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Synthesis and Structure of Group 10 Metal Complexes with New Tripodal Tetradentate Ligand Bearing One Phosphine and Three Thioether Moieties

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A new tripodal tetradentate ligand bearing one phosphine and three thioether moieties, $[2\text{-}(i\text{-PrS})C_6H_4]_3P$ (**1b**), was synthesized by the reaction of $[2\text{-}(i\text{-PrS})C_6H_4]Li$ with PCl_3 in good yield. Ligand **1b** reacted with $NiCl_2\cdot 6H_2O$ in the presence of $NaBF_4$ to afford a five-coordinate complex, [NiCl(**1b**)]BF_4 (**2**), with slightly distorted trigonal-bipyramidal geometry. Reaction of **1b** with $[PdCl_2(PhCN)_2]$ gave a five-coordinate complex, [PdCl(**1b**)]Cl (**3a**). Anion-exchange reaction of palladium(II) complex **3a** with $NaBF_4$ afforded [PdCl(**1b**)]BF_4 (**3b**) with distorted trigonal-bipyramidal structure. Reaction of **1b** with $[PtCl_2(cod)]$ resulted in the formation of a four-coordinate square-planar complex, [$PtCl_2$(**1b**)] (**4**). The structures of **2**, **3b**, and **4** in crystalline state were determined by X-ray structural analysis and are described in detail. The structures of **2**–**4** in solution were also discussed.

In recent years, much attention has been focused on the chemistry of transition-metal complexes bearing tripodal tetradentate ligands from the viewpoints of the activation of small molecules, the stabilization of reactive species with unusual electric and geometric structures, catalytic activities, and so on.[1] Although there are many reports on tripodal tetradentate ligands bearing nitrogen or phosphorus atoms, the chemistry of those bearing one phosphine and three thioether moieties is less explored. Such ligands are expected to show unique structures and reactivities derived from the lability of the coordination of thioether moieties to metals and the property of phosphine as an anchor ligand. Tris(2-methylthiophenyl)phosphine (**1a**) (Chart 1) has been only reported as phosphine ligands tethered with three thioether moieties so far, and there have been several papers on the synthesis and structures of its complexes with nickel(II),[2–5] palladium(II),[6,7] platinum(II),[7] molybdenum(0), and molybdenum(II)[8] metals and the use of **1a** as a ligand in a rhodium-catalyzed reaction.[9]

Meek and co-workers have reported that the methyl-substituted ligand **1a** forms five-coordinate trigonal-bipyramidal complexes with nickel(II), [NiX(**1a**)]ClO_4 (X = Cl, Br, I, and NCS) and [Ni(**1a**)L]$(ClO_4)_2$ (L = $S{=}C(NH_2)_2$, PPh_3, and $PMePh_2$).[2,4] In the case of the palladium(II) complexes, they have isolated only four-coordinate square-planer complexes, [$PdCl_2$(**1a**)]·dmf, [Pd(**1a**)$_2$]$(ClO_4)_2$, [Pd_2Cl_4(**1a**)],[6,7] although the UV–vis spectra of these palladium(II) complexes in solution fit the trends of five-coordinate complexes. Their numerous attempts to isolate a pure five-coordinate complex, [PdCl(**1a**)]ClO_4, have been unsuccessful owing to the precipitation of insoluble [Pd(**1a**)$_2$]$(ClO_4)_2$ and [Pd_2Cl_4(**1a**)]. As for a platinum(II) complex of **1a**, only a four-coordinate square-planar bis(chelate) complex, [Pt(**1a**)$_2$]$(ClO_4)_2$, where **1a** functions as a bidentate ligand, has been synthesized.[7] The structures of these complexes are determined by spectroscopic data and elemental analyses, and the X-ray structural analyses have been only reported for [NiCl(**1a**)]ClO_4[5] and [Pd(**1a**)$_2$]$(ClO_4)_2$.[7]

From these results, we considered that the replacement of methyl groups on the sulfur atoms in ligand **1a** by bulky groups can suppress the formation of bis(chelate) complexes such as [Pd(**1a**)$_2$]$^+$ and [Pt(**1a**)$_2$]$^+$ and lead to the isolation of the corresponding five-coordinate complexes. In this work, we describe the synthesis and structure of the isopropyl-substituted ligand **1b** and its coordination chemistry with group 10 metals.

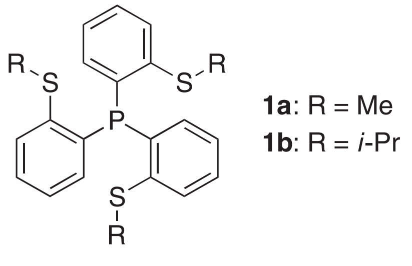


Chart 1.

Experimental

General Procedures. All reactions were carried out under an argon atmosphere unless otherwise noted. Tetrahydrofuran was purified by distillation from sodium diphenyl ketyl before use. Wet column chromatography (WCC) was performed with Merck Silica Gel 60 (70–230 mesh ASTM). The ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{31}P NMR (202 MHz) spectra were measured in $CDCl_3$ with a JEOL JNM-λ500 spectrometer using $SiMe_4$ (0 ppm) as internal standards for ^{1}H 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 Shimadzu UV-2500PC 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.

Preparation of Tris(2-isopropylthiophenyl)phosphine (1b). To a mixture of hexane (15 mL), isopropyl phenyl sulfide[10] (1.00 g, 6.57 mmol), and TMEDA (2.0 mL, 13.1 mmol) was added a hexane solution of butyllithium (1.65 M, 4.79 mL, 7.90 mmol) at 25 °C. After heating at 50 °C for 1 h, the mixture was cooled to −40 °C, and PCl_3 (0.23 mL, 2.63 mmol) was added at this temperature. The reaction mixture was stirred at −40 °C for 3 h, then warmed to 25 °C over 12 h. After addition of a saturated aqueous solution of NH_4Cl, the mixture was extracted with hexane/chloroform (1:1), and the organic layer was dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure, and the residue was separated by WCC (SiO_2, hexane:chloroform = 1:1) to afford pure tris(2-isopropylthiophenyl)phosphine (**1b**) (1.02 g, 2.10 mmol, 96%). **1b**: colorless crystals, mp 143–145 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (brs, 18H, CH_3), 3.61 (sep, $^3J_{HH} = 7$ Hz, 3H), 6.65 (d, $^3J_{HH} = 8$ Hz, 3H), 7.12 (dd, $^3J_{HH} = 8$, 8 Hz, 3H), 7.27 (dd, $^3J_{HH} = 8$, 8 Hz, 3H), 7.53 (dd, $^3J_{HH} = 8$ Hz, $^2J_{HP} = 4$ Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 23.1 (CH_3), 40.0 (d, $J_{CP} = 7$ Hz, CH), 127.8 (CH), 128.7 (CH), 134.1 (CH), 134.5 (d, $J_{CP} = 2$ Hz, CH), 140.1 (d, $^1J_{CP} = 31$ Hz), 143.3 (d, $^2J_{CP} = 11$ Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −24.7. Anal. Calcd for $C_{27}H_{33}PS_3$: C, 66.90; H, 6.86%. Found: C, 66.93; H, 6.72%.

Reaction of 1b with $NiCl_2 \cdot 6H_2O$. To a mixture of **1b** (0.10 g, 0.21 mmol), $NiCl_2 \cdot 6H_2O$ (50 mg, 0.21 mmol), and $NaBF_4$ (1.0 g, 9.1 mmol) was added dichloromethane (4 mL), and the mixture was stirred at reflux for 72 h. After filtration of the reaction mixture, the filtrate was concentrated. The residue was reprecipitated from hexane/dichloromethane to give [NiCl{P[C_6H_4S(*i*-Pr)]$_3$}]BF_4 (**2**) (0.13 g, 0.20 mmol, 95%) as blue crystals. **2**: blue crystals, mp 220 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, 7.5 mM): δ 1.31 (d, $^3J_{HH} = 7$ Hz, 18H), 3.72 (sepd, $^3J_{HH} = 7$ Hz, $J_{PH} = 2$ Hz, 3H), 7.71 (dddd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $J_{PH} = 2$ Hz, 3H), 7.79 (dd, $^3J_{HH} = 8$ Hz, $J_{PH} = 4$ Hz, 3H), 7.92 (dddd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $J_{PH} = 2$ Hz, 3H), 8.59 (dd, $^3J_{HH} = 8$ Hz, $J_{PH} = 8$ Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 22.3 (CH_3), 50.5 (CH), 133.1 (d, $J_{CP} = 7$ Hz, CH), 133.1 (d, $^2J_{CP} = 27$ Hz, CH), 133.6 (CH), 134.6 (CH), 135.2 (d, $^1J_{CP} = 64$ Hz), 136.7 (d, $^2J_{CP} = 25$ Hz). ^{31}P NMR (202 MHz, $CDCl_3$, 7.5 mM): δ 102.3; UV–vis (chloroform): λ_{max} 273 (ε 10000), 334 (ε 4300), 468 (ε 250), 634 (ε 1400) nm. Anal. Calcd for $C_{27}H_{33}BClF_4NiPS_3$: C, 48.72; H, 5.00%. Found: C, 48.36; H, 5.04%.

Reaction of 1b with [$PdCl_2(PhCN)_2$]. To **1b** (0.25 g, 0.52 mmol) and [$PdCl_2(PhCN)_2$][11] (0.20 g, 0.52 mmol) was added dichloromethane (4 mL), and the mixture was stirred at 25 °C for 72 h. After filtration of the reaction mixture, the filtrate was concentrated. The residue was reprecipitated from hexane/chloroform to give [PdCl{P[2-(*i*-PrS)C_6H_4]$_3$}]Cl$\cdot$2H_2O (**3a**$\cdot$2H_2O) (0.26 g, 0.39 mmol, 76%) as red crystals. **3a**$\cdot$2H_2O: red crystals, mp 113 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, 60 mM): δ 1.30 (d, $^3J_{HH} = 7$ Hz, 18H), 3.50 (sep, $^3J_{HH} = 7$ Hz, 3H), 7.69–7.85 (m, 9H), 8.34–8.44 (m, 3H); ^{1}H NMR (500 MHz, $CDCl_3$, 7.6 mM): δ 1.29 (d, $^3J_{HH} = 7$ Hz, 18H), 3.49 (sep, $^3J_{HH} = 7$ Hz, 3H), 7.67 (br, 6H) 7.77 (br, 3H), 8.52 (br, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 22.5 (CH_3), 47.4 (CH), 131.4 (CH), 132.5 (d, $^1J_{CP} = 60$ Hz), 133.9 (d, $^2J_{CP} = 13$ Hz, CH), 134.6 (CH), 136.4 (CH), 137.6 (d, $^2J_{CP} = 20$ Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 7.6 mM): δ 72.0; UV–vis (chloroform): λ_{max} 283 (ε 10000), 364 (ε 3300), 495.5 (ε 380) nm. Anal. Calcd for $C_{27}H_{33}Cl_2PPdS_3 \cdot 2H_2O$: C, 46.45; H, 5.34%. Found: C, 46.26; H, 5.35%.

Reaction of 3a$\cdot$2H_2O with $NaBF_4$. To **3a**$\cdot$2H_2O (0.10 g, 0.15 mmol) and $NaBF_4$ (1.0 g, 9.1 mmol) was added dichloromethane (4 mL), and the mixture was stirred at 25 °C for 24 h. After addition of a saturated aqueous solution of NH_4Cl, the mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was reprecipitated from hexane/chloroform to afford pure [PdCl{P[2-(*i*-PrS)C_6H_4]$_3$}]BF_4 (**3b**) (97.2 mg, 0.14 mmol, 90%) as red crystals. **3b**: red crystals, mp 208 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, 7.0 mM): δ 1.29 (d, $^3J_{HH} = 7$ Hz, 18H), 3.45 (sep, $^3J_{HH} = 7$ Hz, 3H), 7.71 (ddd, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $^4J_{PH} = 4$ Hz, 3H), 7.74 (dddd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $J_{PH} = 3$ Hz, 3H), 7.88 (dddd, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $J_{PH} = 3$ Hz, 3H), 8.20 (ddd, $^3J_{HH} = 8$ Hz, $^3J_{HP} = 11$ Hz, $^4J_{HH} = 1$ Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 22.4 (CH_3), 48.1 (CH), 132.0 (d, $J_{CP} = 8$ Hz, CH), 132.4 (d, $^1J_{CP} = 65$ Hz), 134.2 (d, $^2J_{CP} = 13$ Hz, CH), 135.0 (CH), 135.4 (CH), 137.4 (d, $^2J_{CP} = 20$ Hz); ^{31}P NMR (202 MHz, $CDCl_3$, 7.0 mM): δ 81.0; UV–vis (chloroform): λ_{max} 284 (ε 8700), 365 (ε 3500), 499 (ε 390) nm. Anal. Calcd for $C_{27}H_{33}BClF_4PPdS_3$: C, 45.46; H, 4.66%. Found: C, 45.24; H, 4.89%.

Reaction of 1b with [$PtCl_2$(cod)]. To **1b** (0.13 g, 0.27 mmol) and [$PtCl_2$(cod)][12] (0.10 g, 0.27 mmol) was added dichloromethane (2 mL), and the mixture was stirred at 25 °C for 48 h. After filtration of the reaction mixture, the filtrate was concentrated. The residue was reprecipitated from hexane/chloroform to give [$PtCl_2${P[2-(*i*-PrS)C_6H_4]$_3$}] (**4**) (0.18 g, 0.24 mmol, 89%) as yellow crystals. **4**: yellow crystals, mp 126 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$, 53 mM): δ 1.28 (brs, 18H), 3.56 (br, 3H), 7.2–7.9 (m, 9H), 8.28 (brs, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 22.1 (CH_3), 48.0 (CH), 128.5 (CH), 131.3 (d, $^1J_{CP} = 82$ Hz), 131.6 (CH), 133.8 (d, $^2J_{CP} = 10$ Hz, CH), 134.8 (CH), 139.0 (d, $^2J_{CP} = 9$ Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 50.3 (s, $^1J_{PPt} = 3150$ Hz); UV–vis (chloroform): λ_{max} 283 (ε 8140), 341 (ε 1975) nm. Anal. Calcd for $C_{27}H_{33}Cl_2PPtS_3 \cdot 0.3CHCl_3$: C, 41.69; H, 4.27%. Found: C, 41.63; H, 4.24%.

X-ray Crystallography of 1b, 2, 3b$_i$, 3b$_{ii}$, and 4. Single crystals of **1b**, **2**, **3b$_i$**, **3b$_{ii}$**, and **4** suitable for X-ray structural analysis were obtained by slow recrystallization from hexane/$CHCl_3$. For **3b**, two types of crystals, **3b$_i$** and **3b$_{ii}$**, were obtained. The crystals were mounted on a glass fiber. The intensity data were collected on a Rigaku R-AXIS IV^{++} diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The structures were solved by direct methods (SHELXS-97[13] or SIR-97[14]), and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97[13]). All the non-hydrogen atoms were refined anisotropically. All hydrogens were placed using AFIX instructions. The crystal data and refinement details are shown in Tables 1 and 2. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-755459, CCDC-755460, CCDC-755461, CCDC-755462, and CCDC-755463 for compounds **1b**, **2**, **3b$_i$**, **3b$_{ii}$**, and **4**, 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).

Table 1. Crystal Data and Refinement Details for **1b** and **2**

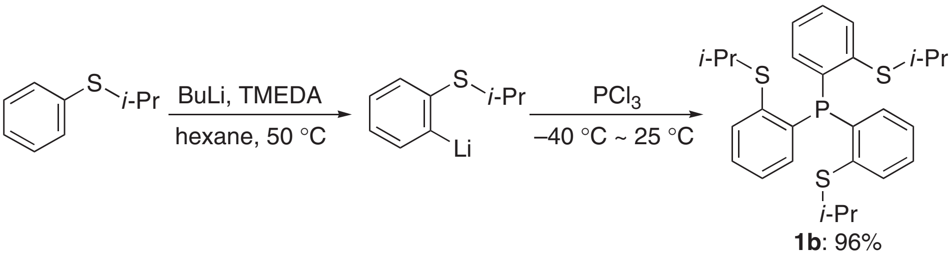
	1b	**2**
Empirical formula	$C_{27}H_{33}PS_3$	$[C_{27}H_{33}ClNiPS_3]BF_4$
Formula weight	484.68	665.65
Temperature/K	123(2)	123(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	10.5003(5)	11.2735(5)
b/Å	15.5086(8)	9.6868(5)
c/Å	16.4401(9)	26.7013(11)
α/°	90.853(3)	90
β/°	90.073(3)	90.0725(5)
γ/°	92.902(3)	90
V/Å^3	2673.5(2)	2915.9(2)
Z	4	4
D_{calcd}/Mg m^{-3}	1.204	1.516
μ(Mo Kα)/mm^{-1}	0.350	1.070
Crystal size/mm^3	0.40 × 0.20 × 0.10	0.30 × 0.15 × 0.15
θ range	2.60 to 25.50°	2.24 to 25.50°
No. of reflns measd	18404	19381
No. of indep reflns	9342	5394
R_{int}	0.0277	0.0207
Completeness	93.8%	99.4%
Data/restraints/parameters	9342/0/559	5394/0/343
Goodness-of-fit on F^2	1.318	1.165
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0661$ $wR_2 = 0.1223$	$R_1 = 0.0381$ $wR_2 = 0.0761$
R indices (all data)[a]	$R_1 = 0.0676$ $wR_2 = 0.1229$	$R_1 = 0.0383$ $wR_2 = 0.0761$
Largest diff./e Å^{-3} peak and hole	0.288 and −0.272	1.068 and −0.829

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [(\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Table 2. Crystal Data and Refinement Details for **3b$_\mathrm{i}$**, **3b$_\mathrm{ii}$**, and **4**

	3b$_\mathrm{i}$	**3b$_\mathrm{ii}$**	**4**
Empirical formula	$[C_{27}H_{33}ClPPdS_3]BF_4$	$[C_{27}H_{33}ClPPdS_3]BF_4$	$[C_{27}H_{33}Cl_2PPtS_3]$
Formula weight	713.34	713.34	750.67
Temperature/K	123(2)	123(2)	123(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a/Å	9.8425(18)	11.2784(10)	8.7082(4)
b/Å	13.6688(18)	9.7531(11)	18.2944(9)
c/Å	23.137(3)	26.855(3)	18.3037(11)
α/°	90	90	90
β/°	95.4931(19)	90.2427(14)	94.2085(7)
γ/°	90	90	90
V/Å^3	3098.5(8)	2954.0(5)	2908.1(3)
Z	4	4	4
D_{calcd}/Mg m^{-3}	1.529	1.604	1.715
μ(Mo Kα)/mm^{-1}	0.980	1.027	5.295
Crystal size/mm^3	0.30 × 0.20 × 0.20	0.40 × 0.10 × 0.05	0.50 × 0.20 × 0.20
θ range	2.56 to 25.50°	2.76 to 25.50°	2.60 to 25.50°
No. of reflns measd	20415	19522	17452
No. of indep reflns	5718	5356	5103
R_{int}	0.0485	0.0679	0.0523
Completeness	99.1%	97.4%	94.1%
Data/restraints/parameters	5718/0/343	5356/0/343	5103/0/307
Goodness-of-fit on F^2	1.312	1.212	1.193
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0761$ $wR_2 = 0.1659$	$R_1 = 0.0523$ $wR_2 = 0.1063$	$R_1 = 0.0442$ $wR_2 = 0.1259$
R indices (all data)[a]	$R_1 = 0.0767$ $wR_2 = 0.1663$	$R_1 = 0.0573$ $wR_2 = 0.1089$	$R_1 = 0.0465$ $wR_2 = 0.1275$
Largest diff./e Å^{-3} peak and hole	0.788 and −1.398	1.129 and −1.101	2.003 and −1.768

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [(\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.



Scheme 1. Synthesis of ligand **1b**.

Figure 1. ORTEP drawing of **1b** with thermal ellipsoids (50% probability).

Results and Discussion

Synthesis and Structure of Tris(2-isopropylthiophenyl)phosphine Ligand 1b. New tripodal tetradentate ligand **1b** was synthesized by the reaction of PCl_3 with [2-(*i*-PrS)-C_6H_4]Li,[15] prepared from (*i*-PrS)C_6H_5,[10] BuLi, and TMEDA in hexane at 50 °C (Scheme 1). The structure of **1b** was determined by the ^{1}H, ^{13}C, and ^{31}P NMR spectra, elemental analysis, and X-ray crystallography. The X-ray structural analysis of **1b** showed that the three sulfur atoms situated in the same side of the lone pair of the phosphorus (Figure 1). This pre-organized structure suggests that **1b** can behave as a tetradentate ligand.

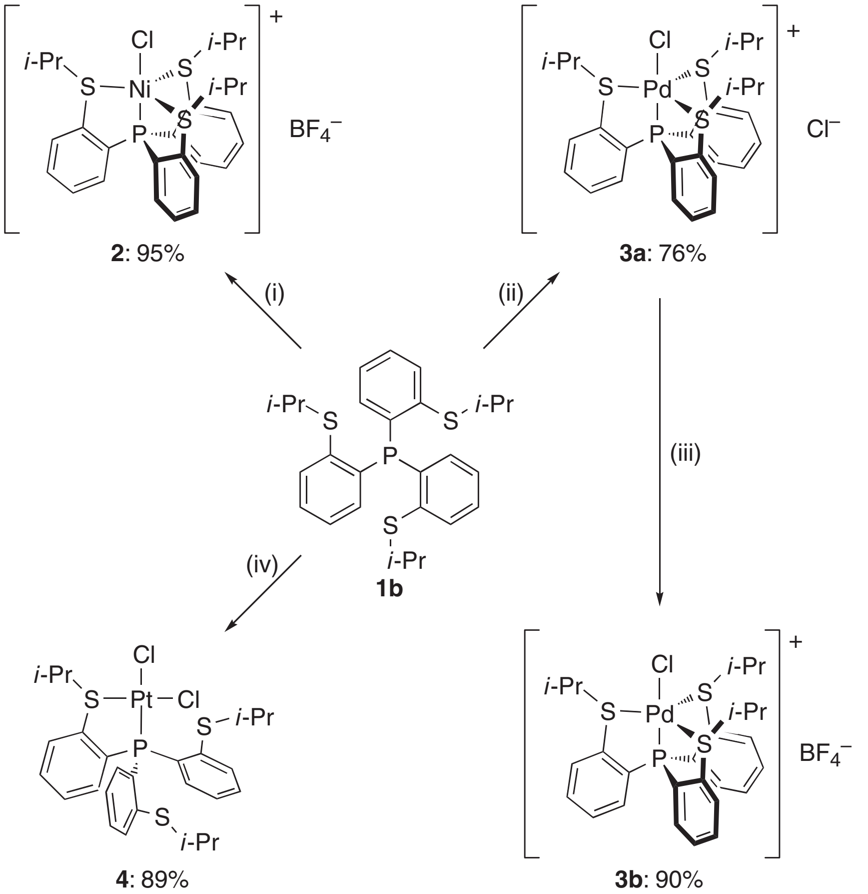
Synthesis of Group 10 Metal Complexes with Ligand 1b. Ligand **1b** reacted with $NiCl_2\cdot6H_2O$ in refluxing CH_2Cl_2 in the presence of $NaBF_4$ for 72 h to afford a five-coordinate, cationic complex **2** with trigonal-bipyramidal geometry as blue crystals in 95% yield (Scheme 2). The formation of the five-coordinate complex **2** is similar to the case of the use of methyl derivative **1a** as a ligand.[2,4,5] Reaction in the absence of $NaBF_4$ resulted in the quantitative recovery of ligand **1b**.

Reaction of **1b** with $[PdCl_2(PhCN)_2]$ in CH_2Cl_2 at 25 °C for 72 h gave the corresponding five-coordinate trigonal-bipyramidal complex **3a** in good yield (Scheme 2). In addition, anion-exchange reaction of **3a** with BF_4^- was performed by the treatment of **3a** with $NaBF_4$ in CH_2Cl_2 at 25 °C for 24 h to afford the corresponding five-coordinate trigonal-bipyramidal complex **3b** in 90% yield (Scheme 2). Generally, palladium(II) complexes possess square-planar geometry around the palladium(II) atom, and five-coordinate palladium(II) complexes are very rare. There are only a few reports of X-ray structural analysis of five-coordinate palladium(II) complexes bearing bi-, tri-, and tetra dentate ligands.[16] The formation of the five-coordinate complexes **3a** and **3b** is very interesting. In addition, the formation of the five-coordinate complexes **3a** and **3b** is in sharp contrast to the case of the methyl derivative **1a**, where four-coordinate square-planar complexes, [$PdCl_2$(**1a**)]•dmf, [Pd(**1a**)$_2$]$(ClO_4)_2$, and [Pd_2Cl_4(**1a**)], have been isolated.[6,7] A possible explanation for this difference is as follows. The steric repulsion between bulkier isopropyl groups on the sulfur atoms probably suppress the formation of a bis(chelate) complex, [Pd(**1b**)$_2$]$^{2+}$. However, this explanation cannot be applied to the suppression of the formation of a four-coordinate complex, [$PdCl_2$(**1b**)], where **1b** acts as a bidentate ligand, since the bulkier substituents on the sulfur atoms seem to favor the four-coordinated structure, which is less congested than the five-coordinate structure. It has been reported that the UV–vis spectra of the palladium(II) complexes with **1a** in solution fit the trends of five-coordinate complexes.[6] Therefore, in these palladium(II) complexes with **1a** and **1b**, an equilibrium between four- and five-coordinate complexes may exist, and the complex with better crystallinity can be isolated. In the isopropyl derivative, the five-coordinate complex **3b** may have better crystallinity, while, in the methyl derivative, the four-coordinate complexes do.

Reaction of **1b** with [$PtCl_2$(cod)] in CH_2Cl_2 at 25 °C for 48 h yielded the corresponding four-coordinate square-planar complex **4** in good yield (Scheme 2). As for a platinum(II) complex of the methyl-substituted ligand **1a**, the isolation of a bis(chelate) complex, [Pt(**1a**)$_2$]$(ClO_4)_2$, has been reported.[7] This difference can be also explained by the steric repulsion between bulkier isopropyl groups on the sulfur atoms. In addition, anion-exchange reaction of platinum(II) complex **4** was attempted by the treatment of **4** with $NaBF_4$ in C_6H_6 at 25 °C, however it unsuccessfully resulted in the quantitative recovery of **4**.

The structures of complexes **2**–**4** were determined by ^{1}H, ^{13}C, and ^{31}P NMR spectra, UV–vis spectra, and elemental analyses. In addition, the structures of **2**, **3b**, and **4** in the crystalline state were revealed by X-ray crystallography. The details of the structures in the crystalline state and in solution will be discussed in the following sections.

Crystal Structures of Group 10 Metal Complexes. The crystal structures of **2**, **3b**, and **4** were determined by X-ray crystallography. The slow recrystallization of **3b** from hexane/$CHCl_3$ gave two types of crystals, **3b**$_\mathbf{i}$ and **3b**$_\mathbf{ii}$. The ORTEP drawings of **2**, **3b**$_\mathbf{i}$, **3b**$_\mathbf{ii}$, and **4** are shown in Figures 2–5,



(i) $NiCl_2 \cdot 6H_2O$, $NaBF_4$, CH_2Cl_2, reflux, 72 h; (ii) $[PdCl_2(PhCN)_2]$, CH_2Cl_2, 25 °C, 72 h; (iii) $NaBF_4$, CH_2Cl_2, 25 °C, 24 h; (iv) $[PtCl_2(cod)]$, CH_2Cl_2, 25 °C, 48 h.

Scheme 2. Synthesis of group 10 metal complexes with **1b**.

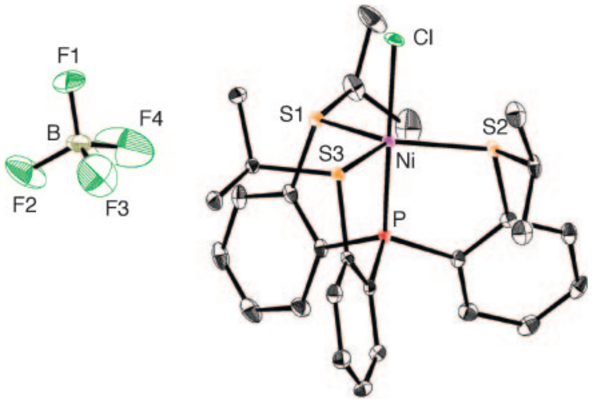


Figure 2. ORTEP drawing of **2** with thermal ellipsoids (50% probability).

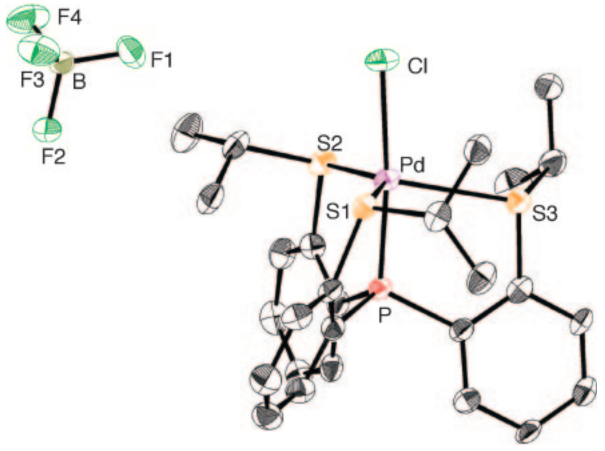


Figure 3. ORTEP drawing of **3b**$_{\mathrm{i}}$ with thermal ellipsoids (50% probability).

respectively, and selective bond lengths and angles of these complexes are shown in Tables 3 and 4.

As shown in Figure 2, nickel(II) complex **2** possesses a slightly distorted trigonal-bipyramidal geometry, where the three S atoms are located in the equatorial positions and the P and Cl atoms are located in the apical positions (P–Ni–Cl 178.60(3)°). The bond distances and angles around the nickel(II) center in **2**, except for the Ni–S3 bond distance, are similar to those for the reported trigonal-bipyramidal nickel(II) complex of the methyl-substituted ligand **1a**, [NiCl(**1a**)]ClO_4 (**6**).[5] The Ni–S3 bond distance (2.3510(7) Å) in **2** is slightly longer than the other two Ni–S bonds (2.2678(7) and 2.2454(7) Å), while the three Ni–S bond distances of the methyl derivative **6** are similar values (2.269(6), 2.242(8), and

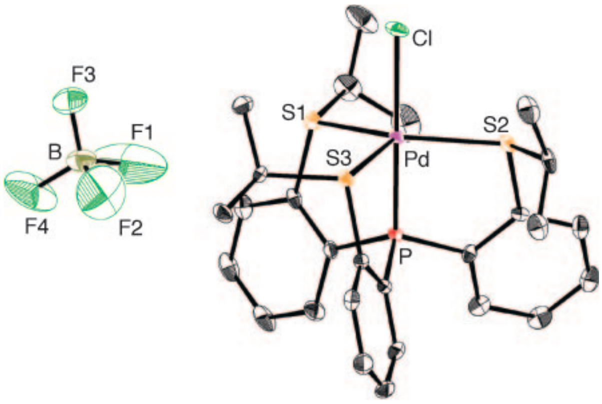


Figure 4. ORTEP drawing of **3b**$_\mathrm{ii}$ with thermal ellipsoids (50% probability).

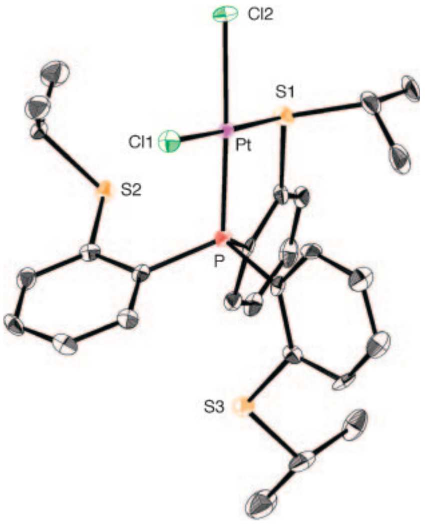


Figure 5. ORTEP drawing of **4** with thermal ellipsoids (50% probability).

Table 3. Selected Bond Lengths/Å and Angles/° for **2**, **3b**$_\mathrm{i}$, and **3b**$_\mathrm{ii}$

	2 (M = Ni)	**3b**$_\mathrm{i}$ (M = Pd)	**3b**$_\mathrm{ii}$ (M = Pd)
M–P	2.1108(7)	2.1787(16)	2.1700(11)
M–S1	2.2678(7)	2.3818(16)	2.3893(12)
M–S2	2.2454(7)	2.3437(17)	2.3685(12)
M–S3	2.3510(7)	2.6515(16)	2.5840(11)
M–Cl	2.2437(7)	2.3782(16)	2.3768(11)
P–M–Cl	178.60(3)	174.12(6)	179.54(4)
P–M–S1	87.50(3)	85.78(6)	86.33(4)
P–M–S2	87.23(3)	87.89(6)	86.05(4)
P–M–S3	86.98(2)	83.06(6)	84.38(4)
Cl–M–S1	92.10(3)	94.23(6)	93.57(4)
Cl –M–S2	92.01(3)	88.07(6)	94.33(4)
Cl –M–S3	94.42(2)	102.56(6)	95.22(4)
S1–M–S2	130.74(3)	136.62(6)	135.03(4)
S2–M–S3	119.03(3)	115.72(6)	116.59(4)
S3–M–S1	109.53(3)	106.01(5)	106.62(4)

Table 4. Selected Bond Lengths/Å and Angles/° for **4**

Pt–P	2.2194(18)	P–Pt–S1	89.46(7)
Pt–Cl1	2.3269(17)	P–Pt–Cl1	92.45(7)
Pt–Cl2	2.3647(17)	S1–Pt–Cl2	86.03(7)
Pt–S1	2.2446(19)	Cl1–Pt–Cl2	92.20(6)
Pt–S2	3.6228(19)		

2.290(7) Å).[5] In addition, the S1–Ni–S2 bond angle (130.74(3)°) in **2** is larger than the S2–Ni–S3 and S3–Ni–S1 bond angles (119.03(3) and 109.53(3)°, respectively). This elongation of the Ni–S3 bonds together with the expansion of the S1–Ni–S2 bond angle, that is, the approach to four-coordinate square-planar structure from five-coordinate trigonal-bipyramidal structure, is probably due to the reduction of the steric repulsion between the bulkier isopropyl groups.

Figures 3 and 4 show the five-coordinate distorted trigonal-bipyramidal structures of **3b**$_\mathrm{i}$ and **3b**$_\mathrm{ii}$, where the P and Cl atoms are located in the apical positions (**3b**$_\mathrm{i}$: P–Pd–Cl 174.12(6)°, **3b**$_\mathrm{ii}$: P–Pd–Cl 179.54(4)°) and the Pd center is out of the equatorial plane constructed by the three S atoms in the direction of the Cl atom. The remarkable differences between **3b**$_\mathrm{i}$ and **3b**$_\mathrm{ii}$ are the position of the BF_4^- anion relative to the cationic part and the conformation of one isopropyl group. The Pd–S1 and Pd–S2 bond lengths (**3b**$_\mathrm{i}$: 2.3818(16) and 2.3437(17) Å, **3b**$_\mathrm{ii}$: 2.3893(12) and 2.3685(12) Å, respectively) are slightly longer than those for the reported four-coordinate palladium(II) complexes (2.290–2.302 Å),[17] and the Pd–S3 bond lengths (**3b**$_\mathrm{i}$: 2.6515(16) Å, **3b**$_\mathrm{ii}$: 2.5840(11) Å) are much longer than the Pd–S1 and Pd–S2 bond lengths. In addition, the S1–Pd–S2 bond angles (**3b**$_\mathrm{i}$: 136.62(6)°, **3b**$_\mathrm{ii}$: 135.03(4)°) are larger than the S2–Pd–S3 and S3–Pd–S1 bond angles (**3b**$_\mathrm{i}$: 115.72(6) and 106.01(5)°, **3b**$_\mathrm{ii}$: 116.59(4) and 106.62(4)°, respectively). This elongation of the Pd–S3 bonds with the expansion of the S1–Pd–S2 bond angle, that is, the approach to four-coordinate square-planar structure from five-coordinate trigonal-bipyramidal structure, is also probably due to the reduction of the steric repulsion between the isopropyl groups as in the case of nickel(II) complex **2**. The Pd–Cl bond lengths (**3b**$_\mathrm{i}$: 2.3782(16) Å, **3b**$_\mathrm{ii}$: 2.3768(11) Å) are slightly longer than those of four-coordinate palladium(II) complexes bearing phosphine and chloro ligands in the *trans* position to each other, e.g., *cis*-$[PdCl_2\{PPh_2\{2\text{-}[(MeOC_{10}H_7)S(O)]C_6H_4\}\text{-}\kappa^2P,S\}]$ (2.356(2) Å)[18] and *cis*-$[PdCl_2\{2\text{-}Ph_2P\text{-}2'\text{-}MeS(1,1'\text{-}binaphthyl)\text{-}\kappa^2P,S\}]$ (2.350(2) Å).[19] The Pd–P bond lengths (**3b**$_\mathrm{i}$: 2.1787(16) Å, **3b**$_\mathrm{ii}$: 2.1700(11) Å) are slightly shorter than those of four-coordinate palladium(II) complexes bearing phosphine and chloro ligands in the *trans* position to each other, e.g., $[PdCl_2\{PPh_2\{2\text{-}[(MeOC_{10}H_7)S]C_6H_4\}\}]$ (2.229(2) Å)[18] and *cis*-$[PdCl_2\{2\text{-}Ph_2P\text{-}2'\text{-}MeS(1,1'\text{-}binaphthyl)\text{-}\kappa^2P,S\}]$ (2.258(2) Å).[19] The shortness of the Pd–P bond lengths can be explained by the coordination of three thioether moieties tethered with the P atom. The slight elongation of the Pd–Cl distances might be interpreted by the *trans* influence of the phosphine ligand with short P–Pd bond length.

Figure 5 shows the four-coordinate square-planar structure of platinum(II) complex **4**. The Pt–S1 and Pt–Cl1 bond lengths (2.2446(19) and 2.3269(17) Å, respectively) are nearly within the range of the reported values for four-coordinated platinum(II) complexes (Pt–S: 2.245–2.289 Å, Pt–Cl: 2.297–2.349 Å),[17] and the Pt–P and Pt–Cl2 bond lengths (2.2194(18) and 2.3647(17) Å, respectively) are close to those of four-coordinate platinum(II) complexes bearing phosphine and chloro ligands in the *trans* position to each other, e.g., *cis*-[$\mathrm{PtCl_2\{1\text{-}Ph_2P\text{-}8\text{-}Ph_2P(S)(naphthalene)\text{-}}\kappa^2 P,S\}$] (Pt–P: 2.2220(6) Å and Pt–Cl: 2.3694(6) Å).[17] The Pt–S2 distance (3.623 Å) is very near to the sum of van der Waals radii of Pt (1.72 Å) and S (1.80 Å) atoms,[20] therefore, very weak interaction between the Pt and S2 atoms may exist. The greater length of the Pt–Cl2 bond (2.3647(17) Å) compared with that of the Pt–Cl1 bond (2.3269(17) Å) is probably due to the larger *trans* influence of Pt–P bonds compared with that of Pt–S bonds.

Structures of Group 10 Metal Complexes in Solution. Figure 6 shows the UV–vis spectra of **2**–**4**. It is known that the UV–vis spectra of five-coordinate group 10 metal complexes show red shifts compared with those of the corresponding square-planar complexes.[2,3,6,21–23] The UV–vis spectra of **2**, **3a**, and **3b** are similar to those of reported five-coordinate complexes, [NiX(**1a**)]$\mathrm{ClO_4}$ (X = Cl, Br, I, and NCS)[2] and [$\mathrm{PdCl\{E[2\text{-}(Ph_2E)C_6H_4]_3\}}$]X (E = P, X = Cl, $\mathrm{BPh_4}$;[21] E = As, X = $\mathrm{ClO_4}$[22]), while the UV–vis spectrum of **4** is similar to those of reported square-planar complexes, [$\mathrm{PtCl_2\{PPh_{3-\mathit{n}}\text{-}[2\text{-}(Me_2N)C_6H_4]_{\mathit{n}}\}}$] ($n = 1$, 2, and 3).[23] These results strongly suggest that nickel(II) and palladium(II) complexes **2**, **3a**, and **3b** have five-coordinated trigonal-bipyramidal structures and platinum(II) complex **4** has a square-planar structure in solution as well as in the crystalline states.

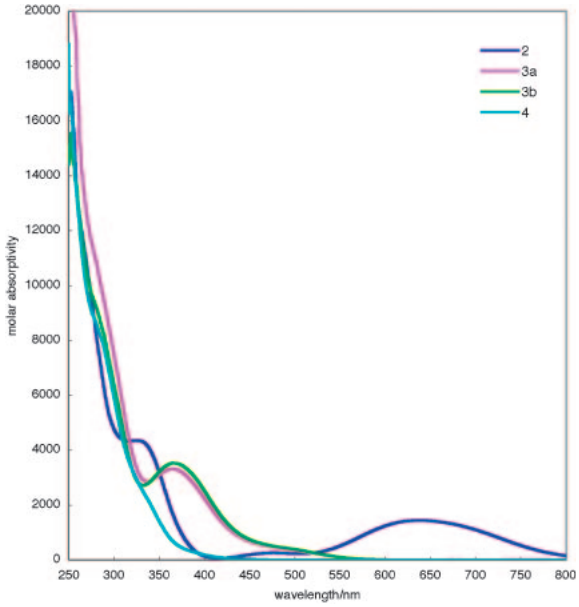
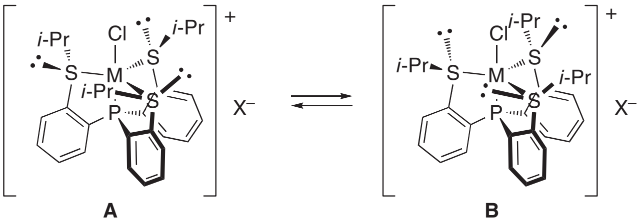


Figure 6. UV–vis spectra of **2**–**4** in chloroform.

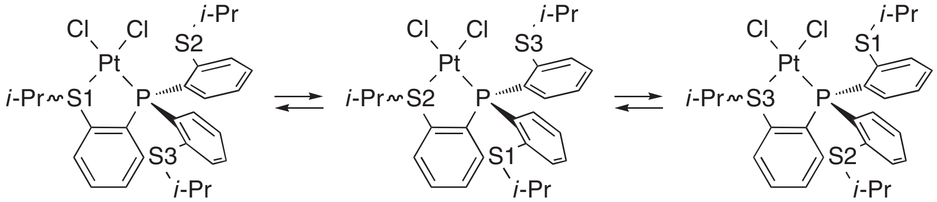
In the ^{1}H and ^{13}C NMR spectra of **2**, **3a**, and **3b**, only one peak for the methyl groups of the isopropyl groups was observed. This suggests the rapid pyramidal inversion of the S atoms (Scheme 3).

To clarify the detailed structure in solution, the effects of temperature and concentration on the NMR spectra were investigated. In the ^{1}H NMR spectrum of palladium(II) complex **3a** at −40 °C, no change was observed in the number of methyl signals. This result suggests the rapid pyramidal inversion of the S atoms even at −40 °C. In addition, this spectrum at −40 °C displayed the up-field shift of the aromatic peak from 8.34 to 8.44 ppm at 20 °C to 8.20–8.34 ppm at −40 °C and down-field shift of the aromatic peak from 7.69 to 7.85 ppm at 20 °C to 7.77–7.94 ppm at −40 °C, while there is little change in the chemical shift of other signals. Furthermore, the concentration effects on the ^{1}H NMR spectra of **3a** was observed; the aromatic proton signal observed at 8.34–8.44 ppm in a 60 mM $\mathrm{CDCl_3}$ solution of **3a** shifted to 8.52 ppm in a 7.6 mM $\mathrm{CDCl_3}$ solution, and other peaks little changed in solutions with various concentrations. These results may suggest interaction between the cationic [PdCl(**1b**)]$^+$ and the counter anion Cl$^-$. A similar concentration effect was observed in nickel(II) and palladium(II) complexes, **2** and **3b**, therefore, a similar interaction between the cationic parts, [NiCl(**1b**)]$^+$ and [PdCl(**1b**)]$^+$, and the counter anion $\mathrm{BF_4}^-$ may exist.

The ^{1}H NMR spectrum of the four-coordinate platinum(II) complex **4** also showed only one peak for the methyl groups of the isopropyl groups. This ^{1}H NMR spectrum may seem to be consistent with that of a five-coordinate trigonal-bipyramidal complex, however the UV–vis spectrum of **4** is similar to those of four-coordinate square-planar complexes as described above. Therefore, it is concluded that platinum(II) complex **4** possesses four-coordinate square-planar geometry in a $\mathrm{CDCl_3}$ solution as in the crystalline state, and the coordinated and uncoordinated sulfur atoms are rapidly exchanged to each other (Scheme 4). The ^{1}H NMR spectrum of **4** at −60 °C showed no split in the methyl signal but the appearance of several small peaks. In addition, in the ^{31}P NMR spectrum at −60 °C, new two small signals appeared, although no split in the main signal was observed. These results indicate the rapid exchange of the



Scheme 3. Pyramidal inversion of S atoms.



Scheme 4. Rapid exchange among thioether moieties.

S atoms even at −60 °C and the existence of an equilibrium among a small amount of isomers, the structures of which have not been determined. These behaviors of platinum(II) complex **4** are very different from those of a square-planar complex $[PtCl_2\{PPh[2\text{-}MeSC_6H_4]_2\}]$ in solution, the ^1H NMR spectrum of which showed four methyl signals at 10 °C, indicating slower pyramidal inversion of the sulfur atoms and slower exchange between coordinated and uncoordinated sulfur atoms than the time scale of ^1H NMR spectrometry.[7] This difference may be ascribed to the isopropyl groups being larger than the methyl groups, which leads to weaker coordination of sulfur to the platinum.

Conclusion

A new tripodal tetradentate ligand **1b** bearing one phosphine and three thioether moieties was synthesized by the reaction of $[2\text{-}(i\text{-}PrS)C_6H_4]Li$ with PCl_3 in good yield. Ligand **1b** formed 1:1 complexes with group 10 metals, and their structures in crystalline states and in solution were discussed.

Nickel(II) and palladium(II) complexes, **2** and **3b**, possess distorted trigonal-bipyramidal geometry, and the distortion of palladium(II) complex **3b** is larger than that of nickel(II) complex **2**. Platinum(II) complex **4** possesses four-coordinate square-planar structure. These results are consistent with the tendency to form five-coordinate complex in the order of $Ni^{II} > Pd^{II} > Pt^{II}$.[24]

The NMR experiments suggest the rapid pyramidal inversion of the sulfur atom in **2**, **3a**, and **3b** and the rapid exchange among the coordinated and uncoordinated sulfur atoms in **4** in solution. In addition, in five-coordinate nickel(II) and palladium(II) complexes, **2**, **3a**, and **3b**, the interaction between the cationic and the anionic portions was suggested.

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