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Cyclic Platina(borasiloxane)s and Platina(siloxane)s and Their Chemical Properties

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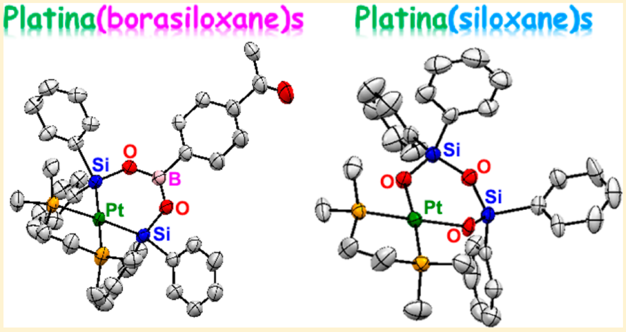
Supporting Information

ABSTRACT: $[\mathrm{Pt(SiHPh_2)_2(dmpe)}]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) reacts with arylboronic acids to produce six-membered platinacycles $[\overline{\mathrm{Pt(SiPh_2\text{-}O\text{-}BAr\text{-}O\text{-}SiPh_2}})\mathrm{(dmpe)}]$ (Ar = C_6H_4-4-COMe (**1a**), C_6H_4-4-CF_3 (**1b**)). X-ray crystallography of **1a** revealed the structure having a planar six-membered ring, composed of Pt, O, B, and Si atoms. Reaction of H_2O with $[\mathrm{Pt(SiHPh_2)_2(dmpe)}]$ formed a four-membered cyclic complex, $[\overline{\mathrm{Pt(SiPh_2\text{-}O\text{-}SiPh_2}})\mathrm{(dmpe)}]$ (**2**), which was observed in the initial reaction mixture of 4-acetylphenylboronic acid with $[\mathrm{Pt(SiHPh_2)_2(dmpe)}]$. Exposure of solutions of $[\mathrm{Pt(SiHPh_2)_2(dmpe)}]$ and of $[\mathrm{Pt(SiHAr_2)_2(PMe_3)_2}]$ (Ar = Ph, C_6H_4-4-Me) to air resulted in the formation of the cyclic platina(siloxane)s, $[\overline{\mathrm{Pt(O\text{-}SiPh_2\text{-}O\text{-}SiPh_2\text{-}O}})\mathrm{(dmpe)}]$ (**3**) and $[\overline{\mathrm{Pt(O\text{-}SiAr_2\text{-}O\text{-}SiAr_2\text{-}O}})\mathrm{(PMe_3)_2}]$ (**4**: Ar = Ph; **5**: Ar = C_6H_4-4-Me), respectively. The six-membered platina(borasiloxane) **1a** reacts with H_2GePh_2 and with CF_3CO_2H to release the cyclic borasiloxanes as the products. The former reaction affords $[\mathrm{Pt(GeHPh_2)_2(dmpe)}]$, while the latter produces $[\mathrm{Pt(OCOCF_3)_2(dmpe)}]$ as the Pt-containing products. A similar reaction of HCl with platina(siloxane) **4** gives a disiloxanediol via cleavage of the Pt−O bonds. Complex **4** reacts with H_2SiPh_2 to form a triplatinum complex, $[\{\mathrm{Pt(PMe_3)}\}_3(\mu\text{-}\mathrm{SiPh_2})_3]$ (**15**), which is obtained under milder conditions than the previously reported reaction starting from $[\mathrm{Pt(SiHPh_2)_2(PMe_3)_2}]$.



INTRODUCTION

Linear, branched, cyclic, and cage-shaped polysiloxanes, composed of the Si−O−Si bonds, have been known as extensively used inorganic polymers.[1,2] They have advantages in thermal stability, water-repellent properties, as well as biocompatibility. These properties of the polysiloxanes are attributed to high stability of the Si−O bond with bond energy of 452 kJ mol^{-1} and weak cohesive force of the molecules having −Si−O−Si− linkage and alkyl substituents on the Si atoms. Linear and cyclic oligosiloxanes are easily available as the starting materials of the polysiloxanes.

Polymers with borasiloxane units, containing both Si−O bonds and B−O bonds (bond energy 536 kJ mol^{-1}), are expected to show new properties arising from the presence of a B atom in the polymer chain. Several research groups have reported on the synthesis of borasiloxane polymers and oligomers. Condensation reactions of phenylboronic acid with 1,3-dichlorodisiloxane and trisiloxane derivatives yield the six- and eight-membered cyclic compounds containing both Si−O and B−O bonds.[3,4] π-Conjugated polymers, containing an eight-membered cyclic borasiloxane group, change their color rapidly on exposure to amine moisture.[5] Polysiloxane, having a boronic acid terminus, exhibits self-healing properties because of the network formation via intermolecular coordination of the OH groups to the B atom.[6] A 10-membered cyclic compound having B−O−Si bonds was prepared by dimerization of the five-membered cyclic precursor.[7] Recently, Matsumi et al. reported dehydrogenative copolymerization of diphenyldisilanol with mesitylborane catalyzed by Rh and Pd complexes. The obtained polymer has a regulated structure, composed of $-\mathrm{O{-}B(C_6H_2\text{-}2,4,6\text{-}Me_3){-}O{-}SiPh_2}-$ repeating units and functions as an efficient sensor of fluoride anion.[8] Dehydrogenative condensation of diorganosilanes with arylboronic acids using transition metal catalysis would also form the −B−O−Si−O− linkage because Tilley, Esteruelas, and Zargarian already reported condensation of organosilanes with OH-containing compounds to form the Si−O bonds.[9] In this study, we conducted reactions of arylboronic acids with Pt complexes having $SiHPh_2$ ligands and obtained new platinacyclohexanes that contain two Si−O−B bonds in the molecule. The reaction proceeds via unexpected double condensation of the boronic acid with the Si ligands rather than formation of the −OBOAr ligand and its coupling with the silyl ligands. This paper presents the synthesis, structure, and chemical properties of the Pt complexes with a new ligand.

RESULTS AND DISCUSSION

Bis(silyl)platinum complex $[\mathrm{Pt(SiHPh_2)_2(dmpe)}]$ reacts with 4-acetylphenylboronic acid and with 4-(trifluoromethyl)phenylboronic

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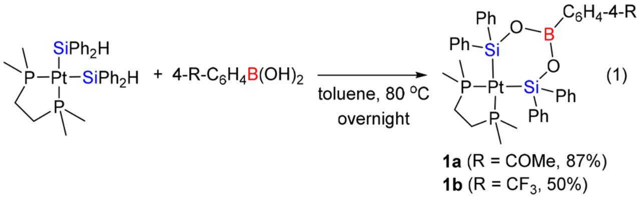
acid to form six-membered cyclic platinum complexes [Pt(SiPh$_2$-O-B(C$_6$H$_4$-4-R)-O-SiPh$_2$)(dmpe)] (**1a**: R = COMe; **1b**: R = CF$_3$) in 87 and 50% isolated yields, respectively, as shown in eq 1. Figure 1 shows the molecular structure of **1a**. The Pt center adopts a square-planar coordination with common Pt−Si bond distances (Pt−Si = 2.352(3), 2.354(3) Å). The six-membered cyclic platina(borasiloxane) is almost planar, and the two axial phenyl substituents on the Si atoms are orientated to the same side relative to the PtP$_2$Si$_2$ plane. Boardman synthesized a six-membered cyclic platina(siloxane), [PtH(Cp)(SiMe$_2$-O-SiMe$_2$-O-SiMe$_2$)] (Cp = cyclopentadienyl), from the reaction of trisiloxane with the Pt precursor, but did not report its crystal structure.[10] The ^{31}P{^{1}H} NMR spectrum of **1a** contains a single signal at δ_P 36.2 with a ^{195}Pt−^{31}P coupling constant of 1331 Hz, which is smaller than that of [Pt(SiHPh$_2$)$_2$(dmpe)] (1445 Hz). The ^{29}Si{^{1}H} NMR signal at δ_{Si} 19.4 is observed with coupling constants of $^{2}J_{PSi}$ = 12, 157 Hz and J_{PtSi} = 1318 Hz, while the ^{11}B{^{1}H} NMR signal is broadened significantly (δ_B 1.46).



1a (R = COMe, 87%)
1b (R = CF$_3$, 50%)

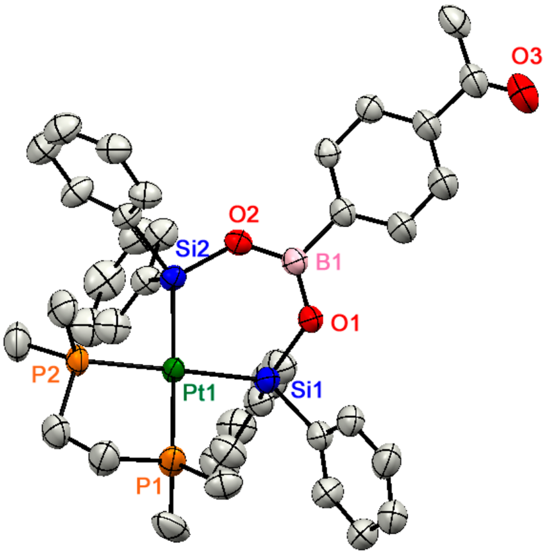
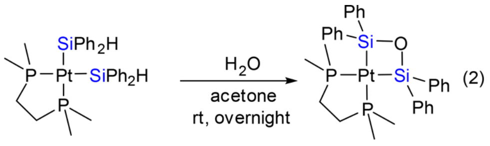


Figure 1. Thermal ellipsoids of **1a** (50% probability). Selected bond distances (Å) and angles (deg): Pt1−P1 2.338(3), Pt1−P2 2.322(3), Pt1−Si1 2.352(3), Pt1−Si2 2.354(3), Si1−O1 1.687(8), B1−O1 1.35(2), B1−O2 1.35(2), Si2−O2 1.678(8). P1−Pt1−P2 84.4(1), Si1−Pt1−Si2 83.3(1), P1−Pt1−Si1 97.6(1), P2−Pt1−Si2 94.7(1), P1−Pt1−Si2 178.9(1), P2−Pt1−Si1 174.5(1).

The above reaction involves double condensation between the OH groups of the arylboronic acid and the two SiHPh$_2$ ligands. We conducted the reaction of water with [Pt(SiHPh$_2$)$_2$(dmpe)] with expectation of a similar dehydrogenative condensation of the OH and SiH groups. Keeping a hydrated acetone solution of [Pt(SiHPh$_2$)$_2$(dmpe)] under nitrogen atmosphere at room temperature produces a platinacycle having an oxygen and two Si atoms within the four-membered ring, [Pt(SiPh$_2$-O-SiPh$_2$)(dmpe)] (**2**, eq 2). Figure 2 shows the molecular structure of complex **2**. The Pt center has a square-planar coordination with Pt−Si bond distances of 2.353(1) and 2.332(3) Å. The Si1−Pt1−Si2 angle (65.6(1)°) is smaller than that of **1a** (83.3(1)°) because of the four-membered chelate ring. Complex **2** is the major product of the reaction, as revealed by the NMR spectra of the reaction mixture, but its isolation in high yields by fractional crystallization was not feasible due to its slow conversion to other complexes in the solution.



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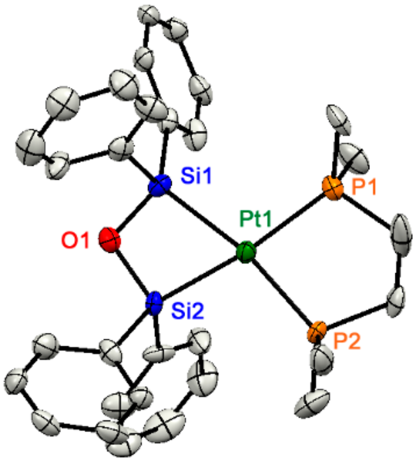


Figure 2. Thermal ellipsoids (50% probability) of **2**. Selected bond distances (Å) and angles (deg): Pt1−P1 2.307(3), Pt1−P2 2.299(3), Pt1−Si1 2.353(1), Pt1−Si2 2.332(3), Si1−O1 1.70(1), Si2−O1 1.70(1), P1−Pt1−P2 84.7(1), Si1−Pt1−Si2 65.6(1), P1−Pt1−Si1 106.2(1), P2−Pt1−Si2 103.6(1), P1−Pt1−Si2 166.3(1), P2−Pt1−Si1 169.1(1).

Figure 3 shows a change of the ^{31}P{^{1}H} NMR spectra during the reaction of 4-acetylphenylboronic acid with [Pt(SiHPh$_2$)$_2$(dmpe)], which affords complex **1a** as the final product (eq 1). The spectrum after the reaction for 1 h at room temperature indicated the formation of four-membered platinacycle **2** (δ_P 38.0, J_{PtSi} = 1443 Hz) and six-membered platina(borasiloxane) **1a**. Further reaction caused decrease of once formed **2** and formation of an insoluble solid. Dissolution of the insoluble products in CD$_2$Cl$_2$ and NMR analyses of the solution did not reveal the structure.

The reaction of 2-methoxyphenylboronic acid with [Pt(SiHPh$_2$)$_2$(dmpe)] formed complex **2** after 2 h at room temperature, and it became the major species in 24 h, as monitored by ^{31}P{^{1}H} NMR spectroscopy (Figure 4). Heating the solution at 60 °C caused the appearance of a minor signal at δ_P 35.2 (J_{PtP} = 1310 Hz), which was assigned to platina(borasiloxane) complex [Pt(SiPh$_2$-O-B(C$_6$H$_4$-2-OMe)-O-SiPh$_2$)(dmpe)] (**1c**).

Schemes 1 and 2 depict possible pathways for the formation of the platina(borasiloxane) (eq 1). As shown in Scheme 1, dehydrocoupling of an OH group of the arylboronic acid with an SiH group of the bis(silyl)platinum complex results in the formation of an acyclic intermediate **A** having a new Si−O−B bond. The second intramolecular Si−O bond formation occurs

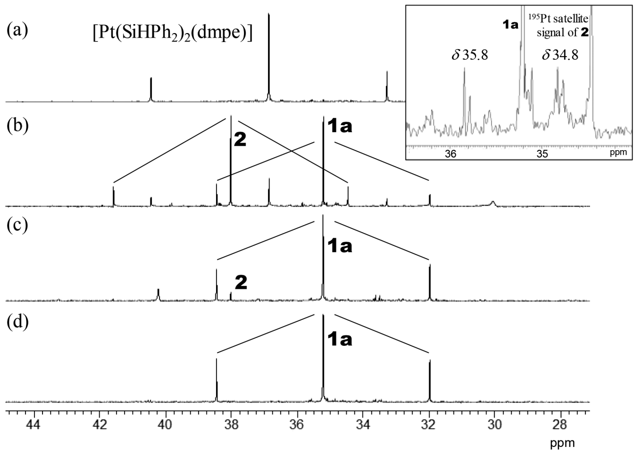


Figure 3. ^{31}P{^{1}H} NMR spectra (202 M Hz, toluene-d_8, rt) of the reaction mixtures of [Pt(SiHPh$_2$)$_2$(dmpe)] and 4-acetylphenylboronic acid in 1:2 ratio at 60 °C: (a) before addition of the arylboronic acid, (b) after 1 h. Inset: Expanded spectrum around **1a** after 1 h exhibiting two doublets at δ_{P} 34.8 and δ_{P} 35.8 ($^{2}J_{\text{PP}}$ = 12 Hz), (c) after 3.5 h, and (d) after 20 h.

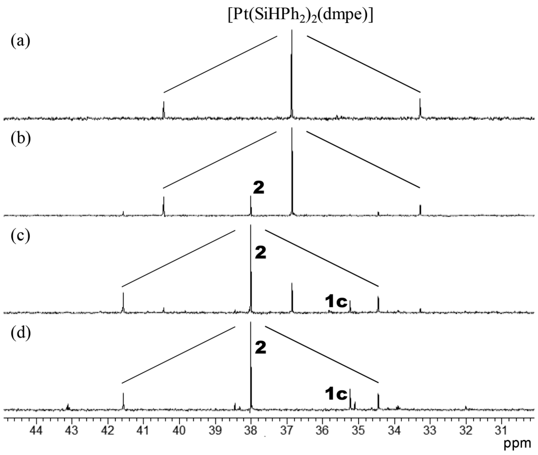
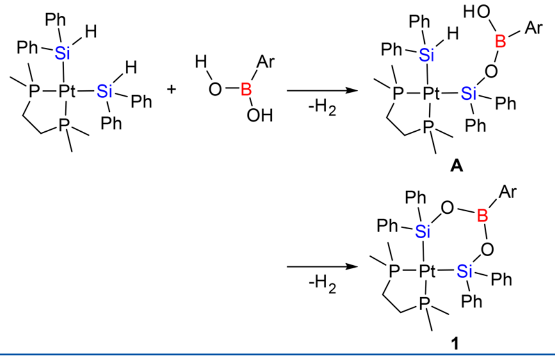


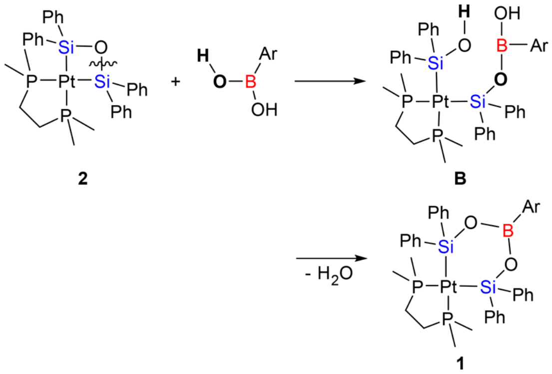
Figure 4. ^{31}P{^{1}H} NMR spectra (202 M Hz, toluene-d_8, rt) of the reaction mixture of [Pt(SiHPh$_2$)$_2$(dmpe)] and 2-methoxyphenylboronic acid in 1:2 ratio (a) before addition of the boronic acid, (b) for 2 h at rt after addition of the arylboronic acid, (c) after 24 h at rt, and (d) after heating for 6.5 h at 60 °C.

Scheme 1. Plausible Pathway for the Formation of Platina(borasiloxane) Complexes 1



more easily than the intermolecular one and produces stable six-membered cyclic platina(borasiloxane) complexes **1**.

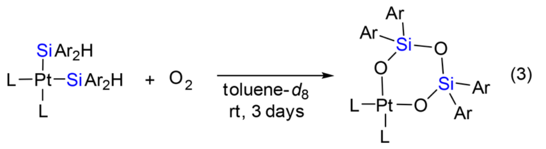
Scheme 2. Pathway for the Formation of 1 via Four-Membered Platinacycle Intermediate 2



Scheme 2 depicts the other pathway. An OH bond of the arylboronic acids adds to an Si–O bond of the ring-strained complex **2**, resulting in the formation of an acyclic intermediate **B** with a new Si–O–B bond. The subsequent intramolecular bond exchange releases an H_2O molecule and produces stable six-membered cyclic platina(borasiloxane) complexes **1**. Arylboronic acid is equilibrated with the corresponding boroxine via reversible cyclotrimerization and hydration of the formed boroxine. Water, generated by the former reaction, may be responsible for formation of complex **2** from [Pt(SiHPh$_2$)$_2$(dmpe)]. The reaction of water with [Pt(SiHPh$_2$)$_2$(dmpe)] (eq 2) occurs at a temperature lower than that of the arylboronic acids in reaction (eq 1), although the arylboronic acid is a stronger Brønsted acid (pK_a = 8.83) than water.

In order to compare the pathways in Schemes 1 and 2, we conducted the reaction of 4-acetylphenylboronic acid with complex **2**. An excess amount of 4-acetylphenylboronic acid reacts with complex **2** (5:1 molar ratio) at 70 °C to form **1a** as the major product. An equimolar reaction at the same temperature, however, results in generation of multiple uncharacterized complexes in considerable amounts. Thus, equimolar reaction of 4-acetylphenylboronic acid with [Pt(SiHPh$_2$)$_2$(dmpe)] (eq 1) occurs via the pathway shown in Scheme 1 rather than that involving complex **2** as the intermediate (Scheme 2). The spectra in Figure 3c,d suggest the disappearance of once formed **2**, but it is due to its conversion into uncharacterized insoluble product rather than to formation of **1a** via the pathway in Scheme 2. 2-Methoxyphenylboronic acid shows reactivity much lower than that of 4-acetylphenylboronic acid, and the reaction yielded complex **2** via contact of H_2O with [Pt(SiHPh$_2$)$_2$(dmpe)] as the main product.

West reported the reaction of oxygen with platinum-η^2-disilene complexes [Pt(η^2-R$_2$Si═SiR$_2$)(dppe)] (R = Me, ^{i}Pr; dppe = 1,2-bis(diphenylphosphino)ethane) to produce the complex having a $\overline{\text{Pt–Si–O–Si}}$ four-membered ring, [$\overline{\text{Pt(SiR}_2\text{-O-SiR}_2\text{)}}$-(dppe)], which has a similar structure to complex **2**.[11] Dioxygen cleaved the Si–Si bond of the complex to form the four-membered platinacycle. In order to compare the reaction with those in this study, we conducted the reaction of oxygen with [Pt(SiHPh$_2$)$_2$(dmpe)]. Exposure of a solution of [Pt(SiHPh$_2$)$_2$(dmpe)] to air at room temperature produces the complex [$\overline{\text{Pt(O-SiPh}_2\text{-O-SiPh}_2\text{-O)}}$(dmpe)] (**3**) which shows the ^{31}P{^{1}H} NMR signal at δ_{P} 18.0 with a large Pt–P coupling constant (3566 Hz), as shown in eq 3. Similar complexes having PMe$_3$ ligands, [$\overline{\text{Pt(O-SiAr}_2\text{-O-SiAr}_2\text{-O)}}$(PMe$_3$)$_2$] (**4**: Ar = C_6H_5, 77%, **5**: Ar = C_6H_4-4-Me, 47%), were obtained from O_2 exposure of a toluene solution of [Pt(SiHAr$_2$)$_2$(PMe$_3$)$_2$] (Ar = C_6H_5, C_6H_4-4-Me) at room temperature.



(3)

3 (L = 1/2·dmpe, Ar = C_6H_5)
4 (L = PMe_3, Ar = C_6H_5, 77%)
5 (L = PMe_3, Ar = C_6H_4-4-Me, 47%)

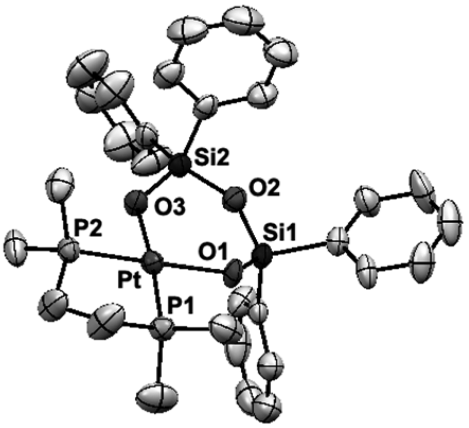
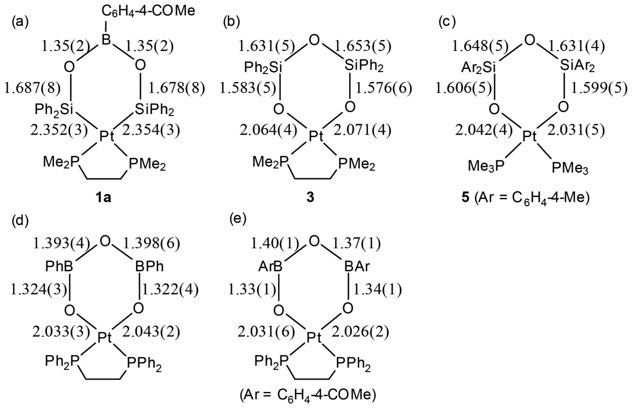


Figure 5. Thermal ellipsoids (50% probability) of **3**. Selected bond distances (Å) and angles (deg): Pt−P1 2.196(3), Pt−P2 2.192(2), Pt−O1 2.071(5), Pt−O3 2.064(4), O1−Si1 1.576(5), Si1−O2 1.653(5), O2−Si2 1.631(5), Si2−O3 1.583(5). P1−Pt−P2 87.13(8), O1−Pt−O3 92.8(2), P1−Pt−O1 91.2(2), P2−Pt−O3 89.0(2), P1−Pt−O3 174.9(2), P2−Pt−O1 176.6(2).

The isolated complexes, **3**−**5**, were identified by X-ray crystallography and NMR spectroscopy. The molecule of **3** has a six-membered ring containing two Pt−O bonds (Figure 5). The Pt center adopted a typical square-planar coordination. The Pt−O bond lengths of **3**−**5** (2.031(5)−2.071(5) Å) are similar to those of the reported bis(silanolate)platinum complexes (1.982(7)−2.036(4) Å).[12] The six-membered ring containing a Pt center has skewed (**3** and **4**) or distorted boat (**5**) conformation. The $^{31}P\{^1H\}$ NMR spectra of **3**−**5** show a singlet with large J_{PtP} values (3518−3566 Hz). The coupling constants are similar to the reported coupling constants of other bis(silanolate) platinum complexes, $[Pt(OSiMe_3)_2(dppe)]$ (J_{PtP} = 3595 Hz)[13] and $[Pt(OSiMe_3)_2(PMe_3)_2]$ (J_{PtP} = 3400 Hz),[14] and much larger than those of **1** (1304−1336 Hz) due to smaller trans influence of the O ligand than the Si ligand. The $^{29}Si\{^1H\}$ NMR spectrum of **4** exhibits a resonance at δ_{Si} −37.0, which is close to the position of hexaphenylcyclotrisiloxane (δ_{Si} −33.8).[15] The ^1H NMR spectra of **3**−**5** show a single resonance for the *ortho*-hydrogens of the aryl group, indicating that the platinasiloxane ring undergoes rapid inversion between the conformers on the NMR time scale. The reaction in eq 3 involves insertion of an oxygen atom into the Pt−Si bond. Schubert reported oxygenation of the two Pt−Si bonds of $[(\kappa^2\text{-}P,N)\text{-}(PN)Pt\{o\text{-}(SiMe_2)_2C_6H_4\}]$ (PN = 2-(diphenylphosphino)-*N*,*N*-dimethylaniline) to form the bis(silanolate)complex $[(\kappa^2\text{-}P,N)\text{-}(PN)Pt\{o\text{-}(OSiMe_2)_2C_6H_4\}]$.[12b] The formation of complexes **3**−**5** also involves the reaction of oxygen to form Si−O−Pt bonds, and it is accompanied by elimination of the two Si−H hydrogens and formation of a new O−Si−O bond.

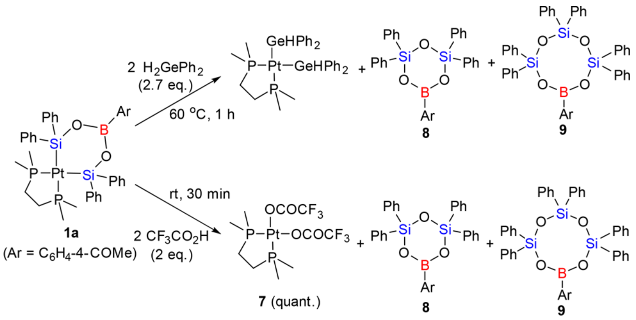
Scheme 3. Bond Distances (Å) of Platina(borasiloxane), Platina(siloxane)s, and Platina(boroxine)s



Scheme 3 compares the bond parameters of the cyclic platina(borasiloxane), platina(siloxane)s, and platina(boroxine)s. We reported that arylboronic acid reacts with dichloroplatinum (II) complex to produce the six-membered cyclic complexes having a $\overline{\mathrm{Pt{-}O{-}B{-}O{-}B{-}O}}$ linkage.[16] Its bond parameters and NMR data are compared with those of complexes **1a**, **3**, and **5**. The Si−O (1.687(8), 1.678(8) Å) and B−O bonds (1.35(2) Å) of **1a** are almost within the range of the typical bond distances (Si−O: 1.66, B−O: 1.36 Å).[17] The Si−O bonds close to the Pt center of **3** (1.583(5), 1.576(6) Å) and **5** (1.599(5), 1.606(5) Å) are shorter than the other Si−O bonds (1.631(4)−1.653(5) Å). The electron-rich oxygen atom coordinated by the Pt atom[18] interacts with the Si atom more significantly than that in the Si−O−Si linkage. Similar contraction of the proximal B−O bonds to the Pt center (1.322(4)−1.34(1) Å) is shown compared to the B−O bonds within the B−O−B linkage of the platina(boroxine)s (1.37(1)−1.40(1) Å).

Complex **1a** reacts with an excess amount of H_2GePh_2 and 2 equiv of CF_3CO_2H to release the cyclic borasiloxanes (six-membered **8** and eight-membered **9**), as shown in Scheme 4.

Scheme 4. Formation of Cyclic Borasiloxanes from the Pt Precursor 1a



The cyclic borasiloxanes were characterized by mass spectrometry, and the former reaction forms **8** as the product. These reactions form the platinum complex with two germyl ligands $[Pt(GeHPh_2)_2(dmpe)]$ and that with two carboxylate ligands, $[Pt(OCOCF_3)_2(dmpe)]$[19] (**7**), respectively. The $^{31}P\{^1H\}$ NMR spectrum in the former reaction mixture displays the signals of $[Pt(GeHPh_2)_2(dmpe)]$ and unreacted complex **1a**, which suggests clean exchange of Ge−H bonds with Pt−Si bonds of the complex (Figure 6). Continuing the reaction causes formation of Ge-containing metallacycles, $[\overline{\mathrm{Pt(GePh_2GePh_2GePh_2})}(\mathrm{dmpe})]$ (δ_p = 36.4, J_{PtP} = 1816 Hz) or $[\overline{\mathrm{Pt(GePh_2GePh_2GePh_2GePh_2})}(\mathrm{dmpe})]$ (δ_p = 34.1, J_{PtP} = 1890 Hz),[20] which are characterized by $^{31}P\{^1H\}$ NMR spectroscopy. Recently, we reported

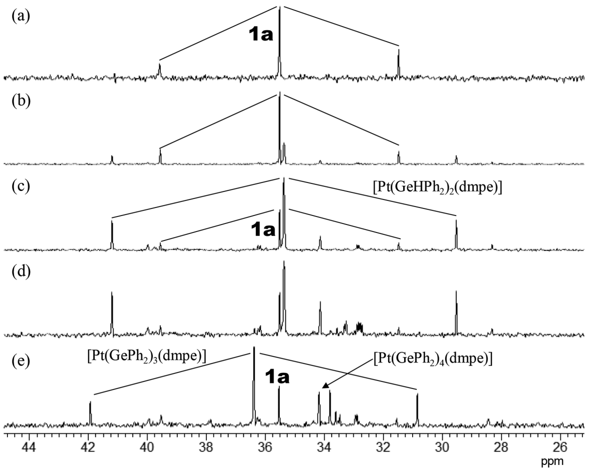
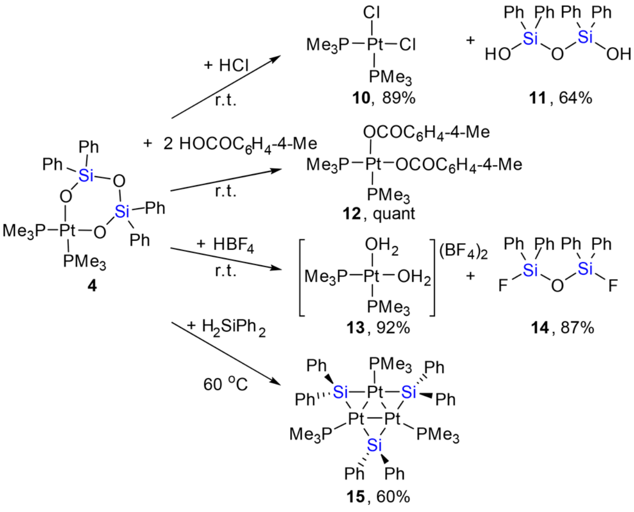


Figure 6. ^{31}P{^{1}H} NMR spectra (162 M Hz, toluene-d_8, rt) of the reaction mixture of **1a** and H_2GePh_2 in a 1:2.7 ratio at 60 °C (a) before addition of H_2GePh_2, (b) 1 h after addition of H_2GePh_2, (c) after 1 day, (d) after 2 days, and (e) after 6 days.

formation of the metallacycles from the dehydrogenative condensations of [Pt($GeHPh_2$)$_2$(dmpe)] with an excess amount of H_2GePh_2.

Scheme 5 summarizes the reactivity of the cyclic platina(siloxane) complex **4**. The reactions with excess HCl occur immediately to produce a mixture of *cis*-[$PtCl_2(PMe_3)_2$][21] (**10**) and 1,1,3,3-tetraphenyldisiloxane-1,3-diol[22] (**11**) in 89 and 64% yields. A similar reaction of **4** with 4-methylbenzoic acid in 1:2 ratio yielded a bis(carboxylate)platinum complex *cis*-[Pt($OCOC_6H_4$-4-Me)$_2$(PMe_3)$_2$] (**12**) in a quantitative yield. The siloxane byproduct was not identified in the reaction. The acid interacts favorably with the M−O bonds of **4**, similar to the alkoxide or aryloxide complexes of group 10 metals, because the oxygen bonded to the late transition metals exhibits high affinity to the proton due to repulsion between filled d$^\pi$ orbitals of the metals and p orbital of the O atom.[18] In contrast, the reaction of HBF_4 with **4** yields the cationic Pt complex *cis*-[Pt(OH_2)$_2$(PMe_3)$_2$](BF_4)$_2$[23] (**13**, 92%) and 1,3-difluoro-1,1,3,3-tetraphenyldisiloxane[24] (**14**, 87%). The F$^-$ ion generated from HBF_4 attacks the electropositive Si atom, forming the stable Si−F bonds.

Scheme 5. Reactivity of Platina(siloxane) Complex 4



The reaction of **4** with H_2SiPh_2 in a 1:3 molar ratio at 60 °C produced [{Pt(PMe_3)}$_3$(μ-$SiPh_2$)$_3$] (**15**)[25] in 60% yield. The formal trimerization of a Pt-silylene complex[26,27] occurs, but it can be ascribed to initial formation of [Pt($SiHPh_2$)$_2$(PMe_3)$_2$] or [Pt($SiHPh_2$)($OSiPh_2OSiPh_2OH$)(PMe_3)$_2$] and subsequent condensation of such monoplatinum complexes. Previously, we reported that heating of bis(silyl)platinum complex [Pt($SiHPh_2$)$_2$(PMe_3)$_2$] at 100 °C also formed **15** in much lower yield (28%).[25a]

In summary, we presented the preparation and characterization of the six-membered platinacycles composed of borasiloxane or siloxane rings. The platina(borasiloxane)s were obtained from the double condensation of the arylboronic acids with two Si−H groups of [Pt($SiHPh_2$)$_2$(dmpe)]. It is contrasted with the previous reports on the catalytic dehydrogenative condensation of organosilanes with OH compounds, which proceeds via coupling of the Si and O ligands. Cyclic platina(siloxane)s are produced by the reactions of O_2 with the same starting material via a cyclic four-membered intermediate complex. The platina(borasiloxane)s and platina(siloxane)s release the corresponding siloxane units via the exchange reactions of the Pt−Si and Pt−O bonds.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk line techniques under an atmosphere of argon or nitrogen or in a nitrogen-filled glovebox (Miwa MFG). Hexane, toluene, and tetrahydrofuran (THF) were purified by using a Grubbs-type solvent purification system (Glass Contour).[28] Dehydrated CH_2Cl_2 and acetone were purchased from Kanto Chemical and used as received. ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H}, ^{19}F{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian Mercury 300 MHz, Bruker Biospin Avance III 400 MHz, and Avance III HD 500 MHz NMR spectrometers. The chemical shifts in the ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual peaks of the solvents used.[29] The peak positions of the ^{11}B{^{1}H}, ^{19}F{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were referenced to external $BF_3 \cdot OEt_2$ (δ 0), $CFCl_3$ (δ 0), $SiMe_4$ (δ 0), and 85% H_3PO_4 (δ 0) in deuterated solvents. The IR spectrum was recorded on a JASCO FTIR-4100 spectrometer. Mass spectroscopic data were obtained on a Bruker Daltonics micrOTOF II (ESI and APCI) spectrometer. Elemental analyses were performed using a J-science JM10 or Yanaco HSU-20 autorecorder. The chemical reagents, 4-acetylphenylboronic acid (Combi-Blocks), 4-(trifluoromethyl)phenylboronic acid (TCI), 2-methoxyphenylboronic acid (Aldrich), CF_3CO_2H (TCI), 4.0 M HCl in 1,4-dioxane (Aldrich), 54 wt % HBF_4 in Et_2O (Aldrich), and 4-methylbenzoic acid (TCI) were used as received. [Pt($SiHPh_2$)$_2$(dmpe)] and [Pt($SiHPh_2$)$_2$(PMe_3)$_2$] were prepared according to the literature.[30] H_2GePh_2 was obtained from reduction of Cl_2GePh_2 (Aldrich) by $LiAlH_4$.

Preparation of [Pt($SiPh_2$-O-B(C_6H_4-4-COMe)-O-$SiPh_2$)(dmpe)] (1a). To a toluene (8 mL) solution of [Pt($SiHPh_2$)$_2$(dmpe)] (712 mg, 1.0 mmol) was added 4-acetylphenylboronic acid (164 mg, 1.0 mmol). The orange solution was stirred at 80 °C overnight, resulting in precipitation of a small amount of dark green solid. To remove the impurity by filtration, the solvent was removed under reduced pressure to give a yellow solid, which was washed with hexane (3 mL) and Et_2O (1 mL) and dried in vacuo to give **1a** as a yellow solid (756 mg, 87%). Recrystallization of **1a** in THF/hexane at −18 °C under inert gas gave a small amount of crystals suitable for X-ray crystallography. Anal. Calcd for $C_{38}H_{43}BO_3P_2Si_2Pt$: C, 52.36; H, 4.97. Found; C, 52.05; H, 5.03. ^{1}H NMR (500 MHz, CD_2Cl_2, rt): δ 7.93 (d, 2H, BC_6H_4 *ortho*, $^3J_{HH}$ = 8.0 Hz), 7.81 (d, 2H, BC_6H_4 *meta*, $^3J_{HH}$ = 7.5 Hz), 7.61 (d, 8H, SiC_6H_5 *ortho*, $^3J_{HH}$ = 6.0 Hz), 7.24−7.27 (m, 12H, SiC_6H_5 *meta* and *para*), 2.53 (s, 3H, COCH_3), 1.58−1.54 (m, 4H, PCH_2), 0.88 (m, 12H, PCH_3, $^2J_{PH}$ = 10 Hz). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, rt): δ 1.46 (br). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, rt): δ 198.9 ($COCH_3$), 147.3 (apparent triplet, SiC_6H_5 *ipso*, $^3J_{PC}$ = 7.0 Hz), 138.6 (CH_3COC and BC, overlapped), 135.6 (apparent triplet, SiC_6H_5 *ortho*, $^4J_{PC}$ = 7.5 Hz), 135.2, 128.3, 127.6, and 127.2 (SiC_6H_5 *meta* or *para*, or BC_6H_4 *ortho* or *meta*), 30.6 (m, PCH_2), 27.0 (COCH_3), 13.3 (m, PCH_3). ^{29}Si{^{1}H} NMR (99 MHz, CD_2Cl_2, rt): δ 19.4 (dd, $^2J_{PSi}$ = 12, 157 Hz, J_{PtSi} = 1318 Hz).

^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$, rt): δ 36.2 ($^2J_{SiP}$ = 12, 157 Hz, J_{PtP} = 1331 Hz). In a NMR tube, to a toluene-d_8 solution (0.5 mL) of [Pt(SiHPh$_2$)$_2$(dmpe)] (5.0 mg, 7 μmol) was added 2 equiv of 4-acetylphenylboronic acid (2.3 mg, 14 μmol). The reaction mixture was monitored by the ^{31}P{^{1}H} NMR spectroscopy, as shown in Figure 3.

Preparation of [Pt(SiPh$_2$–O-B(C$_6$H$_4$-4-CF$_3$)-O-SiPh$_2$)(dmpe)] (1b). The reaction of [Pt(SiHPh$_2$)$_2$(dmpe)] (71 mg, 0.1 mmol) and 4-(trifluoromethyl)phenylboronic acid (38 mg, 0.2 mmol) gave **1b** (45 mg, 50%) as a green solid. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, rt): δ 7.97 (d, 2H, BC$_6$*H*$_4$ *ortho*, $^3J_{HH}$ = 10 Hz), 7.61 (d, 8H, SiC$_6$*H*$_5$ *ortho*, $^3J_{HH}$ = 5.0 Hz), 7.51 (d, 2H, BC$_6$*H*$_4$ *meta*, $^3J_{HH}$ = 10 Hz), 7.25–7.26 (m, 12H, C$_6$*H*$_5$ *meta* and *para*), 1.55–1.58 (m, 4H, PC*H*$_2$), 0.88 (d, 12H, PC*H*$_3$, $^2J_{PH}$ = 10 Hz). ^{11}B{^{1}H} NMR (160 MHz, CD$_2$Cl$_2$, rt): δ 1.27 (br). ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, rt): 147.2 (apparent triplet, SiC$_6$H$_5$ *ipso*, $^3J_{PC}$ = 6.3 Hz), 135.2 (apparent triplet, SiC$_6$H$_5$ *ortho*, $^4J_{PC}$ = 7.5 Hz), 134.9, 127.9, 127.2 (SiC$_6$H$_5$ *meta*, *para* and BC$_6$H$_4$ *ortho*, *meta*), 123.6 (quartet, BC$_6$H$_4$ *meta*, $^3J_{FC}$ = 3.8 Hz), 30.3 (m, PCH$_2$), 12.9 (m, PCH$_3$). The *ipso* carbon was not observed due to low intensity. ^{19}F{^{1}H} NMR (471 MHz, CD$_2$Cl$_2$, rt): δ −62.9 (s). ^{29}Si{^{1}H} NMR (99 MHz, CD$_2$Cl$_2$, rt): δ 19.6 (dd, $^2J_{PSi}$ = 12, 158 Hz, J_{PtSi} = 1313 Hz). ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$, rt): δ 36.2 ($^2J_{SiP}$ = 12, 158 Hz, J_{PtP} = 1336 Hz). HRMS (ESI): calcd for C$_{37}$H$_{40}$BF$_3$NaO$_2$P$_2$PtSi$_2$ [M + Na]$^+$ 920.1638; found *m/z* 920.1614.

Preparation of [Pt(SiPh$_2$-O-SiPh$_2$)(dmpe)] (2). To an acetone (2 mL) solution of [Pt(SiHPh$_2$)$_2$(dmpe)] (36 mg, 0.05 mmol) was added an excess amount of H$_2$O (200 μL). The light yellow solution was stirred at room temperature overnight, and the solution color changed to green. The solvent was removed under reduced pressure to give a light green solid (24 mg) containing **2**. The solid product recovered from the solution containing complex **2** [^{31}P{^{1}H} NMR (202 MHz, toluene-d_8, rt): δ 38.0 (J_{PtP} = 1443 Hz)] as the major species, but its isolation as the analytically pure crystals was not feasible because complex **2** was easily oxidized at room temperature under air, resulting in the formation of **3** and the oxidized products.

Reaction of [Pt(SiHPh$_2$)$_2$(dmpe)] with 2-Methoxyphenylboronic Acid. To a toluene (8 mL) solution of [Pt(SiHPh$_2$)$_2$(dmpe)] (71.2 mg, 0.1 mmol) was added 2-methoxyphenylboronic acid (30.4 mg, 0.2 mmol). The light yellow solution was stirred at 60 °C for 3 h, resulting in a change to orange and precipitation of a gray solid. After filtration, the solvent was removed to give a brown solid containing **2**, [Pt(SiPh$_2$–O-B(C$_6$H$_4$-2-OMe)-O-SiPh$_2$)(dmpe)] (**1c**), and unreacted [Pt(SiHPh$_2$)$_2$(dmpe)]. Data for **1c**: ^{31}P{^{1}H} NMR (202 MHz, toluene-d_8, rt): δ 35.2 (J_{PtP} = 1310 Hz). Recrystallization of this solid in CH$_2$Cl$_2$/hexane at −18 °C under inert gas gave a small amount of crystals of **2** suitable for X-ray crystallography.

Reaction of (HO)$_2$B(C$_6$H$_4$-4-COMe) with 2. 4-Acetylphenylboronic acid (10.7 mg, 65 μmol) was added to a toluene-d_8 solution (0.5 mL) of **2** (10.0 mg, 13 μmol), which was obtained as a crude product. The ^{31}P{^{1}H} NMR spectrum of the mixture at 70 °C for 1 h showed the major signals of **1a** (δ 35.2, J_{PtP} = 1314 Hz), accompanied by unidentified products. Further reaction for 5.5 h at the same temperature increased the signal of **2** as the major product and disappearance of the signal of **2**. An equimolar reaction at the same temperature, however, resulted in the complexes being composed of multiple uncharacterized products.

Preparation of [Pt(O-SiPh$_2$-O-SiPh$_2$-O)(dmpe)] (3). In a NMR tube, a toluene-d_8 solution of [Pt(SiHPh$_2$)$_2$(dmpe)] (5.0 mg, 7 μmol) was stored at room temperature in air. After 3 days, the ^{31}P{^{1}H} NMR spectrum of the mixture showed two ^{31}P signals assigned as **3** (δ 18.0, J_{PtP} = 3566 Hz) and unreacted [Pt(SiHPh$_2$)$_2$(dmpe)]. Slow evaporation of the solution at room temperature afforded a tiny amount of colorless crystals of **3**, which was suitable for X-ray crystallography.

Preparation of [Pt(O-SiPh$_2$-O-SiPh$_2$-O)(PMe$_3$)$_2$] (4). A toluene (10 mL) suspension of [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$] (503 mg, 0.70 mmol) was stirred under O$_2$ atmosphere for 15 h at room temperature. The complex was dissolved in toluene. The solution gradually turned from yellow to brown, accompanied by precipitation of a white solid. The solid was collected through filtration and washed with hexane three times (10 mL) and dried in vacuo to afford **4** as a white solid (412 mg, 77%). The crystals of **4** suitable for X-ray crystallography were obtained by slow diffusion of toluene to hexane solution. Anal. Calcd for C$_{30}$H$_{38}$O$_3$P$_2$PtSi$_2$: C, 47.42; H, 5.04. Found: C, 47.18; H, 4.96. ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 7.76 (d, 8H, C$_6$*H*$_5$ *ortho*, $^3J_{HH}$ = 8.0 Hz), 7.24–7.29 (m, 12H, C$_6$*H*$_5$ *meta* and *para*), 1.40 (d, 18H, PC*H*$_3$, $^2J_{HP}$ = 11 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, rt): δ 141.0 (*C*$_6$H$_5$ *ipso*), 134.6 (*C*$_6$H$_5$ *ortho*), 128.2 (*C*$_6$H$_5$ *para*), 127.0 (*C*$_6$H$_5$ *meta*), 14.7 (m, PCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ −28.9 (J_{PPt} = 3526 Hz). ^{29}Si{^{1}H} NMR (79 MHz, CDCl$_3$, rt): δ −37.0. IR (KBr): 1115 (ν_{Si-OSi}), 996 and 947 (ν_{Si-OPt}) cm^{-1}.

Preparation of [Pt{O–Si(Tol)$_2$–O-Si(Tol)$_2$-O}(PMe$_3$)$_2$] (5). Complex **5** was obtained similarly in 47% yield, and the crystals of **5** suitable for X-ray crystallography were obtained by slow diffusion of toluene to hexane solution. Anal. Calcd for C$_{34}$H$_{46}$O$_3$P$_2$PtSi$_2$: C, 50.05; H, 5.68. Found: C, 50.17; H, 5.86. ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 7.62 (d, 8H, C$_6$*H*$_4$ *ortho*, $^3J_{HH}$ = 7.6 Hz), 7.05 (d, 8H, C$_6$*H*$_4$ *meta*, $^3J_{HH}$ = 7.6 Hz), 2.30 (s, C$_6$H$_4$C*H*$_3$, 12H), 1.41 (d, 18H, PC*H*$_3$, $^2J_{HP}$ = 11 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, rt): δ 137.9 (*C*$_6$H$_4$ *ipso*), 137.6 (*C*$_6$H$_4$ *para*), 134.7 (*C*$_6$H$_4$ *ortho*), 127.8 (*C*$_6$H$_4$ *meta*), 21.5 (s, C$_6$H$_4$CH$_3$), 14.7 (m, PCH$_3$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, rt): δ −29.0 (J_{PPt} = 3518 Hz).

Reaction of H$_2$GePh$_2$ with 1a. To a toluene-d_8 solution (0.6 mL) of **1a** (8.7 mg, 10 μmol) in a J-Young NMR tube under inert gas was added H$_2$GePh$_2$ (5.0 μL, 27 μmol). The ^{31}P{^{1}H} NMR spectrum of the reaction mixture after 1 h at 60 °C appeared at δ 35.5 (J_{PtP} = 1890 Hz), which was assigned to [Pt(GeHPh$_2$)$_2$(dmpe)].[20] Further reaction at the same temperature caused the formation of [Pt(GePh$_2$GePh$_2$GePh$_2$)-(dmpe)] (δ_p = 36.4, J_{PtP} = 1816 Hz) or [Pt(GePh$_2$GePh$_2$GePh$_2$GePh$_2$)-(dmpe)] (δ_p = 34.1, J_{PtP} = 1890 Hz). The HRMS data (APCI) of the mixture revealed the signals assigned as cyclic borasiloxanes (MeCO-4-C$_6$H$_4$BO)(SiPh$_2$O)$_2$ (**8**) and (MeCO-4-C$_6$H$_4$BO)(SiPh$_2$O)$_3$ (**9**). Data for **8**: calcd for C$_{32}$H$_{28}$BO$_4$Si$_2$ [M + H]$^+$ 543.1620; found *m/z* 543.1604. Data for **9**: calcd for C$_{44}$H$_{38}$BO$_5$Si$_3$ [M + H]$^+$ 741.2123; found *m/z* 741.2120.

Reaction of 1a with CF$_3$CO$_2$H. To a THF solution of **1a** (174 mg, 0.2 mmol) was added trifluoroacetic acid (31 μL, 0.4 mmol). The solution changed from yellow to dark green after being stirred at room temperature for 30 min, and the reaction was continued overnight. The solvent was removed under reduced pressure to give a mixture of [Pt(OCOCF$_3$)$_2$(dmpe)][19] (**7**) and the borasiloxane compound. The latter product was extracted by 15 mL of Et$_2$O and evaporated to give a mixture of cyclic borasiloxanes **8** and **9** in a 7:3 ratio as a brown solid (106 mg), which was identified as mixtures by HRMS (APCI) and NMR spectroscopy. ^{1}H NMR assignment for **8** (400 MHz, CD$_2$Cl$_2$, rt): δ 8.13 (d, 2H, BC$_6$*H*$_4$ *ortho*, $^3J_{HH}$ = 8.0 Hz), 7.96 (d, 2H, BC$_6$*H*$_4$ *meta*, $^3J_{HH}$ = 8.0 Hz), 7.72 (d, 8H, SiC$_6$*H*$_5$ *ortho*, $^3J_{HH}$ = 6.8 Hz), 7.38–7.43 (m, 12H, SiC$_6$*H*$_5$ *meta* and *para*), 2.60 (s, 3H, COC*H*$_3$). ^{1}H NMR assignment for **9**: δ 8.17 (d, 2H, BC$_6$*H*$_4$ *ortho*, $^3J_{HH}$ = 8.3 Hz), 8.00 (d, 2H, BC$_6$*H*$_4$ *meta*, $^3J_{HH}$ = 8.3 Hz), 2.62 (s, 3H, COC*H*$_3$). The SiC$_6$*H*$_5$ signals are not characterized clearly due to overlapping with other signals. ^{29}Si{^{1}H} NMR (99 MHz, CD$_2$Cl$_2$, rt): δ −21.7 (s for **8**), −39.5 (s, 1Si for **9**), −41.5 (s, 2Si for **9**). ^{11}B{^{1}H} NMR (160 MHz, CD$_2$Cl$_2$, rt): δ 16.8 (br for **8** and **9**). IR (KBr): 1319, 997 (ν_{BOSi}), 1126 cm^{-1} (ν_{SiOSi}).

Reaction of 4 with HCl. To a CH$_2$Cl$_2$ solution (5 mL) of **4** (248 mg, 0.33 mmol) was added three times molar amounts of 4.0 M HCl in 1,4-dioxane (248 μL, 0.99 mmol). A white solid was rapidly precipitated from the reaction mixture. The solid was collected through filtration, washed with hexane twice (3 mL), and dried in vacuo to give *cis*-[PtCl$_2$(PMe$_3$)$_2$] (**10**, 123 mg, 89%), which was consistent with the literature data (δ −23.9, J_{PPt} = 3468 Hz).[21] 1,1,3,3-Tetraphenyldisiloxane-1,3-diol was isolated from the supernatant solution (**11**, 87 mg, 64%) and characterized by IR spectroscopy.[22] IR (KBr): 3230 (ν_{OH}), 1128 (ν_{SiO}), 1086, 885, 848 (ν_{SiOH}) cm^{-1}.

Reaction of 4 with 4-Methylbenzoic Acid. To a toluene suspension (5 mL) of **4** (145 mg, 0.19 mmol) was added 4-methylbenzoic acid (52 mg, 0.38 mmol) under air to become a yellow solution immediately with stirring for 1 h. The solution was passed through filter paper and evaporated under reduced pressure. Addition of 2 mL of ether to the resulting material separated a platinum complex as a white solid.

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The solid was collected through filtration, washed with 2 mL of ether three times, and dried in vacuo to obtain a di(carboxylate)platinum complex *cis*-[Pt(OCOCF$_3$)$_2$(PMe$_3$)$_2$] (**12**, 109 mg, 93%), which was crystallized by toluene/hexane solutions. The organosiloxane compounds as byproducts were not characterized in the mixture. Data for **12**: Anal. Calcd for $C_{22}H_{32}O_4P_2Pt$: C, 42.79; H, 5.22. Found: C, 43.39; H, 5.40. ^{1}H NMR (300 MHz, CDCl$_3$, rt): δ 7.87 (d, 4H, C_6H_4, J_{HH} = 8.1 Hz), 7.07 (d, 4H, C_6H_4, J_{HH} = 8.1 Hz), 2.30 (s, 6H, $C_6H_4CH_3$), 1.68 (d, 18H, PCH_3, J_{HP} = 11 Hz, J_{HPt} = 50 Hz). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6, rt): δ 206.1 (C═O), 140.7 (C_6H_4 *para*), 135.6 (C_6H_4 *ipso*), 130.4 (C_6H_4 *ortho*), 128.9 (C_6H_4 *meta*), 21.3 ($C_6H_4CH_3$), 15.0 (d, PCH_3, J_{CP} = 43 Hz, $^2J_{CPt}$ = 31 Hz). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, rt): δ −31.2 (J_{PPt} = 3650 Hz). IR (KBr): 1611 ($\nu_{C=O}$), 1556 and 1363 (ν_{CO}) cm^{-1}.

Reaction of 4 with HBF$_4$. To a CH$_2$Cl$_2$ solution (5 mL) of **4** (109 mg, 0.14 mmol) was added three times molar amounts of 54 wt % HBF$_4$ in diethyl ether (98 μL, 0.43 mmol). Immediately, a white solid was precipitated from the reaction mixture. The solid was collected through filtration, washed with hexane twice (3 mL), and dried in vacuo to give a dicationic aquaplatinum complex *cis*-[Pt(OH$_2$)$_2$(PMe$_3$)$_2$](BF$_4$)$_2$[23] (**13**) (72 mg, 92%). 1,3-Difluoro-1,1,3,3-tetraphenyldisiloxane[24] (**14**) was isolated as a white solid from the supernatant solution (51 mg, 87%). Data for **13**: ^{1}H NMR (300 MHz, acetone-d_6, rt): δ 1.94 (m, 18H, C_6H_4 *ortho*, J_{HH} = 7.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, rt): δ −24.6 (J_{PPt} = 3752 Hz). Data for **14**: ^{1}H NMR (300 MHz, CDCl$_3$, rt): δ 7.66 (m, 8H, C_6H_4 *ortho*, J_{HH} = 7.5 Hz), 7.50 (m, 4H, C_6H_4 *para*, J_{HH} = 7.5 Hz), 7.39 (m, 8H, C_6H_4 *meta*, J_{HH} = 7.2 Hz). ^{29}Si{^{1}H} NMR (79 MHz, CDCl$_3$, rt): δ −36.1, J_{SiF} = 281 Hz). GC-MS (70 eV): *m*/*z* = 418.

Reaction of 4 with H$_2$SiPh$_2$. To a toluene solution (5 mL) of complex **4** (399 mg, 0.53 mmol) was added three times molar amounts of H$_2$SiPh$_2$ (292 μL, 1.58 mmol). The solution was stirred at 60 °C for 12 h, and the resultant red solution was evaporated to dryness. The solid product was washed with Et$_2$O (5 mL) and dried in vacuo to yield [{Pt(PMe$_3$)}$_3$(μ-SiPh$_2$)$_3$][25a] (**15**, 145 mg, 60%). The ^{1}H NMR spectrum of the supernatant solution showed the presence of octaphenylcyclotetrasiloxane (OSiPh$_2$)$_4$ that was characterized by ^{1}H and ^{29}Si{^{1}H} NMR spectroscopy. ^{1}H NMR (CDCl$_3$, 500 MHz, rt): δ 7.48 (d, 16H, SiC_6H_5 *ortho*, $^3J_{HH}$ = 5 Hz), 7.35 (t, 8H, SiC_6H_5 *para*, $^3J_{HH}$ = 7.5 Hz), 7.18 (t, 16H, SiC_6H_5 *meta*, $^3J_{HH}$ = 7.5 Hz). ^{29}Si{^{1}H} NMR (CDCl$_3$, 99 MHz, rt) δ −43.0.

X-ray Crystal Structure Analyses. Single crystals of **1a**, **2**, **3**, **4**, **5**, and **12** suitable for X-ray diffraction were mounted on MicroMounts (MiTeGen). The crystallographic data were collected on Rigaku Saturn CCD area detector for **1a**, **2**, **3**, **4**, and **12** or Rigaku AFC5R automated four-cycle diffractometer for **5** equipped with monochromated Mo Kα radiation (λ = 0.71073 Å) at 113 or 293 K. Calculations were carried out using the program package Crystal Structure 4.2 for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method using SHELXL-2014. Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00690.

Crystal structure and data of **1a**, **2**, **3**, **4**, **5**, and **12** and NMR spectra of the products (PDF)

Accession Codes

CCDC 1570088−1570093 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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