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SYNTHESES OF PALLADIUM(II) COMPLEXES WITH THIOLATE AND PHOSPHINE LIGANDS. X-RAY CRYSTAL STRUCTURES OF [Pd(tdt)(PPh₃)₂] · C₂H₄Cl₂ AND [Pd₂(Hmp)₂(PPh₃)₂Cl₂]

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Abstract—By the reactions of Pd^{2+} , 1,1-dithiolate $[SC_6H_3(CH_3)S^{2-}$, $SCH_2CH_2S^{2-}$ or SCH_2CH $(CH_3)S^{2-}]$ or thiolate $(HOC_6H_4S^{-})$ and PR_3 (R = Ph, Et) in MeOH, the complexes $[Pd(tdt)(PPh_3)_2]$ (1), $[Pd_2(edt)_2(PPh_3)_2]$ (2), $[Pd_2(pdt)_2(PPh_3)_2]$ (3), $[Pd_2(edt)_2(PEt_3)_2]$ (4), $[Pd_2(pdt)_2(PEt_3)_2]$ (5), $[Pd_2(Hmp)_2(PPh_3)_2Cl_2]$ (6) and $[Pd_2(tdt)_2(PEt_3)_2]$ (7) $(tdt = 1, 2-toluenedithiolate, edt = 1, 2-ethanedithiol, pdt = 1, 2-propanedithiol and mp = mercaptophenol) were prepared and analysed by X-ray diffraction. All palladium atoms are tetra-coordinated with distorted square-planar geometry of phosphorus and/or sulfur atoms. The reaction mechanism of <math>Pd^{2+}$, 1,2-dithiolate and PR_3 (R = Et, Ph) is discussed. Copyright \bigcirc 1996 Elsevier Science Ltd

Transition metal complexes with phosphine ligands have been studied extensively, not only due to their variation in geometric and electronic structures and properties, but also because of their application for homogeneous or heterogeneous catalytic functions.¹ Metal thiolate complexes are known as ubiquitous biological electron-transfer mediators and have been studied for two decades.^{2,3} However, the complexes blending both phosphine and thiolate ligands have received attention only in recent years. The earlier studies on this project were mainly in the syntheses of simple complexes and survey of their properties and a few have been structurally analysed.⁴⁻⁹ Very recently, the studies of metal-thiolate-phosphine complexes began in our laboratory and a series of complexes, such as $(Et_4N)[Co(SPh)_3(PPh_3)]$,¹⁰ $[Co(SPh)_2L]$ $[L = Ph_2P$ $(CH_2)_3PPh_2$, Ph_2P $(CH_2)_2$ $P(Ph)(CH_2)_2PPh_2]$,¹¹ $[Co_2(SPh)_4(dppx)]$ $[dppx = Ph_2PCH_2PPh_2, Ph_2P$ $(CH_2)_2 PPh_2]$, ¹²⁻¹⁴ $[Co_3(SC_6H_4S)_3(PBu_3^n)_3]$, ¹⁵ [Ni $(SR)_2(PBu_3^n)_2$] (R = Ph, p-tol),¹⁶ [Ni(SC₂H₄SC₂

 $H_4S)PR_3$],¹⁷ have been reported. By the reactions of Ni²⁺, edt²⁻ and PR₃ (R = Ph, Et) in MeOH, we have also isolated the complexes [Ni(tpdt)(PPh₃)], [Ni₂(edt)₂(PPh₃)₂] and [Ni₂(edt)₂(PEt₃)₂].^{18.19}

Surveying the works of the studies on metaldithiolate-phosphine complexes, the structural types can be divided into those shown in Fig. 1.

Although some research groups carried out preliminary work on palladium complexes, surprisingly few pursued the systematic studies, particularly for the structures and spectroscopic analyses. Herein we report the syntheses and properties of the complexes, $[Pd(tdt)(PPh_3)_2]$ (1), $[Pd_2(edt)_2(PPh_3)_2]$ (2), $[Pd_2(pdt)_2(PPh_3)_2]$ (3), $[Pd_2(edt)_2(PEt_3)_2]$ (4), $[Pd_2(pdt)_2(PEt_3)_2]$ (5), $[Pd_2(Hmp)_2(PPh_3)_2Cl_2]$ (6) and $[Pd_2(tdt)_2(PEt_3)_2]$ (7) (tdt = 1,2-toluenedithiolate, edt = 1,2-ethanedithiol, pdt = 1,2-propanedithiol and mp = mercaptophenol) and the crystal structures of 1 and 6 together with their reaction mechanism; the crystal structure of 2 has been reported by our group.²⁰

EXPERIMENTAL

All operations were carried out under dinitrogen with standard Schlenk techniques unless otherwise

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

indicated. The reagent PEt₃ was purchased from Aldrich, PdCl₂, H₂edt and H₂pdt from Merck, H₂tdt from Fluka, and solvents and PPh₃ from Shanghai Chemical Company. Na₂edt, Na₂pdt and Na₂tdt were prepared from the stoichiometric reaction of H₂edt, H₂pdt and H₂tdt with sodium metal in MeOH, respectively. All elemental analyses were carried out at this institute. IR spectra were recorded on a Magna 750 IR spectrometer. ³¹P NMR spectra were measured in CH₂Cl₂ on a Bruker MSL-400 spectrometer with saturated H₃PO₄ as the external standard. Ni₂(pdt)₂(PEt₃)₂, Ni₂(pdt)₂(PPh₃)₂ and Ni₂(edt)₂(PPh₃)₂ were prepared according to our previous report.¹⁸

Preparation of the complexes

 $[Pd(tdt)(PPh_3)_2 \cdot C_2H_4Cl_2]$ (1). To a solution of PPh₃ (1.04 g, 4 mmol) in MeOH (35 cm³) was added Na₂tdt (0.40 g, 2 mmol) in MeOH (5 cm³) and the solution was stirred for 20 min. Anhydrous PdCl₂ (0.53 g, 3 mmol) was added to the solution which turned brown gradually. After stirring for 24 h a dark brown precipitate was formed and collected by filtration. The precipitate was dissolved in C₂H₄Cl₂ (30 cm³) to give dark-red solution, which was mixed with MeOH (30 cm³). The final solution was filtered again and the filtrate was kept in an ice box for 2 weeks to yield dark-red cubic crystals of 1 (30%). IR (KBr): 457(m), 431(m), 410(w), 380(w), 335(w) cm⁻¹.

 $[Pd_2(edt)_2(PPh_3)_2]$ (2). To a solution of PPh₃ (1.52 g, 6 mmol) in MeOH (35 cm³) was added Na₂edt (0.42 g, 3 mmol) in MeOH (5 cm³) and stirred for 20 min. Solid PdCl₂ (0.53 g, 3 mmol) was then added to the solution that turned red-brown and gradually formed an orange-red precipitate. The precipitate was collected by filtration and dissolved in $C_2H_4Cl_2$ (35 cm³). The violet solution was filtered again and the filtrate was kept at 4°C. After 2 weeks violet plate crystals of **2** were obtained (22%). Found: C, 52.1; H, 4.4. Calc. For $C_{40}H_{38}Pd_2S_4P_2$: C, 52.1; H, 4.2%. IR (KBr): 445(m), 426(m), 375(w), 340(w), 318(w), 300(w), 270(w) cm⁻¹.

 $[Pd_2(pdt)_2(PPh_3)_2]$ (3). Sodium metal (0.14 g, 6 mmol) was added to a solution of H_2pdt (0.30 cm³, 3 mmol) in MeOH (35 cm³) and stirred until dissolution. PPh₃ (1.52 g, 6 mmol) and PdCl₂ (0.53 g, 6 mmol) were then added to the solution and stirred for 24 h. The precipitate thus formed was collected by filtration and dissolved in $C_2H_4Cl_2$ (35 cm³). The violet–red solution was filtered again and the filtrate was kept at 4°C for 2 weeks to give microcrystals of 3 (27%). Found: C, 53.0; H, 4.2. Calc. for $C_{42}H_{42}Pd_2S_4P_2$: C, 53.1; H, 4.5%. IR (KBr): 450(m), 433(m), 364(w), 310(w), and 294(w) cm⁻¹.

 $[Pd_2(edt)_2(PEt_3)_2$ (4). To a solution of PEt₃ (0.71 g, 6 mmol) in MeOH (35 cm³) was added Na₂edt (0.42 g, 3 mmol) in MeOH (5 cm³) and stirred for 20 min. Solid PdCl₂ (0.53 g, 3 mmol) was then added to the solution that turned orange-yellow. The mixture was stirred for 24 h and filtered, and the dark-brown filtrate was kept at 4°C for 1 week to give orange-red microcrystals of 4 (12%). Found : Pd, 33.0; S, 19.8; P, 10.1; C, 30.3; H, 6.2.

Calc. for $C_{16}H_{38}Pd_2S_4P_4$: Pd, 33.6; S, 20.3; P, 9.8; C, 30.4; H, 6.0%. IR (KBr): 457(m), 431(m), 410(w), 380(w), 335(w) cm⁻¹.

[Pd₂(pdt)₂(PEt₃)₂] (5). To a solution of PEt₃ (0.71 g, 6 mmol) in MeOH (35 cm³) was added Na₂pdt (0.46 g, 3 mmol) in MeOH and stirred for 20 min. Solid PdCl₂ (0.53 g, 3 mmol) was then added to the solution that turned yellow. The mixture was stirred for 22 h and filtered, and the filtrate was kept at 4°C for 1 week to give yellow microcrystals of 5 (10%). Found: Pd, 32.7; S, 19.0; P, 9.6; C, 32.0; H, 6.4. Calc. for $C_{18}H_{42}Pd_2S_4P_2$: Pd, 32.2; S, 19.4; P,9.4; C, 32.7; H, 6.4%.

[Pd₂(Hmp)₂(PPh₃)₂Cl₂] (6). To a solution of PPh₃ (1.52 g, 6 mmol) and H₂mp (0.30 cm³, 3 mmol) in MeOH (35 cm³) was added sodium metal (0.14 g, 6 mmol) and stirred until dissolved. PdCl₂ (0.53 g, 3 mmol) was then added to the reaction mixture and stirred for 24 h and filtered, the bright-red precipitate was collected and dissolved in C₂H₄Cl₂ (30 cm³). The final solution was filtered again and the filtrate was evaporated in air for 2 weeks to yield bright red crystals of **6** (10%). Found: C, 54.6; H, 3.5. Calc. for C₄₈H₄₀Pd₂S₂P₂Cl₂O₂: C, 54.5; H, 3.8%. IR (KBr): 466(m), 420(w), 340(w), 297(w) cm⁻¹

[Pd₂(tdt)₂(PEt₃)₂] (7). To a solution of PEt₃ (0.47 g, 4 mmol) and Na₂tdt (0.40 g, 2 mmol) in MeOH (25 cm³) was added a solid of PdCl₂ (0.35 g, 2 mmol). The reaction solution was stirred for 24 h and filtered, and the violet–red filtrate was kept at 4°C for 1 week to give violet microcrystals of 7 (41%). Found : Pd, 28.2; S, 16.6; P, 8.0; C, 40.5; H, 6.0. Calc. for C₂₆H₄₄Pd₂S₄P₂: Pd, 28.1;S, 16.9; P, 8.2; C, 41.2; H, 5.6%. IR (KBr) : 436(m), 412(m), 345(w) cm⁻¹.

X-ray structural analysis

Suitable single crystal of 1 and 6 were mounted on glass fibres and data collections were performed at ambient temperature on a Rigaku AFC5R diffractometer using graphite-monochromatized Mo- K_x radiation ($\lambda = 0.71069$ Å). The crystallographic and data collection parameters are summarized in Table 1. Intensity data were corrected for the fluctuation of the monitored reflections, Lorentz-polarization factors, the empirical absorption correction was based on psi-scans and the program DIFABS.²¹ The coordinates of the metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference-Fourier syntheses. The structure of 1 was refined by the fullmatrix least-squares technique with anisotropic temperature factors for Pd, S and P atoms and isotropic temperature factors for all carbon and solvent atoms. The structure of **2** was refined by the full-matrix least-squares technique with anisotropic temperature factors for all non-hydrogen atoms. All calculations were performed on a VAX 11/785 computer with the SDP program package and the H atoms were not included in the calculations. Atomic scattering factors were taken from International Tables for X-ray Crystallography.²²

RESULTS AND DISCUSSION

Syntheses of the complexes

From the reaction system of Pd²⁺, bidentate ligands [SC₆H₄(CH₃)S²⁻, SCH₂CH₂S²⁻, SCH₂CH $(CH_3)S^{2-}$, $HOC_6H_4S^{-}$] and PR_3 (R = Et, Ph) in a 1:1:2 molar ratio in methanol, complexes 1-7 with three different structural types can be isolated. It is interesting that if tdt²⁻ and PPh₃ were used as the initial reactant, the mononuclear complex 1 was obtained. If the 1,2-alkydithiolate [SCH₂ CH₂S²⁻ or $SCH_2CH(CH_3)S^{2-}$ and PR₃ (R = Et, Ph) were used as the initial reactant, instead of mononuclear, the dinuclear complexes were isolated. However, when $HOC_6H_4S^-$ and triphenylphosphine were reacted with PdCl₂, the dinuclear complex with Hmp, Cl and phosphine mixed ligands was obtained.

The related reactions of Ni²⁺ and the bidentate ligand of SCH₂CH₂S²⁻ in methanol without the presence of PR₃, when the molar ratio of Ni²⁺: SRS²⁻ is 1:1, immediately gave rise to insoluble polymers $[(Ni(SRS))_n]$.^{2,3,4} It is similar to the nickel reaction system, where palladium ions react with edt²⁻ or pdt²⁻ first to form the polymer species $[(Pd(SRS))_n]$. The presence of phosphine ligands in the reaction system interrupts the polymerization and leads to the formation of different complexes with mixed ligands.

Assisted with the facts mentioned above, the reactions of these complexes may be deduced and illustrated in Fig. 2.

The Pd²⁺ ions react first with SRS²⁻ to form the intermediate $[Pd(SRS)_2]^{2-}$ (I), from which one of the Pd—S bonds is broken under the attack of the PR₃ ligand, forming the species $[Pd(SRS)_2(PR_3)]^{2-}$ (II) which then reacts with the solvent molecule or free phosphine ligands. The other Pd—S bond of SRS² which plays as a monodentate thiolate is now broken and this cleaved SRS²⁻ ligand is replaced by the solvent molecule to form a new intermediate [Pd(SRS)(PR₃)(solv.)] (III). The reaction of free PR₃ with III by substitution of the solvent molecule forms the complex [Pd(SRS)(PR₃)₂] (IV) or the condensation of two III by losing a solvent molecule

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	1	6	
Formula	$C_{45}H_{40}P_2S_2Cl_2Pd$	$C_{48}H_{40}O_2P_2S_2Cl_2Pd_2$	
Mol. wt	884.20	1058.20	
Crystal system	Monoclinic	Triclinic	
Space group	$P2_1/n$	$P\overline{1}$	
a (Å)	12.860(6)	11.039(4)	
<i>b</i> (Å)	11.168(6)	12.101(4)	
c (Å)	28.948(10)	10.146(3)	
α (°)	90	93.97(4)	
β (°)	90.11(3)	108.47(5)	
γ (°)	90	66.83(3)	
$V(Å^3)$	4157.49	1179.40	
Ζ	4	1	
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.413	1.488	
μ (cm ⁻¹)	7.720	10.539	
F (000)	1808	530	
R	0.76	0.071	
R _w	0.82	0.079	
Crystal dimensions (mm ³)	$0.20 \times 0.20 \times 0.35$	$0.30 \times 0.35 \times 0.35$	
Scan mode	ω –2 $ heta$	ω –2 θ	
2θ range (°)	2-50	2–46	
hkl range	h = 0-15, k = 0-13, l = -34-34	h = 0-12, k = -12-13, l = -11-11	
No. of reflections measured	8134	3523	
No. of reflections refined	1799 with $I > 2\sigma$ (<i>I</i>)	1800 with $I > 2\sigma$ (I)	
Parameters refined	234	262	
w	Unit weights	Unit weights	
Highest residue (e Å ³)	0.96	0.68	
Lowest residue (e Å ³)	-0.83	-0.64	

Table 1. Crystallographic data and refinement parameters for [Pd(tdt)PPh₃)₂ · C₂H₄Cl₂] and [Pd₂(Hmp)₂(PPh₃)₂Cl₂]

yields the dinuclear complexes $[Pd_2(SRS)_2(PR_3)_2]$ (V).

In our previous work, cleavage of the C—S bond and condensation of two edt ligands was observed during the reaction of Ni²⁺, bidental ligand of SCH₂ CH₂S²⁻ and PR₃ (R = Et, Ph) in 1 : 1 : 2 molar ratio in methanol.¹⁸ However, this was not observed in the reaction system of Pd²⁺, bidentate ligands [SC₆H₃(CH₃)S²⁻, SCH₂CH₂S²⁻, SCH₂CH(CH₃)S²⁻, HOC₆H₄S⁻] and PR₃ (R = Et, Ph).

Structure of $[Pd(tdt)(PPh_3)_2 \cdot C_2H_4Cl_2]$ (1)

Selected bond distances and bond angles are listed in Table 2. The molecular structure consists of a discrete monopalladium complex and $C_2H_4Cl_2$ solvent molecules. As depicted in Fig. 3, 1 does not possess any crystallographic symmetry. Each of the palladium atoms is surrounded by two phosphorus and two sulfur atoms from tdt ligand in a distorted square-planar geometry. The dihedral angles of PdS₂ and PdP₂ planes is 169.28°. The Pd atom is 0.16 Å above the least-squares plane

S(1)S(2)P(1)P(2). The five-membered chelate ring [S(1)S(2)C(1)C(2)Pd] and other carbon atoms of tdt ligand are exactly planar. All S atoms in the molecule adopt sp^3 configuration to induce the chelate rings to be planar. The average Pd—S—C angle in the chelate ring $[104.5(3)^{\circ}]$ is smaller than 109° , because of the constraint of the five-membered ring. The average Pd—S bond lengths is 2.297(5) Å longer than those found in the nickel complexes containing monodentate thiolate and phosphine ligands, such as Ni(S-p-Tol)₂(PBuⁿ)₂ (2.213 Å) and $Ni(SPh)_2(PBu^n)_2$ (2.217 Å).¹⁶ The average Pd—P bond length of 2.330(5) Å is longer than those reported in the Ni-S-P complexes^{16,19} and those $Co_2(SPh)_4(dppe)$ $(2.210 Å^{14})$ and in Pt. (SPh)₂(dppm) (2.247 Å).²⁵ The C-S bond distance (1.77 Å) is similar to those (1.76 Å) in other Mtdt complexes, indicating that no trans-P influence occurred in Ni(edt)(dppe).²⁶

Structure of $[Pd_2(edt)_2(PPh_3)_2]$ (2)

The crystal structure of 2 has been published elsewhere.²⁰ The molecular structure as depicted in



Fig. 2. Reaction scheme of Pd^{2+} with dithiolate and phosphine ligands.

Fig. 4 is the isomorph of $Ni_2(edt)_2(PPh_3)_2^{19}$ and possesses a non-crystallographic two-fold axis. Each of the palladium atoms is surrounded by one phosphorus and three sulfur atoms in a distorted square-planar arrangement and one sulfur atom of each edt ligand is shared by two Pd atoms forming the sulfur bridge. The dihedral angles of PdS₂ and PdSP planes fall in the range 159.42–165.03⁰. The Pd(1) atom is 0.11 Å above the least-squares plane S(1)S(2)S(3)P(1), while the Pd(2) atom is 0.10 Å above the least-squares plane S(2)S(3)S(4)P(4). The dihedral angle of two five-membered chelate rings [S(1)S(2)C(1)C(2)Pd(1) and S(3)S(4)C(3) C(4)Ni(2)] is greater than that found in Ni₂(tpdt)₂ (104.37),¹⁸ but similar to those found in Ni₂ (edt)²⁻₃ (119.8°).²⁷ All S atoms in the molecule adopt an *sp*³ configuration to induce the chelate rings to be non-planar and the molecule to be bent at the sulfur bridges with the dihedral angle between the S(1)S(2)S(3)P(1) and S(1)S(3)S(4)P) planes being 108.5(2)°; the average Pd—S—C angle in a chelate ring [103.3(3)°] is smaller than 109° because of the constraint of the five-membered ring. The Pd—Pd distance is 3.038(2) Å, indicating that no direct M—M interaction exists in the molecule. Grouping the Pd—S_b bonds, i.e. Pd—S_t and

Pd—S(1)	2.316(6)		PdS(2)	2.283(6)	
Pd - P(1)	2.309(7)		Pd—P(2)	2.350(6)	
S(1) - C(1)	1.83(1)		S(2) - C(6)	1.71(1)	
P(1) - C(111)	1.91(3)		P(1) - C(121)	1.98(3)	
P(1) - C(131)	1.80(2)		P(2) - C(211)	1.87(3)	
P(2) - C(221)	1.84(3)		P(2)—C(231)	1.78(3)	
C(1) - C(2)	1.44(4)		C(1)—C(6)	1.39(3)	
C(2) - C(3)	1.40(3)		C(3) - C(4)	1.26(3)	
C(3) - C(7)	1.46(3)		C(4) - C(5)	1.51(3)	
C(5) - C(6)	1.33(2)				
S(1)-Pd-S(2) 89.0(2	2)	Pd-P(2)-C(2)	221)	110(1)
S(1)-Pd-P(1) 89.5(2	2)	Pd-P(2)-C(2)	231)	119(1)
S(1)—Pd—P(2) 169.2(2	2)	C(211) - P(2) -	-C(221)	111(1)
S(2) - Pd - P(1)) 172.3(2	2)	C(211)—P(2)-	-C(231)	106(1)
S(2)-Pd-P(2	84.7(2	2)	C(221)-P(2)-	-C(231)	101(1)
P(1)— Pd — $P(2)$	97.9(2	2)	S(1) - C(1) - C(1)	2(2)	111(1)
P(d) - S(1) - C	(1) 101(1)		S(1) - C(1) - C(1)	2(6)	124(1)
P(d) - S(2) - C	(6) 108(1)		C(1) - C(2) -	C(3)	113(2)
Pd - P(1) - C(1)	11) 116(1)		C(2) - C(3) - C(3)	C(4)	124(2)
Pd - P(1) - C(1)	21) 106.7(9))	C(2) - C(3) - C(3)	C(7)	128(2)
Pd - P(1) - C(1)	31) 118(1)		C(4) - C(3) -	C(7)	108(1)
C(111)P(1)-	-C121 113(1)	1	C(4) - C(5) - C(5)	C(6)	116(1)
C(111)-P(1)-	-C131 100(1)		S(2)—C(6)—C	(1)	118(1)
C(121)-P(1)-	-C131 103(1)		S(2) - C(6) - C	2(5)	123(1)
Pd—P(2)—C(2	211) 109(1)		C(1)—C(6)—C	C(5)	119(1)

Table 2. Selected bond distances (Å) and bond angles (°) for $[Pd(tdt)(PPh_3)_2 \cdot C_2H_4Cl_2]$

Pd—S_b, gives the average lengths: 2.296(3) and 2.312(3) Å, respectively. The average Pd—P bond length of 2.281(3) Å is longer than those reported in the Ni—S—P complexes.^{16,19}

Structure of $[Pd_2(Hmp)_2(PPh_3)_2Cl_2]$ (6)

Selected atomic distances and bond angles are given in Table 3. Figure 5 shows the molecular structure. The structure is analogous to that of $Pt_2(SC_5H_9)_2(PPh_3)_2I_4^7$ and possesses a crystallographic inversion centre. Each of the palladium atoms is surrounded by one phosphorus, two sulfur and one chlorine atoms in a slightly distorted square-planar arrangement. The sulfur atom of each mp ligand is shared by two Pd atoms forming the sulfur bridge. Remaining as OH the oxygen atoms are not coordinated to the meal atoms. The core of the molecule lies exactly on a plane $(Pd_2S_2P_2Cl_2)$ with a Pd—Pd distance of 3.495(2) Å, much longer than that in $Pd_2(edt)_2(PPh_3)_2$ [3.038(2) Å], but slightly shorter than that in $Pt_2(SC_5H_9)_2$ $(PPh_3)_2I_2$ [3.539(1) Å].⁷ The planes of two mp ligands are almost vertical to the Pd₂S₂ plane of the four-membered ring (with a dihedral angle of

96.60°). The average Pd—S—Pd angle $[98.6(2)^{\circ}]$ is much more obtuse than those in Ni₂(edt)₂(PPh₃)₂ (82.41°) and Ni₂(pdt)₂(PPh₃)₂ (81.11°). The average Pd—P bond length of 2.291(6) Å is similar to those reported in the Pd—S—P complexes.

Comparison of the structures

The significant molecular parameters for the complexes and related ones are listed in Table 4. All the palladium atoms in these complexes are tetra-coordinated in distorted square-planar geometry. Complex 1 contains a P2S2 square-planar coordination geometry, while complex 2 can be viewed as two PdS₃P and 6 as two PdS₂PCl quadrilateral quadrangles sharing sides. The complexes with hinged square-planar geometry have a shorter M-M distance than those with flat square-planar complexes. Thus, the Pd—Pd distance in 2 [3.038(2) Å] is much shorter than that in 6 [3.495(2) Å], but longer than those of the corresponding hinged square-planar nickel complexes, due to the larger atomic radius of the palladium. The Pd-S and Pd—P distances are almost the same in these complexes, but longer than those in corresponding



Fig. 3. Structure of complex 1 with H atoms omitted.



Fig. 4. Structure of complex 2 with H atoms omitted.

Pd—Pd 3.	495(3)	Pd—Cl	2.318(8)
Pd—S 2.	333(6)	Pd—S	2.277(6)
Pd—P 2.	304(6)	S—C(1)	1.711(3)
P—C(11) 1.	806(8)	P-C(21)	1.820(8)
P — C (31) 1.	782(9)	OC(6)	1.42(1)
Cl—Pd—S	90.8(3)	Cl—Pd—S	171.6(3)
Cl—Pd—P	90.9(4)	S—Pd—S	81.4(2)
S—Pd—P	175.5(3)	S—Pd—P	97.3(3)
Pd—S—Pd	98.6(4)	O—C(6)—	C(1) 120.2(4)
O-C(6)-C(5	5) 117.5(3)	P - C(11) - C(11)	-C(12) 120.1(2)
P-C(11)-C(16) 121.1(3)	P-C(31)-	-C(36) 120.0(3)
P-C(21)-C(22) 118.2(3)	C(21)—P—	-C(23) 108.6(2)
PC(21)C(26) 121.1(3)	C(21)—P—	-C(23) 108.6(2)
P-C(31)-C(32) 120.0(3)	C(21)—P—	-C(23) 108.6(2)

Table 3. Selected bond distances (Å) and angles (°) for $[Pd_2(Hmp)_2(PPh_3)_2Cl_2]$



Fig. 5. Structure of complex 6 with H atoms omitted.

Complex	M—M	$M - S_t^a$	$M - S_b$	M—P	d.a."	Ref.
1		2.297(5)		2.330(3)		This work
2	3.038(2)	2.296(3)	2.312(3)	2.281(3)	108.55	This work
6	3.495(2)		2.305(6)	2.291(6)	0	This work
8	3.539(1)		2.367(3)	2.267(3)	0	7
9	2.893(2)	2.158(2)	2.198(3)	2.188(3)	112.33	19
10	2.867(2)	2.170(1)	2.205(2)	2.193(2)	110.64	29
11	3.025(2)	2.158(3)	2.201(2)	2.184(3)	127.92	30

Table 4. Comparison of the significant molecular parameters for some M—S—P (M = Pd, Ni) complexes

^{*a*} dihedral angle.

8, $[Pt_2(SC_5H_9)_2(PPh_3)_2I_2]$; 9, $[Ni_2(edt)_2(PPh_3)_2]$; 10, $[Ni_2(pdt)_2(PPh_3)_2]$; 11, $[Ni_2(pdt)_2(PEt_3)_2]$.

Table 5. ³¹P NMR chemical shifts of the complexes

Complex	Chemical shift (ppm)
$[Pd_2(edt)_2(PPh_3)_2]$	30.4, 29.7
$[Pd_2(pdt)_2(PPh_3)_2]$	29.4, 29.0
$[Pd_2(Hmp)_2(PPh_3)_2Cl_2]$	30.7, 25.9
$[Ni_2(edt)_2(PPh_3)_2]$	29.5, 29.0
PPh ₃	-5.6^{a}
$[Ni_2(pdt)_2(PEt_3)_2]$	20.8, 19.4
$[Pd_2(tdt)_2(PEt_3)_2]$	26.7, 16.6
$[Ni_2(edt)_2(PEt_3)_2]$	20.8
PEt ₃	-20.1^{a}

" Ref. 31.

nickel complexes. The dihedral angles between mean coordination planes for the complexes together with some nickel complexes are given in Table 4. The dihedral angles for the hinged squareplanar complexes vary with the change of central metal atoms, thiolate ligands and R substituent of the phosphine ligands. The dihedral angles for the palladium complexes are more acute than those for the nickel ones. The angles and M—M distances exhibit a parallel relationship, i.e. the longer the distance, the larger the angle. This indicates that the M—M distances are the most important factor influencing the dihedral angles in these complexes.

³¹P NMR spectra

The chemical shifts of the ³¹P NMR spectra of the complexes studied are listed in Table 5. It is shown that the chemical shifts of the PPh₃ ligand are in the range 25.9–30.7 ppm, while those of PEt₃ are 16.6–26.7 ppm. It is clear in Table 5 that the P nucleus is deshielded downfield, varying with the change of substituent R of PR₃; Et (46 ppm) > Ph (36 ppm). The discussion above is confirmed by the quantum chemistry calculation qualitatively. The EHMO calculation presents that the net charges of P atoms in these complexes are in the range 0.32– 0.41,²⁸ indicating that the electrons are transferred from phosphorus to metal atoms to cause the P nucleus to be deshielded downfield and the chemical shifts increased.

For dinuclear complexes, although the environments of the two phosphorus atoms in each complex are identical, except [Ni₂(edt)₂(PEt₃)₂] two ³¹P NMR signals are observed in solution.

From the molecular structure information and related studies⁷ we can deduce the complexes adopt two structural modes in solution. Thus, for com-



flat-square planar

hinged-square planar



flat-square planar

plexes with 1,2-dithiolate and phosphine ligands, the process in solution may be interpreted as follows:

For the complexes with thiolate and phosphine, such as $Pd_2(Hmp)_2(PPh_3)_2Cl_2$, there are also two structural types in solution and both are equilibrium in solution.

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hinged-square planar

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