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Synthesis of a Bis(silanolate) Complex from a Bis(silyl) Complex by Air Oxidation: Evidence for the Participation of Silanolate Complexes in the Transition-Metal-Catalyzed Formation of Disiloxanes from Hydridosilanes

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Summary: In a novel type of reaction, the bis(silyl) complex (κ^2-P,N)-(PN)Pt[o-($Me_2Si)_2C_6H_4$] (PN = 2-(diphenylphosphino)-N,N-dimethylaniline) was quantitatively converted to the bis(silanolate) analogue (κ^2-P,N)-(PN)-Pt[o-($OMe_2Si)_2C_6H_4$]. Reaction of the bis(silanolate) complex with 1,2-bis(dimethylsilyl)benzene under argon leads to the starting bis(silyl) complex along with 1,1,3,3-tetramethyl-4,5-benzo-2-oxa-1,3-disilacyclopent-4-ene. In air the bis(silane) is quantitatively converted to the siloxane by catalytic amounts of the bis(silanolate) complex.

A frequently encountered problem in reactions involving metal silyl complexes[1] is the easy formation of organic compounds containing Si−O bonds whenever oxygen sources (moisture, oxygen, Si−OH groups of the glassware[2]) are not strictly excluded. Silanoles or siloxanes are often formed as major byproducts or even as the exclusive products in transition-metal-catalyzed reactions of hydridosilanes in the presence of oxygen or in the thermal decomposition of silyl complexes. For example, despite the presence of a nitrogen atmosphere with dry solvents, $(HMe_2Si)_2O$ was formed among other organosilicon products upon thermolysis of *cis*-$(HMe_2Si)_2Pt(PEt_3)_2$.[3] In experiments directed toward the metal-catalyzed dehydrogenative coupling of hydridosilanes, disiloxanes were the major products instead of disilanes when the reaction was conducted in air.[4a] Oxygen was shown to be necessary to activate platinum catalysts for hydrosilylation reactions, but an excess of oxygen led to the formation of siloxanes.[4b]

These arbitrarily selected examples show that the oxygen incorporation is a major issue in the chemistry of metal silyl complexes, although the extent of this problem is not always realized. For example, early reports on the supposed reductive elimination of disilanes from bis(silyl) complexes often do not include the ^{29}Si NMR spectroscopic identification of the organosilicon products, and therefore there is a high chance that siloxanes were formed instead of the reported di- or oligosilanes. Almost nothing is known about mechanisms or potential intermediates leading to the oxidation products. We report here on the quantitative conversion of a metal−silicon bond into a stable M−O−Si entity when the metal silyl complex was reacted with air under controlled conditions and on the subsequent formation of a disiloxane from a bis(silanolate) complex by treatment with a hydridosilane.

During our studies on the chemistry of bis(silyl) complexes bearing P,N-chelating ligands,[5] we found that (κ^2-*P*,*N*)-(PN)Pt[*o*-$(Me_2Si)_2C_6H_4$] (**1**;[6] PN = 2-(diphenylphosphino)-*N*,*N*-dimethylaniline) gave (κ^2-*P*,*N*)-(PN)-Pt{*o*-$[O(Me_2)Si]_2C_6H_4$} (**2**) in nearly quantitative yield when exposed to air for 6 h at 60 °C in benzene (Scheme 1).[8] Complex **2** is surprisingly stable: No decomposition was observed when a solution in toluene-d_8 was heated

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[1] For recent reviews see: (a) Tilley, T. D. In *The Chemistry of Organo Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1415. (b) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419. (c) Schubert, U. In *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach: New York, 1995; p 287. (d) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

[2] See, for example: van der Boom, M. E.; Ott, J.; Milstein, D. *Organometallics* **1998**, *17*, 4263.

[3] Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227.

[4] (a) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590. (b) Onopchenko, A.; Sabourin, E. T. *J. Org. Chem.* **1987**, *52*, 4118.

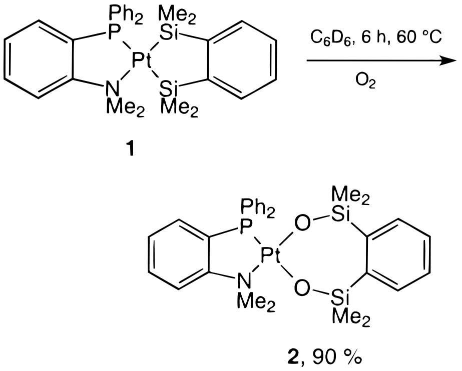
[5] (a) Pfeiffer, J.; Schubert, U. *Organometallics* **1999**, *18*, 3245. (b) Pfeiffer, J.; Kickelbick, G.; Schubert, U. *Organometallics* **2000**, *19*, 62.

[6] Synthesis of **1**: To a solution of 0.5 mmol (0.265 g) of (PN)$PtMe_2$[7] in 2 mL benzene was added 1.0 mmol (0.196 g) of 1,2-bis(dimethylsilyl)benzene dropwise. After the reaction mixture was stirred for 60 h at 60 °C, the solution was cooled to room temperature and transferred into 20 mL of petroleum ether (30/50) by syringe. After storage at −30 °C for 24 h to complete precipitation, the products were filtered off, washed with three portions of 2 mL petroleum ether each, and dried under reduced pressure: pale yellow powder, yield 84%. Anal. Calcd. for $C_{30}H_{36}NPPtSi_2 \cdot C_3H_6O$ (M_r 750.93): C, 52.78; H, 5.64; N, 1.87. Found: C, 52.64; H, 5.66; N, 1.81. $^{31}P\{^1H\}$ NMR (101.25 MHz, acetone-d_6): δ 51.37 (s with Pt and Si satellites, $^1J_{PtP} = 1481.90$ Hz, $^2J_{SiPtP}{}^{trans} = 161.13$ Hz). ^{29}Si NMR (79.49 MHz, INEPT, acetone-d_6): δ −1.38 (d with Pt satellites, $^1J_{PtSi} = 1510.31$ Hz, $^2J_{PPtSi} = 3.60$ Hz, *cis*-Si), 30.04 (d with Pt satellites, $^1J_{PtSi} = 1490.44$ Hz, $^2J_{PPtSi} = 163.99$ Hz, *trans*-Si). $^{13}C\{^1H\}$ NMR (62.5 MHz, acetone-d_6): δ 4.30 (d, $^3J_{PPtSiC} = 3.61$ Hz, *cis*-$Si(CH_3)_2$), 4.99 (d, $^3J_{PPtSiC} = 8.27$ Hz, *trans*-$Si(CH_3)_2$), 54.12 (s, $N(CH_3)_2$), 121.67 (d, $J_{PC} = 8.28$ Hz, Ar C_t), 127.10 (s, Ar C_t), 127.30 (s, Ar C_t), 127.99 (d, $^1J_{PC} = 23.9$ Hz, Ph C_q), 128.40 (d, $J_{PC} = 10.11$ Hz, Ar C_t), 128.95 (d, $J_{PC} = 9.19$ Hz, Ph C_t), 130.20 (s, Ar C_t), 130.81 (s, Ph C_t), 131.29 (d, $J_{PC} = 24.82$ Hz, Ar C_q), 133.06 (d, $J_{PC} = 9.19$ Hz, Ar C_t), 133.53 (d, $J_{PC} = 11.03$ Hz, Ar−C_t), 134.45 (d, $J_{PC} = 14.71$ Hz, Ph C_t), 135.30 (s, Ar C_t), 152.80 (s, SiC^{Ar}), 157.60 (s, SiC^{Ar}), 160.05 (d, $^2J_{PC} = 21.14$ Hz, Ar C_q). ^1H NMR (250 MHz, acetone-d_6): δ −0.04 (s with Pt satellites, $^3J_{PtSiCH} = 32.51$ Hz, 6 H, *cis*-$Si(CH_3)_2$), 0.46 (d with Pt satellites, $^3J_{PtSiCH} = 22.54$ Hz, $^4J_{PPtSiCH} = 2.85$ Hz, 6 H, *trans*-$Si(CH_3)_2$), 3.41 (s with Pt satellites, $^3J_{PtNCH} = 15.36$ Hz, 6 H, $N(CH_3)_2$), 7.12 (t, $J_{HH} = 7.04$ Hz, 1 H, Ar H), 7.17 (t, $J_{HH} = 7.04$, 1 H, Ar H), 7.32 (d, $J_{HH} = 6.91$, 1 H, Ar H), 7.36 (t, $J_{HH} = 7.55$ Hz, 1 H, Ar H), 7.45−7.58 (m, 8 H, Ar H), 7.64 (t, $J_{HH} = 7.68$, 1 H, Ar H), 7.75−7.85 (m, 4 H, Ar H), 7.90 (dd, $J = 4.35, 8.19$ Hz, 1 H, Ar H).

[7] (PN)$PtMe_2$ was prepared from (η^4-2,5-norbornadiene)$Pt(CH_3)_2$ and 2-(diphenylphosphino)-*N*,*N*-dimethylaniline as described for the corresponding 2-(diphenylphosphino)ethyldimethylamine complex in ref 5a.

10.1021/om990947d CCC: $19.00

Scheme 1. Synthesis of 2



to 100 °C in air for 24 h. The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of a singlet with platinum satellites at 8.70 ppm with the coupling constant $^1J_{PtP} = 4128.42$ Hz, typical for platinum complexes bearing a ligand with a weak *trans* influence *trans* to the phosphorus nucleus.[9] In contrast, the $^1J_{PtP}$ value of **1** was much smaller (1481.9 Hz), which is attributed to the strong *trans* influence of the silyl ligand.[10] The resonances of the silicon atoms in the ^{29}Si NMR (INEPT) spectrum at −1.57 and 2.68 ppm are in the characteristic region for $Me_2PhSiO-$ groups (for example, $Me_2PhSi-O-SiPhMe_2$ δ −0.88 ppm).

Crystals of **2** containing 1 equiv of C_6D_6 suitable for a X-ray crystal structure analysis were obtained from a saturated benzene-d_6 solution by slow evaporation of the solvent.[11] The solid-state structure of **2** (Figure 1) is characterized by the typical square-planar coordination around platinum (sum of angles 360.03°). The angle P(1)−Pt−O(23) (94.91°) is slightly widened, presumably due to the steric strain caused by the phenyl substituents of the Ph_2P group. The five-membered chelate ring formed by the PN ligand is almost planar, whereas the seven-membered ring containing the bis(silanolate) ligand adopts a puckered configuration with the oxygen atoms below and above the plane formed by Si(24), C(27), C(32), and Si(33). In comparison to the molecular structure of **1**,[5b] the Pt−N and Pt−P bonds of **2** are shortened (**1**: Pt−N = 236.8(5) pm, Pt−P = 230.3(2) pm) by 29.3 (!) and 14.3 pm, respectively, revealing the strong *trans* influence of silicon compared to oxygen. The Pt−O bond lengths of **2** are within the range expected from other complexes.[12]

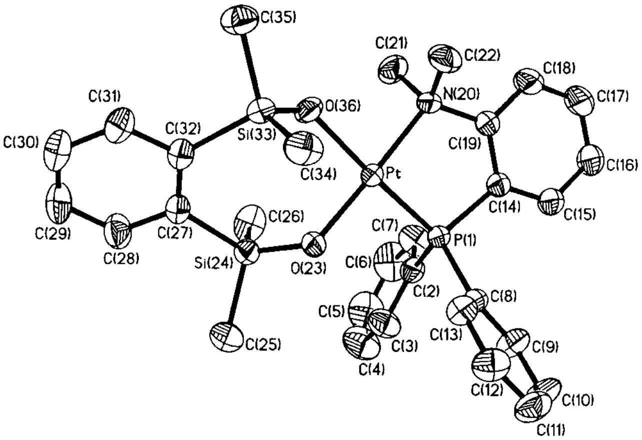


Figure 1. Molecular structure of **2**. Selected bond lengths (pm) and angles (deg): Pt−O(23) = 198.8(2), Pt−O(36) = 201.6(2), Pt−N(20) = 207.5(3), Pt−P(1) = 215.9(1); O(23)−Pt−O(36) = 89.17(9), O(23)−Pt−N(20) = 177.49(8), O(36)−Pt−N(20) = 88.42(9), O(23)−Pt−P(1) = 94.91(7), O(36)−Pt−P(1) = 174.84(6), N(20)−Pt−P(1) = 87.53(7).

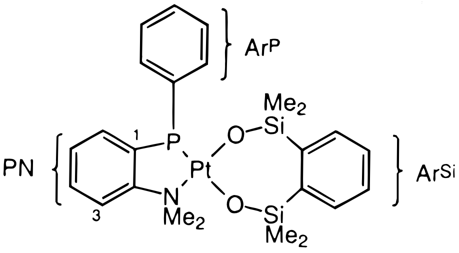


Figure 2. Atom labeling for **2** (NMR spectra).

To the best of our knowledge, the synthesis of bis(silanolate) complex **2** from the bis(silyl) complex **1** is the first example of the deliberate formation of a stable silanolate complex from a metal silyl complex.

Analogues of **2** may be involved in the formation of siloxane byproducts in metal-complex-catalyzed reactions of hydridosilanes as well as in the air-induced

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(8) Synthesis of **2**: 69.2 mg (0.1 mmol) of **1** was dissolved in 0.6 mL of C_6D_6 in a NMR tube. Monitoring by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed that **1** was completely consumed after heating the solution to 60 °C for 6 h in air. During this period a finely divided white powder started to precipitate. After addition of 3 mL of petroleum ether (30/50) to complete precipitation, the product was filtered off, washed with three 2 mL portions of petroleum ether, and dried under reduced pressure: colorless powder, yield 65.1 mg (0.09 mmol, 90%). $^{31}P\{^1H\}$ NMR (101.25 MHz, acetone-d_6): δ 8.70 (s with Pt satellites, $^1J_{PtP} = 4128.42$ Hz). ^{29}Si NMR (79.49 MHz, INEPT, acetone-d_6): δ −1.57, 2.68. $^{13}C\{^1H\}$ NMR (62.5 MHz, acetone-d_6): δ 4.09 (s, 2 C, $Si(CH_3)_2$), 4.48 (s, $Si(CH_3)_2$), 54.98 (s, $N(CH_3)_2$), 122.67 (d, $^4J_{PH} = 10.11$ Hz, PN C^3), 126.37 (s, Ar^{Si} C_t), 126.48 (s, Ar^{Si} C_t), 129.02 (d, $J_{PC} = 11.04$ Hz, Ar^P C_t), 130.35 (d, $^1J_{PC} = 46.88$ Hz, Ar^P C^1), 131.43 (d, $^4J_{PC} = 1.84$ Hz, Ar^P C^4), 133.00 (s, 2 × Ar^{Si} C_t), 133.52 (d, $J_{PC} = 11.03$ Hz, Ar^P C_t and PN C^6), 133.80 (d, $^4J_{PC} = 5.52$ Hz, PN C^4), 152.71 (s, Ar^{Si} C_q), 152.75 (s, Ar^{Si} C_q), 164.84 (d, $^1J_{PC} = 15.62$ Hz, PN C^1). ^1H NMR (400 MHz, acetone-d_6): δ 0.05 (s, 6 H, $Si(CH_3)_2$), 0.42 (s, 6 H, $Si(CH_3)_2$), 3.61 (s, 6 H, $N(CH_3)_2$), 7.13 (t, $J_{HH} = 7.54$ Hz, 1 H, Ar^{Si} H), 7.16 (t, $J_{HH} = 7.31$, 1 H, Ar^{Si} H), 7.39 (d, $J_{HH} = 7.01$, 1 H, Ar^{Si} H), 7.50−7.65 (m, 8 H, 6 × Ar^P H, 1 Ar^{Si} H, PN H^5), 7.74 (t, $^3J_{HH} = 8.18$ Hz, 1 H, PN H^4), 7.89 (dd, $^3J_{HH} = 7.10$, $^3J_{PH} = 8.98$ Hz, 1 H, PN H^6), 7.95 (dd, $^3J_{HH} = 7.01$ Hz, $^3J_{PH} = 12.32$ Hz, 4 H, Ar^P H^2 and Ar^P H^6), 8.08 (dd, $^3J_{HH} = 8.18$, $^3J_{PH} = 4.27$ Hz, 1 H, PN H^3). Assignments according to Figure 2 have been made on the basis of $^1H\{^{31}P\}$, gs-HH-HMQC, gs-CH-HMQC, and gs-SiH-HMBC experiments. The resonances of the carbon atoms PN C^1 and PN C^5 could not be unambigiously assigned in the ^{13}C NMR spectrum due to the low solubility of **2** and overlap of the signals.

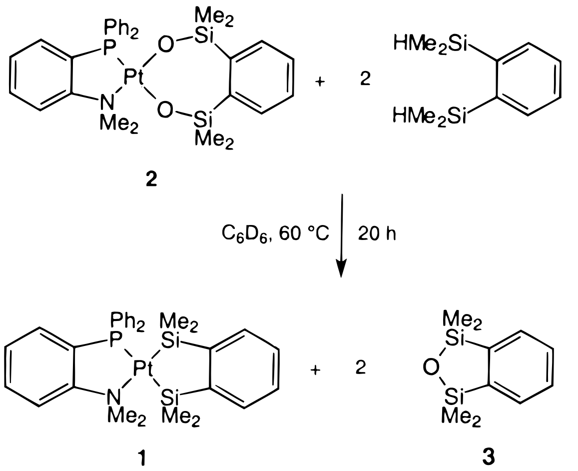
(9) The data known from other platinum complexes bearing silanolate ligands are consistent with the found coupling constant. (a) (dppe)$Pt(OSiMe_3)_2$, $^1J_{PtP} = 3595$ Hz: Andrews, M. A.; Gould, G. L. *Organometallics* **1991**, *10*, 387. (b) $(Me_3P)_2Pt(OSiMe_3)_2$, $^1J_{PtP} = 3400$ Hz: Schmidbauer, H.; Adlkofer, J. *Chem. Ber.* **1974**, *107*, 3680.

(10) Pregosin, P. S.; Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR Basic Principles and Progress 16; Springer: Berlin and Heidelberg, 1979.

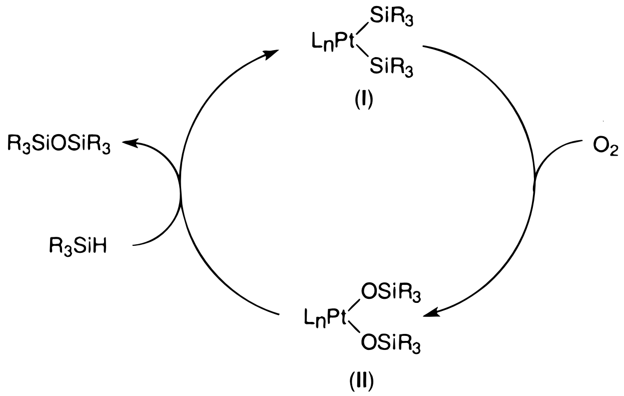
(11) Crystal data for **2**: $C_{30}H_{36}NO_2PPtSi_2 \cdot C_6D_6$ (M_r 806.91), colorless crystal, size 0.40 × 0.20 × 0.14 mm; triclinic, space group $P\bar{1}$; $a = 970.0(5)$ pm, $b = 1075.2(6)$ pm, $c = 1689.2(9)$ pm, $\alpha = 107.736(14)°$, $\beta = 100.47(2)°$, $\gamma = 95.66(2)°$, $V = 1627(2) \times 10^6$ pm^3, $Z = 2$, $D_{calcd} = 1.559$ g/cm^3; Siemens SMART diffractometer with a CCD area detector; 293(2) K; Mo Kα radiation ($\lambda = 71.073$ pm); data collection range 2.01−30.51°; number of independent reflections 9219 ($R_{int} = 0.0183$). The structure was solved by the Patterson method (SHELXS86) and refined by the full-matrix least-squares method based on F^2 (SHELXL97). Hydrogen atoms were added in ideal positions and refined by a riding model: $R = 0.026$ and $R_w = 0.0623$ for reflections with $I > 2\sigma(I)$; goodness of fit 1.094. The crystallographic data for the reported structure has been deposited as Supplementary Publication No. CCDC 135994 at the Cambridge Crystallographic Data Centre. Copies are available free of charge at CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax, (+44)1223-336-033; E-mail, deposit@ccdc.cam.ac.uk).

(12) (a) Kim, K. W.; Sohn, Y. S. *Inorg. Chem.* **1998**, *37*, 6109. (b) Kuroda, R.; Neidle, S.; Ismail, I. M.; Sadler, P. J. *Inorg. Chem.* **1983**, *22*, 3620. (c) Goto, M.; Hirose, J.; Noji, M.; Lee, K. I.; Saito, R.; Kidani, Y. *Chem. Pharm. Bull.* **1992**, *40*, 1022.

Scheme 2. Reaction of 2 with 1,2-Bis(dimethylsilyl)benzene



Scheme 3. Proposed Mechanism for the Platinum-Catalyzed Formation of Siloxanes from Hydridosilanes



decomposition of transition-metal bis(silyl) complexes.[9b,13,14] To prove these assumptions, bis(silanolate) complex **2** was reacted with 2 equiv of 1,2-bis(dimethylsilyl)benzene in the absence of air. Heating to 60 °C leads to complete consumption of **2** within 20 h.[15] The only products (according to the ^{1}H, ^{31}P, ^{29}Si, and ^{1}H-^{29}Si-HMBC NMR spectra) were the bis(silyl) complex **1** and the cyclic siloxane 1,1,3,3-tetramethyl-4,5-benzo-2-oxa-1,3-disilacyclopent-4-ene (**3**) in a 1:2 ratio (Scheme 2). The reaction is indeed catalytic: heating of a benzene solution of 1,2-bis(dimethylsilyl)benzene and bis(silanolate) complex **2** (5 mol %) in air to 60 °C leads to complete consumption of the hydridosilane and formation of **3** within 16 h. ^{31}P NMR spectra showed the presence of both **1** and **2** during the reaction.[16] On the basis of these results, a catalytic cycle for the formation of disiloxanes from hydridosilanes can be proposed (Scheme 3): Reaction of a bis(silyl) complex (**I**; formed from a hydridosilane and a suitable metal precursor) with oxygen leads to the formation of a bis(silanolate) complex (**II**). A ligand exchange reaction with a hydridosilane results in the formation of a siloxane and regenerates the bis(silyl) complex.

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Supporting Information Available: Figures giving NMR spectra of **1** and **2** and tables giving X-ray crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The elimination of $Et_3SiOSiMe_3$ from (COD)Ru(H)($SiEt_3$)($OSiMe_3$) has been reported: Marciniec, B.; Krzyzanowski, P. *J. Organomet. Chem.* **1995**, *493*, 261.

[14] (a) Hornbaker, E. D.; Conrad, F. *J. Org. Chem.* **1959**, *24*, 1858. (b) Schindler, F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 683 and references therein.

[15] A 0.05 mmol amount (36.2 mg) of **2** and 0.1 mmol (19.4 mg, 21.4 μL) of 1,2-bis(dimethylsilyl)benzene were dissolved in 0.6 mL of benzene-d_6 under argon and heated to 60 °C for 20 h.

[16] A 0.05 mmol amount (36.2 mg) of **2** and 1 mmol (194 mg, 0.21 mL) of 1,2-bis(dimethylsilyl)benzene were dissolved in 0.5 mL of toluene-d_8 and heated to 60 °C for 16 h to give 1,1,3,3-tetramethyl-4,5-benzo-2-oxa-1,3-disilacyclopent-4-ene as the only silicon-containing product. Spectroscopic data: ^{1}H NMR (toluene-d_8, 300 MHz) δ 0.35 (s, 12 H, 2 × Si(CH_3)$_2$), 7.23 (dd, $J_{HH} = 3.14, 5.35$ Hz, 2 H, Ar H), 7.44 (dd, $J_{HH} = 3.14, 5.35$ Hz, 2 H, Ar H); ^{29}Si INEPT (toluene-d_8, 59.6 MHz) δ 14.40.