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Introduction

Isolable silvlenes (divalent silicon species) that are stabilized kinetically and/or electronically constitute an attractive research area in organosilicon chemistry.1 A variety of stable silvlenes have been synthesized and used as unique reagents for transformation reactions of organic compounds, and as key starting materials for functional organosilicon compounds such as multiply-bonded silicon compounds.² Isolable silylenes have also attracted much attention as useful ligands for transition-metal complexes³ and some of these silvlene-ligated transition-metal complexes have found applications as catalysts in useful transformation reactions such as [2 + 2 + 2]cycloadditions,⁴ C-H borylations,⁵ as well as Kumada,⁶ Negishi,⁶ and Sonogashira cross-coupling reactions.⁷

Recently, we have synthesized a novel platinum(0) complex (2) that bears a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) ligand and an isolable cyclic dialkylsilylene (1) (Chart 1).⁸ Although 2 demonstrated weaker π -back-donation from Pt to Si than the corresponding bis(phosphine)-coordinated silvlene-platinum complexes,⁹ the π -back-donation



A Pt(0) complex with cyclic (alkyl)(amino)silylene

A platinum(0) complex bearing a cyclic (alkyl)(amino)silylene and a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) was synthesized and isolated in the form of colorless crystals. The single-crystal X-ray diffraction analysis of this complex in combination with theoretical calculations indicated that the Pt→Si

 π -back-donation in this complex is weaker than that in the corresponding cyclic-dialkylsilylene-ligated Pt

complex. The performance of this complex in the catalytic hydrosilylation of (Me₃SiO)₂MeSi-H with

various terminal alkenes that contain functional groups was comparable to that of the corresponding

and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane

ligands: synthesis, molecular structure, and

Tomohiro limura, 回 ^{a,b} Naohiko Akasaka, 回 ^b Tomoyuki Kosai 回 ^b and

catalytic hydrosilylation activity*

Takeaki Iwamoto 匝 *^b

cyclic dialkylsilylene/DVTMS Pt(0) complex.

Chart 1 Dialkylsilylene 1, as well as related silylenes and DVTMSligated Pt complexes.

in 2 is stronger than those in N-heterocyclic carbene (NHC)/ DVTMS ligated Pt(0) complexes $(3a)^{10}$ or three-coordinate silvlene-ligated Pt complex 4,^{9k} due to the presence of a lowlying vacant 3p orbital in 1. Interestingly, 2 showed catalytic activity in the hydrosilylation of terminal alkenes with $(Me_3SiO)_2MeSiH$. Although 2 is stable at ambient temperature, it exhibits a lower decomposition temperature (95 °C) than 3 (3b: 189 °C) and 4 (244–245 °C), which may restrict the range of catalytic applications for 2 (Chart 1). Considering the electronic structure and thermal stability of 1, the lower decomposition temperature of 2 may be related to the lower thermal stability of dialkylsilylene 1.

Very recently, we have reported the synthesis of the twocoordinate cyclic (alkyl)(amino)silylene (CAASi) 5,¹ⁱ which is reminiscent of the cyclic (alkyl)(amino)carbenes (CAACs) developed by Bertrand et al.¹¹ CAASi 5 showed improved thermal

^aScience & Technology, Dow Corning Toray, Ichihara, Chiba 299-0108, Japan ^bDepartment of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan. E-mail: iwamoto@m.tohoku.ac.jp

[†]Electronic supplementary information (ESI) available: Figures for NMR and UV-vis spectra, additional ORTEP drawings of 6 and NMR spectra of the reaction mixture of hydrosilylation as well as the detailed theoretical calculations. CCDC 1535615. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt01113j

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stability compared to dialkylsilylene 1, while high reactivity was retained. In contrast to 1, signs of degradation were not observed for 5, even after two days at 150 °C. The high thermal stability of 5 prompted us to examine the performance of 5 as a ligand for transition-metal complexes. Herein, we report the synthesis and properties of a Pt complex bearing DVTMS and 5 (6). The thermal stability of 6 was considerably improved compared to 2 and its catalytic performance in the catalytic hydrosilylation of terminal alkenes was comparable to that of 2.

Results and discussion

Synthesis of DVTMS/CAASi-Pt(0) complex 6

The reaction between silylene **5** and Karstedt's catalyst $(7)^{12}$ in hexane at room temperature afforded **6** in 52% yield as an airand moisture-sensitive white crystalline solid (Scheme 1). As expected from the high thermal stability of **5**, the decomposition temperature of **6** (185 °C) is drastically increased relative to that of **2** (95 °C). Complex **6** also exhibited considerable stability in solution: even after several days at 70 °C in C₆D₆, decomposition of **6** was not observed. The molecular structure of **6** was determined by multinuclear NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis.

Molecular structure of 6

Fig. 1 shows the molecular structure of **6** as determined by X-ray diffraction (XRD) analysis. In the asymmetric unit, two



Scheme 1 Synthesis of 6



Fig. 1 ORTEP drawing of 6 (atomic displacement parameters set at 50% probability; hydrogen atoms are omitted for clarity). One of the two crystallographically independent molecules is shown. The adamantyl group on N1 is disordered over two positions (0.866(5): 0.134(5)), and only the structure with the major site occupancy factor is shown.

crystallographically independent molecules with similar structural characteristics were observed; structural parameters of one of the two molecules are discussed hereafter. The Pt center in 6 adopts a trigonal-planar coordination geometry and is ligated by one silylene and two DVTMS vinyl moieties similar to 2 (Fig. 1). The two vinyl carbon atoms (C30 and C34), the disiloxane unit (Si-O-Si) in the DVTMS ligand, and the Pt atom form a chair-like six-membered ring, which is almost similar to that of 2. The least-squares plane of the fivemembered ring in the silvlene ligand is oriented perpendicular to the plane containing the Pt atom and the four vinyl carbon atoms of DVTMS, which includes a dihedral angle (89.7°) that is similar to that of 2 (81.4°). The adamantylamino moiety adopts a syn conformation with respect to the disiloxane unit and the plane including the Si, Pt, and vinyl carbons. The Pt-C (vinyl) distances in 6 [2.139(3)-2.162(3) Å] are shorter than those in 2 [2.170(5)-2.181(5) Å], while the C=C distances [1.421(5)–1.427(4) Å] in the DVTMS ligand of 6 are longer than those in 2 [1.415(6)–1.422(4) Å]. These structural parameters indicate that π -back-donation from the Pt center to the vinyl moieties in the DVTMS ligand of 6 is significantly enhanced compared to that of 2. The Si-Pt distance in 6 [Pt1-Si1: 2.2504 (8) Å] is slightly shorter than that in 2 [2.2572(13) Å], and the Si-N distance in 6 [Si1-N1 1.690(3) Å] is shorter than that in free silylene 5 [1.7143(15) Å].¹ⁱ The shorter Pt-C(vinyl) and Si-Pt distances in 6 compared to those in 2 might be responsible for the increased thermal stability.

The ¹H NMR spectrum of **6** in C_6D_6 exhibits two conformers in an \sim 3:1 ratio, while the XRD analysis exhibited only one isomer bearing the adamantylamino moiety in a syn (6a) conformation with respect to the six-membered ring that contains the Pt-DVTMS moiety. The presence of four singlet ¹H NMR signals for the geminal methyl groups on the silicon atoms in the DVTMS group is consistent with the presence of two conformers in solution. The ¹H NMR signals of the two conformers did not change significantly in toluene- d_8 between -70and 70 °C. Theoretical calculations at the B3PW91-D3/B level of theory [Basis B: SDD for Pt; 6-311G(d) for Si, O, N, C, H] suggested that the two conformers should bear the adamantylamino groups in the syn $(6a_{opt})$ and anti conformations $(6b_{opt})$, whereby the free energy of $6a_{opt}$ is by 4.3 kJ mol⁻¹ lower than that of $6b_{opt}$,¹³ which is consistent with the observation of both conformers in solution.

The observed ²⁹Si NMR resonances of the unsaturated silicon nuclei (δ_{Si}) in 6 (6a: 281.3 ppm, 6b: 285.7 ppm) are downfield shifted compared to the corresponding resonance of free silylene 5 (274 ppm),¹ⁱ which stands in sharp contrast to the observed upfield shift of the δ_{Si} of 2 (478.6 ppm)^{8b} relative to that of free silylene 1 (564.7 ppm).^{8a} This result suggests that the bonding between the Pt and Si atoms consists predominantly of the σ -donation from Si(silylene) to Pt, instead of a π -back-donation. This conclusion is based on the fact that the isotropic chemical shift of divalent silicon nuclei in silylenes is roughly proportional to the reciprocal of the energy difference between the n(Si) and the vacant 3p(Si) orbitals,¹⁴ and that a similar downfield shift of δ_{Si} was reported for Kato's

silylene complex **4** upon coordination.^{9k} In the ¹⁹⁵Pt NMR spectrum, two signals were observed for the two different conformers **6a** (5846 ppm) and **6b** (5838 ppm). The J_{PtSi} coupling constants for **6a** (2335 Hz) and **6b** (2335 Hz) are slightly larger than that of **2** (2250 Hz), which is consistent with the shorter Pt–Si bond length in **6** [2.2504(8) Å] compared to that of complex **2** [2.2572(13) Å].^{8b}

The structural features of 6 were also examined theoretically by DFT calculations. The optimized structure of 6 (6a_{opt}), calculated at the B3PW91-D3/B level of theory, was in good agreement with the structural parameters of 6 determined by the single-crystal XRD analysis (for details, see the ESI^{\dagger}). The HOMO and HOMO-5 represent the Si \rightarrow Pt σ -donation and the weak Pt \rightarrow Si π -back-donation, respectively (Fig. 2). Our previous DFT calculations demonstrated that both silylenes $\mathbf{1}_{opt}$ and $\mathbf{5}_{opt}$ exhibit a lone pair orbital on the silicon atom [n(Si)] as the HOMO and an empty 3p orbital on the silicon atom [3p(Si)] as the LUMO, which can contribute to the Si \rightarrow Pt σ -donation and the Pt \rightarrow Si π -back-donation, respectively. While the energy level of the HOMO in 5_{opt} (-5.56 eV) is virtually identical to that of 1_{opt} (-5.55 eV), the LUMO of 5_{opt} (–1.13 eV) lies substantially higher than that of 1_{opt} (-1.84 eV) due to the electron donation from the neighbouring amino group,¹ⁱ which suggests a weaker $Pt \rightarrow Si$ π -back-donation in $6a_{opt}$ compared to that in 2_{opt} . This notion is supported by smaller Wiberg bond indices (WBI)¹⁵ for the Pt-Si bond in $6a_{opt}$ (0.58) compared to that in 2_{opt} (0.66). Nevertheless, the Si-Pt bond in 6aopt [2.255 Å] is slightly shorter than that in 2_{opt} [2.257 Å]. The increased s-character of the Si orbital in the Pt-Si bond, owing to the substitution of the more electronegative nitrogen atom at the Si centre, may be responsible for the shorter Pt-Si bond: a natural bond orbital (NBO) analysis suggested a sp^{0.74} hybridization for the Si orbital in the Pt-Si bond in 6a_{opt}, while that in 2_{opt} is sp^{1.14} (for details, see the ESI†). The reduced Pt \rightarrow Si π -back-donation can thus induce an increased electron density on the Pt center in $6a_{\rm opt}$, which would enhance the π -back-donation from Pt to the vinyl moiety in the DVTMS ligand. This hypothesis is consistent with the shorter Pt-C (vinyl) distances observed in 6 and the larger WBI values for the Pt…CH₂ [0.37 (average)] and Pt…CH [0.29 (average)] bonds of $6a_{opt}$ compared to the corresponding values of 2_{opt} [0.35 and 0.26].



Fig. 2 HOMO (left) and HOMO–5 (right) of $6_{\rm opt}$, calculated at the B3PW91-D3/B level of theory [B: SDD for Pt; 6-311G(d) for H, C, N, O, Si]. Hydrogen atoms are omitted for clarity.

Hydrosilylation of terminal alkenes in the presence of 6

Similar to 2,^{8b} 6 catalyzes the hydrosilylation of various terminal alkenes with $(Me_3SiO)_2MeSi-H$ (8). In the presence of 6 [30 ppm (w/w) of Pt (~7 × 10⁻⁴ mol%)] at 50 °C for 5 h, 1-hexene (9a) was completely transformed into 10a (entry 1 in Table 1). Even when the amount of 6 was reduced to 3 ppm, 10a was obtained in high yield within one hour (entry 2). Notably, 6 also catalyzes the hydrosilylation of terminal

Table 1 Hydrosilylation of terminal alkenes with 8 in the presence of 6^a or related catalysts

		(Me ₃ SiO) ₂ I cata	MeSi—H alyst	(8) (Me₃SiO)₂MeSi ∖_) (Me₃SiO)₂MeSi	
	К	50	O°C		<pre></pre>	
	9			10		
-ξ-(CH ₂)₃CH ₃ (a),			$-\xi$ -CH ₂ OCH ₂ - \swarrow ^O (b), $-\xi$ -CH ₂ N(SiMe ₃) ₂ (c),			
	-§-	(d) , −O	`ş́~C	O Me (e), `ξ∽' O	[⊃] ∼Et (f)	
Enti	y Cat.	Cat. (ppm)	Time	Alkene	Product yield	
1	6	30	5 h	(9a)	>95% (10a)	
2	6	3	1 h	9a	91% (10a)	
3^b	7	3	1 h	9a	85% (10a)	
4^b	2	3	1 h	9a	87% (10a)	
5^{b}	3a	3	1 h	9a	6% (10a)	
6	6	30	5 h		>95% (10b)	
_	_	_		(de)		
7	6	3	1 h	9b	>95% (10b)	
8°	7	3	1 h	9b	91% (10b)	
9 ⁰	2	3	1 h	9b	>95% (10b)	
10^{5}	3a	3	1 h	96	0% (10b)	
11	6	30	5 h	N(SiMe ₃) (9c)	>95% (10c)	
12	6	3	1 h	9c	65% (10c)	
13 ^{<i>b</i>}	7	3	1 h	9c	58% (10c)	
$14^{b}_{,}$	2	3	1 h	9c	80% (10c)	
15"	3a	3	1 h	9c	0% (10c)	
16	6	3	1 h	(bg)	>95% (10d)	
17^b	7	3	1 h	Qd	>05% (10d)	
19 ^b	2	3	1 h	9d 9d	>95% (10d)	
10^{b}	2 3a	3	1 h	9d	18% (10d)	
20	6	30	1 h	Me	67% (10e)	
				O (9e)		
21	7	30	1 h	9e	65% (10e)	
22	2	30	1 h	9e	66% (10e)	
23	6	3	1 h	O_Et (9f)	66% (10f)	
24	7	3	1 h	9f	49% (10f)	
25	2	3	1 h	9f	64% (10f)	
<i>a</i> p		11/1	T / . 11			

alkenes that contain functional groups such as 9b, 9c, 9d, 9e, and 9f (entries 6, 7, 11, 12, 16, 20, and 23). The catalytic performance of 6 in this hydrosilylation is comparable to that of Karstedt's catalyst (7) or dialkylsilylene-ligated Pt catalyst 2 and better than that of 3a.^{8b} Although the actual catalytically active species for these reactions remains unclear at this stage, the catalytic performance of 6 in the reaction of 9f (entry 23) is slightly superior to that of 7 (entry 24), which suggests that 6 is an effective precatalyst, or that cyclic (alkyl)(amino)silylene 5 works as an effective ligand for the hydrosilylation. The stronger π -back-donation from Pt to Si in 6 and 2 compared to that of other N-heterocyclic carbenes and silvlenes such as 3 and 4 might reduce the π -back-donation from Pt to the vinvl moieties in the DVTMS ligand, which would result in facile elimination of the vinyl moiety from Pt to open a reactive coordination site on the Pt center.

Conclusions

We synthesized the novel Pt(0) complex **6**, which bears a DVTMS and a cyclic (alkyl)(amino)silylene ligand (5). The π -back-donation from Pt to Si in **6** is weaker than that in the corresponding (dialkylsilylene)Pt(0) complexes with a DVTMS ligand (2) on account of the higher-lying empty 3p orbital in 5 due to the electron donation of the amino group to the silylene center. Similar to analogous (dialkylsilylene)Pt(0) complexes with a DVTMS ligand, **6** catalyzes the hydrosilylation of various terminal alkenes that bear functional groups. The present study demonstrated that silylene **5** should be a useful ligand with both σ -donor and π -acceptor properties, as well as high thermal stability.

Experimental

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 glove box, as well as dry and oxygen-free solvents. Multinuclear NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. ¹H and ¹³C NMR chemical shifts are referenced to residual ¹H and ¹³C signals of the solvents: C_6D_6 (¹H: δ 7.16 and ¹³C: δ 128.0). ²⁹Si NMR chemical shifts are referenced relative to Me₄Si (δ 0.00). ¹⁹⁵Pt NMR chemical shifts are referenced relative to Na₂PtCl₆ (δ 0.00). Sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 glove box. Mass spectra were recorded on JEOL JMS-Q1050 and Bruker Daltonics SolariX 9.4T spectrometers. UV-vis spectra were recorded on a JASCO V-660 spectrometer.

Materials

Benzene- d_6 , hexane, and toluene were dried in a tube covered with a potassium mirror, and vacuum-distilled prior to use. Karstedt's catalyst (7), 1,1,1,3,5,5,5-heptamethyltrisiloxane (8),

and allylbis(trimethylsilyl)amine (9c) were supplied by Dow Corning Toray. These reagents were dried with molecular sieves (3A) and degassed under reduced pressure prior to use. 1-Hexene (9a), allyl glycidyl ether (9b), vinylcyclohexene oxide (9d), allyl acetate (9e), and allyl ethyl ether (9f) were obtained from common commercial sources, and used after drying over molecular sieves (3A) and degassing under reduced pressure. Complex 2^{8b} and silylene 5¹ⁱ were prepared according to published procedures.

Synthesis of 6

A Schlenk tube (50 mL) equipped with a magnetic stir bar was charged with Karstedt's catalyst (20% Pt, 1.62 g, 0.34 mmol of 7). A hexane solution (5 mL) of 5 (0.25 g, 0.68 mmol) was added to the tube at room temperature under stirring. The reaction mixture was stirred for one hour at room temperature, before all volatiles were removed under reduced pressure. Recrystallization of the resulting solid from hexane at -30 °C provided a colorless solid, which was washed with cold hexane. Removal of the volatiles from the solid under reduced pressure afforded the title compound as air-sensitive colorless crystals (0.26 g, 0.35 mmol) in 52% yield.

6a and 6b (~3:1 mixture): air and moisture sensitive colorless crystals; mp. 185 °C (decomp.); $\delta_{\rm H}$ (500 MHz; C₆D₆; Me₄Si; 298 K) -0.13 (6H, s, SiMe₂, 6a), -0.01 (6H, s, SiMe₂, 6b), 0.17 (18H, s, SiMe₃, 6a), 0.22 (18H, s, SiMe₃, 6b), 0.62 (6H, s, SiMe₂, 6a), 0.63 (6H, s, SiMe₂, 6b), 1.42-1.51 (6H, m, adamantyl (Ad), 6a and 6b), 1.78-1.94 (9H, m, Ad, 6a and 6b), 2.08 (2H, t, ${}^{3}J$ = 10.0 Hz, $CH_{2}C(SiMe_{3})_{2}$, 6a and 6b), 2.17–2.27 (2H, m, CH₂=CH-, 6a and 6b), 2.47 (2H, d, ³J = 15.0 Hz, CH=C H_2 , 6a), 2.54 (2H, d, J = 15.0 Hz, CH=C H_2 , 6b), 2.93 $(2H, d, {}^{3}J = 10.0 \text{ Hz}, CH = CH_{2}, 6a), 2.99 (2H, d, {}^{3}J = 10.0 \text{ Hz},$ CH=CH₂, **6b**), 3.17 (2H, t, ${}^{3}J$ = 5.0 Hz, N-CH₂-CH₂, **6a** and **6b**); $\delta_{\rm C}$ {¹H} (126 MHz; C₆D₆; Me₄Si, 298 K) -2.05 (Si*Me*₂, **6a**), -1.26 (SiMe₂, **6b**), 1.53 (SiMe₃, **6a**), 1.65 (SiMe₃, **6b**), 1.78 (SiMe₂, 6a), 1.97 (SiMe₂, 6b), 29.4 (N-CH₂CH₂-C, 6a), 29.5 (N-CH₂CH₂-C, 6b), 30.3 (CH in Ad, 6a), 30.5 (CH in Ad, 6b), 33.8 (C in Ad, 6a and 6b), 36.7 (CH₂ in Ad, 6a), 36.8 (CH₂ in Ad, **6b**), 39.2 (*C*H=CH₂, **6a**), 39.5 (*C*H=CH₂, **6b**), 44.1 (*C*H=*C*H₂, 6a), 44.4 (CH=CH₂, 6b), 45.3 (CH₂ in Ad, 6b), 45.4 (CH₂ in Ad, 6a), 47.8 (CH₂-N, 6a), 48.0 (CH₂-N, 6b), 55.1 [C(SiMe₃)₂, **6b**], 55.2 [C(SiMe₃)₂, **6a**]; δ_{Si} {¹H} (99 MHz, C₆D₆, Me₄Si, 298 K) 1.38 (SiMe₃, 6a and 6b), 2.45 [=CH-SiMe₂, s with satellites due to coupling with ¹⁹⁵Pt, ${}^{2}J({}^{29}\text{Si}-{}^{195}\text{Pt}) = 37$ Hz, **6a**], 2.78 (=CH-SiMe₂, 6b), 281.3 [Pt-Si, s with satellites due to coupling with 195 Pt, ${}^{1}J({}^{29}$ Si- 195 Pt) = 2335 Hz], 285.7 [Pt-Si, s with satellites due to coupling with ¹⁹⁵Pt, ${}^{1}J({}^{29}Si-{}^{195}Pt) = 2335$ Hz], δ_{Pt} (106.87 MHz; C₆D₆; Na₂PtCl₆; 299 K) –5846 (sept with satellites due to coupling with ²⁹Si, ²J(Pt-H) = 5 × 10 Hz, ${}^{1}J({}^{195}\text{Pt-Si}{}^{29}) = 2335 \text{ Hz}, 6a), -5839 \text{ (sept with satellites due }$ to coupling with ²⁹Si, ²J(Pt-H) = 5 × 10 Hz, ¹J(¹⁹⁵Pt-Si²⁹) = 2335 Hz, 6b); Found: C, 43.80; H, 7.58; N, 1.82%. Calcd for $C_{27}H_{55}OPtSi_5$: C, 43.52; H, 7.44; N, 1.88%; λ_{max} (hexane, 298 K) $nm^{-1} 228 (\epsilon/dm^3 mol^{-1} cm^{-1} 32 100), 329 (1077).$

A representative catalytic hydrosilylation procedure: reaction of 9a with 8 in the presence of 6

A Schlenk tube (20 mL) was charged with 1,1,1,3,5,5,5-heptamethyltrisiloxane (8; 0.50 g, 2.3 mmol) and 1-hexene (9a; 0.13 g, 1.81 mmol). As an internal standard, toluene (0.044 g, 0.48 mmol) was added to the reaction mixture. A benzene- d_6 solution of catalyst 6 (26.0 mmol L⁻¹, 3.5 µL, 9.1 × 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 (Fig. S10†) indicated that 3-hexyl-1,1,1,3,5,5,5-heptamethyltrisiloxane (10a; 504 mg, 1.72 mmol, 95%) had formed, which was identified by comparison of its ¹H NMR spectral data with those reported in the literature.¹⁶ The ¹H NMR spectra of the reaction mixture for entry 1 in Table 1 are shown in the ESI.†

Large-scale hydrosilylation of 9e

A Schlenk tube (20 mL) was charged with 1,1,1,3,5,5,5-heptamethyltrisiloxane (8; 0.99 g, 4.4 mmol) and allyl acetate (9e; 0.37 g, 3.7 mmol). As an internal standard, toluene (0.053 g, 0.58 mmol) was added to the reaction mixture. A benzene- d_6 solution of **6** (3.2 mmol L⁻¹, 62 µL, 2.0 × 10⁻⁴ mmol) was added to the reaction mixture. The mixture was aged at 50 °C for 1 h. The ¹H NMR spectrum of the reaction mixture indicated the presence of 3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl acetate (10e; 798 mg, 2.47 mmol, 67%) before 1,1,1,3,5,5,5-heptamethyltrisiloxane was removed under reduced pressure. Product **10e** was obtained in 55% after distillation (114 °C, 9 hPa).

10e: $\delta_{\rm H}$ (500 MHz, C₆D₆, Me₄Si, 298 K) -0.08 (3H, s, SiMe), 0.15 (18H, s, OSiMe₃), 0.47-0.52 (2H, m, CH₂-Si), 1.66-1.73 (2H, m, CH₂-CH₂-CH₂), 1.69 (3H, s, CO-CH₃), 4.02 (2H, t, *J* = 7.0 Hz, CH₂-O); $\delta_{\rm C}$ {¹H} (126 MHz, C₆D₆, Me₄Si, 298 K) -0.3 (SiMe₂), 1.9 (SiMe₃), 13.8 (CH₂), 20.5 (C(O)-CH₃), 22.9 (CH₂), 66.6 (CH₂O), 170.0 (*C*=O); $\delta_{\rm Si}$ {¹H} (99 MHz, C₆D₆, Me₄Si, 298 K) 7.6 [(Me₃SiO)₂MeSi], -21.6 [(Me₃SiO)₂MeSi], MS (EI, 70 eV) *m*/*z* 307 (9.5%), 265 (67.1), 221 (59.5), 207 (100), 191 (33.1), 73 (48.3); Found: C, 44.62; H, 9.47%. Calcd for C₁₂H₃₀O₄Si₃: C, 44.68; H, 9.37%.

Large-scale hydrosilylation of 9f

A Schlenk tube (20 mL) was charged with 1,1,1,3,5,5,5-heptamethyltrisiloxane (8; 7.1 g, 32 mmol) and allyl ethyl ether (2.3 g, 26.6 mmol). A benzene- d_6 solution of 6 (3.2 mmol L⁻¹, 150 µL, 4.8 × 10⁻⁴ mmol) was added to the reaction mixture. The mixture was aged at 50 °C for 1 h. Excess 8 was removed under reduced pressure, before 3-(3-ethoxypropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (10f) was obtained in 52% after distillation (86–87 °C, 6.7 hPa).

10f: $\delta_{\rm H}$ (500 MHz, C₆D₆, Me₄Si, 298 K) 0.14 (3H, s, SiMe), 0.17 (18H, s, OSiMe₃), 0.65–0.69 (2H, m, CH₂–Si), 1.14 (3H, t, J = 7.0 Hz, CH₂–CH₃), 1.77–1.81 (2H, m, CH₂–CH₂–CH₂), 3.32–3.35 (4H, m, CH₂–O–CH₂); $\delta_{\rm C}$ {¹H} (126 MHz, C₆D₆, Me₄Si, 298 K) –0.1 (SiMe), 2.0 (SiMe₃), 14.2 (CH₂), 15.5 (CH₃), 24.1 (CH₂), 66.1 (CH₂), 73.4 (CH₂); $\delta_{\rm Si}$ {¹H} (99 MHz, C₆D₆, $\begin{array}{l} Me_4 Si,\ 298\ K)\ 7.3\ [(Me_3 SiO)_2 MeSi],\ -20.8\ [(Me_3 SiO)_2 MeSi],\ MS \\ (EI,\ 70\ eV)\ m/z\ 293\ (12.1\%),\ 265\ (11.5),\ 251\ (9.9),\ 221\ (90.0), \\ 207\ (100),\ 191\ (24.5),\ 73\ (43.9);\ Found:\ C,\ 46.65;\ H,\ 10.50\%. \\ Calcd\ for\ C_{12} H_{32} O_3 Si_3;\ C,\ 46.70;\ H,\ 10.45\%. \end{array}$

Single-crystal X-ray diffraction analysis of 6

Single crystals of **6**, suitable for X-ray diffraction analysis, were obtained by recrystallization from hexane at -35 °C. Under an atmosphere of nitrogen, the crystals were coated with Apiezon grease, mounted on a glass fiber, and transferred to 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 For the analysis of the molecular structure, the Yadokari-XG software was used.¹⁹

Crystal data. $C_{27}H_{55}N_1O_1Pt_1Si_5$ [CCDC 1535615], M = 745.26, triclinic, a = 13.0764(4), b = 15.2793(5), c = 17.7828(5) Å, V = 3369.18 Å³, T = 100 K, space group $P\overline{1}$ (no. 2), Z = 2, 63 682 reflections measured, 12 543 unique ($R_{int} = 0.0285$), which were used in all calculations. The final $wR(F^2)$ was 0.0482 (all data).

Theoretical calculations

All theoretical calculations were performed using the Gaussian 09²⁰ and GRRM14²¹ programs. Geometry optimizations and frequency analyses for $6a_{opt}$ and $6b_{opt}$ were carried out at the B3PW91-D3/B level [Basis B: SDD for Pt; 6-311G(d) for H, C, N, O, Si]. Imaginary frequencies were not found in any of the optimized structures. Atomic coordinates for $6a_{opt}$ and $6b_{opt}$ are summarized in the ESI.† The transition energies and oscillator strengths of the electron transition of $6a_{opt}$ were calculated using a time-dependent hybrid DFT method (TD DFT) at the B3PW91-D3/B level of theory. The NBO analysis was carried out using the NBO6.0 program.¹⁵ UV-vis spectra of $6a_{opt}$ superimposed with the experimental spectrum of 6 are shown in Fig. S31.† Selected Kohn–Sham orbitals and important orbital interactions of $6a_{opt}$ are shown in Fig. S32 and S33,† respectively.

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