ORGANOMETALLICS-

A Dialkylsilylene-Pt(0) Complex with a DVTMS Ligand for the Catalytic Hydrosilylation of Functional Olefins

Tomohiro Iimura,^{†,‡} Naohiko Akasaka,[‡] and Takeaki Iwamoto^{*,‡}

[†]Science & Technology, Dow Corning Toray Co., Ltd, 2-2, Chigusa-Kaigan, Ichihara 299-0108, Japan

[‡]Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Supporting Information

ABSTRACT: A platinum(0) complex, bearing a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) and an isolable dialkylsilylene ligand, was successfully synthesized by the reaction between the dialkylsilylene and Karstedt's catalyst. The downfield-shifted ²⁹Si NMR resonance, the smaller ${}^{1}J_{Si,Pt}$ value, and the longer Si–Pt distance in this complex relative to the corresponding parameters in related bis(phosphine)-coordinated silylene-platinum complexes suggest weaker π -back-donation from the Pt center to the silylene, which is,



however, still significant when compared to related DVTMS-ligated Pt complexes bearing *N*-heterocyclic carbenes, *N*-heterocyclic two-coordinate silylenes, or base-stabilized three-coordinate silylenes. The title complex displays excellent catalytic activity in the hydrosilylation of terminal olefins that contain functional groups such as epoxide and amine moieties.

INTRODUCTION

A wide range of stable silylenes has been used to prepare a variety of silylene-ligated transition-metal complexes, which have received much attention due to their characteristic molecular structures and their utility in catalytic transformations.¹ Among the reported silylene-ligated transition-





metal complexes, the main focus has been placed on platinum,^{2,3} as Pt(0) catalysts are often used in hydrosilylation reactions.⁴ However, catalytically active silylene-Pt(0) complexes still remain rare, as the reactivity of their Pt centers is often reduced by the coordination of strong donor ligands such as phosphines. Silylene-Pt(0) complexes that are stabilized by 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS), which coordinates weakly to the active Pt center and thus maintains the reactivity of the metal, should represent a promising catalyst class for hydrosilylation reactions. Among the family of DVTMS-coordinated Pt complexes,⁵ Karstedt's catalyst (1)⁶ and the NHC/DVTMS-stabilized Pt complexes (2) by Markó et al.⁷ have been reported as efficient catalysts for such reactions (Chart 1). Very recently, Baceiredo and Kato et al. reported a

DVTMS-stabilized Pt complex with a strongly donating threecoordinate silylene ligand (3) that was able to catalyze the hydrosilylation of 1-octene more effectively than 1 or $2^{2j,k}$

We have previously reported the synthesis and isolation of cyclic dialkylsilylenes R_2^HSi (4, $R_2^H = 1,1,4,4$ -tetrakis(trimethyl-silyl)butane-1,4-diyl),⁸ which are kinetically stabilized by bulky R^H₂ substituents and can be used as ligands for transition-metal fragments.⁹ As the LUMO of silylene 4 is the vacant 3p orbital on Si, which is energetically lower than those of other stable Nheterocyclic silylenes, it can stabilize low-coordinate transitionmetal centers kinetically (steric bulk) and thermodynamically (σ -donation and π -back-donation). During the course of our studies on silvlenes as ligands for transition-metal fragments, we successfully synthesized a novel dialkylsilylene-Pt complex containing a DVTMS ligand (5), which was structurally characterized by multinuclear NMR spectroscopy, single-crystal X-ray diffraction (XRD) analysis, mass spectrometry, and elemental analysis. We found that 5 efficiently catalyzes not only the hydrosilylation of 1-hexene, similarly to 1 and 2, but also the hydrosilvlation of terminal alkenes that contain functional groups such as amine and epoxy moieties, which remained intact during the reaction.

RESULTS AND DISCUSSION

Complex 5 was obtained in 69% yield from the reaction of dialkylsilylene 4 and Karstedt's catalyst (1) in hexane at room temperature (Scheme 1). Recrystallization from hexane afforded analytically pure 5 as air- and moisture-sensitive yellow crystals that exhibited a decomposition temperature of

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Scheme 1. Synthesis of Dialkylsilylene/DVTMS-Stabilized Pt Complex 5



95 °C. Complex **5** also exhibited considerable stability in solution: even after several days at 70 °C in C_6D_6 , decomposition of **5** was not observed, indicating that **4** does not dissociate from **5** at this temperature.⁸

The XRD analysis of **5** revealed a trigonal planar Pt center that is coordinated to one silylene ligand and two vinyl moieties from one DVTMS ligand (Figure 1). The silacyclopentane ring



Figure 1. ORTEP drawing of 5 (atomic displacement parameters set at 50% probability; hydrogen atoms omitted for clarity).

of silylene 4 adopts an almost orthogonal orientation relative to the plane defined by the Pt center and the four vinyl carbons of DVTMS, which includes a dihedral angle of 81.4° . The sixmembered ring formed by the Pt atom and the DVTMS ligand adopts a chairlike structure, similar to those of 2^{7} and $3.^{2k}$ The Si–Pt bond length in 5 [2.2572(10) Å] is longer than the corresponding Si–Pt distance in related base-free bisphosphine silylene-Pt(0) complexes 6a [2.210(2) Å]^{2b} and 7 [2.2117(11) Å]^{2f} (Chart 2) but shorter than that in DVTMS-stabilized Pt

Chart 2. Related Base-Free Silylene-Ligated Bis(phosphine)platinum(0) Complexes



complex 3 [2.3015(15) Å].^{2k} The Pt–C(vinyl) distances in 5 [2.170(5)–2.181(5) Å] are significantly longer than those in 2a [2.107(4)–2.141(3) Å],¹⁰ 2b [2.130(6)–2.150(8) Å],^{7b} 2c [2.115(5)–2.139(5) Å],^{7b} and 3 [2.122(5)–2.150(5) Å].^{2k} In contrast, the C=C distances in the DVTMS ligand in 5 [1.415(6)–1.424(6) Å] are slightly shorter than those in 2a [1.422(5)–1.436(5) Å],¹⁰ 2b [1.433(6) Å],^{7b} 2c [1.420(9)–1.436(8) Å],^{7b} and 3 [1.426(7)–1.434(7) Å].^{2k} These structural features of 5 suggest that π -back-donation from Pt to Si is weaker in 5 than in 6 and 7, probably due to the absence of phosphine ligands as effective donors. Nevertheless,

it is stronger than in DVTMS-Pt complexes 2 and 3, owing to the presence of the low-lying vacant 3p orbital in 4, which is supported by the corresponding ²⁹Si NMR resonances and DFT calculations (*vide infra*).

The ¹H NMR spectrum of **5** in solution revealed a facile rotation around the Si(silylene)–Pt bond, which is reflected in the appearance of two singlets for the 36 protons of the four trimethylsilyl groups and the four methylene protons on the silacyclopentane ring. Conversely, two singlets, due to the geminal methyl groups on the silicon atoms of DVTMS, were observed, suggesting that the conformation around the DVTMS ligand remains unchanged on the NMR time scale.

The ²⁹Si NMR resonance corresponding to the unsaturated silicon nuclei in 5 (δ_{s_i} = 478.6 ppm) is upfield-shifted compared to the corresponding resonance of free silylene 4 (δ_{Si} = 567.4 ppm),⁸ but considerably downfield-shifted relative to those of bis(phosphine)-stabilized two-coordinate silvlene-Pt(0) complexes such as **6a** ($\delta_{\text{Si}} = 358 \text{ ppm}$),^{2b} **6b** ($\delta_{\text{Si}} = 367 \text{ ppm}$),^{2c} or 7 ($\delta_{\text{Si}} = 394.6 \text{ ppm}$).^{2f} The ²⁹Si-¹⁹⁵Pt coupling constant for **5** ${}^{(1)}_{Si,Pt} = 2250 \text{ Hz}$ is also smaller than that for **6b** ${}^{(1)}_{Si,Pt} = 2973 \text{ Hz}$.^{2c} The downfield-shifted ²⁹Si NMR resonance and small ${}^{1}J_{\text{Si,Pt}}$ value observed for 5 suggest weaker π -back-donation from Pt to Si in 5 than in 6 and 7, which is consistent with the correspondingly longer Si-Pt distance in 5 compared to those in 6 and 7. Interestingly, the upfield shift of δ_{Si} upon coordination to Pt observed for 5 [$\Delta \delta_{si} = \delta_{si}$ (Pt complex) – $\delta_{\rm Si}$ (free silvlene) = -88.8 ppm] stands in contrast to the downfield shift observed for a DVTMS-stabilized Pt complex of a base-stabilized three-coordinate silylene 3 [$\Delta \delta_{s_i}$ = +63.0 ppm; 3: $\delta_{Si} = -24.4$ ppm; 8: -87.4 ppm (Chart 3)]. As the δ_{Si} of

Chart 3. Related Silylenes and Silylene-Ligated Complex



silylenes is roughly proportional to the reciprocal of the excitation energy from the n(Si) to 3p(Si) orbitals,¹¹ the upfield shift of δ_{Si} in **5** suggests that the π -back-donation from Pt to Si elevates the energy level of the 3p(Si) orbital, which thus still contributes to the bonding between Si and Pt atoms. This result is also consistent with the shorter Si–Pt distance in **5** compared to that in **3**, wherein a σ -donation from the three-coordinate silylene center to Pt contributes predominantly to the Si–Pt bond.^{2k} Thus, the intrinsic characteristics of the silylene remain preserved in **5** upon complexation to the Pt center.

The weaker π -back-donation in **5** compared to those in **6** and 7 was also supported by theoretical studies at the B3PW91-D3/ B1 level of theory (Basis B1: SDD for Pt, 6-311G(d) for P, Si, O, C, H) (Figure 2). The optimized structure of **5** ($\mathbf{5}_{opt}$) was in good agreement with the experimentally observed structure of **5**. The HOMO shows a σ -donation from the silylene to the Pt d-orbital, while the HOMO-4 clearly represents the π -back-donation from the Pt center. However, the contribution of the Si 3p orbital to the HOMO-4 is small. Evidence for the weaker π -back-donation in **5** compared to that in **6** and 7 is provided by the significantly lower Wiberg bond index (WBI) of the Si-Pt bond in $\mathbf{5}_{opt}$ (0.93) relative to those in $\mathbf{6a}_{opt}$ (1.04) and 7_{opt}



Figure 2. Selected orbitals of S_{opt} calculated at the B3PW91-D3/B1 level of theory [Basis B1: SDD for Pt, 6-311G(d) for Si, O, C, H]. (a) HOMO [d(Pt) + n(Si)], (b) HOMO-4 [d(Pt) + 3p(Si)]; isoelectronic surface = 0.04 e⁻/Å³.

(1.18). This weaker π -back-donation should be attributed to the absence of phosphine ligands.

To further understand the characteristic electronic properties of 5, a comparison between the theoretically derived bonding situation in 5_{opt} with those of the corresponding Pt-DVTMS complex containing West's unsaturated cyclic diaminosilylene $[CHN(t-Bu)]_2$ Si: **10Si** (9_{opt}, Chart 3), N-heterocyclic carbene $[CHNMe]_2C: 10C (2a_{opt}, Chart 1)$, and base-stabilized three-coordinate dialkylsilylene 8 (3_{opt}) should be most helpful. Our previous theoretical study on model silylenes,^{9b} a recent systematic theoretical study on various silylene ligands by Szilvási et al.,¹² and the following theoretical calculations suggest that the dialkylsilylene acts as a strong σ -donor relative to N-heterocyclic carbenes and N-heterocyclic two-coordinate silvlenes, as a weak σ -donor relative to base-stabilized threecoordinate dialkylsilylenes (8, Chart 3), and as a strong π acceptor relative to N-heterocyclic carbenes, N-heterocyclic two-coordinate silvlenes, and base-stabilized three-coordinate dialkylsilylene. The lone pair orbital of the low coordinate Si center in dialkylsilylene 4_{opt} (-5.55 eV at the B3PW91-D3/6-311G(d) level of theory; see Figure S33), which should contribute to the electron donation toward the Pt center, is slightly higher in energy than those of cyclic diaminosilylene $10Si_{opt}$ (-6.16 eV) and cyclic diaminocarbene $10C_{opt}$ (-5.69 eV), but lower in energy than that of base-stabilized three-coordinate silylene 8_{opt} (-4.78 eV). Conversely, the vacant orbital of the low-coordinate Si center in 4_{opt} (-1.84 eV), which can participate in π -back-donation, is much lower than those of $10Si_{opt}$ (-0.45 eV), $10C_{opt}$ (+1.30 eV), and 8_{opt} (+1.28 eV). Accordingly, the WBI of the Pt–Si bond in 5_{opt} (0.93) is higher than those of 9_{opt} (0.89), $2a_{opt}$ (0.65), and 3_{opt} (0.77), when calculated at the same level of theory.¹³ The natural population analysis (NPA) charge on the Pt atom of $\mathbf{5}_{opt}$ [-0.290] at the B3PW91-D3/B1 level of theory is similar to those of silvlene complexes 3_{opt} [-0.141] and 9_{opt} [-0.290], but much more negative compared to that of carbene complex $2a_{opt}$ [0.278], which should be attributed to the more electropositive nature of the Si atom.

The catalytic activity of **5** was assessed for the hydrosilylation of $(Me_3SiO)_2SiMe-H$ (11) and 1-hexene (12a) in the presence of 30 ppm (w/w) of Pt (~7 × 10⁻⁴ mol %) at 50 °C for 5 h. In this reaction, 12a was completely transformed into 13a (entry 1 in Table 1). This reaction provided only the α regioisomer. When the catalyst loading was reduced to 3 or 0.3 ppm, **5** still exhibited high performance levels (entries 2 and 5) similar to that of Karstedt's catalyst 1 (entries 3 and 6) and superior to that of 2a⁷ (entry 4) under the same conditions. The catalytic hydrosilylation of 1-octene with 11 using similarly low loadings of **3** (3 × 10⁻⁵ mol %, t = 24 h, T = 72 °C in Table 1. Hydrosilylation of Terminal Alkenes with 11 in the Presence of Catalytic Amounts of 5^a or Related Catalysts

$$R \xrightarrow{(Me_3SiO)_2MeSi-H (11)}{Catalyst} (Me_3SiO)_2MeSi R$$
12 13

 $R = -\xi^{-}CH_{2}CH_{2}CH_{2}CH_{3}(\mathbf{a}), -\xi^{-}CH_{2}OCH_{2} - \bigvee^{O}_{i}(\mathbf{b}), -\xi^{-}CH_{2}N(SiMe_{3})_{2}(\mathbf{c}),$

$$-\xi$$
 (d)

entry	cat.	cat. amt (ppm)	time	Alkene	yield of product
1	5	30	5 h	///(12a)	>95% (13a)
2	5	3	1 h	12a	87% (13a)
3	1	3	1 h	12a	85% (13a)
4	$2a^{b}$	3	1 h	12a	6% (13a)
5	5	0.3	1 h	12a	83% (1 3 a)
6	1	0.3	1 h	12a	84% (13a)
7	5	30	5 h	(12b)	>95% (13b)
8	5	3	1 h	12b	>95% (13b)
9	1	3	1h	12b	91% (13b)
10	$2a^{b}$	3	1h	12b	0% (13b)
11	5	30	5 h	N(SiMe ₃) (12c)	93% ^c (13c)
12	5	3	1h	12c	80% (13c)
13	1	3	1h	12c	58% (13c)
14	2a ^b	3	1h	12c	0% (13c)
15	5	3	1 h	(12d)	93% ^c (13d)
16	1	3	1 h	12d	>95% (13d)
17	2a ^b	3	1 h	12d	18 % (13d)

^{*a*}Reaction conditions: SiH/alkene = 1.2, T = 50 °C. The conversion was determined by NMR analysis using toluene as the internal standard. ^{*b*}R = Me. ^{*c*}Yield after isolation.

xylene, product yield = 81%) was recently reported by Baceiredo and Kato.^{2j,k} Notably, 5 also catalyzes the hydrosilvlation of terminal alkenes that contain functional groups, e.g., 12b, 12c, and 12d (entries 7, 8, 11, 12, and 15). In these cases, 5 performs substantially better than 2a (entries 10, 14, and 17). Markó et al. reported that the hydrosilylation of 12b and 12d with 11 in the presence of NHC/DVTMS-ligated Pt catalysts **2d** (R = 2,6-diisopropylphenyl) or **2c** (R = cyclohexyl) at higher catalyst loadings (13b: 0.1 mol %, T = 60 °C, t = 1 h, no solvent, product yield = 78%,¹⁴ and **13d**: 30 ppm, T = 72°C, in xylene, product yield = >95%).^{7a} Although it remains difficult at this stage to ascertain whether 5 represents the catalytically active species, or merely a source of platinum colloids,¹⁵ the catalytic performance of **5** in the reaction of **12b** and 12c (e.g., entries 8 vs 9 and 12 vs 13) is superior to that of Karstedt's catalyst 1, which suggests that 5 is an effective precatalyst or at least that dialkylsilylene 4 works as an effective ligand for the hydrosilylation.

CONCLUSION

In conclusion, we successfully synthesized dialkylsilylene-Pt(0) complex **5** bearing a DVTMS ligand. The spectroscopic data suggest that π -back-donation from Pt to Si in **5** is weaker than those in analogous (silylene)bis(phosphine)platinum(0) complexes, but still significant when compared to those in DVTMS-ligated Pt complexes bearing *N*-heterocyclic carbenes, *N*-heterocyclic silylenes, and base-stabilized three-coordinate dialkylsilylene. Even though **5** bears a silylene ligand without significant electronic perturbation from the substituents to the silicon center, it is an efficient catalyst for the hydrosilylation of terminal alkenes that contain functional groups.

EXPERIMENTAL SECTION

General Procedures. All reactions involving air-sensitive compounds were carried out under an argon atmosphere using a high-vacuum line and standard Schlenk techniques, or a glovebox, as well as dry and oxygen-free solvents. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ¹H and ¹³C NMR chemical shifts were referenced to residual ¹H and ¹³C signals of the solvents: benzene- d_6 (¹H: δ 7.16 and ¹³C: δ 128.0). The ²⁹Si NMR chemical shifts were referenced relative to Me₄Si (δ 0.00). The ¹⁹⁵Pt NMR chemical shifts were referenced relative to Na₂PtCl₆ (δ 0.00). Sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glovebox. Mass spectra were recorded on JEOL JMS-600W and Bruker Daltonics SolariX 9.4T spectrometers. X-ray diffraction analyses were carried out using a Bruker AXS APEXII CCD diffractometer. UV–vis spectra were recorded on a JASCO V-660 spectrometer.

Materials. Benzene- $d_{6^{\circ}}$ hexane, and toluene were dried in a tube covered with a potassium mirror, and then vacuum-distilled prior to use. Karstedt's catalyst (1), 1,1,1,3,5,5,5-heptamethyltrisiloxane (11), and allylbis(trimethylsilyl)amine (12c) were supplied by Dow Corning Toray. These reagents were dried by molecular sieves (3A) and degassed under reduced pressure prior to use. Allyl glycidyl ether (12b), 1-hexene (12a), and vinylcyclohexene oxide (12d) were obtained from common commercial sources and used after drying over molecular sieves (3A) and degassing under reduced pressure. Dialkylsilylene 4 was prepared according to a published procedure.⁸ NHC carbene catalyst 2 (R = Me, 2a) was prepared according to a previously published procedure.^{7b}

Synthesis of 5. A Schlenk tube (50 mL) equipped with a magnetic stir bar was loaded with 1 (4% Pt atom, 13.1 g, 2.69 mmol). A hexane solution (10 mL) of dialkylsilylene 4 (1.0 g, 2.69 mmol) was added to the mixture at room temperature under stirring. The reaction mixture was stirred for an hour at room temperature, before the volatiles, including the solvent and excess 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, were partially removed under reduced pressure. The resulting solid and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane were separated by filtration, before the solid was washed with cold hexane and dried under reduced pressure to afford crystalline 5 in 69.0% yield (1.41 g, 1.87 mmol). 5: air- and moisture-sensitive pale yellow crystals; mp. 95 °C (decomp.); ¹H NMR (500 MHz, C₆D₆, 299 K) -0.018 (s, 6H, SiMe(vinyl)), 0.224 (s, 36H, SiMe₃), 0.579 (s, 6H, SiMe(vinyl)), 2.119 (s, 4H, CH_2CH_2), 2.308 (dd, J = 12 Hz, 15 Hz, 2H, $CH_2=CH-$), 2.505 (d with satellites due to ¹⁹⁵Pt, ³J_{H,H} = 15 Hz, ²J_{H,Pt} = 58 Hz, 2H, $CH_2=CH-$), 2.939 (d with satellites due to ¹⁹⁵Pt, ³J_{H,H} = 12 Hz, ²J_{H,Pt} = 10 Hz, ²J_{H,Pt} = 10 Hz, ²J_{H,Pt} = 10 Hz, ²J_{Hz} = 10 Hz, ³J_{Hz} = 10 = 56 Hz, 2H, CH_2 =CH-); ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 299 K) -1.19 (=CH-SiC), 1.79 (=CH-SiC), 3.56 (SiCH₃), 34.77 (s with satellites due to ¹⁹⁵Pt, ¹ $J_{C,Pt} = 53$ Hz, CH₂CH₂), 45.17 (s with satellites due to ¹⁹⁵Pt, ¹ $J_{C,Pt} = 74$ Hz, CH₂=CH-), 49.93 (C(SiMe₃)₂), 50.83 (s with satellites due to ¹⁹⁵Pt, ¹ $J_{C,Pt} = 74$ Hz, CH₂=CH-), 49.93 $CH_2 = CH_3; {}^{29}Si{}^{1}H$ NMR (99.4 MHz, $C_6D_6, {}^{299}K) -0.20$ $(C(SiMe_3)_2)$, 3.61 (=CH-SiMe_2O), 478.6 (s with satellite due to ¹⁹⁵Pt, Pt–Si, ¹ $J_{Si, Pt}$ = 2250 Hz), ¹⁹⁵Pt NMR (106.87 MHz, C₆D₆, 299 K) -5702; Anal. Calcd for C24H58OPtSi7; C, 38.21; H, 7.75%. Found: C, 38.60; H, 7.79%; HRMS (APCI) *m/z* Calcd for C₂₄H₅₈OPtSi₇:

753.25148. Found: 753.25154; UV–vis (hexane, 298 K) $\lambda_{\rm max}/{\rm nm}$ (ε) 231 (26200), 323 (740), 389 (163).

A Representative Hydrosilylation Procedure: Hydrosilylation of 1-Hexene (12a) in the Presence of 5. 1,1,1,3,5,5,5-Heptamethyltrisiloxane (11) (600 μ L, 2.21 mmol) and 1-hexene (12a) (170 μ L, 1.64 mmol) were loaded in a Schlenk tube (20 mL). As an internal standard, toluene (50 μ L, 0.47 mmol) was added to the reaction mixture. A benzene- d_6 solution of catalyst 5 (23.6 mmol/L, 3.6 μ L, 2.45 × 10⁻⁵ mmol) was added to the reaction mixture. The mixture was kept at 50 °C for 5 h. The ¹H NMR spectrum of the reaction mixture (Figure S7) indicated that 3-hexyl-1,1,1,3,5,5,5-heptamethyltrisiloxane¹⁶ (13a) (480 mg, 1.58 mmol, 95%) had formed. Product 13b was identified by comparison of its ¹H NMR spectral data with those reported in the literature.¹⁴ The ¹H NMR spectra of the reactions mixture for entries 1–17 in Table 1 are shown in the Supporting Information.

Large-Scale Hydrosilylation of Allylbis(trimethylsilyl)amine 12c in the Presence of 5 (Entry 11 in Table 1). A Schlenk flask was loaded with 1,1,1,3,5,5,5-heptamethyltrisiloxane (11) (15.0 g, 67.4 mmol) and a benzene- d_6 solution (66.0 mmol/L, 58.8 μ L, 1.10 × 10⁻³ mmol) of 5, before allylbis(trimethylsilyl)amine (12c) (10.4 g, 51.7 mmol) was added gradually. The mixture was kept at 50 °C for 5 h, before excess 1,1,1,3,5,5,5-heptamethyltrisiloxane was removed under reduced pressure. 1,1,1,3,5,5,5-Heptamethylt-3-[3-(bis(trimethylsilyl)amino)propyl)]trisiloxane (13c) (20.5 g, 48.4 mmol) was obtained in 93.3% yield after distillation (70–72 °C, 1 Pa).

13c: A moisture-sensitive colorless liquid; bp. 70–72 °C (1 Pa); ¹H NMR (500 MHz, C_6D_6 , 299 K) 0.159 (s, 3H, SiCH₃), 0.191 (s, 18H, Si(CH₃)₃), 0.211 (s, 18H, Si(CH₃)₃), 0.461–0.495 (m, 2H, SiCH₂CH₂), 1.565–1.632 (m, 2H, -CH₂CH₂CH₂-), 2.819–2.852 (m, 2H, CH₂-N-); ¹³C{¹H} NMR (125.8 MHz, C_6D_6 , 299 K) 0.06 (SiCH₃), 2.17 (Si(CH₃)₃), 2.47 (Si(CH₃)₃), 15.60 (SiCH₂CH₂CH₂N), 29.58 (SiCH₂CH₂CH₂N), 49.61(SiCH₂CH₂CH₂N); ²⁹Si{¹H} NMR (99.4 MHz, C_6D_6 , 299 K) –21.46 (SiMe), 5.41 (SiMe₃), 7.34 (NSiMe₃); MS (EI, 70 eV) *m*/*z* (%) 423 (0.08), 355 (33.9), 281 (13.7), 207 (100), 208 (21.1), 96 (12.5), 73 (19.0); Anal. Calcd for C₁₆H₄₅NO₂Si₅; C, 45.33; H, 10.70; N, 3.30%. Found: C, 45.38; H, 10.77; N, 3.42%.

Hydrosilylation of Vinylcyclohexene Oxide in the Presence of 5 (Entry 15 in Table 1). A Schlenk flask was loaded with 1,1,1,3,5,5,5-heptamethyltrisiloxane (11) (0.49 g, 2.20 mmol), a mixture of *cis* and *trans* isomers of vinylcyclohexene oxide (12d; 0.224 g, 1.80 mmol), and a benzene- d_6 solution of 5 (66.0 mmol/L, 4.5 μ L, 2.97 × 10⁻⁵ mmol). The mixture was kept at 50 °C for 1 h, before excess 11 was removed under reduced pressure. The resulting *cis* and *trans* isomers of (2-(7-oxa-bicyclo[4.1.0]heptan-3-yl)ethyl)bis-(trimethylsiloxy)methylsilane (13d) (0.58 g, 1.67 mmol) were isolated in 92.7% yield by Kugelrohr distillation (74–78 °C, 1 Pa).

13d: A colorless liquid; bp. 74–78 $^\circ$ C (1 Pa); ¹H NMR (500 MHz, C₆D₆, 299 K) 0.110 (s, 3H, SiMe), 0.117 (s, 3H, SiMe), 0.162 (s, 18H, SiMe₃), 0.169 (s, 18H, SiMe₃), 0.449-0.512 (m, 4H, SiCH₂CH₂), 0.605-0.690 (m, 1H, proton of the cyclohexylepoxy group (CY)), 0.877-0.969 (m, 1H, CY), 0.982-1.036 (ddd, 1H, J = 14.5, 10.5, 2.0 Hz, CY), 1.172-1.262 (m, 6H, overlapping CY and CH₂CH₂-Si), 1.334-1.409 (m, 3H, CY), 1.430-1.514 (m, 1H, CY), 1.606-1.665 (m, 1H, CY), 1.702-1.801 (m, 2H, CY), 1.943-1.990 (m, 1H, CY), 2.049-2.093 (m, 1H, CY), 2.816-2.889 (m, 4H, O-CH); ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 299 K) -0.16 (SiMe), -0.13 (SiMe), 2.00 (SiMe), 14.8 (CH₂Si), 14.9 (CH₂Si), 24.0 (CH₂), 24.5 (CH₂), 25.8 (CH₂), 27.2 (CH₂), 30.0 (CH₂), 30.5 (CH₂), 30.8 (CH₂), 32.0 (CH₂), 32.4 (CH), 35.7 (CH), 51.2 (CH), 52.0 (CH), 52.6 (CH); ²⁹Si{¹H} NMR (99.4 MHz, C₆D₆, 299 K) -20.7 (SiMe), 7.26 (SiMe₃), 7.29 $(SiMe_3)$; MS (EI, 70 eV) m/z (%) 346 (0.002), 307 (0.11), 303 (3.34), 277 (18.4), 249 (7.13), 221 (100), 191 (16.5), 133 (17.1), 73 (65.6); Anal. Calcd for C₁₅H₃₄O₃Si₃; C, 51.97; H, 9.86. Found: C, 52.12; H, 9.89.

X-ray Diffraction Analyses of 5 and 2a. Single crystals suitable for an X-ray diffraction analysis were obtained by recrystallization from hexane (5) or toluene (2a) at -35 °C under an inert atmosphere. For data collection, single crystals coated in Apiezon grease were mounted on a glass fiber and transferred into the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer using graphite-monochromated Mo–K α radiation. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS,¹⁷ and the structure was solved by direct methods and refined by full-matrix least-squares against F^2 using all data (SHELEX-2014).¹⁸ The molecular structure was analyzed using the Yadokari-XG software.¹⁹

Theoretical Calculations. All theoretical calculations were performed using the Gaussian 09²⁰ or GRRM14²¹ programs. Geometry optimizations and frequency analyses for $2a_{opv}$ 3_{opv} 4_{opv} 5_{opt} 6a_{opt} 7_{opt} 8_{opt} 9_{opt} 10Si_{opt} and 10C_{opt} were carried out at the B3PW91-D3/B1 level of theory (basis B1: SDD for Pt and 6-311G(d) for Si, P, O, C, and H). Imaginary frequencies were not encountered in any of the optimized structures. The XYZ file in the Supporting Information contains the calculated Cartesian coordinates of all molecules reported in this study. The transition energies and oscillator strengths of the electron transition of S_{opt} were calculated using a timedependent hybrid DFT method (TD-DFT) at the B3PW91-D3/B1 level of theory (Table S1). A superimposition of the calculated UV-vis spectrum of 5_{opt} with the experimentally obtained spectrum of 5 is shown in Figure S30. The NBO²² analyses of 2a_{opt} 3_{opt} 5_{opt} 6a_{opt} 7_{opt} and 9_{opt} were carried out at the same level. Selected Kohn–Sham orbitals of $\mathbf{5}_{opt}$ are shown in Figure S31. A comparison of the frontier Kohn-Sham orbitals and their energy levels for 5_{opt} and 7_{opt} is shown in Figure S32. A comparison of the frontier Kohn-Sham orbitals and their energy levels for 4_{opt} , 8_{opt} , $10Si_{opt}$, and $10C_{opt}$ is shown in Figure S33.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00741.

Experimental and theoretical details (PDF)

Crystallographic data for 5 and 2a (CIF)

Cartesian coordinates for calculated structures (XYZ)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: iwamoto@m.tohoku.ac.jp.

ORCID[©]

Takeaki Iwamoto: 0000-0002-8556-5785

Notes

The authors declare no competing financial interest.

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