The solution was then exposed to air and the resulting brown precipitate filtered off. On leaving the green mother liquor at ambient temperature for 3 d brown crystals (*ca* 5%) were obtained. Structure solution, refinement and other calculations: *SHELXTL-Plus* (Sheldrick, 1990). Other programs used: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71190 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1044]

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2-[2,2-Bis(diphenylphosphanyl)ethylsulfanyl]phenylamine (NSPP), a New Hetero-Bifunctional Ligand and its $PdCl_2$ Complex †

Ulrich Flörke and Hans-Jürgen Haupt

Anorganische und Analytische Chemie,
Universität-GH Paderborn, Warburgerstrasse 100,
D-33098 Paderborn, Germany

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Abstract

The new ligand NSPP consists of a bis(diphenylphosphanyl)ethane part with coordination ability by the two P donor atoms, and of a second part, the 2-aminobenzenethio unit, which offers the two donor atoms N and S for coordination with metal atoms. Both P atoms are attached to the same C atom of the central ethane skeleton. The other C atom is linked to the S atom of the thio group. $PdCl_2$ is coordinated *via* the two P donors to give the complex [Pd(NSPP)Cl_2].

Comment

The syntheses of hetero-bifunctional ligands for the coordination of different metals led to the new ligand NSPP with four donor atoms. The ligand was prepared by reaction of 2-aminobenzenethiol and 1,1-bis(diphenylphosphanyl)ethene. Further reaction of the isolated ligand with [M(bn)$_2$Cl$_2$] (M = Pd, Pt; bn = benzonitrile) gave the monometal complexes [M(NSPP)Cl_2]. The detailed synthetic work has been reported elsewhere (Haupt, Kleineberg & Flörke, 1992).

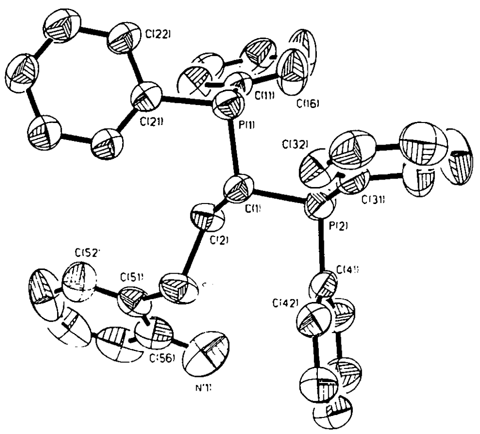

Fig. 1. Molecular structure of the ligand NSPP.

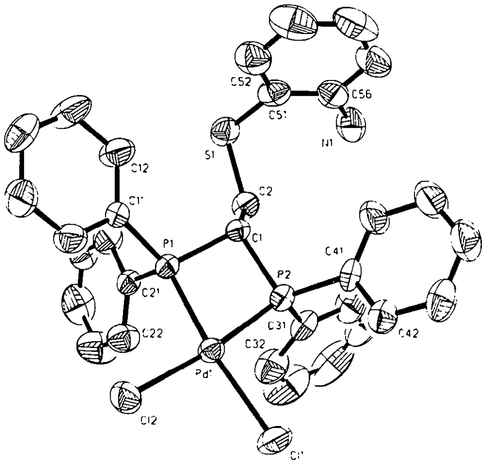

Fig. 2. Molecular structure of the complex [Pd(NSPP)Cl_2].

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† {2-[2,2-Bis(diphenylphosphino)ethylthio]phenylamine-P,P}dichloropalladium(II) dichloromethane solvate.

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The ligand has one bidentate chelate part with the donor atoms N and S and another part with the two P atoms for coordination with metals. The geometry of the free ligand shows no distinct deviations from expected parameters.

In the complex, the Pd atom is coordinated by two terminal Cl ligands and two P atoms from the NSPP ligand. These atoms form an approximately planar coordination with the Pd atom 0.040 Å away from the best plane. The metal atom is also part of a four-membered chelate ring, PdP_2C. This causes rather unfavourable steric interactions of the ligand atoms and leads to strong distortions from ideal geometries. The tetrahedral angle P—C—P reduces from 107.8 (2) in the free NSPP to 92.5 (2)°; the Pd—P—C angles are 95.2 (1) at P(1) and 96.7 (1)° at P(2). The Pd ring angle P—Pd—P is 73.9 (1)°; the opposite angle Cl—Pd—Cl of 92.7 (1)° is closer to the 90° required for square-planar coordination. The ring distortion is also reflected in the difference between the two short Pd—P bond lengths [2.217 (1) and 2.255 (1) Å], whereas the terminal Pd—Cl bonds are equal [2.359 (2) and 2.365 (2) Å, respectively]. The PdP_2C ring deviates from planarity with a dihedral angle PdP_2—P_2C of 13.7°, the Pd atom being 0.42 Å out of the P_2C plane. The other geometrical parameters of the NSPP ligand concerning the N-S part are not affected by complex formation.

Related bonding patterns are similar to those found in other diphenylphosphanylalkane chelate structures containing the PdP_2C ring (Davies, Pinkerton, Syed & Vilmer, 1988; Palenik, Mathew, Steffen & Beran, 1975; Steffen & Palenik, 1976; Wink, 1990). They display almost the same ring angles (P—Pd—P average 73.2, P—C—P average 93.5 and Pd—P—C average 94.8°).

Experimental

NSPP

Crystal data

$C_{32}H_{29}NP_2S$
$M_r = 521.6$
Triclinic
$P\bar{1}$
$a = 11.325\ (2)$ Å
$b = 12.964\ (3)$ Å
$c = 10.038\ (2)$ Å
$\alpha = 104.81\ (2)°$
$\beta = 96.64\ (1)°$
$\gamma = 87.23\ (2)°$
$V = 1414.9\ (5)$ Å^3
$Z = 2$

$D_x = 1.224$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 6$-$15°$
$\mu = 0.24$ mm^{-1}
$T = 293$ K
Prism
0.30 × 0.13 × 0.12 mm
Colourless

Data collection

Siemens $R3m/V$ diffractometer
ω-2θ scans
Absorption correction: none
4934 measured reflections
3708 independent reflections
2351 observed reflections $[F > 4\sigma(F)]$

$R_{\text{int}} = 0.023$
$\theta_{\text{max}} = 22.5°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 10$
4 standard reflections monitored every 400 reflections
intensity variation: none

Refinement

Refinement on F
Final $R = 0.052$
$wR = 0.049$
$S = 2.019$
2351 reflections
266 parameters
H-atom parameters not refined

Calculated weights $w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.53$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.24$ e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* NSPP

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.8244 (1)	0.9907 (1)	0.0115 (2)	0.066 (1)
P1	0.7872 (1)	0.6610 (1)	−0.2359 (2)	0.053 (1)
P2	0.6657 (1)	0.7418 (1)	0.0250 (2)	0.058 (1)
N1	0.6425 (5)	1.1686 (5)	0.0664 (6)	0.113 (5)
C1	0.7761 (4)	0.7762 (4)	−0.0802 (5)	0.048 (3)
C2	0.7421 (4)	0.8847 (4)	−0.1154 (5)	0.056 (4)
C11	0.6563 (3)	0.6814 (3)	−0.3534 (4)	0.051 (4)
C12	0.6563	0.7411	−0.4509	0.066 (4)
C13	0.5532	0.7499	−0.5383	0.074 (5)
C14	0.4502	0.6989	−0.5282	0.078 (5)
C15	0.4501	0.6392	−0.4306	0.116 (7)
C16	0.5532	0.6304	−0.3432	0.093 (5)
C21	0.9092 (3)	0.7005 (3)	−0.3176 (4)	0.049 (4)
C22	0.9276	0.6362	−0.4482	0.065 (4)
C23	1.0233	0.6549	−0.5143	0.074 (5)
C24	1.1004	0.7380	−0.4498	0.070 (4)
C25	1.0819	0.8023	−0.3192	0.065 (4)
C26	0.9863	0.7836	−0.2531	0.058 (4)
C31	0.7357 (4)	0.6296 (3)	0.0870 (4)	0.051 (4)
C32	0.8558	0.6001	0.0876	0.066 (4)
C33	0.8989	0.5158	0.1435	0.073 (5)
C34	0.8219	0.4610	0.1988	0.086 (5)
C35	0.7018	0.4905	0.1982	0.113 (6)
C36	0.6587	0.5748	0.1422	0.087 (5)
C41	0.6849 (4)	0.8498 (3)	0.1851 (3)	0.055 (4)
C42	0.7843	0.8571	0.2828	0.069 (5)
C43	0.7911	0.9395	0.4038	0.084 (5)
C44	0.6984	1.0146	0.4271	0.091 (6)
C45	0.5990	1.0074	0.3294	0.094 (6)
C46	0.5923	0.9250	0.2084	0.075 (5)
C51	0.8043 (4)	1.0985 (3)	−0.0670 (4)	0.057 (4)
C52	0.8821	1.1090	−0.1606	0.080 (5)
C53	0.8721	1.1973	−0.2169	0.118 (7)
C54	0.7842	1.2751	−0.1796	0.108 (7)
C55	0.7063	1.2647	−0.0860	0.095 (6)
C56	0.7164	1.1764	−0.0297	0.070 (5)

Table 2. *Geometric parameters* (Å, °) *for* NSPP

S1—C2	1.826 (5)	P2—C1	1.865 (5)
S1—C51	1.766 (5)	C1—C2	1.556 (7)
P1—C1	1.876 (5)		
C2—S1—C51	102.4 (2)	P2—C1—C2	110.6 (3)
P1—C1—P2	107.8 (2)	S1—C2—C1	108.9 (3)
P1—C1—C2	114.2 (3)		

[Pd(NSPP)Cl$_2$]

Crystal data

[Pd(C$_{32}$H$_{29}$NP$_2$S)Cl$_2$].-
0.5CH$_2$Cl$_2$
M_r = 741.4
Monoclinic
$P2_1/n$
a = 18.299 (4) Å
b = 10.832 (3) Å
c = 18.452 (3) Å
β = 117.02 (1)°
V = 3258.2 (11) Å^3
Z = 4

D_x = 1.511 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 5–15°
μ = 0.99 mm^{-1}
T = 293 K
Plate
0.51 × 0.45 × 0.08 mm
Yellow

Data collection

Siemens *R*3*m*/*V* diffractometer
ω-2θ scans
Absorption correction: empirical *via* ψ-scans
$T_{\min}$ = 0.697, $T_{\max}$ = 0.930
7717 measured reflections
7152 independent reflections
4692 observed reflections [$F > 4\sigma(F)$]

R_{int} = 0.02
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 14$
$l = -24 \rightarrow 24$
4 standard reflections monitored every 400 reflections
intensity variation: none

Refinement

Refinement on F
Final R = 0.043
wR = 0.048
S = 1.838
4692 reflections
299 parameters
H-atom parameters not refined

Calculated weights $w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.76 e Å^{-3}
$\Delta\rho_{\min}$ = −0.88 e Å^{-3}

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* [Pd(NSPP)Cl$_2$]

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd1	0.3071 (1)	0.0284 (1)	0.0775 (1)	0.035 (1)
Cl1	0.1750 (1)	0.1075 (1)	0.0416 (1)	0.059 (1)
Cl2	0.2551 (1)	−0.1347 (1)	−0.0177 (1)	0.052 (1)
P1	0.4400 (1)	−0.0273 (1)	0.1467 (1)	0.034 (1)
P2	0.3700 (1)	0.1829 (1)	0.1617 (1)	0.036 (1)
S1	0.6440 (1)	0.1392 (1)	0.3134 (1)	0.052 (1)
N1	0.6210 (3)	0.4091 (4)	0.3457 (3)	0.071 (1)
C1	0.4763 (3)	0.1266 (4)	0.1951 (3)	0.035 (1)
C2	0.5348 (3)	0.1428 (4)	0.2859 (3)	0.042 (1)
C11	0.5010 (2)	−0.0819 (2)	0.0995 (2)	0.036 (1)
C12	0.5848	−0.0566	0.1335	0.063 (1)
C13	0.6334	−0.1156	0.1037	0.071 (1)
C14	0.5983	−0.1999	0.0399	0.061 (1)
C15	0.5145	−0.2253	0.0059	0.063 (1)
C16	0.4658	−0.1663	0.0357	0.052 (1)
C21	0.4578 (2)	−0.1376 (2)	0.2269 (2)	0.038 (1)
C22	0.3914	−0.1874	0.2348	0.056 (1)
C23	0.4049	−0.2703	0.2975	0.079 (1)
C24	0.4848	−0.3034	0.3523	0.080 (1)
C25	0.5512	−0.2537	0.3445	0.071 (1)
C26	0.5377	−0.1707	0.2818	0.056 (1)
C31	0.3515 (2)	0.2001 (3)	0.2486 (2)	0.047 (1)
C32	0.3143	0.1034	0.2695	0.068 (1)
C33	0.3007	0.1135	0.3377	0.100 (1)
C34	0.3242	0.2203	0.3851	0.108 (1)
C35	0.3614	0.3170	0.3642	0.093 (1)
C36	0.3750	0.3069	0.2960	0.070 (1)
C41	0.3643 (2)	0.3343 (2)	0.1199 (2)	0.040 (1)
C42	0.2896	0.3776	0.0594	0.050 (1)
C43	0.2839	0.4971	0.0291	0.061 (1)
C44	0.3528	0.5734	0.0593	0.069 (1)
C45	0.4275	0.5302	0.1198	0.083 (1)
C46	0.4332	0.4106	0.1501	0.068 (1)
C51	0.6547 (2)	0.2710 (3)	0.2629 (2)	0.048 (1)
C52	0.6780	0.2541	0.2013	0.065 (1)
C53	0.6882	0.3560	0.1606	0.084 (1)
C54	0.6752	0.4748	0.1814	0.086 (1)
C55	0.6519	0.4918	0.2430	0.075 (1)
C56	0.6417	0.3899	0.2837	0.056 (1)
C3	0.0022 (12)	0.4609 (16)	0.0384 (13)	0.105 (8)
Cl3	0.0538 (2)	0.4176 (5)	−0.0122 (2)	0.191 (2)

Table 4. *Geometric parameters* (Å, °) *for* [Pd(NSPP)Cl$_2$]

Pd1—Cl1	2.359 (2)	P2—C1	1.857 (5)
Pd1—Cl2	2.365 (2)	S1—C2	1.825 (5)
Pd1—P1	2.255 (1)	S1—C51	1.765 (3)
Pd1—P2	2.217 (1)	C1—C2	1.535 (6)
P1—C1	1.865 (4)		
Cl1—Pd1—Cl2	92.7 (1)	Pd1—P2—C1	96.7 (1)
Cl1—Pd1—P1	163.8 (1)	C2—S1—C51	101.9 (2)
Cl2—Pd1—P1	100.8 (1)	P1—C1—P2	92.5 (2)
Cl1—Pd1—P2	93.5 (1)	P1—C1—C2	123.0 (3)
Cl2—Pd1—P2	171.9 (1)	P2—C1—C2	115.5 (4)
P1—Pd1—P2	73.9 (1)	S1—C2—C1	115.7 (4)
Pd1—P1—C1	95.2 (1)		

Scattering factors, structure solution, refinement, other calculations and graphics for both structures: *SHELXTL-Plus* (Sheldrick, 1990). Other programs used: *PARST* (Nardelli, 1983), *MISSYM* (Le Page, 1987). For both structures phenyl groups were treated as rigid bodies (C—C 1.395, C—H 0.96 Å) and H atoms were fixed at idealized positions with common isotropic displacement parameters U_{iso} = 0.08 Å^2. For [Pd(NSPP)Cl$_2$] the enclosed dichloromethane solvate molecule is disordered over two sites, with the common centre on a crystallographic inversion centre and an occupation factor for C3 of 0.5.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71221 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1019]

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