Synthesis and solution behavior of mononuclear palladium(II) and platinum(II) complexes containing pyridine-2-thiolate as a ligand. Crystal structure of chloro(pyridine-2-thiolato)-(triphenylphosphine)palladium(II)

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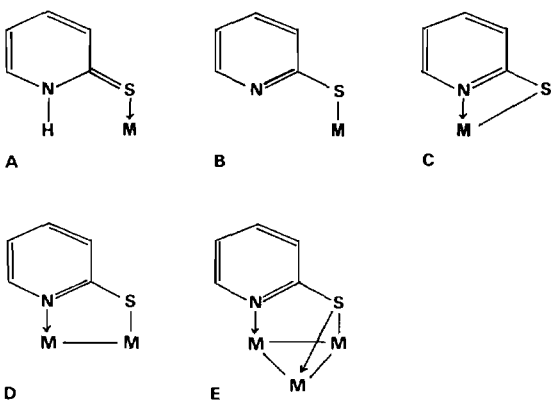
Abstract

Various types of mononuclear pyridine-2-thiolato (pyS) complexes $[M(pyS)_2(PPh_3)_2]$, $[MCl(pyS)(PPh_3)]$, $[M(pyS)_2(PPh_3)]$ (M = Pd(II), Pt(II)) and $[PdCl(pyS)(PPh_3)_2]\cdot CH_2Cl_2$, and the complex of pyridine-2-thiol $[PdCl_2(pySH)(PPh_3)]$ have been prepared. The solution behavior of these complexes has been examined by ^1H and $^{31}P\{^1H\}$ NMR measurements as well as the determination of the molecular weights. The coordination modes of the pyS ligand in the complexes, including chelation, S-unidentate, and the fast exchange between them, have been elucidated. The crystal structure of $[PdCl(pyS)(PPh_3)]$ has been determined. The complex crystallizes in the triclinic space group $P\bar{1}$, $Z=2$, $a=12.969(6)$, $b=10.246(5)$, $c=9.493(3)$ Å, $\alpha=114.53(3)$, $\beta=72.57(3)$, $\gamma=105.71(3)°$. The structure has been determined using conventional heavy atom methods, final $R_w=0.067$ based on 2546 significant ($I>3\sigma(I)$) reflections. The Pd atom is four-coordinated by the Cl, P, S and N donor atoms, constituting a square-planar, *trans*-(P,N) structure; the pyS ligand is chelated with a small bite angle. In the crystals, there are two independent molecules, the structures of which differ from one another in the disposition of the pyridine ring folded in opposite directions on the plane defined by the Pd, Cl, P and S atoms.

Introduction

The ligand pyridine-2-thiol exists predominantly in the 1*H*-pyridine-2-thione form [1] and coordinates as such through the sulfur atom in the most common mode of coordination (**A**) [1–3]. However, the deprotonated thiolate form is very versatile, exhibiting various modes of bonding to the metal atom; S-unidentate (**B**) [3–5], N,S-chelating (**C**) [3–6], μ_2-N,S-η^2-bridging (**D**) [7] and μ_3-N,S-η^2-bridging (**E**) [6g, 7e, 8].



Pyridine-2-thiolato complexes having six-coordinate, octahedral structures have been prepared for a number of transition metals including Fe(II), Ni(II), Mo(V), Ru(II), Ru(III), Rh(III), Os(II) and Ir(III) and their four-membered chelate structures with small bite angles have been established by X-ray analyses [6]. On the other hand, for almost all complexes of Pd(II) and Pt(II) favoring four-coordinate, square-planar stereochemistry, the μ_2-N,S-η^2-bridging structure (**D**) without a metal–metal bond was preferred [7]; the only evidence for the presence of the mononuclear complexes $[M(pyS)(pyS\text{-}S)(PPh_3)]$ (M = Pd(II), Pt(II)) with a chelated pyS ligand in solution has been adduced from ^{31}P NMR spectra when $[M(pyS\text{-}S)_2(PPh_3)_2]$ were dissolved in CD_2Cl_2. In this paper, synthesis of some mononuclear pyridine-2-thiolato Pd(II) and Pt(II) complexes, solution behavior of the complexes based on the detailed consideration of the NMR spectra, and the X-ray crystal structure of the first isolated complex of Pd(II) containing a chelated pyridine-2-thiolato ligand, $[PdCl(pyS)(PPh_3)]$, are reported.

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Experimental

All reactions were carried out in an atmosphere of nitrogen. The complex $[Pd_2(pyS)_4]$ was prepared by the published method [7c]. Special grade pyridine-2-thiol and dipyridyl-2,2'-disulfide (pySSpy) were purchased and used without further purification.

Synthesis of $[Pd(pyS)_2(PPh_3)_2]$ (1a)

$[Pd(PPh_3)_4]$ (1.16 g, 1.00 mmol) and pySSpy (0.220 g, 1.00 mmol) were suspended in toluene (20 cm^3) and heated at 90 °C for 2 h. The resulting reddish orange solution was cooled and hexane was added to deposit a yellow precipitate, which was filtered, washed with hexane and ether, and dried *in vacuo*. Yellowish orange powder, yield 0.82 g (96%). *Anal.* Found: C, 65.19; H, 4.50; N, 3.29%; *MW*, 455. Calc. for $C_{46}H_{38}N_2P_2S_2Pd$: C, 64.90; H, 4.50; N, 3.27%; *MW*, 851. ^1H NMR (C_6D_6): pyS $\delta = 6.12$ (ddd, $J_4 = 7.3$, $J_6 = 5.1$, $J_3 = 1.3$ Hz, H^5), 6.59 (ddd, $J_3 = 8.1$, $J_5 = 7.3$, $J_6 = 2.0$ Hz, H^4), 6.93 (d, $J_4 = 8.1$ Hz, H^3), 7.98 (ddd, $J_5 = 5.1$, $J_4 = 2.0$, $J_3 = 1.0$ Hz, H^6) ppm; phenyl protons $\delta = 7.0$ (broad), 7.6 (broad) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -4.6$ (broad, free PPh_3), 32.0 (broad, PPh_3) ppm.

Synthesis of $[Pt(pyS)_2(PPh_3)_2]$ (1b)

A suspension of $[Pt(PPh_3)_4]$ (1.230 g, 1.00 mmol) and pySSpy (0.220 g, 1.00 mmol) in toluene (50 cm^3) was refluxed for 1 h. On cooling to room temperature, pale yellow crystals separated out, which were filtered, washed with hexane and ether, and then dried *in vacuo*. Yield 0.80 g (85%). *Anal.* Found: C, 59.28; H, 4.12; N, 2.90%; *MW*, 522. Calc. for $C_{46}H_{38}N_2P_2S_2Pt$: C, 58.78; H, 4.07; N, 2.98%; *MW*, 940. ^1H NMR: not assigned owing to broad signals. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -5.3$ (s, free PPh_3), 7.3 (s, $J_{Pt} = 3860$ Hz) ppm.

Synthesis of $[PdCl(pyS)(PPh_3)]$ (2a)

Method 1. $[Pd_2Cl_4(PPh_3)_2]$ (0.879 g, 1.00 mmol) and pySH (0.222 g, 2.00 mmol) were suspended in tetrahydrofuran (THF) (25 cm^3). A 28%-methanol solution of NaOMe (2.00 mmol) was added to the suspension. After being stirred for 2 h, the solvent was evaporated to dryness and the residue was extracted with benzene. On addition of hexane, an orange–yellow solid precipitated, which was filtered, washed with hexane and ether, and then dried *in vacuo*. Yield 0.72 g (70%). Recrystallization from benzene–hexane gave reddish orange crystals. *Anal.* Found: C, 54.12; H, 3.66; N, 2.71%; *MW*, 506. Calc. for $C_{23}H_{19}NClSPd$: C, 53.71; H, 3.72; N, 2.72%; *MW*, 514. ^1H NMR (C_6D_6): pyS $\delta = 5.93$ (dddd, $J_4 = 7.6$, $J_6 = 5.4$, $J_3 = 1.2$, $J_P = 2.4$ Hz, H^5), 6.27 (ddd, $J_4 = 8.1$, $J_5 = 1.2$, $J_6 = 1.0$ Hz, H^3), 6.53 (ddd, $J_3 = 8.1$, $J_5 = 7.6$, $J_6 = 1.7$ Hz, H^4), 8.23 (dddd, $J_5 = 5.4$, $J_4 = 1.7$, $J_3 = 1.0$, $J_P = 3.0$ Hz, H^6) ppm; phenyl protons $\delta = 6.99$–7.02 (m), 7.82–7.87 (m) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 29.4$ (s) ppm.

Method 2. A suspension of **1a** (0.851 g, 1.00 mmol) and $[PdCl_2(PhCN)_2]$ (0.359 g, 1.00 mmol) in THF (40 cm^3) was stirred for 1 h at room temperature. The resulting orange solution was concentrated to one-half its initial volume and hexane was added to deposit a precipitate, which was treated as described in method 1. Yield 0.90 g (87%). *Anal.* Found: C, 53.75; H, 3.71; N, 2.76%; *MW*, 500.

Synthesis of $[PtCl(pyS)(PPh_3)]$ (2b)

A suspension of **1b** (0.625 g, 0.660 mmol) and $[PtCl_2(PhCN)_2]$ (0.312 g, 0.660 mmol) in benzene (40 cm^3) was stirred for 3 h at room temperature. The resulting solution was filtered and hexane was added to deposit a yellow precipitate, which was collected and washed with hexane and ether. Recrystallization from benzene–hexane afforded yellow crystals. Yield 0.66 g (83%). *Anal.* Found: C, 46.20; H, 3.17; N, 2.35%; *MW*, 612. Calc. for $C_{23}H_{19}NClSPt$: C, 45.81; H, 3.18; N, 2.32%; *MW*, 603. ^1H NMR ($CDCl_3$): pyS $\delta = 6.65$ (d, $J_4 = 7.9$ Hz, H^3), 6.94 (dt, $J_4 = J_6 = 6.0$, $J_3 = 0.9$ Hz, H^5), 7.49 (t, $J_3 = J_4 = 8.4$ Hz, H^4), 8.30 (m, $J_{Pt} = 41.2$ Hz, H^6) ppm; phenyl protons $\delta = 7.42$–7.46 (m), 7.67–7.72 (m) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 3.6$ (s, $J_{Pt} = 3829$ Hz) ppm.

Synthesis of $[Pd(pyS)_2(PPh_3)]$ (3a)

Method 1. PySH (0.044 g, 0.40 mmol) and **2a** (0.205 g, 0.400 mmol) were dissolved in THF (20 cm^3). A 28% methanol solution of NaOMe (0.40 mmol) was added to the solution. After being stirred for 1 h, the solvent was evaporated to dryness and the residue was extracted with benzene. On addition of hexane, a yellow precipitate separated out, which was filtered and dried *in vacuo*. Recrystallization from benzene–hexane afforded orange needles. Yield 0.19 g (82%). *Anal.* Found: C, 56.97; H, 3.95; N, 4.69%; *MW*, 605. Calc. for $C_{28}H_{23}N_2PS_2Pd$: C, 57.10; H, 3.94; N, 4.76%; *MW*, 589. ^1H NMR ($CDCl_3$): pyS $\delta = 6.63$ (dt, $J_4 = J_6 = 5.2$, $J_3 = 0.9$ Hz, H^5), 7.15 (d, $J_4 = 8.2$ Hz, H^3), 7.21 (dt, $J_3 = J_5 = 6.0$, $J_6 = 1.5$ Hz, H^4), 7.82 (d, $J_5 = 4.9$ Hz, H^6) ppm; phenyl protons $\delta = 7.35$–7.46 (m), 7.67–7.72 (m) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 32.8$ (s) ppm.

Method 2. To a suspension of $[Pd_2(pyS)_4]$ (0.131 g, 0.200 mmol) in CH_2Cl_2 (15 cm^3) was added a CH_2Cl_2 (5 cm^3) solution of PPh_3 (0.104 g, 0.400 mmol). After being stirred for 30 min, the resulting reddish orange solution was concentrated and hexane was added to deposit an orange precipitate, which was collected and dried *in vacuo*. Yield 0.20 g (86%). *Anal.* Found: C, 57.29; H, 3.93; N, 4.78%; *MW*, 562.

Synthesis of [Pt(pyS)$_2$(PPh$_3$)] (3b)

To a solution of pySH (0.022 g, 0.20 mmol) in THF (5 cm^3) was added a 28%-methanol solution of NaOMe (0.20 mmol). The resulting solution was added to a solution of **2b** in THF (5 cm^3). After being stirred for 2 h, the solvent was evaporated to dryness. The solid was extracted with benzene and hexane was added to the extract. On standing overnight, pale yellow needles were obtained, which were filtered, washed with ether, and then dried *in vacuo*. Yield 0.10 g, (77%). *Anal.* Found: C, 48.89; H, 3.39; N, 4.13%; *MW*, 672. Calc. for $C_{28}H_{23}N_2PS_2Pt$: C, 49.63; H, 3.42; N, 4.13%; *MW*, 678. ^{1}H NMR ($CDCl_3$): not assigned owing to broad signals. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 7.3$ (s, $J_{Pt} = 3870$ Hz) ppm.

Synthesis of [PdCl(pyS)(PPh$_3$)$_2$]·CH$_2$Cl$_2$ (4)

To a solution of **2a** (0.102 g, 0.200 mmol) in CH_2Cl_2 (10 cm^3) was added a solution of PPh_3 (0.111 g, 0.420 mmol) in CH_2Cl_2 (5 cm^3). After being stirred for 30 min, the solution was concentrated to one-half its initial volume and hexane was added. On standing overnight, orange needles were deposited, which were collected, washed with hexane and ether, and then air-dried. Yield 0.070 g (41%). *Anal.* Found: C, 58.75; H, 4.19; N, 1.67. Calc. for $C_{42}H_{36}NCl_3P_2SPd$: C, 58.55; H, 4.21; N, 1.63%. The solvent of crystallization was lost by prolonged vacuum drying. Found: *MW*, 407; calc. for $C_{41}H_{34}NClP_2SPd$: *MW*, 777. ^{1}H NMR (C_6D_6): pyS $\delta = 5.97$ (t, $J_4 = J_6 = 6.3$ Hz, H^5), 6.28 (d, $J_3 = J_4 = 8.2$ Hz, H^3), 6.46 (dt, $J_3 = J_5 = 7.8$, $J_6 = 1.8$ Hz, H^4), 8.21 (d, $J_5 = 5.2$ Hz, H^6) ppm; phenyl protons, $\delta = 7.02$ (broad), 7.67 (broad) ppm.

Synthesis of [PdCl$_2$(pySH)(PPh$_3$)] (5)

[$Pd_2Cl_4(PPh_3)_2$] (0.220 g, 0.250 mmol) and pySH (0.056 g, 0.50 mmol) were dissolved in CH_2Cl_2 (20 cm^3), giving a reddish orange solution, from which an orange precipitate separated out on standing for 1 h. The product was filtered, washed with ether and hexane, and then dried *in vacuo*. Orange powder, yield 0.23 g (83%). *Anal.* Found: C, 49.51; H, 3.64; N, 2.54. Calc. for $C_{23}H_{20}NCl_2PSPd$: C, 50.16; H, 3.66; N, 2.54%. IR: ν(NH) = 3090 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): pySH $\delta = 6.76$ (dd, $J_4 = 8.1$, $J_5 = 0.7$ Hz, H^3), 6.82 (dt, $J_4 = J_6 = 6.4$, $J_3 = 1.1$ Hz, H^5), 7.52 (triplet-like, overlapped with phenyl proton signals, H^4), 8.22 (t, $J = 2.6$ Hz, H^6) ppm; phenyl protons $\delta = 4.72$–7.50 (m), 7.70–7.75 (m) ppm.

Measurements

IR spectra were obtained in Nujol mull with a JASCO DS-701G spectrometer. Proton NMR spectra at 400 MHz were recorded on a JEOL JNM GX-400 instrument using $SiMe_4$ as an internal reference. ^{31}P NMR spectra at 24.2 MHz were taken with a JEOL FX-60Q spectrometer with H_3PO_4 as an external reference. Molecular weight was determined in CH_2Cl_2 at 25 °C with a vapor pressure osmometer manufactured by Knauer, Berlin, FRG.

Crystal structure determination of complex 2a

A yellow plate crystal of dimensions $0.11 \times 0.45 \times 0.53$ mm was mounted on a Philips PW1100 automated diffractometer. The lattice parameters were determined from 35 reflections with $12 \leqslant 2\theta \leqslant 24$. The intensities were measured at room temperature with Mo Kα radiation ($\lambda = 0.71069$ Å). Three standard reflections monitored every 4 h showed no significant variation. The intensities were corrected for Lorentz–polarization effects [9], but not for absorption. The crystal data and summary of data collection and structure refinement are given in Table 1.

The positions of all non-hydrogen atoms were obtained from SHELXS 86 [10]. The least-squares refinement gave $R = 0.044$ and $R' = (\Sigma w \Delta F^2 / \Sigma w F_o^2)^{1/2} = 0.067$. In the final cycles of the refinement, hydrogen atoms placed at idealized positions (C–H = 0.96 Å, $\beta = 8.0$ Å^2) were included, but their parameters were not refined. The function minimized was $\Sigma w(F_o - kF_c)^2$, where $w = [\sigma^2(F_o) + 0.01F_o^2]^{-1}$. Atomic scattering factors with corrections for anomalous scattering for Pd, Cl, S and P atoms were taken from ref. 11. Final atomic coordinates are given in Table 2. Figure 1 was drawn by the use of ORTEP [12]. The computer programs used in the calculations were a local version of UNICS

TABLE 1. Crystal data and summary of data collection and structure refinement

Compound	**2a**
Formula	$C_{23}H_{19}ClNPPdS$
Molecular weight	514
Space group	*P*1
a (Å)	12.969(6)
b (Å)	10.246(5)
c (Å)	9.493(3)
α (°)	114.53(3)
β (°)	72.57(3)
γ (°)	105.71(3)
V (Å^3)	1079.2(7)
Z	2
D_{obs} (g cm^{-3})	1.59
D_{calc} (g cm^{-3})	1.58
F(000)	516
μ (Mo Kα) (cm^{-1})	11.4
$2\theta_{max}$ (°)	$3 \leqslant 2\theta \leqslant 50$
Scan type	ω
Scan speed (° s^{-1})	0.033
Scan width (°)	2.0 + 0.4 tan θ
Data used [$F_o^2 \geqslant 3\sigma(F_o^2)$]	2546
$(\Delta/\sigma)_{max}$	0.7
$(\Delta\rho)_{max}$ (e Å^{-3})	0.6

TABLE 2. Atomic coordinates and equivalent isotropic temperature factors (B_{eq} (Å^2)) for (**2a**) with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}
Pd(1)	0.0	0.0	0.0	3.243(3)
Cl(1)	−0.02992(39)	−0.15569(45)	0.12496(54)	5.156(17)
S(1)	0.02031(48)	0.12311(62)	−0.16641(64)	6.446(23)
P(1)	0.09453(28)	0.18075(37)	0.17326(41)	2.942(11)
N(1)	−0.0663(10)	−0.1523(13)	−0.1961(14)	3.5(4)
C(1)	0.2179(8)	0.1190(12)	0.1556(13)	1.8(3)
C(2)	0.2325(10)	0.0927(15)	0.2828(14)	2.8(4)
C(3)	0.3191(14)	0.0380(20)	0.2588(18)	4.7(6)
C(4)	0.3900(13)	−0.0084(20)	0.1238(27)	6.0(7)
C(5)	0.3802(14)	0.0259(21)	−0.0019(21)	5.5(6)
C(6)	0.2908(11)	0.0884(14)	0.0091(16)	3.2(4)
C(7)	0.0270(8)	0.2429(11)	0.3844(13)	1.8(3)
C(8)	0.0774(9)	0.3585(13)	0.4891(16)	2.8(3)
C(9)	0.0398(14)	0.4086(18)	0.6515(18)	4.5(5)
C(10)	−0.0654(12)	0.3349(15)	0.6982(16)	3.4(4)
C(11)	−0.1250(14)	0.2343(21)	0.6062(20)	5.2(6)
C(12)	−0.0709(13)	0.1716(17)	0.4233(21)	4.8(6)
C(13)	0.1371(9)	0.3445(11)	0.1267(13)	1.9(3)
C(14)	0.2446(17)	0.4032(20)	0.0832(21)	5.4(6)
C(15)	0.2728(16)	0.5335(23)	0.0616(28)	6.5(8)
C(16)	0.1879(19)	0.5987(24)	0.0610(22)	7.4(8)
C(17)	0.0821(21)	0.5457(24)	0.1048(31)	7.8(10)
C(18)	0.0571(14)	0.4111(19)	0.1409(23)	5.5(7)
C(19)	−0.0397(10)	−0.0565(20)	−0.2737(15)	3.8(5)
C(20)	−0.0442(22)	−0.1240(31)	−0.4451(28)	8.4(10)
C(21)	−0.0925(17)	−0.2683(26)	−0.4930(22)	6.8(8)
C(22)	−0.1173(15)	−0.3605(21)	−0.4046(18)	4.9(6)
C(23)	−0.1012(16)	−0.2944(18)	−0.2532(20)	5.6(6)
Pd(2)	−0.39518(9)	−0.23078(12)	−0.29019(13)	3.040(3)
Cl(2)	−0.37432(32)	−0.07108(37)	−0.42708(44)	3.969(12)
S(2)	−0.41419(30)	−0.33748(38)	−0.11242(42)	3.398(11)
P(2)	−0.48943(29)	−0.41093(39)	−0.45692(45)	3.370(12)
N(2)	−0.3322(10)	−0.0920(14)	−0.0959(15)	3.6(4)
C(24)	−0.5380(24)	−0.5796(28)	−0.4214(28)	8.6(11)
C(25)	−0.6432(12)	−0.6435(15)	−0.3763(18)	3.8(4)
C(26)	−0.6598(15)	−0.7681(18)	−0.3382(16)	4.8(5)
C(27)	−0.5807(17)	−0.8342(16)	−0.3577(18)	5.2(6)
C(28)	−0.4779(18)	−0.7677(20)	−0.3953(22)	6.1(7)
C(29)	−0.4536(15)	−0.6472(21)	−0.4170(22)	5.3(7)
C(30)	−0.6100(17)	−0.3470(20)	−0.4490(28)	6.6(8)
C(31)	−0.6850(15)	−0.2933(18)	−0.2986(20)	4.6(6)
C(32)	−0.7718(12)	−0.2426(16)	−0.2742(21)	4.6(5)
C(33)	−0.7941(14)	−0.2342(18)	−0.3958(19)	4.4(5)
C(34)	−0.7223(18)	−0.2597(23)	−0.5512(32)	7.2(9)
C(35)	−0.6338(19)	−0.3322(25)	−0.5698(30)	7.8(9)
C(36)	−0.4275(14)	−0.4758(21)	−0.6598(21)	5.1(6)
C(37)	−0.3204(11)	−0.4062(16)	−0.7298(16)	3.4(4)
C(38)	−0.2818(12)	−0.4464(16)	−0.8731(20)	4.0(5)
C(39)	−0.3287(18)	−0.5774(25)	−0.9894(21)	6.7(8)
C(40)	−0.4286(14)	−0.6413(18)	−0.9299(19)	4.7(5)
C(41)	−0.4891(18)	−0.6038(21)	−0.7689(21)	5.7(7)
C(42)	−0.3652(15)	−0.1623(17)	0.0093(19)	4.8(6)
C(43)	−0.3435(12)	−0.1134(18)	0.1436(15)	3.7(5)
C(44)	−0.3064(20)	0.0257(29)	0.2166(27)	7.5(10)
C(45)	−0.2754(16)	0.1006(25)	0.1357(29)	7.8(9)
C(46)	−0.2907(11)	0.0448(21)	−0.0364(22)	4.9(7)

(RSLC-3, HBLS-IV, RSSFR-5 and DAPH) [13]. Calculations were performed on a HITAC M-660K computer at Osaka City University.

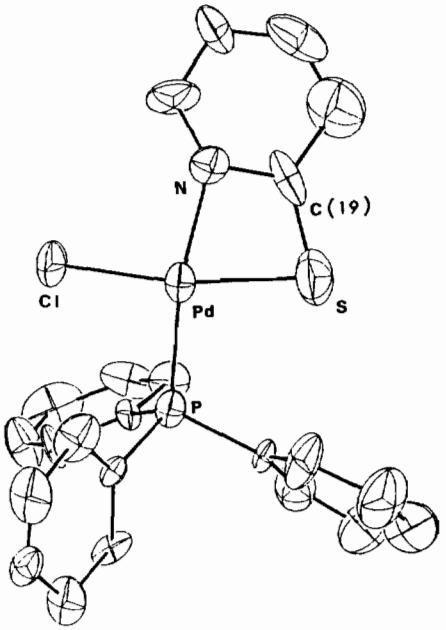
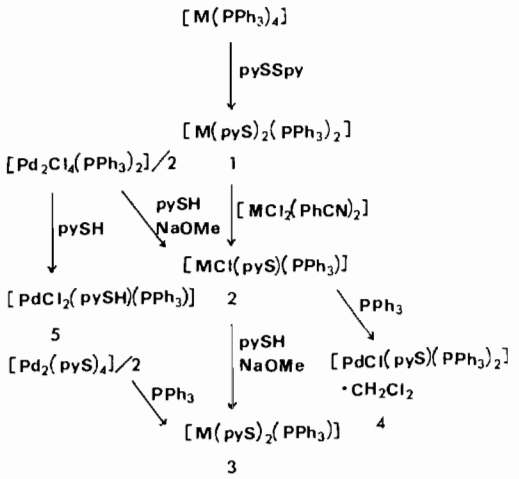


Fig. 1. ORTEP diagram of [PdCl(pyS)(PPh$_3$)] (**2a**-A). Thermal ellipsoids are drawn at the 50% probability level.



Scheme 1. **a**: M = Pd; **b**: M = Pt.

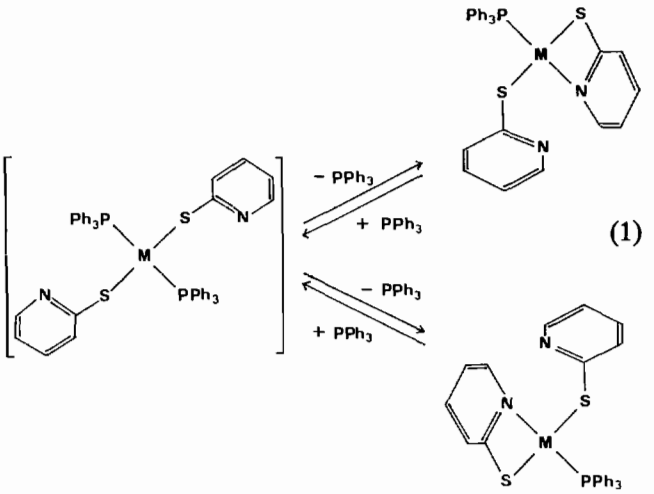
Results and discussion

Synthesis

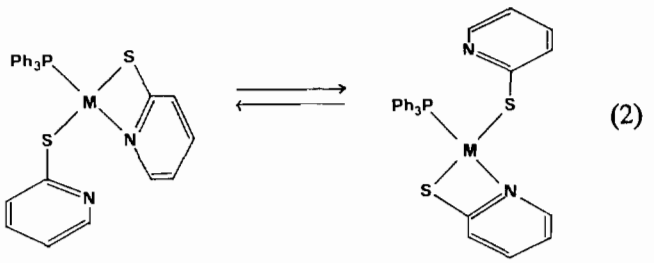
The synthetic routes to the pyS$^-$ or pySH-containing mononuclear Pd(II) and Pt(II) complexes prepared in this paper are presented in Scheme 1.

Oxidative addition of dipyridyl-2,2′-disulfide (pySSpy) to [M(PPh$_3$)$_4$] (M = Pd, Pt) in toluene readily affords [M(pyS)$_2$(PPh$_3$)$_2$] (**1a**: M = Pd; **1b**: M = Pt) in high yields. Previously, the same complexes were prepared by the reaction of [MCl$_2$(PPh$_3$)$_2$] with TlpyS [4], but the procedure needed long hours for completion and the yields were not so high: the presence of fluxional behavior in solution was based on ^{1}H and ^{31}P NMR spectral

evidence. The molecular weights of **1a** and **1b** were determined by us to be one-half the formular weights, respectively, suggesting phosphine dissociation in solution. This is supported by the NMR data, but **1a** and **1b** differ from one another in the dynamic behavior caused by phosphine dissociation, i.e. phosphine exchange (eqn. (1)) and ligand scrambling (eqn. (2)) (*vide infra*).



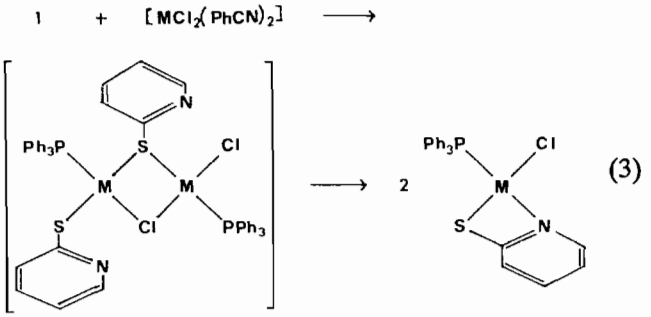
(1)



(2)

When $[Pd_2Cl_4(PPh_3)_2]$ was allowed to react with pySH and NaOMe in THF with the aim of obtaining the pyS-bridged dinuclear complex $[PdCl(pyS)(PPh_3)]_2$, a reddish orange crystalline product **2a** was isolated. The analytical result is consistent with the above formulation, but the molecular weight determined shows this complex to be monomeric. The $^{31}P\{^1H\}$ NMR spectrum of **2a** in $CDCl_3$ reveals that the value is not one caused by phosphine dissociation from the dinuclear structure (*vide infra*). The ^1H NMR spectrum and X-ray analysis confirmed the chelate structure of the pyS ligand in **2a**. Strange to say, the corresponding trimethylphosphine complex $[PdCl(pyS)(PMe_3)]_2$ was revealed to have the pyS-bridged dinuclear structure by X-ray analysis [14]. Chloride-bridge splitting by pySH, followed by elimination of hydrogen chloride by NaOMe, or the direct reaction with the sodium salt of pySH will result in a formation of **2a**. In fact, the intermediate in the former process, namely, $[PdCl_2(pySH)(PPh_3)]$ (**5**) was isolatad from the reaction mixture of $[Pd_2Cl_4(PPh_3)_2]$ and pySH in the absence of the base. Although the ^1H NMR spectrum of **5** in $CDCl_3$ does not show a NH proton signal within the 10–15 ppm region, the IR spectrum exhibits a weak band assignable to ν(NH) at 3090 cm^{-1}, strongly supporting coordination of the ligand as 1*H*-pyridine-2-thione [3]. Recently, one of us (S.O.) revealed the molecular structure of the complex $[Pd(pySH)_4]Cl_2$ involving S-unidentate pySH [7c].

Complex **2a** can be alternatively formed by the ligand scrambling reaction between **1a** and $[PdCl_2(PhCN)_2]$ in THF. Similarly the corresponding platinum complex **2b** was prepared using **1b** and $[PtCl_2(PhCN)_2]$ as reactants. However, such ligand scrambling has never occurred between $[Pt(SPh)_2(PPh_3)_2]$ and $[PdCl_2(MeCN)_2]$, and these reactants gave simply the benzenethiolato-bridged dinuclear complex $[(Ph_3P)_2Pt(SPh)_2PdCl_2]$ [15], suggesting that one more donor atom like nitrogen is necessary to cause scrambling. If we consider dissociation of one of the phosphine ligands from **1** in solution, the formation of the S- and Cl-bridged dinuclear complex is not difficult to suppose. These bridging ligands will be readily transfered to the other metal center, respectively, with assistance of the N-donor atom to form the mononuclear complex **2** (eqn. (3)). The high stability of the chelate ring in **2a** and **2b** may be a dominant factor for the formation of these complexes.



(3)

One more chloride abstraction from complexes **2a** and **2b** by a further mole of NaOMe in the presence of pySH affords **3a** and **3b**, respectively, in high yield. The Pd(II) complex **3a** can be alternatively prepared from $[Pd_2(pyS)_4]$ by the addition of PPh_3, indicating that the pyS-bridging is readily cleaved by PPh_3. The molecular weights determined indicate that these complexes are monomeric and no phosphine dissociation occurs in solution. Hence, the complexes are formally represented as $[M(pyS\text{-}N,S)(pyS\text{-}S)(PPh_3)]$. The chelate ring opening of complex **2a** has never occurred on addition of an equivalent amount of PPh_3 and simply an adduct $[PdCl(pyS\text{-}N,S)(PPh_3)_2]$ (**4**) was isolated from the reaction mixture.

NMR spectra and solution behavior

The ^1H NMR spectrum of **2a** in C_6D_6 is shown in Fig. 2. The spectrum consists of all sharp and well-resolved signals, revealing the stereochemically rigid structure of **2a** in solution. In contrast with $[PdCl(pyS)(PMe_3)]_2$, in which the monomer–dimer equilibrium was found in solution [14], there was no sign of such an equilibrium at room temperature. The assignment of each pyridine-ring proton is based on a comparison of the coupling constants for **2a** with those for trimethyl-2-pyridylsilane ($J_{34}=8.4, J_{35}=1.5, J_{36}=1.2, J_{45}=7.5, J_{46}=1.4, J_{56}=4.8$ Hz) [16]. As is seen from the data, H^6 and H^5 protons of **2a** couple to the P atom, indicating that the complex has a *trans*-(P,N) structure with a chelated pyS ligand. The $^{31}P\{^1H\}$ NMR spectrum of **2a** in $CDCl_3$ exhibits only one singlet, confirming that the molecular weight of **2a** decided as monomeric is not that caused by phosphine dissociation from the dinuclear structure $[Pd_2Cl_2(\mu\text{-}pyS)_2(PPh_3)_2]$, although the analogous 2-picolyl complex $[Pd_2Cl_2(\mu\text{-}CH_2C_5H_4N\text{-}C,N)(PPh_3)_2]$ was found to be dinuclear [17]. It is evident from the ^1H and $^{31}P\{^1H\}$ NMR data and the molecular weight determined that the corresponding Pt(II) complex **2b** has the same *trans*-(P,N) chelate structure as that of **2a**.

The complex **2a** reacts with an equivalent mole of PPh_3 in CH_2Cl_2 to give the five-coordinate phosphine adduct **4**. The ^1H NMR spectrum of **4** in C_6D_6 shows four sharp and well-resolved signals assignable to ring protons of the chelated pyS ligand. On the other hand, phenyl proton signals of the phosphine ligands are broadened because of the slow phosphine exchange occurring between the coordinated and freed PPh_3 ligands.

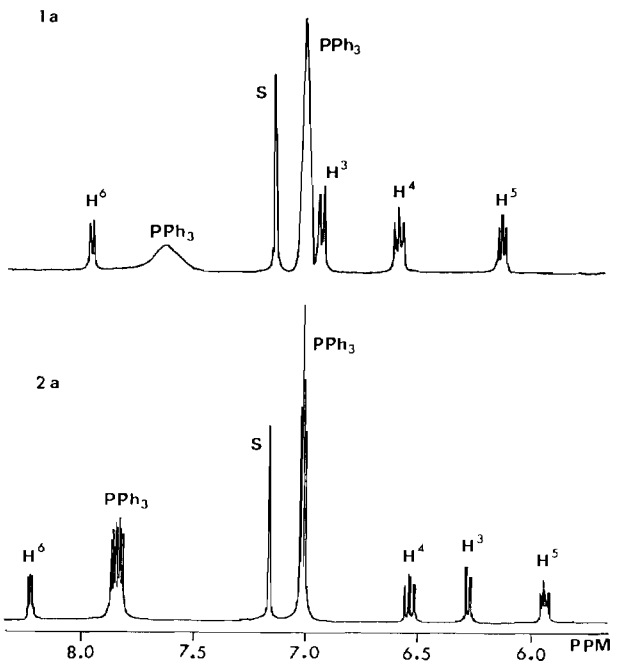


Fig. 2. ^1H NMR spectra of $[Pd(pyS)_2(PPh_3)_2]$ (**1a**) and of $[PdCl(pyS)(PPh_3)]$ (**2a**) in C_6D_6. S denotes solvent.

As shown in Fig. 2, the ^1H NMR spectrum of **1a** in C_6D_6 consists of a set of four sharp and well-resolved signals of the pyridine ring protons and two broad signals from the phosphine ligand. By comparison with the magnitude of the coupling constants for $Me_3Si(C_5H_4N\text{-}C^2)$, the signals at 6.12, 6.59, 6.93 and 7.98 ppm are assigned to H^5, H^4, H^3 and H^6, respectively. No coupling to the phosphorus atom for any protons was observed, suggesting that the nitrogen atom does not coordinate to the metal atom or phosphine exchange occurs rapidly in solution. The $^{31}P\{^1H\}$ NMR spectrum of **1a** in $CDCl_3$ observed two broad signals, one of which was assignable to the free phosphine. These observations, together with the broad phenyl proton signals for PPh_3, suggest that the two equilibria (eqns. (1) and (2)) are present. The result of the molecular weight determination is consistent with the above view.

The ^1H NMR spectrum of the analogous Pt(II) complex **1b** showed broad signals in the whole spectral region, and hence precise assignment of the signals was impossible. On the other hand, the $^{31}P\{^1H\}$ NMR spectrum of **1b** exhibits two comparatively sharp signals, one being accompanied by the ^{195}Pt satellites. These phenomena are in contrast to those observed for the ^1H and $^{31}P\{^1H\}$ NMR spectra of **1a**. In conclusion, the above-mentioned results suggest that in the case of the Pd(II) complex the ligand scrambling process is more rapid than the process of phosphine exchange, while in the Pt(II) case the latter process is extremely slow, if present, and the former is also not so rapid.

The ^1H NMR spectrum of **3a** in $CDCl_3$ at 20 °C showed sharp phenyl proton signals of the phosphine ligand. The observed pyridine-ring proton signals are also sharp and, further, only one set of the signals is found, indicating that rapid ligand scrambling is occurring in solution at room temperature. With a decrease in temperature, the four sharp pyridine-ring proton signals observed at the higher temperature gradually broadened with the apparent shift, and changed to almost flat signals at −60 °C, showing that even at this temperature complex **3a** is not still stereochemically rigid. As was so in the case of **1**, the dynamic behavior of **3** in solution is also slower in the Pt(II) complex than that in the Pd(II), and as a result the ^1H NMR spectrum of **3b** exhibits very broad signals in the whole spectral region.

Molecular structure of [PdCl(pyS)(PPh$_3$)] (2a)

The unit cell contains two crystallographically distinct but chemically equivalent molecules (molecules A and B). Figure 1 shows the structure of molecule A and Table 3 lists selected bond distances and angles.

TABLE 3. Selected bond distances (Å) and angles (°) for [PdCl(pyS)(PPh_3)] (**2a**) with e.s.d.s in parentheses

Pd(1)–Cl(1)	2.250(6)
Pd(1)–S(1)	2.320(7)
Pd(1)–P(1)	2.255(4)
Pd(1)–N(1)	2.112(13)
S(1)–C(19)	1.781(21)
Pd(2)–Cl(2)	2.399(5)
Pd(2)–S(2)	2.289(5)
Pd(2)–P(2)	2.218(5)
Pd(2)–N(2)	2.046(14)
S(2)–C(42)	1.750(19)
Cl(1)–Pd(1)–S(1)	169.5(2)
Cl(1)–Pd(1)–P(1)	93.8(2)
Cl(1)–Pd(1)–N(1)	95.7(4)
S(1)–Pd(1)–P(1)	96.4(2)
S(1)–Pd(1)–N(1)	73.9(4)
P(1)–Pd(1)–N(1)	168.5(4)
Pd(1)–S(1)–C(19)	77.3(7)
Pd(1)–N(1)–C(19)	93.9(11)
S(1)–C(19)–N(1)	114.8(14)
Cl(2)–Pd(2)–S(2)	167.6(2)
Cl(2)–Pd(2)–P(2)	92.1(2)
Cl(2)–Pd(2)–N(2)	101.4(4)
S(2)–Pd(2)–P(2)	98.6(2)
S(2)–Pd(2)–N(2)	67.3(4)
P(2)–Pd(2)–N(2)	164.8(4)
Pd(2)–S(2)–C(42)	84.9(7)
Pd(2)–N(2)–C(42)	105.8(11)
S(2)–C(42)–N(2)	100.5(13)

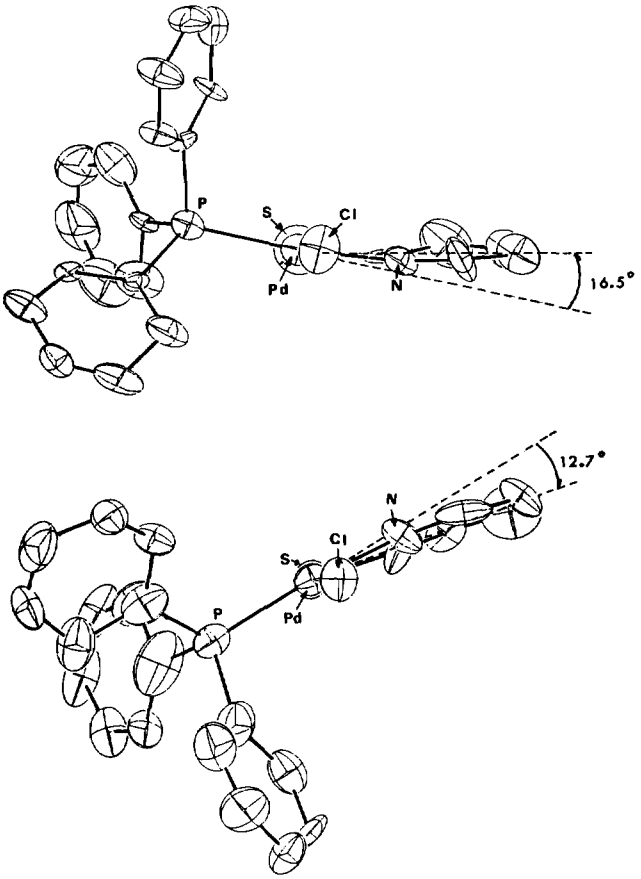


Fig. 3. Structures of **2a**-A (upper) and **2a**-B (lower) showing the disposition of pyridine ring folded in opposite directions on the plane defined by the Pd, Cl, P and S atoms.

The complexes are monomeric and each Pd atom has a square-planar coordination with four donor atoms of N, S, P and Cl. The Pd atom is deviated 0.0962 Å (**2a**-A) and 0.1183 Å (**2a**-B) on the opposite side of the N and P atoms from the coordination plane defined by the N, S, P and Cl atoms. The pyS ligand together with the Pd atom forms a four-membered chelate ring, and the P atom is situated in position *trans* to the N atom, constituting a *trans*-(P,N) structure. As shown in Fig. 3, the plane of the pyridine ring is folded on the plane defined by the Pd, Cl, P and S atoms with dihedral angles of 163.5° for **2a**-A and 12.7° for **2a**-B; this is the major difference between the structures of **2a**-A and **2a**-B.

Some of the bond distances and angles in **2a**-A are also different from the corresponding ones in **2a**-B to such an extent that cannot be ignored. However, the Pd–N (2.112(13), 2.046(14) Å) and the Pd–S (2.320(7), 2.289(5) Å) bond distances are comparable to those in the pyS-bridged dinuclear Pd(II) complexes [$Pd_2(pyS)_4$] (2.112 (mean) Å for Pd–N, 2.293 (mean) Å for Pd–S) [7d], [$Pd_4I_2(pyS)_6$] (2.032 (mean) Å for Pd–N and 2.314 (mean) Å for Pd–S) [7d], and [$Pd_2Cl_2(pyS)_2(PMe_3)_2$] (2.134 (mean) Å for Pd–N, 2.295 (mean) Å for Pd–S) [14]. Generally speaking, these bond distances are significantly shorter in **2a**-B than in **2a**-A, and hence the pyS–chelate bond is a little bit stronger in **2a**-B. Reflecting the stronger Pd–S bond, the Pd–Cl bond distance (2.399(5) Å) in **2a**-B is stretched 0.149 Å compared with the corresponding one in **2a**-A.

The pyS ligand is chelated to the Pd atom with small bite angles of 73.9° (**2a**-A) and 67.3° (**2a**-B). Because no other pyS-chelated Pd(II) complexes have been prepared and crystallographically analyzed, we do not have any data to compare with these bite angle values; nevertheless the value for **2a**-B is comparable to those in the pyS-chelated complexes of many other transition metals: [$Ru(pyS)_2(CO)(PPh_3)$] (67.8(1), 67.51(9)°) [5], [$Ru(pyS)_2(PPh_3)_2$] (66.6(2), 67.7(2)°) [6a], [$Fe(pyS)_3$]$^-$ (65.9(1)–66.3(1)°) [6e], [$Ni(pyS)_3$]$^-$ (67.4(1)–67.8(1)°) [6f] and [$Os(pyS)_2(CO)_2$] (66.7(1), 67.5(1)°) [6h]. The N..S bites (2.67(1) Å for **2a**-A, 2.419(1) Å for **2a**-B) are well correlated to the above-mentioned bite angle values. Why complex **2a** is mononuclear and does not make the pyS-bridged dinuclear complex like [$PdCl(pyS)(PMe_3)]_2$ remains unknown.

Supplementary material

Anisotropic temperature parameters, the hydrogen atom coordinates, a complete list of bond distances and angles, and ORTEP diagram of [PdCl(pyS)(PPh_3)] (**2a**-B), as well as tables of observed and calculated structure factors are available from the authors on request.

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