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Synthesis of Ni(II), Pd(II) and Pt(II) complexes containing chiral phosphino-thiol and -thioether ligands

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The chiral P,S ligand 1-(diphenylphosphino)butane-2-thiol, L^1H, and its thioether methyl derivative L^1Me have been synthesized. L^1H reacts with divalent Ni, Pd and Pt salts to form phosphinothiolato complexes of general formula $[M(L^1)Cl]_2$ (**1**, M = Ni), (**2**, M = Pd), $M(L^1)_2$ (**3**, M = Ni), (**4**, M = Pd), (**5**, M = Pt) and $M(L^1)(PR_3)X$, (**6**, M = Pd, R = Ph, X = Cl), (**7**, M = Pd, R = ^{n}Bu, X = Cl), (**8**, M = Pt, R = Ph, X = H). Single crystal X-ray crystallography reveals a 'butterfly' shape for the dimeric structures of nickel and palladium complexes, **1** and **2** respectively. The P,S chelate ring, according to solid state structural data and NMR analysis, adopts a preferred δ skew-conformation for the *S* isomer and a λ conformation for the *R* isomer. Complex **6** dissociates in chloroform solutions to form the dimeric species **2** and free PPh_3. Thermodynamic parameters for this process have been calculated.

Introduction

In recent years there has been great interest in developing chiral bidentate systems as suitable candidates for catalytic precursors where only one of the donor atoms is phosphorus. For example, mixed P,O-[1] and P,N-donor[2] ligands have been extensively applied in catalysis and there is a growing interest with respect to potential applications of chiral P,S-ligands.[3] Thioether-phosphite and -phosphine ligands have been used in a number of asymmetric reactions such as hydroformylations, hydrogenations, allylic alkylations and aminations.[4–6] In addition, achiral phosphinothiolate ligands have been reported previously to show good regioselectivities in the catalytic formation of branched carboxylic esters from styrene.[7]

P,S ligands consist of two soft donors but break the steric symmetry of more classical chiral P,P ligands such BINAP and DIOP. Hence, P,S systems may prove useful in reactions where the large steric difference of the two coordination sites of the chelate could influence reaction selectivities by accommodating the more bulky side of the participating ligand adjacent to the thiolate. Additionally, the electronic differences of the P and S donors of the chelate ligand might control reaction selectivities *via* operation of the *trans* effect.

In the present study our objectives were to develop efficient routes for the formation of late transition metal complexes with the P,S ligands 1-(diphenylphosphino)butane-2-thiol (L^1) and its methyl thioether derivative L^1Me. Such complexes at a later stage of the project could be tested as catalyst precursors in selected reactions.

Herein, we report on the synthesis, characterisation and properties of chiral phosphino-thiol and -thioether bidentate ligands and their corresponding late transition metal complexes.

Results and discussion

Ligand synthesis

Both the racemic and *S*-isomer of L^1H were prepared as representative examples for this class of ligands, the reaction sequence for their synthesis is shown in Scheme 1.[8] The source of chirality in this example is based on the hydrolytic kinetic resolution of epoxides according to Jacobsen and coworkers.[9] Conversion of the resolved (*R*)-1,2-epoxybutane to the corresponding thiirane is achieved by the action of potassium thiocyanate, this reaction proceeds with inversion of the stereogenic centre. The enantiomeric purity of the thiirane was determined by chiral GC to be ≥99%. Subsequent reaction with diphenylphosphide followed by hydrolysis afforded (*S*)-L^1H. Attack of the lithiophosphide is regioselective and ring opening occurs at the least hindered carbon. The corresponding phosphinothioether ligand L^1Me was formed by deprotonation of L^1H by butyllithium and subsequent reaction with methyliodide. Hauptman *et al.* have previously reported the syntheses of analogous substituted 2-phosphinoethane thioethers by following similar procedures.[4b]

The main features in the ^1H NMR of L^1H and L^1Me are the methinic proton resonances of the α-protons with respect to sulfur, which appear at δ 2.69 and 2.65, respectively, as broad unresolved signals due to vicinal coupling with the diastereotopic protons at the 2 and 4 positions (Fig. 1) as well as ^1H–^{31}P coupling. Resonances for the methylene protons at the 4 position appear as doublets of doublets (dd) and those at the 2 position as unresolved multiplets in the δ 2.3–2.6 and 1.5–1.9 regions, respectively. The thiol proton of L^1H resonates at δ 1.80, overlapping with one of the H^2 protons. In the ^{13}C spectra of LH^1 resonances for the diastereotopic axial and equatorial phenyl groups appear as pairs. The upfield ^{13}C resonances are assigned to the axial phenyl groups as the J_{PC} couplings are consistently smaller on these signals.[10,11]

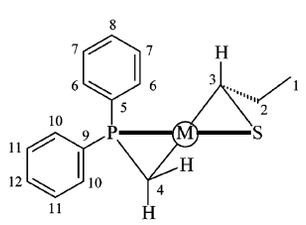

Fig. 1 Adopted numbering for ligands L^1H, L^1Me and their respective complexes.

Synthesis of metal complexes

In order to gain some insight of the coordination properties of ligands L^1H and L^1Me we prepared a number of transition metal complexes with Ni, Pd and Pt. The types of thiolato complexes obtained from L^1H are sulfur-bridged dimeric species (**1**, **2**), bis-chelating (**3**, **4**, **5**) and mixed phosphine

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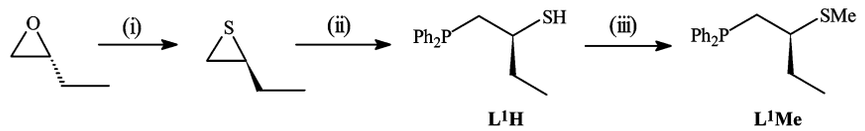
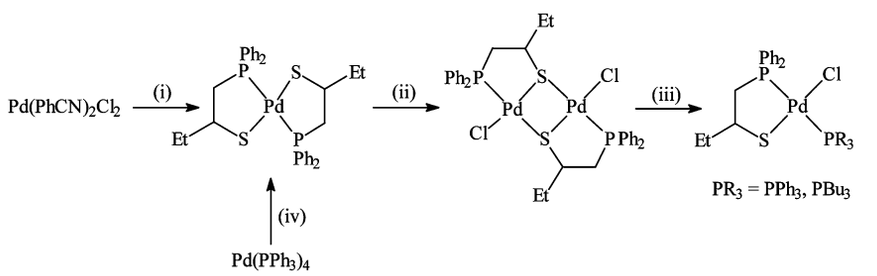
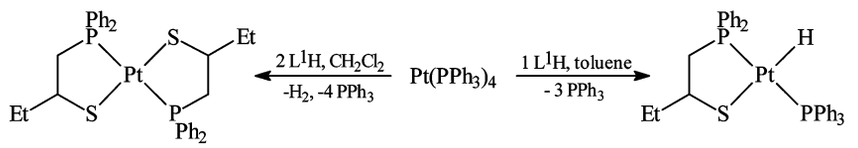


Scheme 1 Reagents and conditions: (i) KSCN, H_2O, 3 days; (ii) Ph_2PLi, Et_2O, H_2O, (iii) BuLi, MeI, thf.



Scheme 2 Reagents and conditions: (i) 2 equiv. L^1H, CH_2Cl_2; (ii) $Pd(CH_3CN)_2Cl_2$, toluene, 110 °C, 1 day; (iii) 2 equiv. PR_3, CH_2Cl_2, 2 h, (iv) 2 equiv. L^1H, CH_2Cl_2.



Scheme 3 Reagents and conditions for the synthesis of the platinum complexes **5** and **8**.

species (**6**, **7**, **8**) as shown in Schemes 2 and 3. The same complexes were prepared with the resolved ligand, (*S*)-L^1H, in order to assign spectroscopically the *meso* and *rac* diastereomeric isomers formed with the racemic ligand, L^1H. The thiolato complexes of L^1H were prepared by the simple addition of the phosphinothiol ligand L^1H to a solution of the metal precursor. Formation of HCl from elimination of the acidic thiol hydrogen did not appear to affect adversely the reaction. Alternatively the palladium complexes **2** and **6** may be prepared from complex **4**, as illustrated in Scheme 2. The ligand L^1Me affords the neutral phosphinothioether complex **9**.

$[M(L^1)Cl]_2$ complexes

Thiolato ligands are well known in forming sulfur-bridged species in the absence of other suitable ligands. Several methods have been used for preparing sulfur-bridged dimers of d^8 transition metals. The palladium and platinum sulfur-bridged dimers of a ferrocenyl phosphinothiolato ligand were prepared by reacting the free thiol ligand with $M(CH_3CN)_2Cl_2$ (M = Pd, Pt).[5a] The complex [Pd(dpppt)Cl]$_2$, dppptH = $Ph_2P(CH_3)_2SH$, was prepared by reacting $Pd(PPh_3)_2Cl_2$ and dppptH without formation of the expected triphenylphosphine complex Pd(dpppt)(PPh_3)Cl.[7] Sulfur-bridged dimers have also been obtained by cleavage of the S–C thioether bond, the complex [Pd{$PCy_2CH_2CH(CH_3)S$}Cl]$_2$ was obtained according to this method.[4b]

The nickel dimer [Ni{$Ph_2PCH_2CH(Et)S$}Cl]$_2$ (**1**) was isolated as a deep red solid after reacting equimolar amounts of $NiCl_2 \cdot 6H_2O$ and L^1H in a dichloromethane solution. Starting from racemic L^1H the dimer obtained reveals only one singlet in its $^{31}P\{^1H\}$ spectrum at δ 37.2 instead of the expected two singlets due to the diastereomeric *meso* and *rac* isomers of **1**. The existence of two different stereoisomers was also not observed in both ^1H and ^{13}C NMR spectra of **1**. This behaviour may be attributed to the long distance between the two stereogenic centres. However, it is possible that only one diastereomer exists in solution, although the large distance between stereogenic centres precludes a rigorous assignment.

The analogous sulfur-bridged dimer [Pd(L^1)Cl]$_2$ (**2**) was isolated after the reaction of L^1H with $Pd(PhCN)_2Cl_2$ in equimolar amounts. Alternatively, **2** may be obtained from [Pd(L^1)]$_2$ **4**, and an equimolar amount of a palladium dichloride source, for example $Pd(CH_3CN)_2Cl_2$ (Scheme 2). As it was previously observed with the corresponding nickel complex only one singlet appears in its ^{31}P spectrum at δ 40.9.

Crystallographic data were obtained for both complexes confirming their dimeric structures as shown in Figs. 2 and 3, respectively, where the five-membered chelates adopt an *S*(δ)

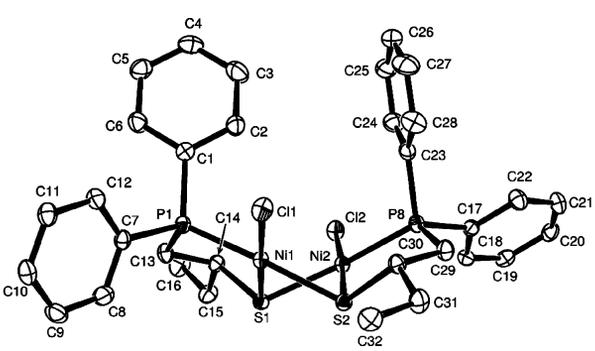


Fig. 2 ORTEP drawing of [Ni(L^1)Cl]$_2$ (**1**) with 40% thermal probability ellipsoids. Hydrogen atoms and water molecule are omitted for clarity.

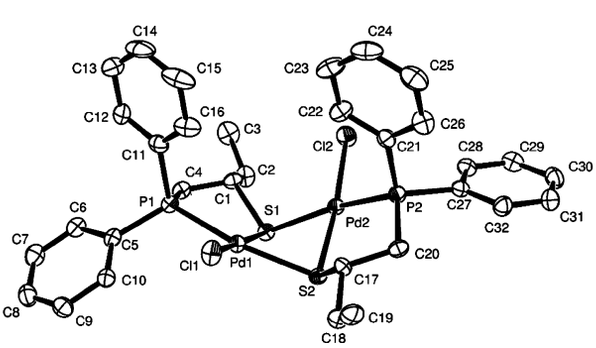


Fig. 3 ORTEP drawing of [Pd(L^1)Cl]$_2$ (**2**) with 40% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1 Crystallographic data for **1**, **2**, **4**, **5**, **6** and **9**

Compound	**1**	**2**	**4**	*cis*-**5**	*trans*-**6**	**9**
Empirical formula	$C_{32}H_{36.4}Cl_2Ni_2O_{0.20}P_2S_2$	$C_{32}H_{36}Cl_2P_2Pd_2S_2$	$C_{32}H_{36}P_2PdS_2$	$C_{32}H_{36}P_2PtS_2$	$C_{34}H_{33}Cl\ P_2PdS$	$C_{17}H_{21}Cl_2PPdS$
Formula weight	738.59	830.37	653.07	741.76	677.45	465.67
Temperature/K	120(2)	120(2)	150(2)	150(2)	293(2)	150(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	11.523(2)	14.955(3)	9.0549(18)	20.104(4)	8.509(2)	8.8678(18)
b/Å	12.031(2)	14.401(3)	10.873(2)	9.885(2)	10.5654(13)	15.492(3)
c/Å	13.325(3)	15.281(3)	15.972(3)	15.240(3)	17.553(2)	13.085(3)
α/°	76.37(3)	90	109.06(3)	90	90	90
β/°	79.93(3)	92.33(3)	90.56(3)	103.69(3)	99.021(14)	95.49(3)
γ/°	65.29(3)	90	101.02(3)	90	90	90
V/Å^3	1624.9(6)	3288.3(11)	1454.4(5)	2942.7(10)	1558.5(4)	1789.4(6)
Z	2	4	2	4	2	4
D_c/g cm^{-3}	1.510	1.677	1.491	1.674	1.444	1.729
Crystal shape; colour	Prism; dark red	Plate; yellow	Plate; orange	Needle; colourless	Prism; orange	Block; yellow
GoF on F^2	1.114	1.001	1.010	1.026	1.060	1.031
R	0.0299	0.0441	0.0682	0.0393	0.0311	0.0331
R_w	0.0701	0.0875	0.1645	0.0990	0.0650	0.0882
Absolute structure parameter			0.00(4)			

Table 2 Selected bond lengths (Å) and angles (°) in complexes **1** and **2**

	1 (M = Ni)	**3** (M = Pd)
P(1)–M(1)	2.1460(7)	2.2469(11)
P(2)–M(2)	2.1591(9)	2.2570(12)
S(1)–M(1)	2.1583(9)	2.2732(10)
S(1)–M(2)	2.2378(9)	2.3918(12)
S(2)–M(2)	2.1713(7)	2.2746(11)
S(2)–M(1)	2.2303(7)	2.3616(11)
M(1)–Cl(1)	2.1835(9)	2.3326(11)
M(2)–Cl(2)	2.1853(7)	2.3562(11)
M(1)–M(2)	2.7583(12)	3.0266(9)
M(1)–S(1)–M(2)	77.70(4)	80.86(4)
P(1)–M(1)–S(1)	88.52(4)	87.10(4)
S(1)–M(1)–S(2)	80.06(4)	80.56(4)
P(2)–M(2)–Cl(2)	94.76(3)	97.78(4)
M(2)–S(2)–M(1)	77.59(3)	81.48(4)
S(2)–M(2)–Cl(2)	176.412(19)	175.08(4)
S(2)–M(2)–S(1)	79.61(4)	79.88(4)
Cl(2)–M(2)–S(1)	96.93(4)	96.51(4)

skew conformation. Collection data and refinement parameters are listed in Table 1 and selected bond lengths and angles are presented in Table 2. In both complexes the geometry around the two metal atoms is distorted square planar and the molecule is bent about the S–S axis adopting a 'butterfly' core structure with a *syn* orientation of the sulfur substituents. For μ-SR^- complexes both *syn* and *anti* orientations of the sulfur substituents have been observed.[5a] The preference in a *syn* orientation of the μ-SR^- substituents in complexes **1** and **2** is likely to arise from the prevailing skew conformation that places the ethyl substituents of the metallacycle in the sterically favoured pseudo-equatorial position. The dihedral angle defined by the two MS_2 planes is 110.88(3)° for complex **1**, one of the smallest reported so far, and 116.02(4)° for complex **2**.

For the nickel dimer the S–Ni–S angles are 80.06(4) and 79.61(4)°, respectively, and are at the lower end of the literature range of 80–86°.[12] For similar complexes the rather small S–Ni–S angles and *syn* orientation of the sulfur substituents have been attributed to the repulsive interaction between the lone pairs on the sulfur atom and metal d-electrons.[12] The Ni–S bond lengths *trans* to phosphorus are 2.2378(9) and 2.2303(7) Å, respectively, and compare well with other reported Ni–S distances for bridging thiolates.[13] However, the Ni–S distances *trans* to the chloride, 2.1583(9) and 2.1713(7) Å, are much shorter due to the lower *trans* influence of the chloride. A similar trend was observed for the analogous thiolate complex [Ni(dppet)Cl]$_2$ (**10**), dppetH = $Ph_2P(CH_2)_2SH$, where the corresponding Ni–S distances were 2.230(3) and 2.164(3) Å, respectively.[14] The Ni–Ni distance of 2.7583(12) Å is somewhat longer than that of **10** at 2.679(1) Å.

The hinged structure of the palladium dimer **2** brings the two metal atoms in close proximity (3.0266(9) Å) but no bonding interactions are observed. The S–Pd–S angles, 80.56(4) and 79.88(4)°, are at the lower end of the literature range of 80–88°.[4b,5a,7] The Pd–S–Pd angles of 80.86(4) and 81.48(4)°, respectively, are in good agreement with those reported for the related complexes [Pd(dpppt)Cl]$_2$[7] and [Pd(Cy_2PCH_2CH(Me)-S)Cl]$_2$.[4b] As was the case for the nickel dimer **1** two different sets of M–S distances are observed one *trans* to the phosphorus atom and one *trans* to the chlorine atom. The average Pd–S bond length *trans* to phosphorus is 2.3767 Å compared with 2.2739 Å *trans* to the chloride ligands.

M(L^1)$_2$ complexes

The most common type of coordination compounds formed between phosphinothiolate ligands and the group 10 metals are bis-chelating complexes of the type M(P–S)$_2$. Most of the bis-chelating complexes reported so far adopt a *trans* arrangement around the metal centre due to the bulky nature of the PPh_2 part of the chelate. However, there are a few examples even with nickel, the smallest metal of the triad, that a *cis* geometry is preferred. The unsubstituted analogue of L^1, dppet, forms *trans* complexes with nickel and palladium although a *cis* arrangement is adopted in the bridging thiolato complex [Ni(dppet)$_2$-$Mo(CO)_4$].[7,12,15,16] The platinum analogue, Pt(dppet)$_2$, has been reported to adopt a *cis* geometry.[16] The nickel and palladium complexes of the ligand 2-(dimethylphosphino)ethane-1-thiolato (dmsp) are known as the *trans* isomers, in contrast, the platinum complex has a *cis* geometry.[16] Bis-chelating complexes of the nickel triad have also been obtained with the *o*-(diphenylphosphino)benzenethiolate ligand. The palladium complex has been found to exist in solution as an equilibrium *cis*–*trans* mixture.[17,18]

The bis-chelating complex [Ni{Ph_2PCH_2CH(Et)S}$_2$] (**3**) was isolated as a green solid from the reaction of Ni(acac)$_2$ and two equivalents of L^{1}H in toluene using $acac^-$ as a base. The diastereomeric mixture obtained contained only *trans*-**3** in approximately equal quantities of *meso* and *rac* isomers. The $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ consisted of two distinct singlets, one at δ 53.1 for the *meso* isomer and one at δ 54.2 for the *rac* isomer. Assignment of these signals was made after comparison with the spectrum of the same complex obtained

Table 3 Selected bond lengths (Å) and angles (°) in **4**

Molecule A				Molecule B			
P(1)–Pd(1)	2.298(3)	P(1)–C(1)	1.810(9)	P(3)–Pd(2)	2.299(3)	P(3)–C(33)	1.825(8)
P(2)–Pd(1)	2.297(2)	P(1)–C(7)	1.824(8)	P(4)–Pd(2)	2.295(2)	P(3)–C(39)	1.819(10)
S(1)–Pd(1)	2.326(2)	P(1)–C(13)	1.820(8)	S(3)–Pd(2)	2.327(2)	P(3)–C(45)	1.830(8)
S(2)–Pd(1)	2.319(2)	P(2)–C(20)	1.815(7)	S(4)–Pd(2)	2.324(2)	P(4)–C(49)	1.826(8)
S(1)–C(14)	1.843(8)	P(2)–C(21)	1.810(8)	S(3)–C(46)	1.854(8)	P(4)–C(55)	1.828(9)
S(2)–C(17)	1.846(8)	P(2)–C(27)	1.830(9)	S(4)–C(62)	1.830(8)	P(4)–C(61)	1.814(7)
P(2)–Pd(1)–P(1)	177.31(11)	P(2)–Pd(1)–S(1)	94.85(9)	P(4)–Pd(2)–P(3)	177.13(10)	P(4)–Pd(2)–P(3)	177.13(10)
P(2)–Pd(1)–S(2)	85.86(9)	P(1)–Pd(1)–S(1)	85.99(9)	P(4)–Pd(2)–S(4)	85.84(9)	P(4)–Pd(2)–S(4)	85.84(9)
P(1)–Pd(1)–S(2)	93.36(9)	S(2)–Pd(1)–S(1)	178.45(14)	P(3)–Pd(2)–S(4)	93.45(9)	P(3)–Pd(2)–S(4)	93.45(9)

from the *S* isomer of L^1H, which should be identical with that from the *rac* isomer. After crystallisation from slow diffusion of petroleum ether into a CH_2Cl_2 solution of **3** the *rac* isomer crystallises out preferentially, in this way it is possible to separate the two diastereomers. The *trans* arrangement of the ligands around the metal centre in $CDCl_3$ solutions was confirmed from their ^{13}C NMR spectrum, which revealed apparent triplets for the C^2–C^4 carbons of the chelate ring and aromatic carbons.

Reaction of two equivalents of L^1H with $Pd(PhCN)_2Cl_2$ or $Pd(OAc)_2$ in dichloromethane affords the bis-chelating, thiolato complex $[Pd(L^1)]_2$ **4**. In agreement with previous observations for complex **3** the diastereomeric mixture of **4** contains only the *trans* isomer in approximately equal quantities of *meso* and *rac* isomers. The $^{31}P\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ consisted of two distinct singlets, one at δ 47.4 for the *meso* isomer and one at δ 45.3 for the *rac* isomer, as assigned after comparison with spectra of (*S*)-**4**. The $^{13}C\{^1H\}$ NMR spectrum of **4** confirms the *trans* arrangement of the ligands around the metal centre in $CDCl_3$ solutions since apparent triplets for the α- and β-carbons of the chelate ring and aromatic carbons are observed. However, $^{31}P\{^1H\}$ NMR spectra recorded in polar solvents such as deuterated acetonitrile and methanol revealed the existence of *cis*/*trans* geometrical isomers, not observed in CH_2Cl_2 solutions, in *ca.* 1 : 2 and 1 : 1 ratios, respectively. Formation of *cis* isomers despite the unfavourable steric interaction of the phosphine groups is attributed to the higher *trans* influence of the phosphorus *versus* the sulfur donor which disfavours the two phosphine groups being placed *trans* to each other. Attempts to isolate the *cis* isomer after crystallization were unsuccessful, implying that the kinetics of *cis*/*trans* isomerisation are more rapid than those of crystallisation.[17]

Complex **4** was also isolated by the reaction of $Pd(PPh_3)_4$ with two equivalents of L^1H. The reaction is thought to proceed *via* the oxidative addition of L^1H to palladium(0) to form an unstable intermediate hydride complex which reacts further with free L^1H to form **4**. The same reactivity has been previously observed with the phosphinothiol ligands dppet and dpppt.[7] As we shall see in the discussion for the platinum complexes an analogous platinum–hydride intermediate has been characterised spectroscopically.

From the reaction of $Pd(OAc)_2$ with (*S*)-L^1H, orange crystals of (*S*)-**4** suitable for X-ray crystallographic analysis were obtained after slow diffusion of petroleum ether into a dichloromethane solution. The unit cell comprises two independent molecules (A and B) which show no anomalies in their structural data summarised in Table 3. An ORTEP view of molecule B is presented in Fig. 4 showing the *trans* arrangement and δ skew conformation of the two ligand fragments around the metal centre. The Pd–P bonds at 2.298(3) and 2.297(2) Å are close to those reported for the analogous complex with the 2-(diphenylphosphino)thiophenolato ligand, $Ph_2P(C_6H_4S)$[19] and the Pd–S bonds at 2.326(2) and 2.319(2) Å are within the expected range.

The platinum complex $Pt(L^1)_2$ **5** was prepared from the reaction of $PtCl_2$ and L^1H in hot acetonitrile. This method affords both *cis* and *trans* geometric isomers which were then separated

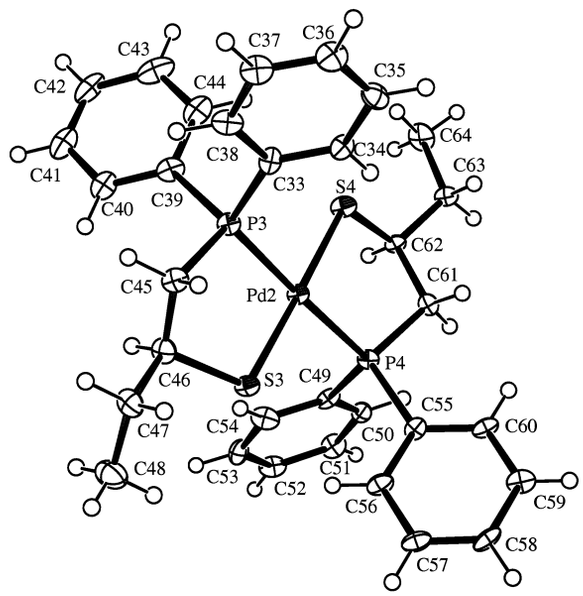


Fig. 4 ORTEP drawing of molecule B of $[Pd(L^1)_2]$ (**4**) with 40% thermal probability ellipsoids. Molecule A is omitted for clarity.

by crystallisation. In the $^{31}P\{^1H\}$ NMR spectrum of **5** two sets of singlets in a 2 : 3 ratio were observed at δ 47.6 (*rac*, J_{PtP} = 2758.6 Hz), 50.5 (*meso*, J_{PtP} = 2630 Hz) for the *trans* isomers and δ 38.2 (*rac*, J_{PtP} = 2818.23 Hz), 42.3 (*meso*, J_{PtP} = 2824.18 Hz) for the *cis* isomers. Assignment of the *rac* and *meso* isomers was made after comparison with spectra of (*S*)-**5**. *Cis* and *trans* isomers were identified from their ^{13}C NMR spectra, which for the *trans*-*rac* isomer reveal apparent triplets in the aromatic region. In addition, for the *cis*-*rac* complex all six aromatic resonances are observed in the ^1H NMR spectrum.

Slow crystallisation from CH_2Cl_2–petroleum ether afforded the less soluble *cis*-*rac* isomer, as later confirmed by X-ray diffraction. The *trans*-*rac* isomer was isolated by crystallisation from CH_3CN–Et_2O. In this case the deprotonation of the thiol ligand was somewhat surprising since it has been found that for the formation of platinum–thiolato complexes the presence of a base is necessary.[20]

Complex **5** was also obtained from the reaction of $Pt(PPh_3)_4$ and two equivalents of L^1H in CH_2Cl_2 (Scheme 3). The reaction is thought to proceed *via* initial formation of the Pt–H complex **8** and subsequent molecular hydrogen elimination. The high *cis*/*trans* ratio (4 : 1) obtained under these reaction conditions is surprising since CH_2Cl_2 is a solvent of low polarity and thus *trans* complexes are expected to be more stable. This predominance of the *cis* isomer may be associated with the reaction mechanism leading to the formation of the thiolate complex.

Colourless crystals of the *cis*-*rac* isomer suitable for X-ray diffraction were obtained after fractional crystallisation from a diastereomeric mixture of **5**. *Cis*-**5** crystallises in the *C*2/*c* centrosymmetric space group and in the unit cell **5** is ordered in layers of *S*(δ) and *R*(λ) enantiomers. Selected bond lengths and

Table 4 Selected bond lengths (Å) and angles (°) in *cis*-**5**[a]

P(1)–Pt(1)	2.2560(12)	C(13)–P(1)	1.838(4)
S(1)–Pt(1)	2.3284(11)	C(7)–P(1)	1.811(4)
C(1)–P(1)	1.815(4)	C(14)–S(1)	1.848(4)
P(1)–Pt(1)–P(1^{i})	99.98(6)	P(1)–Pt(1)–S(1)	86.53(4)
P(1)–Pt(1)–S(1^{i})	172.77(4)	S(1^{i})–Pt(1)–S(1)	87.16(5)

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x+1, y, -z+1/2$.

angles for **5** are shown in Table 4. In Fig. 5 an ORTEP view of **5** shows the interfering phenyl groups in near parallel positions. The *cis* orientation of the two bulky phosphine groups results in the opening up of the P–Pt–P angle to 99.98(6)° and compression of the S–Pt–S and P–Pt–S angles to 87.16(5) and 86.53(4)°, respectively. The Pt–P and Pt–S bonds at 2.2560(12) and 2.3284(11) Å, respectively, are amongst the shortest ones reported for platinum complexes bearing a phosphine ligand *trans* to a thiolate.[21]

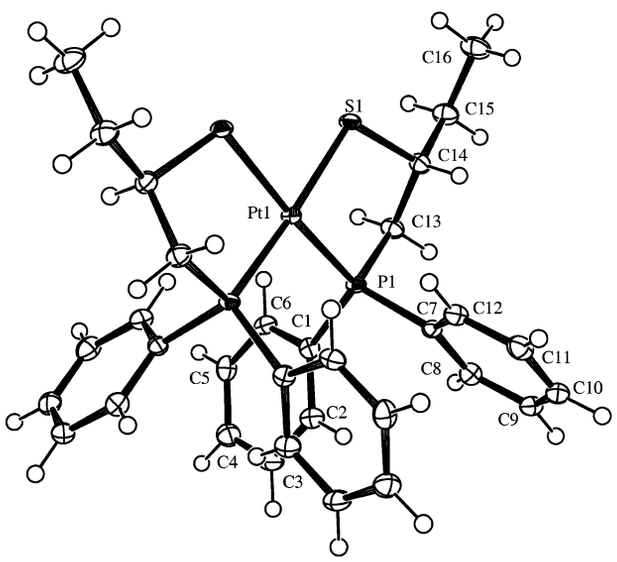


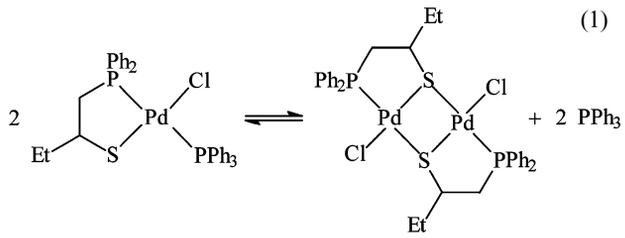
Fig. 5 ORTEP drawing of [Pt(L^{1})$_2$] (**5**) with 40% thermal probability ellipsoids.

M(L^{1})(PR$_3$)X complexes

The phosphinothiolato complex [Pd{Ph$_2$PCH$_2$CH(Et)S}(PPh$_3$)Cl] **6** has been prepared by the reaction of equimolar amounts of L^{1}H, Pd(PhCN)$_2$Cl$_2$ and PPh$_3$. Alternatively, **6** can be prepared from the reaction of complex **2** with two equivalents of PPh$_3$ (Scheme 2). According to the room-temperature ^{31}P{^{1}H} NMR data in CDCl$_3$, the equilibrium mixture of **6** contains the *trans* isomer as the major product with *ca.* 6% of the *cis* isomer present in solution. The ^{31}P{^{1}H} NMR spectrum of **6** reveals two doublets at δ 50.3 (L^{1}) and δ 24.0 (PPh$_3$) with a large coupling constant, $^{2}J_{PP}$ = 460 Hz, characteristic of a *trans* arrangement of the two phosphorus atoms. The *cis* isomer of **6** displays two doublets in the ^{31}P{^{1}H} NMR spectrum positioned at δ 57.5 (L^{1}) and δ 23.0 (PPh$_3$), respectively, with a significantly smaller coupling constant, $^{2}J_{PP}$ = 13.4 Hz.

Complex **6** dissociates in CDCl$_3$ solutions to the palladium dimer **2** and free PPh$_3$, this dissociation process is shown in eqn. (1).

In order to obtain thermodynamic parameters for this dissociation process variable temperature ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded in the temperature range −40 to +60 °C. At −40 °C signals only due to *cis*- and *trans*-**6** are detected, but as the temperature was raised signals due to free PPh$_3$ and dimer **2** appear that steadily increase with temperature. The *cis*/*trans* ratio did not appear to change in that temperature range

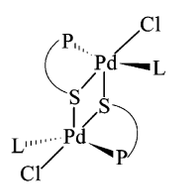


(1)

which suggests that the entropy dependence of this process is rather small. The thermodynamic parameters determined show a rather small dissociation constant for the dimer formation with a value of $K_{298} = 5.6 \times 10^{-4}$ M. Dimer formation has also a small but negative value for the free Gibbs energy ($\Delta G°$) at −18.5 kJ mol^{-1} and a large negative value for the entropy change ($\Delta S° = -153.44$ kJ mol^{-1} K^{-1}). This behaviour contrasts with that reported for the related complex Pd(dppet)(PPh$_3$)Cl where dissociation to a palladium dimer was not observed.[7] In the same study it was reported that under similar conditions the ligand dpppt does not form the expected triphenylphosphine complex Pd(dpppt)(PPh$_3$)Cl, instead the dimer [Pd(dpppt)Cl]$_2$ forms quantitatively. These differences were attributed by the authors to the greater chelate size of dpppt complexes. However, when comparing complexes of dppet and L^{1} where the chelate size is the same such differences in the ability to form sulfur bridged complexes may be attributed to the higher *trans* influence of L^{1}.

The above observations prompted us to explore the lability of L^{1} complexes in the presence of other phosphorus containing ligands. Under similar conditions that afford **6**, *n*-tributylphosphine and triethylphosphite were tested. In the case of P(^{n}Bu$_3$) *trans*-[Pd{Ph$_2$PCH$_2$CH(Et)S}(P^{n}Bu$_3$)Cl], **7**, together with ~6% of the *cis* isomer was obtained without formation of the palladium dimer **2**. However, with P(OEt)$_3$ the only product isolated was pure dimer **2**. ^{31}P{^{1}H} NMR spectra recorded during this reaction reveal that a transient complex analogous to **6** is also formed with P(OEt)$_3$, this assignment was made on the basis of the characteristic J_{P-P} values for *trans* phosphines.

Although we have not carried out kinetic experiments, complex **11** is a likely intermediate in the dissociation of complex **6**



11

in agreement with five-coordinate species usually suggested for substitution reactions in d^{8} transition metal complexes.[22] The reactions with P(^{n}Bu$_3$) and P(OEt)$_3$ also agree with such an intermediate formed. The ligands S, P and Cl retain their relationship in both the tbp intermediate **11** and the initial complex (*e.g. trans*-**6**) leaving the ligands L, P and incoming thiolate in the trigonal plane of **11**. In the case of **7** the *trans* effect of the ligands in the equatorial plane increases in the order: P(^{n}Bu$_3$) > PPh$_2$R > $^{-}$SR and as a result the leaving group is the thiolate and intermediate **11** reverts to complex **7**. When L = P(OEt)$_3$, triethylphospite becomes the leaving group as it has the lower *trans*-effect of the three equatorial ligands. PPh$_3$ falls in between these two situations and an equilibrium of monomer **6** and dimer **2** is observed. Thus it may be suggested that formation of monomeric complexes depends on the *trans*-effect of the monodentate neutral ligand (L), which must be greater than that of the thiolate in order to prevent sulfur-bridged dimers formed.

Table 5 Selected bond lengths (Å) and angles (°) in *trans*-**6**

Pd(1)–S(1)	2.278(2)	P(1)–C(1)	1.816(6)
Pd(1)–P(1)	2.283(2)	P(1)–C(11)	1.825(3)
Pd(1)–P(2)	2.344(2)	P(2)–C(17)	1.822(3)
Pd(1)–Cl(1)	2.345(2)	P(2)–C(23)	1.825(4)
S(1)–C(2)	1.847(6)	P(2)–C(29)	1.829(3)
P(1)–C(5)	1.816(3)		
S(1)–Pd(1)–P(1)	85.57(6)	S(1)–Pd(1)–Cl(1)	176.98(8)
S(1)–Pd(1)–P(2)	88.07(6)	P(1)–Pd(1)–Cl(1)	93.15(6)
P(1)–Pd(1)–P(2)	173.61(6)	P(2)–Pd(1)–Cl(1)	93.17(6)

Orange crystals of *trans*-**6** were isolated from the slow diffusion of petroleum ether into a dichloromethane solution of **6**. Selected bond lengths and angles are collected in Table 5. The structure of *trans*-**6** is illustrated in Fig. 6 showing the *S* isomer adopting the δ skew conformation. The Pd–P, Pd–S and Pd–Cl bonds around the coordination plane are close to the values reported for the analogues complex [Pd(dppet)(PPh_3)Cl].[7]

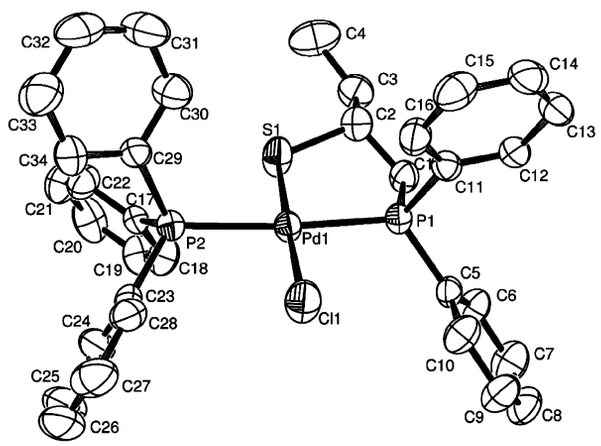


Fig. 6 ORTEP drawing of [Pd(L^1)(PPh_3)Cl] (**6**) with 40% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

As we saw earlier from the reaction of L^1H with $Pd(PPh_3)_4$ a palladium–hydride intermediate was not detected and only the bis-chelating complex **4** was isolated. However, under the same conditions the platinum–hydride complex **8** was formed from the oxidative addition of L^1H to $Pt(PPh_3)_4$. The reaction is best carried out in aromatic solvents (benzene or toluene) since in dichloromethane solutions the bis-chelating complex **5** is quantitatively formed, as illustrated in Scheme 3. The hydride complex is stable in aromatic solutions even with excess of L^1H (1.5 equivalents) present and it is only after several days that complex **5** is observed in solution. *Trans*-**8** is the major isomer with ~10% of the *cis* isomer present in toluene solutions.

The main drawback of this synthetic approach is the difficult separation of **8** from free PPh_3 since they display comparable solubilities in hydrocarbon solutions. However, the ^1H and $^{31}P\{^1H\}$ NMR data collected show unambiguously the formation of **8**. Due to the large excess of PPh_3 present (threefold excess with respect to **8**) rapid exchange is observed between coordinated and free PPh_3. As a result, signals for *trans*-**8** in the $^{31}P\{^1H\}$ NMR spectrum are broad ($w_{1/2}$ = 19 Hz for L^1) and no coupling is observed between the coordinated L^1 and PPh_3 ligands. The $^{31}P\{^1H\}$ NMR resonance for L^1 is observed at δ 54.15 (J_{PtP} = 2921.6 Hz) as a singlet whereas the PPh_3 resonance is coalescing with that of the free ligand at δ 7. This fluxional process can be observed in the ^1H NMR spectrum of *trans*-**8** as well, where the hydride resonance appears as a broad singlet at δ −6.70 (J_{PtH} = 950 Hz). In contrast, the *cis* isomer does not show the same fluxional behaviour, both $^{31}P\{^1H\}$ and ^1H NMR spectra show the expected coupled signals. In $^{31}P\{^1H\}$ NMR two doublets appear with their respective platinum satellites at δ 25.38 (J_{PP} = 10 Hz, J_{PtP} = 3036.2 Hz) for PPh_3 and δ 52.26 (J_{PP} = 10 Hz, J_{PtP} = 1880.1 Hz) for L^1. Accordingly, in ^1H NMR a doublet of doublets appears for the hydridic proton at δ −3.4 ($J_{HP_{trans}}$ = 192.1 Hz, $J_{HP_{cis}}$ = 24.2 Hz, J_{HPt} = 986.4 Hz). The difference in the exchange rates of PPh_3 in the *trans* and *cis* isomers of **8** may be attributed to the higher *trans*-effect of the PPh_2 than the thiolate entity in L^1. In the *trans* isomer of **8** the PPh_3 is *trans* to the phosphine ligand and as a result becomes more labile than in *cis*-**8** where it is *trans* to the thiolate. The same fluxional behaviour of coordinated PPh_3 was observed previously in the dissociation of the complex Pd(L^1)(PPh_3)Cl to the palladium dimer **2** and free PPh_3.

Table 6 Selected bond lengths (Å) and angles (°) for **9**

P(1)–Pd(1)	2.2441(7)	C(4)–P(1)	1.840(3)
S(1)–Pd(1)	2.2688(7)	C(5)–P(1)	1.819(2)
Cl(1)–Pd(1)	2.3713(7)	C(5)–P(1)	1.819(2)
Cl(2)–Pd(1)	2.3037(7)	C(11)–P(1)	1.809(2)
C(1)–C(4)	1.512(4)	C(17)–S(1)	1.810(3)
C(1)–S(1)	1.846(3)		
P(1)–Pd(1)–S(1)	86.98(3)	C(11)–P(1)–Pd(1)	118.88(8)
P(1)–Pd(1)–Cl(2)	93.89(3)	C(5)–P(1)–Pd(1)	114.30(8)
S(1)–Pd(1)–Cl(2)	177.75(2)	C(4)–P(1)–Pd(1)	105.64(9)
P(1)–Pd(1)–Cl(1)	174.37(2)	C(17)–S(1)–C(1)	98.90(15)
S(1)–Pd(1)–Cl(1)	88.18(3)	C(17)–S(1)–Pd(1)	106.66(12)

Pd(L^1Me)Cl_2

Reaction of L^1Me with $Pd(PhCN)_2Cl_2$ afforded the palladium dichloride complex [Pd(L^1Me)Cl_2] **9**, with the phosphinothioether ligand bonded in a chelating fashion as illustrated in the crystal structure shown in Fig. 7. Upon complexation, a shift of the $^{31}P\{^1H\}$ NMR signal of L^1Me from δ −20.3 to δ +52.1 is observed. The phosphinothioether complex **9** is sparingly soluble in common organic solvents thus making it difficult to obtain good quality NMR spectra, a noisy ^1H NMR spectrum was obtained from acetonitrile-d_3.

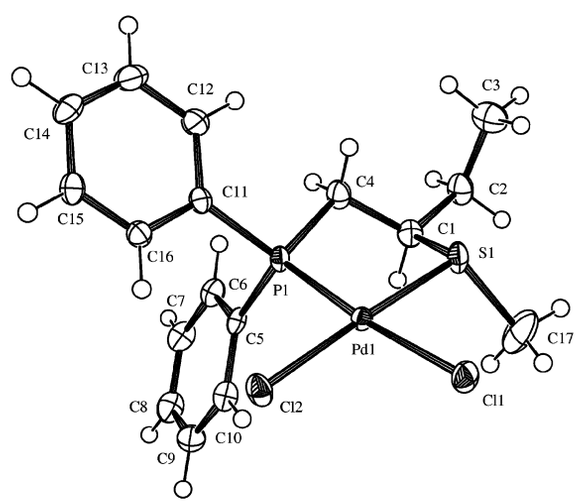
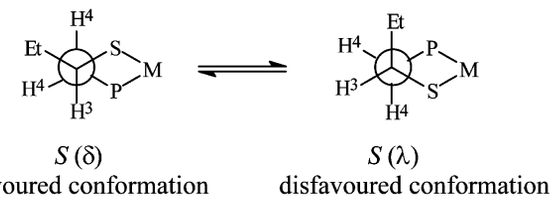


Fig. 7 ORTEP drawing of [Pd(L^1Me)Cl_2] (**9**) with 40% thermal probability ellipsoids.

The structure of complex **9** was verified by X-ray structural determination from yellow crystals grown by diethyl ether diffusion in a dichloromethane solution. Selected bond lengths and angles are given in Table 6. In the solid state **9** adopts the more sterically favoured conformation which places the *syn* Ph and Et groups in a pseudo-equatorial position and the Me substituent of sulfur pseudo-axial (Fig. 7). The same orientation of the sulfur substituent has been previously observed in similar complexes of P,S ligands, however in solution slow inversion of the sulfur has been observed.[4b,5b,23]

Conformational solution NMR studies

A full assignment of the proton resonances of the complexes was made on the basis of a combination of $^{1}H^{1}H$, $^{31}P^{1}H$ and $^{195}Pt^{1}H$ (for **5** and **8**) long-range correlations, together with two-dimensional COSY experiments. The P,S chelate conformation in solution was determined by taking into consideration the dihedral angle dependence of the vicinal coupling constants ^{3}J(H,H) and ^{3}J(Pt,H) of the chelate ring protons H^3 and H^4, according to the Karplus relation. As shown in Scheme 4 significantly different vicinal couplings are expected between an *S*(δ) and an *S*(λ) conformation. In the former case $^{3}J(H^3,H^4_{ax}) \gg {}^{3}J(H^3,H^4_{eq})$, due to the *trans* arrangement of the H^3 and H^4_{ax} protons. Whereas in an *S*(λ) conformation both H^4 protons are *gauche* with respect to H^3 and consequently $^{3}J(H^3,H^4_{ax}) \approx {}^{3}J(H^3,H^4_{eq})$.



Scheme 4 Newman projection down the C^3–C^4 bond of the fragment ML^1, showing the dihedral angle relation for $^{3}J(H^3, H^4_{ax})$, $^{3}J(H^3, H^4_{eq})$ and $^{3}J(Pt, H^4_{eq})$. Although only the *S*(δ) and *S*(λ) conformers are pictured here, the relation between *R*(λ) and *R*(δ) is identical.

Due to the lack of C_2 symmetry in the L^1 ligand if the chelate ring is interconverting between a λ and δ conformation two different magnetic environments should be observed (two diastereomers). NMR data though show only one set of resonances (axial and equatorial) for the diastereotopic Ph and methylene protons, which suggests that only one skew conformation is adopted in solution for each optical isomer of L^1. For the discussion that is following it will be useful to note the nomenclature shown in Fig. 1.

The ^{1}H NMR spectrum of **1** reveals well-resolved signals for the diastereotopic H^2 and H^4 methylene protons. H^4_{ax} resonates at δ 2.30 and its signal splits into an apparent triplet of doublets. The triplet splitting is due to the similar values for geminal and vicinal coupling to protons H^4_{eq} and H^3 respectively, at 13.5 Hz, whereas the doublet arises from geminal coupling to phosphorus, 6.6 Hz, as determined from its $^{1}H\{^{31}P\}$ NMR spectrum. The methylene proton, H^4_{eq}, gives a doublet of doublets of doublets (ddd) at δ 2.72, which collapses into a dd in the phosphorus decoupled spectrum, with a geminal coupling value for ^{2}J(P,H) at 11.2 Hz. In contrast to H^4_{ax}, the equatorial proton, H^4_{eq}, couples only weakly to the methinic proton H^3, $^{3}J(H^3,H^4_{eq}) = 4.5$ Hz. This large difference in size of the vicinal couplings of the H^4 diastereotopic protons suggests that the equilibrium shown in Scheme 4 lies largely on the left. The existence of only one chelate conformation in solution is further demonstrated by the appearance of just one set of signals for the aromatic *ortho* protons at δ 7.93 (pseudo-axial) and δ 8.19 (pseudo-equatorial). Similarly, in the ^{13}C NMR spectrum one set of aromatic resonances is observed for each of the diastereotopic phenyl rings. The lower chemical shift of the pseudo-axial *ortho* protons has been attributed to the shielding effect of the metal d-electrons. Previously, Tóth and Hanson have attributed the shielding of the pseudo-axial *ortho* protons in chelating diphosphine complexes to substituent effects of the ligand backbone.[10] In our complexes, however, the ethyl substituent is pointing away from the phenyl ring on the phosphorus thus an electronic interaction of the pseudo-axial *ortho* protons, which point directly above the coordination plane, with the metal d-electrons seems more likely.

The corresponding palladium dimer **2** reveals an analogous pattern to **1** in its ^{1}H NMR spectrum. The vicinal couplings $^{3}J(H^3,H^4_{ax})$ and $^{3}J(H^3,H^4_{eq})$ at 13.8 and 3.8 Hz, respectively, have again values which agree with an axial and equatorial arrangement of the H^4_{ax} and H^4_{eq} protons with respect to H^3. In the aromatic region signals for the pseudo-axial and pseudo-equatorial protons are overlapping, however, in the ^{13}C NMR spectrum separate sets of aromatic resonances are observed for the pseudo-axial and pseudo-equatorial aryl rings.

The P,S chelate conformation in solution for the platinum complex **5**, was determined for the *cis-rac* isomer only from the four possible isomers. In the ^{1}H NMR spectrum of **5** coupling to platinum is observed only for the methylene proton, H^4_{eq}, which resonates at δ 2.72 with a ^{3}J(Pt,H) value of 66.4 Hz. This is in accordance with an adopted *S*(δ)/*R*(λ) conformation where the pseudo-equatorial proton is *trans* to the platinum atom, whereas H^4_{ax} and H^3 protons are nearly at right angles with it and thus close to the expected minimum in the Karplus relation. In accordance with our previous observations there is a large difference in the values for the vicinal couplings of H^4_{ax} and H^4_{eq} protons to H^3, at 12.1 and 2.4 Hz, respectively. The NOEdiff spectrum shows an interaction between H^4_{ax} and H^{10} (Fig. 1), the *ortho* proton of the pseudo-equatorial phenyl ring, but no interaction between the ethyl group with the aromatic rings again in agreement with an adopted *S*(δ)/*R*(λ) conformation. In the aromatic region six separate, well-defined signals are visible assigned to the six different types of protons of the pseudo-axial and pseudo-equatorial phenyls.

The ^{1}H NMR spectrum of **6** reveals two separate ddd for the axial and equatorial H^4 protons at δ 2.44 and 2.84, respectively. The vicinal coupling constants of H^4_{ax} and H^4_{eq} to H^3 are 11.6 and 3.5 Hz, respectively.

Conclusions

A new chiral P,S ligand and its coordination chemistry have been described. L^1 reacts with group 10 metals to form analogous complexes with that of the homologue ligand dppet. However, substitution at the ethylene backbone of L^1 makes the λ and δ conformers no longer thermodynamically equivalent. Spectroscopic evidence and crystallographic data show that the chelate ring in these complexes adopts the preferred *S*(λ)/*R*(δ) conformations both in the solid state and in solution. This preorganisation of the P,S ligand around the metal centre might prove useful in asymmetric transformations. Unlike dppet, both *cis* and *trans* isomers were observed for the palladium and platinum complexes of L^1 in solution,[7] with the relative *cis*/*trans* ratio depending on the polarity of the solvent. The complex $Pd(L^1)(PPh_3)Cl$ dissociates in solution to form the dinuclear complex $[Pd(L^1)Cl]_2$. In contrast, dissociation of triphenylphosphine was not observed in the analogous complex of dppet demonstrating the better σ-donor ability of L^1 when compared to dppet. Oxidative addition of the S–H bond to a Pt(0) or a Pd(0) complex was observed in the synthesis of the complexes $Pt(L^1)(PPh_3)H$ (**8**) and $Pd(L^1)_2$; where an unstable Pd–H intermediate complex analogous to **8** was postulated for the formation of $Pd(L^1)_2$. Addition of the S–H bond to zerovalent platinum complexes has been previously reported by Real *et al.* for cysteine derivatives.[24] We are currently exploring applications of L^1 and other derivatives in asymmetric catalysis.

Experimental

Materials and methods

All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. All metal complexes were prepared under an inert atmosphere but after their formation they are air-stable, with the exception of complex **8**, and thus manipulated under aerobic conditions. All other reagents were used as received. Petroleum ether had a bp range of 40–60 °C. Solvents were

purified by standard literature methods.[25] Microanalyses were obtained within the department using a Perkin-Elmer 2400 CHN elemental analyser and electronic spectra in dichloromethane solution using a Perkin-Elmer Lambda 20. NMR spectra were obtained on Bruker Avance AMX 400 or JEOL Eclipse 300 sprectrometers and referenced to external TMS; *J* values are in Hz. The nomeclature adopted for assignment of ^{1}H and ^{13}C resonances is shown in Fig. 1. Mass spectra were obtained in APCI (Atmospheric Pressure Chemical Ionisation) mode unless otherwise reported on a VG Platform II Fisons Instruments spectrometer. Racemic 2-butylenesulfide and its *S*-isomer were prepared by following a literature procedure.[26] (*R*)-2-butyleneoxide, required for the synthesis of (*S*)-2-butylenesulfide, was prepared by following a procedure reported by Jacobsen and coworkers for the asymmetric resolution of epoxides.[9]

L^{1}H

Diphenylphosphine (4.9 mL, 27.9 mmol) was syringed into diethyl ether (30 mL) at −40 °C and subsequently 11.2 mL of *n*-BuLi (2.5 M, 28 mmol) were added. After 30 min 2-butylenesulfide was added dropwise and the yellow solution was left to reach ambient temperature and stirred further for another 30 min. Water (15 mL) was then added and the diethyl ether layer collected, subsequently the water layer was washed with diethyl ether (2 × 20 mL) and the ethereal extracts collected. Evaporation of diethyl ether under vacuum afforded L^{1}H as a clear colourless liquid (6.84 g, 90%). The ligand was used without further purification. δ_H ($CDCl_3$, 400 MHz): 0.92 (3H, t, $^{3}J_{HH}$ = 7.3, H^{1}), 1.53 (1H, m, $^{2}J_{HH}$ = 6.9, H^{2}), 1.80 (2H, m, $^{2}J_{HH}$ = 6.9, H^{2}, SH), 2.27 (1H, dd, $^{2}J_{HH}$ = 6.3, $^{2}J_{HP}$ = 13.8, H^{4}), 2.39 (1H, dd, $^{2}J_{HH}$ = 6.3, $^{2}J_{HP}$ = 13.0, H^{4}), 2.69 (1H, br m, H^{3}), 7.26 (6H, m, ArH), 7.35 (4H, m, ArH); δ_C ($CDCl_3$, 100 MHz): 10.27 (1C, s, C^{1}), 31.42 (1C, d, $^{3}J_{CP}$ = 8.2, C^{2}), 38.11 (1C, d, $^{1}J_{CP}$ = 13.3, C^{4}), 38.91 (1C, d, $^{2}J_{CP}$ = 16.6, C^{3}), 127.47 (2C, d, $^{3}J_{CP}$ = 4.8, C^{7}), 127.53 (2C, d, $^{3}J_{CP}$ = 4.9, C^{11}), 127.60 (1C, s), 127.85 (1C, s), 131.57 (2C, d, $^{2}J_{CP}$ = 18.6, C^{6}), 131.94 (2C, d, $^{2}J_{CP}$ = 19.3, C^{10}), 136.90 (1C, d, $^{1}J_{CP}$ = 13.2, C^{9}), 137.29 (1C, d, $^{1}J_{CP}$ = 12.8, C^{5}); δ_P ($CDCl_3$, 121 MHz): −19.4.

L^{1}Me

L^{1}H (0.69 g, 2.5 mmol) was dissolved in thf (20 mL) and subsequently 1 mL of BuLi (2.5 M, 2.5 mmol) was syringed into the flask. After 30 min MeI (0.16 mL, 2.5 mmol) was introduced and the reaction was left to stir for another hour. Similar workup as for L^{1}H followed to yield L^{1}Me (0.5 g, 70%). The ligand was used without further purification. δ_H ($CDCl_3$, 300 MHz): 1.03 (3H, t, $^{3}J_{HH}$ = 7.3, H^{1}), 1.72 (1H, m, $^{3}J_{HH}$ = 7.3, H^{2}), 1.89 (1H, m, $^{3}J_{HH}$ = 7.3, H^{2}), 2.00 (3H, s, SMe), 2.30–2.65 (3H, overlapping m, H^{3} and H^{4}), 7.34 (6H, m, ArH), 7.50 (4H, m, ArH); δ_P ($CDCl_3$, 121 MHz): −20.3.

[Ni(L^{1})Cl]$_2$ 1

To a suspension of anhydrous $NiCl_2$ (0.065 g, 0.5 mmol) in CH_2Cl_2 (10 mL) L^{1}H (0.137 g, 0.5 mmol) was added. The yellow slurry within a few minutes turned lime green and subsequently changed into a deep maroon solution. After stirring the solution overnight at room temperature volatiles were evaporated *in vacuo*. The resulting red solid was washed twice with diethyl ether (20 mL) and dried (0.142 g, 77%). The sample was further purified by the slow diffusion of diethyl ether in a CH_2Cl_2 or thf solution of the complex, which afforded deep red coloured crystals (Found: C, 52.38; H, 5.18. $C_{32}H_{36}Cl_2Ni_2P_2S_2$ requires C, 52.29; H, 4.94%); λ_{max}/nm (CH_2Cl_2): 495 (ε/dm^3 mol^{-1} cm^{-1} 3010), 386.3 (sh, 3600). δ_H ($CDCl_3$, 300 MHz): 0.91 (3H, t, $^{3}J_{HH}$ = 7.3, H^{1}), 1.59 (1H, m, $^{2}J_{HH}$ = 6.9, H^{2}), 1.71 (1H, m, $^{2}J_{HH}$ = 6.9, H^{2}), 2.30 (1H, td, $^{2}J_{HH} \cong {}^{3}J_{HH}$ = 13.5, $^{2}J_{HP}$ = 6.6, H$^{4}_{ax}$), 2.72 (1H, ddd, $^{2}J_{HH}$ = 13.5, $^{3}J_{HH}$ = 4.5, $^{2}J_{HP}$ = 11.2, H$^{4}_{eq}$), 3.10 (1H, br m, H^{3}), 7.30–7.60 (6H, m, ArH), 7.93 (2H, t, $^{3}J_{HH} \cong {}^{3}J_{HP}$ = 6.4, H^{6}), 8.19 (2H, t, $^{3}J_{HH} \cong {}^{3}J_{HP}$ = 7.0, H^{10}); δ_C ($CDCl_3$, 100 MHz): 14.29 (1C, s, C^{1}), 28.62 (1C, t, J_{CP} = 8.7, C^{2}), 41.3 (1C, m, C^{4}), 43.53 (1C, m, C^{3}), 127.76 (2C, t, J_{CP} = 5.1), 127.91 (2C, t, J_{CP} = 5.1), 128.9 (1C, dd, $^{1}J_{CP}$ = 26.2, $^{5}J_{CP}$ = 2.9, C^{9}), 129.4 (1C, dd, $^{1}J_{CP}$ = 25.3, $^{5}J_{CP}$ = 2.9, C^{5}), 130.05 (1C, s), 130.17 (1C, s), 132.25 (2C, t, J_{CP} = 4.9, C^{6}), 132.44 (2C, t, J_{CP} = 5.3, C^{10}); δ_P ($CDCl_3$, 121 MHz): 37.2; *m*/*z* 734 (M$^+$, 1%).

[Pd(L^{1})Cl]$_2$ 2

Method A. To a solution of $Pd(PhCN)_2Cl_2$ (0.192 g, 0.5 mmol) in CH_2Cl_2 (20 mL) L^{1}H (0.138 g, 0.5 mmol) was added. The resulted bright orange solution was left stirring overnight; subsequently volatiles were evaporated *in vacuo*. The resulting bright orange solid was washed twice with diethyl ether (20 mL) and dried (0.187 g, 90%). The pure compound was obtained after slow diffusion of diethyl ether into an acetonitrile solution of **2** (Found: C, 46.03; H, 4.29. $C_{32}H_{36}Cl_2Pd_2P_2S_2$ requires C, 46.28; H, 4.37%); δ_H ($CDCl_3$, 400 MHz): 1.05 (3H, t, $^{3}J_{HH}$ = 7.3, H^{1}), 1.84 (1H, m, $^{2}J_{HH} \cong {}^{3}J_{HH}$ = 7.3, H^{2}), 2.10 (1H, m, $^{2}J_{HH} \cong {}^{3}J_{HH}$ = 7.3, H^{2}), 2.62 (1H, td, $^{2}J_{HH} \cong {}^{3}J_{HH}$ = 13.8, $^{2}J_{HP}$ = 6.6, H$^{4}_{ax}$), 2.91 (1H, ddd, $^{2}J_{HH}$ = 13.8, $^{2}J_{HP}$ = 11.4, $^{3}J_{HH}$ = 3.8, H$^{4}_{eq}$), 3.71 (1H, br m, H^{3}), 7.20–7.75 (6H, m, ArH), 7.93 (4H, m, ArH); δ_C ($CDCl_3$, 100 MHz): 12.76 (1C, s, C^{1}), 30.35 (1C, m, C^{2}), 43.65 (1C, m), 46.29 (1C, s), 129.41 (4C, m, C^{11}, C^{7}), 130.0 (1C, m), 130.5 (1C, m), 131.90 (1C, s), 132.00 (1C, s), 133.63 (2C, t, J_{CP} = 5.1, C^{6}), 133.80 (2C, t, J_{CP} = 5.7, C^{10}); δ_P ($CDCl_3$, 121 MHz): 40.9.

Method B. Complex **2** may also be obtained from Pd(L^{1})$_2$. To a solution of Pd(L^{1})$_2$ (0.123 g, 0.19 mmol) in toluene (10 mL), $Pd(CH_3CN)_2Cl_2$ (0.49 g, 0.19 mmol) was added. The orange solution was stirred for 1 day at 110 °C. Subsequently the volume of the toluene solution was reduced to *ca.* 1 mL and diethyl ether (10 mL) was added to afford complex **2** as an orange solid (0.12 g, 80%). This material had identical properties to that prepared by method A.

Ni(L^{1})$_2$ 3

Ligand L^{1}H (0.274 g, 1 mmol) was added to a slurry of Ni(acac)$_2$ (0.128 g, 0.5 mmol) in toluene (15 mL). The resulting green mixture was stirred overnight at room temperature, after which the solvent was reduced to *ca.* 4 mL volume. Petroleum ether was subsequently added to complete precipitation of **3** as a green solid (0.26 g, 86%). The complex was further purified by crystallisation from CH_2Cl_2–petroleum ether (Found: C, 63.29; H, 5.94. $C_{32}H_{36}S_2P_2Ni$ requires C, 63.49; H, 5.99%); λ_{max}/nm (CH_2Cl_2) 590.7 (ε/dm^3 mol^{-1} cm^{-1} 95). ***rac*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.79 (3H, m, H^{1}), 1.44 (1H, m, H^{2}), 1.59 (1H, m, H^{2}), 2.34 (1H, br m, H$^{4}_{ax}$), 2.56 (1H, br m, H^{3}), 2.76 (1H, m, H$^{4}_{eq}$), 7.20–7.50 (6H, m, ArH), 7.58 (2H, m, H^{10}), 7.93 (2H, m, H^{6}); δ_C ($CDCl_3$, 100 MHz): 15.27 (1C, s, C^{1}), 34.35 (1C, t, J_{CP} = 6.8, C^{2}), 44.92 (1C, t, J_{CP} = 13.7, C^{3}), 45.27 (1C, t, J_{CP} = 18.3, C^{4}), 129.77 (2C, m), 130.04 (2C, m), 131.67 (1C, s), 132.10 (1C, s), 134.29 (2C, t, J_{CP} = 5.7, C^{6}), 135.49 (2C, t, J_{CP} = 5.9, C^{10}); δ_P ($CDCl_3$, 121 MHz): 54.2; ***meso*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.79 (3H, m, H^{1}), 1.66 (1H, m, H^{2}), 2.16 (1H, m, H$^{4}_{ax}$), 2.43 (1H, br m, H^{3}), 7.20–7.50 (6H, m, ArH), 7.43 (2H, m, H^{10}), 8.0 (2H, m, H^{6}); δ_C ($CDCl_3$, 100 MHz): 15.53 (1C, s, C^{1}), 33.83 (1C, t, J_{CP} = 7.0, C^{2}), 43.91 (1C, t, J_{CP} = 13.6, C^{3}), 44.27 (1C, t, J_{CP} = 18.5, C^{4}), 129.77 (2C, m), 130.04 (2C, m), 131.55 (1C, s), 132.23 (1C, s), 133.85 (2C, t, J_{CP} = 5.5, C^{6}), 135.89 (2C, t, $^{1}J_{CP}$ = 6.1, C^{10}); δ_P ($CDCl_3$, 121 MHz): 53.1.

Pd(L^{1})$_2$·1/2CH_2Cl_2 4

Method A. To a solution of Pd(OAc)$_2$ (0.11 g, 0.5 mmol) in methanol (10 mL) L^{1}H (0.28 g, 1.0 mmol) was added. After a few minutes a heavy orange precipitate was formed. The supernatant solution was decanted and the remaining solid washed

with diethyl ether (2 × 10 mL) and dried *in vacuo* (0.29 g, 90%). Good quality crystals were obtained from CH_2Cl_2–petroleum ether (Found: C, 56.70; H, 5.39. $C_{32.5}H_{37}ClS_2P_2Pd$ requires C, 56.16; H, 5.29%). ***trans-rac*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.89 (3H, t, $^3J_{HH}$ = 7.4, H^1), 1.64 (1H, m, $^3J_{HH}$ = 7.4, H^2), 1.72 (1H, m, $^3J_{HH}$ = 7.4, H^2), 2.32 (1H, td, $^2J_{HH} \cong {}^3J_{HP}$ = 12.4, $^3J_{HH}$ = 3.0, H^4), 2.73 (1H, br m, H^3), 2.89 (1H, m, H^4), 7.35 (6H, m, ArH), 7.56 (2H, m, ArH), 7.87 (2H, m, ArH); δ_C ($CDCl_3$, 100 MHz): 14.61 (1C, s, C^1), 32.70 (1C, t, J_{CP} = 10.3, C^2), 43.28 (1C, t, J_{CP} = 9.8, C^3), 43.68 (1C, t, J_{CP} = 17.5, C^4), 128.90 (2C, t, J_{CP} = 4.9, C^7), 129.06 (2C, t, J_{CP} = 5.1, C^{11}), 130.78 (1C, s), 131.23 (1C, s), 132.73 (2C, t, J_{CP} = 6.2, C^6), 134.64 (2C, t, J_{CP} = 7.1, C^{10}); δ_P ($CDCl_3$, 121 MHz): 48.6; ***trans-meso*-isomer:** δ_H ($CDCl_3$, 400 MHz): 2.46 (1H, m, H^4), 7.64 (2H, m, ArH), 7.81 (2H, m, ArH); all other ^{1}H resonances coincide with that of the *trans-rac*-isomer; δ_P ($CDCl_3$, 121 MHz): 51.1, ***cis-rac*-isomer:** δ_H ($CDCl_3$, 400 MHz): 2.46 (1H, m, H^4), 6.84 (2H, m, ArH), 6.96 (2H, m, ArH), 7.11 (1H, m, ArH), 7.19 (2H, m, ArH), 7.46 (2H, m, ArH); all other ^{1}H resonances coincide with that of the *trans-rac*-isomer; δ_P ($CDCl_3$, 121 MHz): 44.5; *m/z* 652 (M^+, 100%).

Method B. Complex **4** was also obtained by the following procedure: $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) was dissolved in toluene (30 mL), subsequently L^1H (0.14 g, 0.52 mmol) was added and the resulting red solution was stirred overnight. Then the volume was reduced to *ca.* 5mL and petroleum ether (20 mL) was added to complete precipitation of **4** (0.16 g, 92%). The compound isolated had identical spectroscopic properties with that prepared by method A.

$Pt(L^1)_2$ 5

To a suspension of $PtCl_2$ (0.133 g, 0.5 mmol) in 20 mL of acetonitrile L^1H (0.275 g, 1.0 mmol) was added at 50 °C. Immediately a pale yellow solution formed that was stirred overnight at room temperature. After reducing the solution to *ca.* 8 mL in volume and placing it in the fridge for 1 day pale yellow crystals were obtained. These were later identified as the *trans* isomer of **5** containing *ca.* 5% of the *cis*-isomer. The *cis* isomer crystallises preferentially from a mixture of CH_2Cl_2 and petroleum ether. Yield 0.32 g (86%) (Found: C, 51.55; H, 4.74. $C_{32}H_{36}S_2P_2Pt$ requires C, 51.81; H, 4.89%). ***trans-rac*-isomer:** δ_H ($CDCl_3$, 300 MHz): 0.97 (3H, t, $^3J_{HH}$ = 7.3, H^1), 1.77 (2H, overlapping m, H^2), 2.20 (1H, m, H^3), 2.80 (2H, m, H^4), 7.4 (6H, m, ArH), 7.68 (2H, m, H^6), 7.97 (2H, m, H^{10}); δ_C ($CDCl_3$, 100 MHz): 14.40 (1C, s, C^1), 31.12 (1C, m, C^2), 40.92 (1C, m, C^3), 48.02 (1C, m, C^4), 128.23 (2C, t, J_{CP} = 4.9, C^7), 128.44 (2C, t, J_{CP} = 5.1, C^{11}), 130.62 (2C, s), 131.40 (2C, s), 132.32 (2C, t, J_{CP} = 5.2, C^6), 135.05 (2C, t, J_{CP} = 6.1, C^{10}); δ_P ($CDCl_3$, 121 MHz): 47.6 (J_{PtP} = 2758.6). ***cis-rac*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.89 (3H, t, $^3J_{HH}$ = 7.3, H^1), 1.73 (2H, m, H^2, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 2.4), 2.44 (1H, td, $^2J_{HH} \cong {}^3J_{HH}$ = 12.1, $^2J_{HP}$ = 6.8, H^4_{ax}), 2.51 (1H, m, $^3J_{HH}$ = 2.4, H^3), 2.72 (1H, td, $^2J_{HH} \cong {}^3J_{HP} \cong$ 12.1, $^3J_{HH}$ = 2.6, $^3J_{PtH}$ = 66.4, H^4_{eq}), 6.88 (2H, t, $^3J_{HP} \cong {}^3J_{HH}$ = 7.2, H^6), 6.96 (2H, t, $^3J_{HH}$ = 7.2, H^7), 7.07 (1H, t, $^3J_{HH}$ = 7.2, H^8), 7.18 (2H, t, $^3J_{HH}$ = 7.4, H^{11}), 7.30 (1H, t, $^3J_{HH}$ = 7.4, H^{12}), 7.53 (2H, t, $^3J_{HP} \cong {}^3J_{HH}$ = 7.4, H^{10}); δ_P ($CDCl_3$, 121 MHz): 38.2 ($^1J_{PtP}$ = 2818.23); ***cis-meso*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.83 (3H, t, $^3J_{HH}$ = 7.3, H^1), 1.52 (2H, m, H^2, $^3J_{HH}$ = 7.3), all other ^{1}H resonances coincide with that of the *cis-rac*-isomer; δ_P ($CDCl_3$, 121 MHz): 42.3 ($^1J_{PtP}$ = 2824.18); ***trans-meso*-isomer:** δ_P ($CDCl_3$, 121 MHz): 50.5 ($^1J_{PtP}$ = 2630); *m/z* 741 (M^+, 100%).

$Pd(L^1)(PPh_3)Cl$ 6

Method A. $Pd(PhCN)_2Cl_2$ (0.192 g, 0.5 mmol) and L^1H (0.137 g, 0.5 mmol) were dissolved in CH_2Cl_2 (40 mL), next triphenylphosphine (0.134 g, 0.5 mmol) was added and the resulting orange solution was left to stir overnight. The solution was condensed to *ca.* 5 mL volume and diethyl ether (30 mL) was added to complete precipitation of **6** as an orange solid (0.295 g, 87%). Crystallisation from CH_2Cl_2–petroleum ether afforded good quality orange crystals (Found: C, 59.68; H, 4.82. $C_{34}H_{33}ClP_2PdS$ requires C, 60.27; H, 4.91%); ***trans*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.76 (3H, t, $^3J_{HH}$ = 7.3, H^1), 1.52 (2H, m, $^3J_{HH}$ = 7.3, H^2), 2.44 (1H, ddd, $^2J_{HH}$ = 13.1, $^3J_{HH}$ = 11.6, $^2J_{HP}$ = 6.9, H^4_{ax}), 2.69 (1H, br m, H^3), 2.84 (1H, ddd, $^2J_{HH}$ = 13.1, $^2J_{HP}$ = 11.5, $^3J_{HH}$ = 3.5, H^4_{eq}), 7.1–7.5 (17H, m, ArH), 7.6–7.8 (6H, m, ArH), 7.8–8.0 (2H, m, ArH); δ_C ($CDCl_3$, 100 MHz): 14.18 (1C, s, C^1), 31.89 (1C, m, C^3), 44.34 (1C, s, C^2), 44.70 (1C, m, C^4), 128.47 (6C, d, J_{CP} = 10.1, PPh_3), 128.84 (2C, d, J_{CP} = 10.5, C^7), 129.17 (2C, d, J_{CP} = 10.5, C^{11}), 130.80 (3C, d, J_{CP} = 2.3, PPh_3), 131.11 (1C, d, J_{CP} = 1.8, C^8), 131.61 (1C, d, J_{CP} = 1.8, C^{12}), 133.47 (2C, d, J_{CP} = 11.0, C^6), 134.54 (2C, d, J_{CP} = 12.0, C^{10}), 135.34 (6C, d, J_{CP} = 11.4, PPh_3); δ_P ($CDCl_3$, 121 MHz): 50.3 (d, $^2J_{PP}$ = 460), 24.0 (d, $^2J_{PP}$ = 460); ***cis*-isomer:** δ_P ($CDCl_3$, 121 MHz): 57.5 ($^2J_{PP}$ = 13.4), 23.0 ($^2J_{PP}$ = 13.4); *m/z* 678 (MH^+, 5%), 641 (M − Cl, 1).

Method B. Complex **6** may also be obtained from dimer **2** and PPh_3 according to the following procedure: $[Pd(L^1)Cl]_2$ (22 mg, 0.027 mmol) and triphenylphosphine (0.014 g, 0.054 mmol) were dissolved in CH_2Cl_2 (10 mL). The orange solution formed was stirred for two hours at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of a sample taken from the reaction solution showed that reaction was complete. An orange solid (34 mg, 95%) was obtained after standard workup procedures that had identical spectroscopic properties with the compound obtained by method A.

$Pd(L^1)(PBu_3)Cl$ 7

The tributulphosphine analogue was obtained by following the same protocols described in methods A and B for complex 6, typical yields were 79–85% (Found: C, 54.68; H, 7.32. $C_{28}H_{45}ClP_2PdS$ requires C, 54.46; H, 7.34%); ***trans*-isomer:** δ_H ($CDCl_3$, 400 MHz): 0.84 (9H, t, $^3J_{HH}$ = 7.3, $P(CH_2)_3CH_3$); 0.90 (3H, t, $^3J_{HH}$ = 7.3, H^1), 1.36 (6H, m, $^3J_{HH}$ = 7.3, $P(CH_2)_3CH_3$), 1.48 (6H, m, $P(CH_2)_3CH_3$), 1.61 (2H, m, H^2), 1.81 (6H, m, $P(CH_2)_3CH_3$), 2.18 (1H, m, H^4), 2.74 (2H, m, H^3 and H^4), 7.2–7.4 (4H, m, ArH), 7.52 (2H, m, ArH), 7.67 (2H, m, ArH), 7.84 (2H, m, ArH); δ_P ($CDCl_3$, 121 MHz): 46.0 (d, $^2J_{PP}$ = 466), 12.0 (d, $^2J_{PP}$ = 466), ***cis*-isomer:** δ_P ($CDCl_3$, 121 MHz): 54.2 (d, $^2J_{PP}$ = 11), 8.9 (d, $^2J_{PP}$ = 11).

$Pt(L^1)(PPh_3)(H)$, 8

Ligand L^1H (0.121 g, 0.44 mmol) was added to a slurry of $Pt(PPh_3)_4$ (0.543 g, 0.44 mmol) in benzene (15 mL). The resulting pale yellow solution was stirred overnight at room temperature, after which the solvent was evaporated to afford a pale yellow oil. ***trans*-isomer:** δ_H ($CDCl_3$, 400 MHz): −6.70 (1H, br s, $^1J_{PtH}$ = 950, PtH), 1.05 (3H, t, $^3J_{HH}$ = 7.3, H^1), 1.95 (2H, br, H^2), 2.25 (1H, br, H^4), 2.85 (1H, br, H^3), 3.16 (1H, br, H^4), 6.9–7.2 (17H, m, ArH), 7.3–7.6 (6H, m, ArH), 7.87 (2H, m, ArH); δ_P ($CDCl_3$, 121 MHz): 54.15 (br s, $^1J_{PtP}$ = 2921.6, L^1), 7.0 (br, PPh_3); ***cis*-isomer:** δ_H ($CDCl_3$, 400 MHz): −3.4 (1H, dd, $^2J_{HP_{trans}}$ = 192.1, $^2J_{HP_{cis}}$ = 24.2 $^1J_{HPt}$ = 986.4, PtH); δ_P ($CDCl_3$, 121 MHz): 25.38 (d, $^2J_{PP}$ = 10, $^1J_{PtP}$ = 3036.2), 52.26 (d, $^2J_{PP}$ = 10, $^1J_{PtP}$ = 1880.1).

$Pd(L^1Me)Cl_2$ 9

To a solution of $Pd(PhCN)_2Cl_2$ (0.24 g, 0.62 mmol) in CH_2Cl_2 (20 mL) L^1Me (0.18 g, 0.62 mmol) was added. The yellow solution formed was stirred for 2 h, subsequently it was condensed to *ca.* 5 mL volume and diethyl ether (30 mL) was added to complete precipitation of a bright yellow solid (0.25 g, 88%). Crystallisation from CH_2Cl_2–diethyl ether afforded good quality yellow coloured crystals (Found: C, 42.23; H, 4.10. $C_{17}H_{21}ClPPdS$ requires C, 43.84; H, 4.55%); δ_H (CD_3CN, 400 MHz): 0.94 (3H, br, H^1), 1.70 (1H, br, H^2), 2.59 (1H, br, H^4), 2.68 (3H, br s, SMe), 2.84 (1H, br, H^3), 2.96 (1H, br, H^4), 7.3–7.7 (8H, m,

ArH), 8.02 (2H, m, ArH); δ_P ($CDCl_3$, 121 MHz): 52.1; ES-MS: *m*/*z* 467 (MH^+, 100%). We were unable to record the $^{13}C\{^1H\}$ NMR spectrum of **9** due to its poor solubility in organic solvents.

For the preparation of metal complexes with the resolved ligand, (*S*)-L^1H, the same experimental procedures were followed as for the racemic ligand, L^1H.

X-Ray crystallography

Data for the complexes **1**, **2**, **4**, **5** and **9** were collected on a Nonius Kappa CCD area detector diffractometer located at the window of a Nonius FR591 rotating anode X-ray generator equipped with a molybdenum target (λ(Mo-Kα) = 0.71073 Å). Data were corrected for absorption effects by means of comparison of equivalent reflections using the program SORTAV.[27] Compound **4** contained two molecules in the asymmetric unit, which showed a pseudo-symmetry centre. Refinement of the structure in the centrosymmetric space group ($P\bar{1}$) resulted in non-convergence of the model and a structure that contained almost entirely 'non positive definite' atoms. Data for complex **6** were collected on an Enraf Nonius CAD4 diffractometer (ω-scan mode) using monochromated Mo-Kα radiation (λ = 0.71071 Å). Empirical absorption corrections were applied by the x-scan method.[28] Structures were solved and refined using the SHELX[29] suite of programs. Molecular structures were drawn using ORTEP-III[30] Non-hydrogen atoms were refined anisotropically with the exception of the oxygen atom in the water molecule of structure **1** which was isotropically refined. Hydrogen atoms were included in calculated positions (riding model). Pertinent data collection and refinement parameters are collated in Table 1.

CCDC reference numbers 194251–194256.

See http://www.rsc.org/suppdata/dt/b2/b209142a/ for crystallographic data in CIF or other electronic format.

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References and comments

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