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Synthesis of an Arylbromosilylene–Platinum Complex by Using a 1,2-Dibromodisilene As a Silylene Source

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Supporting Information

ABSTRACT: Kinetically stabilized 1,2-dibromodisilene, Bbt(Br)Si=Si(Br)Bbt (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) (2), was treated with $[Pt(PCy_3)_2]$ to afford the corresponding arylbromosily-lene-Pt complex, Bbt(Br)Si=Pt(PCy_3)_2 (1), as stable orange crystals. The molecular structure of 1 was elucidated by spectroscopic and X-ray crystallo-



graphic analyses. The nature of the Si-Pt bond in 1 was investigated with the aid of DFT calcualtions.

 ilylene—transition metal complexes have been postulated as Ney intermediates in transition metal-catalyzed transformations of organosilicon compounds, and thus their synthesis as stable species had been attempted since the middle of the last century.¹ Since the seminal work on the synthesis of base-stabilized² and base-free³ silylene complexes two decades ago, a number of stable silvlene complexes have been synthesized and isolated by incorporating various transition metals and silylene ligands, allowing us to understand not only fundamental characteristics but also the unsual reactivity of silylene-transition metal complexes.⁴ The present synthetic methodology of silylene complexes can be classified into several categories,⁵ including (i) anion abstraction from silyl complexes $(R_2XSi-ML_n \rightarrow [R_2Si=ML_n]^+ + X^-, X^- = halide and$ pseudohalide), (ii) direct coordination of free silylenes to low-valent transion metals ($R_2Si: + ML_n \rightarrow R_2Si=ML_n$), (iii) [1,2]-migration of a substituent from silicon to transition metal centers in silvl complexes $(R_2XSi-ML_n \rightarrow R_2Si=M(L_n)X)$, (iv) salt elimination from 1,1-dimetallosilanes (or their equivalents) and transition metal dihalides $(R_2SiM'_2 + L_nMX_2)$ \rightarrow R₂Si=ML_n + M'X₂, M' = Li, etc., X = halogen), and (v) addition of an anion to silvlidyne complexes $(X^- + RSi \equiv ML_n)$ \rightarrow [R(X)Si=ML_n]⁻).⁶ Method (ii) was employed in the synthesis of the first neutral silylene complexes, Mes₂Si= $Pt(PR_3)_2$ (I: R = Cy, II: R = *i*-Pr),⁷ and it was recently found to be applicable to the synthesis of dialkylsilylene-transition metal complexes.8 Method (iv) has been recently developed9 and applied to synthesize the first example of Schrock-type silylene complexes.¹⁰ Although these methodologies have their own advantages and are complementary to each other, there are still limitations in the availability of stable silvlene-transition metal complexes. Especially, introduction of a functional group such as a halogen to the silylene center of the silylene-transition metal complex is not straightforward yet due to the difficulty of preparation of an appropriate silylene ligand source.¹¹

We have recently reported the synthesis and properties of kinetically stabilized 1,2-dibromodisilene Bbt(Br)Si=Si(Br)Bbt (2) (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-

(trimethylsilyl)methyl]phenyl).¹² During the course of our study on its reactivity, 1,2-dibromodisilene 2 was found to exhibit reactivity as a bromosilylene toward ketones, alcohols, alkenes, alkynes, and a diene, playing a role as a bottleable source of arylbromosilylene Bbt(Br)Si: by proper choice of the reaction conditions and partners.^{12,13} These results prompted us to examine the reaction of 2 with a low-valent transition metal complex in the expectation of obtaining the corresponding bromosilylene complex, demonstraiting a new synthetic method of silvlene complexes bearing a reactive functional group on the low-coordianted silicon (i.e., 2 + 2 $ML_n \rightarrow 2$ $Bbt(Br)Si=ML_n$). Here, we report the synthesis of a bromosilylene-Pt complex, $Bbt(Br)Si=Pt(PCy_3)_2$ (1), by the reaction of disilene 2 with $[Pt(PCy_3)_2]$, and the structure and properties of 1 were investigated experimentally and theoretically.¹⁴

Disilene 2 was treated with 2 equiv of $[M(PCy_3)_2]$ (M = Pd, Pt) in C_6D_6 at 25 °C, and the reactions were monitored by multinuclear NMR spectroscopy. In the case of the reaction with $[Pd(PCy_3)_2]$,¹⁵ the color of the reaction mixture turned from yellow to black within minuites, and then intractable mixtures containing palladium black were obtained. Conversely, the reaction of 2 with $[Pt(PCy_3)_2]$ afforded bromosilylene-Pt complex 1 as the sole product, judging from the ¹H and ³¹P NMR spectra of the reaction mixture. Complex 1 was isolated in 56% yield as orange-colored, air- and moisture-sensitive crystals by the careful recrystallization from the reaction mixture (Scheme 1). Although the formation mechanism of complex 1 is still unclear, the reaction was clean and did not contain any intermediates detectable by means of multinuclear NMR spectroscopy.¹⁶ The ²⁹Si NMR spectrum of 1 in C₆D₆ shows a triplet signal with a set of satellite signals in characteristic low-field region (δ_{Si} 298.11, ${}^{2}J_{SiP}$ = 137 Hz, ${}^{1}J_{\text{SiPt}}$ = 3660 Hz), revealing the low-coordinated silicon character of 1. Compared to the previously reported

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Scheme 1. Reactions of Disilene 2 with $[M(PCy_3)_2]$ (M = Pt, Pt)



silylene–Pt complexes (δ_{Si} 309–394), the ²⁹Si resonance of 1 is slightly high-field shifted. The ${}^{2}J_{SiP}$ value of 1 is ranked between those of the neutral silylene–Pt complexes (${}^{2}J_{SiP}$ 107–118 Hz) and that of cationic silvene –Pt complex {Mes₂Si=Pt(H)[(i- $Pr_{2}PCH_{2}CH_{2}P(i-Pr_{2}) [MeB(C_{6}F_{5})_{3}] (^{2}J_{SiP(trans)} = 188 \text{ Hz}).^{1}$ Meanwhile, the ${}^{1}J_{SiPt}$ coupling constant of 1 (3660 Hz) is much larger than those of the previously reported silylene-Pt(0)complexes (e.g., II: ${}^{1}J_{SiPt} = 2973$ Hz), suggesting the enhanced s-character of the Si-Pt bond in 1 as compared with those of the previously reported silvlene-Pt(0) complexes. The ${}^{1}J_{PPt}$ coupling constant of 1 (3300 Hz) also increased compared to those of the other silylene–Pt(0) complexes (e.g., I: ${}^{1}J_{PPt}$ = 3068 Hz; II: ${}^{1}J_{PPt}$ = 3119 Hz). These NMR spectroscopic features of 1 indicate the arylbromosilylene ligand Bbt(Br)Si: should exhibit larger π -accepting ability than carbon-substituted silvlene ligands such as Mes₂Si:.

The solid-state structure of 1 was determined by the X-ray crystallographic analysis (Figure 1). The Si1-Pt1 bond length



Figure 1. Molecular structure of **1**. (a) Thermal ellipsoids are drawn at the 30% probability level, and only the major parts of the disorderd molecules are shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Pt1 2.2076(15), Si1–C(Bbt) 1.916(5), Si1–Br1 2.3143(15), Pt1–P1 2.3170(13), Pt1–P2 2.3289(14), Pt1–Si1–C(Bbt) 151.86(17), C(Bbt)–Si1–Br1 98.16(16), Br1–Si1–Pt1 109.88(6), Si1–Pt1–P1 120.85(5), Si1–Pt1–P2 124.36(5), P1–Pt1–P2 113.98(5). (b) Ball-and-stick representation of the core structure of **1** showing the angle between the coordination planes of Si1 and Pt1 atoms.

of 1 (2.2076(15) Å) is shorter than the shortest end of the Si– Pt single bond lengths $(2.224-2.451 \text{ Å})^{18}$ and comparable to the reported Si=Pt double-bond lengths (2.21-2.27 Å),4,7 revealing the Si=Pt double-bond character of 1 in the solid state. The Si1–Br1 bond of 1 (2.3143(15) Å) is elongated from those of 1,2-dibromodisilene 2 (2.243(3), 2.254(3) Å), probably because of the 5d(Pt1) $\rightarrow \pi^*$ (Si1-Br1) electronic interaction. The presence of such a donor/acceptor-type interaction was indicated by the DFT calculations (vide infra). Both the Si1 and Pt1 atoms of 1 show planar geometries, as shown by the summations of the bond angles around them. The angle between the least-squares plane of the silvlene ligand (defined by the Si1, Pt1, Br1, and C(Bbt) atoms) and the platinum coordination plane (defined by the Si1, Pt1, P1, and P2 atoms) is 72° (Figure 1b), which is close to the value reported for complex I (69°). One noticeable structural feature of 1 is that the geometry around the Si1 atom substantially deviates from trigonal-planar one and approaches a T-shaped geometry (Pt1-Si1-C(Bbt) angle: 151.86(17)°, Pt1-Si1-Br1 angle: 109.88(6)°). In contrast, previously reported silvlene-Pt complexes exhibit trigonal or Y-shaped geometries around the silylene ligands (e.g., Pt-Si-C(Mes) angles of complex I: 123.8(2)°, 130.6(2)°). Such a structural anomaly in 1 would be due to the steric repulsion between the Bbt and cyclohexyl groups, judging from the results of DFT calculations on less hindered model complexes as shown in Table 1. The optimized geometries of model complex 6 bearing a Bbt' group, where the $C(SiMe_3)_3$ group at the para-position of Bbt group was replaced by a H atom, well reproduced the experimentally observed structure of 1. Therefore, the subsequent calculations were carried out by using the optimized structure of 6.

The UV-vis spectra of complex 1 in THF and benzene are almost identical, both of which exhibit two strong absorption bands at λ_{max} = 382 and 312 nm, respectively (Figure 2). In addition to these distinct absorption bands, complex 1 exhibits a weak, shoulder-like absorption extended to 560 nm, resulting in the orange-red color of 1. The negligible solvent effect in the UV-vis absorption spectra indicates no apparent coordination of a THF molecule to complex 1 under these conditions. The origins of these absorptions were investigated by using TDDFT calculations on model complex 6, and the simulated spectra are shown by vertical green lines in Figure 2, exhibiting a good agreement between the simulated and experimental absorption spectra. The simulated spectrum contains two intense absorption peaks at 397 nm (f = 0.1200, HOMO-1 \rightarrow LUMO) and 321 nm (f = 0.1121, HOMO-5 \rightarrow LUMO) and a red-shifted weak transition at 518 nm (f = 0.0092, HOMO \rightarrow LUMO), well reproducing the experimentally observed absorption peaks of 1.

The electronic character of the Si–Pt bond of model complex 6 was investigated by using DFT calculations, and the selected Kohn–Sham molecular orbitals of 6 are shown in Figure 3. The HOMO and HOMO–1 of 6 correspond to the σ - and π -type bonding orbitals of the Si–Pt bond, respectively. These orbitals also contain small contributions of the Si–Br antibonding interactions. The LUMO of 6 corresponds to the Si–Pt π -antibonding orbital and mainly consists of the vacant 3p(Si) orbital on the bromosilylene ligand. Meanwhile, the LUMO+1 of 6 could be described as a mixture of an in-plane Si–Pt π -bonding orbital and the Si–Br σ^* orbital.

The interactions between the bromosilylene ligand and the Pt center in model complex 6 were further analyzed on the basis of NBO calculations. The calculated natural bonding orbital corresponding to the Si–Pt bonding interaction is

Table 1. Selected Bond	Lengths (Å) a	and Angles (deg)	around the Silvl	lene Ligands in 1 ;	and Model Complexes 3–6

		R ¹ P Si=Pt Br P	$ \begin{array}{l} \textbf{3: } R^1 = R^2 = \textbf{M} \\ \textbf{4: } R^1 = \text{Dip, } R^2 \\ \textbf{5: } R^1 = \text{Bbt', } R^2 \\ \textbf{6: } R^1 = \text{Bbt', } R^2 \end{array} $	$ \begin{array}{c} \mathbf{e} \\ = \mathbf{M}\mathbf{e} \\ \mathbf{e} = \mathbf{M}\mathbf{e} \\ \mathbf{e} = \mathbf{C}\mathbf{y} \end{array} $	Dip: $R^3 = Me$ R^3 Bbt': $R^3 = SiMe_3$		
	Si-Pt/Å	Si-Br/Å	$Si-C(R^1)/Å$	$Pt-Si-C(R^1)/deg$	$C(R^1)$ –Si–Br/deg	Br-Si-Pt/deg	$\theta/{\rm deg}^a$
1^b	2.2076(15)	2.3143(15)	1.916(5)	151.86(17)	98.16(16)	109.88(6)	72
3 ^c	2.21660	2.29392	1.89861	133.536	100.148	126.316	89
4 ^{<i>c</i>}	2.21665	2.25851	1.89527	135.735	101.170	123.081	90
5 ^c	2.22571	2.31782	1.90797	145.848	100.700	113.452	90
6 ^{<i>c</i>}	2.24376	2.34099	1.93727	151.288	94.994	106.878	64

^{*a*}Angles between the coordination planes of the low-coordinated silicon (defined by Si, Pt, $C(R^1)$, and Br atoms) and platinum (Pt, Si, and the two P atoms) atoms (θ /deg). ^{*b*}Experimental values obtained by X-ray diffraction analysis. ^{*c*}Optimized geometry calculated at the B3PW91/LanL2DZ[Pt]:6-31G(d)[C,H,Br,P,Si] level of theory.



Figure 2. UV-vis absorption spectra of 1 in THF (blue line) or benzene (red line) and TDDFT-simulated spectra (vertical green lines).



Figure 3. Kohn–Sham molecular orbitals of the model complex 6 (isovalue = 0.03). Hydrogen atoms are not shown for clarity.

predominantly formed from the 3s(Si) and 6s(Pt) orbitals $(\sigma(\text{Si}-\text{Pt}) = 0.8844(3s3p^{0.79})\text{Si} + 0.4667(6s6p^{0.29})\text{Pt})$, showing that the main bonding interaction between the bromosilylene and platinum moieties originates from the 3s(Si) \rightarrow 6s*(Pt) σ -donation. The large s-character of the Si–Pt bond was also suggested by the observed large ${}^{1}J_{\text{SiPt}}$ and ${}^{2}J_{\text{SiP}}$ coupling

constants of 1 in the NMR spectra (*vide supra*). On the other hand, the Si-Pt π -back-bonding was evaluated as a relatively strong donor/acceptor interaction rather than a distinct covalent bond, and the stabilization energy by the 5d(Pt) \rightarrow 3p*(Si) interaction was estimated to be 20.89 kcal·mol⁻¹ by the second-order perturbation theory. These calculational results showed that the Si-Pt bond in 1 is mainly composed of the Si-Pt σ bond, and the contribution of the π -back-donation interaction is much smaller compared to the σ bond. Therefore, the Si-Pt bond in the bromosilylene-Pt complex would be best described as a single bond rather than a genuine double bond. Such description was further confirmed by the Wiberg bond index of the Si-Pt bond in 6 (0.9924).

SUMMARY

In conclusion, bromosilylene–Pt complex 1 was successfully synthesized by the reaction of stable 1,2-dibromodisilene 2 with $[Pt(PCy_3)_2]$. The structure of 1 was unambiguously confirmed on the basis of multinuclear NMR spectra and single-crystal Xray diffraction analysis. Compared to the previously reported silylene–Pt complexes, 1 exhibited increased ${}^{1}J_{\text{SiPt}}$ and ${}^{2}J_{\text{SiP}}$ coupling constants, indicating the enhanced s-character of the Si–Pt bond of 1. The bonding character between the bromosilylene and Pt moieties in 1 was theoretically investigated, revealing the high s-character of the Si–Pt bond as predicted by the experimental data. In addition, the NBO analysis showed that the π -back-donation from the Pt to Si center should be much weaker than the σ -donation from the Si to Pt. A reactivity study of 1 is currently in progress.

EXPERIMENTAL SECTION

General Procedures and Instrumentation. All the manipulations were performed in a glovebox filled with argon. Solvents were purified by standard methods and/or the Ultimate Solvent System, Glass Contour Company,¹⁹ and the remaing trace water and oxygen were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. ¹H (300 MHz), ¹³C (75 MHz), ³¹P (121 MHz), and ²⁹Si (59 MHz) NMR spectra were recorded on a JEOL JNM AL-300 NMR spectrometer. ¹H and ¹³C NMR spectra were referenced to the signals due to residual C₆D₅H (7.15 ppm) or C₆D₆ (128 ppm), respectively, while ³¹P and ²⁹Si NMR spectra were referenced to the signals of 85% H₃PO₄ (0 ppm) or tetramethylsilane (0 ppm), respectively. ¹⁹⁵Pt (129 MHz) NMR spectra were recorded on a Bruker AVANCE-600 spectrometer and referenced to the signal of 1.2 M Na₂PtCl₆ in D₂O ($\hat{0}$ ppm). UV-vis spectra were recorded on a JASCO Ubest V-570 spectrometer. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

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Bbt(Br)Si=Si(Br)Bbt (2)¹²a and $[Pt(PCy_3)_2]^{20}$ were synthesized according to the literature.

Synthetic Procedure for 1. In a 5 mm φ NMR tube connected to a J.Young joint, 2 (97 mg, 0.066 mmol) and [Pt(PCy₃)₂] (0.10 g, 0.13 mmol) were dissolved in C_6D_6 (0.5 mL), and the tube was sealed and moderately shaken at 25 °C with a homemade shaker to afford an orange solution and reddish-orange crystals after 10 h. The crystals were filtered in a glovebox, washed with hexane, and dried in vacuo to give analytically pure 1 as orange crystals (0.11 g, 0.074 mmol, 56%). Mp: 146 °C (dec). ¹H NMR (300 MHz, C₆D₆, rt): δ 0.43 (s, 27H), 0.46 (s, 36H), 1.28-1.39 (m, 12H), 1.61-1.77 (m, 24H), 1.83-1.91 (m, 12H), 2.22–2.35 (m, 18H), 3.13 (s, 2H); 6.89 (s, 2H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75 MHz, C_6D_6 , rt): δ 2.94 (s, $CH(SiMe_3)_2$), 6.20 (s, C(Si<u>Me</u>₃)₃), 22.25 (s, <u>C</u>(SiMe₃)₃), 26.94 (brs, CH₂), 28.09 (brs, CH₂), 31.27 (s, CH(SiMe₃)₂), 31.40 (brs, CH₂), 41.07 (brs, P-CH), 127.68 (s, C3), 146.51 (s, C4), 148.30 (s, C2), 154.48 (t, ${}^{3}J_{CP} = 9.8$ Hz, C1). ²⁹Si{¹H} NMR (59 MHz, C₆D₆, rt): δ 1.03 (s), 1.71 (s), 297.50 (t, ²J_{SiP} = 138 Hz, ${}^{1}J_{\text{SiPt}}$ = 3660 Hz). ${}^{31}P{}^{1}H{}$ NMR (121 MHz, C₆D₆, rt): δ 54.33 (${}^{1}J_{PPt}$ = 3300 Hz, ${}^{2}J_{PSi}$ = 138 Hz). No signal was observed in ¹⁹⁵Pt NMR spectra even after long-time measurement for a few days. Anal. Calcd for C₆₆H₁₃₃BrP₂PtSi₈: C, 53.26; H, 9.01. Found: C, 53.03; H, 9.04.

X-ray Crystallographic Analysis of 1. The intensity data of 1 were collected on a Rigaku Saturn CCD diffractometer equipped with a VariMax X-ray optics system using graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å). Preliminary reflection data were collected on a BL38B1 beamline in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) with a diffractometer equipped with an ADSC Quantum315 CCD detector (2011A1409). The structure was solved by a direct method (SHELXS-97) and refined by full-matrix least-squares method on F^2 for all reflections (SHELXL-97).²¹ All hydrogen atoms were placed using AFIX instructions, while the other atoms were refined anisotropically. The tris(trimethylsilyl)methyl group is disordered over two positions with 58% and 42% occupancy, and one of the trimethylsilyl groups in one bis(trimethylsilyl)methyl group is also disordered over two positions with 62% and 38% occupancy. Crystal data for 1: $C_{66}H_{133}BrP_2PtSi_8$, fw = 1488.38 g·mol⁻¹, T = 123(2) K, trigonal, space group $R\overline{3}$ (#148), a = 54.9060(5) Å, c = 14.2772(2) Å, V = 37274.6(6) Å³, Z = 18, $D_{calcd} = 1.194$ g·cm⁻³, crystal size 0.10 × $0.03 \times 0.01 \text{ mm}^3$, $0.74^\circ < \theta < 25.50^\circ$, independent reflections = 15287 $(R_{int} = 0.0797)$, completeness = 99.2%, GOF = 1.074, $R_1 (I > 2\sigma(I)) =$ 0.0428, wR_2 (all data) = 0.1340, largest diffraction peak and hole 3.045 and $-1.042 \text{ e}\cdot\text{Å}^{-3}$ (around Pt1 atom).

Theoretical Calculations for Model Complexes $R(Br)Si = Pt-(PMe_3)_2$ (3, R = Me; 4, $R = 2,6-(i-Pr)_2-C_6H_3$; 5, R = Bbt') and $Bbt'(Br)Si = Pt(PCy_3)_2$ (6) ($Bbt' = 2,6-[CH(SiMe_3)_2]_2-C_6H_3$). Geometry optimizations and TD-DFT calculations were performed using the Gaussian 03 (Rev. E.01) program package²² at the B3PW91 density functional level of theory using LanL2DZ[Pt]:6-31G(d)[Br,P,Si,C,H] mixed basis sets. The optimized geometries of these model complexes are included in the Supporting Information. NBO calculations on 6 were carried out using the NBO program (Version 3.1)²³ included in the Gaussian 03 program package at the B3PW91/LanL2TZ(f)[Pt]:6-311G(2df)[Br,P,Si]:6-31G(d)[C,H] level.

ASSOCIATED CONTENT

S Supporting Information

CIF file of 1 and the optimized geometries of model complexes 3-6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) Addition of PCy_3 to the C_6D_6 solution of disilene 2 did not show any detectable change in the NMR spectra, indicating that PCy_3 does not participate in the generation of reactive bromosilylene Bbt(Br)Si: from 2.

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