Abstract

The cyclopalladation of 3,5-bis(diphenylphosphinothioyl)pyridine afforded new $\kappa^3$S,C,S-pincer palladium complexes with a $\sigma$-bond between Pd and 4-C of the centered 3,5-pyridinediyl unit. By utilizing the quaternization and complexation ability of the pyridine imine nitrogen ($N_{py}$) atom, various new pincer-type complexes, including hetero-binuclear complexes, have been synthesized.

Keywords: pincer complex; palladium; pyridine; quaternization; binuclear complexes

1. Introduction

Pincer palladium complexes have been intensively investigated in the field of catalysis and material science [1]. Self-assembled metallosupramolecules have also been the subject of recent interest [2,3]. To construct metallosupramolecules of pincer complexes, the introduction of several functional groups at the $para$-position of the centered arene ring of pincer ligands (e.g., the pincer complex with structure (a) in Scheme
1) has been achieved [1a,1b,3]. Recently, pincer complexes attached to terpyridine and porphyrin units have also been synthesized, and their interesting chemical properties have been revealed [3k,3l,3r].

![Scheme 1](image)

**Scheme 1.** Pincer complexes: E = chelating donor atom; F = Functional or coordinating substituent.

We previously reported the preparation of pincer palladium complexes with a centered phenylene-type ligand bearing phosphine sulfide auxiliary ligands at the \( \alpha \)-positions (cf. molecular formula (b) in Scheme 1) [4]. As an extension of the research, we have prepared new pincer complexes of type (c) depicted in Scheme 1. Replacing the centered phenylene unit in the pincer ligand by a pyridine unit offers interesting possibilities. The presence of a reacting and coordinating pyridine imine nitrogen \( N_{py} \) atom will make it possible to create various new pincer complexes derived from the complex of type (c). Examples of such pincer ligands with a 3,5-pyridinediyl moiety, however, have been limited [5], because the presence of \( N_{py} \) sometimes leads to a number of unexpected coordination modes [5b]. Milstein et al. successfully demonstrated that \( \kappa^3P,C,P \)-pincer rhodium and palladium complexes of a monoanionic bis(phosphine)pyridine ligand, \([3,5-(\text{Ph}_2\text{PCH}_2)_2\text{C}_5\text{H}_2\text{N}]^-\), serve as a metalloligand for a second metal center [5a]. We herein report the synthesis of a new pincer complex of type (c) and the quaternization and complexation reactions of the pincer complex.

**2. Results and Discussion**

The Pd-catalyzed aryl phosphination of 3,5-dibromopyridine with two equivalents of diphenylphosphine followed by sulfurization with elemental sulfur afforded ligand 1, as shown in Scheme 2 [4,6]. The pincer palladium complex 2a was obtained via the \( \text{ortho,ortho}-\text{cyclopalladation} \) of 1 with \( \text{PdCl}_2(\text{PhCN})_2 \). The addition of sodium acetate led to regioselective cyclopalladation at the 4-C position of the centered pyridine.
The treatment of 2a with AgBF₄ followed by the addition of Bu₄NX (X = Br, I) gave the corresponding bromo- (2b) and iodo- (2c) complexes.

Scheme 2.

The chemical structures of 1 and 2a-c were confirmed by NMR, FAB-mass spectroscopy, and elemental analysis. In the ¹H NMR spectrum of 2a, the signal assigned to the 4-H of the centered pyridine ring disappeared, and an upfield shift (0.15 ppm) of the signal, assigned to the 2,6-H of the pyridine ring, was observed. The cyclopalladation led to a downfield shift of the ¹³C NMR signal of C(ipso) by 37 ppm due to the σ-bonding to Pd. The ³¹P NMR spectrum of 2a exhibited a downfield shift of the signal by 16 ppm due to the S-coordination mainly, and the two phosphine sulfide groups were magnetically equivalent in the complex. Evidence of S-coordination was also supported by the ν(P=S) position of 2a (603 cm⁻¹), which appeared at a lower frequency than that of 1 (645 cm⁻¹).

The ORTEP drawings of 1 and 2a are presented in Figure 1. Detailed results of X-ray crystallography and selected bond lengths are summarized in Tables 1 and 2, respectively. 2a has a distorted square-planar geometry, and the Pd-C, Pd-S, and Pd-Cl bond lengths lie within the range of lengths found in related pincer palladium complexes [4]. The P=S bond lengths of 2a (2.003(3) and 2.012(3) Å) are somewhat longer, while the P-C bond lengths of the phosphine sulfide and the centered pyridine ring in 2a (1.810(9) and 1.793(7) Å) are shorter than those of 1 (P-S, 1.9460(10) Å; P-C, 1.814(2) Å). A similar structural feature was observed for 2b and 2c; the ORTEP drawings and detailed results of X-ray crystallography of 2b and 2c are given in Supplementary material. These data suggest that the cyclopalladation leads to the delocalization of electrons within the unsaturated part of the ligand, as shown in B in Scheme 3. A similar suggestion has been made for
\( \kappa^3 \text{S,P,S-pincer complexes composed of a phosphinine ring bearing two phosphine sulfide side arms} \ [7]. \)

\[
\begin{align*}
\text{A} & \quad \text{Ph}_2\text{P}=\text{S} & \quad \text{Ph}_2\text{P}=\text{S} \\
\text{N} & \quad \text{Ph}_2\text{P}=\text{S} & \quad \text{Ph}_2\text{P}=\text{S} \\
\quad & \quad \text{N} & \quad \text{Ph}_2\text{P}=\text{S} \\
\end{align*}
\]

Scheme 3. Delocalization of electron in the pincer ligand.

The treatment of 2b and 2c with alkylhalides afforded \( \text{N}_\text{py} \)-quaternized pyridinium complexes 3-5.

The \(^1\text{H} \) NMR spectra of 3-5 were consistent with their molecular structures. The \(^{13}\text{C} \) NMR spectra of 3-5 showed the Pd-C\text{ipso} signal at a considerably lower field (\( \delta 212-206 \)) than those of 2b and 2c (\( \delta 186 \) for 2b and \( \delta 191 \) for 2c). The Pd-C\text{ipso} signal position was at a lower magnetic field than those of related Pd-pyridinium/pyridinylidene complexes (\( \delta 178-190 \)) [8] and similar to those of Pd-quinolin-4-ylidene complexes with a C=Pd\(^+\) bond (\( \delta 208-201 \)) [9]. Consequently, the NMR spectra of 3-5 are considered to have a contribution from the resonance structure such as 3B in Scheme 5.

\[
\begin{align*}
\text{2b,c} & \xrightarrow{1) \text{R-X}} \left[ \begin{array}{c}
\text{Ph}_2\text{P}=\text{S} \\
\text{R-N} \\
\text{Pd-X} \\
\text{Ph}_2\text{P}=\text{S}
\end{array} \right] \\
3: & \quad \text{R = Me, X = I (from 2c)} \\
4: & \quad \text{R = Benzyl, X = Br (from 2b)} \\
5: & \quad \text{R = } \sigma\text{-allyl, X = Br (from 2b)}
\end{align*}
\]

Scheme 4

\[
\begin{align*}
\text{Me} & \quad \text{N} & \quad \text{Ph}_2\text{P}=\text{S} \\
\quad & \quad \text{Me} & \quad \text{N} & \quad \text{Ph}_2\text{P}=\text{S} \\
\quad & \quad \text{Me} & \quad \text{N} & \quad \text{Ph}_2\text{P}=\text{S} \\
\quad & \quad \text{Me} & \quad \text{N} & \quad \text{Ph}_2\text{P}=\text{S} \\
\end{align*}
\]

Scheme 5

X-ray quality single crystals of 3 and 5 were obtained from their ion exchange with \( \text{NH}_4\text{PF}_6 \) to give hexafluorophosphate salts, 3' and 5', respectively. Figure 2 shows the ORTEP drawings of 3' and 5'. Detailed
results of X-ray crystallography and selected bond lengths are shown in Tables 1 and 2, respectively. The Pd-C_\text{ipso} bond lengths of 3' (1.994(6) Å) and 5' (1.994(5) Å) are slightly shorter than those of 2c (2.005(5) Å) and 2b (2.006(11) Å), respectively. The bond lengths are comparable to those of the reported Pd-pyridinium/pyridinylidene complexes [8b,8c] and the Pd-quinolin-4-ylidene complexes with a C=\text{Pd}^+ bond [9]. Raubenheimer et al. reported that there is little difference between a Pd-quinolin-6-ylidene complex and a Pd-quinolin-6-yl complex in terms of the Pd-C bond lengths [10].

The coordinating ability of the N_{py} atom of 2a allowed the binding of 2a to other metal centers. The reactions of 2a with [RuCl_2(\eta^6-C_6H_6)]_2 and [PtCl_2(PhCN)_2] led to the formation of hetero-binuclear complexes, 6 and 7, respectively, as exhibited in Scheme 6.

In the \textsuperscript{1}H NMR spectra of 6 and 7, the 2,6-H signal of the pyridine ring showed respective downfield shifts of 0.42 and 0.24 ppm from that of 2a. For 6, the signal of H at \eta^6-benzene was observed at \delta 5.43.

The ORTEP drawing of 6 is presented in Figure 3. The molecular structure reveals that the Ru(II) center of 6 is located in a piano-stool conformation, and the pincer fragment of 6 maintains the same geometry, with bond lengths and angles essentially similar to those of 2a, as shown in Table 2. The Ru-N_{py} bond length (N_{py}-Ru = 2.152(8) Å) falls within the range reported for related complexes such as [RuCl_2(\eta^1,3,5-Me_3C_6H_3)(pyridine)] [11]. These results indicate that 2a serves as an N_{py}-coordinating metalloligand and does not change the basic structure of the connecting metal complexes upon coordination.

UV-vis absorption data for the complexes are summarized in Table 3, and the spectra are shown in
Figure S2. 2-5 have absorption bands in the region of 350-470 nm, and the shape of the spectra in the region is similar to that of reported pincer palladium complexes such as [3,5-bis(diphenylphosphinothioyl)toluene-C^4,S,S’]chloropalladium(II) (8, cf. Scheme 1(b)), in which the absorption bands have been tentatively assigned to a metal-to-ligand charge-transfer (MLCT) transition [4a]. The absorption band of 2a is observed in an energy region that is about 20 nm lower than that of 8, suggesting that replacing the centered phenylene unit in the pincer ligand by a pyridine unit resulted in a reduction in the energy level of the π* orbital of the ligand. For complexes 2a (X = Cl, λ_{max,MLCT} = 346 nm), 2b (X = Br, λ_{max,MLCT} = 352 nm), and 2c (X = I, λ_{max,MLCT} = 392 nm), the peak position shifts in the lower-energy direction with magnitude in the order of Cl > Br > I; these data suggest that an enhancement in the σ-donor characteristic of the halide ligand stabilizes the excited states [12]. The λ_{max,MLCT} of the quaternized complexes 3 (R = Me, X = I), 4 (R = CH_2Ph, X = Br), and 5 (R = CH=CH_2, X = Br) is observed at 405, 367, and 363 nm, respectively, which is shifted to longer wavelength by about 20 nm than those of the iodide complex 2c and the bromide complex 2b. These results indicate that N_{py}-alkylation causes a bathochromic shift in the MLCT band. The electron-withdrawing substitution resulted in a reduction in the π* level, and the bathochromic shift suggested that the N_{py}-alkylation slightly affects the electron density of the metal [5a,c]. For the N_{py}-coordination (6 and 7), only a slight shift in the band was observed, and the complexes exhibited absorption profiles with long tails.

8 was light-emissive in the glassy frozen state (λ_{em} = 590 nm, φ_f = 0.14, τ = 240 μs) [4], whereas 2a exhibited only weak emission in the glassy frozen state (λ_{em} = 607 nm, φ_f = 0.01); the quaternization and coordination reactions of 2a did not improve the emission ability.

As described above, new pincer Pd complexes 2 with a pyridine moiety have been prepared. Because of the quaternizing and coordinating reactivity of N_{py} in 2, these complexes are considered to be starting complexes for the formation of various pincer complexes. The preparation of a variety of hetero-binuclear pincer complexes would be of interest because there have recently been extensive studies on the catalytic reactions using the pincer palladium complexes [1].
3. Experimental

General procedure.

NMR spectra were recorded on JEOL JNM-EX-400 and Lambda-300 NMR spectrometer. Mass spectra were recorded on JEOL JMS-700 and Shimadzu LCMS-2010 Mass spectrometer. IR spectra were recorded on a JASCO FTIR-460Plus spectrometer. Elemental analyses were carried out with a Yanaco CHN Corder MT-5 and a Yanaco SX-Elements Micro Analyzer YS-10. UV-visible absorption spectra and emission spectra were recorded on a Shimadzu UV-2550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Dichlorobis(benzonitrile)palladium, PdCl₂(PhCN)₂ [13] and dichlorobis(benzonitrile)platinum, PtCl₂(PhCN)₂ [14] were prepared according to literatures. Benzeneruthenium(II) chloride dimer, [RuCl₂(η⁶-C₆H₆)]₂, was purchased and used as received.

Synthesis of 3,5-bis(diphenylphosphinothioyl)pyridine (1).

A mixture of 3,5-dibromopyridine (1.42 g, 6 mmol) and diphenylphosphine (2.79 g, 15 mmol) was dissolved in DMF (20 mL). Palladium chloride (53 mg, 0.3 mmol) and sodium acetate (1.48 g, 18 mmol) were added to the solution, and the reaction mixture was stirred at 130 °C for 24 h under N₂. After cooling to room temperature, sulfur (480 mg, 15 mmol as elemental sulfur) was added and the reaction mixture was stirred at 120 °C for 4 h under N₂. After cooling to room temperature, an aqueous solution of EDTA-2Na (100 mL) and CHCl₃ (200 mL) were added, and the mixture was stirred for 30 min. The organic phase was separated and the solvent was evaporated. The crude product was purified by column chromatography and recrystallization from THF to give 1 as a white powder (1.96 g, 64% yield). FAB-mass: m/z = 512 [M+H]+. ¹H NMR (400 MHz in CDCl₃): δ 8.96 (ddd, J = 6.8 Hz, 2.3 Hz, 1.2 Hz, 2H), 8.19 (tt, J = 12.5 Hz, 2.0 Hz, 1H), 7.68-7.58 (m, 8H), 7.56-7.48 (m, 4H), 7.46-7.38 (m, 8H). ¹³C NMR (100 MHz in CDCl₃): δ 154.5 (d, J = 12.3 Hz), 142.9 (d, J = 9.1 Hz), 132.1, 132.0 (d, J = 11.5 Hz), 131.1 (d, J = 85.8 Hz), 129.9 (dd, J = 79.2 Hz, 4.0 Hz), 128.8 (d, J = 13.3 Hz). ³¹P NMR (160 MHz in CDCl₃): δ 39.2. Anal. Calcd for C₂₉H₂₃NP₂S₂: C, 68.09; H, 4.53; N, 2.74; S, 12.54. Found:
Synthesis of [3,5-bis(diphenylphosphinothioyl)pyridine-C\(^4\),S,S']chloropalladium(II) (2a).

A mixture of 1 (256 mg, 0.5 mmol), PdCl\(_2\)(PhCN)\(_2\) (270 mg, 0.7 mmol), and sodium acetate (123 mg, 1.5 mmol) in 1,1,2,2-tetrachloroethane (30 mL) was stirring at 150 °C for 24 h under N\(_2\). The resulting yellow precipitate was filtered and washed with hexane, ether, methanol, and water. The product was purified by recrystallization from a mixture of CHCl\(_3\) and hexane to give a yellow powder of 2a (88 mg, 27% yield). FAB-mass: \(m/z = 616\) [M-Cl]+.

\(^1^H\) NMR (400 MHz in CDCl\(_3\)): \(\delta 8.04\) (dd, \(J = 3.4\) Hz, 2.8 Hz, 2H), 7.87-7.76 (m, 8H), 7.68-7.61 (m, 4H), 7.60-7.50 (m, 8H).

\(^{13}\)C NMR (100 MHz in CDCl\(_3\)): \(\delta 180.0\), 150.9 (d, \(J = 18.5\) Hz), 145.7 (dd, \(J = 102.4\) Hz, 13.3 Hz), 133.4, 132.4 (d, \(J = 12.0\) Hz), 129.3 (d, \(J = 13.3\) Hz), 128.1 (d, \(J = 81.8\) Hz).

\(^{31}\)P NMR (160 MHz in CDCl\(_3\)): \(\delta 55.4\). Anal. Calcd for C\(_{29}\)H\(_{22}\)ClNP\(_2\)PdS\(_2\): C, 53.39; H, 3.40; N, 2.15; S, 9.83. Found: C, 53.33; H, 3.24; N, 2.20; S, 9.66.

Synthesis of [3,5-bis(diphenylphosphinothioyl)pyridine-C\(^4\),S,S']bromopalladium(II) (2b).

To a THF (1 mL) solution of 2a (9.8 mg, 0.015 mmol) was added AgBF\(_4\) (5.0 mg, 0.026 mmol), and an addition of Bu\(_4\)NBr (32 mg, 0.1 mmol) led to precipitation of the product. The precipitate was filtered and washed with methanol and water. The product was purified by recrystallization from a mixture of CHCl\(_3\) and hexane to give a yellow powder of 2b (5.1 mg, 49% yield). FAB-mass : \(m/z = 616\) [M-Br]+.

\(^1^H\) NMR (400 MHz in CDCl\(_3\)): \(\delta 8.08\) (dd, \(J = 3.3\) Hz, 3.0 Hz, 2H), 7.86-7.76 (m, 8H), 7.68-7.62 (m, 4H), 7.59-7.52 (m, 8H).

\(^{13}\)C NMR (100 MHz in CDCl\(_3\)): \(\delta 186.0\), 150.9 (d, \(J = 18.6\) Hz), 145.1 (dd, \(J = 102.1\) Hz, 13.3 Hz), 133.4, 132.4 (d, \(J = 12.0\) Hz), 129.3 (d, \(J = 13.3\) Hz), 128.1 (d, \(J = 81.8\) Hz).

\(^{31}\)P NMR (160 MHz in CDCl\(_3\)): \(\delta 59.8\). Anal. Calcd for C\(_{29}\)H\(_{22}\)BrNP\(_2\)PdS\(_2\): C, 49.98; H, 3.18; N, 2.01; S, 9.20. Found: C, 50.02; H, 3.21; N, 1.98; S, 9.23.

Synthesis of [3,5-bis(diphenylphosphinothioyl)pyridine-C\(^4\),S,S']iodopalladium(II) (2c).

Similar procedure described above was adopted using Bu\(_4\)NI (37 mg, 0.1 mmol) to give 2c (5.7 mg, 52% yield). FAB-mass : \(m/z = 616\) [M-I]+.

\(^1^H\) NMR (400 MHz in CDCl\(_3\)): \(\delta 8.18\) (dd, \(J = 3.1\) Hz, 3.0 Hz, 2H), 7.83-7.72 (m, 8H), 7.66-7.60 (m, 4H), 7.57-7.50 (m, 8H).

\(^{13}\)C NMR (100 MHz in CDCl\(_3\)): \(\delta 190.7\), 150.6 (d, \(J = 18.5\) Hz), 145.2 (dd, \(J = 102.1\) Hz, 13.3 Hz), 133.4, 132.4 (d, \(J = 12.0\) Hz), 129.3 (d, \(J = 13.3\) Hz), 128.1 (d, \(J = 81.8\) Hz).
143.8 (dd, J = 102.0 Hz, 13.9 Hz), 133.4, 132.3 (d, J = 11.9 Hz), 129.4 (d, J = 11.9 Hz), 128.2 (d, J = 79.8 Hz).

\(^{31}\)P NMR (160 MHz in CDCl\(_3\)): \(\delta\) 68.6.  Anal. Calcd for C\(_{29}\)H\(_{22}\)INP\(_2\)PdS\(_2\): C, 46.82; H, 2.98; N, 1.88; S, 8.62. Found: C, 49.55; H, 3.20; N, 1.88; S, 8.58.

**Synthesis of [N-methyl-3,5-bis(diphenylphosphinothioyl)pyridinium-C\(_4\),S,S’] iodopalladium(II) iodide (3).**

To a THF (2 mL) solution of 2c (9.7 mg, 0.013 mmol) was added CH\(_3\)I (1 mL) and refluxed for 6 h. The solvent was evaporated, and the residue was washed with CHCl\(_3\), acetone and water. The product was purified by recrystallization from a mixture of CH\(_3\)CN and ether to give a yellow powder of 3 (7.4 mg, 64% yield). ESI-mass: \(m/z = 758\ [M-I]^+\).  \(^1\)H NMR (400 MHz in CD\(_3\)CN): \(\delta\) 8.23 (dd, J = 4.8 Hz, 2.2 Hz, 2H), 7.93-7.80 (m, 12H), 7.73-7.66 (m, 8H), 3.94 (s, 3H). \(^{13}\)C NMR (100 MHz in DMSO-d\(_6\)): \(\delta\) 206.3, 144.8 (d, J = 26.6 Hz), 144.4 (dd, J = 107.8 Hz, 15.9 Hz), 134.5, 132.5 (d, J = 11.9 Hz), 129.8 (d, J = 13.3 Hz), 125.9 (d, J = 80.9 Hz), 47.6. \(^{31}\)P NMR (160 MHz in CD\(_3\)CN): \(\delta\) 67.5.  Anal. Calcd for C\(_{30}\)H\(_{25}\)I\(_2\)NP\(_2\)PdS\(_2\): C, 40.68; H, 2.84; N, 1.58. Found: C, 39.73; H, 2.92; N, 1.50.

X-ray quality single crystals of 3 were obtained from ion exchange of 3 with NH\(_4\)PF\(_6\) to give the hexafluorophosphate salt of 3 (3').

**Synthesis of [N-benzyl-3,5-bis(diphenylphosphinothioyl)pyridinium-C\(_4\),S,S’] bromopalladium(II) bromide (4).**

To a THF (5 mL) solution of 2b (9.1 mg, 0.013 mmol) was added benzyl bromide (1 mL) and refluxed for 12 h. The solvent was evaporated, and the residue was washed with hexane, ether and water. The product was purified by recrystallization from a mixture of CH\(_3\)CN and ether to give a yellow powder of 4 (8.7 mg, 77% yield).  ESI-mass: \(m/z = 787\ [M-Br]^+\).  HRMS: calcd for C\(_{36}\)H\(_{29}\)NBrP\(_2\)PdS\(_2\): 787.9434. Found: 787.9395.  \(^1\)H NMR (400 MHz in DMSO-d\(_6\)): \(\delta\) 9.18 (d, J = 7.3 Hz, 2H), 7.98-7.90 (m, 8H), 7.88-7.70 (m, 4H), 7.78-7.68 (m, 8H), 7.33 (m, 5H), 5.60 (s, 2H). \(^{13}\)C NMR (100 MHz in DMSO-d\(_6\)): \(\delta\) 207.1, 146.7 (dd, J = 107.8 Hz, 15.9 Hz), 144.2 (d, J = 26.6 Hz), 134.5, 132.6 (d, J = 11.9 Hz), 129.7 (d, J = 13.3 Hz), 128.9, 128.8, 128.5, 127.8, 125.8 (d, J = 82.5 Hz), 62.6. \(^{31}\)P NMR (160 MHz in DMSO-d\(_6\)): \(\delta\) 62.9.
Synthesis of \([N\text{-allyl-3,5-bis(diphenylphosphinothioyl)pyridinium-C}^4\text{,S,S'}]\) bromopalladium(II) bromide (5).

Similar reaction described above was carried out using 2b and allyl bromide to give 5 (6.8 mg, 64% yield).

ESI-mass: \(m/z = 738 \ [M-Br]^+\).


\(^1\)H NMR (400 MHz in DMSO-d\(_6\)): \(\delta 9.03 (d, J = 5.6 \text{ Hz}, 2\text{H}), 8.00-7.80 (m, 12\text{H}), 7.78-7.64 (m, 8\text{H}), 5.95-6.05 (m, 1\text{H}), 5.26 (d, J = 11.0 \text{ Hz}, 1\text{H}), 5.22 (d, J = 18.0 \text{ Hz}, 1\text{H}), 5.02 (s, 2\text{H}).

\(^{31}\)P NMR (160 MHz in DMSO-d\(_6\)): \(\delta 211.7, 146.3 (d, J = 105.1 \text{ Hz}, 14.6 \text{ Hz}), 144.2 (d, J = 23.9 \text{ Hz}), 134.5, 132.5 (d, J = 11.9 \text{ Hz}), 131.6, 129.7 (d, J = 13.3 \text{ Hz}), 126.0 (d, J = 80.3 \text{ Hz}), 120.6, 61.8.

X-ray quality single crystals of 5 were obtained from ion exchange of 5 with NH\(_4\)PF\(_6\) to give the hexafluorophosphate salt of 5 (5').

Synthesis of Dichloro(\(\eta^6\)-benzene){[3,5-bis(diphenylphosphinothioyl)pyridine-C\(^4\),S,S']} chloropalladium(II) ruthenium(II) (6)

To a THF (5 mL) solution of 2a (9.8 mg, 0.015 mmol) was added [RuCl\(_2\)(\(\eta^6\)-C\(_6\)H\(_6\))]\(_2\) (10.0 mg, 0.020 mmol), and refluxed for 12 h. The solvent was evaporated, and the residue was washed with ether and hexane. The product was purified by recrystallization from CHCl\(_3\) to give a pale brown powder of 6 (8.8 mg, 65% yield).

FAB-mass: \(m/z = 866 \ [M-Cl]^+\).

\(^1\)H NMR (400 MHz in CDCl\(_3\)): \(\delta 8.46 (d, J = 5.3 \text{ Hz, 2H}), 7.90-7.80 \ (m, 8\text{H}), 7.70-7.50 \ (m, 12\text{H}), 5.43 \ (s, 6\text{H}).

\(^{31}\)P NMR (160 MHz in CDCl\(_3\)): \(\delta 56.2.

Anal. Calcd for C\(_{35}\)H\(_{28}\)Cl\(_3\)NP\(_2\)PdRuS\(_2\): C, 46.58; H, 3.13; N, 1.55. Found: C, 45.74; H, 2.78; N, 1.50. Because of low solubility of 6 in CDCl\(_3\), satisfactory \(^{13}\)C NMR spectrum has not been obtained.

Synthesis of Dichloro(benzonitrile){[3,5-bis(diphenylphosphinothioyl)pyridine-C\(^4\),S,S']} chloropalladium(II) platinum(II) (7)

To a THF (5 mL) solution of 2a (9.8 mg, 0.015 mmol) was added PtCl\(_2\)(PhCN)\(_2\) (7.1 mg, 0.015 mmol), and stirred for 12 h. The solvent was evaporated, and the residue was washed with water, CH\(_3\)CN, and ether. The product was purified by recrystallization from a mixture of CH\(_2\)Cl\(_2\) and CH\(_3\)CN to give a yellow powder of 7.
(5.1 mg, 33% yield).

FAB-mass: \( m/z = 1020 \ [\text{M+H}^+] \).  

\(^1\text{H} \) NMR (400 MHz in CDCl\(_3\)): \( \delta 8.28 \) (dd, \( J = 5.6 \) Hz, 1.7 Hz, 2H), 7.88-7.80 (m, 8H), 7.74-7.68 (m, 7H), 7.65-7.58 (m, 8H), 7.53 (dd, \( J = 8.2 \) Hz, 7.0 Hz, 2H). \(^31\text{P} \) NMR (160 MHz in CDCl\(_3\)): \( \delta 56.1 \). Because of low solubility of 7 in CDCl\(_3\), satisfactory \(^{13}\text{C} \) NMR spectrum has not been obtained.

IR (KBr, cm\(^{-1}\)): 2288 (\( \nu(\text{C=\(\equiv\)N}) \)). Anal. Calcd for C\(_{36}\)H\(_{27}\)Cl\(_3\)N\(_2\)P\(_2\)PdPtS\(_2\): C, 42.33; H, 2.66; N, 2.74. Found: C, 42.03; H, 2.98; N, 2.68.

**X-ray Crystallographic Study.**

The diffraction data were collected with a Rigaku Saturn CCD area detector with graphite monochromated MoK\(\alpha\) (\( \lambda = 0.71070 \ \text{Å} \)) at \(-160\) °C. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods (SIR 2002) and expanded using Fourier techniques. In general, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

For 2a, a solved CHCl\(_3\) molecule was located by using a rigid group due to disordering. For 6, hydrogen atoms excepted for those of the \( \eta^6 \)-benzene were refined using the riding model due to disordering.

**4. Supplementary material**

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; publication numbers CCDC 659442 (1), 659443 (2a·2CHCl\(_3\)), 659444 (2b·2CHCl\(_3\)), 659445 (2c·CHCl\(_3\)), 659446 (3·2CH\(_3\)CN), 659447 (5·CH\(_3\)CN), 659448 (6·CHCl\(_3\)).

Figures giving ORTEP drawings of 2b and 2c, and UV-vis spectra of the complexes are provided as Supplementary material. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.026.
Acknowledgement

The authors are grateful to Prof. K. Tanaka, Dr. R. Okamura, and Ms. K. Tsutsui of Institute for Molecular Science for ESI-MS measurement.
References


Captions of Figures

Figure 1. X-ray crystal structures of (a) 1 and (b) 2a with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvated CHCl₃ molecules are omitted for simplicity.

Figure 2. X-ray crystal structures of (a) 3’ and (b) 5’ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, an PF₆⁻ anion, and solvated CH₃CN molecules are omitted for simplicity.

Figure 3. X-ray crystal structure of 6 with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and a solvated CHCl₃ molecule are omitted for simplicity.
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<td>C₁₂H₁₂BrF₆N₃P₂PdS₂</td>
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<td>P2₁/n (No.14)</td>
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Table 2. Selected bond lengths (Å) for 1, 2a, 3', 5', and 6

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<th>3'</th>
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<th>6</th>
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<td>Pd−halogen</td>
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<sup>a</sup> N<sub>py</sub>-quaternized substituent of 3' and 5'.

"
Table 3 UV-vis absorption spectroscopic data for 1-8<sup>a</sup>

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<td>8&lt;sup&gt;b&lt;/sup&gt;</td>
<td>265 (3.1), 323 (5.5)</td>
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<sup>a</sup> in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> from ref. 4a and 4b.
### Table S1. Crystal data and details of the structure refinements for 2b and 2c

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<td>3160.7(11)</td>
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### Table S2. Selected bond lengths for 2b and 2c

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<td>Pd-S</td>
<td>2.345(3)</td>
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<td>P-S</td>
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<td>P-S</td>
<td>2.021(5)</td>
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<td>C(βᵢₚₛ)−P</td>
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<td>C(βᵢₚₛ)−P</td>
<td>1.809(10)</td>
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Figure 1. X-ray crystal structures of (a) 1 and (b) 2a with thermal ellipsoids drawn at the 50% probability level.

Hydrogen atoms and solvated CHCl₃ molecules are omitted for simplicity.
Figure 2. X-ray crystal structures of (a) 3’ and (b) 5’ with thermal ellipsoids drawn at the 50% probability level.

Hydrogen atoms, an PF$_6^-$ anion, and solvated CH$_3$CN molecules are omitted for simplicity.
Figure 3. X-ray crystal structure of 6 with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and a solvated CHCl₃ molecule are omitted for simplicity.
Figure S1. X-ray crystal structures of (a) 2b and (b) 2c with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvated CHCl₃ molecules are omitted for simplicity.
Figure S2. UV-vis absorption spectra of the ligands and the complexes in CH₂Cl₂ at room temperature: (a) 1 and 2a-c, (b) 3, 4, and 5, (c) 6 and 7.
Corresponding author: Takaki Kanbara
Graduate School of Pure and Applied Sciences, Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan
Tel.: +81-29-853-5066; fax: +81-29-853-4490; E-mail: kanbara@ims.tsukuba.ac.jp

Graphical Abstract
Title: Synthesis, Structure, and Quaternization and Complexation Reactions of \( \kappa^3 \)SCS Pincer Palladium Complexes Having 3,5-Pyridinediyl Unit
Authors: Hikaru Meguro\(^a\), Take-aki Koizumi\(^a\), Takakazu Yamamoto\(^a\), and Takaki Kanbara\(^{b,c,*}\)
Address: \(^a\)Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
\(^b\)Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan
\(^c\)Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8573, Japan
Abstract: The cyclopalladation of 3,5-bis(diphenylphosphinothioyl)pyridine afforded new \( \kappa^3 \)S,C,S-pincer palladium complexes with a \( \sigma \)-bond between Pd and 4-C of the centered 3,5-pyridinediyl unit. By utilizing the quaternization and complexation ability of the pyridine imine nitrogen (N\(_\text{py}\)) atom, various new pincer-type complexes, including hetero-binuclear complexes, have been synthesized.
Keywords: Pincer complex; Palladium; Pyridine; Quaternization; Binuclear complexes