Double Addition of the Si−H Bonds of $Pt(SiHPh_2)_2(PMe_3)_2$ to Nitriles to Afford 3-Aza-2,4-disilaplatinacyclobutanes

Makoto Tanabe and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Summary: The reactions of PhCN and MeCN with $Pt(SiHPh_2)_2(PMe_3)_2$ led to double addition of Si−H bonds to the C≡N triple bond of the nitriles to produce the 3-aza-2,4-disilaplatinacyclobutanes, $Pt(SiPh_2\text{-}NR\text{-}SiPh_2)(PMe_3)_2$ (R = CH_2Ph, Et). Structure determined by X-ray crystallography of the complexes revealed mononuclear structures with planar four-membered rings composed of a disilazanediyl ligand and a platinum center.

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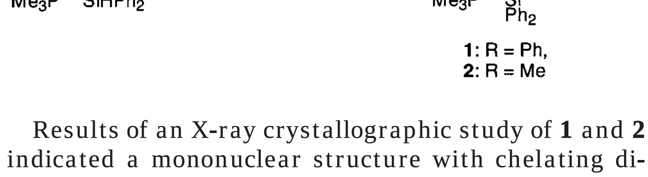
Introduction

Transition metal complex-promoted catalytic or stoichiometric addition of the Si−H bond to the C≡N bond has been reported to a lesser extent than the hydrosilylation of C=C, C≡C, and C=O bonds. The Rh complex-catalyzed reaction of organosilanes with acrylonitrile results in the addition of an Si−H bond to the C=C double bond to yield β-silylpropionitriles,[1] which suggests hydrosilylation of the C≡N bond is more difficult compared to the C=C bond. Hydrosilylation of nitriles was achieved using $Co_2(CO)_8$ as a catalyst, producing disilazanes via the addition of two Si−H bonds to the C≡N bond.[2,3] A related stoichiometric Si−N bond formation was reported in the reaction of 2,5-disilaferracyclopentane, $(CO)_4FeSiPh_2\text{-}CR{=}CR\text{-}SiPh_2$, with a nitrile to afford the corresponding five-membered cyclic disilazane.[4] We report here a new reaction, the stoichiometric addition of the Si−H bonds of $SiHPh_2$ ligands bonded to Pt to the C≡N bond to afford 3-aza-2,4-disilaplatinacyclobutanes.

Results and Discussion

Heating $Pt(SiHPh_2)_2(PMe_3)_2$[5] in benzonitrile and in acetonitrile at 70−80 °C afforded 3-aza-2,4-disilaplatinacyclobutanes, $(Me_3P)_2Pt(SiPh_2{-}N(CH_2R)\text{-}SiPh_2)$ (**1**: R = Ph, **2**: R = Me), in 62% and 64% yield, respectively (eq 1). The reaction mixture does not contain other possible products such as those from the insertion of the C≡N bond into the Pt−Si bond or those from bis-silylation of the nitriles.[3]



Results of an X-ray crystallographic study of **1** and **2** indicated a mononuclear structure with chelating disilazanediyl ligands as shown in Figure 1 rather than alternative di- or multinuclear structures with bridging ligands. An analogous 3-aza-2,4-disilaplatinacyclobu-

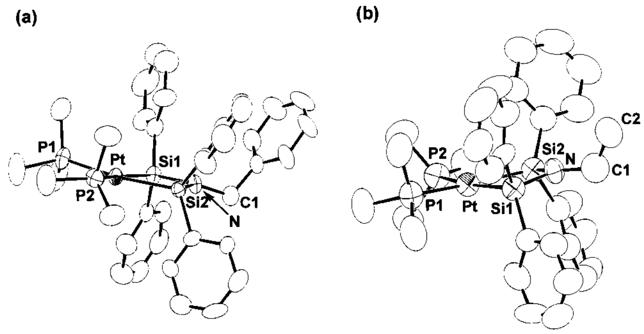


Figure 1. (a) ORTEP drawing of **1** at 50% ellipsoidal level. Selected bond distances (Å) and angles (deg): Pt−P1 2.338(3), Pt−P2 2.328(3), Pt−Si1 2.366(4), Pt−Si2 2.377(3), Si1−N 1.734(8), Si2−N 1.726(8), N−C1 1.47(1), C1−C2 1.49(1), Si1···Si2 2.630(4), P1−Pt−P2 102.8(1), P1−Pt−Si1 93.3(1), P1−Pt−Si2 160.3(1), P2−Pt−Si1 163.2(1), P2−Pt−Si2 96.3(1), Si1−Pt−Si2 67.3(1), Pt−Si1−N 96.9(3), Pt−Si2−N 96.7(3), Si1−N−Si2 98.9(4), Si1−N−C1 129.7(6), Si2−N−C1 128.9(7), N−C1−C2 113.9(9). (b) ORTEP drawing **2**·toluene at 50% ellipsoidal level. Solvated toluene was omitted for simplicity. Selected bond distances (Å) and angles (deg): Pt−P1 2.323(3), Pt−P2 2.318(3), Pt−Si1 2.365(3), Pt−Si2 2.350(3), Si1−N 1.730(8), Si2−N 1.732(7), N−C1 1.44(1), C1−C2 1.38(2), Si1···Si2 2.627(4), P1−Pt−P2 98.9(1), P1−Pt−Si1 95.6(1), P1−Pt−Si2 162.4(1), P2−Pt−Si1 165.5(1), P2−Pt−Si2 97.8(1), Si1−Pt−Si2 67.7(1), Pt−Si1−N 96.2(3), Pt−Si2−N 96.7(3), Si1−N−Si2 98.7(4), Si1−N−C1 130.3(7), Si2−N−C1 129.4(7), N−C1−C2 120(1).

(1) (a) Nozakura, K.; Konotsune, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 322. (b) Belyakova, Z. V.; Golubstov, S. A.; Yakusheva, T. M. *Zh. Obshch. Khim.* **1962**, *32*, 1997; *Chem. Abstr.* **1963**, *58*, 4591. (c) Chalk, A. J. *J. Organomet. Chem.* **1970**, *21*, 207. (d) Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1976**, *111*, 43.

(2) Murai, T.; Sakane, T.; Kato, S. *Tetrahedron Lett.* **1985**, *26*, 5145.

(3) Pt complex promoted 1,2-bissilylation of nitriles by 1,2-bis(dimethylsilyl)benzene was reported to give the corresponding heterocyclic products. Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett.* **1992**, 45.

(4) Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623.

(5) The complex exists as an equilibrium mixture of the cis and trans isomers in solution. See: Kim, Y.-J.; Park, J.-I.; Lee, S.-C.; Osakada, K.; Tanabe, M.; Choi, J.-C.; Koizumi, T.; Yamamoto, T. *Organometallics* **1999**, *18*, 1349.

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tane without N-alkyl substituents, $\overline{Pt(SiMe_2\text{-}NH\text{-}SiMe_2)}$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) was prepared by the reaction of Pt(η^2-$SiMe_2SiMe_2$)(dppe) with NH_3,[6] but its precise bond parameters were not determined. The bond parameters of the platinacyclobutane part of the complexes **1** and **2** are similar to each other and also to those of $\overline{Pt(SiMe_2\text{-}O\text{-}SiMe_2)}$(dppe).[6] The four-membered rings composed of Pt, Si, and N (or O) atoms are essentially planar; the sum of the four bond angles of the chelating ligand and the metal center are approximately 360°. Complexes **1** and **2** contain close SiSi contacts (2.630(4) and 2.627(4) Å) and acute Si−Pt−Si bond angles (67.3(1)° and 67.7(1)°). These bond distances and angles are somewhat larger than those in $\overline{Pt(SiMe_2\text{-}O\text{-}SiMe_2)}$(dppe) (2.549(2) Å and 65.0(1)°).[6,7]

The NMR spectra of **1** and **2** also support structures with a disilazanediyl ligand bonded to the square-planar Pt center in a chelating manner. The ^{1}H and ^{13}C{^{1}H} NMR signals of the PMe_3 ligands indicate the presence of two equivalent phosphine ligands at the cis positions. The ^{29}Si{^{1}H} NMR signal shows splitting due to two ^{31}P nuclei in the trans and cis positions ($^2J_{SiP}$ = 154, 18 Hz for **1** and 154, 17 Hz for **2**). The peak positions (δ −10.6 (**1**) and −13.5 (**2**)) are similar to those reported for the NH containing 3-aza-2,4-disilaplatinacyclobutane (δ −12.1 for $\overline{Pt(SiMe_2\text{-}NH\text{-}SiMe_2)}$(dppe)).[6] The CH_2-N carbon in the ^{13}C{^{1}H} NMR spectra of the complexes exhibits symmetrical triplet signals due to two equivalent phosphorus nuclei ($^4J_{CP}$ = 6 Hz).

In summary, this study provides a convenient method for the preparation of 2,4-disila-3-azaplatinacyclobutanes with N-substituents. The addition of the Si−H bond of the silyl ligand to the C≡N bond occurs at elevated temperature to afford the products selectively.

Table 1. Crystallographic Data and Details of Refinement of 1 and 2·Toluene

	1	**2**·toluene
chemical formula	$C_{37}H_{45}NP_2Si_2Pt$	$C_{39}H_{51}NP_2Si_2Pt$
fomula weight	816.98	847.05
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	10.932(8)	9.965(4)
b, Å	19.284(7)	16.034(3)
c, Å	9.583(5)	25.097(3)
α, deg	102.56(4)	
β, deg	112.04(4)	98.46(2)
γ, deg	79.73(5)	
V, Å^3	1817(2)	3966(2)
Z	2	4
μ, mm^{-1}	4.025	3.691
F(000)	820	1712
D_{calcd}, g cm^{-3}	1.493	1.418
cryst size, mm × mm × mm	0.61 × 0.57 × 0.34	0.68 × 0.34 × 0.20
2θ range, deg	5.0−55.0	5.0−55.0
unique reflections	8347	9428
used reflections ($I > 3.0\sigma(I)$)	6368	4235
no. of variables	388	371
R	0.050	0.048
R_w	0.057	0.046

Experimental Section

General Methods. All manipulations of the Pt complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. $Pt(SiHPh_2)_2(PMe_3)_2$ was prepared according to the literature method.[5] Benzonitrile, distilled from CaH_2, and dry acetonitrile purchased from Kanto Chemical Co., Inc. were stored under nitrogen. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, ^{31}P{^{1}H}) were recorded on JEOL EX-400 or Varian Mercury 300 spectrometers. ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR peak positions are referenced to external 85% H_3PO_4 and external $SiMe_4$, respectively. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of $\overline{Pt(SiPh_2\text{-}NCH_2Ph\text{-}SiPh_2)}(PMe_3)_2$ (1) and $\overline{Pt(SiPh_2\text{-}NEt\text{-}SiPh_2)}(PMe_3)_2$ (2). A solution of Pt-$(SiHPh_2)_2(PMe_3)_2$ (478 mg, 0.67 mmol) in benzonitrile (15 mL) was heated for 12 h at 70−80 °C. The color of the solution turned from yellow to orange during the course of the reaction. The solvent was removed at reduced pressure. Addition of hexane to the resulting red residue caused the separation of an orange solid that was collected by filtration, washed repeatedly with hexane, and dried *in vacuo* to give **1** as a pale yellow solid (336 mg, 62%). Recrystallization from toluene−hexane afforded pale yellow crystals suitable for X-ray crystallography. Anal. Calcd for $C_{37}H_{45}NP_2PtSi_2$: C, 54.40; H, 5.55; N, 1.71. Found: C, 54.63; H, 5.81; N, 1.72. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.22 (m, 18H, PMe_3, $^2J_{HP}$ = 7 Hz, $^3J_{HPt}$ = 21 Hz), 3.72 (s, 2H, CH_2, $^4J_{HPt}$ = 8 Hz), 6.60 (d, 2H, $CH_2C_6H_5$-*o*, J_{HH} = 7 Hz), 6.73 (t, 2H, $CH_2C_6H_5$-*m*, J_{HH} = 7 Hz), 6.83 (t, 1H, $CH_2C_6H_5$-*p*, J_{HH} = 7 Hz), 7.27 (m, 12H, SiC_6H_5-*m* and -*p*), 7.69 (m, 8H, SiC_6H_5-*o*). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 19.1 (apparent triplet, PMe_3, J_{CP} = 14 Hz, $^2J_{CPt}$ = 28 Hz), 51.9 (t, CH_2, $^4J_{CP}$ = 6 Hz, $^3J_{CPt}$ = 138 Hz), 124.8 ($CH_2C_6H_5$-*p*), 126.6 (SiC_6H_5-*m*), 126.8 ($CH_2C_6H_5$-*m*), 127.2 ($CH_2C_6H_5$-*o*), 128.5 (SiC_6H_5-*p*), 136.2 (SiC_6H_5-*o*, $^3J_{CPt}$ = 20 Hz), 142.6 ($CH_2C_6H_5$-*ipso*), 143.9 (t, SiC_6H_5-*ipso*, $^3J_{CP}$ = 5 Hz, $^2J_{CPt}$ = 38.9 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ −15.4 ($^2J_{PSi}$ = 129 Hz, J_{PPt} = 1661 Hz). ^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, −70 °C): δ −10.6 ($^2J_{SiP}$ cis = 18 Hz, $^2J_{SiP}$ trans = 154 Hz, J_{SiPt} = 1050 Hz).

Complex **2** was obtained similarly as a yellow solid (343 mg, 64%) and recrystallized from toluene−hexane. Anal. Calcd for $C_{32}H_{43}NP_2PtSi_2$: C, 50.91; H, 5.74; N, 1.86. Found: C, 51.25; H, 5.90; N, 2.16. ^{1}H NMR (400 MHz, C_6D_6): δ 0.87 (d, 18H, PMe_3, $^2J_{HP}$ = 7 Hz, $^3J_{HPt}$ = 23 Hz), 0.95 (t, 3H, CH_3, $^3J_{HH}$ = 7 Hz), 3.07 (q, 2H, CH_2, $^3J_{HH}$ = 7 Hz, $^4J_{HPt}$ = 8 Hz), 7.24 (t, 8H, C_6H_5-*p*, J_{HH} = 7 Hz) 7.34 (t, 8H, C_6H_5-*m*, J_{HH} = 7 Hz), 8.14 (d, 8H, C_6H_5-*o*, J_{HH} = 7 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 18.1 (CH_3), 19.8 (apparent triplet, PMe_3, J_{CP} = 13 Hz, $^2J_{CPt}$ = 28 Hz), 42.0 (t, CH_2, $^4J_{CP}$ = 6 Hz, $^3J_{CPt}$ = 132 Hz), 126.6 (C_6H_5-*m*), 127.4 (C_6H_5-*p*), 136.5 (C_6H_5-*o*, $^3J_{CPt}$ = 20 Hz), 144.8 (t, C_6H_5-*ipso*, $^3J_{CP}$ = 6 Hz, $^2J_{CPt}$ = 39 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −16.2 ($^2J_{PSi}$ = 125 Hz, J_{PPt} = 1650 Hz). ^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2, −70 °C): δ −13.5 ($^2J_{SiP}$ cis = 17 Hz, $^2J_{SiP}$ trans = 154 Hz, J_{SiPt} = 1048 Hz).

Crystal Structure Determination. Crystals of **1** and **2**·toluene were mounted in glass capillary tubes under Ar. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using MoKα radiation (λ = 0.710 69 Å) and $\omega - 2\theta$ scan method, and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out by using a program package teXsan for Windows. Atomic scattering factors were obtained from the literature.[8] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Carbon atoms of solvated toluene of **2**·

(6) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. See also: Osakada, K.; Tanabe, M.; Tanase, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4053.

(7) Other examples of SiSi contact: Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068; Anderson, A. B.; Shiller, P.; Zarate, E. A.; Tessier-Youngs, C. A.; Tessier-Youngs, W. J. *Organometallics* **1989**, *8*, 2320. See also: Alemany, P.; Alvarez, S. *Inorg. Chem.* **1992**, *31*, 4266. Aullón, G.; Alemany, P.; Alvarez, S. *J. Organomet. Chem.* **1994**, *478*, 75.

toluene were refined isotropically. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. Crystal data and details of refinement of **1** and **2** are summarized in Table 1.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Crystallographic data of **1** and **2**·toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

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Additions and Corrections

2001, Volume 20

Kande K. D. Amarasinghe, Sanjoy K. Chowdhury, Mary Jane Heeg, and John Montgomery*: Structure of an η^1 Nickel *O*-Enolate: Mechanistic Implications in Catalytic Enyne Cyclizations.

Page 370. A relevant reference (Kaschube, W.; Schröder, W.; Pörschke, K. R.; Angermund, K.; Krüger, C. *J. Organomet. Chem.* **1990**, *389*, 399) that describes the formation of a nickel metallacyclopentene by the intermolecular coupling of an alkene and an alkyne was omitted. A second relevant reference (Büch, H. M.; Binger, P.; Benn, R.; Rufinska, A. *Organometallics* **1987**, *6*, 1130) that describes the formation of a nickel metallacyclopentane which incorporates methyl acrylate was also omitted.

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