Unusual Double Silylation Reaction of a $PtSi_2P_2$ Complex with an *o*-Carboranyl Unit

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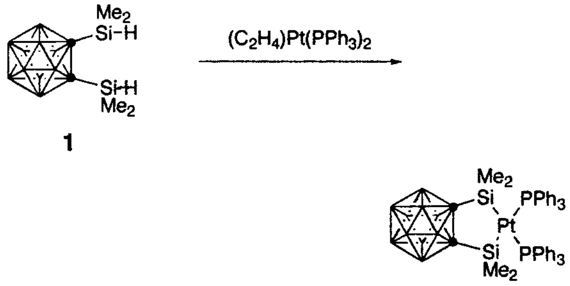
Summary: Reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ and o-bis(dimethylsilyl)carborane provides the cyclic bis(silyl)platinum complex **2**. *The complex* **2** *reacts with a variety of substrates such as an alkyne, dione, and nitrile, generating a new class of heterocyclic compounds incorporating an alkene, ketonate, imine, and amine.*

The double silylation of unsaturated organic compounds catalyzed by group 10 metals[1] is a convenient synthetic route to obtain disilacyclic compounds. Platinum complexes, in particular, provide excellent catalysts for the transformation of disilanes. Cyclic bis(silyl)platinum complexes, which Eaborn et al.[2] and Tanaka et al.[3] had already reported, have been implicated as key intermediates in the platinum-catalyzed double silylation of alkynes. However, the complexes have not been structurally characterized. Here we report the general synthesis of a new class of thermally stable cyclic bis(silyl)platinum complexes with a bulky *o*-carborane unit and some unusual reaction chemistry with unsaturated organic compounds.

The reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.05 mmol) and *o*-bis(silyl)carborane **1** (1.4 equiv) in benzene leads to **2** in good yield (eq 1). The compound **2** is a yellow solid stable to air and to brief heating to 120−130 °C.



(1)

The ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR data for **2** support the proposed structure. In particular, the ^{29}Si NMR chemical shift of 37.17 ppm as a doublet of doublets ($J_{Pt-Si} = 1281.6$ Hz, $J_{Si-P(trans)} = 148.82$ Hz, $J_{Si-P(cis)} = 12.80$ Hz) is close to the literature values for *cis*-$PtSi_2P_2$ complexes.[4] The structure of **2** was established by a single-crystal X-ray analysis.[5]

Compound **2** was found to be a good precursor for the double-silylation reaction.[6−8] Thus, thermolysis of a toluene solution of **2** (0.153 mmol) and 1-hexyne (1.23 mmol) at 120 °C for 6 h afforded a 54% yield of **3** as a colorless oil. A key feature in the ^1H NMR spectrum of **3** is a singlet at 6.24 ppm assigned to the vinyl proton. A characteristic low-frequency ^{13}C NMR resonance at δ 138.50 provides evidence for a tethered carbon atom of the two silicon moieties[9] (Scheme 1).

Treatment of **2** with 3 equiv of 3-phenyl-2-propenal in refluxing toluene-d_8 while the reaction progress was monitored by ^1H NMR spectroscopy resulted in the disappearance of the aldehyde hydrogen peak and the formation of a new methine peak (δ 1.56).[10] The IR spectrum of **4** shows a new absorption due to a ν_{C-O} stretch at 1448 cm^{-1}. The mass spectrum of the product showed a molecular ion at *m/z* 538. To our surprise, an X-ray study of **4** showed it to be the insertion product of two carbonyl ligands into the C−Si bond in **2** (Figure 1).[11] The reaction has the potential for developing a new method for double C−C bond formation between the carboranyl unit and carbonyl compounds. Such an insertion of the carbonyl functionality into the *o*-carborane has

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[2] Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organmet. Chem.* **1973**, *63*, 107.

[3] (a) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (b) Uchimaru, Y.; Lautenschlager, H. J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639. (c) Tanaka, M.; Uchimaru, Y. *Bull. Soc. Chim. Fr.* **1992**, *129*, 667.

[4] (a) Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873. (b) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667.

[5] Crystal data for **2**: fw = 1054.32, monoclinic space group $C2/c$, $a = 22.435(1)$ Å, $b = 15.855(2)$ Å, $c = 14.859(2)$ Å, $\alpha = 90.012(8)°$, $\beta = 114.544(5)°$, $\gamma = 89.994(6)°$, $V = 4807.8(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.456$ g cm^{-3}, λ(Mo Kα) = 0.7107 Å, 8219 unique data, 3210 observations with $I > 3\sigma(I)$, goodness of fit = 1.695, $R = 0.0377$, $R_w = 0.0456$.

[6] (a) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16. (b) Uchimaru, Y.; Brandl, P.; Tanaka, M.; Goto, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

[7] (a) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organomet. Chem.* **1992**, *428*, 1.

[8] Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H.-J.; Tanaka, M. *Chem. Lett.* **1992**, 45.

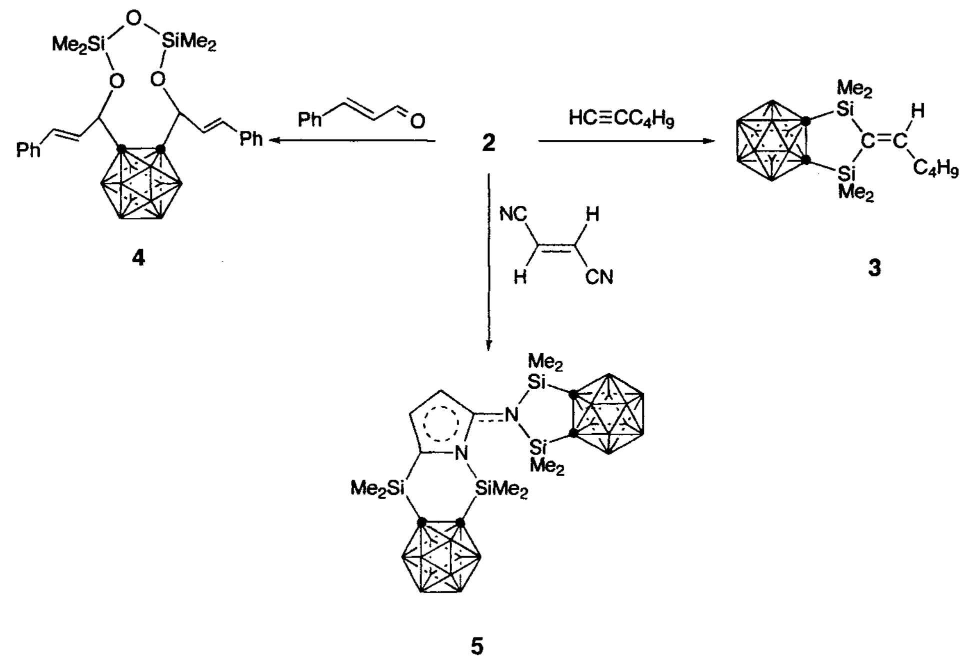
[9] Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics* **1996**, *15*, 1101.

[10] A mixture of **2** (0.2 g, 0.2 mmol) and *trans*-cinamaldehyde (0.21 g, 1.6 mmol) in toluene (15 mL) was heated under reflux for 16 h, and volatiles were removed under vacuum. The resulting oil was purified by chromatography over silica gel, with benzene and hexane as eluent (1:1). The residue was left to crystallize at −15 °C in hexane: yield 0.06 g (56%); colorless crystals; mp 56 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.52−6.18 (m, 10H, *Ph*), 6.88 (dd, 1H, J(H,H) = 12.3 Hz, J(H,H) = 5.8 Hz, =C*H*), 6.74 (dd, 1H, J(H,H) = 12.3 Hz, J(H,H) = 4.4 Hz, =C*H*), 1.56 (dd. 1H, J(H,H) = 5.8 Hz, J(H,H) = 4.4 Hz, C*H*), 0.84 (s, 12H, Si(C*H*$_3$)). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.47, 133.64, 132.15, 129.19, 128.7 (*Ph*), 127.60 (s, 1C, =*C*H), 126.43 (s, 1C, =*C*H), 31.59 (s, 1C, *C*H), 14.03 (s, 1C, Si(*C*H$_3$)). ^{29}Si NMR (50 MHz, $CDCl_3$): δ 17.48. MS (EI): *m/z*: 538. Anal. Calcd for $C_{24}H_{38}B_{10}O_3Si_2$: C, 53.45; H, 7.05. Found: C, 53.12; H, 6.88.

[11] Crystal data for **4**: fw = 1077.67, monoclinic, space group $P2_1/m$, $a = 10.711(1)$ Å, $b = 24.060(1)$ Å, $c = 12.654(1)$ Å, $\alpha = 89.997(8)°$, $\beta = 97.978(8)°$, $\gamma = 90.001(7)°$, $V = 3229.3(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.108$ g cm^{-3}, λ(Mo Kα) = 0.7107 Å, 6513 unique data, 2808 observations with $I > 3\sigma(I)$, $R = 0.1130$, $R_w = 0.1403$.

10.1021/om990105e CCC: $18.00

Scheme 1



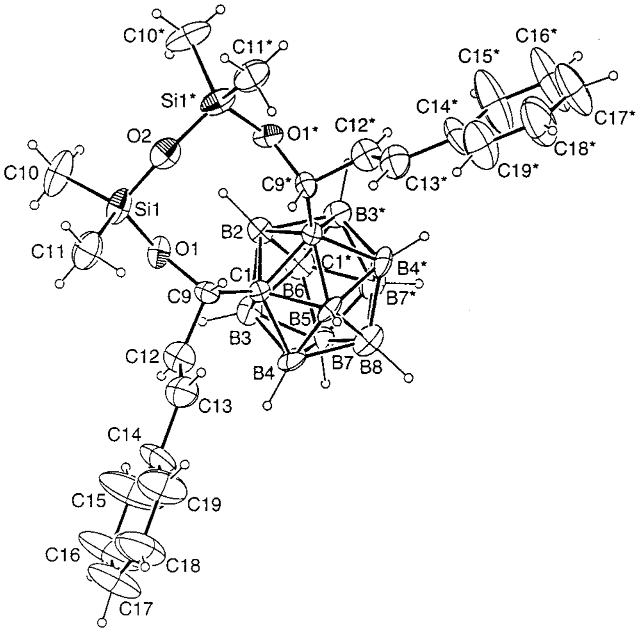


Figure 1. Crystal structure of **4**. Selected bond distances (Å): Si1−O1, 1.648(6); Si1−O2, 1.625(4); O1−C9, 1.421(10); C1−C9, 1.58(1); C1−C1*, 1.71(2).

been observed in Yamamoto's work on the chemoselective addition of *o*-carborane to the aldehyde groups by a palladium-catalyzed[12] or a fluoride-promoted reaction.[13]

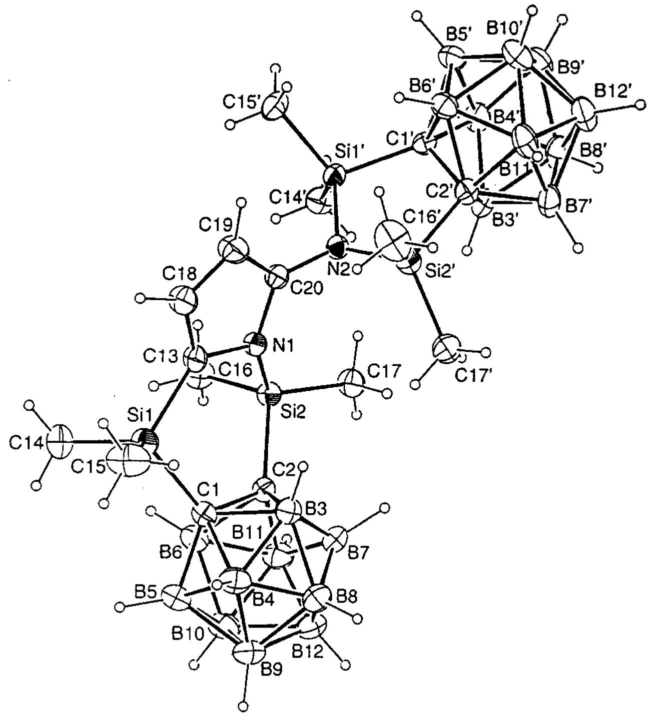


Figure 2. Crystal structure of **5**. Selected bond distances (Å) and angles (deg): Si1′−N2, 1.749(2); Si2′−N2, 1.750(2); Si1′−C1′, 1.896(2); Si2′−C2′, 1.899(3); N2−C20, 1.422(3); N1−C20, 1.393(3); N1−C13, 1.419(3); Si2−N1, 1.764(2); Si1−C13, 1.850(3); C13−C18, 1.363(4); C18−C19, 1.398(4); C19−C20, 1.370(3); Si1′-N2−Si2′, 120.5(1); N2−C20−N1, 122.9(2); C20−N1−C13, 107.5(2); Si2−N1−C13, 118.1(2); N1−C13−Si1, 129.1(2).

The reaction between **2** and 4 equiv of fumaronitrile in refluxing toluene for 8 h produced **5** as colorless crystals.[14] Three singlets (δ 12.53, 4.36, −6.51) in the ^{29}Si NMR spectrum and four singlets (δ 2.20, 0.93, 0.40, −0.047) in the ^{13}C NMR spectrum of **5** assigned to the methyl groups on the silicon atom demonstrate that the four dimethyl groups are not equivalent. The IR spectrum of **5** failed to show a new signal for a terminal CN.

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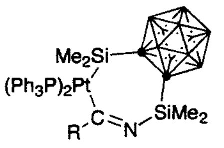
(13) Cai, J.; Nemoto, H.; Nakamura, H.; Singaram, B.; Yamamoto, Y. *Chem. Lett.* **1996**, 792.

(14) **5** was prepared similarly, but using a 1:8 molar ratio of **2** to fumaronitrile. The crude product was chromatographed with benzene and hexane as eluent (1:1) and recrystallized from hexane: yield 75%; mp 158−162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (d, 1H, *J*(H,H) = 5.1 Hz, C*H*), 5.67 (d, 1H, *J*(H,H) = 5.1 Hz, C*H*), 0.63 (s, 6H, Si−C*H*$_3$), 0.44 (s, 6H, Si−C*H*$_3$), 0.35 (s, 6H, Si−C*H*$_3$), 0.29 (s, 6H, Si−C*H*$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 128.6, 128.2, 125.4, 124.9 (S, 1C, *C*N), 2.20 (s, 2C, Si−*C*H$_3$), 0.93 (s, 2C, Si−*C*H$_3$), 0.40 (s, 2C, Si−*C*H$_3$), −0.04 (s, 2C, Si−*C*H$_3$). ^{29}Si NMR (50 MHz, $CDCl_3$): δ 12.53, 4.36, −6.51. Anal. Calcd for $C_{16}H_{46}B_{20}N_2Si_4$: C, 32.26; H, 7.73. Found: C, 32.02; H, 7.56.

The ambiguous spectroscopic data led us to carry out a single-crystal X-ray diffraction study in order to elucidate the structure for **5** (Figure 2).[15] To our surprise, an X-ray study revealed **5** to be a cyclization product with two types of disilyl moieties such as the imine and *N*,*N*-bis(silyl)amine, which are connected by a five-membered ring. The five-membered ring (C_4N) is nearly planar, with the largest deviation of the ring atoms from the mean plane at N(1) (0.03 Å). The C−C bond lengths (1.363−1.398 Å) and C−N bond lengths (1.393−1.422 Å) in the ring fall between a single and double bond,[16] demonstrating the delocalized ring system. Such a transformation of nitriles to imines or *N*,*N*-bis(silyl)-enamines has been observed during the photochemical reaction[17] or catalysis by a platinum complex.[8]

A reasonable mechanism for the formation of **5** involves the initial insertion of the cyano group into one of the platinum−silicon bonds, leading to intermediate **6**, followed by the cyclization to the imine **7**. It lends some credence to the notion that nucleophilic attack of the imine is at the platinum carbene intermediate **8** formed from the migration of the silicon atom to the nitrogen atom that leads to compound **5**.[18]



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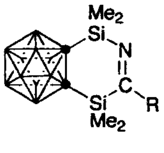

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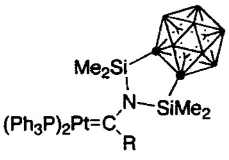

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In summary, the organometallic cyclic bis(silyl)-platinum complex reacts with a variety of substrates such as an alkyne, enone, and nitrile, generating a new class of heterocyclic compounds incorporating an alkene, ketonate, imine, and amine. In contrast to similar $PtSi_2P_2$ compounds, **2** is relatively robust and not as readily attacked by unsaturated organic substrates. Studies are in progress to clarify the mechanistic details of compounds **4** and **5**.

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Supporting Information Available: Text giving details on the synthesis and characterization of compounds **2**−**5** and tables giving X-ray crystallographic data for **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for **5**: fw = 595.09, monoclinic, space group $P2_1/c$, a = 9.322(1) Å, b = 22.191(2) Å, c = 17.580(1) Å, α = 90.010(6)°, β = 99.499(8)°, γ = 90.022(8)°, V = 3587.2(5) Å^3, Z = 4, D_{calcd} = 1.102 g cm^{-3}, λ(Mo Kα) = 0.7107 Å, 7270 unique data, 5056 observations with $I > 3\sigma(I)$, goodness of fit = 2.253, R = 0.0444, R_w = 0.0568.

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(18) Gunnoe, T. B.; White, P. S.; Templeton, J. L.; Casarrubois, L. *J. Am. Chem. Soc.* **1997**, *119*, 3171.