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Synthesis and properties of amido- and alkoxopalladium(II) complexes with tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) ligand

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Abstract

$PdCl_2(tmeda)$ reacts with $NaN(SiMe_3)_2$ to give $PdCl[N(SiMe_3)_2](tmeda)$ (**1**). Single crystal X-ray analysis shows the structure of **1** which has a slightly distorted square planar coordination around the Pd center with Pd–N(amido) bond distance of 2.043(6) Å and Pd–N(amine) bond distances of 2.104(7) and 2.102(7) Å, respectively. Reactions of complex **1** with 1,1,1,3,3,3-hexafluoro-2-propanol and with phenol cause substitution of the amido ligand to give the corresponding alkoxide and phenoxide palladium complexes, PdCl(OR)(tmeda) (**2**: $R = CH(CF_3)_2$, **3**: $R = C_6H_5$, respectively). Reactions of dimethylpalladium complex, $PdMe_2(tmeda)$, with the fluoro alcohol and with phenol give $PdMe(OCH(CF_3)_2)(tmeda)$ (**4**) and $PdMe(OC_6H_5)(tmeda)$ (**5**), respectively. Complex **5** reacts further with HOPh to give $PdMe(OC_6H_5)(tmeda) \cdot (HOPh)$ (**6**) whose ^1H NMR spectrum shows the OH hydrogen peak at extremely low magnetic field position (10.3 ppm) due to strong O–H ⋯ O hydrogen bonding between the phenoxide ligand and phenol. The tmeda ligand in complex **4** is easily displaced by addition of phosphine ligands such as dppm (bis(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane), and dppp (1, 3-bis(diphenylphosphino)propane) to give the corresponding palladium alkoxide complexes with the phosphine ligand, $PdMe(OCH(CF_3)_2)(L)$ (**7**: L = dppm; **8**: L = dppe; **9**: L = dppp).

Keywords: Palladium; Alkoxide; Crystal structure; Amide

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1. Introduction

Recent progress in the study of alkoxide and amide complexes of Group 10 metals [1–8] has revealed details of unique reactions of the complexes such as insertion of CO and olefins into the M–O and M–N bonds, amido and alkoxido ligand exchange caused by addition of protic compounds as well as association of the alkoxide ligand with alcohols through O–H ⋯ O hydrogen bonding [9–11]. These reactions seem to be relevant to the pathways of Pd complexes, catalyzed oxidation and carbonylation of alcohols and olefin functionalization as well as transesterification [12–13]. Many of the already known alkoxide and amide complexes of Pd with phosphine ligand have been prepared by metathesis reaction of halogeno or pseudohalogeno complexes with sodium or lithium alkoxide or amide. Alcoholysis of organopalladium complexes and reaction of alcohol with amide Pd complexes also provide the corresponding alkoxide palladium complexes. On the other hand, there have been fewer reports on alkoxide and amide Pd complexes stabilized with nitrogen donor ligands [14].

In this paper we report preparation, characterization, and chemical properties of various palladium alkoxide (or aryloxide) complexes with tmeda ligand as well as preparation and structure of $PdCl[N(SiMe_3)_2]$(tmeda) which serves as a precursor of alkoxide Pd complexes with the amine ligand.

2. Results and discussion

2.1. Preparation and structure of $PdCl(N(SiMe_3)_2)$ (tmeda) (1)

$PdCl_2$(tmeda) reacts with two equivalents of $NaN(SiMe_3)_2$ at room temperature to give PdCl-

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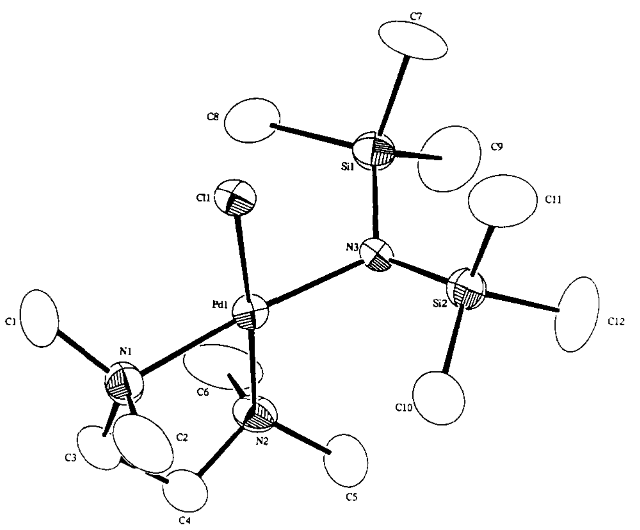
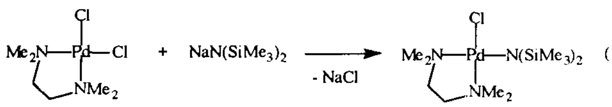


Fig. 1. ORTEP view of the molecular structure of **1**. Ellipsoids represent 50% probability.

$[N(SiMe_3)_2](tmeda)$ (**1**) as air-stable deep violet crystals. Formation of diamide complexes such as $Pd[N(SiMe_3)_2]_2(tmeda)$ is not observed in the reaction mixture probably due to sterically bulky $SiMe_3$ groups on the amido ligand. Similar reaction with $LiN(SiMe_3)_2$ to obtain complex **1** requires much longer reaction time.



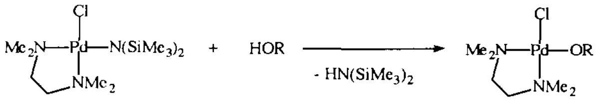
(1)

1

The ^1H NMR spectrum of **1** shows a singlet at 0.20 ppm due to $SiMe_3$ hydrogens of the amido ligand and peaks at 2.4–2.8 ppm due to the tmeda ligand. Fig. 1 shows molecular structure of **1** by X-ray single crystal structure determination. The molecule has a slightly distorted square-planar coordination around the palladium center. The Pd–N3 bond distance of the complex is 2.043(6) Å which is shorter than Pd–N1 and Pd–N2 bonds (2.104(7) and 2.102(7) Å, respectively). Almost similar distances between Pd–N1 and Pd–N2 bond suggest that the chloro and amido ligands have no significant difference in the degree of trans influence. Amidopalladium complex with a P–N–P chelating ligand, $PdCl[N(SiMe_2CH_2PPh_2)_2]$ [15], has similar Pd–N(amido) bond distance (2.063(2) Å) to that of **1**, while dinuclear complex with bridging amido ligands, $[Pd(C_6F_5)(^tBuNC)(\mu\text{-}NHPh)]_2$ [7], has similar or slightly longer Pd–N bonds (2.06–2.14 Å). The Si1–N3–Si2 bond angle of **1** is considerably larger (125.4(8)°) due to steric repulsion between $SiMe_3$ groups.

Preparation of bis(trimethylsilyl)amido complexes of other 8–10 group transition metals, Rh, Ru [16] and Ni [17], has been already reported. Relatively high stability of these amido complexes can be attributed to bulkiness of $SiMe_3$ groups and stability toward β-elimination of the ligand. However, there has been no report on preparation of similar bis(trimethylsilyl)amido palladium complexes. Already known amidopalladium complexes have phenyl substituents on the amido nitrogen except for $PdCl[N(SiMe_2CH_2PPh_2)_2]$. Reaction (1) provides the amidopalladium complex which is not stabilized by phenyl substituent on the coordinated nitrogen atom nor by chelation of the amido ligand.

Complex **1** reacts readily with two equivalents of 1,1,1,3,3,3-hexafluoro-2-propanol to give $PdCl(OCH(CF_3)_2)(tmeda)$ (**2**) in 74% yield as yellow crystalline solids. Reaction of **1** with phenol gives $PdCl(OC_6H_5)(tmeda)$ (**3**) analogously (83%). The isolated complexes were characterized by elemental analyses and spectroscopic data.



(2)

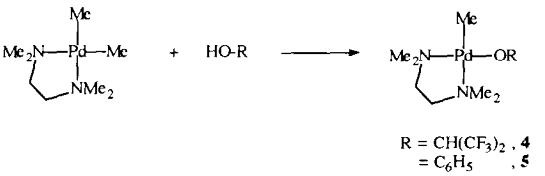
R = $CH(CF_3)_2$, **2**
= C_6H_5, **3**

M–O bonds of late transition metal alkoxide complexes have been estimated to be more thermodynamically stable than M–N bonds in the corresponding metal amido complexes. Motivation of the above reaction seems to be the higher stability of Pd–O bond than Pd–N bond [18].

2.2. *Preparation and properties of methylpalladium alkoxide complexes with tmeda ligand*

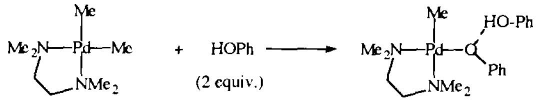
Previously we have reported that dimethylpalladium complexes with dppe or dmpe (1,2-bis(dimethylphosphino)ethane) react easily with fluoro alcohol or phenol to give methylpalladium fluoroalkoxide or phenoxide complexes [9a,b]. On the other hand, dimethylpalladium complexes with diamine ligands have quite different reactivity toward electrophilic reagents from those with phosphine ligands. $PdMe_2(bpy)$ reacts with MeI to give the Pd(IV) complex, $PdMe_3I(bpy)$ [19], while similar reaction of $PdMe_2(PR_3)_2$ gives $Pd(Me)I(PR_3)_2$ [20]. Reaction of dimethylpalladium complexes with diamine ligands with fluoro alcohol or phenol might give dimethylpalladium(IV) alkoxide complex as the oxidative addition product or methylpalladium alkoxide(II) complex as alcoholysis product.

Actually, reactions of $PdMe_2(tmeda)$ with an equimolar amount of 1,1,1,3,3,3-hexafluoro-2-propanol and with phenol in Et_2O at room temperature give $PdMe(OCH(CF_3)_2)(tmeda)$ (**4**) and $PdMe(OC_6H_5)(tmeda)$ (**5**), respectively. Pd(IV) complexes are not observed in the reaction mixture. Similar reaction with methanol does not cause alcoholysis of the dimethylpalladium complex at all.



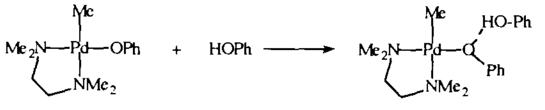
(3)

The reaction with excess phenol does not give the diphenoxide complex $Pd(OC_6H_5)_2$(tmeda), but affords $PdMe(OC_6H_5)$(tmeda) · (HOPh) (**6**) which contains O–H · · · O hydrogen bonding between phenol and the phenoxide ligand. Reaction of **5** with equimolar amount of phenol also gives **6** as shown in Eq. (5).



(4)

6



(5)

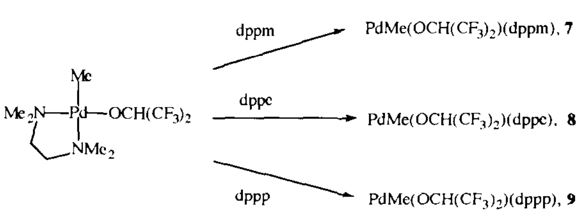
5 **6**

Complexes **4**–**6** were characterized by IR and NMR (^{1}H and $^{13}C\{^1H\}$) spectroscopy as well as elemental analyses. The IR spectrum of **6** shows a broad absorption band around 2500 cm^{-1} due to ν(O–H), whose peak position is characteristic of strong hydrogen bond. The ^{1}H spectrum shows an O–H hydrogen peak at δ 10.3 ppm. The extremely high chemical shift of the hydrogen is also attributed to the hydrogen bonding similarly to already reported phenoxide palladium complexes having hydrogen bonded phenol moiety such as $[Pd(OPh)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ · HOPh [11], *trans*-$PdMe(OPh)(PMe_3)_2$ · HOPh [9b], and *trans*-$PdH(OPh)(PCy_3)_2$ · HOPh [10].

Complex **4** reacts with phenol to give complex **5** at ambient conditions. Substitution of fluoroalkoxide ligand by phenoxide has been reported in Ru, Pd, and Pt complexes having phosphine ligands [9].

2.3. Ligand exchange reaction of $PdMe(OCH(CF_3)_2)$(tmeda) with chelated phosphine

The tmeda ligand in complex **4** is easily displaced by chelated phosphine such as dppm, dppe, and dppp in a stoichiometric ratio to give complexes **7**–**9** as shown in Scheme 1.



Scheme 1. Ligand exchange reactions.

Complex **8** with dppe ligand shows the IR and ^{1}H NMR spectra which are identical to those of the authentic sample independently prepared from the reaction of $PdMe_2$(dppe) and $HOCH(CF_3)_2$. The ^{1}H and $^{13}C\{^1H\}$ NMR peaks due to Pd–Me carbon and hydrogens of **9** having dppp ligand appear as doublets of doublets in a quite similar manner to those of **8**. The $^{31}P\{^1H\}$ NMR spectrum showing two doublets as well as the above results indicate the square-planar coordination around the palladium center with *cis* configuration. The ^{1}H NMR signal of methyl ligand of **7** having a dppm ligand appears as a broadened singlet. Two peaks are observed due to two CH_2 hydrogens in dppm. The $^{31}P\{^1H\}$ NMR spectrum shows a single peak even at −40°C. All the spectroscopic features of **7** seem to be attributed to the structure which is deviated seriously from common square-planar coordination and some fluxional behaviors although these details are not clear at present.

Chelating phosphine ligands undergo facile substitution of coordinated diamine ligands in organotransition metal complexes of 10 group metals. $NiMe_2$(bpy) [21] and $PdMe_2$(tmeda) [22] were reported to react with mono and bis(phosphine)s to give the corresponding dialkylpalladium complexes with the phosphine ligands. The above methylpalladium alkoxide complex **4** also undergoes substitution of the diamine ligand by diphosphine ligand, while complex **1** does not undergo ligand exchange with dppe ligand. Presumably sterically bulky bis(trimethylsiyl) amido group of **1** precludes σ-donor attack of phosphine. Reaction (2) proceeds smoothly because of smaller steric repulsion between the alcohol oxygen and the palladium center than that between diphenylphosphino group and the metal center.

In summary several new amido- and alkoxo palladium complexes with tmeda ligands were prepared in the present study. These complexes undergo substitution of the alkoxo, amido, and tmeda ligands depending on the conditions. Further investigation of properties of the complexes including reactivity toward insertion of small molecules into the Pd–O and Pd–N bonds is under way.

3. Experimental section

All manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with use of standard Schlenk technique. Solvents were distilled from Na-benzophenone. 1,1,1,3,3,3-Hexafluoro-2-propanol, dppm, dppe, and dppp were purchased from Aldrich Co. $PdCl_2$(tmeda) and $PdMe_2$(tmeda) were prepared according to the literature [22].

Elemental analyses were carried out by the analytical laboratory at Tokyo Institute of Technology. NMR spectra were recorded on Varian XL-200 and JEOL-FX 100GX-270 spectrometers. IR spectra were recorded on a Hitachi 270-30 spectrophotometer.

3.1. Preparation of $PdCl[N(SiMe_3)_2](tmeda)$ (1)

To an ethereal solution (90 ml) containing $PdCl_2(tmeda)$ (3.0 g, 10 mmol) was slowly added $NaN(SiMe_3)_2$ (20 mmol, 1.0 M in THF solution). After stirring for 1h at room temperature the reaction mixture was concentrated, stored at freezing point to afford reddish-violet crystals. The crude product was dissolved in CH_2Cl_2 and filtered through celite. The final crystals were recrystallized from CH_2Cl_2/hexane (1.3 g, 30%).

A similar reaction using $LiN(SiMe_3)_2$ (1.0 M solution in hexane) also results in complex **1** in 51% yields but the reaction needs about 48 h stirring to complete. M.p.: 172°C. IR (KBr): 2944, 1461, 1236, 980, 873, 872 cm^{-1}. ^1H NMR(CD_2Cl_2, 100 MHz, δ): 0.20 (s, 18H), 2.5, 2.6 (s, 12H, NMe_2), 2.4–2.8 (m, 4H, $N-CH_2$). Anal. Calc. for $C_{12}H_{34}N_3ClSi_2Pd$: C, 34.4; H, 8.2; N, 10.0. Found: C, 33.9; H, 8.0; N, 9.6.

3.2. Preparation of $PdCl(OCH(CF_3)_2)(tmeda)$ (2) and $PdCl(OC_6H_5)(tmeda)$(3)

To a CH_2Cl_2 (4 ml) solution containing $PdCl[N(SiMe_3)_2](tmeda)$ (200 mg, 0.47 mmol) was added 1,1,1,3,3,3-hexafluoro-2-propanol (156 mg, 0.94 mmol). The initial deep violet solution was turned into a yellow solution on stirring at room temperature. After stirring for 30 min the solution was concentrated and stored at −20°C to afford yellow crystalline solids which were recrystallized from CH_2Cl_2/hexane (150 mg, 74%). IR(KBr): 2936, 1280, 1204 cm^{-1}. ^1H NMR(CD_2Cl_2, 100 MHz, δ): 2.6, 2.8 (s, 12H, $N-Me_2$), 2.5–2.7 (m, 4H, $N-CH_2$) 4.5 (sep, J(HF) = 7 Hz, 1H). Anal. Calc. for $C_9H_{17}N_2OClF_6Pd$: C, 25.4; H, 4.0; N, 6.6. Found: C, 25.4; H, 4.2; N, 6.8.

Complex **3** was prepared analogously from reaction of **1** with equimolar phenol in 83% yield. IR(KBr): 3010, 1584, 1473, 1292 cm^{-1}. ^1H NMR(DMSO-d^6, 100MHz, δ): 2.5, 2.7 (s, $N-Me_2$, 12H), 2.5–2.8(m, 4H, $N-CH_2$), 6.2–7.1(m, 5H, aromatic). Anal. Calc. for $C_{12}H_{21}N_2OClPd$: C, 41.0; H, 6.0; N, 8.0. Found: C, 41.3; H, 6.2; N, 7.8.

3.3. Preparation of $PdMe(OCH(CF_3)_2)(tmeda)$ (4) and $PdMe(OC_6H_5)(tmeda)$ (5)

To an ether (30 ml) solution of $PdMe_2(tmeda)$ (1.37 g, 5.4 mmol) was added 1,1,1,3,3,3-hexafluoro-2-propanol (910 mg, 5.4 mmol). The initially colorless solution was turned into a bright yellow solution on stirring at room temperature. After the reaction the solution was cooled at −70°C for 2 h to yield pale green precipitates which were filtered and dried in vacuo. Recrystallization from ether gave crystals of **4** (1.3 g, 60%). M.p.: 115°C. IR(KBr): 2940 cm^{-1} (strong, aliphatic C–H), 1190 cm^{-1} (strong, C–F). ^1H NMR ($CDCl_3$, 200 MHz, δ): 0.22 (s, 3H, Pd–Me), 2.5, 2.6 (s, 12H, $N-Me_2$), 2.4–2.7 (m, 4H, $N-CH_2$), 4.0 (sep, 1H, J(HF) = 7 Hz, -CH). ^{13}C NMR{^1H} NMR(50 MHz, $CDCl_3$, δ): −0.71(s, Pd–Me), 46.8, 51.1(s, $N-Me_2$), 57.4, 63.3(s, $N-CH_2$), 76.2(sep, J(CF) = 29 Hz), 124(q, J(CF) = 289 Hz). Anal. Calc. for $C_{10}H_{20}ON_2F_6Pd$: C, 29.7; H, 5.0; N, 6.9. Found: C, 30.0; H, 5.2; N, 7.1.

Complex **5** was prepared analogously (1.4 g, 78%). M.p.: 139°C. IR(KBr): 1600, 1495, 1305 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, δ): 0.38 (s, 3H, Pd–Me), 2.5, 2.7 (s, 12H, $N-Me_2$), 2.5–2.7 (m, 4H, $N-CH_2$), 6.4, 7.0 (m, 5H, aromatic). ^{13}C NMR{^1H} NMR(50 MHz, $CDCl_3$, δ): −3.3(s, Pd–Me), 47.7, 51.0(s, $N-Me_2$), 57.3, 63.4(s, $N-CH_2$), 113, 120, 129, 139(s, aromatic). Anal. Calc. for $C_{13}H_{24}ON_2Pd$: C, 47.2; H, 7.3; N, 8.5. Found: C, 47.1; H, 7.3; N, 8.7.

3.4. Preparation of $PdMe(OC_6H_5)(tmeda) \cdot (HOPh)$ (6)

To an ether (10 ml) solution of $PdMe_2(tmeda)$ (0.29 g, 1.1 mmol) was added phenol (227 mg, 2.4 mmol). After stirring for 2h at room temperature the reaction mixture was evaporated to give a pale green precipitate which was filtered and washed with hexane (320 mg, 68%). IR(KBr): 2900, 2500, 1598, 1480, 1270 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, δ): 0.47 (s, 3H, Pd–Me), 2.5, 2.7 (s, 12H, $N-Me_2$), 2.5–2.7 (m, 4H, $N-CH_2$), 10.3 (s, 1H, OH), 6.5–7.3(m, 10H, aromatic). ^{13}C NMR{^1H} NMR(50 MHz, $CDCl_3$, δ): −2.8(s, Pd–Me), 47.6, 51.0(s, $N-Me_2$), 57.2, 63.9(s, $N-CH_2$), 114, 116, 119, 120, 129, 140, 158(s, aromatic). Anal. Calc. for $C_{19}H_{30}O_2N_2Pd$: C, 53.7; H, 7.1; 6.6. Found: C, 54.0; H, 7.3; N, 6.4.

Reaction of **5** with equimolar phenol also gives **6**.

3.5. Ligand Exchange of $PdMe(OCH(CF_3)_2)(tmeda)$ with dppm, dppe, and dppp

A benzene solution (5 ml) containing dppm (408 mg, 1.1 mmol) was added slowly to an ether (20 ml) solution of $PdMe(OCH(CF_3)_2)(tmeda)$ (430 mg, 1.1 mmol) at 0°C. After stirring for 1 h the orange solution was evaporated under reduced pressure to give oily materials which were dissolved in small amounts of ether. The solution was stored at −20°C overnight to yield yellow solids which were filtered and washed with ether below 0°C. The resulting yellow solids were confirmed as solvent coordinated form, $PdMe(OCH(CF_3)_2)(dppm) \cdot 0.5(ether)$ (7) (250 mg, 56%). IR(KBr): 1180, 1145 cm^{-1}. ^1H NMR(100 MHz, CD_2Cl_2, δ, −40°C): −0.1 (broad triplet, 3H, Pd–Me), 3.1 (m, 1H, -CH), 4.6 (m, 1H, -CH), 4,3(sep, 1H, -CH), 7.0–7.9(m, 20H, aromatic). $^{31}P\{^1H\}$ NMR(40 MHz, CD_2Cl_2, δ, −40°C): 15.2(s). Anal. Calc. for $C_{29}H_{26}F_6OP_2Pd \cdot 0.5Et_2O$: C, 52.4; H, 4.4. Found: C, 52.8; H, 4.7.

Dppe (250 mg, 0.61 mmol) was added to a benzene (20 ml) solution containing $PdMe(OCH(CF_3)_2)(tmeda)$ (250 mg, 0.61 mmol). After stirring for 1h the reaction mixture was evaporated to give white solids of **8** which were filtered and washed with ether (620 mg, 62%). IR(KBr): 1200, 1170 cm^{-1}. ^1H NMR(200 MHz, C_6D_6, δ): 0.85 (dd, 3H, $J(HP) = 8, 2$ Hz, Pd–Me), 1.4–2.2 (m, $-CH_2$), 5.4(sep, 1H, $J(HF) = 7$ Hz, -CH), 6.8–8.1 (m, aromatic). These data were identified by the literature data [9a].

Complex **9** was prepared analogously (93%). IR(KBr): 1190 cm^{-1}(C–F). ^1H NMR (100 MHz, CD_2Cl_2, δ): 0.30 (dd, 3H, $J(HP) = 2.4, 7.6$ Hz, Pd–Me), 1.8 (m, 2H, $-CH_2$), 2.4 (m, 4H, $-CH_2$), 4.6 (sep, 1H, $J(HF) = 4.0$ Hz, -CH), 7.2–7.9 (m, 20H, aromatic). $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_2Cl_2, δ): 15.6 (dd, J(CP) = 3.1, 95 Hz, Pd–Me), 19.2 (d, $J(CP) = 5.3$ Hz, $-CH_2$), 27.0 (d, $J(CP) = 19$ Hz, P–CH_2), 29.7 (dd, $J(CP) = 8.8$, 31 Hz, $-CH_2$), 73.0 (sep, $J(CF) = 29$ Hz, $CH(CF_3)_2$), 124.0 (q, $J(CF) = 289$ Hz, C–F), 129–134 (m, aromatic). $^{31}P\{^1H\}$ NMR (40 MHz, CD_2Cl_2, δ): −9.2, 28.0 (d, $J(PP) = 49$ Hz). Anal. Calc. for $C_{31}H_{30}F_6OP_2Pd$: C, 53.1; H, 4.3. Found: C, 52.7; H, 4.6.

3.6. X-Ray structure determination

A crystal of **1** suitable for crystallography was obtained from a CH_2Cl_2–hexane mixture and mounted in a glass capillary tube under argon. The unit cell parameters were obtained by least-squares refinement of setting angles of 20 reflections with $25 \leq 2\ \theta \leq 35°$. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo Kα radiation ($\lambda = 0.710\ 69$ Å) and the ω-2θ method. Calculations were carried out by using a program package TEXSAN on a DEC Micro VAXII computer. A full

Table 1
Crystallographic data for **1**

formula	$C_{12}H_{34}ClN_3Si_2Pd$
formula weight	418.47
crystal system	monoclinic
space group	C2/c (No. 15)
a, Å	31.342(4)Å
b, Å	9.349(3)Å
c, Å	15.303(3)Å
β, °	113.11(1)°
V, Å^3	4124(1)Å
Dcalcd, g cm^{-3}	1.3489 g cm^{-3}
Z	8
μ, cm^{-1}	11.28
F(000)	1744
no. of variables	172
2θ range, deg	5.0–50.0
hkl	$0 \leq h \leq 19, 0 \leq k \leq 11, -19 \leq l \leq 19$
Unique reflections	3868
Used reflections ($Fo \geq 3\sigma(Fo)$)	2583
R (*F*o) [a]	0.048
Rw (*F*o) [a]	0.040

[a] $R = [\Sigma(Fo-Fc)/\Sigma Fo$, $Rw = \Sigma(Fo-Fc)^2/\Sigma w(Fo)^2]$ where $w = [(\sigma(Fo))^2]^{-1}$.

Table 2
Atomic coordinates and isotropic thermal parameters (Å^2) for **1**

atom	x	y	z	B*eq*
Pd(1)	0.16442(2)	0.11442(7)	0.58821(5)	3.37(1)
Cl(1)	0.19807(7)	0.3422(2)	0.5989(1)	3.58(5)
Si(1)	0.09493(9)	0.2718(3)	0.6629(2)	4.37(7)
Si(2)	0.0744(1)	0.2663(3)	0.4522(2)	4.88(7)
N(1)	0.2257(2)	0.0072(8)	0.6016(5)	4.8(2)
N(2)	0.1383(2)	−0.0936(7)	0.5850(5)	4.3(2)
N(3)	0.1017(2)	0.2054(6)	0.5658(4)	3.4(2)
C(1)	0.2696(3)	0.065(1)	0.6785(9)	9.2(4)
C(2)	0.2312(4)	0.017(1)	0.5087(8)	8.1(4)
C(3)	0.2194(3)	−0.145(1)	0.6222(7)	5.7(3)
C(4)	0.1716(3)	−0.1923(10)	0.5682(7)	5.3(3)
C(5)	0.0922(3)	−0.120(1)	0.5104(8)	7.8(3)
C(6)	0.1375(4)	−0.126(1)	0.6793(8)	8.8(4)
C(7)	0.0933(4)	0.472(1)	0.6682(8)	9.2(4)
C(8)	0.1427(4)	0.218(1)	0.7786(6)	6.3(3)
C(9)	0.0407(3)	0.207(1)	0.6707(8)	10.1(4)
C(10)	0.0961(4)	0.183(1)	0.3671(7)	8.3(4)
C(11)	0.0786(5)	0.460(1)	0.4330(8)	9.9(4)
C(12)	0.0110(4)	0.226(2)	0.4094(8)	11.2(4)

Table 3
Selected bond distances (Å) and angles (deg) for **1**

Pd(1)–Cl(1)	2.353(2)	Pd(1)–N(1)	2.104(7)
Pd(1)–N(2)	2.102(7)	Pd(1)–N(3)	2.043(6)
Si(1)–N(3)	1.700(6)	Si(1)–C(7)	1.87(1)
Si(1)–C(8)	1.884(10)	Si(1)–C(9)	1.852(9)
Si(2)–N(3)	1.706(6)	Si(2)–C(10)	1.858(10)
Si(2)–C(11)	1.85(1)	Si(2)–C(12)	1.87(1)
N(1)–C(1)	1.52(1)	N(1)–C(2)	1.50(1)
N(1)–C(3)	1.48(1)	N(2)–C(4)	1.49(1)
N(2)–C(5)	1.47(1)	N(2)–C(6)	1.48(1)
C(3)–C(4)	1.47(1)		
Cl(1)–Pd(1)–N(1)	93.3(2)	Cl(1)–Pd(1)–N(2)	176.4(2)
Cl(1)–Pd(1)–N(3)	90.6(2)	N(1)–Pd(1)–N(2)	83.9(3)
N(1)–Pd(1)–N(3)	174.8(3)	N(2)–Pd(1)–N(3)	92.4(3)
N(3)–Si(1)–C(7)	114.7(4)	N(3)–Si(1)–C(8)	113.5(4)
N(3)–Si(1)–C(9)	111.7(4)	C(7)–Si(1)–C(8)	104.6(5)
C(7)–Si(1)–C(9)	106.4(6)	C(8)–Si(1)–C(9)	105.3(5)
N(3)–Si(2)–C(10)	113.6(4)	N(3)–Si(2)–C(11)	116.8(4)
N(3)–Si(2)–C(12)	109.2(5)	C(10)–Si(2)–C(11)	103.2(6)
C(10)–Si(2)–C(12)	107.5(6)	C(11)–Si(2)–C(12)	105.9(6)
Pd(1)–N(1)–C(1)	114.9(6)	Pd(1)–N(1)–C(2)	108.7(6)
Pd(1)–N(1)–C(3)	106.5(6)	C(1)–N(1)–C(2)	107.9(8)
C(1)–N(1)–C(3)	109.4(8)	C(2)–N(1)–C(3)	109.4(8)
Pd(1)–N(2)–C(4)	106.6(5)	Pd(1)–N(2)–C(5)	115.5(6)
Pd(1)–N(2)–C(6)	108.7(6)	C(4)–N(2)–C(5)	107.6(8)
C(4)–N(2)–C(6)	108.8(8)	C(5)–N(2)–C(6)	109.5(8)
Pd(1)–N(3)–Si(1)	116.6(3)	Pd(1)–N(3)–Si(2)	112.0(3)
Si(1)–N(3)–Si(2)	125.8(4)	N(2)–C(4)–C(3)	110.1(8)

matrix least-squares refinement was carried out by applying anisotropic thermal factors to all the non-hydrogen atoms. Hydrogen atoms were located from calculation by assuming the ideal positions (d (C–H) = 0.95 Å) and included the structure calculation without further refinement of the parameters. Absorption correction by ψ scan method of the collected data was applied. Crystallographic data, selected bond distances and angles, and atomic coordinates of the non-hydrogen atoms are listed in Tables 1–3. Atomic coordinates of hydrogen atoms and all bond distances and angles are available from the author (Y.-J. K).

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