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Syntheses and spectroscopic properties of palladium(II) complexes with bidentate phosphine and thiolate ligands. X-ray crystal structure of $[Pd(SCH_2Ph)_2\{Ph_2P(CH_2)_3PPh_2\}]$

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Abstract—By the reactions of Pd^{2+}, thiolate ($PhCH_2S^-$ or pdt) and dppe or dppp [pdt = $SCH_2CH_2CH_2S^{2-}$, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane] in MeOH, the following complexes, $[Pd(SCH_2Ph)_2(dppe)]$ (**1**), $[Pd(SCH_2Ph)_2(dppp)]$ (**2**) and [Pd(pdt)(dppp)] (**3**), were prepared. The crystal structure of **2** was analysed by single-crystal X-ray diffraction. The palladium atom is tetra-coordinated with a distorted square-planar geometry of two phosphorus and two sulfur atoms. Their IR, ^{31}P and ^1H NMR spectra are reported. © 1997 Elsevier Science Ltd

Keywords: palladium(II) complexes; syntheses; crystal structure; NMR spectra; IR spectra.

Owing to their variation in geometric and electronic structures, and their application for homogeneous or heterogeneous catalytic functions, transition metal complexes with phosphine ligands have been studied extensively [1]. In recent years, we have explored the complexes blending both phosphine and thiolate ligands and a series of the complexes, such as $(Et_4N)[Co(SPh)_3(PPh_3)]$ [2], $[Co(SPh)_2L]$ (L = $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$) [3], $[Co_2(SPh)_4(dppx)]$ [dppx = $Ph_2PCH_2PPh_2$, $Ph_2P(CH_2)_2PPh_2$)] [4–6], $[Co_3(SC_6H_4S)_3(PBu_3^n)_3]$ [7], $[Ni(SR)_2(PBu_3^n)_2]$ (R = Ph, *p*-tol) [8] and $[Ni(SC_2H_4SC_2H_4S)PPh_3]$ [9], have been reported. By the reactions of Ni^{2+} or Pd^{2+}, 1,2-dithilates and PR_3 (R = Ph, Et) in MeOH, we have also isolated complexes $Ni_2(edt)_2(PPh_3)_2]$ and $[Ni_2(edt)_2(PEt_3)_2]$ [10,11], $Pd(tdt)(PPh_3)_2$, $Pd_2(edt)_2(PPh_3)_2$, $Pd_2(pdt)_2(PPh_3)_2$, $Pd_2(edt)_2(PEt_3)_2$, $Pd_2(pdt)_2(PEt_3)_2$, $Pd_2(Hmp)_2(PPh_3)_2Cl_2$ and $Pd_2(tdt)_2(PEt_3)_2$ [12] (tdt = 1,2-tolunedithiolate, edt = 1,2-ethanedithiol, pdt = 1,2-propanedithiol and mp = mecaptophenol). Herein we report the syntheses and spectroscopic properties of a series of Pd^{2+} complexes with blending bidentate phosphine and thiolate ligands, $[Pd(SCH_2Ph)_2(dppe)]$ (**1**), $[Pd(SCH_2Ph)_2(dppp)]$ (**2**) and [Pd(pdt)(dppp)] (**3**), of which the crystal structure of **2** has been determined by X-ray single-crystal diffraction. The crystal structures of **1** and **3** have also been reported by our group [13].

EXPERIMENTAL

All operations were carried out under dinitrogen with standard Schlenk techniques. Reagent $PdCl_2$, $HSCH_2Ph$, H_2pdt and phosphine ligands were purchased from Merck, solvents from Shanghai Chemical Company. Na_2pdt and $NaSCH_2Ph$ were obtained from the stoichiometric reaction of H_2pdt and $HSCH_2Ph$ with sodium metal in MeOH, respectively.

All elemental analyses were carried out in this Insti-

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tute. IR spectra were recorded on a Magna 750 IR spectrometer. ^{31}P NMR spectra were measured in DMSO on a Varin Unit-500 spectrometer with saturated H_3PO_4 as the external standard.

Preparation of the complexes

[Pd(SCH$_2$Ph)$_2$(*dppe*)] (**1**). To a stirred solution of dppe (0.38 g, 1 mmol) and anhydrous $PdCl_2$ (0.18 g, 1 mmol) in DMF (20 cm^3) a solution of $NaSCH_2Ph$ (0.27 g, 2 mmol) in MeOH (15 cm^3) was added. After the reaction solution was stirred for 24 h, a black precipitate formed was filtered off. The filtrate was mixed with $CH(CH_3)_2OH$ (10 cm^3). The final solution was filtered again and the filtrate was kept in an icebox for 2 weeks to yield dark-red crystals of **1** (42%). IR (KBr): 528(s), 482(m), 438(w), 380(m), 353(m), 305(m) cm^{-1}. ^{1}H NMR (ppm): 3.36, 3.75, 7.17, 7.40, 7.77; ^{31}P NMR (ppm): 55.8. Found: C, 64.7; H, 5.3; P, 8.0. Calc. for $C_{40}H_{38}PdS_2P_2$: C, 63.9; H, 5.1; P, 8.3%.

[Pd(SCH$_2$Ph)$_2$(*dppp*)] (**2**). To a stirred solution of dppp (0.40 g, 1 mmol) and anhydrous $PdCl_2$ (0.18 g, 1 mmol) in DMF (15 cm^3) a solution of $NaSCH_2Ph$ (0.27 g, 2 mmol) in MeOH (15 cm^3) was added. After the reaction solution was stirred for 24 h, the black precipitate which formed was filtered off. The filtrate was mixed with $CH(CH_3)_2OH$ (10 cm^3). The final solution was filtered again and the filtrate was kept in an icebox for 2 weeks to yield dark-red crystals of **2** (38%). IR (KBr): 509(m), 482(m), 432(w), 372(m), 330(m), 307(m) cm^{-1}. ^{1}H NMR (ppm): 1.61, 2.50, 3.36, 3.72, 7.08, 7.14, 7.37, 7.67; ^{31}P NMR (ppm): 9.17. Found: C, 63.2; H, 5.0; P, 8.2. Calc. for $C_{41}H_{40}PdS_2P_2$: C, 64.3; H, 5.2; P, 8.1%.

[Pd(*pdt*)(*dppp*)] · *CH$_3$CN*] (**3**). To a stirred solution of dppp (0.40 g, 1 mmol) and anhydrous $PdCl_2$ (0.18 g, 1 mmol) in MeCN (35 cm^3) a solution of Na$_2$pdt (0.16 g, 1 mmol) in MeOH (15 cm^3) was added. After the reaction solution was stirred for 24 h, a black precipitate formed was filtered off. The filtrate was mixed with $CH(CH_3)_2OH$ (10 cm^3). The final solution was filtered again and the filtrate was kept in an icebox for 2 weeks to yield dark-red crystals of **3** (35%). IR (KBr): 513(m), 482(m), 449(w), 432(w), 422(w), 360(m), 339(m), 300(m) cm^{-1}. ^{1}H NMR (ppm): 1.85, 2.65, 3.37, 7.37, 7.63; ^{31}P NMR (ppm): 6.87. Found: C, 58.2; H, 5.1; P, 8.9. Calc. for $C_{32}H_{35}NPdS_2P_2$: C, 57.7; H, 5.3; P, 9.3%.

X-ray structural analysis

Suitable single crystal of **2** was mounted on a glass fibre and data collection was performed at ambient temperature on a Rigaku RX-II Imaging Plate diffractometer using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å). The crystallographic and data collection parameters are summarized in Table 1. The coordinates of the metal atom were determined by Patterson method and the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structure was refined by the full-matrix least-squares technique with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were not included in the calculations. All calculations were performed on a Compaq 486 computer with the SHELEXTL-PC program package.

Table 1. Crystallographic data and refinement parameters for **2**

Formula	$C_{41}H_{40}P_2S_2Pd$
Mol. wt	765.20
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	18.381(4)
b (Å)	9.434(2)
c (Å)	22.559(5)
α (°)	90
β (°)	108.30(3)
γ (°)	90
V (Å^3)	3714(2)
Z	4
D_c (g cm^{-3})	1.368
μ (cm^{-1})	7.26
F(000)	1576
R	0.046
R_w	0.052
Crystal dimensions (mm^3)	$0.20 \times 0.25 \times 0.30$
Scan mode	ω
2θ range (°)	2–45
hkl range	$h = 0$–23, $k = -11$-10, $l = -28$-27
No. of reflections measured	12,891
No. of reflections refined	6777 with $F > 4\sigma(F)$
Parameters refined	415
w	$\sigma^2(F) + 0.0001F^2$
Highest residue (e Å^3)	0.54
Lowest residue (e Å^3)	-0.67

RESULTS AND DISCUSSION

Syntheses of the complexes

From the reaction system of Pd^{2+}, the bidentate phosphine ligand (dppe or dppp) and thiolate ($PhCH_2S^-$ or $SCH_2CH_2CH_2S^{2-}$) in DMF/MeOH complexes **1**–**3** were isolated. If the bidentate phosphine ligands and Pd^{2+} were used as initial reactant to react with either thiolate or 1,2-dithiolate, the products obtained are always mononuclear, which is different from the reaction system of Pd^{2+}, PR$_3$ (R = Et, Ph) and thiolate where both mononuclear and binuclear complexes were isolated [12].

In our previous work, a cleavage of the C—S bond and a condensation of two edt ligands was observed during the reaction of Ni^{2+}, a bidentate ligand of

$SCH_2CH_2S^{2-}$ and PR_3 (R = Et, Ph) in 1 : 1 : 2 molar ratio in methanol [10]. However, similar to the reaction system of Pd^{2+}, PR_3 (R = Et, Ph) and bidentate ligands $[SC_6H_3(CH_3)S^{2-}$ $SCH_2CH_2S^{2-}$, $SCH_2CH(CH_3)S^{2-}$, $HOC_6H_4S^-]$ [12], the cleavage of the C—S bond was not observed in this reaction system of Pd^{2+}, bidentate phosphine ligands and $SCH_2CH_2CH_2S^{2-}$, $PhCH_2S^-$).

Structure of $[Pd(S_2CH_2Ph)_2(dppp)]$ (2)

Selected bond distances and bond angles are listed in Table 2. The molecular structure of **2**, as depicted in Fig. 1, does not possess any crystallographic symmetry. The palladium atoms is coordinated by two phosphorus atoms from phosphine and two sulfur atoms from the thiolate ligands in a distorted square-planar geometry. The bidentate dppp ligand chelates to the Pd atom to form a six-membered ring, [(P(1)P(2)C(1)C(2)C(3)Pd], which is in a chair form. The dihedral angle of PdS_2 and PdP_2 planes is 169.28°. The Pd Atom is 0.18 Å above the least-squares plane S(1)S(2)P(1)P(2). Two Pd—S—C angles are quite different, being 100.0(1) and 109.5(1)°. The average Pd—S bond length is 2.364(9) Å, longer than those found in the nickel complexes containing monodentate thiolate and phosphine ligands, such as $[Ni(S\text{-}p\text{-}Tol)_2(PBu_3^n)_2]$ (2.213 Å) and $[Ni(SPh)_2(PBu^n)_2]$ (2.217 Å) [8]. The average Pd—P bond length of 2.284(3) Å is longer than those reported in the Ni—S—P complexes [8,11] and those in $[Co_2(SPh)_4(dppe)]$ (2.210 Å) [14] and $[Pt(SPh)_2(dppm)]$ (2.247 Å) [15]. The comparison of the significant molecular parameters for some M—S—P (M = Pd, Ni) complexes are listed in Table 3. The average C—S bond distance (1.839 Å) is much longer than (1.74–1.80 Å) found in other M-thiolate complexes.

All sulfur atoms in the molecule adopt the sp^3 configuration. As shown in Scheme 1, such configuration may induce that the two $PhCH_2S^-$ ligands and metal atom form three conformations: C, M, and S types. For instance, the conformation of $Pt(dppe)(SPh)_2$ is C type [15] and that of $Co(dppp)(SPh)_2$ is M type [3]. The conformation of **2** is S type, because there is a considerable torsion in the MS_2P_2 plane due to the arrangement of the atoms in C or M conformation.

^{31}P *NMR spectra*

The ^{31}P NMR chemical shifts of the complexes and some relating compounds are listed in Table 4. It is shown that the chemical shifts of the ligand dppp in the complexes are in the range 6.87–9.17 ppm, while that of dppe is 55.8 ppm. It is clear that electrons are transferred from phosphorus atoms to the metal atoms to cause the P nucleus to be deshielded to downfield and the increased chemical shifts and the deshielding of P in dppe complexes is much higher than that in dppp complexes. As mentioned above, the five-membered chelating ring PdP_2C_2 in the dppe complex is in a nearly planar form, while the six-membered chelating ring PdP_2C_3 in dppp complexes is non-planar chair form. The coordination of P atoms to metal atoms may be stronger in the dppe complex than in the dppp complexes and more electrons are transferred from phosphorus atoms to the metal atoms to cause the higher deshielding.

Table 2. Selected bond distances (Å) and bond angles (°) for $Pd(SCH2Ph)_2(dppp)$

Pd(1)—P(1)	2.283 (1)	Pd(1)—P(2)	2.285 (1)
Pd(1)—S(1)	2.372 (1)	Pd(1)—S(2)	2.355 (1)
P(1)—C(1)	1.834 (3)	P(1)—C(11)	1.829 (4)
P(1)—C(21)	1.819 (4)	P(2)—C(3)	1.831 (4)
P(2)—C(31)	1.824 (5)	P(2)—C(41)	1.823 (4)
S(1)—C(4)	1.831 (6)	S(2)—C(5)	1.846 (4)
C(1)—C(2)	1.528 (6)	C(2)—C(3)	1.551 (5)
C(4)—C(51)	1.508 (6)	C(5)—C(61)	1.499 (7)
P(1)—Pd(1)—P(2)	92.8(1)	P(1)—Pd(1)—S(1)	174.0(1)
P(2)—Pd(1)—S(1)	86.7(1)	P(1)—Pd(1)—S(2)	86.2(1)
P(2)—Pd(1)—S(2)	178.9(1)	S(1)—Pd(1)—S(2)	94.4(1)
Pd(1)—P(1)—C(1)	116.5(1)	Pd(1)—P(1)—C(11)	109.9(1)
C(1)—P(1)—C(11)	105.0(2)	Pd(1)—P(1)—C(21)	117.6(1)
C(1)—P(1)—C(21)	99.2(2)	C(11)—P(1)—C(21)	107.3(2)
Pd(1)—P(2)—C(3)	117.8(1)	Pd(1)—P(2)—C(31)	110.2(1)
C(3)—P(2)—C(31)	104.6(2)	Pd(1)—P(2)—C(41)	117.2(1)
C(3)—P(2)—C(41)	97.9(2)	C(31)—P(2)—C(41)	107.8(2)
Pd(1)—S(1)—C(4)	100.0(1)	Pd(1)—S(2)—C(5)	109.5(1)
P(1)—C(1)—C(2)	116.9(3)	C(1)—C(2)—C(3)	111.3(4)
P(2)—C(3)—C(2)	114.5(3)	S(1)—C(4)—C(51)	110.3(4)
S(2)—C(5)—C(61)	112.9(3)		

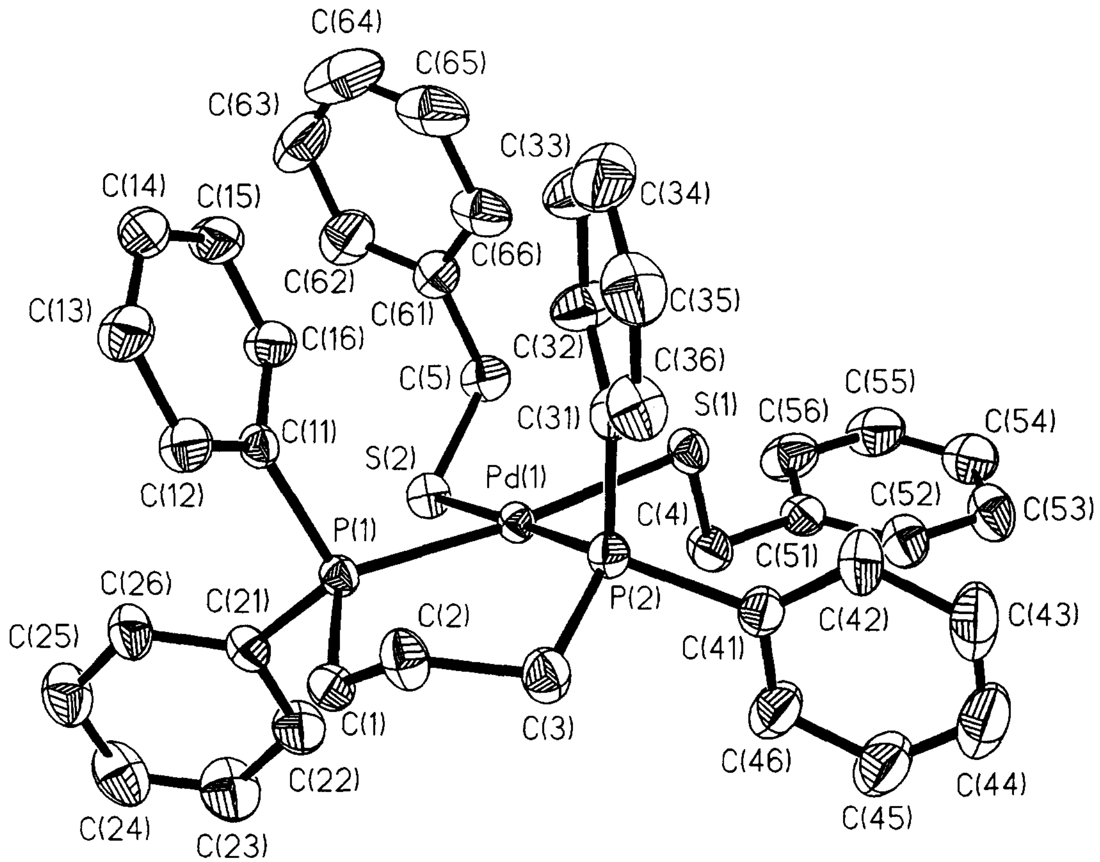
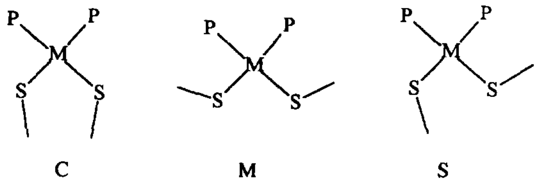


Fig. 1. Structure of complex **2** with H atoms omitted.

Table 3. Comparison of the significant molecular parameters for some M—S—P (M = Pd, Ni) complexes

Complex	M—S_t^{a}	M—S_b	M—P	Reference
1	2.360(2)		2.277(2)	[13]
2	2.296(3)		2.281(3)	This work
3	2.327(8)		2.298(6)	[13]
4	2.297(5)		2.330(3)	[12]
5	2.305(6)		2.291(6)	[12]
6	2.158(2)	2.198(3)	2.188(3)	[10]
7	2.170(1)	2.205(2)	2.193(2)	[10]
8	2.158(3)	2.201(2)	2.184(3)	[10]

4 Pd(tdt) $(PPh_3)_2$], **5** [Pd_2(tdt)$PEt_3)_2$], **6** [$Ni_2(edt)_2(PPh_3)_2$], **7** [$Ni_2(pdt)_2(PPh_3)_2$], **8** [$Ni_2(pdt)_2(PEt_3)_2$].



Scheme 1. Structural types of mononuclear transition metal complexes with dithiolate and phosphine ligands.

For these complexes, one ^{31}P NMR signal in DMSO was observed in solution, indicating that the environments of the two phosphorus atoms in each complex are identical. From the molecular structure information and related studies [16], we can deduce that each of these complexes adopts only one structural mode in solution. This is different from the Ni^{2+} complexes with edt and bidentate phosphine ligands, which possess several structural modes in solution [17].

Table 4. IR absorption peaks and ^{31}P NMR chemical shifts of the palladium and some relating complexes

Complex	$\nu_{M—P}$ or $\nu_{M—P}$ (cm^{-1})	δ (ppm)	Reference
[Pd(SCH$_2$Ph)$_2$(dppe)]^a	380, 353, 305	55.8	This work
[Pd(SCH$_2$Ph)$_2$(dppp)]^a	372, 330, 307	9.17	This work
[Pd(pdt) (dppp)]^a	360, 339, 300	6.87	This work
[Ni (edt) (dppp)]^b		43.2, 32.7, 21.4, 5.7	[17]
[Ni (tdt) (dppe)]^a		59.0	[17]
dppe		−12.5	[18]
dppp		−16.7	[18]

^{a} DMSO as solvent.
^{b} CDCl$_3$ as solvent.

The ^{1}H NMR spectra of the complexes in DMSO at ambient temperature exhibit phenyl resonances at the range 7.14–7.77 ppm and the methylene resonances in multiplet with the range 1.61–3.75 ppm. The proton chemical shifts of these complexes are similar to the respective free ligands.

The 400–4000 cm^{-1} region of IR spectra for the complexes is the diphosphine and thiolate ligand fingerprints and very little changes are observed upon complexation with metal atoms. ν(Pd—P) and ν(Pd—S) vibration absorptions of the complexes are in the range 300–380 cm^{-1} and are difficulty to distinguished with each other.

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