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Synthesis and properties of dimethylpalladium complex with new PS_3-type tripodal tetradentate ligand

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Dimethylpalladium complex bearing PS_3-type tripodal tetradentate ligand, $[PdMe_2\{P(C_6H_4\text{-}2\text{-}S\text{-}i\text{-}Pr)_3\}]$, was synthesized by the reaction of $[PdCl\{P(C_6H_4\text{-}2\text{-}S\text{-}i\text{-}Pr)_3\}]X$ ($X = Cl, BF_4$) with methyllithium (Br free). The dimethylpalladium complex reacted with an equimolar amounts of HCl to give the corresponding chloromethylpalladium complex, $[PdClMe\{P(C_6H_4\text{-}2\text{-}S\text{-}i\text{-}Pr)_3\}]$, while the similar reaction using 2 M amounts of HCl afforded the dichloropalladium complex, $[PdCl\{P(C_6H_4\text{-}2\text{-}S\text{-}i\text{-}Pr)_3\}]Cl$. The detailed structures of the complexes were revealed by X-ray crystallography and variable temperature ^1H NMR studies.

1. Introduction

Dimethylpalladium(II) complexes bearing phosphane ligands undergo reductive elimination of ethane to afford zerovalent palladium complexes [1–8], which are active species in various catalytic reactions, such as carbon-carbon and carbon-heteroatom bond forming reactions, etc. [9–16]. Dimethylpalladium(II) complexes with trialkylphosphanes such as $(i\text{-}Pr)_3P$ generate the corresponding zerovalent palladium complexes along with ethane at $>0\,^\circ C$, while, the use of triarylphosphanes or phosphites as ligands of dimethylpalladium(II) complexes results in the formation of zerovalent palladium complexes by heating at 70–80 °C [5]. In addition, dimethylpalladium(II) complexes having bidentate ligands such as $Ph_2PCH_2CH_2PPh_2$ requires heating at the higher temperature for the formation of zerovalent palladium complex along with ethane [7]. In the case of strained dimethylpalladium(II) complex, $[PdMe_2\{PCy_2(CH_2)PCy_2\}]$, the reductive elimination takes place at the lower temperature [8]. These reactivities of dimethylpalladium complexes have been explained by the reaction mechanism described below [2–4]. At first, elimination of a ligand results in the formation of 3-coordinate complex. Since low electron density on the metal accelerates the reductive elimination, the elimination of ethane occurred from the 3-coordinate complex. Therefore, monodentate ligands and strained complexes lead to ready elimination.

We have recently synthesized new PS_3-type tripodal tetradentate ligands and their complexes with group 10 metals [17,18]. As for palladium complexes, dichloropalladium complex **2** was synthesized by reaction of PS_3-type ligand **1** with $[PdCl_2(PhCN)_2]$, and the treatment of **2** with $NaBF_4$ afforded five-coordinate cationic palladium complex **3** (Scheme 1). We have revealed that the PS_3-type ligand **1** can stabilize 5-coordinate structures. This paper presents the synthesis of dimethylpalladium complex **4** from complexes **2**, **3** and its structure and reactivities.

2. Experimental section

2.1. General procedures

All reactions were carried out under an argon atmosphere unless otherwise noted. Tetrahydrofuran was purified by distillation from sodium diphenylketyl before use. Other solvents used in reactions were purified by the reported methods. An ether solution of methyllithium (Br free) and an ether solution of methyllithium (containing LiBr) were bought form Kanto Chemical Co., Inc. Wet column chromatography (WCC) was performed with Merck Silica Gel 60 (70–230 mesh ASTM). The ^1H NMR (600, 500 or 400 MHz), ^{13}C NMR (150 or 126 MHz), and ^{31}P NMR (243 or 202 MHz) spectra

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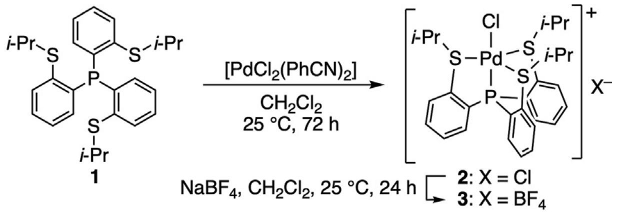


Scheme 1. Synthesis of palladium complexes 2, 3 bearing PS_3-ligand.

were measured in $CDCl_3$ with a JEOL JNM-ECA600, JNM-λ500 or JNM-ECS400 spectrometer using $SiMe_4$ (0 ppm) as internal standards for ^1H NMR spectroscopy, $CDCl_3$ (77.0 ppm) as those for ^{13}C NMR spectroscopy, and H_3PO_4 (85%) in D_2O (0 ppm) as an external standard for ^{31}P NMR spectroscopy. The UV/vis spectra were recorded on a JASCO V-550 UV/vis spectrometer. All melting points were determined on a Yanaco micro melting point apparatus MP-J3 and are uncorrected. Elemental analyses were performed by the Center for Material Research by Instrumental Analysis (CIA), Gunma University.

2.2. *Synthesis of [Pd(CH_3)$_2${P(C_6H_4-2-S-i-Pr)$_3$}] (**4**) from **3***

To a benzene solution (5.0 mL) of [PdCl{P(C_6H_4-2-S-*i*-Pr)$_3$}]BF_4 (**3**) [17] (250 mg, 0.350 mmol) was slowly added an ether solution of methyllithium (1.05 M, Br free; 1.0 mL, 1.05 mmol) with stirring at ambient temperature. After stirring for 15 min, the resulting yellow solution was evaporated under reduced pressure to dryness. Benzene was added to the residue and the mixture was filtrated to remove insoluble materials. The solvent of the filtrate was removed under reduced pressure to afford [Pd(CH_3)$_2${P(C_6H_4-2-S-*i*-Pr)$_3$}] (**4**) (189 mg, 0.304 mmol, 87%). **4**: yellow crystals, mp 130 °C (decomp.); ^1H NMR (500 MHz, C_6D_6): δ 1.05 (d, $^3J_{HH} = 7$ Hz, 9H), 1.14 (d, $^3J_{HH} = 7$ Hz, 9H), 1.22 (brs, 3H), 1.41 (brs, 3H), 3.13 (sep, $^3J_{HH} = 7$ Hz, 3H), 6.78 (dd, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$ Hz, 3H), 6.94 (dd, $^3J_{HH} = 7$, 7 Hz, 3H), 7.11 (dd, $^3J_{HH} = 7$ Hz, $J_{HP} = 7$ Hz, 3H), 7.32 (dd, $^3J_{HH} = 7$ Hz, $^4J_{HP} = 3$ Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 2.86 (d, $^2J_{CP} = 116$ Hz, CH_3), 6.24 (d, $^2J_{CP} = 3$Hz, CH_3), 23.1 (CH_3), 41.5 (CH), 127.2 (d, $J_{CP} = 4$ Hz, CH), 128.3 (d, $J_{CP} = 11$Hz, CH), 130.2 (CH), 135.4 (d, $J_{CP} = 3$ Hz, CH), 138.1 (d, $^1J_{CP} = 29$ Hz), 142.7 (d, $^2J_{CP} = 24$ Hz); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 29.9 (s); UV/vis (benzene) λ_{max} 310 (ε 8700) nm. Anal. Calcd. for $C_{29}H_{39}PPdS_3 \cdot 0.5H_2O$: C, 55.27; H, 6.40%. Found: C, 54.97; H, 6.27%.

2.3. *Synthesis of [Pd(CH_3)$_2${P(C_6H_4-2-S-i-Pr)$_3$}] (**4**) from **2***

To a benzene solution (2.0 mL) of [PdCl{P(C_6H_4-2-S-*i*-Pr)$_3$}]Cl (**2**) [17] (50 mg, 0.076 mmol) was slowly added an ether solution of methyllithium (0.96 M, Br free; 0.2 mL, 1.92 mmol) with stirring at ambient temperature. After stirring for 15 min, the resulting solution was evaporated under reduced pressure to dryness. Benzene was added to the residue and the mixture was filtrated to remove insoluble materials. The solvent of the filtrate was removed under reduced pressure to afford [Pd(CH_3)$_2${P(C_6H_4-2-S-*i*-Pr)$_3$}] (**4**) (30 mg, 0.048 mmol, 64%).

2.4. *Reaction of **3** with MeLi (containing LiBr)*

To a benzene solution (2.0 mL) of [PdCl{P(C_6H_4-2-S-*i*-Pr)$_3$}]BF_4 (**3**) (50 mg, 0.07 mmol) was slowly added an ether solution of methyllithium (0.96 M, containing LBr; 0.2 mL, 0.19 mmol) with stirring at ambient temperature. After stirring for 15 min, the resulting solution was evaporated under reduced pressure to dryness. Benzene was added to the residue and the mixture was filtrated to remove insoluble materials. The solvent of the filtrate was removed under reduced pressure and the resulting residue was reprecipitated from hexane/$CHCl_3$ to give a mixture (20 mg) mainly containing [PdBr(CH_3){P(C_6H_4-2-S-*i*-Pr)$_3$}] (**5**). **5**: red crystals; ^1H NMR (500 MHz, $CDCl_3$): δ 1.11 (d, $^3J_{HP} = 3$ Hz, 3H), 1.25 (d, $^3J_{HH} = 7$Hz, 18H), 3.42 (sep, $^3J_{HH} = 7$ Hz, 3H), 7.17–7.24 (m, 3H), 7.39–7.48 (m, 6H), 7.58 (dd, $^3J_{HH} = 8$ Hz, $J_{HP} = 4$ Hz, 3H); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 43.8 (s).

2.5. *Reaction of **4** with an equimolar amount of $R^{Si}Cl$ ($R^{Si} = SiMe_3$, $SiMe_2Ph$)*

To a C_6D_6 solution (0.6 mL) of **4** (25 mg, 0.040 mmol) and a small amount of H_2O was added $R^{Si}Cl$ ($R^{Si} = SiMe_3$: 4 mg, 0.040 mmol; $R^{Si} = SiMe_2Ph$: 7 mg, 0.040 mmol) at ambient temperature and the mixture was stirred for 10 min at the same temperature. After removal of the solvent under reduced pressure, the residue was washed with hexane. The dryness under vacuum afforded [PdCl(CH_3){P(C_6H_4-2-S-*i*-Pr)$_3$}] (**6**) (23 mg, 0.036 mmol, 90% for $R^{Si} = SiMe_3$; 21 mg, 0.033 mmol, 81% for $R^{Si} = SiMe_2Ph$). **6**: orange crystals, mp 170 °C (decomp.); ^1H NMR (500 MHz, $CDCl_3$): δ 1.00 (d, $^3J_{HP} = 2$ Hz, 3H), 1.19 (d, $^3J_{HH} = 7$ Hz, 18H), 3.36 (sep, $^3J_{HH} = 7$ Hz, 3H), 7.15 (dd, $^3J_{HH} = 8$, 8 Hz, 3H), 7.35 (dd, $^3J_{HH} = 8$Hz, $^3J_{HP} = 11$ Hz, 3H), 7.39 (dd, $^3J_{HH} = 8$, 8 Hz, 3H), 7.51 (dd, $^3J_{HH} = 8$Hz, $^4J_{HP} = 4$Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 12.8 (d, $^2J_{CP} = 5$ Hz, CH_3), 22.9 (CH_3), 41.8 (CH), 126.7 (d, $J_{CP} = 8$ Hz, CH), 131.6 (d, $J_{CP} = 2$ Hz, CH), 132.5 (d, $J_{CP} = 8$ Hz, CH) 133.3 (d, $^1J_{CP} = 53$ Hz), 136.3 (d, $J_{CP} = 8$ Hz, CH), 141.0 (d, $^2J_{CP} = 15$ Hz); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 43.8 (s). UV/vis (chloroform) λ_{max} 310 (ε 8200), 350 (ε 2600) nm. Anal. Calcd. for $C_{28}H_{36}ClPPdS_3 \cdot H_2O$: C, 50.98; H, 5.81%. Found: C, 51.17; H, 5.63%.

2.6. *Reaction of **4** with 2 M amounts of $R^{Si}Cl$ ($R^{Si} = SiMe_3$, $SiMe_2Ph$)*

To a C_6D_6 solution (0.6 mL) of **4** (25 mg, 0.040 mmol), ethylbenzene 20 mg (0.19 mmol) (standard), and a small amount of H_2O was added $R^{Si}Cl$ ($R^{Si} = SiMe_3$: 9 mg, 0.080 mmol; $R^{Si} = SiMe_2Ph$: 14 mg, 0.080 mmol) at ambient temperature and the mixture was stirred for 10 min at the same temperature. The ^1H NMR spectrum of the reaction mixture represented the formation of $R^{Si}{}_2O$ ($R^{Si} = SiMe_3$: 60%; $R^{Si} = SiMe_2Ph$: 80%. The yields were estimated by the ratio with the integrals of peaks for ethylbenzene). After removal of the solvent under reduced pressure, the residue was washed with hexane. The dryness under vacuum afforded [$PdCl_2${P(C_6H_4-2-S-*i*-Pr)$_3$}] (**2**) (25 mg, 0.038 mmol, 94% for $R^{Si} = SiMe_3$; 23 mg, 0.035 mmol, 86% for $R^{Si} = SiMe_2Ph$) [18].

2.7. *Reaction of **4** with excess of $R^{Si}Cl$ ($R^{Si} = SiMe_3$, $SiMe_2Ph$)*

To a C_6D_6 solution (0.6 mL) of **4** (21 mg, 0.034 mmol) and a small amount of H_2O was added $R^{Si}Cl$ ($R^{Si} = SiMe_3$: 74 mg, 0.68 mmol; $R^{Si} = SiMe_2Ph$: 116 mg, 0.68 mmol) at ambient temperature and the mixture was stirred for 10 min at the same temperature. After removal of the solvent under reduced pressure, the residue was washed with hexane. The dryness under vacuum afforded [$PdCl_2${P(C_6H_4-2-S-*i*-Pr)$_3$}] (**2**) (19 mg, 0.028 mmol, 86% for $R^{Si} = SiMe_3$; 15 mg, 0.023 mmol, 68% for $R^{Si} = SiMe_2Ph$) [18].

2.8. *Reaction of **4** with HCl*

To a benzene solution (2 mL) of **4** (25 mg, 0.040 mmol) was added an ether solution of HCl [0.05 M solution, 0.80 mL (0.040 mmol) for run 1; 1.0 M solution, 0.080 mL (0.080 mmol) for run 2; 1.0 M solution, 0.80 mL (0.80 mmol) for run 3), and the mixture was stirred for 10 min at room temperature. After removal of the precipitates by filtration, the filtrate was evaporated to dryness. The residue was washed with hexane and then dried under vacuum to afford [PdCl(CH$_3$){P(C$_6$H$_4$-2-S-*i*-Pr)$_3$}] (**6**) (25 mg, 0.039 mmol, 97%) for run 1, or [PdCl$_2${P(C$_6$H$_4$-2-S-*i*-Pr)$_3$}] (**2**) (26 mg, 0.039 mmol, 98%) for runs 2 and 3.

2.9. X-ray crystallography of **4**, **5**, and **6**

Single crystals of **4**, **5**, and **6** suitable for X-ray structural analysis were obtained by slow recrystallization from hexane/benzene for **4** and hexane/CHCl$_3$ for **5** and **6**. The crystals were mounted on glass fibers for **4** and **5**. The crystal of **6** was immersed in a drop of oil and mounted on a MicroMount. The intensity data were collected on Rigaku R-AXIS IV^{++} diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) for **4** and **5** and on a Rigaku Vari-Max with an XtaLab P200 diffractometer with multi-layer mirror monochromated Mo Kα radiation ($\lambda = 0.71075$ Å) for **6**. The structures were solved by direct methods (SHELXS-97 [19]) for **4** and **5** and by using SHELXT [20] for **6**, and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97 [19] for **4** and **5** and SHELXL-2014/7 [21] for **6**). All the non-hydrogen atoms were refined anisotropically. All hydrogens were placed using AFIX instructions. The crystal data and refinement details are shown in Table 1. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-1896333, CCDC-1896334, and CCDC-1896335 for compounds **4**, **5**, and **6**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Synthesis of dimethylpalladium complex **4**

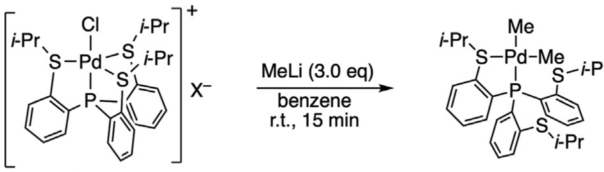
When cationic palladium complex **3** was treated with 3 M amounts of MeLi (Br free), the corresponding dimethylpalladium complex **4** was obtained in 87% yield (Scheme 2). The structure of complex **4** was determined by ^{1}H, ^{13}C, and ^{31}P NMR spectra, and characteristic peaks assigned to two methyl groups were observed at 1.22 and 1.41 ppm as broad peaks in the ^{1}H NMR spectrum and at 2.86 (d, $^2J_{CP} = 116$ Hz) and 6.24 (d, $^2J_{CP} = 3$ Hz) ppm as doublet peaks in the ^{13}C{^{1}H} NMR spectrum. The molecular structure of **4** was finally determined by X-ray crystallography, showing 4-coordinate square planar structure (Fig. 1). The detailed discussion on the structure in the crystalline state and in solution will be shown below.

The treatment of dichloropalladium complex **2** with 3 M amounts of MeLi also afford dimethylpalladium complex **4** in 64% yield (Scheme 2).

On the other hand, the methylation of **3** by the use of an ether solution of MeLi containing LiBr did not afford dimethylpalladium complex **4**, and a mixture mainly containing bromomethylpalladium complex **5** was obtained. The structure of **5** was determined by ^{1}H NMR spectrum and X-ray crystallography (Fig. 2), although complex **5** could not be isolated.

3.2. Reactivities of dimethylpalladium complex **4**

Dimethylpalladium complex **4** is stable in the solid state at room temperature in air, and can be stored under such conditions. In addition, a C$_6$D$_6$ solution of **4** is also stable at room temperature in



2: X = Cl; **3**: X = BF$_4$

4

Scheme 2. Synthesis of dimethylpalladium complex **4**.

Table 1
Crystal data and refinement details for **4**, **5**, and **6**.

	4	**5**	**6**
empirical formula	$C_{29}H_{39}PPdS_3$	$C_{28}H_{36}BrPPdS_3$	$C_{28}H_{36}ClPPdS_3$
formula weight	621.15	686.03	641.57
temperature (K)	153(2)	153(2)	130(2)
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	P–1 (No. 2)	P–1 (No. 2)
a (Å)	17.430(2)	9.5871(5)	9.591(3)
b (Å)	9.6606(10)	11.3925(4)	11.181(3)
c (Å)	19.903(2)	15.1277(17)	15.130(5)
α (deg)	90	77.156(13)	77.561(17)
β (deg)	112.3141(10)	87.783(15)	88.097(19)
γ (deg)	90	65.614(11)	65.473(14)
V (Å^3)	3100.5(6)	1464.58(19)	1438.6(8)
Z	4	2	2
D_{calc} (Mg m^{-3})	1.331	1.556	1.481
absorp coeff (mm^{-1})	0.867	2.282	1.027
crystal size (mm)	0.30 × 0.20 × 0.10	0.30 × 0.10 × 0.05	0.03 × 0.01 × 0.01
θ range	3.39–25.49°	3.39–25.50°	2.640–27.497°
no. of reflns measd	21415	10068	23563
no. of indep reflns	5750	5107	6575
R_{int}	0.0853	0.0458	0. 1554
completeness	99.6%	93.4%	99.5%
data/restraints/parameters	5750/0/307	5107/0/307	6575/0/314
goodness–of–fit on F^2	1. 282	1.106	1. 155
final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.$ 0755 w$R_2 = 0.1977$	$R_1 = 0.$ 0586 w$R_2 = 0.1116$	$R_1 = 0.$ 0870 w$R_2 = 0.$ 1609
R indices (all data)[a]	$R_1 = 0.$ 0784 w$R_2 = 0.2003$	$R_1 = 0.$ 0777 w$R_2 = 0.1212$	$R_1 = 0.$ 1632 w$R_2 = 0.$ 2020
largest diff. peak and hole (e Å^{-3})	1.213 and −1.274	0.652 and −1.233	2.634 and −0.858

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = [(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

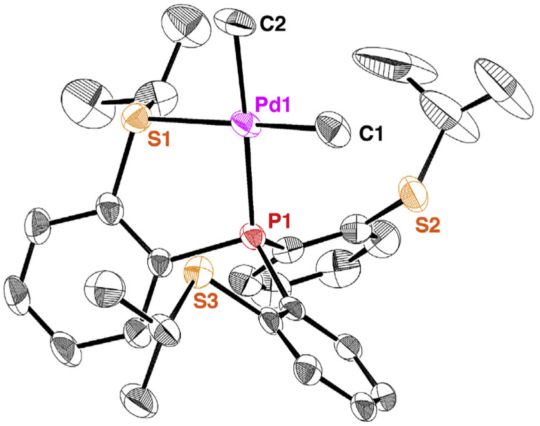


Fig. 1. ORTEP drawing of complex **4** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

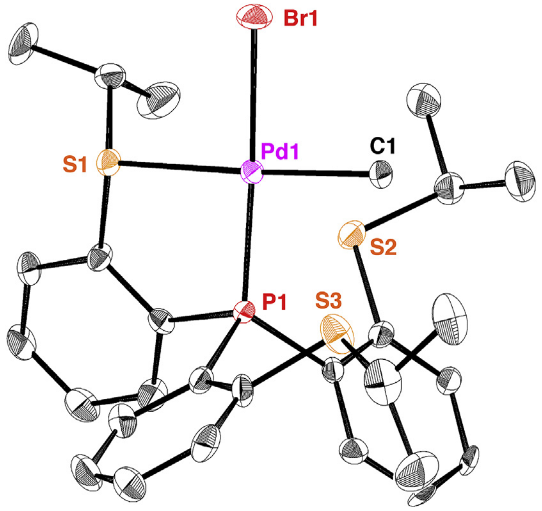
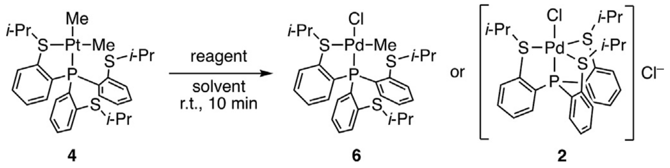


Fig. 2. ORTEP drawing of complex **5** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.



Scheme 3. Reaction of dimethylpalladium complex **4** with chlorosilanes or HCl.

Table 2
Reaction of dimethylpalladium complex **4** with $R^{Si}Cl$ or HCl.

reagent	solvent	6	2
Me_3SiCl (1.0 eq), H_2O	C_6D_6	90%	
Me_3SiCl (2.0 eq), H_2O	C_6D_6		94%
Me_3SiCl (excess), H_2O	C_6D_6		86%
$Me_2PhSiCl$ (1.0 eq), H_2O	C_6D_6	81%	
$Me_2PhSiCl$ (2.0 eq), H_2O	C_6D_6		86%
$Me_2PhSiCl$ (excess), H_2O	C_6D_6		68%
HCl (1.0 eq)	benzene	97%	
HCl (2.0 eq)	benzene		98%
HCl (excess)	benzene		98%

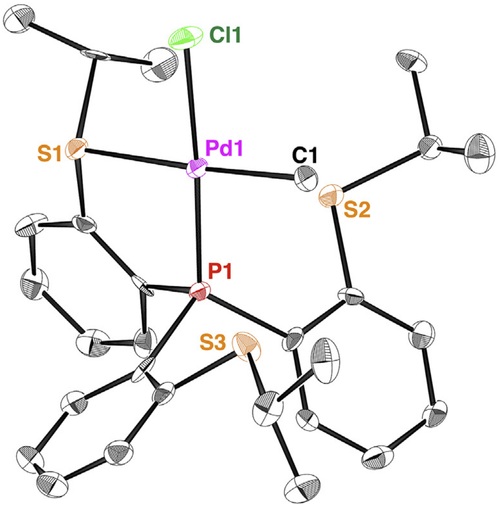


Fig. 3. ORTEP drawing of complex **6** with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

air for several hours and it can be handled in air. When a solution of **4** in C_6D_6 stood at 25 °C for 1 d under Ar atmosphere, no change was observed in the ^1H NMR spectrum. However, when the solution was further left at 25 °C for 6 d, the gradual decomposition of **4** took place to afford a complicated mixture containing the starting material **4** without observation of the formation of ethane. When a C_6D_6 solution of **4** was treated with trapping reagents such as PhI, Ph_2SiH_2, Ph_3SiH, Et_3SiH, hex-1-ene, CH_3CN, or S_8, the expected adducts such as [PdI(Ph)(L)], [PdH(R^{Si})(L)] (R^{Si} = $SiHPh_2$, $SiPh_3$, $SiEt_3$), or [Pd(L)(L′)] (L′ = hex-1-ene, CH_3CN) (L = **1**) could not be observed. It was revealed that dimethylpalladium complex **4** gradually decomposes at 25 °C in C_6D_6 solution although the reductive elimination of ethane from **4** could not be confirmed.

When dimethylpalladium complex **4** was treated with an equimolar amount of Me_3SiCl in the presence of a small amount of H_2O in C_6D_6, chloromethylpalladium complex **6** was formed in 88% yield (Scheme 3 and Table 2). The structure of **6** was determined by the ^1H, ^{13}C, and ^{31}P NMR spectra and X-ray crystallography (Fig. 3). The ORTEP drawing showed that the structure in the crystalline state is 4-coordinate square planar structure where the methyl group is on the *cis* position of the phosphorus atom. In the ^1H and ^{13}C NMR spectra, characteristic peaks assigned to methyl group were observed at 1.00 (d, $^3J_{HP} = 2$ Hz, 3H) ppm as a sharp doublet peak in the ^1H NMR spectrum and at 12.8 (d, $^2J_{CP} = 5$ Hz) ppm as a doublet peak in the $^{13}C\{^1H\}$ NMR spectrum. The values of the coupling constant with the ^{31}P nucleus, $^3J_{HP} = 2$ Hz and $^2J_{CP} = 5$ Hz, strongly suggest that the methyl group is situated on the *cis* position of the ^{31}P nucleus also in solution [22–24]. The detailed structure of **6** will be discussed in the following sections.

On the other hand, the reaction of **4** with 2 M amounts or excess of Me_3SiCl resulted in the substitution of both methyl groups by Cl atoms to afford dichloropalladium complex **2** in 94% or 86% yield, respectively (Scheme 3 and Table 2). In addition, the similar reactions using $PhMe_2SiCl$ instead of Me_3SiCl also lead to the similar results.

The reaction of **4** with freshly distilled $PhMe_2SiCl$ without the addition of H_2O in C_6D_6, resulted in the formation of a mixture of dimethylpalladium complex **4**, chloromethylpalladium complex **6**, $PhMe_2SiCl$, and $(PhMe_2Si)_2O$ with the ratio of 3.9:5.5:2.3:1. The existence of both **4** and $PhMe_2SiCl$ in the mixture suggests that complex **4** does not react directly with $PhMe_2SiCl$. The formation of **6** can be explained by hydrolysis of $PhMe_2SiCl$ giving HCl and $(PhMe_2Si)_2O$ and the subsequent reaction of **4** with HCl yielding **6**

Table 3
Selected bond lengths (Å) and angles (°) for **4**, **5**, and **6**.

	4 (X = C2)	**5** (X = Br)	**6** (X = Cl)
Pd–X[i]	2.088(6)	2.4970(8)	2.371(3)
Pd–C1	2.067(6)	2.105(5)	2.058(9)
Pd–P	2.3107(14)	2.2449(17)	2.230(3)
Pd–S1	2.3894(15)	2.4064(15)	2.405(3)
Pd···S2	3.8336(17)	3.4000(16)	3.432(2)
Pd···S3	3.6112(17)	3.785(2)	3.781(3)
X–Pd–P	177.5(2)	177.04(5)	176.47(11)
S1–Pd–C1	172.90(19)	174.83(19)	174.3(3)
X–Pd–C1[i]	84.2(3)	86.89(18)	88.1(3)
C1–Pd–P	98.2(2)	94.98(18)	94.7(3)
P–Pd–S1	84.27(5)	86.79(6)	86.33(9)
S1–Pd–X[i]	93.2(2)	91.54(5)	91.16(9)

[i] X = C2 for **4**, X = Br for **5**, X = Cl for **6**.

along with methane. This mechanism is supported by the formation of $(PhMe_2Si)_2O$ or $(Me_3Si)_2O$ in the reaction of **4** with $PhMe_2SiCl$ or Me_3SiCl, respectively. In addition, this mechanism was further supported by the reaction of **4** with HCl. The treatment of dimethylpalladium complex **4** with an equimolar amount of HCl resulted in the formation of chloromethylpalladium complex **6** in 97% yield, while the use of 2 M amounts of HCl afforded dichloropalladium complex **2** in 98% yield (Scheme 3 and Table 2).

3.3. Crystal structure of complexes **4**–**6**

The X-ray structural analyses of **4** and **5** are the first structural analyses of dialkyl- and bromoalkyl-palladium complexes bearing phosphine and thioether ligands, although some alkylchloropalladium complexes bearing phosphine and thioether ligands has been reported [22–25]. Figs. 1–3 show the square planar structure around the Pd atoms of complexes **4**–**6**. The selected bond lengths and angles of complexes **4**–**6** are shown in Table 3. Since the Pd···S2 and Pd···S3 distances of complexes **4**–**6** are very near or longer compared with the sum of van der Waals radii of Pd (1.63 Å) and S (1.80 Å) atoms [26], it can be concluded that there is no or very weak interaction between Pd and S2 or S3 atoms. The Pd–C1 bond lengths of **4**–**6** are very close each other, although the value of **5** (2.105(5) Å) is slightly longer than those of **4** and **6** (2.067(6) and 2.058(9) Å). They are also close to the reported Pd–C bond lengths situated in the *trans* position of thioether ligands, 2.069(6) Å for $[PdClMe(Ph_2PCH_2C_6H_4\text{-}2\text{-}SMe\text{-}\kappa^2P,S)]$ [23], 2.068(4) Å for $[PdClMe(Ph_2PC_6H_4\text{-}2\text{-}CH_2SPh\text{-}\kappa^2P,S)]$ [24], and 2.049(5) Å for $[PdClMe\{Fe(\eta^5\text{-}C_5H_5)(Ph_2P\text{-}\eta^5\text{-}C_5H_3\text{-}2\text{-}S\text{-}t\text{-}Bu)\text{-}\kappa^2P,S\}]$ [22]. In dimethylpalladium complex **4**, the bond distance of the Pd–C2 bond (2.088(6) Å) situated in the *trans* position of the phosphine ligand is slightly longer than that of the Pd–C1 bond situated in the *trans* position of the thioether ligand. This difference can be explained by stronger *trans* influence of phosphine ligands than that of thioether ligands. The Pd–C2 bond length is normal value as Pd–C bond lengths of dimethylpalladium complexes bearing bisphosphine ligands, 2.084(3) and 2.087(3) Å for $[PdMe_2\{Ph_2P(CH_2)_3PPh_2\text{-}\kappa^2P,P\}]$ [6], and 2.090(3) and 2.089(3) Å for *cis*-$[PdMe_2(PMePh_2)_2]$ [27].

3.4. Dynamic behavior of dimethylpalladium complex **4** and chloridomethylpalladium complex **6**

The dynamic behaviors of dimethylpalladium complex **4** and chloridomethylpalladium complex **6** in solution were investigated by the variable temperature (VT) ^1H NMR studies.

The VT ^1H NMR spectra of **4** (Fig. 4) show that the methyl groups of isopropyl groups were observed as one set of broaden doublet peak at 100 °C, as one broad peak at 60 °C, and as two sets of doublet peaks at 20 and 0 °C. The measurements at the lower

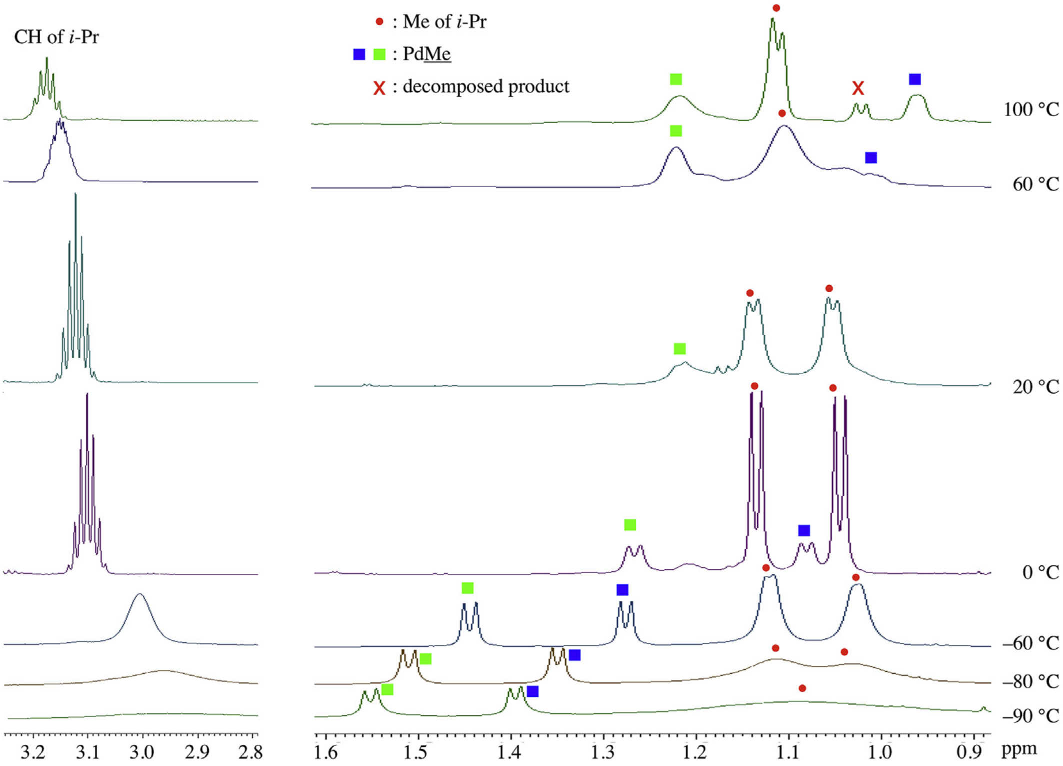


Fig. 4. Variable temperature ^1H NMR spectra of **4** (600 MHz, toluene-d_8).

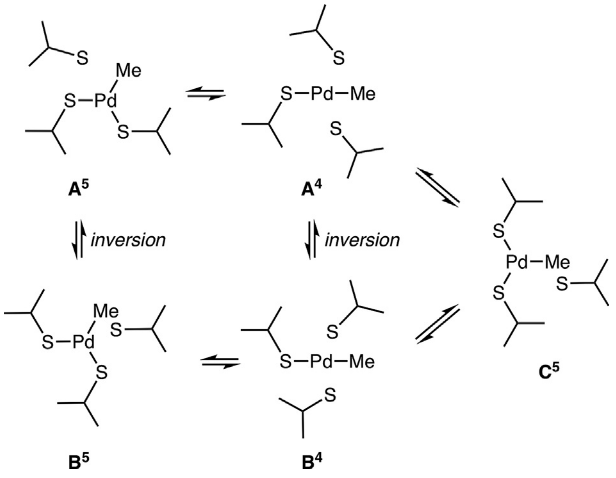
temperature (−20, −60, −80, and −90 °C) result in the broadening of the peaks. On the other hand, the methine protons of the isopropyl groups were observed always as one peak at −90 to 100 °C, although the methine peaks were broadened at 60, −60, −80, and −90 °C. These observations can be explained by the dynamic behavior described below. At 100 and 60 °C, all the methyl and methine groups of isopropyl groups are equivalent, which indicates rapid equilibrium among **A^5**, **A^4**, **C^5**, **B^4** and **B^5** (Scheme 4). At 20, 0, −60, and −80 °C, the three isopropyl groups are equivalent although the two methyl groups of the isopropyl group are non-equivalent. These results can be interpreted by the rapid coordination/elimination of thioether ligands on the palladium metal (*e.g.* rapid equilibrium between **A^5** and **A^4** structures) along with the restricted inversion on the sulfur atoms and the restricted equilibrium among **A^4**, **C^5**, and **B^4** (Scheme 4).

On the other hand, the ^{1}H NMR spectrum of chloromethylpalladium complex **6** always showed one methyl and one methine peaks of the isopropyl groups at −60 to 60 °C, and these signals broadened at the lower temperatures (at −20 and −60 °C) (Fig. 5), which suggests the rapid equilibrium among **A^5**, **A^4**, **C^5**, **B^4** and **B^5** at −60 to 60 °C (Scheme 4).

This difference in the dynamic behaviors of complexes **4** and **6** can be explained by the lower electron density on the palladium atom of **6** than that of **4** derived from the higher electron negativity of Cl than Me. The lower electron density on the palladium results in the stabilization of 5-coordinate structure **C^5**, which is an intermediate of the interconversion between **A^4** and **B^4**. Therefore, it is considered that the stabilization of 5-coordinate structure **C^5** leads to the rapid interconversion among **A^5**, **A^4**, **C^5**, **B^4** and **B^5**.

4. Conclusion

Dimethylpalladium complex **4** bearing PS_3-type tripodal tetradentate ligand was synthesized by the reaction of $[PdCl\{P(C_6H_4\text{-}2\text{-}S\text{-}i\text{-}Pr)_3\}]X$ (**2**: X = Cl, **3**: X = BF_4) with 3 M amounts of methyllithium (LiBr free). The use of methyllithium (containing LiBr) in this reaction resulted in the formation of bromomethylpalladium complex **5**. Dimethylpalladium complex **4** is stable in the solid state at room temperature in air, and its solution in C_6D_6 is also stable at 25 °C for several hours in air. However, when the solution stood at 25 °C for 6 d under argon atmosphere, dimethylpalladium complex **4** underwent gradual decomposition to give complicated mixture although the reductive elimination of ethane from **4** could not be confirmed. Dimethylpalladium complex **4** reacted with an equimolar amount of chlorosilanes in the presence of small amounts of H_2O to give the corresponding chloromethylpalladium complex, $[PdClMe\{P(C_6H_4\text{-}2\text{-}S\text{-}i\text{-}Pr)_3\}]$ (**6**), while the similar reaction of **4** using 2 M amounts of chlorosilanes afforded the dichloropalladium complex **2**. The reaction of **4** with an equimolar amount of HCl also afforded **6** selectively, and the use of 2 M amounts of HCl resulted in the formation of **2**. The variable temperature ^{1}H NMR spectra of **4** and **6** suggested the existence of the equilibrium between 4- and 5-coordinate structures.



Scheme 4. Equilibrium between 4- and 5-coordinate structures. The view from the direction along the X–Pd–P bond, extracting the Pd, Me, and *i*-PrS parts.

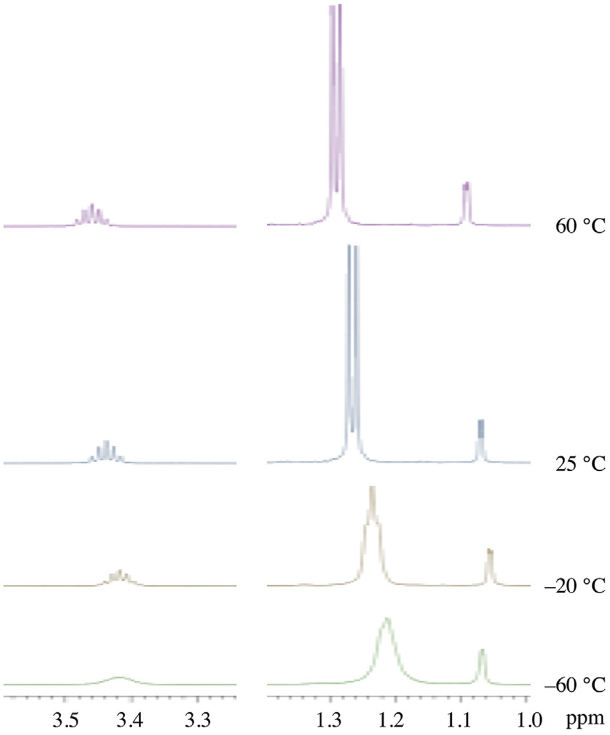


Fig. 5. Variable temperature ^{1}H NMR spectra of **6** (600 MHz, $CDCl_3$).

It was revealed that dimethylpalladium complex **4** is easily handled in air and the reaction of **4** with HCl selectively affords chloromethylpalladium complex **6** or dichloropalladium complex **2** depending on the molar ratio of HCl. The application of complex **4** to the synthesis of new organopalladium complexes bearing the PS_3 ligand and the catalyst for organic reactions are strongly expected.

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