$_2$–allenyl/propargyl ligands [Cp′ = (Me$_3$Si)$_2$(C$_5$H$_2$)], we synthesized new compounds [(Me$_3$Si)$_2$(C$_5$H$_3$)]SiMe$_2$CH$_2$C≡CSiR$_3$ [**1a** (R = Me) and **1b** (R = Ph)], which had bis-Me$_3$Si–cyclopentadiene and trimethyl- or triphenylsilyl substituted propyne linked by a Me$_2$Si bridging group. Both ligands **1a** and **1b** were obtained by the sequential additions of (Me$_3$Si)$_2$CpLi and LiCH$_2$C≡CSiR$_3$ to Me$_2$SiCl$_2$ followed by trap-to-trap distillation (Scheme 1). The NMR spectra indicated that **1a** and **1b** existed as mixtures of isomers with respect to the positions of substituents and/or double bonds on the Cp ring. In addition, although we describe **1a** and **2a** as propargyl compounds for clarity in Scheme 1, the precise structure of the allenyl/propargyl moiety could not be determined from the NMR spectra.

The reaction of a dilithium salt of **1a** with SmCl$_3$ in THF at 23°C in the presence of *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA) yielded a Sm(III) complex **2a** as dark red needle-like crystals (Scheme 2). Owing to the high solubility of **2a** in organic solvents, the complex was obtained only in trace yield. The characterization of **2a** was carried out by X-ray crystallographic analysis and the ORTEP drawing is shown in Fig. 1. Although the poor quality of the data does not allow us to discuss the detailed bond distances and angles of **2a**, the established atom connectivity in Fig. 1 suggests that the three carbon atoms are coordinated to a Sm center in an η^3-fashion along with the coordination of the η^5-cyclopentadienyl ring and three Cl atoms [7]. However, considering the standard deviations of C(1)–C(2) and C(2)–C(3) bond lengths in the analysis, it is not possible to determine which C–C bond is shorter than the other in the C(1)–C(2)–C(3) sequence.

In order to decrease the solubility and improve the crystallinity of the resulting complexes, we used the ligand **1b** having a Ph$_3$Si group as a substituent. Changing the substituent on the terminal carbon of the allenyl/propargyl group from Me$_3$Si to Ph$_3$Si resulted in a

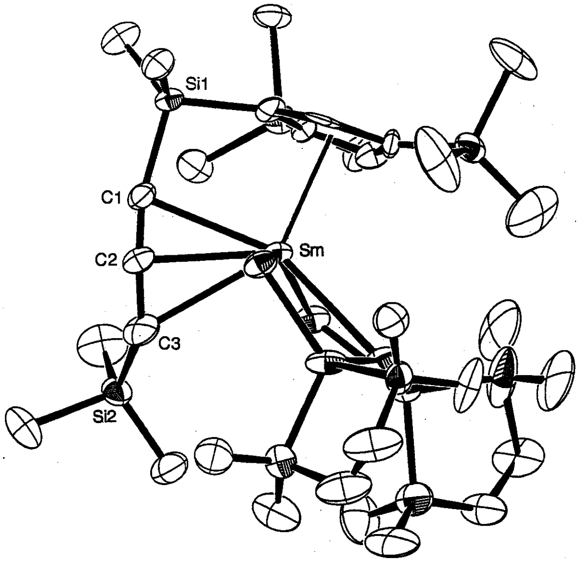


Fig. 1. Molecular structure of **2a**.

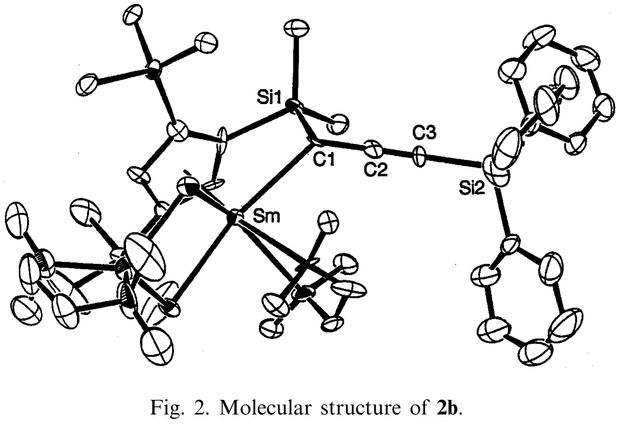
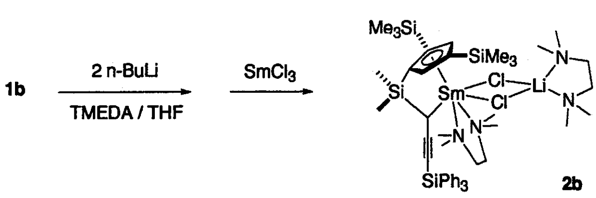


Fig. 2. Molecular structure of **2b**.



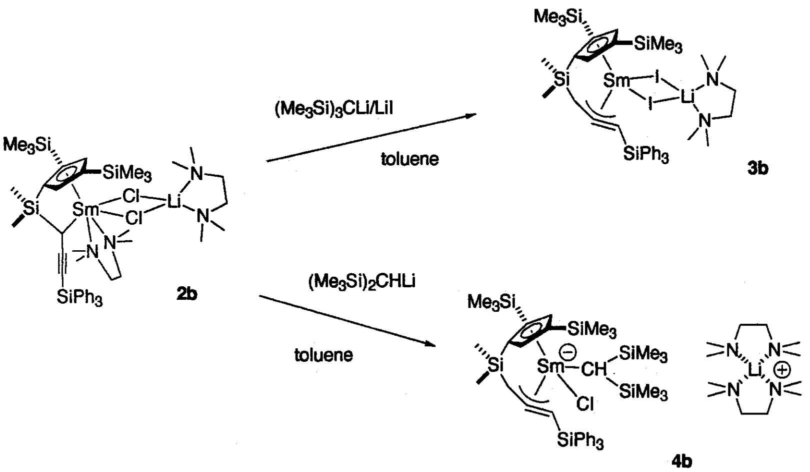
Scheme 3.

drastic change in the coordination mode of the allenyl/propargyl anion. Fig. 2 shows the crystal structure of the Sm complex **2b** obtained by the reaction of a dilithium salt of **1b** with $SmCl_3$ in the identical reaction conditions to the synthesis of **2a** (Scheme 3). Unfortunately, the quality of the data of the highly air-sensitive crystals of **2b** were not sufficient for a detailed discussion of the structure and only the connectivity of the atoms can be reliably described [7]. Nevertheless, the ORTEP drawing in Fig. 2 reveals that the interaction between the allenyl/propargyl anion and the Sm center exists only through the Sm–C(1) σ-bond, resulting in an η^1-propargyl coordination. In accord with the η^1-propargyl coordination, both C(2) and C(3) carbons seem to assume sp-hybridization, forming a linear arrangement with C(1) and Si(2) atoms. It is noteworthy that in the structure of **2b** with the η^1-propargyl bonding, the coordinative unsaturation on the highly electrophilic Sm cation is compensated by the direct coordination of a TMEDA molecule through two nitrogen atoms.

A conversion of the bonding mode from η^1-propargyl to η^3-allenyl was observed by removing the coordinated TMEDA molecule on the Sm center and exchanging two Cl anions for two I anions in **2b**. The transformation was achieved by the reaction of **2b** with $(Me_3Si)_3CLi/LiI$ in toluene at 23°C. Removal of the TMEDA by $(Me_3Si)_3CLi$ and anion exchange by LiI resulted in the formation of an η^3-allenyl samarium complex **3b** (Scheme 4). The conversion of the bonding mode from η^1-propargyl to η^3-allenyl most probably originated from the increase in both electronic and steric coordinative unsaturation on the Sm center, which would be mainly caused by the removal of the TMEDA molecule.

The same structural conversion was also observed by the transformation of **2b** to an anionic samarium ate complex **4b**. The reaction of **2b** with $(Me_3Si)_2CHLi$ in toluene at 23°C resulted in the introduction of the alkyl group on the Sm center, affording the anionic ate complex **4b** with one of the Cl atoms remaining on Sm (Scheme 4). By the transformation from **2b** to **4b**, the electron density on the Sm center substantially increased as indicated by the presence of an anionic charge on the Sm in the ate complex **4b**. Therefore, the conversion of the bonding mode from η^1-propargyl to η^3-allenyl in this case should arise only from the steric constraint imparted by the change of the $Cl_3Li_2(TMEDA)_2$ moiety to the $Cl[CH(SiMe_3)_2]$.

The precise structures of the η^3-allenyl complexes **3b** and **4b** were determined by X-ray diffraction studies. The molecular structures of **3b** and **4b** are shown in Figs. 3 and 4, respectively. Selected bond distances and bond angles are listed in Tables 1 and 2 and illustrated in Fig. 5. As shown in Table 2 and Fig. 5, structural parameters of the η^3-allenyl coordinations of C(1), C(2), and C(3) to Sm in **3b** and **4b** are very similar except that the bond distances of Sm to the three carbons in **4b** are slightly longer than those in **3b**. The longer bond lengths in **4b** should arise from the presence of the anionic charge on the Sm center in the complex, which renders the Sm–C bonds in **4b** weaker than those bonds in neutral complex **3b**. The following points should be noted as common structural features of η^3-allenyl coordination in **3b** and **4b**: (i) the bond distances of Sm–C(2) and Sm–C(3) are nearly equal, and they are about 0.3 Å shorter than Sm–C(1) bonds; (ii) C(2)–C(3) bonds are about 0.1 Å shorter than



Scheme 4.

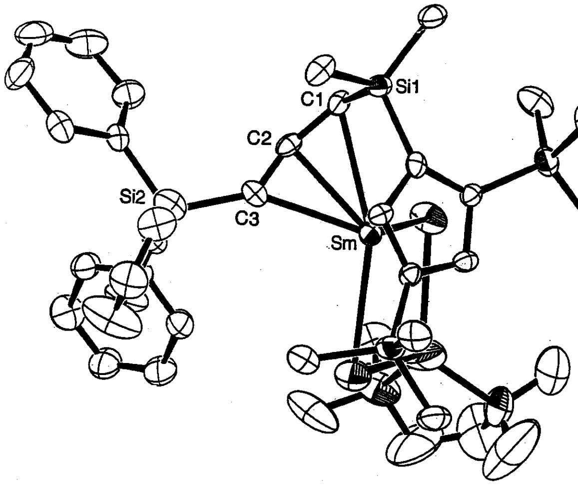


Fig. 3. Molecular structure of **3b**.

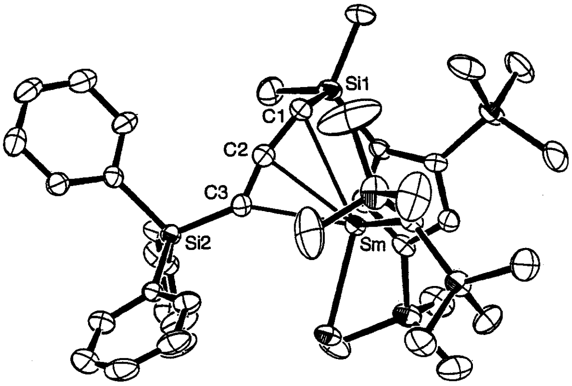


Fig. 4. Molecular structure of the anion **4b**.

C(1)–C(2) bonds; (iii) the bond angles C(1)–C(2)–C(3) are ca. 163° and they are 17° smaller than the ideal value of sp hybridization on C(2) carbons (180°); (iv) Si(1)–C(1)–C(2) angles are close to 120°, which is the ideal value of sp^2 hybridization on C(1) carbons, and C(2)–C(3)–Si(2) angles are about 16° larger than the ideal value. On the basis of these observations, we can reasonably conclude that C(2)–C(3) bonds are stronger than C(1)–C(2) bonds and a H atom attaches to the C(1) carbon in both complexes, although we could not locate the position of the H atom near C(1), C(2), or C(3) from the electron density in the diffraction studies of **3b** and **4b**. These are the first examples of complete structural characterization of the bonding interaction between lanthanide metals and allenyl/propargyl anions.

In conclusion, although we have not yet elucidated the behavior of **2a**, **2b**, **3b**, and **4b** in solution [8], we have for the first time succeeded in revealing the solid state bonding structures of two types (η^3-allenyl and η^1-propargyl) on lanthanide allenyl/propargyl complexes. These findings will extend the chemistry of transition metal allenyl/propargyl complexes to Group III elements.

3. Experimental

3.1. General considerations

All manipulations were performed on a high-vacuum line using standard Schlenk techniques under a purified Ar atmosphere. Solvents were distilled from Na/K alloy/benzophenone ketyl, except for toluene, which was distilled from Na/benzophenone ketyl. Me_2SiCl_2 (Shin-Etsu), 1-trimethylsilyl-1-propyne ($CH_3–C{\equiv}C–SiMe_3$, Tokyo Kasei), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, Tokyo Kasei) were stored with CaH_2 and used without distillation. Ph_3SiCl (Shin-Etsu), *n*-

Table 1
Crystal data for **3b** and **4b**

	3b	**4b**
Formula	$C_{40}H_{58}SmSi_4N_2$-LiI_2	$C_{55}H_{98}N_4SmSi_6Li$-$ClO_{0.5}$
Formula weight	1090.40	1184.67
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.584(3)	15.211(6)
b (Å)	17.532(3)	19.811(5)
c (Å)	11.050(2)	11.881(5)
α (°)	90.71(2)	104.50(3)
β (°)	99.61(2)	92.03(4)
γ (°)	108.52(1)	79.19(3)
V (Å^3)	2454.2(9)	3404(2)
Z	2	2
D_{calc} (g cm^{-3})	1.475	1.163
F(000)	1078	1260
μ (Mo–K_α) (cm^{-1})	25.81	10.44
Number of measured reflections	11748	16217
Number of observed reflections ($F_o \cong 3.0\sigma(F_o)$)	6205	8584
R [a] (R_w) [b]	0.060 (0.061)	0.058 (0.059)
GOF	1.50	1.36

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_w = (\Sigma\, w(|F_o|-|F_o|)^2/\Sigma\, w|F_o|^2)^{1/2}$; $w = 1/\sigma^2(F_o)$.

Table 2
Selected bond lengths (Å) and angles (°) of **3b** and **4b**

Compound	**3b**	**4b**
Bond lengths		
Sm–C(1)	2.827(10)	2.962(7)
Sm–C(2)	2.551(9)	2.662(7)
Sm–C(3)	2.58(1)	2.657(7)
C(1)–C(2)	1.35(1)	1.368(10)
C(2)–C(3)	1.25(1)	1.255(9)
Bond angles		
Si(1)–C(1)–C(2)	120.4(7)	118.4(6)
C(1)–C(2)–C(3)	163.5(10)	162.8(8)
C(2)–C(3)–Si(2)	136.7(9)	136.3(6)

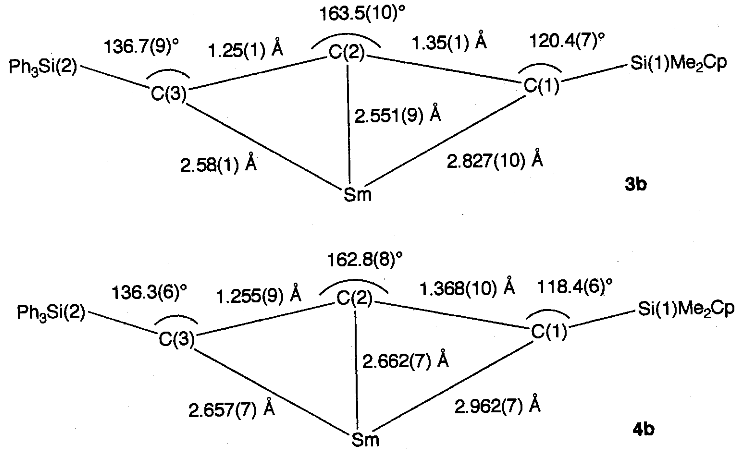


Fig. 5. Selected bond lengths and angles of **3b** and **4b**.

BuLi (1.6 M solution in hexane, Kanto Chemicals), and 1-propynylmagnesium bromide ($CH_3–C{\equiv}CMgBr$, 0.5 M solution in THF, Aldrich) were used as received. Me_3SiCpH was prepared by the reaction of CpNa with Me_3SiCl. $(Me_3Si)_2CpH$ was prepared by the reaction of $Me_3SiCpNa$ with Me_3SiCl. $SmCl_3$ was prepared by the reaction of Sm_2O_3 with HCl in the presence of excess NH_4Cl, followed by removal of excess NH_4Cl by sublimation at 360° under vacuum. $(Me_3Si)_3CH$ [9] and $(Me_3Si)_2CHLi$ [10] were prepared following the reported procedures. ^1H-NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer (395.75 MHz) in sealed tubes at ambient probe temperature. Chemical shifts were reported versus $SiMe_4$ and were determined by reference to the residual solvent peaks. New ligands **1a** and **1b** cannot be characterized by NMR spectroscopy because they exist as mixtures of isomers both in terms of the positions of substituents and C–C double bonds on the Cp ring. Complexometric metal analyses were conducted by the method reported by Atwood and Evans [11].

3.2. Preparation of $[(Me_3Si)_2(C_5H_3)]SiMe_2CH_2C{\equiv}CSiMe$ (**1a**)

A solution of $(Me_3Si)_2CpH$ (10.0 ml, 40.4 mmol) in THF (60 ml) was cooled to 0°C. *n*-BuLi (1.63 M solution in hexane, 24.5 ml, 39.9 mmol) was added to the solution dropwise and the mixture was stirred at 0°C for 5 h. Me_2SiCl_2 (4.8 ml, 40 mmol) was added to the mixture at 0°C and the resulting mixture was stirred at 23°C for 3 h to give a solution of $(Me_3Si)_2(C_5H_3)SiMe_2Cl$. A solution of $CH_3–C{\equiv}C–SiMe_3$ (6.0 ml, 41 mmol) and TMEDA (6.4 ml, 42.4 mmol) in THF (60 ml) was cooled to 0°C. *n*-BuLi (1.63 M solution in hexane, 24.5 ml, 39.9 mmol) was added to the solution dropwise and the mixture was stirred at 23°C for 2 h to generate a solution of $LiCH_2–C{\equiv}C–SiMe_3$. The $LiCH_2–C{\equiv}C–SiMe_3$ solution was added dropwise to the solution of $(Me_3Si)_2(C_5H_3)SiMe_2Cl$ held at 0°C and the mixture was stirred at 23°C for 12 h. The reaction mixture was poured into a saturated aqueous solution of $NaHCO_3$ (500 ml) and the organic layer was separated. The aqueous layer was extracted with hexane (2 × 100 ml) and the combined organic layer was dried over Na_2SO_4. After the volatiles were removed by flash distillation, **1a** was obtained by trap-to-trap distillation (120°C, 1 mmHg) as a yellow oil (11.7 g, 30.9 mmol, 78.3%).

3.3. Preparation of 1-triphenylsilyl-1-propyne

A solution of Ph_3SiCl (2.46 g, 8.33 mmol) in THF (50 ml) was cooled to 0°C. $CH_3–C{\equiv}CMgBr$ (0.50 M solution in THF, 16.0 ml, 8.00 mmol) was added to the solution dropwise at 0°C and the mixture was stirred and gradually warmed to 23°C over 20 h. The mixture was poured into a saturated aqueous solution of $NaHCO_3$ and the organic layer was separated. The aqueous layer was extracted with hexane and the combined organic layer was dried over Na_2SO_4. Removal of the volatiles afforded 1-triphenylsilyl-1-propyne as a white solid (1.60 g, 5.35 mmol, 66.9%). ^1H-NMR ($CDCl_3$): δ 7.34–7.68 (m, 15H, Ph–H), 2.05 (s, 3H, CH_3).

3.4. Preparation of $[(Me_3Si)_2(C_5H_3)]SiMe_2CH_2C{\equiv}CSiPh$ (**1b**)

The procedure described above for **1a** was employed using $(Me_3Si)_2CpH$ (6.00 ml, 24.3 mmol) in THF (90 ml), *n*-BuLi (1.59 M solution in hexane, 15.0 ml, 23.9 mmol), and Me_2SiCl_2 (2.9 ml, 24 mmol) to generate $(Me_3Si)_2CpSiMe_2Cl$, and $CH_3–C{\equiv}C–SiPh_3$ (7.19 g, 24.0 mmol), TMEDA (4.0 ml, 27 mmol) in THF (90 ml), and *n*-BuLi (1.59 M solution in hexane, 15.0 ml, 23.9 mmol) to generate $LiCH_2–C{\equiv}C–SiPh_3$. **1b** was obtained by trap-to-trap distillation (230°C, 1 mmHg) as a yellow oil (10.1 g, 17.8 mmol, 74.6%).

3.5. Preparation of {[$(Me_3Si)_2(C_5H_2)$]$SiMe_2$(η^3-C=C=C[H]$SiMe_3$)}$SmCl_3Li_2(TMEDA)_2$ (**2a**)

A solution of **1a** (3.59 g, 9.46 mmol) and TMEDA (3.0 ml, 20 mmol) in THF (60 ml) was cooled to 0°C. *n*-BuLi (1.66 M solution in hexane, 11.4 ml, 18.9 mmol) was added dropwise to the solution at 0°C and the mixture was stirred at 23°C for 5 h. The mixture was added to a suspension of $SmCl_3$ (2.43 g, 9.45 mmol) in THF (75 ml) at 23°C and the mixture was stirred at 23°C for 12 h. The volatiles were removed under vacuum and the residual solid was dissolved into toluene (90 ml). After a small amount of an insoluble solid was removed by centrifugation, toluene was removed under vacuum. Recrystallization of the residual solid from hexane afforded red needle-like crystals of **2a**, which were suitable for X-ray crystallographic analyses. Because of the high solubility of **2a**, **2a** was obtained only in trace yield and improving the yield has been difficult so far. ^{1}H-NMR spectrum of the crystals of **2a** indicated that the complex existed as a mixture of isomers. ^{1}H-NMR (the main isomer, C_6D_6): δ 14.27 (s, 1H, Cp–*H* or Me_3Si[*H*]C=C=C), 7.10 (s, 1H, Cp–*H* or Me_3Si-[*H*]C=C=C), 3.84 (s, 1H, Cp–*H* or Me_3Si[*H*]C=C=C), 2.27 (s, 24H, CH_3N), 2.07 (s, 8H, CH_2N), 1.79 (s, 3H, Me_2Si), 1.42 (s, 3H, Me_2Si), 0.24 (s, 9H, Me_3SiCp or Me_3Si[*H*]C=C=C), −0.13 (s, 9H, Me_3SiCp or Me_3Si-[*H*]C=C=C), −0.95 (s, 9H, Me_3SiCp or Me_3Si-[*H*]C=C=C). Anal. Calc. for $C_{31}H_{68}Cl_3Li_2N_4Si_4Sm$: Sm, 17.09. Found: Sm, 16.94%.

3.6. Preparation of {[$(Me_3Si)_2(C_5H_2)$]$SiMe_2$(η^1-CHC≡$CSiPh_3$)}Sm(TMEDA)[$Cl_2Li(TMEDA)_2$] (**2b**)

A solution of **1b** (3.86 g, 6.83 mmol) and TMEDA (2.1 ml, 14 mmol) in THF (60 ml) was cooled to 0°C. *n*-BuLi (1.59 M solution in hexane, 8.50 ml, 13.5 mmol) was added to the solution dropwise at 0°C and the mixture was stirred at 23°C for 7 h. The mixture was added to a suspension of $SmCl_3$ (1.73 g, 6.75 mmol) in THF (60 ml) at 23°C and was then stirred at 23°C for 12 h. The volatiles were removed under vacuum and the residual solid was dissolved in toluene (80 ml). After a small amount of an insoluble solid was removed by centrifugation, toluene was removed under vacuum. Recrystallization of the residual solid from diethyl ether afforded red needle-like crystals of **2b** (2.54 g, 2.48 mmol, 36.8%). The ^{1}H-NMR spectrum of the crystals of **2a** was too complicated to assign because the complex existed as a mixture of isomers. Anal. Calc. for $C_{46}H_{74}Cl_2LiN_4Si_4Sm$: Sm, 14.69. Found: Sm, 14.42%.

3.7. Preparation of $(Me_3Si)_3CI$

A solution of $(Me_3Si)_3CH$ (46.3 g, 199 mmol) in THF (300 ml) was cooled to 0°C. MeLi (1.0 M in Et_2O, 200 ml, 200 mmol) was added dropwise to the solution at 0°C and the mixture was refluxed for 12 h. After the mixture was cooled to −78°C, a solution of 1,2-diiodoethane (58 g, 200 mmol) in THF (60 ml) was added. After the mixture was stirred for 1 h at −78°C, it was gradually warmed to 23°C with stirring. The reaction mixture was washed with a aqueous $Na_2S_2O_3$ solution and the separated organic layer was dried over Na_2SO_4. After the volatiles were removed under reduced pressure, the residual solid was dissolved in hexane and an unsolved solid was removed by filtration. Removal of hexane afforded $(Me_3Si)_3CI$ as a pale yellow powder. (59.0 g, 0.165 mol, 83% yield). ^{1}H-NMR ($CDCl_3$): δ 0.24 (s, 27H, Me_3Si).

3.8. Preparation of Et_2O solution of $(Me_3Si)_3CLi/LiI$

A suspension of Li powder (3.14 g, 453 mmol) in Et_2O (210 ml) was cooled to −78°C. A solution of $(Me_3Si)_3CI$ (65.0 g, 181 mmol) in Et_2O (210 ml) was added dropwise to the suspension at −78°C and the reaction mixture was stirred and gradually warmed to 23°C over 4 h. Removal of a part of LiI, which appeared as a solid, and excess Li powder by centrifugation and filtration through glass wool afforded an Et_2O solution of $(Me_3Si)_3CLi/LiI$, whose concentration of $(Me_3Si)_3CLi$ was determined by titration with HCl–NaOH (yield of $(Me_3Si)_3CLi$ was quantitative).

3.9. Preparation of {[$(Me_3Si)_2(C_5H_2)$]$SiMe_2$(η^3-CH=C=$CSiPh_3$)}$SmI_2Li(TMEDA)_2$ (**3b**)

A solution of **2b** (0.65 g, 0.64 mmol) in toluene (45 ml) was cooled to 0°C. $(Me_3Si)_3CLi/LiI$ ($(Me_3Si)_3CLi$ = 0.69 M in Et_2O, 1.1 ml, 0.76 mmol) was added dropwise to the solution at 0°C and the mixture was stirred at 23°C for 48 h. After an insoluble solid was removed by centrifugation, volatiles were removed under vacuum. Recrystallization of the residual solid from Et_2O afforded orange needle-like crystals of **3b**, which were suitable for X-ray crystallographic analyses. The crystals of **3b** were obtained only in trace yield because of the high solubility of the complex. The ^{1}H-NMR spectrum of the crystals of **3b** was too complicated to assign because the complex existed as a mixture of isomers. Anal. Calc. for $C_{40}H_{58}I_2LiN_2Si_4Sm$: Sm, 13.79. Found: Sm, 13.54%.

3.10. Preparation of $(\{[(Me_3Si)_2(C_5H_2)]SiMe_2(\eta^3\text{-}CH{=}C{=}CSiPh_3)\}SmCl[CH(SiMe_3)_2])[Li(TMEDA)_2]$ (**4b**)

A solution of **2b** (1.72 g, 1.68 mmol) in toluene (45 ml) was cooled to 0°C. $(Me_3Si)_2CHLi$ (0.96 M in Et_2O, 2.1 ml, 2.02 mmol) was added dropwise to the solution at 0°C and the mixture was stirred at 23°C for 48 h. After an insoluble solid was removed by centrifugation, volatiles were removed under vacuum. The residual solid was washed with hexane (60 ml) to remove unreacted $(Me_3Si)_2CHLi$. Recrystallization of the hexane insoluble solid from Et_2O afforded yellow needle-like crystals of **4b** (1.02 g, 0.89 mmol, 52.9%). The ^{1}H-NMR spectrum of the crystals of **4b** indicated that the complex existed as a mixture of isomers. ^{1}H-NMR (the main isomer, C_6D_6): δ 9.78 (s, 1H, Cp–*H* or $Ph_3SiC{=}C{=}CH$), 8.21 (d, 6H, $^3J_{HH} = 7.1$ Hz, *o*-Ph), 7.87 (s, 1H, Cp–*H* or $Ph_3SiC{=}C{=}CH$), 7.36 (t, 6H, $^3J_{HH} = 7.1$ Hz, *m*-Ph), 7.27 (t, 3H, $^3J_{HH} = 7.5$ Hz, *p*-Ph), 1.88 (s, 8H, CH_2N), 1.84 (s, 24H, CH_3N), 0.95 (s, 9H, Me_3Si), 0.71 (s, 9H, Me_3Si), 0.46 (s, 3H, Me_2Si), 0.10 (s, 3H, Me_2Si), -0.14 (s, 9H, Me_3Si), -0.40 (s, 9H, Me_3Si). One of the Cp–*H* or $Ph_3SiC{=}C{=}CH$ signals and a $CH(SiMe_3)_2$ signal were obscured by the other resonances. Anal. Calc. for $C_{53}H_{93}ClLiN_4Si_6Sm$: Sm, 13.10. Found: Sm, 12.97%.

4. Supplementary material

Crystal data and data collection parameters are contained in Table 1. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 140444 (**2a**), 140445 (**2b**), 140446 (**3b**), and 140447 (**4b**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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