

Investigación

New Palladium(II) Tetraorganodichalcogenoimido Diphosphinates. Crystal and Molecular Structure of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ and $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$

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Dedicated to the memory of Dr. Jacobo Gómez-Lara, a remarkable man, scientist and friend

Abstract. Bis(tetraorganodichalcogenoimidodiphosphinato)palladium(II), $\text{Pd}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_2$, were prepared and investigated by means of IR and multinuclear (^1H , ^{13}C , ^{31}P) NMR spectroscopy. The crystal and molecular structures of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ (**1**) and $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ (**2**) were determined by X-ray diffractometry. The crystals of both compounds contain discrete mononuclear molecules. The ligands act as monometallic biconnective units through both chalcogen atoms which results in a spiro-bicyclic system with distorted square planar PdS_4 and PdSe_2O_2 core, respectively.

Key Words. Bis(tetraorganodichalcogenoimidodiphosphinato)palladium(II), X-ray diffractometry, monometallic biconnective units, spiro-bicyclic system

Resumen. Bis(tetraorganodichalcogenoimidodifosfinato) de paladio (II), $\text{Pd}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_2$ fueron preparados e investigados por espectroscopía de infrarrojo y resonancia magnética multinuclear (^1H , ^{13}C , ^{31}P). Las estructuras moleculares y cristalinas de $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ (**1**) y $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ (**2**) fueron determinadas por difracción de rayos X. Los cristales de ambos compuestos contienen moléculas mononucleares discretas. Los ligandos actúan como unidades biconectivas monometálicas a través de ambos átomos chalcogénicos resultando un sistema espiro bicíclico con un núcleo planar cuadrado distorsionado, PdS_4 y PdSe_2O_2 , respectivamente.

Palabras clave: Bis(tetraorganodichalcogenoimidodifosfinato) de paladio (II), difracción de rayos X, unidades biconectivas monometálicas, sistema espiro bicíclico.

Introduction

The synthesis of several Pd(II) complexes of tetraorganodichalcogenoimidodiphosphinato ligands has been described in the literature [1-14] and the molecular structure of either neutral or anionic compounds has been established by X-ray diffractometry. Most of the known bis(tetraorganodichalcogenoimidodiphosphinato)palladium(II) complexes contain symmetric organophosphorus moieties, $\text{Pd}[(\text{XPR}_2)_2\text{N}]_2$ [1-5,13]. Few complexes of asymmetric ligands, *i.e.* different chalcogen atoms and/or organic groups attached to phosphorus atoms, $\text{Pd}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_2$, have been described so far: $\text{Pd}[(\text{SPPh}_2)(\text{SP}(\text{OEt})_2)\text{N}]_2$ [6], $\text{Pd}[(\text{OPPh}_2)(\text{YPPH}_2)\text{N}]_2$, $\text{Pd}[(\text{OPPh}_2)(\text{YPPH}_2)\text{N}]_2(\text{en})$ ($\text{Y} = \text{S}, \text{Se}$) [9,10], $\text{Pd}[(\text{OPPh}_2)(\text{SP}(\text{OEt})_2)\text{N}]_2$, $\text{Pd}[(\text{SPPH}_2)(\text{OP}(\text{OEt})_2)\text{N}]_2$ [11], $\text{Pd}[(\text{OP}(\text{OEt})_2)(\text{SP}(\text{OEt})_2)\text{N}]_2$ [14]. Regardless of the nature of the organophosphorus ligands, with one exception, both chalcogen atoms are involved in coordination to the metal center (**a**), and this results in a square planar coordination geometry for the bis (tetraorganodichalcogenoimido-diphosphinato)palladium(II) complexes.

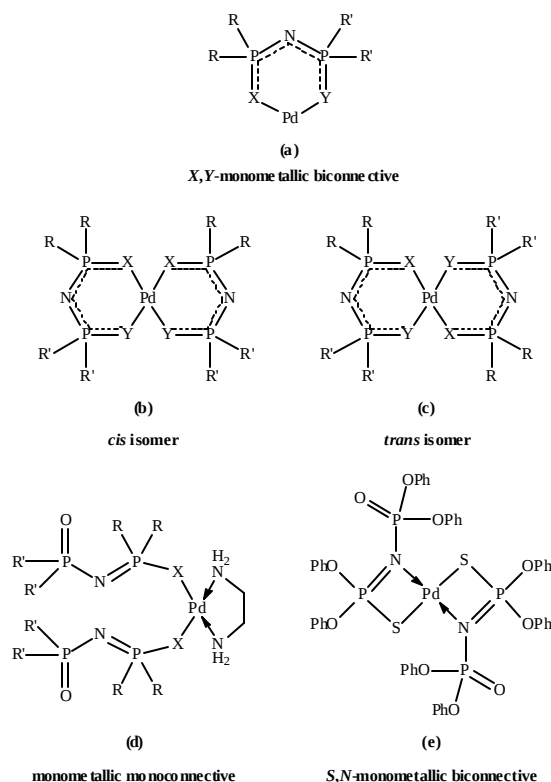
When asymmetric ligands have been used, NMR spectroscopic evidence has suggested in some cases that both *cis* (**b**) and *trans* (**c**) isomers are present in solution [6,11]. For

$\text{Pd}[(\text{SPPH}_2)(\text{SP}(\text{OEt})_2)\text{N}]_2$, the *trans*-isomer (with respect to the organic groups attached to phosphorus atoms) was isolated in the solid state [6], while only the *cis* isomers have been isolated and characterized by single crystal X-ray diffractometry for $\text{Pd}[(\text{OPR}_2)(\text{YPR}'_2)\text{N}]_2$ ($\text{Y} = \text{S}, \text{Se}$). Only for the $\text{Pd}[(\text{OP}(\text{OEt})_2)(\text{SP}(\text{OEt})_2)\text{N}]_2$ complex was a different molecular structure found; in this case the organophosphorus ligands exhibit a S,N-monometallic biconnective coordination pattern, resulting in a *trans*- NiS_2N_2 square planar core (**e**) [14]. When ethylenediamine was used as a chelating agent the $[(\text{OPPh}_2)(\text{YPPH}_2)\text{N}]^-$ ($\text{Y} = \text{S}, \text{Se}$) ligands were found to exhibit a monometallic monoconnective coordination pattern only through the "soft" chalcogen atom (**d**) [9,10].

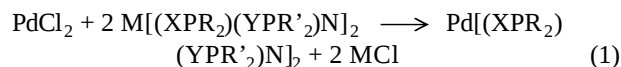
We report here on the synthesis and spectroscopic characterization of new $\text{Pd}[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]_2$ complexes, and the crystal and molecular structures of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ and $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$.

Results and Discussion

The title compounds were prepared as red-orange to red-brown crystalline solids, by reacting palladium dichloride,



PdCl_2 , with the appropriate sodium or potassium salts of the tetraorgano-dichalcogenoimidodiphosphinic acids in acetone, according to equation (1):



$\text{M} = \text{Na}, \text{K}; \quad \text{R}, \text{R}' = \text{Me}, \text{Ph}, \text{OEt}, \quad \text{X}, \text{Y} = \text{O}, \text{S}$

Details concerning the preparation, including yields and melting points, are given in the Experimental Section. All compounds were recrystallized by slow diffusion of *n*-hexane into an acetone solution of the Pd(II) complex.

The new Pd(II) complexes were investigated by IR, and multinuclear (^1H , ^{13}C , ^{31}P) NMR spectroscopy, and the crystal and molecular structures of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ and $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ were determined by X-ray diffractometry.

The strong IR absorptions observed for the Pd(II) complexes in the regions 1250–1150, 1070–1050 and 560–510 cm^{-1} were assigned to $\nu_{\text{as}}(\text{P}_2\text{N})$, $\nu(\text{PO})$, and $\nu(\text{PS})$ stretching vibrations, respectively, by comparison with the spectra of the free acids and their alkali metal salts. This behavior is consistent with the coordination of the ligands in the deprotonated form through both chalcogens to the metal atom.

^1H and ^{13}C NMR spectra show characteristic signals for the organic groups attached to phosphorus, with the expected pattern due to phosphorus-proton/carbon couplings. Thus, for example, the ^1H NMR spectrum of $\text{Pd}[(\text{OPPh}_2)(\text{OP}(\text{OEt})_2)\text{N}]_2$ exhibits two resonances with the expected splitting pattern for

$\text{P-OCH}_2\text{CH}_3$ (triplet) and $\text{P-OCH}_2\text{CH}_3$ (doublet of quartets) in the aliphatic region, and two resonances ($\text{P-C}_6\text{H}_5$ -*ortho* - doublet of doublets, and $\text{P-C}_6\text{H}_5$ -*meta+para* - multiplet) in the aromatic region, respectively. This indicates the equivalence of the organic groups attached to the same phosphorus atom on the NMR time-scale.

The ^{31}P NMR spectra of compounds **1**–**3** are of the typical AX type, thus indicating the presence of only one isomer in solution for complexes **2** and **3**. By contrast, for $\text{Pd}[(\text{SPMe}_2)(\text{SPPH}_2)\text{N}]_2$ (**4**) two AX spectra with very similar chemical shifts were observed. This behavior is most likely due to the presence of both *cis* and *trans* isomers in solution. All four resonances exhibit a doublet pattern due to the phosphorus-phosphorus coupling. Similar behavior was previously described for the $\text{Pd}[(\text{SPPH}_2)(\text{SP}(\text{OEt})_2)\text{N}]_2$ complex [6]. The ^{31}P NMR spectra are consistent with a coordination pattern of the tetraorgano-dichalcogenoimidodiphosphinato ligands through both chalcogens to the metal atom.

Crystal and molecular structure of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ (**1**) and $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ (**2**)

The solid state structures of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ (**1**) and $\text{cis-Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ (**2**) were determined by single-crystal X-ray diffraction. For both compounds the crystal contains discrete monomeric molecules separated by normal van der Waals distances. The ORTEP plots of the molecular structures of **1** and **2** are displayed in Fig. 1 and 2. Important bond lengths and angles are listed in Table 1.

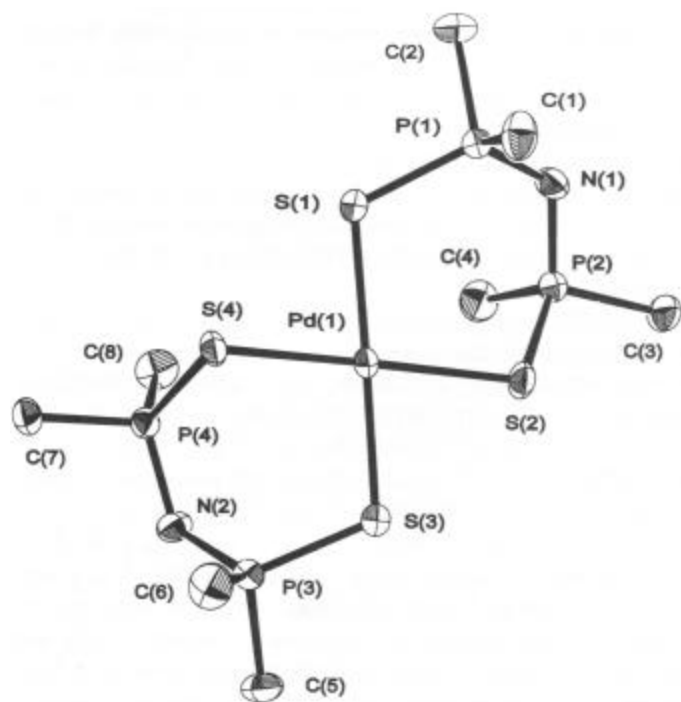


Fig. 1. ORTEP plot of the molecule $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ (**1**) (the atoms are drawn with 30% probability ellipsoids and hydrogen atoms are omitted for clarity).

Table 1. Important bond lengths (Å) and angles (°) for Pd[(SPMe₂)₂N]₂ (**1**) and Pd[(OPPh₂)(SPMe₂)N]₂ (**2**)

Pd[(SPMe ₂) ₂ N] ₂ (1)				Pd[(OPPh ₂)(SPMe ₂)N] ₂ (2)	
Pd(1)-S(1)	2.3483(8)	Pd(1)-S(3)	2.3321(9)	Pd(1)-S(1)	2.292(1)
Pd(1)-S(2)	2.3401(8)	Pd(1)-S(4)	2.3526(7)	Pd(1)-O(1)	2.071(3)
P(1)-S(1)	2.034(1)	P(3)-S(3)	2.036(1)	P(1)-O(1)	1.512(3)
P(1)-N(1)	1.600(3)	P(3)-N(2)	1.591(3)	P(1)-N(1)	1.593(4)
P(2)-N(1)	1.592(3)	P(4)-N(2)	1.600(3)	P(2)-N(1)	1.580(4)
P(2)-S(2)	2.028(1)	P(4)-S(4)	2.035(1)	P(2)-S(1)	2.042(2)
S(1)1/4S(2)a	3.581(1)	S(3)1/4S(4)a	3.537(1)	O(1)1/4S(1)	3.160(3)
S(1)1/4S(4)a	3.103(1)	S(2)1/4S(3)a	3.016(1)	O(1)1/4O(1)'	2.845(6)
				S(1)1/4S(1)'	3.186(3)
S(1)-Pd(1)-S(2)	99.61(3)	S(3)-Pd(1)-S(4)	98.07(3)	O(1)-Pd(1)-S(1)	92.66(9)
S(1)-Pd(1)-S(4)	82.62(3)	S(2)-Pd(1)-S(3)	80.42(3)	O(1)-Pd(1)-O(1)'	86.8(2)
				S(1)-Pd(1)-S(1)'	88.03(8)
S(1)-Pd(1)-S(3)	174.29(3)	S(2)-Pd(1)-S(4)	172.75(3)	O(1)-Pd(1)-S(1)'	177.12(8)
Pd(1)-S(1)-P(1)	112.20(4)	Pd(1)-S(3)-P(3)	110.02(4)	Pd(1)-O(1)-P(1)	120.3(2)
Pd(1)-S(2)-P(2)	104.82(4)	Pd(1)-S(4)-P(4)	103.33(4)	Pd(1)-S(1)-P(2)	101.15(7)
S(1)-P(1)-N(1)	117.3(1)	S(3)-P(3)-N(2)	116.3(1)	O(1)-P(1)-N(1)	117.7(2)
P(1)-N(1)-P(2)	122.9(2)	P(3)-N(2)-P(4)	124.8(2)	P(1)-N(1)-P(2)	130.1(2)
S(2)-P(2)-N(1)	116.5(1)	S(4)-P(4)-N(2)	115.9(1)	S(1)-P(2)-N(1)	117.7(2)

^a Non-bonding distances. ^b Symmetry equivalent position (1 - x, y, 1/2 - z) given by a prime.

The molecular structure of **1** and **2** complexes contains monometallic biconnective tetraorganodichalcogenoimidodiphosphinato ligands, coordinated to the metal center through both chalcogen atoms. The result is a spiro-bicyclic system with a square-planar PdS₂X₂ core slightly distorted to tetrahedral [dihedral angle Pd(1)S(1)S(2) / Pd(1)S(3)S(4) 8.4° in **1**, and Pd(1)O(1)S(1) / Pd(1)O(1a)S(1a) 3.9° in **2**, respectively], and a *cis* arrangement of the donor atoms around the palladium center in the monothioimidodiphosphinato complex **2**, as observed for other Pd[(OPR₂)(YPR'₂)N]₂ (Y = S, Se) derivatives [10,11].

The Pd-S [range 2.332(1)-2.353(1) Å in **1**, and 2.292(1) Å in **2**] bond distances are very close to those found in the related palladium(II) derivatives, *e.g.* Pd[(SPPh₂){SP(OEt)₂}N]₂ (av. 2.335 Å) [6], Pd[{SP(OPh)₂}₂N]₂ (av. 2.345 Å) [13], or Pd[{OP(OPh)₂}{SP(OPh)₂}N]₂ (av. 2.342 Å) [14], while the Pd-O [2.071(3) Å] bond distances in **2** are similar to those found in Pd[(OPPh₂)(SePPh₂)N]₂ (av. 2.080 Å) [10].

The P-S [range 2.028(1)-2.036(1) Å in **1**, and 2.042(2) Å in **2**] and the P-N bonds [range 1.591(3)-1.600(3) Å in **1**, and 1.580(4)-1.593(4) Å in **2**] are equal, within the experimental errors, and their lengths are intermediate between single and double phosphorus-sulphur and phosphorus-nitrogen bonds, *cf.* the free acids (S=PMe₂)₂NH [15]: P=S 1.939(2), 1.962(2), P-N 1.679(3), 1.675(3) Å; (O=PPh₂)(S=PMe₂)NH [16]: P=S 1.944(3), (S)P-N 1.681(7), (O)P-N 1.662(7), P=O 1.480(5) Å; Ph₂P(S)SH [17]: P=S 1.954(1), P-S 2.077(1) Å; and

[(Me₃Si)₂N-P(=NBu^t)S]₂ [18]: P=N 1.529(2), P-N 1.662(2) Å. The P-O [1.512(3) Å in **2**] bond distances have also intermediate values between single and double phosphorus-oxygen bonds (*cf.* Ph₂P(=O)OH [19]: P-O 1.526(6), P=O 1.486(6) Å), and are comparable with those observed in *cis*-Pd[(OPPh₂)(SePPh₂)N-O,Se]₂ (av. P-O 1.521 Å) [10]. In the *trans*-Pd[{OP(OPh)₂}{SP(OPh)₂}N]₂ complex, containing *S,N*-coordinated ligands, the corresponding P=O bond distance is significantly shorter [1.450(3) Å] [14].

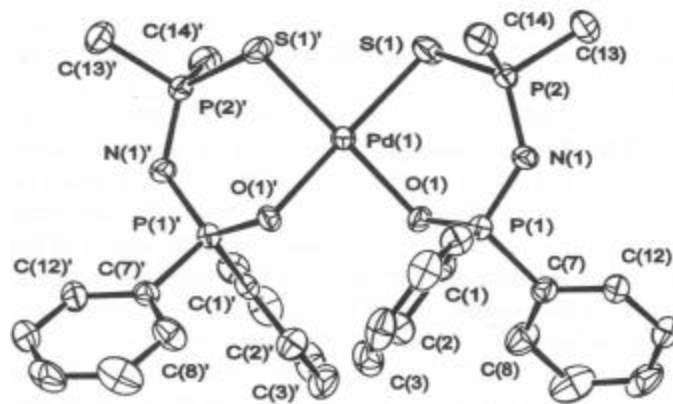


Fig. 2. ORTEP plot of the molecule Pd[(OPPh₂)(SPMe₂)N]₂ (**2**) (the atoms are drawn with 30% probability ellipsoids and hydrogen atoms are omitted for clarity).

Table 2. Torsion angles (°) for Pd[(SPMe₂)₂N]₂ (**1**) and Pd[(OPPh₂)(SPMe₂)N]₂ (**2**).

Pd[(SPMe ₂) ₂ N] ₂ (1)				Pd[(OPPh ₂)(SPMe ₂)N] ₂ (2)	
Pd(1)S(1)P(1)N(1)	51.1	Pd(1)S(3)P(3)N(2)	39.7	N(1)P(1)O(1)Pd(1)	−48.3
S(1)P(1)N(1)P(2)	−26.7	S(3)P(3)N(2)P(4)	−58.4	O(1)P(1)N(1)P(2)	17.8
S(2)P(2)N(1)P(1)	−39.8	S(4)P(4)N(2)P(3)	2.6	S(1)P(2)N(1)P(1)	−19.8
Pd(1)S(2)P(2)N(1)	71.3	Pd(1)S(4)P(4)N(2)	58.0	Ni(1)S(1)P(2)N(1)	42.0
S(1)Pd(1)S(2)P(2)	−34.4	S(3)Pd(1)S(4)P(4)	−56.6	O(1)Ni(1)S(1)P(2)	−53.8
S(2)Pd(1)S(1)P(1)	−12.6	S(4)Pd(1)S(3)P(3)	6.2	S(1)Ni(1)O(1)P(1)	66.7
twisted-boat		twisted-boat		twisted-chair	

The six-membered PdSXP₂N rings in both Pd(II) complexes are not planar and their conformation, as reflected by the torsion angles (Table 2), is consistent with a high flexibility of the SPNPX systems. Thus, for **1** the two chelate rings display twisted boat conformations, with P(1)/S(2) and P(3)/S(4) atoms, respectively, in the apices, and are bent on the same side of the PdS₄ core of the spiro-bicyclic NP₂S₂PdS₂P₂N system [deviations from the best PdS₄ plane: N(1) 0.414, N(2) 1.679 Å]. By contrast, in **2** the chelate rings display twisted chair conformations, with Pd(1)/N atoms in the apices, and they are oriented on opposite sides of the PdS₂O₂ core of the *cis* spiro-bicyclic NP₂SOPdOSP₂N system [deviations from the best PdS₄ plane: N(1) −1.779, N(1a) 1.779 Å].

Experimental

Sodium or potassium tetraorganodichalcogenoimidodiphosphinates were prepared according to published methods: K[(SPMe₂)₂N] [15], K[(OPPh₂)(SPMe₂)N] [16], K[(OPPh₂){OP(OEt)₂}N] [20], K[(SPMe₂)(SPPH₂)N] [21]. Palladium dichloride, PdCl₂, was commercially available. The infrared

spectra were recorded using KBr pellets on a Specord 75 IR C. Zeiss-Jena (DDR) instrument, in the range 4000–400 cm^{−1}. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian Gemini 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively. The chemical shifts are reported in ppm relative to TMS and H₃PO₄ 85%, respectively.

Preparation of the title compounds, Pd[(XPR₂)(YPR'₂)N]₂, (Table 3)

A reaction mixture containing stoichiometric amounts of PdCl₂ and the corresponding sodium or potassium tetraorganodichalcogenoimidodiphosphinate, M[(XPR₂)(YPR'₂)N], in 40 mL acetone was stirred at room temperature for 24 h. The insoluble solid was filtered off and from the clear dark-red solution the solvent was removed to dryness in a rotary evaporator. The remaining solid product was recrystallized from organic solvents.

Pd[(SPMe₂)₂N]₂ (1**):** ¹H NMR (CDCl₃, 300 MHz) 1.92 (m, ²J_{PH} + ⁴J_{PH} 12.2 Hz); ¹³C NMR (CDCl₃, 75 MHz) 25.8 (m, ¹J_{PC} + ³J_{PC} 77.3 Hz); ³¹P NMR (CDCl₃, 121.4 MHz) 41.1 (s). **Pd[(OPPh₂)(SPMe₂)N]₂ (**2**):** ¹H NMR (CDCl₃, 300 MHz) 1.55 (d, 3H, ²J_{PH} 14.1 Hz, CH₃), 7.50 (m, 3H, C₆H₅ - *meta* +

Table 3. Preparation of Pd[(XPR₂)(YPR'₂)N]₂ derivatives.

Starting materials		Product [yield: g (%)]	M.p. (°C)	Colour	IR data (cm ^{−1})
PdCl ₂ [g (mmol)]	M[(XPR ₂)(YPR' ₂)N] [g (mmol)]				
0.177 (1.0)	K[(SPMe ₂) ₂ N] 0.478 (2.0)	Pd[(SPMe ₂) ₂ N] ₂ 0.25 (50)	170	red	ν _{as} (P ₂ N) 1180s ν(PS) 530m
0.177 (1.0)	K[(OPPh ₂)(SPMe ₂)N] 0.666 (2.0)	Pd[(OPPh ₂)(SPMe ₂)N] ₂ 0.52 (75)	138– 140	red- Orange	ν _{as} (P ₂ N) 1200s ν(PO) 1050s ν(PS) 540s
0.177 (1.0)	K[(OPPh ₂){OP(OEt) ₂ }N] 0.783 (2.0)	Pd[(OPPh ₂){OP(OEt) ₂ }N] ₂ 0.71 (88)	87–89	red- orange	ν _{as} (P ₂ N) 1250s ν(PO) 1050s
0.177 (1.0)	K[(SPMe ₂)(SPPH ₂)N] 0.698 (2.0)	Pd[(SPMe ₂)(SPPH ₂)N] ₂ 0.61 (84)	257– 258	red- orange	ν _{as} (P ₂ N) 1150s ν(PhPS) 560s ν(MePS) 510s

para), 7.83 (dd, 2H, $^3J_{\text{PH}}$ 12.9, $^3J_{\text{HH}}$ 7.8 Hz, C_6H_5 - *orto*); ^{13}C NMR (CDCl_3 , 75.4 MHz) 25.38dd (dd, $^1J_{\text{PC}}$ 67.8, $^3J_{\text{PC}}$ 6.0 Hz, CH_3), 128.76 (d, $^3J_{\text{PC}}$ 12.2 Hz, C_m), 131.46 (s, C_p), 132.04 (d, $^2J_{\text{PC}}$ 9.5 Hz, C_o) (*ipso*-carbons not observed); ^{31}P NMR (CDCl_3 , 121.4 MHz) 22.6 (d, $^2J_{\text{PP}}$ 8.5 Hz, Ph_2PO), 38.1 (d, $^2J_{\text{PP}}$ 8.5 Hz, Me_2PS).

Pd[(OPPh₂){OP(OEt)₂}N]₂ (3): ^1H NMR ($\text{Me}_2\text{CO}-d_6$, 300 MHz) 1.06 (t, 3H, $^3J_{\text{HH}}$ 7.1 Hz, $\text{P}-\text{OCH}_2\text{CH}_3$), 3.88 (dq, 2H, $^3J_{\text{PH}}$ 6.9, $^3J_{\text{HH}}$ 6.9 Hz, $\text{P}-\text{OCH}_2\text{CH}_3$), 7.29 (m, 3H, $\text{P}-\text{C}_6\text{H}_5$ -*meta+para*), 7.96 (dd, 2H, $^3J_{\text{HH}}$ 7.9, $^3J_{\text{PH}}$ 11.8 Hz, $\text{P}-\text{C}_6\text{H}_5$ -*orto*); ^{13}C NMR ($\text{Me}_2\text{CO}-d_6$, 75.4 MHz) 16.54 (d, $^3J_{\text{PC}}$ 8.0 Hz, $\text{P}-\text{OCH}_2\text{CH}_3$), 61.61 (d, $^2J_{\text{PC}}$ 4.8 Hz, $\text{P}-\text{OCH}_2\text{CH}_3$), 128.31 (d, $^3J_{\text{PC}}$ 12.7 Hz, C_{meta}), 130.26 (s, C_{para}), 132.15 (d, $^2J_{\text{PC}}$ 9.8 Hz, C_{orto}), 141.19 (dd, $^1J_{\text{PC}}$ 131.7, $^3J_{\text{PC}}$ 4.3 Hz, C_{ipso}); ^{31}P NMR ($\text{Me}_2\text{CO}-d_6$, 121.4 MHz) 3.0 (d, $^2J_{\text{PP}}$ 20.9 Hz, EtOPO), 13.3 (s, Ph_2PO).

Pd[(SPMe₂)(SPPH₂)N]₂ (4): ^{31}P NMR (CDCl_3 , 121.4 MHz) 37.15 (d, $^2J_{\text{PP}}$ 4.5 Hz, Ph_2PS), 37.76 (d, $^2J_{\text{PP}}$ 4.5 Hz, Ph_2PS), 43.64 (d, $^2J_{\text{PP}}$ 4.5 Hz, Me_2PS), 43.70 (d, $^2J_{\text{PP}}$ 4.5 Hz, Me_2PS) (see text).

Crystal structure determinations. A red block crystal of $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$, **1**, and an orange block crystal of $\text{Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$, **2** were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Siemens SMART/CCD system at McMaster University with graphite-monochromated Mo-K α radiation, operating at 50 kV and 35 mA. Cell constants corresponded to monoclinic cells whose dimensions are given in Table 4 along with other experimental parameters. Semiempirical absorption corrections were applied which resulted in transmission factors ranging from 0.831 to 0.696 for **1**, and 0.883 to 0.713 for **2**. The structures were solved by direct methods [22]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with C-H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinements [23] were based on 3484 (for **1**) and 2015 (for **2**) observed reflections [$I > 3.00\sigma(I)$] and 172 (for **1**) and 177 (for **2**) variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.0247$ (for **1**) and 0.0390 (for **2**) and $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.0277$ (for **1**) and 0.0352 (for **2**). The standard deviations of an observation of unit weight [24] was 1.31 (for **1**) and 1.37 (for **2**). Plots of $[\sum w(|F_o| - |F_c|)^2]$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.42 and -0.68 e/Å³, respectively (for **1**) and 0.52 and -0.84 (for **2**). Neutral-atom scattering factors were taken from Cromer and Waber [25]. Anomalous dispersion effects were included in F_c [26]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [27]. All calculations were performed using the TEXAN TEXSAN [28] crystallographic package of Molecular Structure Corp. Selected distances and bond angles are given in Table 1 and the molecule is displayed in the ORTEP diagram in

Table 4. Crystallographic data for $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ (**1**) and $\text{Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ (**2**).

Molecular formula	$\text{C}_6\text{H}_{24}\text{N}_2\text{P}_4\text{S}_4\text{Pd}$	$\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_2\text{P}_4\text{S}_2\text{Pd}$
M	506.83	722.99
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
Radiation	Mo-K α	Mo-K α
$a/\text{\AA}$	11.209(4)	22.983(1)
$b/\text{\AA}$	8.557(4)	9.0216(5)
$c/\text{\AA}$	21.214(9)	16.4651(7)
β°	97.82(1)	111.693(2)
$V(\text{\AA}^3)$	2016(1)	3172.2(2)
Z	4	4
D_c / gcm^{-3}	1.67	1.51
F_{000}	1024.00	1472.00
$\mu(\text{Mo-K}\alpha) / \text{mm}^{-1}$	1.64	9.47
$2\theta \text{ max} / ^\circ$	55	55
Reflections measured	13881	11615
Reflections observed [$I_o \geq 3\sigma(I_o)$], N_o	3484	2015
No. of parameters refined, N_p	172	177
Largest shift / e.s.d. in final cycle	0.001	0.001
Largest electron-density peak / e Å ⁻³	0.42	0.52
R^a	0.0247	0.0390
R'^b	0.0277	0.0352
Goodness of fit, ^c S	1.31	1.37

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.

^c $S = [\sum |F_o| - |F_c|] / \sigma / (N_o - N_p)$.

Figures 1 and 2. Additional material available from the Cambridge Crystallographic Data Centre comprises the final atomic coordinates for all atoms, thermal parameters, and a complete listing of bond distances and angles.

Supplementary material. The complete listing of the crystal data is provided in the Supporting Information which contains tables giving final fractional coordinates and $B(\text{eq})$ for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates and $B(\text{eq})$ for hydrogen atoms, all bond lengths and angles and ORTEP drawings for $\text{Pd}[(\text{SPMe}_2)_2\text{N}]_2$ and $\text{Pd}[(\text{OPPh}_2)(\text{SPMe}_2)\text{N}]_2$ (12 pages). Structure-factor tables are available from the authors (J.E.D.).

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