DALTON
FULL PAPER

Chiral palladium complexes from *N*-diphenylphosphinoamino methyl esters

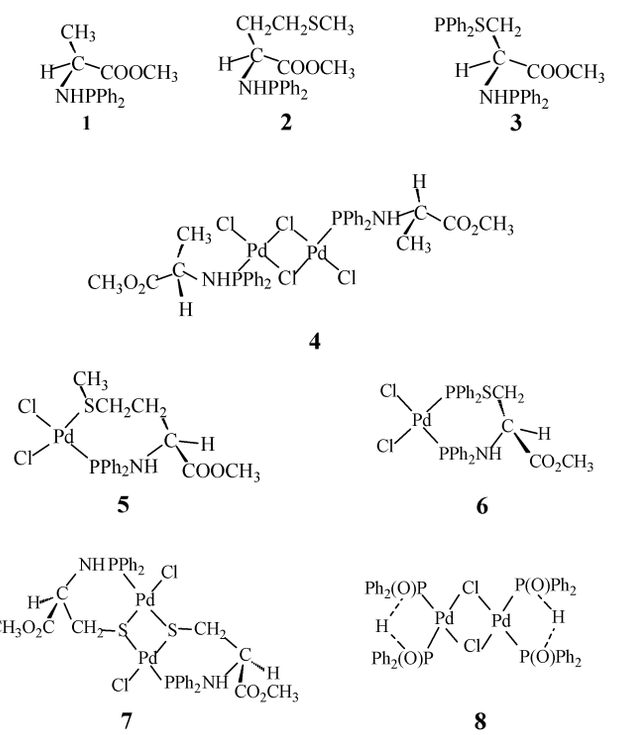
Qingzhi Zhang, Alexandra M. Z. Slawin and J. Derek Woollins *

Department of Chemistry, University of St Andrews, Fife, Scotland KY16 9ST.
E-mail: jdw3@st-and.ac.uk

Received 23rd May 2001, Accepted 5th October 2001
First published as an Advance Article on the web 26th November 2001

(*S*)-*N*,*S*-Bis(diphenylphosphino)cystein methyl ester (bdppcys **3**) is obtained from the reaction of chlorodiphenylphosphine with (*S*)-cystein methyl ester hydrochloride in the presence of Et_3N as (*S*)-*N*-diphenylphosphinoalanine methyl ester (dppal **1**) and (*S*)-*N*-diphenylphosphinomethionine methyl ester (dppmet **2**). Compounds **1**–**3** show different coordination behaviour to [$PdCl_2$(cod)]. Ligand **1** and [$PdCl_2$(cod)] give an unexpected chloro-bridged binuclear complex *trans*-[PdCl(μ-Cl)(dppal-*P*)]$_2$ **4**. Compound **2** interacts with [$PdCl_2$(cod)] to give a chelate complex *cis*-[$PdCl_2$(dppmet-*S*,*P*)] **5**. Reaction of **3** with [$PdCl_2$(cod)] leads to an unstable chelate complex *cis*-[$PdCl_2$(dppcys-*P*,*P*′)] **6**, which gradually decomposes into a novel sulfur-bridged binuclear complex *trans*-[PdCl(μ-*S*)-dppcys-*P*)]$_2$ **7** and a chloro-bridged binuclear complex *trans*-[Pd(μ-Cl)(P(O)Ph_2-*P*)(P(OH)Ph_2-*P*)]$_2$ **8**.

Chiral complexes are very important in catalytic asymmetric synthesis. As natural and readily available chiral compounds, amino acids are often employed as starting materials for chiral ligands.[1–3] There are several reports[4–8] which involve *N*,*N*-bis(diphenylphosphino)amino esters, but to the best of our knowledge, no *N*-mono(diphenylphosphino)amino ester complexes were found apart from one report concerning the stereoselective synthesis of *N*-phosphorus(v) substituted amino acids *via* the *N*-phosphorus(iii) derivative of amino acids.[9] In our preliminary publication,[10] we reported two crystal structures of (*R*)-*N*-diphenylphosphinoalanine methyl ester complexes. Herein we describe several other palladium complexes from *N*-phosphorus(iii) derivated methionine methyl ester and cystein methyl ester. The ligands and complexes involved in this paper are illustrated in Scheme 1.



Scheme 1 Different chiral ligands and palladium complexes.

Experimental

All solvents and reagents were purchased from Aldrich and Lancaster. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Diethyl ether and tetrahydrofuran were purified by reflux over sodium and distillation under nitrogen. (*S*)-α-Amino ester hydrochlorides (97–99%) were used as received. Ligand preparations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Coordination reactions and work-up were performed in dry solvents. [$PdCl_2$(cod)] (cod = cycloocta-1,5-diene)[11] was prepared using literature procedures.

Infrared spectra were recorded from KBr discs on a Perkin-Elmer system 2000 spectrometer, ^{31}P-{^{1}H} NMR spectra (101.3 MHz or 121.4 MHz) and ^{1}H NMR spectra (250 MHz or 300 MHz) on either a Bruker AC250FT or Varian Gemini 2000 spectrometer. Microanalyses were performed by the University Service within this Department and fast atom bombardment (FAB) or chemical ionization (EI) mass spectra by the Swansea Mass Spectrometer Service. Optical rotations were measured on an Optical Activity Polaar 2001 spectrometer in $CHCl_3$ or CH_2Cl_2 (g per 100 cm^3) on a 25 cm cell. Precious metal salt was provided on loan by Johnson Matthey plc.

Preparations

(*S*)-*N*,*S*-Bis(diphenylphosphino)cystein methyl ester 3. To a solution of (*S*)-cysteine methyl ester hydrochloride (1.72 g, 10.0 mmol) in CH_2Cl_2 (100 cm^3) was added Et_3N (4.8 cm^3, 35 mmol). A CH_2Cl_2 (40 ml) solution of Ph_2PCl (3.7 cm^3, 4.55 g, 20.6 mmol) was added dropwise to the above reaction mixture at 0 °C. Stirring was continued for 3 h. The reaction mixture was evaporated to dryness *in vacuo* and thf (100 cm^3) was added. The solution was filtered through a sintered frit under N_2 and the residue washed with thf (3 × 30 cm^3). The filtrate was evaporated to dryness *in vacuo* and the light yellow

 DOI: 10.1039/b104571g

oil was washed with a cold mixture of MeOH and Et_2O (3 × 10 cm^3) to give an off-white solid. Drying *in vacuo* gave 4.52 g of crude product, yield 90%. Purification of the crude product by column chromatography (SiO_2, degassed diethyl ether–petroleum (bp 60–80 °C) = 1 : 1.5) under N_2 gave 1.81 g of white solid, yield 40%. $[\alpha]_D^{25} = +13.1°$ ($c = 6.1$, $CHCl_3$). ^{31}P-{^1H} NMR ($CDCl_3$, ppm): 41.9 (s, P–N). 31.1 (s, P–S). ^1H NMR ($CDCl_3$, ppm): 7.65–7.34 (m, 20H, ArH); 4.23 (m, 1H, CH, [$^3J_{CHCH}$ = 6 Hz]); 3.27 (ddd, 2H, CH_2, [$^2J_{CHH}$ = 11 Hz], [$^3J_{PSCH}$ = 2 Hz]); 2.96 (dd, 1H, NH, [$^3J_{PNCH}$ = 2 Hz], [$^3J_{NHCH}$ = 10 Hz]). Microanalysis (%): Found (Calc. for $C_{28}H_{27}O_2NP_2S$) C, 65.68(66.79); H, 5.32(5.40); N, 2.98(2.78). EIMS (*m*/*z*): 504 $[M]^+$, 318 $[M - SPPh_2]^+$.

***cis*-[PdCl$_2$(dppmet-*S*,*P*)] 5.** To a solution of [$PdCl_2$(cod)] (96 mg, 337 μmol) in CH_2Cl_2 (10 cm^3) was added dropwise a CH_2Cl_2 (40 cm^3) solution of **2** (125 mg, 360 μmol). The reaction mixture was stirred for two days and then concentrated to *ca.* 2 cm^3. A yellow solid precipitated. 65 mg of the product was collected by fitration washed with CH_2Cl_2 (2 × 0.5 cm^3). 90 mg more product was obtained by addition of Et_2O (5 cm^3) to the filtrate and filtration, finally washing with Et_2O (3 × 1 cm^3). The total yield was 155 mg (87%). $[\alpha]_D^{25} = +85.7°$ ($c = 0.28$, CH_2Cl_2, low solubility in $CHCl_3$). ^{31}P-{^1H} NMR (CD_2Cl_2, ppm): 70.9. ^1H NMR (CD_2Cl_2, ppm): 8.13–8.06 (m, 4H, ArH), 7.69–7.40 (m, 6H, ArH), 4.55 (br s, 1H, CH), 3.83 (s, 3H, OCH_3), 3.60 (br s, 1H, NH), 2.63 (m, 2H, SCH_2CH_2), 2.50 (s, 3H, SCH_3), 2.08 (m, 2H, SCH_2CH_2). Microanalysis (%): Found (Calc. for $C_{18}H_{22}Cl_2NO_2PPdS$): C, 40.71(41.28); H, 3.95(4.23); N, 2.89(2.67). FAB (*m*/*z*): 546/548 $[M + Na]^+$, 488 $[M - Cl]^+$, 1015 $[2M - Cl]^+$.

***cis*-[PdCl$_2$(dppcys-*P*,*P*′)] 6.** To a solution of **3** (135 mg, 268 μmol) in CH_2Cl_2 (20 cm^3) was added [$PdCl_2$(cod)] (74 mg, 262 μmol). The reaction mixture was stirred for 10 min and concentrated to *ca.* 1 cm^3. Et_2O (5 cm^3) was added and an orange powder precipitated. The powder was collected by suction filtration, washed with Et_2O (3 × 1 cm^3) and dried *in vacuo* to give 151 mg of the product, yield 85%. $[\alpha]_D^{25} = +2.5°$ ($c = 1.3$, $CHCl_3$). ^{31}P-{^1H} NMR (ppm): 68.9 (d), 64.5 (d) in CH_2Cl_2; 68.2 (d), 66.9 (d) in $CDCl_3$ [$^2J_{P-P}$ = 23 Hz]. Microanalysis (%): Found (Calc. for $C_{28}H_{27}Cl_2NP_2PdS$): C, 49.05(49.47); H, 3.81(4.00); N, 2.04(2.06). FAB (*m*/*z*): 646 $[M - Cl]^+$, 608 $[M - 2Cl]^+$.

***trans*-[PdCl(μ-*S*)-dppcys-*P*)]$_2$ 7.** To a solution of **3** (120 mg, 238 μmol) in CH_2Cl_2 (20 cm^3) was added [$PdCl_2$(cod)] (102 mg, 358 μmol). The reaction mixture was stirred for 4 days and filtered through Celite545. The filtrate was filled in a 60 cm^3 Schlenk tube. 1 cm^3 of Et_2O and petroleum ether (bp 40–60 °C, 40 cm^3) were layered above the CH_2Cl_2 solution to give orange crystals of **7** in two days. The upper layer of petroleum was removed by syringe carefully and the bottom solution was filtered. The crystals were collected mechanically carefully. Yield: 39 mg (36%). $[\alpha]_D^{25} = +92°$ ($c = 0.5$, $CHCl_3$). ^{31}P-{^1H} NMR (ppm): 54.9 (s) in $CDCl_3$; 55.6 (s) in CH_2Cl_2. Microanalysis (%): Found (Calc. for $C_{32}H_{34}Cl_2N_2P_2Pd_2$): C, 39.23(38.78); H, 3.55(3.66); N, 2.95(2.83). FAB (*m*/*z*): 919 $[M]^+$, 942 $[M + Na]^+$, 885 $[M - Cl]^+$, 885 $[M - 2Cl]^+$.

***trans*-[Pd(μ-Cl)(P(O)Ph$_2$-*P*)(P(OH)Ph$_2$-*P*)]$_2$ 8.** After collection of **7**, the filtrate was evaporated to dryness and then dissolved in 2 cm^3 of CH_2Cl_2. To this solution was added Et_2O (10 cm^3). The greenish-yellow powder precipitated and was collected by filtration, washed with Et_2O (3 × 0.5 cm^3) and dried *in vacuo*. Yield: 39 mg (60%). ^{31}P-{^1H} NMR ($CDCl_3$, ppm): 78.4. ^1H NMR ($CDCl_3$, ppm): 7.22–7.62 (m, ArH). Microanalysis (%): Found (Calc. for $C_{48}H_{42}Cl_2O_4P_4Pd_2$): C, 52.41(52.96); H, 3.66(3.89). FAB (*m*/*z*): 1089 $[M]^+$, 1053 $[M - Cl]^+$, 1017 $[M - 2Cl]^+$.

X-Ray crystallography

Table 1 list details of data collections and refinements for **5** and **7**. Data were collected at room temperature using Mo-Kα radiation with a SMART system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[12]

CCDC reference numbers 165075 and 165076.

See http://www.rsc.org/suppdata/dt/b1/b104571g/ for crystallographic data in CIF or other electronic format.

Results and discussion

As previously described,[10,13] (*S*)-alanine methyl ester hydrochloride or cystein methyl ester hydrochloride reacts with chlorodiphenylphosphine in CH_2Cl_2 in the presence of Et_3N to give (*S*)-*N*-diphenylphosphinoalanine methyl ester (**1** dppal) or (*S*)-*N*-diphenylphosphinomethionine (**2** dppmet). Details of the characterisation for **1** and **2** have been reported elsewhere.[13] However, when stoichiometric amounts of cystein methyl ester hydrochloride and Ph_2PCl were reacted together, both P–N and P–S bonds were formed. The reaction of two molar equivalents of chlorodiphenylphosphine with cystein methyl ester gives (*S*)-*N*,*S*-bis(diphenylphosphino)cystein methyl ester (**3** bdppcys) as an off-white solid in good yield.

The ^{31}P-{^1H}-NMR spectrum of **3** shows two singlets. The resonance at δ(P) 41.9 is assigned to the phosphorus of the aminophosphine moiety by comparison with that of **1** and **2**.[13] The singlet at δ(P) 31.1 is assigned to that of the S–P group. The ^1H NMR spectrum of **3** displays well-resolved resonances for all the protons including the two non-magnetically equivalent β-protons of CH_2 at δ(H) 3.27, [$^2J_{H-H}$ = 11 Hz, $^3J_{CH-CH}$ = 6 Hz, $^3J_{PSCH}$ = 2 Hz]. The microanalyses gave good results and the EI mass spectrum shows the expected parent and fragment ions. The IR spectrum shows the $\nu_{(N-H)}$ vibration at 3310 cm^{-1}, $\nu_{(C=O)}$ at 1734 cm^{-1} and $\nu_{(P-N)}$ at 863 cm^{-1}.

Ligands **1** and **2** function as monodentate ligands towards [RhCl(cod)] and [$PtCl_2$(cod)] to give the same type of complex [RhCl(cod)(dppm-*P*)] and *cis*-[$PtCl_2$(dppam-*P*)$_2$].[10,13] However, reaction of **1** and **2** with [$PdCl_2$(cod)] leads to quite different complexes. **1** and [$PdCl_2$(cod)] give the unexpected chloro-bridged binuclear complex *trans*-[PdCl(μ-Cl)(dppal-*P*)] **4**, δ(P) 56.0 (s, $CDCl_3$), the *R*-isomer has been characterised by single crystal X-ray diffraction.[10] In contrast, **2** and [$PdCl_2$(cod)] afford a hybrid chelate complex *cis*-[$PdCl_2$(dppmet-*S*,*P*)] **5**, δ(P) 70.9 (s, CD_2Cl_2).

Both **4** and **5** gave satisfactory microanalyses and the expected molecular and fragment ions. Their IR spectra show $\nu_{(N-H)}$ vibrations at 3330 cm^{-1}, 3205 cm^{-1} and $\nu_{(C=O)}$ at 1734 cm^{-1}, 1737 cm^{-1}, respectively. Compound **4** shows one vibration at 296 cm^{-1} for $\nu_{(Pd-Cl)}$. **5** displays two $\nu_{(Pd-Cl)}$ vibrations at 309, 281 cm^{-1} which is in agreement with the *cis*-geometry. The ^1H NMR spectrum of **4** is well-resolved and shows the NH proton as a triplet at δ(H) 4.44, shifted from that of the free ligand[13] by 1.88 ppm. By selective irradiation at CH_3, NH and CH resonances in **4** respectively, the coupling constants were obtained [$^3J_{PNCH}$ = 8 Hz, $^3J_{NHCH}$ = 10 Hz, $^2J_{PNH}$ = 11 Hz]. However, the signals in the ^1H NMR spectrum of **5** are quite broad and complicated due to the conformational movements of the flexible seven-membered chelate ring in solution.

Slow evaporation of a CH_2Cl_2 solution gave yellow crystals of **5** suitable for X-ray analysis (Fig. 1, Table 2). Fig. 1a reveals a boat-like seven-membered chelate ring with the metal in an approximate square-planar environment. The maximum deviation for Pd(1) from the mean plane of P(1)–S(5)–C(2)–C(1) is 0.05 Å. The prow atom C(1) of the boat lies 0.68 Å above the bottom mean plane N(1)–C(4)–C(5)–P(1) with a fold angle of

Table 1 Details of the X-ray data collections and refinements for compounds **5** and **7**

Compound	**5**	**7**·0.5CH_2Cl_2
Empirical formula	$C_{18}H_{22}Cl_2NO_2PPdS$	$C_{32.50}H_{35}Cl_3N_2O_4P_2Pd_2S_2$
M	524.70	962.84
Crystal colour, habit	Yellow, prism	Orange, block
Crystal dimensions/mm	0.25 × 0.1 × 0.1	0.14 × 0.2 × 0.4
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12$
a/Å	8.8737(1)	11.8621(1)
b/Å	13.5627(2)	18.7870(3)
c/Å	17.5293(1)	9.1333(2)
U/Å^3	2110	2035
Z	4	2
D_c/g cm^{-3}	1.652	1.571
μ/mm^{-1}	1.320	1.297
F(000)	1056	962
Measured reflections	9249	9025
Independent observed reflections (R_{int})	3023(0.0180)	2928(0.0277)
Final *R*1, $\omega R2$ [$I > 2\sigma(I)$]	0.0168, 0.0423	0.0344, 0.0875

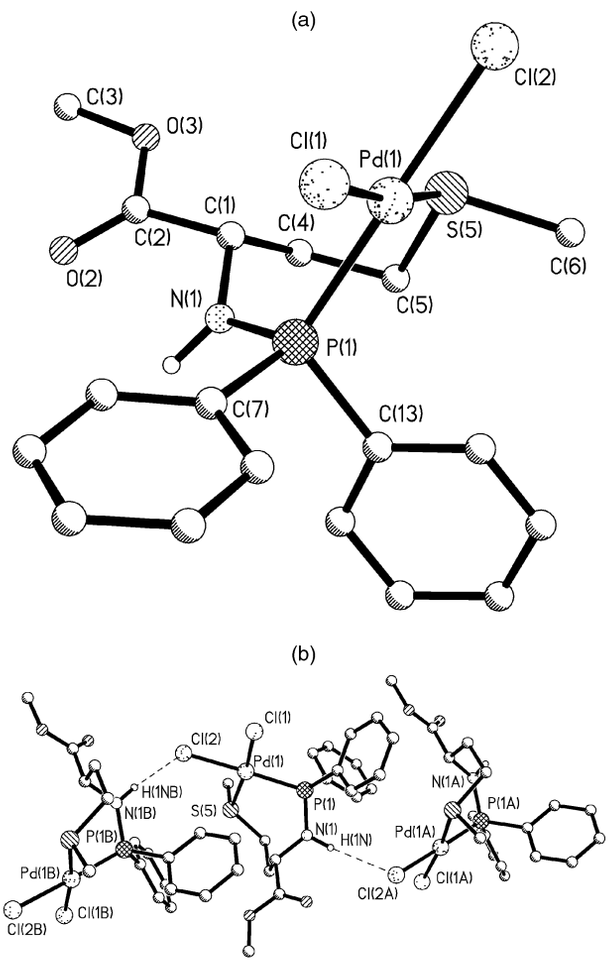


Fig. 1 (a) The crystal structure of **5**. (b) The crystal structure of **5** showing part of the H-bonded chains.

123° between the bottom and C(1)–N(1)–C(4) planes along the N(1)–C(4) axis, while the stern atoms Pd(1) and S(5) lie 1.99 and 1.47 Å respectively above the bottom mean plane respectively with a fold angle of 118° along the P(1)–C(5) axis. The mean deviation of the bottom mean plane N(1)–C(4)–C(5)–P(1) is 0.90 Å and that of Pd(1)–P(1)–C(5)–S(5) is 0.03 Å. In addition to the weak intramolecular H bonding in the complex (H(1*n*) ··· O(2) 2.44 Å, N(1)–H(1*n*)–O(2) 96.78°), weak intermolecular H bonding between the N–H group of one molecule and a chloride ligand of another complex molecule (H(1*n*) ··· Cl(2A) 2.57 Å, N(1)–H(1*n*)–Cl(2A) 174.7°) is also observed (Fig. 1b).

Table 2 Selected bond lengths (Å) and angles (°) in compound **5**

Pd(1)–Cl(1)	2.3039(8)	Pd(1)–Cl(2)	2.3655(7)
Pd(1)–P(1)	2.2500(6)	Pd(1)–S(5)	2.3060(8)
P(1)–N(1)	1.656(2)	P(1)–C(7)	1.814(3)
N(1)–C(1)	1.467(3)	P(1)–C(13)	1.831(2)
C(1)–C(2)	1.517(4)	C(2)–O(2)	1.195(4)
C(2)–O(3)	1.317(4)	C(3)–O(3)	1.435(4)
C(1)–C(4)	1.528(4)	C(4)–C(5)	1.507(4)
C(5)–S(5)	1.827(3)	S(5)–C(6)	1.797(4)
P(1)–Pd(1)–Cl(1)	90.94(3)	P(1)–Pd(1)–S(5)	95.05(3)
Cl(1)–Pd(1)–Cl(2)	91.11(3)	S(5)–Pd(1)–Cl(2)	82.88(3)
Pd(1)–P(1)–N(1)	110.36(8)	N(1)–P(1)–C(7)	104.20(12)
N(1)–P(1)–C(13)	110.03(12)	C(7)–P(1)–C(13)	101.32(11)
C(13)–P(1)–Pd(1)	110.26(9)	C(7)–P(1)–Pd(1)	120.07(9)
P(1)–N(1)–C(1)	123.7(2)	N(1)–C(1)–C(4)	114.3(2)
C(1)–C(4)–C(5)	114.2(2)	C(4)–C(5)–S(5)	110.7(2)
C(5)–S(5)–Pd(1)	115.88(10)	C(5)–S(5)–C(6)	99.5(2)
C(6)–S(5)–Pd(1)	107.30(13)	N(1)–C(1)–C(2)	109.4(2)
C(2)–C(1)–C(4)	110.7(2)		
C(1)–C(2)–O(2)	125.5(3)	O(2)–C(2)–O(3)	124.5(3)
C(1)–C(2)–O(3)	110.0(3)	C(2)–O(3)–C(3)	117.4(3)

In spite of the different chelate ring sizes, the Pd–Cl, Pd–P, Pd–S and S–C bond lengths listed in Table 2 for **5** are comparable to the corresponding parameters of other *P*,*S*-donor chelate palladium chlorides.[14–19] The Pd(1)–Cl(1) bond length of 2.3039(8) Å opposite to sulfur is shorter than the Pd(1)–Cl(2) separation, 2.3655(7) Å, opposite to phosphorus due to the greater *trans* influence of phosphorus. However, compared to the only other example of a seven-membered *P*,*S*-chelate complex we could find *cis*-[$PdCl_2$L-*P*,*S*] (L = *trans*-diphenyl[2-di(phenylthiophosphinoyl)cyclohexyl]phosphinic acid ester)[19] which is chair-like, the bite angle 95.05(3)° is slightly narrower while the P(1)–Pd(1)–Cl(1) angle, 90.94(3)°, slightly wider in **5**.

Reaction of compound **3** with [$PdCl_2$(cod)] is not straight forward. Initially ligand **3** did bind in the anticipated bidentate bis-phosphine coordination mode to give complex **6**. The orange precipitate of **6** that separated from the reaction mixture within 10 min shows two doublets at δ(P) 68.2 and δ(P) 66.9 [$^3J_{P-P}$ = 23 Hz, $CDCl_3$] in the ^{31}P-{^{1}H} NMR spectrum, though as the acquisition continued other peaks appeared. The compound gave satisfactory microanalysis, and the FAB mass spectrum showed the appropriate molecular ion and fragment pattern. However, attempts to obtain a satisfactory ^{1}H NMR spectrum of **6** were not successful owing to the decomposition and conformational movement of the seven-membered ring.

Complex **6** not only decomposed in $CDCl_3$ but also in CH_2Cl_2. A mixture of **3** and [$PdCl_2$(cod)] in a 1 : 1 molar ratio in CH_2Cl_2 displays only two doublets at δ(P) 68.9 and δ(P) 64.5 [$^3J_{P-P}$ = 23 Hz] for approximately 10 minutes, but a single peak at δ(P) 55.6 and broad peaks at δ(P) 78–83 gradually appear as

Table 3 Selected bond lengths (Å) and angles (°) in compound **7**

Pd(1)–P(1)	2.246(2)	Pd(1)–S(4)	2.298(2)
Pd(1)–Cl(1)	2.326(2)	Pd(1)–S(4A)	2.398(2)
P(1)–N(1)	1.667(5)	N(1)–C(1)	1.469(8)
C(1)–C(4)	1.526(9)	C(4)–S(4)	1.816(7)
C(1)–C(2)	1.502(9)	C(2)–O(2)	1.200(8)
C(2)–O(3)	1.335(8)	O(3)–C(3)	1.463(8)
P(1)–Pd(1)–S(4)	96.94(6)	P(1)–Pd(1)–Cl(1)	89.62(6)
Cl(1)–Pd(1)–S(4A)	96.04(6)	S(4)–Pd(1)–S(4A)	77.43(7)
N(1)–P(1)–Pd(1)	112.2(2)	P(1)–N(1)–C(1)	119.5(4)
N(1)–C(1)–C(4)	111.1(5)	C(1)–C(4)–S(4)	115.0(5)
C(4)–S(4)–Pd(1)	115.3(2)	Pd(1)–S(4)–Pd(1A)	78.28(5)

the acquisition continues and the two doublets at δ(P) 68.9 and δ(P) 64.5 gradually decrease. Monitoring the reaction by ^{31}P-{^{1}H} NMR spectroscopy showed that complex **6** decomposed completely within four days in CH_2Cl_2 or in $CDCl_3$.

Dissolving the completely reacted and decomposed mixture in CH_2Cl_2, layering it with petroleum ether and setting aside gave well-formed orange crystals of **7**. The X-ray analysis showed a surprising binuclear structure of *trans*-[PdCl(μ-*S*-dppcys-*P*)]$_2$ (dppcys = $SCH_2NH(PPh_2)COOCH_3$) **7** (Fig. 2, Table 3) which is in agreement with the microanalysis result and FAB mass spectrum.

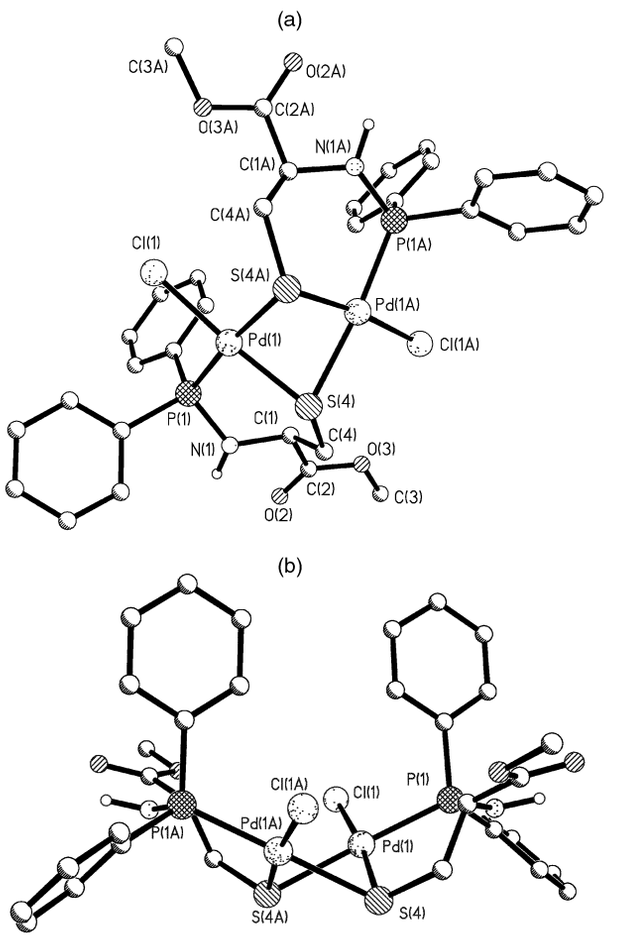


Fig. 2 (a) The crystal structure of **7**. (b) Side view of the crystal structure of **7**.

As shown by Fig. 2 and Table 3, compound **7** possesses crystallographic two-fold symmetry. Compound **7** can be viewed as two Pd(dppcys)Cl fragments that have dimerized to give rise to the folded Pd_2S_2 center. Each palladium of the binuclear complex is coordinated in a roughly square-planar geometry. The maximum deviation for Pd(1) from the mean plane Cl(1)–P(1)–S(4)–S(4A) is 0.02 Å. The chelate six-membered ring at each metal is distorted roughly in an envelope-shape. The maximum deviation of the N(1)–C(4)–S(4)–Pd(1)–P(1) mean envelope plane is 0.12 Å. C(1) is 0.83 Å out of this mean plane forming a 112° folding angle between C(1)–N(1)–C(4) and N(1)–C(4)–S(4)–Pd(1)–P(1) planes. The Pd(1)–S(4) bond length of 2.298(2) Å opposite to chloride is shorter than that of Pd(1)–S(4A) 2.398(2) Å opposite to phosphorus because the phosphorus(III) exerts a stronger *trans* influence than chloride. As has been reported, sulfur-bridged binuclear complexes can be either planar or hinged,[20–23] the hinge angle is usually around 130°.[21,23] However in compound **7**, the hinge angle of 108° between the Pd(1)–S(1)–S(1A) and Pd(1A)–S(1A)–S(1) planes is reduced. The S(4)–Pd(1)–S(4A) bond angle of 77.43(7)° in the core ring of **7** is also not as wide as the S–M–S bond angle (approximately 90°) in other thiolato-bridged binuclear complexes.[21–23] This may be due to the chelate coordination mode of the sulfur–phosphorus ligand, the core and the chelate rings adopt the observed geometry to ease the strain imposed by the coordination environment. The same phenomena were also observed in the closely related structure of [Pd(μ-*S*-dpppt-*P*)$_2$] (dpppt = $S(CH_2)_3PPh_2$) from the reaction of [$PdCl_2(PPh_3)_2$] and $HS(CH_2)_3PPh_2$.[20] Also observed in complex **7** are the intramolecular hydrogen bonds (H(1*n*) ··· O(2) 2.20 Å, N(1)–H(1*n*)–O(2) 150.9°) between the N–H and the C=O groups. In contrast to the two different conformational ester chains in compound **4**,[10] the two ester chains in compound **7** adopt the same conformation, with C=O lying *syn* to the NH group.

Similar to that of [Pd(μ-*S*-dpppt-*P*)$_2$],[20] even though **7** exhibits a sharp signal (δ(P) 54.9 (s), $CDCl_3$ or δ(P) 55.6 (s), CH_2Cl_2) in the ^{31}P-{^{1}H} NMR spectrum, its ^{1}H NMR signals are quite broad and complicated apart from the OCH_3 resonance. Considering that a soft potential energy function has been predicted for the folding process of the bridged dimers,[20,23] the complex appearance of the ^{1}H NMR spectrum of **7** can be interpreted as the combined effect of the ring conformational movements and folding–unfolding motions of the palladium coordination planes over the S ··· S axis.

In addition to complex **7**, compound **8** (δ(P) 78.4 ($CDCl_3$)) was also obtained from the decomposed mixture of compound **6**. Compound **8** was initially presumed to be [Cl_2Pd(μ-*P*,*P*-$PPh_2PPh_2)_2PdCl_2$] from microanalysis, ^{1}H NMR and FAB mass spectra. However, X-ray crystallographic analysis of **8** reveals a chloro-bridged tetraphosphorus binuclear complex. The structure of **8** has been previously reported though the bond lengths and angles are slightly different.[24]

Ligand **3** is stable enough to be purified by column chromatography and stored in the fridge under a nitrogen atmosphere for half a year without change. In contrast, the high instability and decomposition of compound **6** reveals the tendency for the formation of a thiolato-bridge in the presence of palladium. The source of the oxygen and hydrogen in **8** is most likely due to atmospheric moisture as dry solvents were used throughout. Considering the widely reported sulfur-bridged binuclear complexes [{M(μ-SR)L_2}$_2$] (M = Ni, Pd, or Pt),[20–23] it can be presumed that the formation of the stable thiolato-bridged complex is one of the driving forces of the decomposition. The decomposition of complex **6** renders us a new chiral P,S-mixed chelate binuclear complex **7**. Further studies with complexes **7**, **4** and **5** for asymmetric hydrogenation are under way.

Acknowledgements

We wish to thank the JREI for equipment grants and Johnson Matthey plc for loan of precious metals. Qingzhi Zhang is indebted to St Andrews University and the Chinese Scholarship Council for financial support.

References

1 L. R. Falvello, S. Fernandez, R. Navarro and A. Urriolabeitia, *New J. Chem.*, 1997, **21**, 909.

2 P. W. Lednor, W. Beck, H. G. Fick and H. Zippel, *Chem. Ber.*, 1978, **111**, 615.
3 P. W. Lednor, W. Beck and H. G. Fick, *J. Organomet. Chem.*, 1978, **113**, 19.
4 H. Trampisch and W. Beck, *Z. Naturforsch., Teil B*, 1983, **38**, 365.
5 N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 203.
6 N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 223.
7 A. Badia, L. R. Falvello, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1997, **547**, 121.
8 A. Badia, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1998, **554**, 105.
9 O. I. Kolodiazhnyi, E. V. Grishkun, S. V. Galushko and O. R. Golovatyi, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1995, **103**, 183.
10 A. M. Z. Slawin, J. D. Woollins and Q. Zhang, *Inorg. Chem. Commun.*, 1999, **2**, 386.
11 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1991, **28**, 346.
12 G. M. Sheldrick, SHELXTL, Bruker AXS, Madison, WI, 1999.
13 A. M. Z. Slawin, J. D. Woollins and Q. Zhang, *J. Chem. Soc., Dalton Trans.*, 2001, 621.
14 S.-T. Liu, C.-L. Tsao, M.-C. Cheng and S.-M. Peng, *Polyhedron*, 1990, **9**, 2579.
15 P.-H. Leung, S.-K. Loh, K. F. Mok, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 4443.
16 A. S. Abu-Surrah, K. Lappalainen, M. Leskela, H. A. Hodali and B. Rieger, *Acta Crystallogr., Sect. C*, 1999, **55**, 188.
17 K. Aurivillius and G.-I. Bertinsson, *Acta Crystallogr., Sect. B*, 1981, **37**, 2073.
18 L.-F. Zhang, J. Yang, D.-J. Huang and G.-N. Li, *Sci. China, Ser. B.*, 1993, **36**, 513.
19 C. L. Thurner, M. Barz, M. Spiegler and W. R. Thiel, *J. Organomet. Chem.*, 1997, **541**, 39.
20 N. Brugat, A. Polo, Á. Álvarez-Larena, J. F. Piniella and J. Real, *Inorg. Chem.*, 1999, **38**, 4829.
21 A. Albinati, J. Herrmann and P. S. Pregosin, *Inorg. Chim. Acta*, 1997, **264**, 33.
22 R. Cao, M. Hong, F. Jiang, B. Kang, X. Xie and H. Liu, *Polyhedron*, 1996, **15**, 2661.
23 M. Capdevila, W. Clegg, P. Gonzalez-Duarte, A. Jarid and A. Lledos, *Inorg. Chem.*, 1996, **35**, 490.
24 T. Ghaffar, A. Kieszkiewicz, S. C. Nyburg and A. W. Parkins, *Acta Crystallogr., Sect. C*, 1994, **50**, 697.