Preparation and Structure of New Phenylplatinum Complexes Containing Silsesquioxane as a Monodentate or Bidentate Ligand

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Received February 28, 2006

Incompletely condensed silsesquioxanes, $R_7Si_7O_9(OH)_3$ (R = *cyclo*-C_5H_9, *iso*-C_4H_9), react with *trans*-[PtI(Ph)(L)$_2$] (L = PEt_3, PMe_2Ph) at room temperature in the presence of Ag_2O to yield platinum complexes with a monodentate *O*-coordinated silsesquioxane, *trans*-[Pt{$O_{10}Si_7R_7(OH)_2$}(Ph)(L)$_2$] (**1a**: R = *cyclo*-C_5H_9; L = PEt_3, **1b**: R = *iso*-C_4H_9; L = PEt_3, **2a**: R = *cyclo*-C_5H_9; L = PMe_2Ph, **2b**: R = *iso*-C_4H_9; L = PMe_2Ph). Reactions of silsesquioxanes with *trans*-[PtI(Ph)(PPh_3)$_2$] in the presence of Ag_2O at 55 °C afford unexpected Pt−Ag heterobimetallic complexes, [Pt{$O_{11}Si_7R_7(OH)(AgPPh_3)$}(Ph)($PPh_3$)] (**3a**: R = *cyclo*-$C_5H_9$, **3b**: R = *iso*-$C_4H_9$), and a hydroxo-bridged dinuclear platinum complex, *anti*-[{PtPh(PPh_3)}$_2$(μ-OH)$_2$] (**4**). These complexes were isolated and characterized by X-ray crystallography and ^{1}H, ^{31}P, ^{29}Si, and ^{13}C NMR spectroscopy. The crystal structures of **3a** and **3b** show a square-planar coordination around the Pt center bonded to Ph, PPh_3, and bidentate *O*,*O*-coordinated silsesquioxane. One of the coordinated oxygen atoms is also bound to the $AgPPh_3$ group.

Introduction

Incompletely condensed silsesquioxanes[1] contain a network composed of Si−O bonds and OH groups and are regarded as partial structures of the silica surface used for heterogeneous catalysts.[2] Silsesquioxane complexes of transition metals catalyze the polymerization and epoxidation of alkenes.[2d] Inspite of the many reports on early-transition metal complexes with silsesquioxane ligands[3,4] and late-transition metal complexes with silsesquioxane-based phosphine ligands,[5] there have been a few reports on group 10 metal complexes having *O*-bonded silsesquioxanes as ligand. Recently, Abbenhuis[6] and Johnson[7] have reported platinum complexes that contain silsesquioxanes as *O*,*O*-chelating bidentate ligands. Pt complexes with Pt−O−Si bonds were obtained using simple silanolate as ligand. Komiya reported a metathesis reaction of sodium silanolate with an alkylplatinum halogeno complex to afford PtEt($OSiPh_3$)(cod).[8] Recently, we have employed Ag_2O to activate both the OH bond of silanol and the Pt−I bond of *trans*-[PtI(Ph)(PPh_3)$_2$] and obtained *trans*-[Pt{$OSiMe_2(C_6H_4CF_3$-4)}(Ph)(PPh_3)$_2$] as the product of the metathesis reaction.[9] An analogous reaction of silanol, $HOSiMe_2(C_6H_4CF_3$-4) with [PtBr(PEt_3)$_3$]$^+$, however forms diarylplatinum complexes via the initial formation of an intermediate silanolato platinum complex and its C−Si bond cleavage.[10] The introduction of a bulky and partially hydrophilic silsesquioxane ligand to aryl(or alkyl)platinum complexes would provide complexes with unique chemical properties. In this paper, we report the preparation and structure of new platinum-containing silsesquioxanes with monodentate ligands and unexpected Pt−Ag heterobimetallic silsesquioxanes with bidentate ligands.

Results and Discussion

The reaction of silsesquioxanes $R_7Si_7O_9(OH)_3$ (R = *cyclo*-C_5H_9, *iso*-C_4H_9) with *trans*-[PtI(Ph)(L)$_2$] (L = PEt_3, PMe_2Ph) in the presence of Ag_2O produces platinum complexes with monodentate silsesquioxane ligands, *trans*-[Pt{$O_{10}Si_7R_7(OH)_2$}(Ph)(L)$_2$] (**1a**: R = *cyclo*-C_5H_9; L = PEt_3, **1b**: R = *iso*-C_4H_9; L = PEt_3, **2a**: R = *cyclo*-C_5H_9; L = PMe_2Ph, **2b**: R = *iso*-C_4H_9; L = PMe_2Ph), at room temperature, shown by eq 1. The ^{31}P{^{1}H} NMR spectra of the reaction mixture indicate that the completion of the metathesis reaction requires 24−120 h. The

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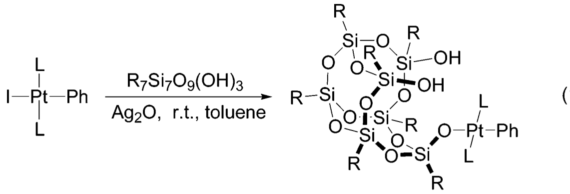
platinum−silsesquioxane complexes **1a**, **1b**, and **2a** were obtained in high yields (74−98%), although the isolated yield of **2b** is much lower (5%) owing to the high solubility of **2b** in organic solvents.



(1)

1a: R = *cyclo*-C_5H_9, L = PEt_3
1b: R = *iso*-C_4H_9, L = PEt_3
2a: R = *cyclo*-C_5H_9, L = PMe_2Ph
2b: R = *iso*-C_4H_9, L = PMe_2Ph

Figure 1a shows the molecular structure of **1a** determined by X-ray crystallography. The selected bond distances and angles of **1a** and **1b** are summarized in Table 1. Both complexes **1a** and **1b** have square-planar Pt(II) centers with two phosphine ligands at *trans* coordination sites. The Pt−O1 bond distances of **1a** (2.129(3) Å) and **1b** (2.113(2) Å) are longer than the Pt−O bond distances of the platinum complexes with bidentate silsesquioxane ligands, $[Pt\{O_{11}Si_7(cyclo\text{-}C_5H_9)_7(OSiMe_3)\}(dppe)]$ (dppe = bis(1,2-diphenylphosphino)ethane) (2.031(6), 2.036(4) Å)[6] and $[Pt\{O_{11}Si_7(cyclo\text{-}C_5H_9)_7(OSiMe_3)\}(\eta^4\text{-}C_8H_{12})]$ (1.987(5), 1.990(5) Å),[7] and those of siloxoplatinum complexes $PtEt(OSiPh_3)(cod)$ (2.003(4) Å), $PtPh(OSiPh_3)(cod)$ (1.992(3) Å),[8] and *trans*-$[Pt\{OSiMe_2(C_6H_4CF_3\text{-}4)\}(Ph)(PPh_3)_2]$ (2.091(4) Å).[9] A large *trans* influence of the phenyl ligand and the electron-withdrawing effect of the silsesquioxane moiety[2a] elongate the Pt−O bond of **1a** and **1b**. The phosphine ligands at the *cis* positions of the silsesquioxane ligand also affect Pt−O bond distances. The complexes have decreasing bond distances in the order **1a** > **1b** > *trans*-$[Pt\{OSiMe_2(C_6H_4CF_3\text{-}4)\}(Ph)(PPh_3)_2]$; the complex with more electron-donating phosphine ligands contains longer a Pt−O bond of the siloxo and silsesquioxane ligands.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 1a and 1b

	1a	**1b**
Pt−P1	2.303(1)	2.297(1)
Pt−P2	2.309(1)	2.304(1)
Pt−O1	2.129(3)	2.113(2)
Pt−C1	2.014(4)	1.998(3)
O1···O6	2.558(4)	2.547(4)
O1···O7	4.104(5)	4.143(3)
O6···O7	2.750(5)	2.757(4)
O1···H1	1.84(6)	1.92(5)
O6···H2	2.13(5)	2.04(5)
P1−Pt−O1	92.02(8)	92.55(8)
P1−Pt−C1	88.5(1)	87.5(1)
P2−Pt−O1	92.70(9)	92.05(8)
P2−Pt−C1	86.6(1)	87.9(1)
Pt−O−Si	134.6(2)	130.2(2)
O1···H1−O6	172(5)	165(5)
O6···H2−O7	175(2)	167(5)

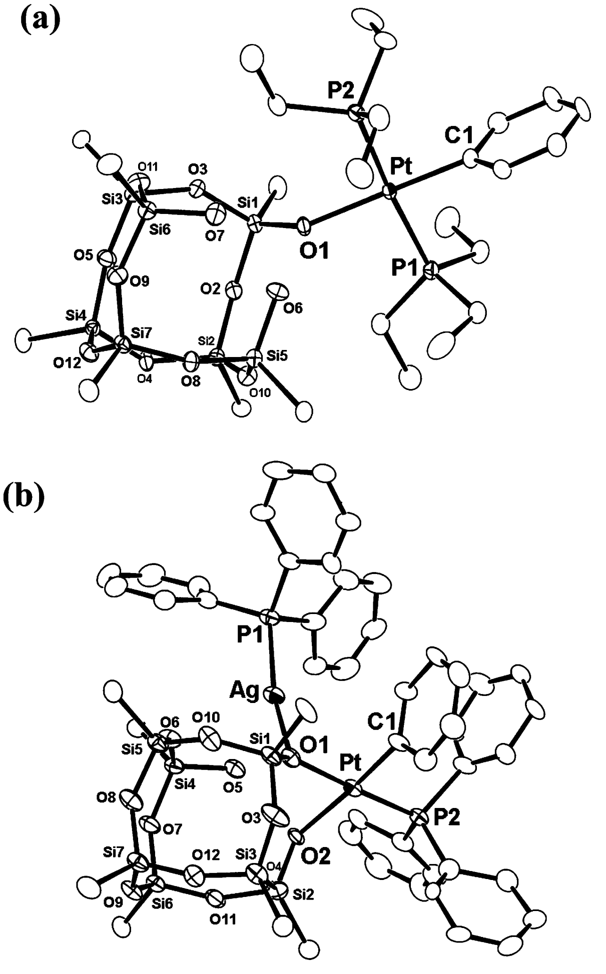


Figure 1. ORTEP drawings of **1a** (a) and **3a** (b) at 50% and 30% ellipsoidal level, respectively. Hydrogens atoms and cyclopentyl substituents attached to Si atoms are omitted for simplicity.

The O1···O6 and O6···O7 distances of **1a** (2.558(4), 2.750(5) Å) are within the range of the O···H−O hydrogen bond lengths. Actually, O6−H1 and O7−H2 bonds are directed toward oxygen atoms, namely, O1 and O6, respectively. The Si−OH groups of **1b** also form two intramolecular hydrogen bonds. The presence of hydrogen bonding is consistent with an almost linear O···H−O arrangement, O1···H1−O6 (**1a**: 172(5)°, **1b**: 165(5)°) and O6···H2−O7 (**1a**: 175(2)°, **1b**: 167(5)°) as well as O1···H1 (**1a**: 1.84(6) Å, **1b**: 1.92(5) Å) and O6···H2 (**1a**: 2.13(5) Å, **1b**: 2.04(5) Å), distances within the sum of the van der Waals radii for H and O atoms (2.72 Å).[11] The O···O and O···H distances of O1···H1−O6 are shorter than those of O6···H2−O7, indicating that the former hydrogen bonds between the OH group and coordinated oxygen are stronger than the latter between two OH groups of the ligand. Ott et al. have reported a similar intramolecular hydrogen bond of iron silsesquioxane complexes (O···H−O angle: 172.7°, O···H distance: 1.947 Å).[12] Fluoroalkoxide and arylalkoxide complexes of Rh, Pd, Pt, and Ru were reported to form a 1:1 aggregate with alcohols through a strong O···H−O bond between the alcohol and the alkoxide ligand in the solid state and in solution.[13−16]

The ^1H NMR spectra of **1** and **2** exhibit signals for OH hydrogens of the silsesquioxane ligand at low magnetic field

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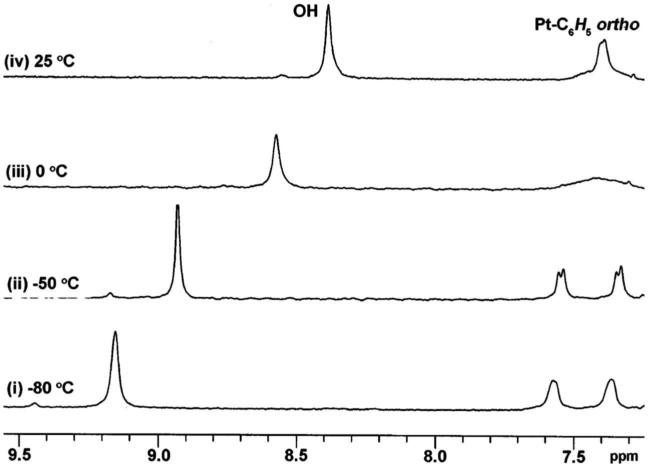
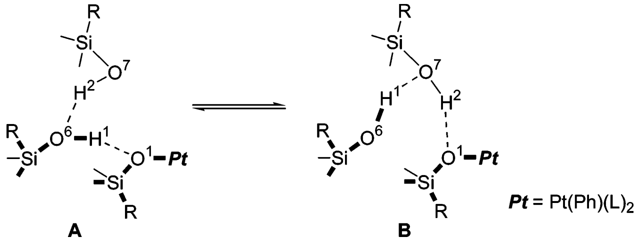


Figure 2. Variable-temperature ^{1}H NMR spectra of **1a** in toluene-d_8 at (i) −80 °C, (ii) −50 °C, (iii) 0 °C, and (iv) 25 °C.

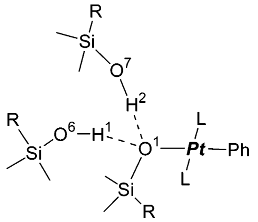
(δ 8.5−9.2). The low magnetic field positions of the signals are ascribed to the O−H···O hydrogen bonding that is observed by X-ray crystallography. The ^{1}H NMR spectrum of [(c-C_6H_{11})$_7$-$Si_7O_{11}(OH)Sn^{II}$]$_2$ was also reported to show the OH hydrogen signal at low-field position, although it was explained by O−H···Sn interaction.[17] The addition of D_2O to an NMR sample in C_6D_6 causes the disappearance of the OH hydrogen signal because of the rapid exchange of hydroxo protons with D_2O. A variable-temperature ^{1}H NMR study of these complexes revealed their dynamic behavior in solution. The ^{1}H NMR spectrum of **1a** in toluene-d_8 at −80 °C (Figure 2 (i)) is consistent with the C_s symmetry of the molecule. The crystal structures of **1a** and **1b** show two different OH hydrogens, whereas the ^{1}H NMR spectra in solution at −80 °C exhibit a single OH hydrogen peak (**1a**: δ 9.15, **1b**: δ 9.48) probably because of the rapid exchange of the two OH hydrogens, shown in Scheme 1.

Scheme 1

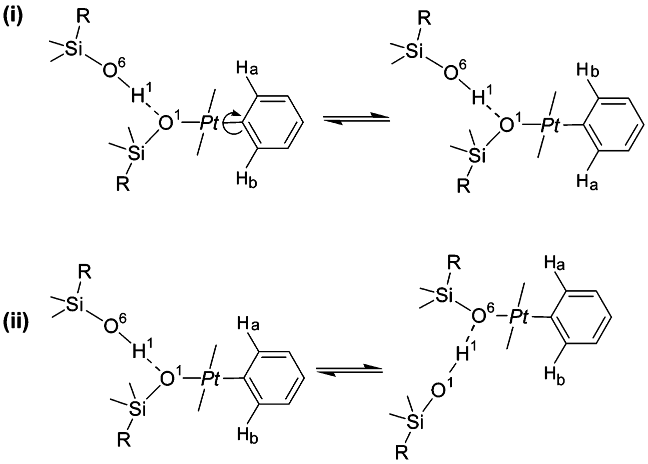


Structure **A** contains a hydrogen bond between H1 and the coordinated oxygen (O1) as well as that between silanol oxygen (O6) and H2. The switching of the hydrogen bond forms structure **B**, having hydrogen bonds between O1 and H2 and between O7 and H1. Another possible explanation for a single OH hydrogen signal may be a structure of the complex with symmetrically bifurcated hydrogen bonds between coordinated oxygen and the two Si−O−H groups, as shown in Scheme 2. However the bifurcated interactions are not consistent with the crystal structure of **1a** or **1b**.

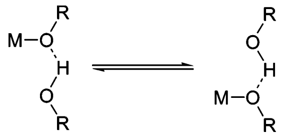
Scheme 2



Scheme 3



Scheme 4



Two peaks at δ 7.57 and 7.37 (Figure 2 (i)) are assigned to the *ortho* hydrogens of the phenyl ligand whose six-membered ring is perpendicular to the coordination plane, as found by X-ray crystallography (Figure 1a). On increasing the temperature, ^{1}H NMR signals of the *ortho* protons of the phenyl ligand are broadened at 0 °C and completely coalesce at 25 °C, as shown in Figure 2 (ii)−(iv). Scheme 3 depicts two possible dynamic behaviors that account for change of the NMR spectra depending on temperature. Rapid rotation of the platinum−aryl bond renders two *ortho* hydrogens of the phenyl ligand magnetically equivalent, as shown in Scheme 3 (i). NMR study of a *cis*-platinum iodo complex with a chelating diphosphine ligand revealed the rotation of the Pt−C bond on the NMR scale.[18] Intramolecular exchange of O−Pt and O−H bonds, including activation of both Pt−O1 and O6−H1 bonds and the concurrent formation of Pt−O6 and H1−O1 (Scheme 3 (ii)), also causes the coalescence of the signals. Late-transition metal alkoxide complexes with associated alcohol through hydrogen bonding cause the intramolecular exchange of an alkoxide ligand and alcohol on the NMR time scale (Scheme 4).[13−16] Thus, either rotation of the Pt−aryl bond or intramolecular exchange of the platinum group between the siloxo ligand and silanol is responsible for the temperature-dependent change of the NMR spectra.

The IR spectra of **1a**, **1b**, and **2a** in the solid state show a broad absorption at 3300−3200 cm^{-1}, which is assigned as the stretching vibration of the OH bond involved in the O···H−O hydrogen bond system. C−H stretching vibrations (2953−2865 cm^{-1}) and strong Si−O broad bands (centered at 1150−1100

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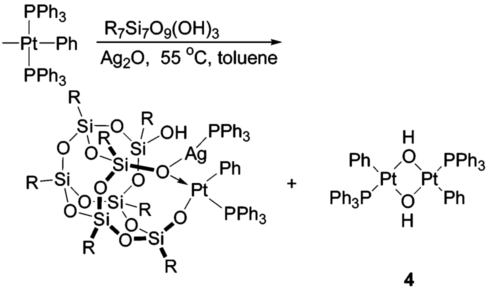
cm^{-1}) are observed at normal positions for silsesquioxane.[19] A new band at approximately 740 cm^{-1} is observed and assigned to the Si−O group bonded to platinum, in agreement with a monodentate-coordinated silsesquioxane.

The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** show a single signal of phosphine ligands, and the coupling constants (J_{PPt} = 2860−2956 Hz) suggest the *trans* position of the ligands of the square-planar Pt(II) center. The $^{13}C\{^1H\}$ NMR spectra of **1a**, **1b**, and **2a** contain five signals for the seven CH carbon atoms of the cyclopentyl groups (**1a** and **2a**) or CH_2 carbon atoms of the isobutyl substituents (**1b**) in 1:2:2:1:1 ratio. The $^{29}Si\{^1H\}$ NMR spectra of complexes **1a**, **1b**, and **2a** at room temperature in solution display five signals in the ratio 2:1:1:1:2 for the seven silicon atoms in the silsesquioxane framework. The number and relative intensity of the peaks are consistent with the rapid exchange of the OH group in solution, shown in Scheme 1. Two pairs of magnetically equivalent Si nuclei, (Si2 and Si3) and (Si5 and Si6) in Figure 1a, show the NMR signals at δ −67.68 and −56.65, respectively. A signal at δ −57.67 is assigned to a Si nucleus that is bonded to coordinated oxygen. The ^{29}Si NMR spectra of the complexes **1a**, **1b**, and **2a** often exhibited a minor peak due to contamination with completely condensed cubic silsesquioxanes (*cyclo*-C_5H_9)Si_8O_{12} or (*iso*-C_4H_9)Si_8O_{12} (δ −65.4 for **1a** and **2a**, δ −66.8 for **1b**).[20] The removal of the impurity from **2a** and **2b** is difficult owing to the similar solubility of the complexes and cubic silsesquioxane, and sufficient elemental analyses were not achieved.

Reactions of the silsesquioxanes with *trans*-[PtI(Ph)$(PPh_3)_2$] in the presence of Ag_2O at 55 °C yield a mixture of unexpected Pt−Ag heterobimetallic silsesquioxane complexes, [Pt{$O_{11}Si_7R_7$(OH)($AgPPh_3$)}Ph(PPh_3)] (**3a**: R = *cyclo*-C_5H_9, **3b**: R = *iso*-C_4H_9), and a hydroxo-bridged platinum dimer, *anti*-[{PtPh(PPh_3)}$_2$(μ-OH)$_2$] (**4**), as shown in eq 2. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture displays a 2:1 ratio of **3** to **4**. Complexes **3a** and **3b** were isolated from the reaction mixture in 47% and 39% yields, respectively.



(2)

3a: R = *cyclo*-C_5H_9
3b: R = *iso*-C_4H_9

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The formation of **3a** and **3b** with a chelating silsesquioxane ligand and a PPh_3 ligand rather than a Ag-free platinum complex with monodentate silsesquioxane and two PPh_3 ligands is partly ascribed to the facile dissociation of PPh_3 prior to or during the reaction, while PEt_3 and PMe_2Ph ligands in eq 1 do not undergo dissociation easily.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 3a and 3b

	3a	**3b**
Pt−P2	2.200(3)	2.192(2)
Pt−O1	2.042(8)	2.076(5)
Pt−O2	2.15(1)	2.141(6)
Pt−C1	1.95(2)	2.01(1)
Ag−P1	2.316(3)	2.327(2)
Ag−O1	2.161(8)	2.142(5)
Pt⋯Ag	3.151(2)	3.0875(7)
Ag⋯O5	2.61(1)	2.572(6)
O1⋯O5	3.25(2)	3.167(8)
O2⋯O5	2.53(1)	2.534(8)
P2−Pt−O2	95.5(2)	98.5(2)
P2−Pt−C1	90.1(3)	88.5(2)
O1−Pt−O2	84.4(4)	84.2(2)
O1−Pt−C1	90.0(5)	88.9(2)
P1−Ag−O1	166.0(3)	168.6(2)
Pt−O1−Ag9	7.1(3)	94.1(2)
Pt−O1−Si1	136.6(5)	133.0(3)
Pt−O2−Si2	124.1(5)	126.1(3)
Si4−O5−O1	101.4(4)	105.1(3)
Si4−O5−Ag	101.1(4)	111.4(3)
Si4−O5−O2	122.7(4)	118.9(3)

Figure 1b shows the molecular structure of **3a** determined by X-ray crystallography. The selected bond distances and angles of **3a** and **3b** are summarized in Table 2. A square-planar Pt(II) center is bonded to a phenyl ring, one PPh_3 ligand, and two oxygen atoms of the deprotonated silsesquioxane. A Ag center is bonded to one of the coordinated oxygen atoms and PPh_3 to form a linear coordination (P1−Ag−O1, **3a**: 166.0(3)°, **3b**: 168.6(2)°). The distances between Pt and Ag atoms (**3a**: 3.151(2) Å, **3b**: 3.0875(7) Å) are longer than the sum of the atomic radii of Pt and Ag (2.83 Å) and that of the dative bond between Pt(II) and Ag(I) reported (2.6781(9)−2.8121(9) Å),[21] indicating the absence of a metal−metal bond in **3a** and **3b**. The Ag−P1 bond distances of the complexes (**3a**: 2.316(3) Å, **3b**: 2.327(2) Å) are shorter than those of the linear Ag(I)−PPh_3 complexes [$AgNO_3(PPh_3)$] (2.369 Å)[22] and [AgCl(PPh_3)]$_4$ (2.382 Å).[23] Although the positions of OH hydrogens in **3a** and **3b** are not determined by crystallography, a short contact between O2 and O5 atoms (**3a**: 2.53(1) Å, **3b**: 2.534(8) Å) suggests an O−H⋯O hydrogen bond between the OH group and coordinated oxygen. A short Ag⋯O5 distance (**3a**: 2.61(1) Å, **3b**: 2.572(6) Å) is also observed.[24] The IR spectra of **3a** and **3b** in the solid state show OH peaks as weak, broad absorptions at slightly higher wavenumbers (3450 cm^{-1}) than those of monodentate platinum silsesquioxanes **1a**, **1b**, and **2a** (3300−3200 cm^{-1}). These values are in the range reported by Dijkstra et al. for mono-hydrogen-bonded and poly-hydrogen-bonded silanols, respectively.[25] The ^1H NMR spectrum of **3a** in toluene-d_8 at −50 °C exhibits a signal of an OH group at a low magnetic field (δ 12.82) due to strong O−H⋯O bonding or O−H⋯Ag interaction.

Figure 3 shows the $^{31}P\{^1H\}$ NMR spectrum of **3a**, which displays two signals assigned to the two phosphorus atoms bonded to Pt and to Ag based on the coupling patterns with ^{195}Pt and $^{107+109}Ag$ nuclei. **3a** and **3b** show large $^{31}P-^{195}Pt$ coupling constants (4945 and 4939 Hz). The resonance for the phosphorus atom coordinated to the Ag center of **3a** and **3b** is observed as two doublets because of coupling with two magnetic isotopes ^{107}Ag and ^{109}Ag (**3a**: J_{P107Ag} = 679 Hz, J_{P109Ag} = 784 Hz, **3b**: J_{P107Ag} = 682 Hz, J_{P109Ag} = 787 Hz) at room

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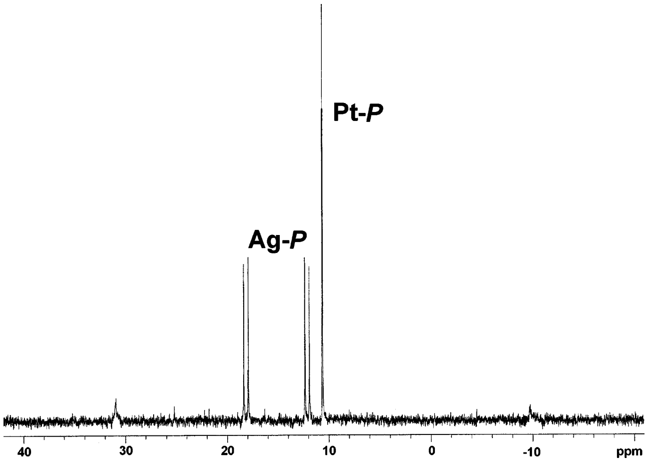

Figure 3. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in C_6D_6 at room temperature.

temperature, although PPh_3 coordinated to Ag(I) often shows a broad peak due to the facile dissociation of the ligand from the labile d^{10} center.[26] Pt−Ag binary complexes with bridging alkynyl ligands $[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PPh_3)](NBu_4)$ (J_{P107Ag} = 570 Hz, J_{P109Ag} = 657 Hz at −60 °C)[27] or a bridging hydrosulfido ligand $[Pt(C_6F_5)_2(PPh_3)\{S(H)Ag(PPh_3)\}]$ (J_{P107Ag} = 570 Hz, J_{P109Ag} = 657 Hz at −50 °C)[28] show smaller coupling constants than **3a** and **3b** with bridging siloxo ligands at low temperatures. A strong coordination of PPh_3 to the Ag(I) center of **3a** and **3b** is evidenced also by short AgP bonds in the crystallographic results.

The $^{29}Si\{^{1}H\}$ NMR spectra of **3a** and **3b** exhibit signals corresponding to seven silicon atoms in their molecules. Four signals at higher magnetic field (δ −65.28, −65.56, −66.73, and −67.20 for **3a**, and −66.86, −66.92, −68.13, and −69.00 for **3b**) are assigned as the internal Si atoms of the silsesquioxane framework, while three signals, at δ −55.84, −56.62, −58.24 (**3a**) and −57.60, −57.95, −59.20 (**3b**), are due to the terminal Si atoms of the silsesquioxane. The signals at −55.84 and −57.95 are split by coupling with a Ag nucleus (4.8 Hz (**3a**) and 2 Hz (**3b**)).[29] In the $^{13}C\{^{1}H\}$ NMR spectra of **3a** and **3b**, the Si−C carbon atoms in the silsesquioxane framework show seven signals in the range δ 23.08−25.60. The IR spectra of **3a** and **3b** show two new bands due to the stretching vibration Si−O of coordinated silanol groups at lower frequencies (695, 745 (**3a**) and 694, 739 cm^{-1} (**3b**)) in comparison with those of free ligands.

A hydroxo-bridged organoplatinum dimer, **4**, obtained from reaction 2 was reported to be synthesized in situ from $[PtPh(PPh_3)(\mu\text{-}Cl)]_2$ and KOH.[30] The NMR spectroscopic data of **4** obtained in reaction 2 are completely consistent with those of the dinuclear platinum complex prepared independently from the thermal reaction of *trans*-$[PtPh(OH)(PPh_3)_2]$.[31] In reaction 2, the addition of an equivalent amount of H_2O leads to a 1:4 ratio of **3a** (or **3b**) to **4**, indicating that the hydrolysis of the Pt complex during reaction 2 produces **4**. A similar reaction of a Pt(II) complex, $[PtBr(PEt_3)_3](BF_4)$, with silanol $(4\text{-}CF_3C_6H_4)SiMe_2OH$ in the presence of Ag_2O also gives a hydroxo-bridged diplatinum complex, $[Pt_2(\mu\text{-}OH)_2(PEt_3)_4](BF_4)_2$, upon the addition of H_2O.[10] The crystal structure of **4**, which is isomorphous to the palladium dimer $[\{PdPh(PPh_3)\}_2(\mu\text{-}OH)_2]$,[32] is determined by X-ray crystallography (Figure 4). The geometry around the Pt center consists of a phenyl, a PPh_3, and two bridging hydroxo groups. The short distance of the Pt−P bond of **4** (2.198(2) Å) is consistent with the large coupling constant between Pt and P atoms (4687 Hz), which is similar to that of the hydroxo-bridged platinum dimer *trans*-$[\{Pt(C_6H_4Me\text{-}4)(PEt_2Ph)\}_2(\mu\text{-}OH)_2]$ (J_{PPt} = 4425 Hz).[33]

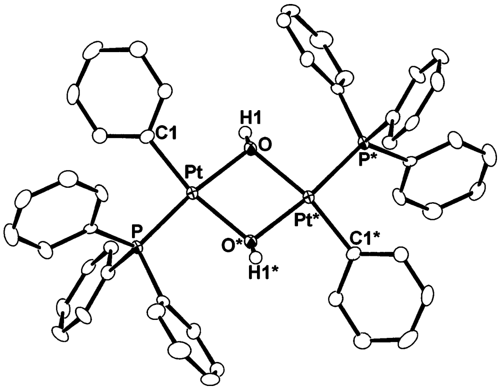

Figure 4. ORTEP drawing of **4** at 50% ellipsoidal level. Hydrogens except for OH hydrogens are omitted for simplicity. The molecule has a C_2 symmetry center at the midpoint of two Pt centers. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. The selected bond distances (Å) and angles (deg) of **4** are as follows: Pt−P 2.198(2), Pt−O 2.069(6), Pt−O* 2.113(6), Pt−C1 2.004(6), P−Pt−O* 96.6(2), P−Pt−C1 95.7(2), O−Pt−O* 76.5(2), O−Pt−C1 91.3(2).

Conclusion

Incompletely condensed silsesquioxane functions as a monodentate ligand of a neutral phenylplatinum complex and as a bidentate ligand of phenylplatinate with one phosphino ligand and $AgPPh_3$ that is bonded to coordinated oxygen depending on the type of phosphine ligand. Two types of platinum complexes with incompletely condensed silsesquioxane were obtained depending on auxiliary phosphine ligands. The silsesquioxane functions as a monodentate ligand of the neutral phenylplatinum complexes *trans*-$[Pt\{O_{10}Si_7R_7(OH)_2\}(Ph)(L)_2]$ with two PEt_3 or $PPhMe_2$ groups in mutually *trans* positions. The phenylplatinate $[Pt\{O_{11}Si_7R_7(OH)(AgPPh_3)\}(Ph)(PPh_3)]$ with a PPh_3 ligand contains the bidentate silsesquioxane ligand in which an oxygen atom is bonded both to the Pt center and to the $AgPPh_3$ fragment. Facile dissociation of PPh_3 from the Pt center induced chelating coordination of the silsesquioxane, to form the platinate with Ag(I).

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. Toluene for reactions was distilled from sodium benzophenone ketyl and stored under nitrogen. The platinum

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complexes *trans*-[PtI(Ph)(PEt_3)$_2$], *trans*-[PtI(Ph)($PPhMe_2$)$_2$], and *trans*-[PtI(Ph)(PPh_3)$_2$] were prepared by replacement of cod (1,5-cyclooctadiene) from [PtI(Ph)(cod)] with corresponding phosphine ligands, as previously reported.[34] The complex [PtI(Ph)(cod)] was synthesized according to the literature method.[35] Silsesquioxanes 1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1(5,11)]heptasiloxane-*endo*-3,7,14-triol ((*cyclo*-C_5H_9)$_7Si_7O_9(OH)_3$) and 1,3,5,7,9,11,14-heptoisobutyltricyclo[7.3.3.1(5,11)]heptasiloxane-*endo*-3,7,14-triol ((*iso*-C_4H_9)$_7Si_7O_9(OH)_3$) are commercial available products of Aldrich Chemical Co. Ag_2O was purchased from Wako Pure Chemical Ind., Ltd. The reagents are used without any purification.

^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian Mercury 300 or JEOL EX-400 spectrometers. Peak positions in the ^{29}Si{^{1}H} and ^{31}P{^{1}H} NMR spectra were referenced to external standard $SiMe_4$ in C_6D_6 and 85% H_3PO_4 in C_6D_6, respectively. To minimize nuclear Overhauser enhancement effects, ^{29}Si NMR spectra were recorded with inverse-gated proton decoupling. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of *trans*-[Pt{$O_{10}Si_7$(*cyclo*-C_5H_9)$_7$(OH)$_2$}(Ph)(PEt_3)$_2$] (1a). To a toluene (10 mL) solution of *trans*-[PtI(Ph)(PEt_3)$_2$] (95 mg, 0.15 mmol) were added (*cyclo*-C_5H_9)$_7Si_7O_9(OH)_3$ (131 mg, 0.15 mmol) and Ag_2O (46 mg, 0.20 mmol). The mixture was stirred for 3 days at room temperature. After completion of the reaction, monitored with ^{31}P{^{1}H} NMR spectroscopy, a gray solid was removed by filtration through Celite. Complete evaporation of the solvent from the filtrate gave **1a** as a white solid (204 mg, 98%). Slow diffusion of acetone in toluene solution of **1a** affords colorless crystals appropriate for X-ray analysis. When the reaction was performed at 55 °C, complex **1a** was obtained as a major product, accompanied by uncharacterized side compounds. No signal for heterobimetallic Pt−Ag complex analogous to **3a** was observed. Anal. Calcd for $C_{53}H_{100}O_{12}P_2Si_7Pt$: C, 46.03; H, 7.29. Found: C, 45.89; H, 6.79. Mp: 164 °C. ^{1}H NMR (300 MHz, benzene-d_6, room temperature): δ 1.07 (m, 18H, PCH_2CH_3), 1.22 (br m, 7H, C*H*-pentyl), 1.5−2.4 (br m, 68H, C*H*$_2$-pentyl and PC*H*$_2$-CH_3), 6.94 (m, 3H, C_6H_5 *meta* and *para*), 7.41 (s, 2H, C_6H_5 *ortho*, J_{HPt} was not observed clearly), 8.53 (s, 2H, O*H*). ^{1}H NMR (400 MHz, toluene-d_8, −80 °C): δ 1.10 (br m, 18H, PCH_2CH_3), 1.2−2.0 (br m, 75H, C*H*$_2$-pentyl; C*H*-pentyl, and PC*H*$_2$CH$_3$), 7.37 (s, 1H, C_6H_5 *ortho*), 7.57 (s, 1H, C_6H_5 *ortho*), 9.15 (s, 2H, O*H*). The C_6H_5 *meta* and *para* signals are overlapped with solvent. ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, room temperature): δ 7.64 (s, PCH_2CH_3), 12.98 (vt, PCH_2CH_3, $^{V}J_{CP}$ = 16.4 Hz,), 23.00, 23.08, 23.85, 23.91, 26.74 (1:1:2:2:1, 7C, *C*H-pentyl), 27.55, 27.58, 27.62, 27.95, 28.26, 28.30, 28.32, 28.34, 29.84 (28C, *C*H$_2$-pentyl), 122.38 (C_6H_5 *meta*), 130.95 (t, $^2J_{CP}$ = 10.2 Hz, C_6H_5 *ipso*), 137.61 (C_6H_5 *ortho*). The C_6H_5 *para* carbon was not observed due to overlap with solvent. ^{29}Si{^{1}H} NMR (79 MHz, benzene-d_6, 0.02 M Cr(acac)$_3$, room temperature): δ −56.65, −57.67, −64.35, −64.69, −67.68 (2:1:1:1:2). ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, room temperature): δ 16.5 (J_{PPt} = 2862 Hz). IR (KBr): 3200 (vw), 2949 (s), 2867 (s), 1508 (w), 1246 (w), 1150 (vs), 922 (m), 878 (m), 763 (w), 739 (w), 708 (w), 505 (m) cm^{-1}.

Preparation of *trans*-[Pt{$O_{10}Si_7$(*iso*-Bu)$_7$(OH)$_2$}(Ph)(PEt_3)$_2$] (1b). Complex **1b** was synthesized from the reaction of (*iso*-Bu)$_7Si_7O_9(OH)_3$ (119 mg, 0.15 mmol) with *trans*-[PtI(Ph)(PEt_3)$_2$] (95 mg, 0.15 mmol) in the presence of Ag_2O (46 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After filtration through Celite, washing with toluene, and removing of the solvent, the crude product was dissolved in 1 mL of acetone and kept at −20 °C for 2 days. Recrystallization from an acetone solution gave **1b** as colorless crystals in 76% yield (148 mg). Anal. Calcd for $C_{46}H_{100}O_{12}P_2Si_7Pt$: C, 42.54; H, 7.76. Found: C, 42.31; H, 7.62. Mp: 86 °C. ^{1}H NMR (300 MHz, benzene-d_6, room temperature): δ 0.89 (d, 14H, C*H*$_2$-^{i}Bu, J_{HH} = 7.2 Hz), 1.03 (vt, 18H, PCH_2CH_3, $^{V}J_{CP}$ = 8.0 Hz), 1.14 (d, 6H, C*H*$_3$-^{i}Bu, J_{HH} = 6.6 Hz), 1.15 (d, 6H, C*H*$_3$-^{i}Bu, J_{HH} = 6.6 Hz), 1.19 (d, 24H, C*H*$_3$-^{i}Bu, J_{HH} = 6.6 Hz), 1.26 (d, 6H, C*H*$_3$-^{i}Bu, J_{HH} = 6.6 Hz), 1.49 (br, 12 H, PC*H*$_2$CH$_3$), 2.21 (m, 7H, C*H*-^{i}Bu, J_{HH} = 6.6 Hz), 6.94 (m, 3H, C_6H_5 *meta* and *para*), 7.41 (s, 2H, C_6H_5-*o*, J_{HPt} was not observed clearly), 8.84 (s, 2H, O*H*). ^{1}H NMR (400 MHz, toluene-d_8, −80 °C): δ 0.97 (br, 14H, C*H*$_2$-^{i}Bu), 1.08 (br, 18H, PCH_2CH_3), 1.2−1.5 (m, 54H, C*H*$_3$-^{i}Bu and PC*H*$_2$CH$_3$), 2.31 (m, 7H, C*H*-^{i}Bu), 7.38 (s, 1H, C_6H_5 *ortho*), 7.54 (s, 1H, C_6H_5 *ortho*), 9.48 (s, 2H, O*H*). Signals for C_6H_5 *meta* and *para* are overlapped with solvent. ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, room temperature): δ 7.58 (s, PCH_2CH_3), 12.73 (vt, PCH_2CH_3, $^{V}J_{PC}$ = 16.1 Hz,), 23.24, 23.37, 23.98, 24.19, 27.37 (1:1:2:2:1, 7C, *C*H$_2$)*, 24.55, 24.60, 24.63, 25.52 (7C, *C*H)*, 25.91, 25.97, 26.03, 26.23, 26.32, 26.52 (14C, *C*H$_3$)*, 122.36 (C_6H_5 meta), 127.85 (C_6H_5 *para*), 131.21 (t, C_6H_5 *ipso*, $^2J_{CP}$ = 9.8 Hz,), 137.63 (C_6H_5 *ortho*). *Chemical shifts for CH, CH$_2$, CH$_3$ carbon atoms originated from *iso*-butyl groups were determined by the DEPT method. ^{29}Si{^{1}H} NMR (79 MHz, benzene-d_6, 0.02 M Cr(acac)$_3$, room temperature): δ −57.42, −57.97, −65.80, −66.11, −68.80 (2:1:1:1:2). ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, room temperature): δ 17.3 (J_{PtP} = 2860 Hz). IR (KBr): 3300 (vw), 2953 (s), 2907 (s), 2874 (s), 1464 (w), 1229 (m), 1100 (s), 908 (w), 835 (w), 768 (w), 739 (m), 710 (w), 486 (m) cm^{-1}.

Preparation of *trans*-[Pt{$O_{10}Si_7$(*cyclo*-C_5H_9)$_7$(OH)$_2$}(Ph)($PPhMe_2$)$_2$] (2a). Preparation of **2a** was carried out similarly from *trans*-[PtI(Ph)(PMe_2Ph)$_2$] (101 mg, 0.15 mmol), (*cyclo*-C_5H_9)$_7Si_7O_9$-(OH)$_3$ (131 mg, 0.15 mmol), and Ag_2O (46 mg, 0.20 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 5 days. The product **2a** was obtained by recrystallization from ether/ethanol solution at −20 °C in 74% yield (158 mg). Mp: 132 °C. ^{1}H NMR (300 MHz, benzene-d_6, room temperature): δ 1.20 (m, 7H, C*H*-pentyl), 1.4−2.3 (br m, 68H, C*H*$_2$-pentyl and PC*H*$_3$), 6.6 (br, 2H, PtC$_6$*H*$_5$ *ortho*), 6.72 (m, 2H, PtC$_6$*H*$_5$ meta), 6.99 (m, 2H, PC$_6$*H*$_5$ *para*, J_{HH} = 7.5 Hz), 7.06 (m, 4H, PC$_6$*H*$_5$ *meta*, J_{HH} = 7.5 Hz), 7.42 (m, 4H, PC$_6$*H*$_5$ *ortho*, J_{HH} = 7.5 Hz), 9.1 (br, 2H, O*H*). PtC$_6$*H*$_5$ *para* signal was not found. ^{1}H NMR (400 MHz, toluene-d_8, −80 °C): 1.2−2.3 (m, 75H, C*H*$_2$-pentyl; C*H*-pentyl; PC*H*$_3$), 6.50 (s, 1H, PtC$_6$*H*$_5$ meta), 6.62 (s, 1H, PtC$_6$*H*$_5$ *ortho*), 6.83 (d, 2H, PtC$_6$*H*$_5$ *meta*), 7.35 (s, 1H, PtC$_6$*H*$_5$ *para*), 7.42 (s, 4H, PC$_6$*H*$_5$ *ortho*), 9.84 (s, 2H, O*H*). ^{13}C{^{1}H} NMR (75 MHz, benzene-d_6, room temperature): δ 11.8 (br, P*C*H$_3$), 23.00, 23.14, 23.79, 23.94, 26.60 (1:1:2:2:1, 7C, *C*H-pentyl), 27.44, 27.55, 27.64, 27.84, 27.97, 28.00, 28.22, 28.26, 28.30, 28.42, 29.64 (28C, *C*H$_2$-pentyl), 122.09 (Pt*C*$_6$H$_5$ *meta*), 127.30 (Pt*C*$_6$H$_5$ *para*), 128.21 (vt, P*C*$_6$H$_5$ *meta*, $^{V}J_{CP}$ = 5.2 Hz), 129.06 (t, Pt*C*$_6$H$_5$ ipso, $^2J_{CP}$ = 10.2 Hz), 129.75 (P*C*$_6$H$_5$ *para*), 131.37 (vt, P*C*$_6$H$_5$ *ortho*, $^{V}J_{CP}$ =5.7 Hz), 134.26 (vt, P*C*$_6$H$_5$ ipso, $^{V}J_{CP}$ = 27.3 Hz), 138.37 (Pt*C*$_6$H$_5$ *ortho*). ^{13}C{^{1}H} NMR (100.4 MHz, toluene-d_8, −70 °C): 9.70 (vt, P*C*H$_3$, $^{V}J_{CP}$ = 18.6 Hz), 12.19 (vt, P*C*H$_3$, $^{V}J_{PC}$ = 18.6 Hz), 22.55, 22.69, 23.51, 23.58, 25.95 (1:1:2:2:1, 7C, *C*H-pentyl), 27.25, 27.33, 27.39, 27.43, 27.66, 27.82, 28.04, 28.09, 28.33, 29.33, 29.90 (28C, *C*H$_2$-pentyl), 121.93 (Pt*C*$_6$H$_5$ *meta*), 129.75 (P*C*$_6$H$_5$ *para*), 131.08 (P*C*$_6$H$_5$ *ortho*), 133.64 (vt, P*C*$_6$H$_5$ ipso, $^{V}J_{CP}$ = 27 Hz), 137.78 (Pt-*C*$_6$H$_5$-*o*). ^{29}Si{^{1}H} NMR (79.3 MHz, benzene-d_6, 0.02 M Cr(acac)$_3$, room temperature): δ −56.75, −57.30, −64.59, −64.87, −67.60 (2:1:1:1:2). ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, room temperature): δ −1.3 (J_{PtP} = 2956 Hz). IR (KBr): 3250 (vw), 2950 (s), 2865 (s), 1450 (w), 1246 (w), 1120 (vs), 945 (w), 907 (m), 741 (w), 503 (m) cm^{-1}.

Preparation of *trans*-[Pt{$O_{10}Si_7$(*iso*-Bu)$_7$(OH)$_2$}(Ph)($PPhMe_2$)$_2$] (2b). Complex **2b** was synthesized analogously by using (*iso*-Bu)$_7Si_7O_9(OH)_3$ (119 mg, 0.15 mmol) and *trans*-[PtI(Ph)($PPhMe_2$)$_2$]

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Table 3. Crystallographic Data and Details of Refinement of 1a, 1b, 3a, 3b, and 4

	1a	**1b**	**3a**	**3b**	**4**
formula	$C_{53}H_{100}O_{12}P_2Si_7Pt$	$C_{46}H_{100}O_{12}P_2Si_7Pt$	$C_{77}H_{99}O_{12}P_2Si_7Pt$	Ag $C_{70}H_{99}O_{12}P_2Si_7Pt\cdot 1/2C_6H_{14}$	$AgC_{48}H_{42}O_2P_2Pt_2$
fw	1383.00	1298.92	1778.13	1737.11	1102.98
color	colorless	colorless	colorless	colorless	colorless
cryst size/mm	0.06 × 0.10 × 0.28	0.22 × 026 × 0.58	0.24 × 0.40 × 0.48	0.15 × 0.17 × 0.23	0.05 × 0.05 × 0.15
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	C_c (No. 9)	$P2_1/n$ (No.14)	$P2_1/n$ (No.14)
a/Å	11.3362(17)	13.580(2)	25.810(6)	12.784(2)	8.792(3)
b/Å	26.444(4)	13.659(2)	13.462(3)	27.027(4)	14.694(4)
c/Å	21.509(3)	19.933(3)	24.976(6)	23.001(4)	15.298(4)
α/deg		71.799(6)			
β/deg	91.964(2)	73.423(6)	114.184(3)	90.520(3)	100.397(3)
γ/deg		68.216(6)			
V/Å^3	6444(2)	3200.8(9)	7916(3)	7947(2)	1944(1)
Z	4	2	4	4	2
D_{calcd}/g cm^{-3}	1.425	1.348	1.492	1.453	1.884
F(000)	2880	1356	3640	3576	1064
μ/mm^{-1}	2.4027	2.4136	2.2096	2.1991	7.2828
no. of reflns measd	47 857	19 756	29 022	55 875	14 334
no. of unique reflns	14 542	12 436	8926	17 542	4416
R_{int}	0.062	0.017	0.070	0.084	0.059
no. of variables	782	719	1035	1016	268
R_1 ($I > 2.00\sigma(I)$)	0.0368	0.0385	0.0478	0.0732	0.0346
wR_2 (all data)	0.1017	0.1093	0.1375	0.2217	0.0864
GOF	0.939	1.063	1.044	1.029	0.943

(101 mg, 0.15 mmol) in the presence of Ag_2O (46 mg, 0.2 mmol). Although the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture displays complete conversion of the starting material after 4 days, the isolated yield of **2b** as a sticky crude product is low (5%) due to its high solubility in common organic solvents. ^1H NMR (300 MHz, benzene-d_6, room temperature): δ 0.84 (m, 14H, CH_2-^{i}Bu), 1.0−1.2 (m, 54H, CH_3-^{i}Bu and PCH_3), 2.1 (m, 7H, CH-^{i}Bu), 6.78 (m, 3H, C_6H_5 *meta* and *para*), 7.02 (m, 6H, PC_6H_5 *meta* and *para*), 7.40 (m, 4H, PC_6H_5 *ortho*), 9.2 (br, 2H, O*H*). $^{31}P\{^1H\}$ NMR (122 MHz, benzene-d_6, room temperature): δ −1.97 (s, J_{PPt} = 2932 Hz).

Preparation of [Pt{$O_{10}Si_7$(*cyclo*-C_5H_9)$_7$(OH)(OAgPPh$_3$)}(Ph)(PPh$_3$)] (3a). To a 10 mL toluene suspension of *trans*-[PtI(Ph)(PPh$_3$)$_2$] (138 mg, 0.15 mmol) were added Ag_2O (46 mg, 0.20 mmol) and (*cyclo*-C_5H_9)$_7Si_7O_9$(OH)$_3$ (131 mg, 0.15 mmol). This mixture was then heated for 12 h at 55 °C and gave a mixture of **3a**, **4**, and Ph_3PO. The same products were obtained when the reaction was carried out for 6 days at room temperature. The reaction mixture was filtered through Celite to remove the gray residue. The filtrate was evaporated to afford an oily material. Complex **3a** was separated from **4**, Ph_3PO, and unreacted silsesquioxane by addition of ethyl acetate, which caused precipitation of a white solid. It was filtrated, washed two times with a 1 mL portion of ethyl acetate, and dried in vacuo to afford complex **3a** (126 mg, 47%). The purification of **4** from the ethyl acetate filtrate failed. To characterize complex **4**, it was prepared by an independent method, as described below. The single crystals of **3a** were prepared by slow evaporation of a THF/hexane solution at room temperature. Anal. Calcd for $C_{77}H_{99}O_{12}P_2Si_7PtAg$: C, 52.01; H, 5.61. Found: C, 51.77; H, 5.36. Decomp > 175 °C. ^1H NMR (300 MHz, benzene-d_6, room temperature): δ 1.2 (m, 7H, C*H*-pentyl), 1.5−2.4 (m, 56H, CH_2-pentyl), 6.40 (t, 2H, PtC_6H_5 *meta*, J_{HH} = 7.2 Hz), 6.63 (t, 1H, PtC_6H_5 *para*, J_{HH} = 7.2 Hz), 7.01 (m, 9H, PC_6H_5 *meta* and *para*), 7.10 (m, 11H, PC_6H_5 *meta* and *para*, and PtC_6H_5 *ortho*)*, 7.65 (m, 6H, PC_6H_5 *ortho*), 7.75 (m, 6H, PC_6H_5 *ortho*). *Peak position of PtC_6H_5 *ortho* protons was determined by H−H COSY. $^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, room temperature): δ 23.08, 23.20, 23.39, 23.88, 24.04, 25.39, 25.60 (1:1:1:1:1:1:1, 7C, *C*H-pentyl), 27.13, 27.58, 27.78. 27.94, 28.12, 28.23, 28.50, 28.80, 29.64, 27.46, 27.62, 27.84, 28.06, 28.18, 28.39, 28.65, 29.29 (28C, *C*H_2-pentyl), 121.80 (PtC_6H_5 *meta*), 127.27 (PtC_6H_5 *para*), 127.74 (PtPC_6H_5 *meta*), 129.29 (d, AgPC_6H_5 *meta*, $^3J_{CP}$ = 11 Hz), 130.13 (d, AgPC_6H_5 *para*, $^4J_{CP}$ = 2.3 Hz), 130.35 (PtC_6H_5 *ipso*), 131.03 (PtPC_6H_5 *para*), 131.17 (d, PtPC_6H_5 *ipso*, J_{CP} = 63 Hz), 131.48 (dd, AgPC_6H_5 *ipso*, J_{CP} = 37 Hz, $^2J_{CAg}$ = 4.6 Hz), 134.46 (dd, AgPC_6H_5 *ortho*, $^2J_{CP}$ =16 Hz, $^3J_{CAg}$ = 2.9 Hz), 135.34 (d, PtPC_6H_5 *ortho*, $^2J_{CP}$ = 11 Hz), 138.73 (PtPC_6H_5 *ortho*). $^{29}Si\{^1H\}$ NMR (79.3 MHz, benzene-d_6, 0.02 M Cr(acac)$_3$, room temperature): δ −55.84 (d, J_{SiAg} = 4.8 Hz), −56.62, −58.24, −65.28, −65.56, −66.73, −67.20. $^{31}P\{^1H\}$ NMR (121 MHz, benzene-d_6, room temperature): δ 10.6 (s, J_{PPt} = 4945 Hz), 15.1 (d, J_{P107Ag} = 679 Hz, J_{P109Ag} = 784 Hz). IR (KBr): 3450 (vw), 3052 (w), 2948 (s), 2865 (s), 1437 (s), 1244 (m), 1100 (vs), 970 (m), 912 (m), 745 (m), 695 (s), 524 (s) cm^{-1}.

Preparation of [Pt{$O_{10}Si_7$(*iso*-Bu)$_7$(OH)(OAgPPh$_3$)}(Ph)(PPh$_3$)] (3b). Complex **3b** was prepared similarly to **3a** using (*iso*-Bu)$_7Si_7O_9$(OH)$_3$ (119 mg, 0.15 mmol). The desired complex was obtained by recrystallization from acetone solution (1 mL) at −20 °C to yield complex **3b** (191 mg, 39%). The reaction of *trans*-[PtI(Ph)(PPh$_3$)$_2$] (20 mg, 0.022 mmol) with (*iso*-C_4H_9)$_7Si_7O_9$(OH)$_3$ (17 mg, 0.022 mmol) in the presence of Ag_2O (6 mg, 0.029 mmol) and a stoichiometric amount of H_2O (0.4 μL, 0.022 mmol) was carried out in degassed C_6D_6 for 12 h at 55 °C. The ratio of the products was estimated by ^{31}P NMR data. Anal. Calcd for $C_{70}H_{99}O_{12}P_2Si_7PtAg$: C, 49.63; H, 5.89. Found: C, 49.29; H, 6.22. Mp: 171 °C (dec). ^1H NMR (300 MHz, benzene-d_6, room temperature): δ 0.88 (m, 14H, CH_2-^{i}Bu), 0.98 (d, 6H, CH_3-^{i}Bu, J_{HH} = 6.6 Hz), 1.06 (d, 3H, CH_3-^{i}Bu, J_{HH} = 6.6 Hz), 1.14 (m, 24H, CH_3-^{i}Bu), 1.22 (m, 3H, CH_3-^{i}Bu), 1.45 (t, 6H, CH_3-^{i}Bu, J_{HH} = 6.3 Hz), 1.86 (m, 1H, C*H*-^{i}Bu), 2.03 (m, 1H, C*H*-^{i}Bu), 2.19 (m, 4H, C*H*-^{i}Bu), 2.53 (m, 1H, C*H*-^{i}Bu), 6.45 (t, 2H, PtC_6H_5 *meta*, J_{HH} = 7.5 Hz), 6.67 (t, 1H, PtC_6H_5 *para*, J_{HH} =7.5 Hz), 7.02 (m, 9H, PC_6H_5 *meta* and *para*), 7.11 (m, 11H, PC_6H_5 *meta* and *para*, and PtC_6H_5 *ortho*)*, 7.62 (m, 6H, PC_6H_5 *ortho*), 7.74 (m, 6H, PC_6H_5 *ortho*). *The signal for PtC_6H_5 *ortho* protons was assigned by the H−H COSY method. $^{13}C\{^1H\}$ NMR (75.3 MHz, benzene-d_6, room temperature): δ 23.22, 23.46, 23.57, 24.30, 24.42, 24.50, 25.36 (1:1:1:1:1:1:1, 7C, *C*H_2-^{i}Bu)*, 24.58, 24.61, 24.66, 24.88, 25.07 (7C, *C*H-^{i}Bu)*, 25.71, 25.90, 25.97, 26.04, 26.07, 26.16, 26.31, 26.36, 26.43, 26.56, 26.71, 27.19 (14C, *C*H_3-^{i}Bu)*, 121.95 (PtC_6H_5 *meta*), 127.28 (PtC_6H_5 *para*), 127.78 (PtPC_6H_5 *meta*), 129.33 (d, AgPC_6H_5 *meta*, $^3J_{CP}$ = 10.4 Hz), 130.17 (AgPC_6H_5 *para*), 130.75 (d, PtPC_6H_5 ipso, J_{CP} = 63 Hz), 131.08 (PtPC_6H_5 *para*), 131.50 (dd, AgPC_6H_5 ipso, J_{CP} = 32 Hz, $^2J_{CAg}$ = 4.6 Hz), 134.43 (dd, AgPC_6H_5 *ortho*, $^2J_{CP}$ = 16 Hz, $^3J_{CAg}$ = 2.9 Hz), 135.40 (d, PtPC_6H_5 *ortho*, $^2J_{CP}$ = 10.3 Hz), 138.73 (PtC_6H_5 *ortho*). *Chemical shifts for the ^{i}Bu group were determined by the DEPT method. ^{29}Si{^{1}H} NMR (79.3 MHz, benzene-d_6, 0.02 M Cr(acac)$_3$, room temperature): δ −57.60, −58.95 (d, J_{SiAg} = 2 Hz), −59.20, −66.86, −68.92, −68.13, −69.00. ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, room temperature): δ 11.0 (J_{PPt} = 4939 Hz), 14.7 (dd, J_{P107Ag} = 682 Hz, J_{P109Ag} = 787 Hz). IR (KBr): 3450 (vw), 3053 (w), 2951 (s), 2866 (m), 1437 (m), 1226 (m), 1098 (vs), 981 (m), 916 (w), 833 (w), 739 (m), 694 (m), 501 (m) cm^{-1}.

Preparation of *anti*-[{PtPh(PPh$_3$)}$_2$(μ-OH)$_2$] (4). A C_6D_6 solution (1 mL) of *trans*-[Pt(Ph)(OH)(PPh$_3$)$_2$][27] (32 mg, 39 mmol) was heated for 14 h at 60 °C. The solvent was removed under reduced pressure. The resulting material was washed twice with a 1 mL portion of acetone to remove Ph$_3$PO and dried in vacuo to yield a mixture of *anti*- and *syn*-platinum dimers **4** in 3:1 ratio (64%). Recrystallization from a CH_2Cl_2/pentane solution afforded colorless crystals appropriate for X-ray analysis. Anal. Calcd for $C_{48}H_{42}O_2P_2Pt_2$: C, 52.27; H, 3.84. Found: C, 52.07; H, 3.86. Decomp > 175 °C. ^{1}H NMR (300 MHz, CDCl$_3$, room temperature): δ −0.46 (d, 2H, O*H*, J_{HP} = 3 Hz), 6.56 (t, 4H, PtC$_6$*H*$_5$ *meta*, J_{HH} = 7 Hz), 6.64 (d, 2H, PtC$_6$*H*$_5$ *para*, J_{HH} = 7.2 Hz), 6.98 (d, 4H, PtC$_6$*H*$_5$ *ortho*, J_{HH} = 8.1 Hz), 7.27 (m, 18H, PC$_6$*H*$_5$ *meta and para*), 7.90 (m, 12H, PC$_6$*H*$_5$ *ortho*). ^{31}P{^{1}H} NMR (122 MHz, CDCl$_3$, room temperature): δ 11.35 (J_{PtP} = 4687 Hz). IR (KBr): ν_{OH} 3630 (vw) cm^{-1}.

X-ray Crystallography. Crystals of **1a**, **1b**, **3a**, **3b**, and **4** suitable for X-ray diffraction study were mounted on a glass capillary tube. The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo Kα radiation (λ = 0.71073 Å) at −160 °C. A sweep of data was done using ω-scans from −110.0° to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 0.0°. The detector swing angle was −20.42°. A second sweep was performed using ω-scans from −110.0° to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 90.0°. The crystal-to-detector distance was 44.84 mm. Readout was performed in the 0.070 mm pixel mode. Calculations were carried out by using the program package Crystal Structure ver. 3.7 for Windows. A full-matrix least-squares refinement was used for the nonhydrogen atoms with anisotropic thermal parameters. One cyclopentyl group bound to Si3 of **3a** is disordered. Two isobutyl groups bound to Si2 and Si6 of **3b** were refined with isotropic thermal parameters. Hydrogen atoms except for the OH hydrogens of **1a**, **1b**, and **4** were located by assuming the ideal geometry and were included in the structure calculation without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 3.

Acknowledgment. N.M. thanks the Japanese Society for Promotion of Science for a postdoctoral fellowship for foreign researchers (2004−2006). This work was financially supported by a Grant-in-Aid for Scientific Research for Young Chemists No. 17750049 and for Scientific Research on Priority Areas, from the Ministry of Education, Culture, Sport, Science, and Technology Japan, and by The 21st Century COE Program “Creation of Molecular Diversity and Development of Functionalities”.

Supporting Information Available: Crystallographic data for **1a**, **1b**, **3a**, **3b**, and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060192S