New mixed-donor unsymmetrical P–N–P ligands and their palladium(II) complexes†

Marek Necas,[a] Mark R. St J. Foreman,[b] Jaromír Marek,[a] J. Derek Woollins[c] and Josef Novosad*[a]

[a] *Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlárská 2, 611 37 Brno, Czech Republic. E-mail: novosad@chemi.muni.cz*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, University of London, South Kensington, UK SW7 2AY*
[c] *Department of Chemistry, University of St. Andrews, St. Andrews, UK KY16 9ST*

Received (in Strasbourg, France) 18th April 2001, Accepted 21st June 2001
First published as an Advance Article on the web 19th September 2001

Unsymmetrical bidentate ligands $R_2P(E)–N(H)–P(E')R'_2$ [R, R′ = Ph, OPh, ^{i}Pr; E, E′ = O, S, Se] have been synthesised using the condensation reaction of an amino compound, $R_2P(E)NH_2$ [R = PhO, Ph; E = O, S, Se], with a phosphorus electrophile, $R'_2P(E')Cl$ [R′ = ^{i}Pr, Ph, OPh; E′ = O, S, Se]. Deprotonated ligands (with KO^{t}Bu) can be treated with $Pd(OAc)_2$ to give $[Ph_2P(S)–N–P(O)(OPh)_2]_2Pd$, $[^iPr_2P(S)–N–P(O)(OPh)_2]_2Pd$ and $[Ph_2P(S)–N–P(S)(OPh)_2]_2Pd$, which show either four-membered or six-membered chelate rings. The new compounds were studied spectroscopically (NMR, IR and Raman) and by X-ray crystallography.

Ligands with P–N–P backbones have been known since 1964.[1] Two classes of compounds are of particular interest: $(RO)_2P(E)–N(H)–P(E)(OR)_2$ (E = O, S), oxidized imidodiphosphate esters,[2] and oxidized imidodiphosphinates,[3] $R_2P(E)–N(H)–P(E)R_2$ (E = O, S, Se). Their anions $[(RO)_2P(E)–N(H)–P(E)(OR)_2]^-$ and $[R_2P(E)–N(H)–P(E)R_2]^-$, closely related to acetylacetonate ($acac^-$), form many complexes with a diverse spectrum of metal ions. Moreover, selected ligands and complexes have found important applications in areas such as NMR shift reagents,[4] selective metal extractants[2] and in catalysis.[5] Very recently, tetraphenyl imidodiphosphinate was shown, in preliminary studies, to form a hydrophobic shell around terbium and europium ions, leading to long-lived, highly luminescent complexes.[6]

In contrast, relatively little work has been done on *mixed* ligands where the nitrogen links both types of phosphorus atoms—phosphate as well as phosphine. These ligands can be prepared using the condensation reaction of an amino compound with a phosphorus electrophile. Two standard methods are known; either a weak base such as triethylamine[7] or a strong base like sodium hydride in tetrahydrofuran (THF) can be used (Scheme 1).[8]

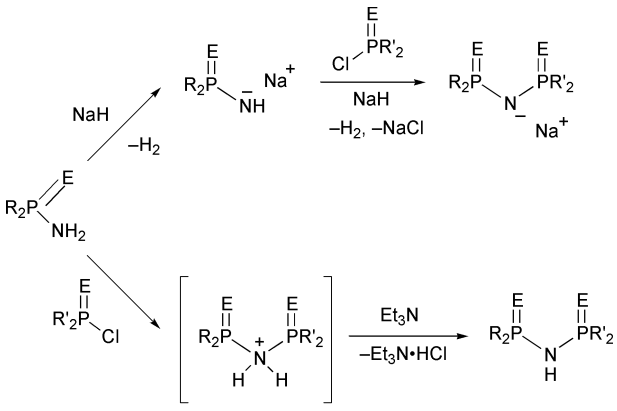
Ten new ligands were prepared and characterized by IR, Raman, ^{1}H-NMR and ^{31}P-NMR spectroscopies and eight of them by X-ray crystallography. Three new Pd complexes were also characterized crystallographically.

Results and discussion

Synthesis

The preparation of the ligands is based on an existing synthetic route.[8,9] As the synthesis in THF was successful in only some cases (compounds **1** to **6**), we postulated that the low solubility of the sodium salts of some starting amino compounds might cause the coupling reaction to be less effective. By increasing the polarity of the solvent (using DMF), the yield of **6** increased remarkably. Using method B (see Experimental), compounds **7**, **8** and **9** were also prepared. Recently, the compound $PhCONHP(S)Ph_2$, which can be viewed as being midway between an acetylacetone and an imidodiphosphinate, has been reported.[10] Using method A, compound **10** [$PhCONHP(S)(OPh)_2$] was prepared as part of our study of the reactions of $(PhO)_2P(S)NH_2$ in the presence of strong bases.

Substitution of phenyl groups for phenoxy and alkyl groups increases the solubility of the prepared ligands in common organic solvents. The nature of the group 16 donor atoms also has a strong influence on ligand solubility. $Ph_2P(O)NHP(O)Ph_2$ is one of the most insoluble P–N–P ligands, probably because of its hydrogen bonded polymeric form in the solid state. The location of oxygen in the ligands synthesised here significantly affects their solubility. The main difference between **1** and **8** is in the location of the donor atoms (O, S) in the structure. While **1** is readily soluble in dichloromethane, dissolving **8** in this solvent takes much more time and heating is needed.

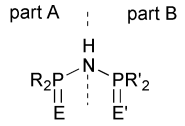


R = alkyl, aryl, alkoxy, aryloxy; E = O, S

Scheme 1

† Dedicated to Professor Zdirad Zák, Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Brno, on the occasion of his sixtieth birthday.

 DOI: 10.1039/b103501k



	Ligand part A		Ligand part B		Derived complex
	R	E	R'	E'	
1	PhO	O	Ph	S	**11**
2	PhO	O	Ph	Se	
3	PhO	O	^{i}Pr	S	**12**
4	PhO	O	^{i}Pr	Se	
5	PhO	S	Ph	Se	
6	PhO	S	Ph	S	**13**
7	PhO	S	^{i}Pr	S	
8	PhO	S	Ph	O	
9	Ph	S	^{i}Pr	S	
10	PhC(O)-		PhO	S	
14	PhO	O	PhO	S	**17**
16	EtO	S	Ph	S	**15**

NMR and vibrational spectra

The ^{31}P-{^{1}H} NMR spectra of the ligands are as expected pairs of doublets. We assumed that based on the ^{31}P chemical shift of the *P*-amino and *P*-chloro starting materials and also on the P–Se coupling in some cases, both of the phosphorus environments in compounds **1** to **9** could be assigned. The $^{2}J[^{31}P–^{31}P]$ coupling constants for compounds **1** to **9** were in the range expected from the literature, and are tabulated in Table 1.[11] As can be seen, the effect of the phenyl/phenoxy replacement on the ^{31}P chemical shift in the $–P(S)R_2$ group is almost negligible. This fact makes the chemical shift assignments in **6** quite unreliable. The ^{1}H chemical shift of the nitrogen bonded proton is rather variable and its coupling with phosphorus nuclei in the ^{31}P NMR spectra is not observed. The ^{31}P NMR resonance in **13** moves upfield upon deprotonation/coordination compared to the free ligand. On the other hand, the different coordination mode in four-membered chelates **11** and **12** causes the ^{31}P NMR resonances to move downfield in general.

In IR and Raman spectra of the ligands, mainly the vibrations in the aromatic and aliphatic (isopropyl groups) skeletons and adjacent C–H bonds can be assigned. The presence of the isopropyl groups in compounds **3**, **4** and **7** was confirmed by Raman spectroscopy, while the presence of the phenyl groups was confirmed by both Raman and IR spectroscopy. For those compounds that have P–O–C bonds, an IR band at 1160 cm^{-1} was observed.[12] As the amine is involved in hydrogen bonding the NH stretching frequency is normally lowered. In accordance with the crystal structures of the ligands, we found the N–H stretching vibrations at lower frequencies (2600–2750 cm^{-1}). Other characteristic bands were observed; *ν*(P=O) around 1190, *ν*(PNP) around 950 and 760, *ν*(P=S) around 625 and 610 and *ν*(P=Se) around 580 cm^{-1}. The *ν*(C=O) stretching vibration in **10** appears at 1664 cm^{-1}, in the analogous compound $Ph_2P(S)–N(H)–C(O)Ph$ there is a corresponding vibration at 1651 cm^{-1}.[10] IR data for the palladium complexes were collected mainly as evidence that the ligand had undergone deprotonation at the nitrogen. If identified, *ν*(PNP) bands appear at higher frequencies and the *ν*(P=S) bands appear at lower frequencies compared to the free ligands, reflecting the increased P–N bond order and decreased P=S character in the deprotonated molecules. Unfortunately, Raman spectra of many complexes showed significant fluorescence, so usually no reasonable data could be obtained and interpreted.

Structure of ligands

The basic crystallographical data are listed in Table 2. With the exception of **9** the ligands crystallise in centrosymmetric space groups. The asymmetric unit is represented by two molecules in **4**, **9** and **10**; in the other cases there is only one molecule present. One of the phenyl groups in **7** is disordered over two sites having approximately the same occupancies; the disordered ring planes are almost mutually perpendicular. Selected bond lengths and angles for P–N–P ligands characterized by X-ray structure analysis are given in Table 3. In cases where two crystallographically independent molecules are present in the structure, both values are listed. Crystals of $(PhO)_2P(O)–N(H)–P(S)(OPh)_2$, **14**,[13] were also prepared, and the crystal structure of **14** was determined for comparison.

For dithioimidodiphosphinates and related compounds two common basic crystal structure types are known. Tetraphenyl diselenoimidodiphosphinate and dithioimidodiphosphinate, as well as imidodiphosphate tetraphenylester molecules, form hydrogen bonded dimers, whilst tetraphenyl dioxoimidodiphosphinate exists as a hydrogen bonded polymer. The crystal structures of compounds **1**, **2**, **5** to **7** and **9** are hydrogen bonded dimers. Along with dimeric molecules in the

Table 1 ^{31}P NMR shifts of ligands and their assignment based on chemical shifts of the parent *P*-amino and *P*-chloro compounds

	δ P_A	δ P_B	$^{2}J[^{31}P–^{31}P]$/Hz	$^{1}J[^{31}P–^{77}Se]$/Hz	Parent compounds corresponding to P_A	δ P	Parent compounds corresponding to P_B	δ P	$^{1}J[^{31}P–^{77}Se]$/Hz
1	−7.2	53.9	11.2	—	$(PhO)_2P(O)NH_2$	2.5	$Ph_2P(S)NH_2$	54.5	—
					$(PhO)_2P(O)Cl$	−5.0	$Ph_2P(S)Cl$	80.2	—
2	−7.7	48.8	12.6	801.3	$(PhO)_2P(O)NH_2$	2.5	$Ph_2P(Se)NH_2$	49.3	774.7
					$(PhO)_2P(O)Cl$	−5.0	$Ph_2P(Se)Cl$	70.3	867.1
3	−6.9	91.6	15.8	—	$(PhO)_2P(O)NH_2$	2.5	$^{i}Pr_2P(S)NH_2$	83.7	—
					$(PhO)_2P(O)Cl$	−5.0	$^{i}Pr_2P(S)Cl$	128.8	—
4	−7.1	89.8	18.5	770.1	$(PhO)_2P(O)NH_2$	2.5	$^{i}Pr_2P(Se)NH_2$		
					$(PhO)_2P(O)Cl$	−5.0	$^{i}Pr_2P(Se)Cl$	125.3	839.8
5	55.3	50.5	26.8	805.0	$(PhO)_2P(S)NH_2$	65.1	$Ph_2P(Se)NH_2$	49.3	774.7
					$(PhO)_2P(S)Cl$	60.0	$Ph_2P(Se)Cl$	70.3	867.1
6[a]	56.0	55.4	23.2	—	$(PhO)_2P(S)NH_2$	65.1	$Ph_2P(S)NH_2$	54.5	—
					$(PhO)_2P(S)Cl$	60.0	$Ph_2P(S)Cl$	80.2	—
7	55.7	94.5	27.8	—	$(PhO)_2P(S)NH_2$	65.1	$^{i}Pr_2P(S)NH_2$	83.7	—
					$(PhO)_2P(S)Cl$	60.0	$^{i}Pr_2P(S)Cl$	128.8	—
8	56.6	21.9	13.5	—	$(PhO)_2P(S)NH_2$	65.1	$Ph_2P(O)NH_2$	22.4	—
					$(PhO)_2P(S)Cl$	60.0	$Ph_2P(O)Cl$	42.7	—
9	52.7	99.7	27.0	—	$Ph_2P(S)NH_2$	54.5	$^{i}Pr_2P(S)NH_2$	83.7	—
					$Ph_2P(S)Cl$	80.2	$^{i}Pr_2P(S)Cl$	128.8	—

[a] Due to their small difference the chemical shifts in **6** can not be unambiguously assigned (see text).

Table 2 Crystallographic data for the ligands and their palladium(II) complexes

	1	**2**	**4**	**5**	**6**	**7**
Empirical formula	$C_{24}H_{21}NO_3P_2S$	$C_{24}H_{21}NO_3P_2Se$	$C_{18}H_{25}NO_3P_2Se$	$C_{24}H_{21}NO_2P_2SSe$	$C_{24}H_{21}NO_2P_2S_2$	$C_{18}H_{25}NO_2P_2S_2$
Formula weight	465.42	512.32	444.29	528.38	481.48	413.45
T/K	150(2)	150(2)	120(2)	150(2)	130(2)	130(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$C2/c$	$P\bar{1}$
a/Å	9.738(1)	9.745(2)	18.491(4)	23.236(5)	23.166(5)	8.494(2)
b/Å	18.582(2)	18.799(4)	23.200(5)	9.654(2)	9.633(2)	9.173(2)
c/Å	12.564(1)	12.423(2)	9.642(2)	22.026(4)	22.060(4)	13.751(3)
α/°	90	90	90	90	90	97.97(3)
β/°	98.84(2)	98.21(3)	98.59(3)	108.97(3)	109.23(3)	104.38(3)
γ/°	90	90	90	90	90	92.35(3)
U/Å^3	2246.5(4)	2252.5(8)	4089.9(15)	4672.5(16)	4648.2(16)	1024.6(4)
Z	4	4	8	8	8	2
μ/mm^{-1}	0.313	1.835	2.009	1.855	0.388	0.428
Reflections all/independent	14 140/3563	12 723/3566	29 324/9677	2880/2789	4134/4026	3764/3602
R_{int}	0.0726	0.1021	0.0464	0.0495	0.0131	0.0163
Final R_1, $wR_2[I > 2\sigma(I)]$[a]	0.0475, 0.0933	0.0571, 0.1239	0.0340, 0.0857	0.0342, 0.0939	0.0430, 0.0936	0.0773, 0.1909
	9	**10**	**11**	**12**	**13**	**14**
Empirical formula	$C_{18}H_{25}NP_2S_2$	$C_{19}H_{16}NO_3PS$	$C_{24}H_{20}NO_3P_2Pd_{0.5}S$	$C_{36}H_{48}N_2O_6P_4PdS_2$	$C_{24}H_{20}NO_2P_2Pd_{0.5}S_2$	$C_{24}H_{21}NO_5P_2S$
Formula weight	381.45	369.36	517.61	899.16	533.67	497.42
T/K	150(2)	120(2)	120(2)	130(2)	130(2)	130(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	Cc
a/Å	10.154(2)	9.974(2)	10.678(2)	11.605(2)	10.698(2)	10.829(2)
b/Å	17.574(4)	13.675(3)	9.294(2)	12.181(2)	10.890(2)	22.400(4)
c/Å	22.213(4)	15.078(3)	23.112(5)	15.930(3)	11.220(2)	10.007(2)
α/°	90	76.93(3)	90	110.77(3)	108.78(3)	90
β/°	90	70.93(3)	99.24(3)	91.19(3)	105.07(3)	98.22(3)
γ/°	90	68.82(3)	90	106.59(3)	95.40(3)	90
U/Å^3	3963.8(14)	1798.7(6)	2263.9(8)	1999.1(6)	1172.2(4)	2402.5(8)
Z	8	4	4	2	2	4
Reflections all/independent	3332/3332	12 158/7912	10 385/3913	7026/6705	4349/4110	2253/2253
R_{int}	0.0000	0.0219	0.0236	0.0564	0.0291	0.0000
Final R_1, wR_2 $[I > 2\sigma(I)]$[a]	0.0275, 0.0737	0.0334, 0.0780	0.0249, 0.0638	0.0422, 0.1030	0.0448, 0.1172	0.0332, 0.0853

[a] Weighting scheme used: $w = 1/[\sigma^2(F_o^2) + (0.0540P)^2 + 0.4286P]$ where $P = (F_o^2 + 2F_c^2)/3$.

crystal structure of **4**, oligomeric chains also occur. Unlike tetraphenyl dioxoimidodiphosphinate, which exists as the $Ph_2P(O)$–N=P(OH)Ph_2 tautomer in the solid state, the hydrogen is bonded to the nitrogen in all the present compounds. Therefore the hydrogen-bonding interactions between P=E and NH groups of adjacent molecules are responsible for oligomer formation in the crystal. As expected, oxygen atoms are involved in hydrogen bonds rather than sulfur or selenium in **1** (Fig. 1), **2** and **4** and sulfur atoms rather than selenium in compound **5**. In cases where both donor atoms are sulfurs, sulfur at the phenoxy group side is involved in hydrogen bonding in **6** (Fig. 2) or at the side of the isopropyl groups in **7** (Fig. 3) and **9**. The P=E bond order is decreased when the chalcogen atom is involved in hydrogen bonding. The hydrogen bond parameters are collected in Table 4. Both values are listed when two molecules are present in the asymmetric unit. As expected, the shortest nitrogen–chalcogen distances in the N–H···E sequence appear in ligands with oxygen donors.

Compound **14** has a chain arrangement in the crystal packing (Fig. 4). Other known examples of P–N–P ligands linearly linked *via* N–H···E hydrogen bonds are

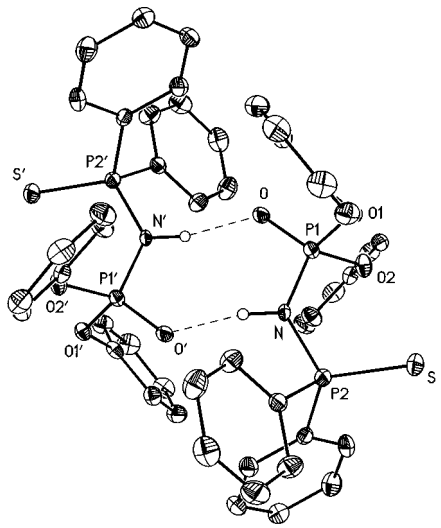


Fig. 1 The solid-state structure of $Ph_2P(S)N(H)P(O)(OPh)_2$, **1**, showing the hydrogen bonded dimer.

Table 3 Selected bond lengths (Å) and angles (°) for synthesised ligands

	P(1)=E	P(2)=E	P(1)–N	P(2)–N	P(1)–N–P(2)
1	1.469(2)	1.934(1)	1.634(3)	1.689(3)	130.7(2)
2	1.473(5)	2.089(2)	1.654(6)	1.671(6)	131.8(4)
4	1.456(1), 1.462(1)	2.093(1), 2.081(1)	1.620(2), 1.621(2)	1.694(2), 1.686(2)	129.3(1), 132.4(1)
5	1.915(1)	2.079(1)	1.627(3)	1.702(3)	131.3(2)
6	1.929(1)	1.915(1)	1.702(2)	1.640(2)	130.2(1)
7	1.877(3)	1.943(2)	1.636(5)	1.686(5)	136.5(4)
9	1.935(1), 1.941(1)	1.957(1), 1.955(1)	1.676(3), 1.670(2)	1.683(2), 1.682(3)	134.9(2), 132.3(2)
14	1.458(3)	1.898(1)	1.640(3)	1.650(3)	127.4(2)

Table 4 Hydrogen bond parameters for synthesised ligands

	N–H/Å	H···E/Å	N···E/Å	N–E···E/°
1	0.73(3)	2.02(4)	2.752(4)	179(4)
2	0.81(7)	1.97(7)	2.743(7)	159(7)
4	0.80(2), 0.83(3)	2.05(2), 1.95(3)	2.795(2), 2.772(2)	154(2), 170(3)
5	0.73(4)	2.71(4)	3.432(4)	170(3)
6	0.79(2)	2.63(2)	3.407(2)	171(2)
7	0.67(5)	2.69(5)	3.331(7)	162(6)
9	0.84(3), 0.83(4)	2.58(3), 2.51(4)	3.395(3), 3.316(3)	165(3), 164(3)
10	0.80(2), 0.83(2)	2.08(2), 2.07(2)	2.866(2), 2.894(2)	169(2), 172(2)
14	0.80(6)	2.04(7)	2.779(9)	153(6)

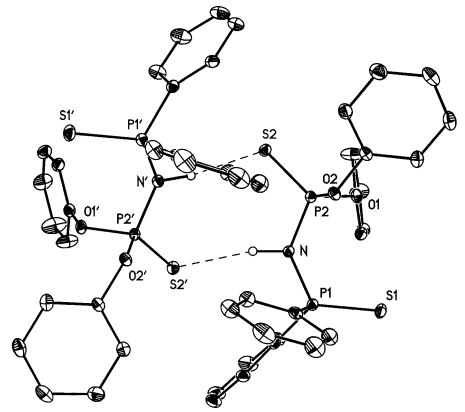


Fig. 2 The solid-state structure of $Ph_2P(S)N(H)P(S)(OPh)_2$, **6**, showing the hydrogen bonded dimer.

$Me_2P(S)–N(H)–P(S)Me_2$,[14] $^iPr_2P(S)–N(H)–P(S)^iPr_2$,[15] $^iBu_2P(S)–N(H)–P(S)^iBu_2$,[16] $(EtO)_2P(S)–N(H)–P(O)Ph_2$,[8] and, in the present work, also one of the two molecules of $^iPr_2P(Se)–N(H)–P(O)(OPh)_2$, **4**. When the donor atoms interchange their positions in $(EtO)_2P(S)–N(H)–P(O)Ph_2$, the chain arrangement transforms into a dimeric arrangement of molecules in $(EtO)_2P(O)–N(H)–P(S)Ph_2$.[8] Although the factors that favour chain rather than dimer formation are not obvious, the chains are more commonly observed in the presence of alkyl groups.

All the synthesised ligands studied crystallographically have the two donor atoms in an *anti* (*trans*) arrangement, which is typical for $Me_2P(S)–N(H)–P(S)Me_2$ (the S–P···P–S 'torsion angle' being 176.9°). The E–P···P–E torsion angles in the ligands vary from 147° for **6** to almost planar (178.3°) for one of the crystallographically independent molecules in **9**. The presence of two different phosphorus centres in a ligand sometimes leads to significant asymmetry in the P–N bond lengths. In common with $Ph_2P(S)–N(H)–(O)Ph$, the structure of **10** shows that the compound is present in the keto form with the proton bonded to nitrogen. There are two crystallographically independent molecules in the crystal structure. The torsion angles S=P···C=O, for the oxygen and sulfur atoms that are arranged *trans* to each another, are remarkably different (−7.4 and −65.4°). In $Ph_2P(S)–N(H)–(O)Ph$ the donor atoms are in a *syn* conformation. Unlike many other ligands described here and in common with $Ph_2P(S)–N(H)–C(O)Ph$ the hydrogen bonding between the C=O oxygen and N–H hydrogen in **10** leads to molecular chain formation (Fig. 5). Bond lengths and angles in both $Ph_2P(S)–N(H)–C(O)Ph$ and **10** are very similar, showing that the influence of electronically different substituents is unimportant.

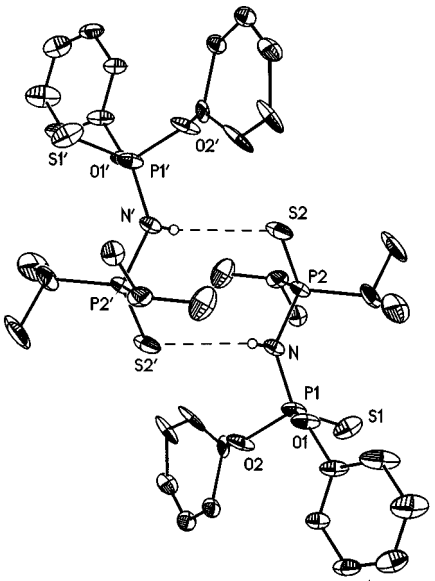


Fig. 3 The solid-state structure of $^iPr_2P(S)N(H)P(S)(OPh)_2$, **7**, showing the hydrogen bonded dimer.

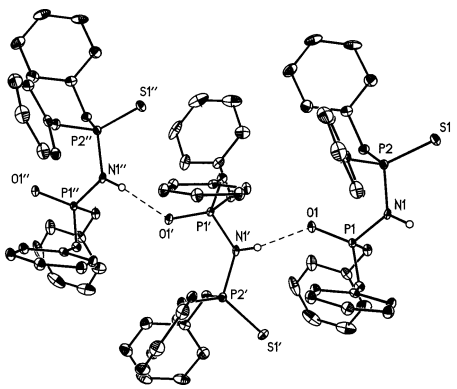


Fig. 4 The solid-state structure of $(PhO)_2P(O)N(H)P(S)(OPh)_2$, **14**, showing the hydrogen bonded chain structure.

Structure of complexes

The palladium complex **13** is constituted of two six-membered chelate rings as both sulfur donors of each ligand are coordinated to the metal centre (Fig. 6). The P–S bonds are elongated and the P–N distances are shorter when compared with the free ligand, thus suggesting that delocalisation occurs in

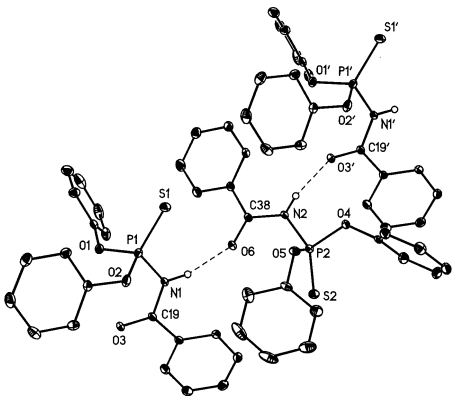


Fig. 5 The solid-state structure of $PhC(O)N(H)P(S)(OPh)_2$, **10**, showing the hydrogen bonded chain structure.

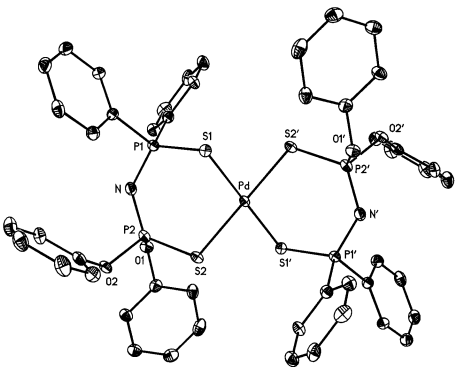


Fig. 6 Crystal structure of $[Ph_2P(S)NP(S)(OPh)_2]_2Pd$, **13**, showing the six-membered chelate rings.

the six-membered chelate ring. Since palladium lies at the centre of symmetry and the sulfur donors are related by a symmetry operation, the palladium environment is perfectly planar. The P(1)S(1)P(2)S(2) plane is almost planar with a mean atomic deviation of 0.04 Å. Palladium deviates 1.51 Å from this plane and nitrogen −0.13 Å, indicating a chair conformation of the chelate rings. The interplanar angle is 113°. A similar compound, $[(EtO)_2P(S)–N–P(S)Ph_2]_2Pd$, **15**, was prepared previously using the ligand $(EtO)_2P(S)–N(H)–P(S)Ph_2$, **16**,[17] and its ring conformation can be described as a boat. Table 5 lists selected bond lengths and angles for **13** and **15** along with the data for their parent ligands. The bond lengths and angles are in reasonable agreement with those found in previously published coordination compounds of imidodiphosphinates.

In the palladium complexes **11** and **12** (Fig. 7 and 8) the coordination is different from that of **13**. With the strong electron withdrawing effect of the phenoxy group, the phosphoryl groups become too "hard" to coordinate to the metal. Instead, four-membered PdSPN chelate rings are observed. A similar complex, **17**, is known with the tetraphenoxy ligand **14**.[18] In all three complexes oxygen and sulfur are arranged *trans* to one another. The chelate rings are almost planar with mean deviations from their planes of 0.08 Å in **11** and 0.06 Å in **12**. The P–S bond lengths of the ligands change upon complex formation, as in the palladium compounds with six-membered rings. Since oxygen is not involved in donation, the difference in the P=O bond lengths is negligible and also the O–P–N angle is quite unaffected by coordination. All three palladium complexes with four-membered chelate rings have very similar bond lengths and angles; they are summarised in Table 6 (included also are the parameters of corresponding ligands, if known). Interestingly, **11** crystallises in two different crystal systems, both monoclinic and triclinic crystals can be isolated from the same solution.

Table 5 Selected bond lengths (Å) and angles (°) for two palladium compounds with six-membered chelate rings and their free ligands. P(2) corresponds to the phosphorus atom with ethoxy or phenoxy substituents

	16	**6**	**15**	**13**
Pd–S(1)	—	—	2.325(mean)	2.344(1)
Pd–S(2)	—	—	2.345	2.332(2)
P(1)–S(1)	1.937(1)	1.929(1)	2.027	2.008(2)
P(2)–S(2)	1.920(2)	1.915(1)	2.011	2.006(2)
P(1)–N	1.681(3)	1.640(2)	1.594	1.596(4)
P(2)–N	1.667(3)	1.702(2)	1.566	1.553(4)
P(1)–N–P(2)	129.9(2)	130.2(1)	125.1	132.9(2)
S–P(1)–N	116.3(1)	113.1(1)	116.7	117.6(2)
N–P(2)–S	112.9(1)	114.1(1)	117.4	120.9(2)
Pd–S(1)–P(1)	—	—	110.1	100.3(1)
Pd–S(2)–P(2)	—	—	101.1	101.9(1)

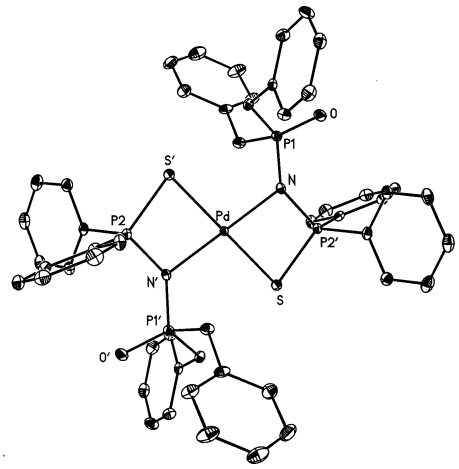


Fig. 7 Crystal structure of $[Ph_2P(S)NP(O)(OPh)_2]_2Pd$, **11**, showing the four-membered chelate rings.

There are two pairs of doublets in the ^{31}P NMR spectra of **11**. In common with the previous work of Cupertino *et al.*,[8] we suppose that there may be three possible structures, and we can now confirm the presence of the third type by X-ray crystallography (Fig. 9).

We postulate that in the case of a ligand with a P–N–P backbone where both donor atoms are sulfur or selenium atoms,[17,19] the palladium(II) atom is coordinated by both chalcogens, regardless of the organic substituents on phosphorus and that the resulting chelate rings are six-membered.

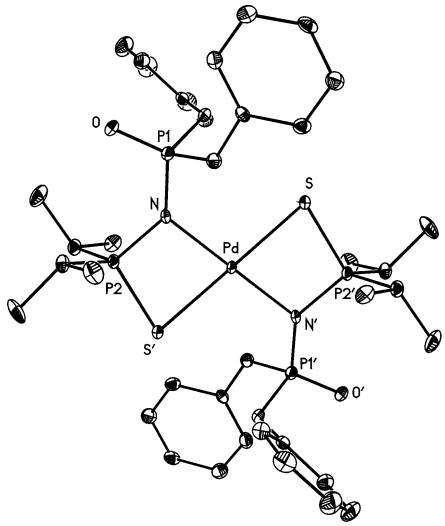


Fig. 8 Crystal structure of $[^iPr_2P(S)NP(O)(OPh)_2]_2Pd$, **12**, showing the four-membered chelate rings.

Table 6 Comparative bond lengths (Å) and angles (°) for Pd compounds with four-membered chelate rings

	14	**1**	**17**	**11**	**12**
Pd–S	—	—	2.342(1)	2.347(2)	2.357(1), 2.346(1)
Pd–N	—	—	2.055(3)	2.054(3)	2.042(4), 2.047(4)
P(1)–O	1.458(3)	1.469(2)	1.450(3)	1.471(3)	1.458(4), 1.453(4)
P(2)–S	1.898(1)	1.934(1)	1.987(2)	2.020(2)	2.015(2), 2.013(2)
P(1)–N	1.640(3)	1.634(3)	1.636(3)	1.622(4)	1.608(4), 1.611(4)
P(2)–N	1.650(3)	1.689(3)	1.592(3)	1.626(5)	1.633(4), 1.633(4)
P(1)–N–P(2)	127.4(2)	130.7(2)	129.2(2)	129.4(2)	129.5(3), 129.1(2)
O–P(1)–N	113.9(2)	110.4(2)	112.8(2)	114.7(2)	115.9(2), 115.7(2)
N–P(2)–S	113.5(1)	113.8(1)	102.0(1)	99.7(1)	99.5(2), 100.3(2)
Pd–S–P(2)	—	—	79.4(1)	80.19(6)	80.6(1), 80.2(1)
Pd–N–P(2)	—	—	98.5(1)	99.6(2)	100.6(2), 100.3(2)

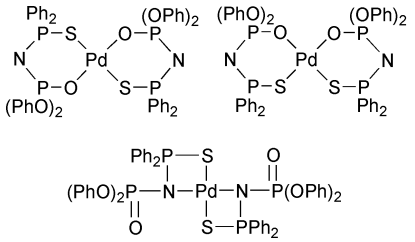


Fig. 9 Possible structures for $[Ph_2P(S)NP(O)(OPh)_2]_2Pd$.

If oxygen is present as a potential donor atom (it is a much 'harder' donor than sulfur), its ability to coordinate to palladium now depends on the nature of the organic substituents in the $R_2P(O)$– group. The electron-donating substituents (phenyl groups) allow oxygen to act as a donor and the resultant chelate ring is six-membered.[20,21] The electron-withdrawing substituents (phenoxy or ethoxy groups) do not allow oxygen to be involved in donation. The resulting complexes now have four-membered chelate rings as found in **11**, **12**, in $[(PhO)_2P(S)NP(O)(OPh)_2]_2Pd$[18] and probably also in $[Ph_2P(S)NP(O)(OEt)_2]_2Pd$.[8]

Experimental

All reactions were performed in the absence of water, under argon gas unless otherwise stated. All reagents were purchased from Aldrich and were used as received, unless otherwise stated.

^1H NMR spectra (in $CDCl_3$) and ^{31}P-$\{^1H\}$ NMR spectra (in CH_2Cl_2) were recorded on a Bruker AVANCE DRX 500 instrument using tetramethylsilane and H_3PO_4 (85%), respectively, as an external reference. IR spectra were recorded on Nujol mulls using a Bruker IFS 28 spectrometer. Raman spectra were recorded on samples in sealed glass capillaries on a Spex Ramalog 3 spectrometer, using a Spectra Physics Model 165-03 argon laser for excitation (100–200 mW at 488 nm). Emission lines of the argon plasma were used for calibration. Microanalyses was preformed using a Fisons EA 1108 instrument at Palacky University, Olomouc, Czech Republic.

Crystals were usually grown by slow diffusion of hexane into dichloromethane solutions. Diffraction data were collected on a KUMA KM-4 κ-axis diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) using either a scintillation counter or an area detector. The intensity data were corrected for Lorentz and polarisation effects. Details of the data collections and refinements are summarised in Table 2. The computer programs used were DATPROC9 and KM4RED from the KM-4 software[22] for the data reduction, SHELXS-86 for the structure solutions,[23] SHELXL-97 for the structure refinement[24] and ORTEP[25] was used to produce drawings (thermal ellipsoids are drawn at the 30% probability level).

CCDC reference numbers 153013–153024. See http://www.rsc.org/suppdata/nj/b1/b103501k/ for crystallographic data in CIF or other electronic format.

Preparation of $Ph_2P(E)Cl$ and $^iPr_2P(E)Cl$ and corresponding amines (E = S, Se)

Equimolar quantities of phosphine and chalcogen were heated under toluene reflux for 5 h. After cooling, the mixture was filtered and toluene was removed *in vacuo*. The corresponding amino compounds were prepared by bubbling ammonia gas through the solution of the chloride in diethyl ether. After the ammonolysis was completed (determined by ^{31}P-$\{^1H\}$ NMR spectroscopy), the mixture was filtered through Celite and the filtrate was evaporated to dryness to give the amine in almost quantitative yield. ^{31}P-$\{^1H\}$ NMR data are summarised in Table 1.

Preparation of $(PhO)_2P(E)Cl$ and corresponding amines (E = O, S)

The $(PhO)_2P(E)Cl$ compounds were prepared according to literature methods.[26,27] $(PhO)_2P(O)NH_2$ was prepared by ammonolysis as described above, while the ammonolysis of $(PhO)_2P(S)Cl$ was performed using a concentrated aqueous ammonia solution.[27] ^{31}P-$\{^1H\}$ NMR data are given in Table 1.

Ligand synthesis (general)

Two similar synthetic methods were employed, using different solvents. Compounds **1** to **6** and **10** were prepared in tetrahydrofuran (method A) while compounds **6** to **9** were prepared in dimethylformamide (method B). Examples of both of these methods are given below. The crude products were usually recrystallised from dichloromethane with the exception of **10**, which was crystallised from methanol. All ligands are colourless and air stable except for **2**, **4** and **5**, which turned red on exposure to light and air, due to the formation of red selenium.

Method A. The amine was added to a suspension of sodium hydride in THF at room temperature. The mixture was stirred (30 min) before the dropwise addition of phosphorus electrophile over 15 min. The mixture was refluxed overnight. After cooling methanol (5 ml) was added to destroy any excess sodium hydride. The volume of the THF was then reduced by half under vacuum and 2 M aqueous hydrochloric acid was added. The mixture was then extracted with dichloromethane. The dichloromethane extract was dried over Na_2SO_4, then the solvent was partially distilled off, before the extract was stored at −18 °C for 3 days to give the product as a crystalline white solid.

Method B. The amine was added to a suspension of sodium hydride in dimethylformamide at room temperature. After 30 min of stirring the phosphorus electrophile was added dropwise over 15 min. The mixture was then heated to *ca.* 100 °C for 5 h. During the heating period the mixture finally took on a creamy appearance. 2 M aqueous HCl was added and the mixture was extracted with dichloromethane. The dichloromethane solution was dried over Na_2SO_4 and its volume reduced under vacuum. A white solid was obtained either by adding hexane with stirring or allowing the mixture to stand at −18 °C.

$Ph_2P(S)NHP(O)(OPh)_2$, 1. *Method A.* Reagents: $(PhO)_2P(O)NH_2$ (6.60 g, 0.026 mol), NaH (1.90 g, 0.079 mol), $Ph_2P(S)Cl$ (6.70 g, 0.026 mol) in THF (100 ml); 2 M HCl (150 ml) used for protonation and CH_2Cl_2 (60 ml × 3) used for extraction. Yield: (4.15 g, 33.7%); mp: 162–163 °C; microanalysis: found C 61.72, H 4.68, N 2.77, S 6.96%; calc. for $C_{24}H_{21}NO_3P_2S$: C 61.93, H 4.55, N 3.01, S 6.89%; selected IR data: 2726s [ν(NH)], 1184s [ν(PO)], 1158s, 960s [ν(PNP)], 768m, 754m, 630m, 616m [ν(PS)] cm^{-1}; ^1H NMR: δ(N–H) 8.3.

$Ph_2P(Se)NHP(O)(OPh)_2$, 2. *Method A.* Reagents: $(PhO)_2P(O)NH_2$ (6.60 g, 0.026 mol), NaH (1.90 g, 0.079 mol), $Ph_2P(Se)Cl$ (7.90 g, 0.026 mol) in THF (100 ml); 2 M HCl (150 ml) used for protonation and CH_2Cl_2 (60 ml × 3) used for extraction. Yield: (3.70 g, 27.3%); mp: 164.5–165.5 °C; microanalysis: found C 56.32, H 4.20, N 2.42%; calc. for $C_{24}H_{21}NO_3P_2Se$: C 56.26, H 4.13, N 2.73%; selected IR data: 2723s [ν(NH)], 1183s [ν(PO)], 1158s, 962s [ν(PNP)], 766m, 751m, 578m, 559m [ν(PSe)] cm^{-1}; ^1H NMR: δ(N–H) 3.7.

$^{i}Pr_2P(S)NHP(O)(OPh)_2$, 3. *Method A.* Reagents: $(PhO)_2P(O)NH_2$ (3.60 g, 0.014 mol), NaH (1.00 g, 0.042 mol), $^{i}Pr_2P(S)Cl$ (2.60 g, 0.014 mol) in THF (60 ml); 2 M HCl (75 ml) used for protonation and CH_2Cl_2 (50 ml × 3) used for extraction. Yield: (1.30 g, 22.6%); mp: 129–130 °C; microanalysis: found C 54.37, H 6.28, N 3.28, S 7.91%; calc. for $C_{18}H_{25}NO_3P_2S$: C 54.40, H 6.34, N 3.52, S 8.07%; selected IR data: 2749m [ν(NH)], 1195s [ν(PO)], 1162m, 958s [ν(PNP)], 775m, 765m, 616w [ν(PS)] cm^{-1}; ^1H NMR: δ(N–H) 5.7.

$^{i}Pr_2P(Se)NHP(O)(OPh)_2$, 4. *Method A.* Reagents: $(PhO)_2P(O)NH_2$ (3.70 g, 0.015 mol), NaH (1.08 g, 0.045 mol), $^{i}Pr_2P(Se)Cl$ (3.50 g, 0.015 mol) in THF (100 ml); 2 M HCl (75 ml) used for protonation and CH_2Cl_2 (50 ml × 3) used for extraction. Yield: (2.25 g, 34.1%); mp: 99–101 °C; microanalysis: found C 48.72, H 5.45, N 2.80%; calc. for $C_{18}H_{25}NO_3P_2Se$: C 48.66, H 5.67, N 3.15%; selected IR data: 2750m [ν(NH)], 1194s [ν(PO)], 1162m, 956s [ν(PNP)], 774m, 767m, 589m, 572m [ν(PSe)] cm^{-1}; ^1H NMR: δ(N–H) 6.2.

$Ph_2P(Se)NHP(S)(OPh)_2$, 5. *Method A.* Reagents: $Ph_2P(Se)NH_2$ (2.70 g, 0.010 mol), NaH (0.70 g, 0.029 mol), $(PhO)_2P(S)Cl$ (2.74 g, 0.010 mol) in THF (50 ml); 2 M HCl (50 ml) used for protonation and CH_2Cl_2 (30 ml × 3) used for extraction. Yield: (0.65 g, 12.8%); mp: 130–132 °C; microanalysis: found C 54.62, H 3.98, N 2.70, S 6.22%; calc. for $C_{24}H_{21}NO_2P_2SSe$: C 54.55, H 4.01, N 2.65, S 6.07%; selected IR data: 3124m, 2600w [ν(NH)], 1157m, 947s [ν(PNP)], 776m, 653m [ν(PS)], 547w [ν(PSe)] cm^{-1}; ^1H NMR: δ(N–H) 3.6.

$Ph_2P(S)NHP(S)(OPh)_2$, 6. *Method A.* Reagents: $Ph_2P(S)NH_2$ (3.00 g, 0.013 mol), NaH (0.93 g, 0.039 mol), $(PhO)_2P(S)Cl$ (3.66 g, 0.013 mol) in THF (50 ml); 2 M HCl (50 ml) used for protonation and CH_2Cl_2 (30 ml × 3) used for extraction. Yield: (1.60 g, 25.8%); mp: 128–129 °C; microanalysis: found C 60.01, H 4.43, N 2.75, S 13.14%; calc. for $C_{24}H_{21}NO_2P_2S_2$: C 59.87, H 4.40, N 2.91, S 13.32%; selected IR data: 3126m, 2600w [ν(NH)], 1157s, 935s [ν(PNP)], 776m, 767m, 627m, 614w [ν(PS)] cm^{-1}; ^1H NMR: δ(N–H) 5.2.

Method B. Reagents: $Ph_2P(S)NH_2$ (3.00 g, 0.013 mol), NaH (0.93 g, 0.039 mol), $(PhO)_2P(S)Cl$ (3.66 g, 0.013 mol) in DMF (70 ml); 2 M HCl (50 ml) used for protonation and CH_2Cl_2 (30 ml × 3) used for extraction. Yield: (3.95 g, 63.8%); mp: 128–129 °C; microanalysis: found C 59.84, H 4.38, N 3.02, S 13.25%; calc. for $C_{24}H_{21}NO_2P_2S_2$: C 59.87, H 4.40, N 2.91, S 13.32%; selected IR data: 3126m, 2600w, 1157s, 935s, 776m, 766m, 627m, 614w cm^{-1}; ^1H NMR: δ(N–H) 5.2.

$^{i}Pr_2P(S)NHP(S)(OPh)_2$, 7. *Method B.* Reagents: $(PhO)_2P(S)NH_2$ (3.90 g, 0.015 mol), NaH (1.10 g, 0.046 mol), $^{i}Pr_2P(S)Cl$ (2.70 g, 0.015 mol) in DMF (80 ml); 2 M HCl (100 ml) used for protonation and CH_2Cl_2 (50 ml × 3) used for extraction. Yield: (4.40 g, 72.4%); mp: 86–87 °C; microanalysis: found C 52.34, H 6.23, N 3.24, S 15.78%; calc. for $C_{18}H_{25}NO_2P_2S_2$: C 52.29, H 6.09, N 3.39, S 15.51%; selected IR data: 2668m [ν(NH)], 1161s, 923s [ν(PNP)], 769m, 762m, 626m, 610m [ν(PS)] cm^{-1}; ^1H NMR: δ(N–H) 4.8.

$Ph_2P(O)NHP(S)(OPh)_2$, 8. *Method B.* Reagents: $(PhO)_2P(S)NH_2$ (3.00 g, 0.011 mol), NaH (0.80 g, 0.033 mol), $Ph_2P(O)Cl$ (2.68 g, 0.011 mol) in DMF (50 ml); 2 M HCl (50 ml) used for protonation and the precipitate was collected by filtration. Yield: (4.30 g, 81.7%); mp: 194–197 °C; microanalysis: found C 62.03, H 4.54, N 2.97, S 6.45%; calc. for $C_{24}H_{21}NO_3P_2S$: C 61.93, H 4.55, N 3.01, S 6.89%; selected IR data: 2629s [ν(NH)], 1182s [ν(PO)], 1162s, 955s, 937s [ν(PNP)], 779s, 620w [ν(PS)] cm^{-1}; ^1H NMR: δ(N–H) 8.5.

$Ph_2P(S)NHP(S)^{i}Pr_2$, 9. *Method B.* Reagents: $Ph_2P(S)NH_2$ (3.40 g, 0.015 mol), NaH (1.10 g, 0.046 mol), $^{i}Pr_2P(S)Cl$ (2.70 g, 0.015 mol) in DMF (80 ml); 2 M HCl (75 ml) used for protonation and CH_2Cl_2 (50 ml × 3) used for extraction. Yield: (3.00 g, 54.0%); mp: 104–105 °C; microanalysis: found C 56.70, H 6.72, N 3.72, S 16.25%; calc. for $C_{18}H_{25}NP_2S_2$: C 56.67, H 6.61, N 3.67, S 16.81%; selected IR data: 2611w [ν(NH)], 918s [ν(PNP)], 781m, 627m, 614w [ν(PS)] cm^{-1}; ^1H NMR: δ(N–H) 3.8.

$PhC(O)NHP(S)(OPh)_2$, 10. *Method A.* Reagents: $(PhO)_2P(S)NH_2$ (2.00 g, 0.008 mol), NaH (0.55 g, 0.023 mol), PhC(O)Cl (1.10 g, 0.008 mol) in THF (50 ml); 50 ml 2 M HCl used for protonation and 3 × 30 ml CH_2Cl_2 used for extraction. Yield: (0.70 g. 25.1%); mp: 124–125 °C; microanalysis: found C 61.88, H 4.26, N 3.75, S 8.51%; calc. for $C_{19}H_{16}NO_3PS$: C 61.78, H 4.37, N 3.79, S 8.68%; selected IR data: 3221m [ν(NH)], 1664s [ν(CO)], 1161m, 641m, 616w [ν(PS)] cm^{-1}; ^{31}P-{^1H} NMR: δ 55.4 (s); ^1H NMR: δ(N–H) 2.2.

Synthesis of palladium complexes

To a stirred suspension of the ligand in methanol, potassium *tert*-butoxide was added. After stirring to obtain a homogenous mixture, $Pd(OAc)_2$ dissolved in methanol was added dropwise. The mixture was stirred for 6 to 12 h. The resulting red precipitate was collected by filtration, washed with methanol and dried *in vacuo*.

$[Ph_2P(S)NP(O)(OPh)_2]_2Pd$, 11. Reagents: **1** (0.233 g, 0.500 mmol) in MeOH (30 ml); $Pd(OAc)_2$ (0.056 g, 0.250 mmol) in MeOH (20 ml); KO^{t}Bu (0.056 g, 0.500 mmol). Yield: (0.210 g, 81.1%); mp: 197 °C; microanalysis: found: C 55.71, H 3.84, N 2.55, S 5.72%; calc. for $C_{48}H_{40}N_2O_6P_4PdS_2$: C 55.69, H 3.89, N 2.71, S 6.19%; selected IR data: 1226m [ν(PNP)], 1192s [ν(PO)], 1158s, 566m, 541w [ν(PS)] cm^{-1}; ^{31}P-{^1H} NMR: δ −2.2 (d) and 87.3 (d) ^2J(P–P) 11.6 Hz; δ 3.0 (d) and 40.3 (d) ^2J(P–P) 18.9 Hz.

$[^{i}Pr_2P(S)NP(O)(OPh)_2]_2Pd$, 12. Reagents: **3** (0.200 g, 0.503 mmol) in MeOH (15 ml); $Pd(OAc)_2$ (0.056 g, 0.250 mmol) in MeOH (20 ml); KO^{t}Bu (0.056 g, 0.503 mmol). Yield: (0.067 g, 29.6%); mp: 164.5–165 °C; microanalysis: found C 47.98, H 5.51, N 3.25, S 8.23%; calc. for $C_{36}H_{48}N_2O_6P_4PdS_2$: C 48.09, H 5.38, N 3.12, S 7.13%; selected IR data: 1238s [ν(PNP)], 1191s [ν(PO)], 1161s, 578s, 572s [ν(PS)] cm^{-1}; ^{31}P-{^1H} NMR: δ − 0.5 (d) and 125.0 (d) ^2J(P–P) 18.0 Hz.

$[Ph_2P(S)NP(S)(OPh)_2]_2Pd$, 13. Reagents: **6** (0.250 g, 0.519 mmol) in MeOH (15 ml); $Pd(OAc)_2$ (0.058 g, 0.258 mmol) in MeOH (20 ml); KO^{t}Bu (0.058 g, 0.519 mmol). Yield: (0.210 g. 75.8%); mp: 196–198 °C; microanalysis: found C 54.07, H 3.63, N 2.47, S 13.15%; calc. for $C_{48}H_{40}N_2O_4P_4PdS_4$: C 54.01, H 3.78, N 2.62, S 12.01%; selected IR data: 1221m [ν(PNP)], 1161s, 562m, 548m [ν(PS)] cm^{-1}; ^{31}P-{^1H} NMR: δ 42.3 (d) and 46.8 (d) ^2J(P–P) 27.3 Hz.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (grant no. 203/99/0067) and by the Ministry of Education of the Czech Republic (MSM 143100011). We also thank Prof. Steinar Husebye, Department of Chemistry, University of Bergen, Norway, for very valuable discussions.

References

1 A. Schmidpeter, R. Böhm and H. Groeger, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 704.
2 O. Navrátil, E. Herrmann and P. Slezák, *Coll. Czech. Chem. Commun.*, 1987, **52**, 1708.

3 J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 2893.
4 L. Barkaoui, M. Charrouf, M.-N. Rager, B. Denise, N. Platzer and H. Rudler, *Bull. Soc. Chim. Fr.*, 1997, **134**, 167.
5 H. Rudler, B. Denise, J. R. Gregorio and J. Vaissermann, *Chem. Commun.*, 1997, 2299.
6 S. W. Magennis, S. Parsons, A. Corval, J. D. Woollins and Z. Pikramenou, *Chem. Commun.*, 1999, 61.
7 E. Fluck, H. Richter and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1983, **498**, 161.
8 D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1998, **17**, 4219.
9 L. Mezník and A. Marecek, *Z. Chem.*, 1981, **8**, 294.
10 D. J. Birdsall, J. Green, T. Q. Ly, J. Novosad, M. Necas, A. M. Z. Slawin, J. D. Woollins and Z. Zak, *Eur. J. Inorg. Chem.*, 1999, 1445.
11 J. C. Tebby, *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*, CRC Press, Boca Raton, FL, 1991.
12 K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, Inc., San Francisco, CA, 1962.
13 E. Herrmann, M. Nouaman, Z. Zak, G. Grossmann and G. Ohms, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1879.
14 C. Silvestru, R. Rösler, I. Haiduc, R. Cea-Olivares and G. Espinosa-Perez, *Inorg. Chem.*, 1995, **34**, 3352.
15 D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 2695.
16 D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1999, **18**, 707.
17 D. C. Cupertino, R. W. Keyte, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1998, **18**, 311.
18 Z. Zak, M. Fofana, J. Kamenicek and T. Glowiak, *Acta Crystallogr., Sect. C*, 1989, **45**, 1686.
19 M. Nouaman, Z. Zak, E. Herrmann and O. Navratil, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1147.
20 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Polyhedron*, 1998, **17**, 4465.
21 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 3659.
22 KM-4 Software, v 6.0, Kuma Diffraction, Wrocław, Poland, 1992.
23 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
24 G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
25 C. K. Johnson and M. N. Burnett, ORTEP3, Report ORNL-6895, Oak Ridge National Laboratory, TN 1996.
26 P. Brigl and H. Müller, *Ber. Dtsch. Chem. Ges.*, 1939, **72**, 2121.
27 W. Autenrieth and O. Hildebrand, *Ber. Dtsch. Chem. Ges.*, 1898, **31**, 1094.