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Preparation and NMR Studies of Palladium Complexes with a Silsesquioxanate Ligand

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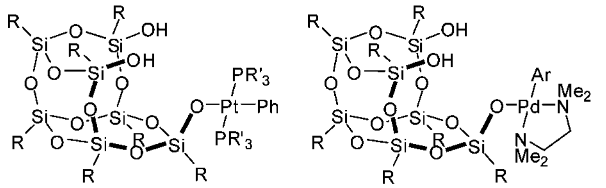
Reaction of an incompletely condensed silsesquioxane trisilanol, (c-$C_5H_9)_7Si_7O_9(OH)_3$, with *trans*-[Pd(I)(Ar)($PMe_3)_2$] in the presence of Ag_2O yielded arylpalladium complexes with a monodentate *O*-coordinated silsesquioxanate ligand, *trans*-[Pd{$O_{10}Si_7$(c-$C_5H_9)_7(OH)_2$}(Ar)($PMe_3)_2$] (**4a**: Ar = Ph, **4b**: Ar = C_6F_5). X-ray crystallographic results of **4b** showed *trans* coordination of the pentafluorophenyl ligand and the *O*-coordinated silsesquioxanate ligand to the square-planar Pd(II) center. Variable-temperature ^1H, $^{19}F\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra of **4a** and **4b** revealed dynamic behavior of the molecules in solution.

Introduction

The metal complexes with silsesquioxane-containing ligands were studied as molecular model compounds of silica-supported transition-metal catalysts or precursors of metal-based heterogeneous catalysts.[1] Incompletely condensed silsesquioxanes that are functionalized with amino and phosphido groups are employed as the ligands of transition-metal complexes.[2,3] Polyhedral oligomeric silsesquioxanes with incompletely condensed structures are coordinated to transition metals as the bulky *O*-ligands.[4] Although the metallasilsesquioxanes of early transition metals are stabilized by the M−O bond of the inherently oxophilic metals, the late transition metal complexes with directly *O*-bonded silsesquioxanate ligands are less common, possibly due to mismatching of the coordinating siloxo groups and electron-rich metals.[5] Abbenhuis[6] and Johnson[7] prepared platinum complexes containing incompletely condensed silsesquioxanates as *O*,*O*-chelating bidentate ligands.



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$PR'_3 = PEt_3, PMe_2Ph$
$R = c\text{-}C_5H_9$

2a: Ar = C_6H_5, R = c-C_5H_9
2b: Ar = C_6F_5, R = c-C_5H_9

Figure 1.

Recently, we reported platinum and palladium complexes with a monodentate silsesquioxanate ligand, *trans*-[Pt{$O_{10}Si_7$(c-$C_5H_9)_7(OH)_2$}(Ph)($PR_3)_2$] (**1**) (PR'_3 = PEt_3, PMe_2Ph)[8] and [Pd{$O_{10}Si_7$(c-$C_5H_9)_7(OH)_2$}(Ar)(tmeda)] (**2a**: Ar = Ph, **2b**: Ar = C_6F_5, tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) (Figure 1).[9] Two OH groups and the coordinated oxygen atom formed two intramolecular O−H···O hydrogen bonds, which were revealed by X-ray crystallography and ^1H NMR spectroscopy. In this paper, we report the preparation and dynamic behavior of the palladium complexes having two PMe_3 ligands and a silsesquioxanate as the *O*-coordinated ligand.

Results and Discussion

The reaction of an incompletely condensed silsesquioxane, (c-$C_5H_9)_7Si_7O_9(OH)_3$, with *trans*-[Pd(I)(Ar)($PMe_3)_2$] (**3a**: Ar = Ph, **3b**: Ar = C_6F_5) in the presence of Ag_2O at room temperature produced the palladium complexes with silsesquioxanate and two *trans* PMe_3 ligands, *trans*-[Pd{$O_{10}Si_7$(c-$C_5H_9)_7(OH)_2$}(Ar)($PMe_3)_2$] (**4a**: Ar = Ph, **4b**: Ar = C_6F_5), in 85% and 78% yields (eq 1). The obtained complexes are stable under air in the solid state but are decomposed slowly in $CHCl_3$.

Complex **4a** was obtained also by exchange of the auxiliary ligand of [Pd{$O_{10}Si_7$(c-$C_5H_9)_7(OH)_2$}(Ph)(tmeda)] (**2a**); treatment of **2a** with excess PMe_3 yielded **4a** at room temperature in 85% yield, accompanied by *cis–trans* isomerization (eq 2).

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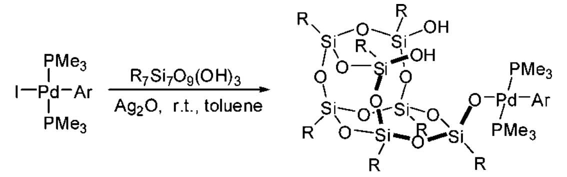
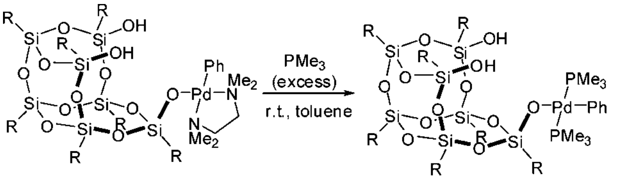


3a: Ar = C_6H_5
3b: Ar = C_6F_5

4a: Ar = C_6H_5, R = c-C_5H_9
4b: Ar = C_6F_5, R = c-C_5H_9

(1)



2a **4a**

(2)

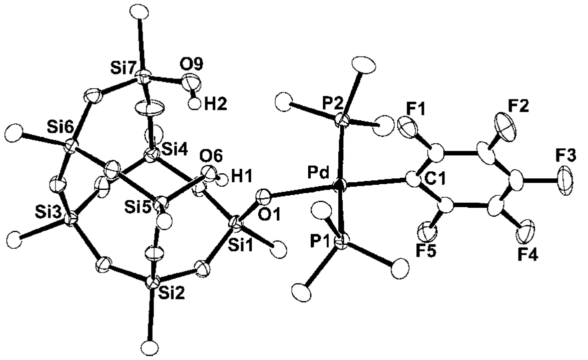


Figure 2. ORTEP drawing of **4b** at the 50% ellipsoidal level. Hydrogen atoms, except for two OH hydrogens, and CH_2 carbons of the cyclopentyl groups are omitted for simplicity.

Table 1. Selected Bond Distances and Angles for 4b

bond distances (Å)		bond angles (deg)	
Pd−O1	2.098(3)	P1−Pd−O1	88.68(8)
Pd−P1	2.322(1)	P1−Pd−C1	87.9(1)
Pd−P2	2.330(1)	P2−Pd−O1	95.69(8)
Pd−C1	2.014(4)	P2−Pd−C1	88.0 (1)
Si1−O1	1.609(3)	Pd−O1−Si1	125.6(2)
O1···O6	2.588(4)	O1···H1−O6	172.0(4)
O6···O9	2.771(5)	O6···H2−O9	170.0(8)
O1···O9	3.826(5)		
O1···H1	1.86(6)		
O6···H2	2.11(6)		

Figure 2 shows the molecular structure of **4b** determined by X-ray crystallography. Selected bond distances and angles are summarized in Table 1. **4b** has a square-planar coordination around the Pd center, having the C_6F_5 group and the *O*-coordinated silsesquioxanate ligand at *trans* positions. The C_6F_5 plane is situated perpendicularly to the coordination plane around the Pd center. The Pd−O1 bond distance of **4b** (2.098(3) Å) is similar to the reported alkoxo-palladium complexes (1.979–2.129 Å),[10] aryloxo-palladium complexes (2.020–2.134 Å),[11] and the palladium silsesquioxanate with tmeda ligand **2b** (2.000(2) Å).[9] The plane formed by Pd, O1, and Si1 atoms is also perpendicular to the coordination plane. The Pd−O1−Si1 bond angle (125.6(2)°) is smaller than those of **2b** (133.0(1)°),[9] [Pd(C_6F_5)(OSiPh$_3$)(tmeda)] (136.9(2)°, 137.9(2)°),[12] and silsesquioxanate platinum complexes **1** (130.2(2)°, 134.6(2)°).[8] The O1···O6 and O6···O9 distances of **4b** (2.588(4) and 2.771(5) Å) indicate the presence of two intramolecular O···H−O hydrogen bonds, and the O6−H1 and O9−H2 bonds are oriented toward O1 and O6, respectively. The shorter distance between the coordinated oxygen O1 and O6 atoms than that between O6 and O9 suggests a stronger hydrogen bond of the former, which is ascribed to the high electron density of the O1 atom coordinated by the Pd center. The complexes of platinum,[8] palladium,[9] and iron[13] with *O*-coordinated silsesquioxanate ligands were reported to form similar hydrogen bonds among OH groups and the coordinated oxygen atoms. IR spectra of **4a** and **4b** show broad ν(OH) peaks at 3200 and 3300 cm^{-1}, respectively, in the solid state. Incompletely condensed silsesquioxanes, having a vicinal trisilanol structure, (*c*-C_5H_9)$_7$Si$_7$O$_9$(OH)$_3$, exhibit a peak at a similar position (3200 cm^{-1}), but the silsesquioxane disilanols formed by its methylation, (*c*-C_5H_9)$_7$Si$_7$O$_9$(OSiMe$_3$)(OH)$_2$, give rise to the ν(OH) peaks at a higher wavenumber (3471 cm^{-1}).[1e] Thus, two OH groups of **4a** form strong hydrogen bonds similarly to (*c*-C_5H_9)$_7$Si$_7$O$_9$(OH)$_3$, while **4b** contains weaker O−H···O hydrogen bonds due to the less electron-donating C_6F_5 ligand of **4b** than the C_6H_5 ligand of **4a**.

^{1}H NMR spectra of **4a** and **4b** at room temperature contain broadened peaks of the OH hydrogens of the silsesquioxanate ligand at δ 9.20 (**4a**) and 8.34 (**4b**). Figure 3 shows variable-temperature ^{1}H NMR spectra of **4a** at −80 to 50 °C. As the temperature of the solution is lowered, the OH signal of **4a** is shifted to a lower magnetic field (δ 9.57 at −50 °C) and is sharpened at −80 °C. Although the crystal structure of **4b** shows the presence of two OH groups that are hydrogen bonded to the coordinated oxygen or oxygen atom of the other OH group, the ^{1}H NMR signal of the OH hydrogens is observed as a single peak even at low temperature; similar results are obtained from the variable-temperature ^{1}H NMR studies of Pt complex **1**.[8]

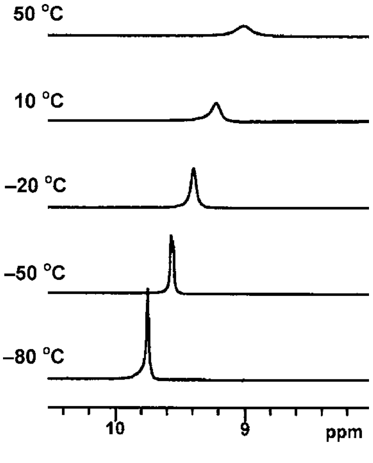


Figure 3. ^{1}H NMR spectra of **4a** in toluene-d_8 at −80, −50, −20, 10, and 50 °C.

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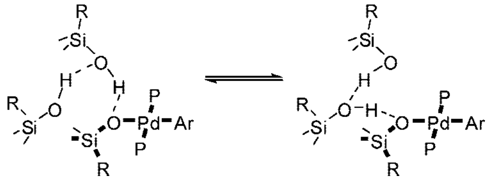
Scheme 1



Consequently, complex **4a** undergoes rapid exchange of the two OH groups over the NMR time scale even at −80 °C, as shown in Scheme 1. Broadening of the OH signals of complex **4a** above 0 °C may suggest the occurrence of a different dynamic behavior.

Variable-temperature $^{29}Si\{^1H\}$ NMR studies of **4a** in toluene-d_8 also demonstrate dynamic behavior of the silsesquioxane molecules, as shown in Figure 4. The $^{29}Si\{^1H\}$ NMR spectrum at −50 °C shows five distinct signals at δ −67.7, −65.6, −65.4, −58.3, and −57.3 (ratio 2:1:1:1:2), similarly to the spectra of analogous Pt complexes **1** (PR_3 = PEt_3, PMe_2Ph) at room temperature.[8] The signal at δ −65.4 remains as a sharp peak even at 50 °C. Two sets of signals at δ −67.7 and −65.6 and δ −58.3 and −57.3 are broadened at 5 °C due to exchange of the ^{29}Si nuclei on the NMR time scale. The peak pair at lower magnetic field with a smaller peak separation ($\Delta\nu$ = 77.2 Hz at −50 °C) approaches the weighted average position at 50 °C, although the peak pair (δ −67.7 and −65.6) with a larger peak separation ($\Delta\nu$ = 169 Hz at −50 °C) does not move from their original position at 50 °C. Coalescence of the latter peak pair would occur at higher temperature. The NMR spectra at 75 °C indicated partial decomposition of the complex and did not provide useful information for the dynamic behavior of the molecule. The $^{29}Si\{^1H\}$ NMR spectrum of complex **4b** changes above room temperature, indicating that the same dynamic process takes place less easily (Figure 5). The spectrum of **4b** at 25 °C shows five signals at δ −67.6, −65.1, −65.0, −58.0, and −56.9 in 2:1:1:1:2 ratio. Heating the solution at 90 °C causes broadening of two sets of signals at δ −67.6 and −65.0 and δ −58.0 and −56.9 to give two broadened signals and a sharp signal. The higher coalescence temperature of the $^{29}Si\{^1H\}$ NMR signals of **4b** than **4a** can be ascribed to the C_6F_5 group situated at the *trans* position of the silsesquioxanate ligand; an electron-withdrawing C_6F_5 ligand stabilizes coordination of the electron-donating silsesquioxanate ligand more significantly than the C_6H_5 ligand.

Scheme 2 depicts a plausible mechanism that accounts for the dynamic behavior of **4a**. The five peaks at δ −67.7, −65.6, −65.4, −58.3, and −57.3 at −50 °C are assigned to $Si_{C',C''}$, Si_C, Si_A, Si_B, and $Si_{B',B''}$ of structure **I**, which is consistent with the 2:1:1:1:2 ratio. Transfer of the Pd to the other OH groups would form the structures **II** and **III**. Approach of the signals at δ −58.3 and −57.3 to the weight averaged position with broadening, broadening of the signal at δ −65.6 and −67.7, and the temperature-independent position of the peak at δ −65.4 (Si_A) are consistent with the dynamic behavior of the molecule. Previously, we proposed intramolecular exchange of the siloxo ligand of the Pt and Pd complexes with an *O*-coordinated silsesquioxanate ligand in order to interpret the ^1H and ^{19}F NMR signals of the C_6H_5 and C_6F_5 ligands bonded to the metal center. The complexes in this study show dynamic behavior via intramolecular exchange of the hydrogen bonds, shown in Scheme 2.

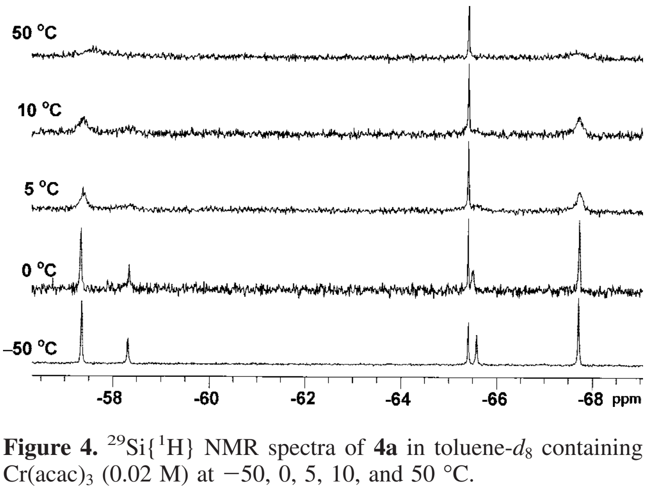


Figure 4. $^{29}Si\{^1H\}$ NMR spectra of **4a** in toluene-d_8 containing $Cr(acac)_3$ (0.02 M) at −50, 0, 5, 10, and 50 °C.

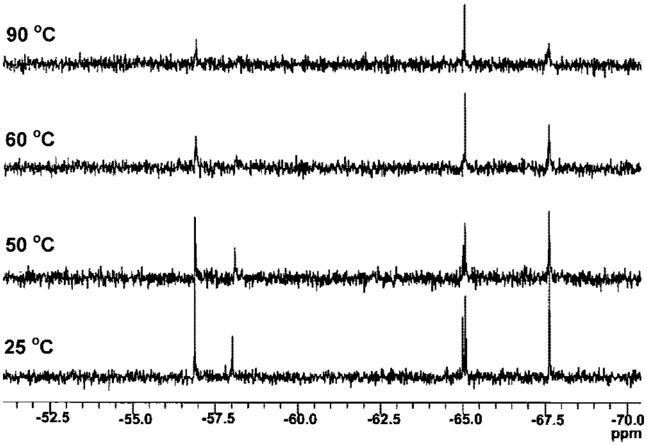


Figure 5. $^{29}Si\{^1H\}$ NMR spectra of **4b** in toluene-d_8 containing $Cr(acac)_3$ (0.02 M) at 25, 50, 60, and 90 °C.

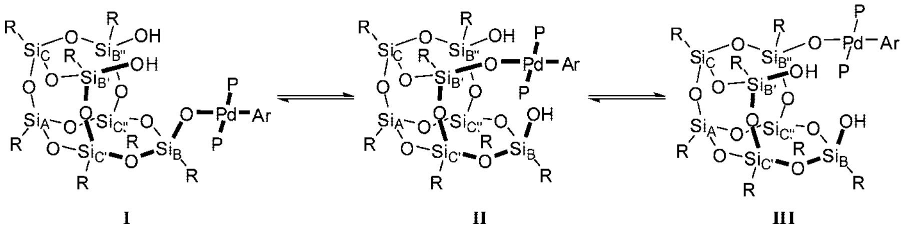
The $^{19}F\{^1H\}$ NMR spectra of **4b** change depending on temperature, as shown in Figure 6. The spectrum at −50 °C contains a signal for the *para* fluorine nucleus (δ −158.7), two signals for *ortho* (δ −117.1, −117.9), and two signals for *meta* (δ −161.5, −162.1) fluorine nuclei. Raising the temperature causes broadening of the signals for the *ortho* and *meta* fluorine peaks, and the signals are coalesced at 0 °C. Separation of the ^{19}F NMR peaks (318 and 252 Hz) is larger than the pairs of ^{29}Si NMR peaks that are broadened on heating (90.8 and 208 Hz), and the fluxional behavior of the ^{19}F NMR spectra is not directly related to that observed in the $^{29}Si\{^1H\}$ NMR spectra. There is a possible dynamic process other than those in Schemes 1 and 2, and rotation of the aryl ring may occur independently from the two dynamic processes shown above.

The present study provided the structure of the palladium complexes with a monodentate silsesquioxanate ligand in the solid state and in solution. Variable-temperature ^{29}Si NMR studies of complexes **4a** and **4b** display the dynamic behavior that involves switching of the O−H···O hydrogen bonds within the *O*-coordinated silsesquioxanate ligand.

Experimental Section

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere. Hexane and toluene were purified by passing through a solvent purification system (Glass Contour). ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, $^{29}Si\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 or JEOL EX-400 spectrometer. Chemical shifts of the signals in ^1H and $^{13}C\{^1H\}$ NMR spectra were adjusted to the residual peaks of the solvents used. The peak positions of the $^{19}F\{^1H\}$, $^{29}Si\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were referenced to external CF_3COOH (δ −76.5) in toluene-d_8, external $SiMe_4$ (δ

Scheme 2



0) in toluene-d_8, and 85% H_3PO_4 (δ 0) in C_6D_6, respectively. The palladium complexes *trans*-[Pd(I)(Ph)(PMe_3)$_2$],[14] [Pd(I)(C_6F_5)(tmeda)],[15] and [Pd{(*c*-C_5H_9)$_7$$Si_7O_{10}(OH)_2$}(Ph)(tmeda)] (**2a**)[9] were prepared according to the previous reports. Silsesquioxanes, 1,3,5,7,9,11,14-heptacyclopentyltricyclo[7.3.3.1(5,11)]heptasiloxane-endo-3,7,14-triol (Gelest), Ag_2O (Wako Pure Chemical), and acetone (Kanto Chemical) are commercially available products. These reagents and solvents are used without any purification. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analysis was carried out with a LECO CHNS-932 CHNS or Yanaco MT-5 CHN autorecorder.

Preparation of *trans*-[Pd(I)(C_6F_5)(PMe_3)$_2$] (3b). To a toluene (10 mL) solution containing [Pd(I)(C_6F_5)(tmeda)] (858 mg, 1.7 mmol) at room temperature was slowly added PMe_3 (0.43 mL, 4.15 mmol) by a syringe. After stirring for 12 h at room temperature, the solvent was removed under reduced pressure to give a white solid, which was washed twice with 3 mL of hexane and dried *in vacuo* to afford **3b** (883 mg, 96%). Anal. Calcd for $C_{12}H_{18}F_5IP_2Pd$: C, 26.08; H, 3.28; F, 17.19; I, 22.97. Found: C, 26.17; H, 3.27; F, 16.97; I, 22.64. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.89 (apparent triplet due to virtual coupling, PCH_3, 18H, splitting 3.6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, room temperature): δ 16.5 (apparent triplet due to virtual coupling, PCH_3, splitting 16.3 Hz), 137.2 (ddd, C_6F_5 *meta*, $J_{\text{F-C}} = 254, 30, 13$ Hz) 138.3 (m, C_6F_5 *para*, $J_{\text{F-C}} = 244$ Hz), 146.6 (dd, C_6F_5 *ortho*, $J_{\text{F-C}} = 221, 16$ Hz). The *ipso*-carbon signal of the C_6F_5 group was not observed due to the low intensity. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, room temperature): δ −163.0 (m, 2F, C_6F_5 *meta*, $J_{\text{F-F}} = 24, 6$ Hz), −160.0 (t, 1F, C_6F_5 *para*, $J_{\text{F-F}} = 20$ Hz), −118.3 (dd, 2F, C_6F_5 *ortho*, $J_{\text{F-F}} = 32, 6$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, room temperature): δ −17.9.

Preparation of *trans*-[Pd{(*c*-C_5H_9)$_7$$Si_7O_{10}(OH)_2$}(Ph)($PMe_3$)$_2$] (4a). To a toluene (10 mL) solution of *trans*-[Pd(I)(Ph)(PMe_3)$_2$] (107 mg, 0.23 mmol) were added (*c*-C_5H_9)$_7$$Si_7O_9(OH)_3$ (199 mg, 0.23 mmol) and Ag_2O (63.4 mg, 0.27 mmol). The mixture was stirred for 46 h at room temperature. When the reaction was completed by monitoring of the $^{31}P\{^1H\}$ NMR spectroscopy, the toluene suspension was filtrated through Celite to remove the precipitation, and the solvent was pumped off. The residual solid substance was washed twice with 3 mL portions of acetone and dried *in vacuo* to give **4b** as a white solid (237 mg, 85%). Anal. Calcd for $C_{47}H_{88}O_{12}P_2PdSi_7$: C, 46.65; H, 7.33. Found: C, 46.34; H, 7.25. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.98 (apparent triplet due to virtual coupling, 18H, PCH_3, splitting 3.2 Hz), 1.21 (m, 7H, C*H* pentyl), 1.57, 1.74, 1.83, 1.97, 2.22 (56H, CH_2 pentyl), 6.88 (m, 3H, C_6H_5 *meta* and *para*), 7.13 (br, 2H, C_6H_5 *ortho*), 9.20 (br, 2H, O*H*). ^{1}H NMR (400 MHz, toluene-d_8, −50 °C): δ 0.91 (br, 18H, PCH_3), 1.23 (m, 7H, C*H* pentyl), 1.61, 1.80, 1.87, 2.03, 2.28 (56H, CH_2 pentyl), 6.88 (m, 3H, C_6H_5 *meta* and *para*), 7.04 (br, 1H, C_6H_5 *ortho*), 7.19 (br, 1H, C_6H_5 *ortho*), 9.57 (br, 2H, O*H*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, room temperature): δ 12.8 (apparent triplet due to virtual coupling, PCH_3, splitting 14 Hz), 23.1, 23.9, 24.1 (*C*H pentyl), 27.7, 28.1, 28.4, 29.8 (*C*H_2 pentyl), 123.1 (C_6H_5 *para*), 136.7 (C_6H_5 *ortho*), 149.0 (t, C_6H_5 *ipso*, $J_{\text{P-C}} = 9.0$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, toluene-d_8, −50 °C): δ 13.5 (apparent triplet due to virtual coupling, PCH_3, splitting 14 Hz), 22.7, 22.9, 23.4, 23.7, 26.9 (1:1:2:2:1, *C*H pentyl), 27.4, 27.4, 27.6, 27.8, 27.9, 28.1, 28.2, 28.3, 29.5 (*C*H_2 pentyl), 122.8 (C_6H_5 *para*), 137.1 (C_6H_5 ortho), 149.2 (t, C_6H_5 *ipso*, $J_{\text{P-C}} = 9.0$ Hz). The *meta*-carbon signal of the C_6H_5 group was overlapped with the solvent signals. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, room temperature): δ −17.9. $^{29}Si\{^1H\}$ NMR (79.3 MHz, toluene-d_8, 0.02 M Cr(acac)$_3$, 25 °C): δ −67.4 (br), −65.1, −58.1 (br), −57.0 (br). $^{29}Si\{^1H\}$ NMR (79.3 MHz, toluene-d_8, 0.02 M Cr(acac)$_3$, −50 °C): δ −67.7, −65.6, −65.4, −58.3, −57.3 (ratio 2:1:1:1:2). IR data (KBr): 3200 (br), 2950 (s), 2867 (s), 1119 (s), 951 (s), 735 (m), 505 (m) cm^{-1}.

Table 2. Crystallographic Data and Details of Refinement for 4b

formula	$C_{47}H_{83}F_5O_{12}P_2PdSi_7 \cdot 1/2C_7H_8$
fw	1346.18
cryst color	orange
cryst syst	triclinic
cryst size/mm	0.15 × 0.35 × 0.40
space group	$P\bar{1}$ (No. 2)
a/Å	13.700(6)
b/Å	14.054(6)
c/Å	17.196(7)
α/deg	102.186(7)
β/deg	99.416(5)
γ/deg	91.966(7)
V/Å^3	3185(2)
Z	2
D_{calcd}/g cm^{-3}	1.411
F(000)	1418
μ/mm^{-1}	0.5425
no. of rflns measd	20 863
no. of unique rflns	12 827 ($R_{\text{int}} = 0.027$)
no. of obsd rflns ($I > 2.00\sigma(I)$)	10 188
no. of variables	797
$R1$ ($I > 2.00\sigma(I)$)	0.0603
$wR2$ ($I > 2.00\sigma(I)$)	0.1326
GOF	1.018

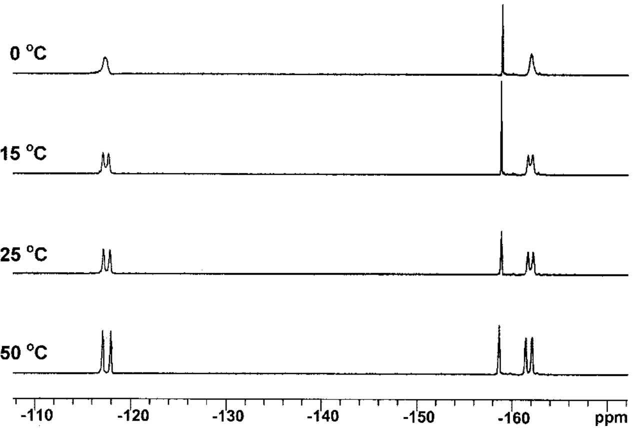


Figure 6. $^{19}F\{^1H\}$ NMR spectra of **4b** in toluene-d_8 at −50, −25, −15, and 0 °C.

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(15) Hughes, R. P.; Ward, A. J.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L.; Zakharov, L. N. *Dalton Trans.* **2004**, 2720.

Preparation of *trans*-[Pd{(c-C_5H_9)$_7$$Si_7O_{10}(OH)_2$}($C_6F_5$)-($PMe_3$)$_2$](4b). To a toluene (10 mL) solution of *trans*-[Pd(I)(C_6F_5)(PMe_3)$_2$] (65.3 mg, 0.12 mmol) were added (c-C_5H_9)$_7$$Si_7O_9(OH)_3$ (105 mg, 0.12 mmol) and Ag_2O (33.4 mg, 0.14 mmol). The mixture was stirred for 4 days at room temperature. The toluene suspension was filtrated through Celite, and the solvent was pumped off. The residual solid substance was washed twice with 3 mL of acetone and dried *in vacuo* to give **4b** as a white solid (122 mg, 78%). Anal. Calcd for $C_{47}H_{83}O_{12}P_2PdSi_7$: C, 43.42; H, 6.43; F, 7.31. Found: C, 43.24; H, 6.47; F, 7.14. ^{1}H NMR (400 MHz, C_6D_6, room temperature): δ 0.93 (apparent triplet due to virtual coupling, 18H, PCH_3, splitting 3.2 Hz), 1.16 (m, 7H, C*H* pentyl), 1.56, 1.74, 1.99, 2.21 (56H, CH_2 pentyl), 8.34 (br, 2H, O*H*). $^{13}C\{^1H\}$ NMR (100 MHz, toluene-d_8, room temperature): δ 13.8 (apparent triplet due to virtual coupling, PCH_3, splitting 15 Hz), 23.1, 23.3, 23.8, 24.0, 27.4 (*C*H pentyl), 27.5, 27.6, 28.1, 28.1, 28.3, 28.4, 28.5, 29.8 (CH_2 pentyl), 113.9 (m, C_6F_5 *ipso*), 137.1 (m, C_6F_5 *meta*, $J_{\text{F-C}} = 254$ Hz) 138.0 (m, C_6F_5 *para*, $J_{\text{F-C}} = 244$ Hz), 146.9 (m, C_6F_5 *ortho*, $J_{\text{F-C}} = 227$ Hz). $^{19}F\{^1H\}$ NMR (376 MHz, toluene-d_8, room temperature): δ −162.1 (2F, C_6F_5 *meta*), −159.3 (1F, C_6F_5 *para*), −117.5 (2F, C_6F_5 *ortho*). $^{19}F\{^1H\}$ NMR (376 MHz, toluene-d_8, −50 °C): δ −162.1 (m, 1F, C_6F_5 *meta*), −161.5 (m, 1F, C_6F_5 *meta*), −158.7 (t, 1F, C_6F_5 *para*, $J_{\text{F-F}} = 20$ Hz), −117.9 (d, 1F, C_6F_5 *ortho*, $J_{\text{F-F}} = 29$ Hz), −117.1 (d, 1F, C_6F_5 *ortho*, $J_{\text{F-F}} = 29$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, room temperature): δ −14.3. $^{29}Si\{^1H\}$ NMR (79.3 MHz, toluene-d_8, 0.02 M Cr(acac)$_3$, room temperature): δ −67.6, −65.1, −65.0, −58.0, −56.9 (ratio 2:1:1:1:2). IR data (KBr): 3300 (br), 2950 (s), 2867 (s), 1504.7 (s), 1458 (s), 1111 (w), 951 (s), 504 (m) cm^{-1}.

Reaction of *trans*-[Pd{(c-C_5H_9)$_7$$Si_7O_{10}(OH)_2$}(Ph)(tmeda)] (2a) with an Excess of PMe_3. To a solution of palladasilsesquioxane **2a** (100 mg, 0.085 mmol) in toluene (3 mL) was added an excess of PMe_3 (35 μL, 0.34 mmol) at room temperature. The reaction mixture was stirred at room temperature for 13 h. The solvent was removed under reduced pressure. The resulting material was washed twice with 3 mL of acetone to yield **4a** as a white solid (87.1 mg, 85%).

X-ray Crystallography. Crystals of **4b** suitable for an X-ray diffraction study were sealed in glass capillaries. Data for **4b** were collected at −160 °C on a Rigaku Saturn CCD diffractometer equipped with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Calculations were carried out using the program package Crystal Structure, version 3.7, for Windows. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms, except for the OH hydrogens of **4b**, were located by assuming the ideal geometry and were included in the structure calculations without further refinement of the parameters. Crystallographic data and details of refinement are summarized in Table 2.

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

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