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# Synthesis and Characterization of Platinasilsesquioxane Complexes and Their Reaction with Arylboronic Acid

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*Summary: Phenyl(iodo)platinum complexes having a 2,2′-bipyridine (bpy) or 1,2-bis(diphenylphosphino)ethane (dppe) ligand react with incompletely condensed silsesquioxane* ($c$-$C_5H_9$)$_7$$Si_7O_9$($OH$)$_3$ *in the presence of* $Ag_2O$ *to yield platinasilsesquioxane complexes* [$Pt\{(c\text{-}C_5H_9)_7Si_7O_{10}(OH)_2\}(C_6H_5)(L)$] (***1**, L = bpy;* ***2**, L = dppe). NMR spectroscopy revealed their square-planar structures with an O-coordinated silsesquioxanate ligand and O−H···O hydrogen bonds within the ligand. Both complexes undergo transmetalation of p-methoxyphenylboronic acid to afford unsymmetrical diarylplatinum complexes* [$Pt(C_6H_4OCH_3\text{-}p)(C_6H_5)(L)$] (***3**, L = bpy;* ***4**, L = dppe).*

## Introduction

Transition metal complexes with silsesquioxanate ligands are regarded as molecular models of the metal catalysts supported on a silica surface or precursors of the heterogeneous catalysts.[1] Pt(II) and Pd(II) complexes with silsesquioxanes were investigated by Abbenhuis, Johnson, and Vogt.[2] We also reported preparation of the pallada- and platinasilsesquioxane complexes such as [$Pd(Ar)\{R_7Si_7O_{10}(OH)_2\}(tmen)$] and *trans*-[$M(Ar)\{R_7Si_7O_{10}(OH)_2\}(PR'_3)_2$] (M = Pt, Pd; Ar = $C_6H_5$, $C_6F_5$; R = $c$-$C_5H_9$, $i$-$C_4H_9$; $PR'_3$ = $PMe_3$, $PEt_3$, $PMe_2Ph$; tmen = *N,N,N′,N′*-tetramethylethylenediamine). The complexes show fluxional NMR spectra due to dynamic exchange of the hydrogen bonds in the silsesquioxanate ligand.[3−5] A palladium complex with an *O,O′*-coordinated bidentate silsesquioxanate ligand, [$Pd\{R_7Si_7O_{11}(OH)\}(bpy)$], reacts with chlorosilane, leading to double silylation of the ligand.[6] Further studies on the reactions of organic molecules with the silsesquioxane complexes would reveal their new chemical properties. In this paper we present our results on transmetalation of aryl groups from boron to the highly reactive Pt−O−Si bond from platinasilsesquioxane complexes.

## Results and Discussion

**Preparation of Platinasilsesquioxane Complexes.** The reaction of silsesquioxane containing trisilanols ($c$-$C_5H_9$)$_7$$Si_7O_9$($OH$)$_3$ with [PtI(Ph)(L)] (L = 2,2′-bipyridine (bpy); 1,2-bis(diphenylphosphino)ethane (dppe)) in the presence of $Ag_2O$ affords platinum complexes with an *O*-coordinated silsesquioxanate ligand, [$PtPh\{(c\text{-}C_5H_9)_7Si_7O_{10}(OH)_2\}(L)$] (**1**, L = bpy, yield 95%; **2**, L = dppe, yield 62%), as shown in Scheme 1.

Complexes **1** and **2** are thermally stable, and their NMR spectra do not change even after 5 days at 60 °C. The $^{31}P\{^1H\}$ NMR spectrum of **2** displays two signals flanked with $^{195}Pt$ satellites (39.4 ppm, $J_{PtP}$ = 1654 Hz and 29.7 ppm, $J_{PtP}$ = 4127 Hz). The respective $^{31}P-^{195}Pt$ coupling constants fall in the typical range of the phosphine ligands bonded at trans positions of an aryl ligand and of an *O*-ligand in Pt(II) complexes.[2a,7−9] Both complexes show $^{29}Si\{^1H\}$ NMR spectra that consist of five signals in 1:2:1:1:2 ratio. These signals are typical for the silsesquioxane framework with $C_s$ symmetry and often observed in the spectrum of transition metal complexes having a monodentate silsesquioxanate ligand.[3,5,10] $^{13}C\{^1H\}$ NMR signals with the same intensity are observed in the range 22.5−26.6 ppm and are assigned to the CH carbons of the cyclopentyl groups.

The $^1H$ NMR spectra of **1** and **2** in toluene-$d_8$ at 25 °C contain OH hydrogen peaks at 8.8 and 8.3 ppm, respectively. Their low magnetic field positions are ascribed to intramolecular hydrogen bonding in the complexes, similar to the reported platina- and palladasilsesquioxane complexes.[3−6] As can be expected,[11] the signals are shifted to low magnetic field with decreasing temperature and reach 11.6 ppm (**1**) and 10.1 ppm (**2**) at −80 °C. Change of the concentration of **1**

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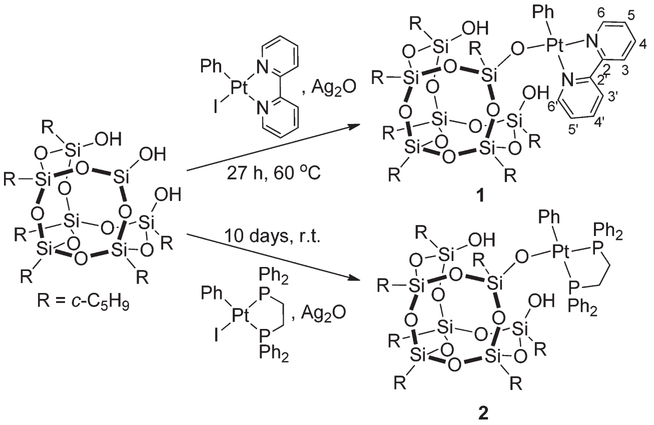
**Scheme 1**



from 40 mM to 5 mM at 25 °C causes a shift of the OH hydrogen peak from 8.54 ppm to 8.23 ppm. Signals of the bipyridine hydrogens are also influenced by the concentration. All the bipyridine hydrogen signals are broadened at low concentration. The peripheral $H_{3,3'}$, $H_4$, and $H_5$ hydrogen signals appear at 8.23, 7.81, and 7.38 ppm at [**1**] = 40 mM, respectively, while they are shifted to 8.52, 7.92, and 7.55 ppm in a dilute solution (5 mM), as shown in Figure 1. Signals of the hydrogens close to the Pt center ($H_6$, $H_{6'}$) are affected to a negligible degree. The above NMR results, including broadening of the signals, may be attributed to partial dissociation of the silsesquioxanate ligand from **1**. Another possible explanation may be intermolecular interaction of the complex molecules in the solution. X-ray analysis of palladium complexes with bipyridine and *O,O'*-coordinated silsesquioxanate ligands revealed an associative interaction between the bipyridine planes of the molecules.[6] The origin of the NMR change depending on the concentration is not clear at present.

**Formation of Diarylplatinum Complexes from the Silsesquioxane Complexes and Arylboronic Acid.** Hydroxopalladium species are regarded as an intermediate of synthetic organic reactions using arylboronic acids as the aryl source and Pd complexes as the catalyst such as Suzuki–Miyaura coupling.[12] The Pd–OH species can be generated from hydrolysis of the halopalladium complexes by $OH^-$ and undergo transmetalation on reaction with arylboronic acid in the catalytic cycles. The reaction of arylboronic acid with a hydroxopalladium complex forms an arylpalladium complex or biaryl via transmetalation.[13] The transfer of an organic group from B to the transition metal center is accelerated by addition of bases such as $F^-$, $OH^-$, or $OR^-$[7,14] or by reaction with cationic platinum or palladium complexes.[15] We expected the reactions of arylboronic acids with the silsesquioxanate ligand of the above Pt complexes.

Platinasilsesquioxane complexes **1** and **2** react with an equimolar amount of (*p*-methoxyphenyl)boronic acid in THF or benzene solution to produce unsymmetrical diarylplatinum complexes [Pt($C_6H_4OCH_3$-*p*)($C_6H_5$)(L)] (**3**, L = bpy; **4**, L = dppe), boric acid, and the trisilanol (Scheme 2). The former reaction mixture was separated into the orange insoluble residue, composed of **3** and of $H_3BO_3$ or its condensation product, and the THF/hexane solution that contains $(c\text{-}C_5H_9)_7Si_7O_{10}(OH)_3$, which is isolated in 69% yield. The evidence for formation of boric acid is its $^1H$ NMR signals in acetone-$d_6$.[8] The silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_{10}(OH)_3$ can be easily isolated from the above THF/hexane filtrate and identified by comparison of the FAB and $^1H$ and $^{29}Si$ NMR spectroscopic data with an authentic sample.[16]

X-ray crystallography of **3** and **4** (Figure 2) showed a square-planar geometry around the platinum center, which is coordinated to two N-donor atoms of the bipyridine ligand in **3** or two P atoms from dppe in **4** and two C atoms from the phenyl and methoxyphenyl rings at the *cis* position. The Pt–N, Pt–P, and Pt–C bond distances are in the typical range in comparison with those of previously reported diarylplatinum complexes.[8,17] The Pt–P1 bond length (2.301(2) Å) in **4** is elongated slightly from Pt–P2 (2.283(2) Å) due to a stronger trans influence of the phenyl ligand, whereas the electron-withdrawing effect of a methoxy group in the aryl ligand shortens the distance Pt–C1 (2.106(6) Å) compared with Pt–C8 (2.115(7) Å). Despite the unsymmetrical diaryl ligands, the two Pt–N bonds and Pt–C1 and Pt–C8 bonds in **3** are very similar. This is in accord with the $^1H$ NMR spectrum, which shows three signals at 8.64, 7.35, and 6.74 ppm for bypiridine hydrogens $H_{6,6'}$, $H_{3,3'}$, and $H_{4,4'}$ and two closely located signals at 6.18 and 6.13 ppm assigned to $H_{5'}$ and $H_5$ of bpy. The doublet signals with coupling H–H and Pt–H at 7.93 ppm ($J_{HH}$ = 8.7 Hz, $J_{PtH}$ = 78 Hz) and 8.09 ppm ($J_{HH}$ = 6.6 Hz, $J_{PtH}$ = 60 Hz) for ortho hydrogens of aryl and phenyl ligands, respectively, are observed quite similarly.

In summary, we obtained and characterized new platinum complexes with *O*-coordinated silsesquioxanate and bpy or dppe ligands. Their reactions with arylboronic acid produce diarylplatinum complexes by transmetalation of an aryl group from B to Pt.

## Experimental Section

**General Procedures.** All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen

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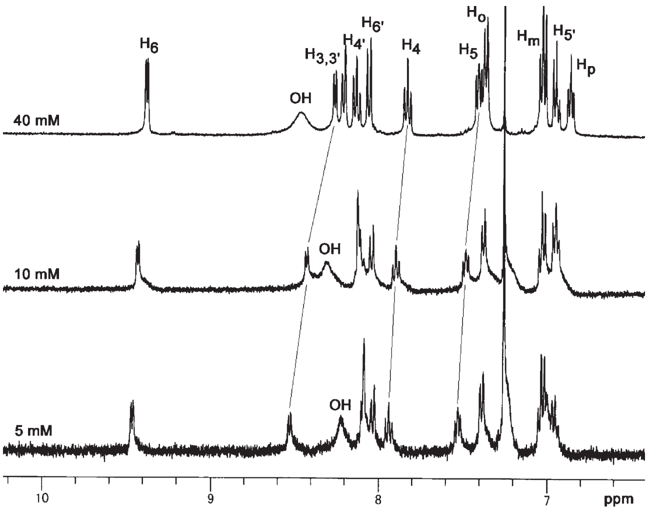
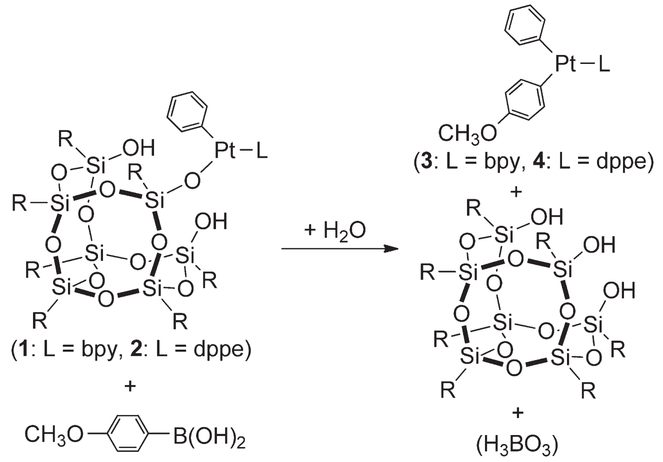


**Figure 1.** $^1$H NMR spectra of **1** in $CDCl_3$ at 5, 10, and 40 mM.

**Scheme 2**



atmosphere. Hexane and toluene were purified by using a solvent purification system (Glass Contour). Phenyl(iodo)platinum(II) compexes [PtI(Ph)(bpy)] and [PtI(Ph)(dppe)] were prepared by ligand replacement of 1,5-cyclooctadiene from [PtI(Ph)(cod)] with 2,2′-bipyridine and dppe, respectively, as previously reported.[18] Silsesquioxane 1,3,5,7,9,11,14- heptacyclopentyltricyclo[7.3.3.1(5,11)]heptasiloxane-endo-3,7,14-triol, $(c\text{-}C_5H_9)_7\text{-}Si_7O_9(OH)_3$, was prepared according to the literature.[16a] $Ag_2O$, bpy, dppe, and *p*-methoxyphenylboronic acid were purchased from Wako Pure Chemical Ind., Ltd. and were used without any purification. $^1$H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded on Varian Mercury 300 or Bruker Biospin Avance III 400 spectrometers. Chemical shifts of the signals in $^1$H and $^{13}C\{^1H\}$ NMR spectra were adjusted to the residual peaks of the solvents used. Peak positions in the $^{29}Si\{^1H\}$ and $^{31}P\{^1H\}$ spectra were referenced to external standard $SiMe_4$ in $CDCl_3$ or $C_6D_6$, and 85% $H_3PO_4$ in $C_6D_6$, respectively. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analyses were carried out using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology.

**Preparation of $[Pt\{(c\text{-}C_5H_9)_7Si_7O_{10}(OH)_2\}(C_6H_5)(bpy)]$ (1).** To a toluene (10 mL) suspension of $[PtI(C_6H_5)(bpy)]$ (83 mg, 0.15 mmol) were added $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (131 mg, 0.15 mmol) and $Ag_2O$ (46 mg, 0.20 mmol). The reaction mixture was heated at 60 °C for 27 h. The gray solid was removed by filtration through Celite, and the filtrate was evaporated under reduced pressure. In order to remove a toluene completely, the residue was washed with 5 mL of hexane three times. The solution was evaporated until a yellow solid was formed, then was dried *in vacuo* to give **1** (186 mg, 95%). Anal. Calcd for $C_{51}H_{78}N_2O_{12}Si_7Pt$: C, 47.02; H, 6.03; N, 2.15. Found: C, 47.19; H, 6.30; N, 2.01. $^1$H NMR (300 MHz, $CDCl_3$, rt): $\delta$ 0.56 (m, 1H, C*H*-pentyl), 0.94 (m, 3H, C*H*-pentyl) 1.14 (m, 3H, C*H*-pentyl), 1.4−2.0 (m, 56H, $CH_2$-pentyl), 6.84 (t, 1H, $PtC_6H_5$-*p*, $J_{HH}$ = 6 Hz), 6.96 (d, 1H, $H_{5'}$-bpy, $J_{HH}$ = 6.9 Hz), 7.03 (t, 2H, $C_6H_5$-*m*, $J_{HH}$ = 7 Hz), 7.35−7.38 (overlapped 3H, $C_6H_5$-*o* and $H_5$-bpy), 7.81 (td, 1H, $H_4$-bpy, $J_{HH}$ = 8, 1.5 Hz), 8.07 (d, 1H, $H_{6'}$-bpy, $J_{HH}$ = 8.1Hz), 8.15 (td, 1H, $H_{4'}$-bpy, $J_{HH}$ = 7.8, 1.2 Hz), 8.23 (t, 2H, $H_{3,3'}$-bpy, $J_{HH}$ = 8.4 Hz), 8.54 (s, 2H, O*H*), 9.37 (d, 1H, $H_6$-bpy, $J_{HH}$ = 4.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rt): $\delta$ 22.47, 22.57, 22.81, 23.20, 24.03 (1:2:2:1:1, 7C, *C*H-pentyl), 27.11, 27.14, 27.21, 27.25, 27.30, 27.38, 27.46, 27.51, 27.54, 27.87 (28C, $CH_2$-pentyl), 122.39 ($C_{6'}$-bpy), 122.78 ($C_{5'}$-bpy), 124.21 ($C_{3'}$-bpy), 126.26 ($C_6H_5$-*p*), 126.37 ($C_6H_5$-*m* + $C_5$-bpy), 137.58 ($C_6H_5$-*o*), 137.82 ($C_{4'}$-bpy), 138.05 ($C_4$-bpy), 140.72 ($C_6H_5$-*i*), 148.31 ($C_6$-bpy), 151.36 ($C_3$-bpy), 153.29 ($C_{2'}$-bpy), 156.91 ($C_2$-bpy). The peak positions for all H and C atoms were assigned according to H−H and C−H COSY diagrams. $^{29}Si\{^1H\}$ NMR (79.3 MHz, $CDCl_3$, 0.02 M $Cr(acac)_3$, rt): $\delta$ −54.62, −56.60, −64.75, −65.17, −67.45 (1:2:1:2:1). IR data (KBr): 3350brw., 2950s, 2865s, 1603w, 1574w, 1468w, 1449m, 1244m, 1115vs, 951m, 910m, 764m, 737w, 727w, 702w, 500m, 447w.

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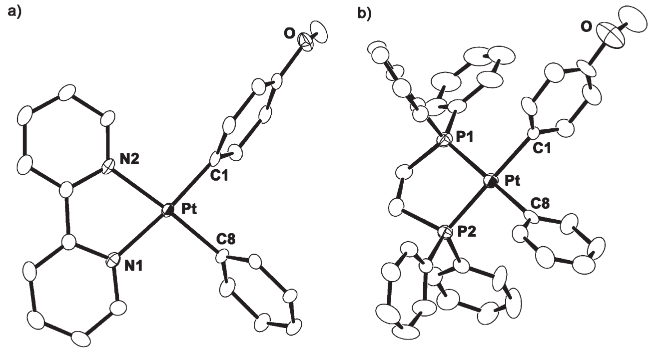

**Figure 2.** ORTEP drawings of (a) **3** and (b) **4** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. (a) One of the two crystallographically independent molecules is shown. Selected bond distances (Å) and angles (deg) of **3**: Pt−N1 = 2.104(8); 2.095(7), Pt−N2 = 2.098(6); 2.098(6), Pt−C1 = 2.00(1); 2.002(9), Pt−C8 = 2.007(8); 2.006(8), N1−Pt−N2 = 77.7(3); 77.4(2), N1−Pt−C8 = 97.8(3); 98.9(3), N2−Pt−C1 = 97.6(3); 98.1(3), C1−Pt−C8 = 86.9(3); 85.8(3). (b) Selected bond distances (Å) and angles (deg) of **4**: Pt−P1 = 2.301(2), Pt−P2 = 2.283(2), Pt−C1 = 2.106(6), Pt−C8 = 2.115(7); P1−Pt−P2 = 85.81(7), P1−Pt−C1 = 93.7(2), P2−Pt−C8 = 94.6(2), C1−Pt−C8 = 86.1(2).

**Preparation of [Pt{(*c*-$C_5H_9)_7Si_7O_{10}(OH)_2\}(C_6H_5)$(dppe)] (2).** To a toluene (10 mL) suspension of [PtI($C_6H_5$)(dppe)] (120 mg, 0.15 mmol) were added (*c*-$C_5H_9)_7Si_7O_9(OH)_3$ (131 mg, 0.15 mmol) and $Ag_2O$ (46 mg, 0.20 mmol). The reaction mixture was stirred at room temperature for 10 days. When the conversion was complete, the gray solid containing $Ag_2O$ and AgI was removed by filtration through Celite and the filtrate was evaporated under reduced pressure. Recrystallization from 1 to 2 mL of ether solution at −20 °C gives **2** (143 mg, 62%). Anal. Calcd for $C_{67}H_{94}O_{12}Si_7P_2Pt$: C, 52.08; H, 6.13. Found: C, 52.02; H, 6.02. The same reaction takes place under heating at 60 °C for 48 h, but minor byproducts are formed and they obstruct crystallization of the final desired complex. Complex **2** can also be obtained by reaction of hydroxoplatinum complex [Pt(OH)($C_6H_5$)(dppe)] and (*c*-$C_5H_9)_7Si_7O_9(OH)_3$ for 24 h at 60 °C. $^1H$ NMR (300 MHz, $C_6D_6$, rt): $\delta$ 1.18 (m, 7H, C*H*-pentyl), 1.4−2.0 (m, 56H, C*H*$_2$-pentyl), 6.94 (m, 12 H, P$C_6$*H*$_5$-*m,p*), 7.04 (m, 2H, Pt$C_6$*H*$_5$-*m*), 7.21 (1H, Pt$C_6$*H*$_5$-*p*), 7.38 (m, 4H, P$C_6$*H*$_5$-*o*), 7.61 (t, 2H, Pt$C_6$*H*$_5$-*o*, $J_{PtH}$ = 45 Hz), 7.96 (m, 4H, P$C_6$*H*$_5$-*o*), 8.4 (s, 2H, O*H*). $^{31}P\{^1H\}$ NMR (121.5 MHz, $C_6D_6$, rt): $\delta$ 39.4 (s, P trans to $C_6H_5$, $J_{PtP}$ = 1654 Hz), 29.7 (s, P trans to silsesquioxane, $J_{PtP}$ = 4127 Hz). $^{29}Si\{^1H\}$ NMR (79.3 MHz, $C_6D_6$, 0.02 M Cr(acac)$_3$, rt): $\delta$ −55.12, −57.20, −65.33, −65.58, −68.24 (1:2:1:1:2). $^{13}C\{^1H\}$ NMR (100.4 MHz, $C_6D_6$, rt): $\delta$ 23.21, 23.37, 23.60, 24.00, 26.62 (7C, *C*H-pentyl, 1:1:2:2:1), 27.5−28.8 (*C*H$_2$-pentyl and dppe), 123.39 (Pt*C*$_6$H$_5$-*p*), 128.67 (d, P*C*$_6$H$_5$-*p*, *J* = 13 Hz), 129.08 (d, P*C*$_6$H$_5$-*o*, *J* = 9 Hz), 131.09 (d, P*C*$_6$H$_5$-*o′*, *J* = 9 Hz), 132.04 (s, Pt*C*$_6$H$_5$-*m*), 133.30 (d, P*C*$_6$H$_5$-*i*, *J* = 11 Hz), 134.13 (d, P*C*$_6$H$_5$-*i′*, *J* = 12 Hz), 137.90 (s, Pt*C*$_6$H$_5$-*o*). IR data (KBr): 3300brw, 2948s, 2865s, 1572w, 1451w, 1435m, 1244m, 1100vs, 920m, 828m, 731w, 690m, 548w, 498m, 450w.

**Reaction of [($C_6H_4OCH_3$-*p*)B(OH)$_2$] with 1.** To 4 mL of THF solution of [Pt{(*c*-$C_5H_9)_7Si_7O_{10}(OH)_2\}(C_6H_5)$(bpy)] (**1**) (80 mg, 0.06 mmol) was added ($C_6H_4OCH_3$-*p*)B(OH)$_2$ (9.2 mg, 0.06 mmol), and the mixture was heated at 60 °C for 4 h. After that the solution was concentrated under reduced pressure and 10 mL of hexane was added. Cooling at −20 °C gave an orange residue, which was filtrated off, washed with water, and dried *in vacuo* to produce [Pt(bpy)($C_6H_5$)($C_6H_4OCH_3$-*p*)] (**3**) (24 mg, 75%). Evaporation of water washings yielded $H_3BO_3$ (2 mg, 54%). $^1H$ NMR (300 MHz, acetone-*d*$_6$, rt): $\delta$ 5.81 (s, OH, boroxine), 2.88 (s, OH, boric acid). Hexane filtrate was evaporated to dryness, washed with acetone, and dried *in vacuo* to give (*c*-$C_5H_9)_7Si_7O_9(OH)_3$ (36 mg, 69%). FAB: *m*/*z* 875. $^{29}Si$ NMR (79 MHz, $CDCl_3$, rt): $\delta$ −57.29, −65.96, −66.85 (3:1:3). Data for **3**: Anal. Calcd for $C_{23}H_{20}N_2OPt \cdot H_2O$: C, 49.91; H, 4.01; N, 5.06. Found: C, 50.46; H, 3.90; N, 5.01. $^1H$ NMR (300 MHz, $C_6D_6$, rt): $\delta$ 3.50 (C*H*$_3$O), 6.13 (t, 1H, *H*$_5$-bpy, $J_{HH}$ = 6.5 Hz), 6.18 (t, 1H, *H*$_{5'}$-bpy, $J_{HH}$ = 6.5 Hz), 6.74 (m, 2H, *H*$_{4,4'}$-bpy), 6.81 (3H, Pt$C_6$*H*$_5$-*m, p*), 7.01 (d, 2H, Pt$C_6$*H*$_4$-*m*, $J_{HH}$ = 8.4 Hz), 7.35 (t, 2H, *H*$_{3,3'}$-bpy, $J_{HH}$ = 7.5 Hz), 7.93 (d, 2H, Pt$C_6$*H*$_4$-*o*, $J_{HH}$ = 8.7 Hz, $J_{PtH}$ = 78 Hz), 8.09 (d, 2H, Pt$C_6$*H*$_5$-*o*, $J_{HH}$ = 6.6 Hz, $J_{PtH}$ = 60 Hz), 8.64 (t, 2H, *H*$_{6,6'}$-bpy, $J_{HH}$ = 6.3 Hz).

**Reaction of [($C_6H_4OCH_3$-*p*)B(OH)$_2$] with 2.** The reaction of ($C_6H_4OCH_3$-*p*)B(OH)$_2$ and **2** takes place at 60 °C for 15 min in THF-*d*$_8$ and for 30 min in $C_6D_6$ and gives **4** in 100% yield calculated by NMR signals. $^1H$ NMR (400 MHz, $C_6D_6$, rt): $\delta$ 1.85 (m, 4H, PC*H*$_2$), 3.30 (s, 3H, OC*H*$_3$), 6,72 (td, 2H, Pt$C_6$*H*$_4$-*m*, $J_{HH}$ = 8 Hz), 6.88 (t, 1H, Pt$C_6$*H*$_5$-*p*, $J_{HH}$ = 8 Hz), 7.00 (m, 12H, P$C_6$*H*$_5$-*m, p*), 7.06 (m, 2H, Pt$C_6$*H*$_5$-*m*), 7.50 (m, 12H, P$C_6$*H*$_5$-*o*), 7.54 (td, 2H, Pt$C_6$*H*$_4$-*o*, $J_{HH}$ = 8 Hz), 7.68 (q, 2H, Pt$C_6$*H*$_5$-*o*, $J_{HH}$ = 8 Hz, $J_{PtH}$ = 60 Hz). $^{31}P\{^1H\}$ NMR (400 MHz, $C_6D_6$, rt): $\delta$ 42.0 (d, $J_{PP}$ = 5 Hz, $J_{PtP}$ = 1694 Hz), 41.3 (d, $J_{PP}$ = 5 Hz, $J_{PtP}$ = 1670 Hz). Complex **4** was isolated from the reaction mixture of a THF solution (5 mL) of [Pt{(*c*-$C_5H_9)_7Si_7O_{10}(OH)_2\}(C_6H_5)$(dppe)] (**2**) (140 mg, 0.09 mmol) and ($C_6H_4OCH_3$-*p*)B(OH)$_2$ (13.6 mg, 0.09 mmol), which was heated at 60 °C for 30 min. The solution was concentrated under reduced pressure, and 10 mL of hexane was added. Cooling at −20 °C gave a white residue, which was filtrated off, washed with water, and dried under vacuum to yield **4** (63 mg, 88%). Anal. Calcd for $C_{39}H_{36}P_2OPt \cdot H_2O$: C, 58.86; H, 4.81. Found: C, 58.86; H, 4.69. Single crystals of **4** were obtained by recrystallization from a $C_6D_6$/hexane solution. Evaporation of water washings and the THF/hexane filtrate yields $H_3BO_3$ (2.8 mg, 50%) and (*c*-$C_5H_9)_7Si_7O_9(OH)_3$ (53 mg, 67%), respectively, which were characterized analogously to the above reaction.

**X-ray Crystallography.** Crystals of **3** and **4** suitable for X-ray diffraction study were mounted on MicroMounts (MiTeGen). The crystallographic data were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 150 K. Calculations were carried out using the program package Crystal Structure, version 3.8, for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on $F^2$ by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. Crystallographic data and details of refinement of **3** and **4** are summarized in the Supporting Information.

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**Supporting Information Available:** Crystallographic data for **3** and **4** as CIF files and a table. This material is available free of charge via the Internet at http://pubs.acs.org.