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Secondary Phosphine Chalcogenides
XI*. The Reaction of the Bis(2,4-pentanedionato) Complexes of the Nickel Triade with Secondary Phosphane Sulfides, $R_2P(S)H$ (R = Ph, Bu^t). Crystal Structure of $[Pd_2(\mu\text{-}SPBu^t{}_2)_2(\eta^2\text{-}SPBu^t{}_2)_2]$. A Comparison of the η^2- and the μ-Coordination Mode of the R_2PS^- Ligand

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Abstract

Treatment of $[M(acac)_2]$ (M = Ni, Pd, Pt) with the secondary phosphane sulfides $R_2P(S)H$ (R = Ph, Bu^t) affords the complexes $[M_2(\mu\text{-}SPR_2)_2(\eta^2\text{-}SPR_2)_2]$ whose structure markedly depends on the organic substituents at phosphorus. Thus, the phosphorus atoms around the metal atoms are mutually *cis* positioned for R = Ph and *trans* positioned for R = Bu^t, respectively. These metal(II) complexes (M = Pd; R = Ph) undergo redox reactions with the metal(0) complexes $[M'(PPh_3)_2L]$ (M' = Pd, Pt; L = $2PPh_3$, C_2H_4) to produce homo- and heterodinuclear metal(I) complexes $[PdM'(\mu\text{-}SPPh_2)_2(PPh_3)_2]$ (M' = Pd, Pt).

The structure of $[Pd_2(\mu\text{-}SPBu^t{}_2)_2(\eta^2\text{-}SPBu^t{}_2)_2]$ has been determined by single crystal X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.315(3)$, $b = 10.668(3)$, $c = 11.181(3)$ Å, $\alpha = 72.95(2)$, $\beta = 75.20(2)$, $\gamma = 71.97(2)°$, $Z = 1$, $D_{exp} = 1.38(1)$, $D_{calc} = 1.392$ g cm^{-3}. The structure was solved by heavy atom method and refined by full-matrix least-squares treatment to $R = 0.053$ ($R_w = 0.052$). The structure represents a centrosymmetric dinuclear complex with a six-membered $(Pd\text{–}P\text{–}S)_2$ core. The $Bu^t{}_2PS^-$ ligands are coordinated in the bridging as well as in the dihapto mode.

Introduction

Continuing our work with the coordination chemistry of secondary phosphane chalcogenides, we investigated the reaction of secondary phosphane sulfides with the bis(2,4-pentanedionato) complexes of nickel, palladium and platinum. In the previous paper [1] we reported on the reaction of diphenylphosphane oxide, $Ph_2P(O)H$, with $[\{M(acac)_2\}_n]$ (M = Ni, $n = 3$; M = Pd, Pt; $n = 1$). These reactions result in complexes with the hydrogen bridged uninegative chelate ligand $[(Ph_2PO)_2H]^-$, $[M(acac)\{(Ph_2PO)_2H\}]$ (M = Ni, Pd) and $[Pt\{(Ph_2PO)_2H\}_2]$, respectively.

Whereas a few complexes are described with the weakly hydrogen bridged O.S ligand $(Ph_2OH\cdots SPPh_2)^-$ [2, 3], diorganophosphane sulfides, when reacted with transition metal complexes, act as neutral S or P bonded ligands or form preferentially the corresponding anionic ligands R_2PS^- adopting the μ-, η^2- or η^1-coordination mode [4].

This paper shows the complete substitution of the $acac^-$ ligands for R_2PS^- in the course of the title reaction, forming dinuclear complexes containing the R_2PS^- ligands in both the bridging and dihapto mode. The results of an X-ray crystal structure analysis performed for one of these complexes enables us to compare the two coordination modes in one molecule.

Experimental

General Procedures and Materials

Reactions were carried out under an argon atmosphere using a conventional Schlenk technique. Melting points were obtained in sealed capillaries under argon and are uncorrected. The compounds analyzed satisfactorily (see 'Supplementary Material').

Starting materials were prepared according to literature procedures: $[\{Ni(acac)_2\}_3]$ [5], $[Pd(acac)_2]$ [6], $[Pt(acac)_2]$ [7], $[Ni(cod)_2]$ [8], $Ph_2P(S)H$ [9]. $Bu^t{}_2P(S)H$ was prepared as described in ref. 9 but was purified by sublimation *in vacuo* (0.05 kPa, 40 °C); melting point (m.p.) 75 °C; $^{31}P\{^1H\}$ NMR (C_6D_6): δ 74.3 s. ^1H and ^{31}P NMR spectra were recorded on the Bruker spectrometers WP 200 (^1H at 200.132 MHz, ^{31}P at 81.026 MHz) and AC 80 (^1H at

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80.13 MHz, ^{31}P at 32.438 MHz). Chemical shift references are the absolute frequencies of Me_4Si (^1H) and external 85% H_3PO_4 (^{31}P), respectively. Positive shifts are to lower field. Spectral simulations were made with the use of the PANIC NMR synthesis program provided by Bruker as part of the standard software. The relative signs could only be established by spectral simulation, with $^1J(PtP)$ taken as positive.

$[Ni_2(\mu\text{-}SPPh_2)_2(\eta^2\text{-}SPPh_2)_2]$ (1)

A benzene solution (50 ml) of 0.9 g (1.17 mmol) $[\{Ni(acac)_2\}_3]$ and 1.5 g (7 mmol) $Ph_2P(S)H$ was stirred for 20 h at room temperature. After filtration the black solution was concentrated *in vacuo* until *c.* 10 ml remained. The product was precipitated with methanol and purified twice by redissolution in benzene and addition of methanol, yield 1.0 g (43.3%), m.p. 174 °C dec.

1 was analogously obtained either from 0.8 g (2.91 mmol) $[Ni(cod)_2]$ and 1.3 g (5.8 mmol) $Ph_2P(S)H$ or from 0.5 ml (3.9 mmol) $[Ni(CO)_4]$ and 1.7 g (7.8 mmol) $Ph_2P(S)H$, yield 70 and 67%, respectively.

$[Pd_2(\mu\text{-}SPR_2)_2(\eta^2\text{-}SPR_2)_2]$ (R = Ph (2), Bu^t (3))

The benzene solution (60 ml) of 0.75 g (2.5 mmol) $[Pd(acac)_2]$ and 1.1 g (5 mmol) $Ph_2P(S)H$ and 0.9 g (5 mmol) $Bu^t{}_2P(S)H$ was stirred for 20 h at room temperature. The orange–red **2** precipitated during this procedure. Removing the solvent *in vacuo* afforded **3** as a red solid. An analytically pure sample was obtained by recrystallization from benzene. Yield: 0.8 g (60%) **2**, 0.8 g (70%) **3**; m.p. 275 °C dec. **2**, 215 °C dec. **3**. ^1H NMR (C_6D_6, **3**): δ 1.35, d, $^3J(PH)$ = 16.1 Hz, δ 169, d, $^3J(PH)$ = 13.7 Hz.

$[Pt_2(\mu\text{-}SPPh_2)_2(\eta^2\text{-}SPPh_2)_2]$ (4)

$[Pt(acac)_2]$ (0.5 g, 1.3 mmol) and $Ph_2P(S)H$ (0.7 g, 3.4 mmol) were dissolved in 50 ml toluene and the solution refluxed for 20 h followed by filtration and removal of solvent *in vacuo*. Addition of 15 ml CH_3OH caused the residue to crystallize. Recrystallization from acetone/methanol (1:4) afforded 0.54 g (84%) bright yellow **4**, m.p. 212 °C dec.

$[Pt_2(\mu\text{-}SPBu^t{}_2)_2(\eta^2\text{-}SPBu^t{}_2)_2]$ (5)

$[Pt(acac)_2]$ (1 g, 2.6 mmol) and $Bu^t{}_2P(S)H$ (0.9 g, 5 mmol) in 30 ml toluene were refluxed for 24 h. During this time the solution gradually became yellow. After removal of 15 ml toluene *in vacuo* **5** began to crystallize. Dropwise addition of 10 ml pentane completed the crystallization. **5** can be recrystallized from toluene. Yield: 0.9 g (66%), m.p. 260 °C dec. ^1H NMR ($CDCl_3$): δ 1.58–1.35 (multiplet, CH_3). No satisfactory analytical data could be obtained, but the spectra gave sufficient evidence for **5**.

The IR and the ^{31}P {^1H} NMR data of **1**–**5** are collected in Table 1.

TABLE 1. IR[a] and ^{31}P {^1H} NMR[b] data of 1–5

Complex	ν (PS)	δ		J									Solvent
		P^1	P^3	$^1J(PtP^1)$	$^1J(PtP^3)$	$^2J(PtP^4)$	$^2J(P^1P^3)$	$^3J(P^1P^4)$	$^3J(P^2P^3)$	$^3J(P^3P^4)$	$^4J(PtP^2)$	$^5J(P^1P^2)$	
1	500, 580	91.4	61.7				47.4						C_6D_6
2	515, 578	62.3	49.3				13.3						$CDCl_3$
3	535, 564	102.5	82.1				−368.2	5.9		26.9[c]		16.9	C_6D_6
4	523, 562	61.5	35.6	4023	3294	<1	−21.6	7.4	7.6	<1	<1	<1	$CDCl_3$
5	520, 551	85.2	68.1	3507	1588	−21.0	−358.2	7.0	12.5	−1.0	−118.3	−1.0	C_6D_6

[a] KBr, cm^{-1}.

[b] Numbering scheme see text, δ(ppm), J(Hz).

[c] Assignment of the values to $^3J(P^3P^4)$ and $^5J(P^1P^2)$, respectively, uncertain.

Reaction of 2 with [Pd(PPh$_3$)$_4$]

The addition of 0.5 g (0.43 mmol) [Pd(PPh$_3$)$_4$] to a suspension of 1.0 g (0.86 mmol) of **2** in 50 ml benzene caused the rapid formation of a red solution from which **6** precipitated quantitatively in a period of 12 h; m.p. 214–215 °C dec. IR(KBr): ν (PS) 575 cm^{-1} [10].

Reaction of 2 with [Pt(PPh$_3$)$_2$C$_2$H$_4$)]

Solid [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (1.2 g, 1.63 mmol) was added to a benzene suspension (40 ml) of **2** (0.9 g, 0.83 mmol). The color of the reaction mixture changed from yellow to deep red and after 30 min. **7** started to precipitate. The solvent was removed under reduced pressure until *c.* 20 ml remained, and **7** was filtered and washed with hexane; m.p. 179–181 °C dec. (benzene/hexane).

X-ray Data Collection and Structure Analysis of 3

Optically clear, reddish-brown crystals of **3** were grown from toluene. A suitable specimen was mounted on a Huber four-circle diffractometer and X-ray diffraction data were measured at room temperature using graphite crystal monochromated Mo Kα radiation. Lattice parameters were determined by a least-squares treatment of the setting angles of 15 reflections. Crystal data and details concerning data collection, structure solution and refinement are summarized in Table 2. The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by Patterson methods and subsequent Fourier syntheses and refined by full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically, the hydrogen positions were calculated geometrically. The methyl groups were treated as rigid groups during refinement. Final positional and displacement parameters for the non-H atoms are given in Table 3.

All calculations were done on IBM compatible PCs of the universities of Halle and Poznań (Poland) using the program packages SHELX-76 [11], SHELXS-86 [12] and EDIT [13].

TABLE 2. Crystal data and details of data collection and structure refinement for [Pd(μ-SPBu^t)$_2$(η^2-SPBu$^t{}_2$)$_2$] (**3**)

Formula	$C_{32}H_{72}P_4Pd_2S_4$
Formula weight (g mol^{-1})	921.9
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.315(3)
b (Å)	10.668(3)
c (Å)	11.181(3)
α (°)	72.95(2)
β (°)	75.20(2)
γ (°)	71.97(2)
V (Å^3)	1100.0(6)
Z	1
F(000)	480
μ(Mo Kα) (cm^{-1})	11.53
D_{exp} (flotation, H$_2$O + KI) (g cm^{-3})	1.38(1)
D_{calc} (g cm^{-3})	1.392
Crystal size (mm)	0.55 × 0.44 × 0.28
Radiation, λ (Å)	Mo Kα, 0.71069
$2\theta_{max}$	58°
Scan mode	$\theta/2\theta$
No. unique reflections collected	5661
No. observed reflections	4340
Condition for observed reflections	$\lvert F_o \rvert \geqslant 3.92\sigma(F_o)$
No. reflections per parameter refined	19.2
R (R_w)	0.053 (0.052)
Weighting scheme	$1/\sigma^2(F_o)$
Max. shift/σ in last l.s. cycle	0.391
$\Delta\rho_{fin}$ (max./min.) (e Å^{-3})	+1.66/−1.49

TABLE 3. Final fractional coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atoms of **3**

Atom	x/a	y/b	z/c	U_{eq} ^{a}
Pd1	0.80521(4)	0.02948(4)	0.16568(4)	0.032(4)
P1	1.0026(1)	−0.1562(1)	0.1706(1)	0.035(7)
P2	0.5970(1)	0.1574(1)	0.2439(1)	0.035(7)
S1	0.8136(2)	0.1386(2)	−0.0476(2)	0.059(9)
S2	0.6689(2)	−0.0072(2)	0.3749(1)	0.047(8)
C1	1.0676(7)	−0.2063(7)	0.3273(6)	0.05(2)
C2	1.2135(8)	−0.3021(9)	0.3249(7)	0.07(2)
C3	1.0714(10)	−0.0726(9)	0.3489(8)	0.07(2)
C4	0.9677(9)	−0.2742(10)	0.4360(8)	0.08(2)
C5	0.9552(8)	−0.3009(7)	0.1408(9)	0.07(2)
C6	0.9384(10)	−0.2544(11)	−0.0002(10)	0.09(3)
C7	0.8174(11)	−0.3209(10)	0.2230(12)	0.10(2)
C8	1.0663(13)	−0.4361(9)	0.1636(15)	0.11(3)
C9	0.4391(6)	0.1539(7)	0.1924(6)	0.05(2)
C10	0.3036(7)	0.1996(9)	0.2795(7)	0.06(2)
C11	0.4358(8)	0.2482(10)	0.0577(7)	0.07(2)
C12	0.4575(9)	0.0121(9)	0.1821(9)	0.07(2)
C13	0.5863(7)	0.3153(6)	0.2926(6)	0.05(2)
C14	0.4857(10)	0.3244(9)	0.4199(8)	0.08(2)
C15	0.7323(9)	0.3049(9)	0.3081(9)	0.07(2)
C16	0.5425(11)	0.4405(8)	0.1884(9)	0.08(2)

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_i U_{ij}a^*{}_i a^*{}_j \mathbf{a}_i \mathbf{a}_j$.

Results and Discussion

Synthesis and Reaction Chemistry

The acetylacetonato complexes of nickel, palladium and platinum react with R$_2$P(S)H in benzene at room temperature (Ni, Pd) or in refluxing toluene (Pt) in the molar ratio 1:2 as shown in eqn. (1). Based on their elemental analysis and their IR and ^{1}H and ^{31}P NMR spectra, **1**–**5** were identified as dinuclear metal(II) complexes bearing exclusively R$_2$PS$^-$ ligands in both the μ- and η^2-coordination mode. A single crystal X-ray diffraction study of **3** gave a conclusive structure proof.

$$2[\{M(acac)_2\}_n] \xrightarrow[-4n\text{Hacac}]{4nR_2P(S)H} n[M_2(\mu\text{-}SPR_2)_2(\eta^2\text{-}SPR_2)_2] \quad (1)$$

	1	2	3	4	5
M	Ni	Pd	Pd	Pt	Pt
n	3	1	1	1	1
R	Ph	Ph	Bu^t	Ph	Bu^t

1 was also obtained in a redox reaction by treatment of $[Ni(CO)_4]$ and $[Ni(cod)_2]$, respectively, with $Ph_2P(S)H$. Reaction of K_2PtCl_4 and $Ph_2P(S)H$ in CH_3OH also results in **4**. The synthesis of **1** is accompanied by the formation of a less soluble by-product of the same constitution, likely the polymeric compound $[\{Ni(\mu\text{-}SPPh_2)_2\}_n]$. This material also slowly precipitates from the solution of **1** in benzene or dichloromethane and thus prevents the cryoscopic molecular weight determination. **2** and **4** themselves are insufficiently soluble in benzene for molecular weight determinations. In order to prevent the formation of such a by-product the reaction was carried out with the sterically more demanding $Bu^t_2P(S)H$. It appears that $[\{Ni(acac)_2\}_3]$ does not react with $Bu^t_2P(S)H$ even in boiling toluene, whereas $[M(acac)_2]$ (M = Pd, Pt) reacts to give red **3** and yellow **5**, respectively.

Lindner reported that mononuclear η^2-SPR_2 complexes of the 3d metals, which may also be formed from μ-SPR_2-bridged dinuclear metalacycles by a dimer–monomer equilibrium, undergo cyclodi- and -trimerization reactions when treated with electron poor alkynes [14]. We found that our complexes do not react with $MeO_2CC{\equiv}CCO_2Me$. This result, which was unexpected at least for the nickel complex **1**, may be related to the absence of a dimer–monomer equilibrium for this complex.

The η^2-SPR_2 ligands of **1**–**5** should enable these complexes to coordinate appropriate metal fragments and thus to build up new complexes and clusters. First results show that **2** undergoes redox reactions with $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_2(C_2H_4)]$ according to eqn. (2).

$$2 + 2[M(PPh_3)_2L] \xrightarrow[-2L]{} 2[PdM(\mu\text{-}SPPh_2)_2(PPh_3)_2] \quad (2)$$

M = Pd (**6**), Pt (**7**); L = $2PPh_3$ (**6**), C_2H_4 (**7**).

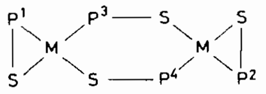
The obtained complexes **6** and **7** belong to a well characterized type of dinuclear metal(I) complex [10, 15] but **7** represents the first heteronuclear example. Contrary to **2** the sterically more crowded complex **3** does not react with $[Pt(PPh_3)_2(C_2H_4)]$ in benzene at room temperature.

Spectroscopy

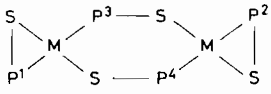
The absence of any bands of the $acac^-$ ligand in the IR and ^1H NMR spectra of **1**–**5** indicates the complete substitution of these ligands for R_2PS^-. The IR spectra revealed two absorptions in the $\nu(PS)$ region typical for R_2PS^- ligands (Table 1). According to the PS bond lengths as determined by the X-ray structure of **3** (see below) we assign the lower wave numbers to the bridging and the higher ones to the dihapto coordinated ligands. This implies a higher PS bond order for the η^2-coordinated ligand compared with that of the μ-ligands.

The ^1H NMR spectra of **1**, **2** and **4** exhibit the complex multiplets for the phenyl protons at *c.* 7 ppm. That of **3** shows two doublets ($^3J(PH)$) of equal intensity according to the methyl groups of the η^2- and μ-bonded $Bu^t_2PS^-$ ligands, respectively. No further assignment of these doublets can be made.

The $^{31}P\{^1H\}$ NMR data of **1**–**5** at room temperature are summarized in Table 1. In principle, *cis* and *trans* complexes are possible depending on the arrangement of the donor atoms around the metal atoms as shown in **A** and **B** (substituents at phosphorus omitted).



A



B

The ^{31}P NMR spectra give evidence that the substituents of the phosphorus atoms determine the actual structure. Thus, complexes containing the Ph_2PS^- ligands adopt the *cis* (**A**) and those containing the $Bu^t_2PS^-$ ligand the *trans* (**B**) arrangement. On the basis of comparison [2, 4, 15, 16] the low field signal is generally assigned to the dihapto coordinated ligand and accordingly the high field signal to the bridging ligand. The ^{31}P spectra of **1** and **2** are of the AX type and hence give no evidence for the dinuclear nature of these molecules. But in analogy to the following discussion the molecules should contain two pairs of chemically equivalent phosphorus nuclei attached to the central atoms in mutual *cis* position (small value of $^2J(P^1P^3)$). The spectrum of **1** shows additionally two singlets at δ 71.6 and δ 71.8 ppm which we suppose to belong to the oligomeric by-product (see above).

Evidence for the dinuclear diphenylthiophosphinito bridged structure of these complexes comes from the $^{31}P\{^1H\}$ NMR spectrum of **4**. The spectrum is complicated compared with those of **1** and **2** by the superposition of the subspectra of the three isotopomers due to the ^{195}Pt nucleus (43.8% AA'MM', 44.8% AA'MM'X, 11.4% AA'MM'XX'; A = η^2-$S^{31}PR_2$, M = μ-$S^{31}PR_2$, X = ^{195}Pt) as well as by the magnetic inequivalence of the ^{31}P nuclei of the bridging ligands which gives rise to the structurally important $^3J(P^1P^4)$ coupling. Of the three isotopomers only the AA'MM' and the AA'MM'X subspectra could be observed. The data obtained for the $Pt_2^{II}(\mu\text{-}SPPh_2)_2$ unit agree well with those of the other known complexes containing this unit [2, 16].

The AA'BB' spin system for **3** follows from the large value of $^2J(P^1P^3)$ which causes a large J/δ ratio [17]. The structural features deduced from the data are the mutual *trans* positions of the phosphorus atoms attached to each palladium atom (large value of $^2J(P^1P^3)$) as well as the dinuclear nature of the complex in solution (long range couplings). The spectrum of **5** which is also complicated by the presence of the three isotopomers, clearly allows the same conclusions. It shows however the presence of another similar compound in a very low concentration. Noteworthy is the extremely small value of $^1J(PtP^3)$ likely due to the *trans* positioned phosphorus atom of the η^2-coordinated ligand.

The ^{31}P {^1H} NMR spectrum ($CDCl_3$) of the dipalladium(I) complex **6** is of the AX type with δ 32.2 (μ-$SPPh_2$) and δ 15.1 (PPh_3), respectively, and $^2J(PP)$ = 6 Hz. The heterodinuclear complex **7** ($[(Ph_3P^2)Pt(\mu\text{-}SP^1Ph_2)(\mu\text{-}Ph_2P^4S)Pd(P^3Ph_3)]$), on the other hand, shows a complicated ^{31}P spectrum due to the four chemically inequivalent phosphorus atoms and the existence of two isotopomers due to the ^{195}Pt isotope.

The data obtained are: δ 12.9 (P^1), δ 20.5 (P^2), δ 24.7 (P^3), δ 20.9 (P^4), $^1J(PtP^1) = 3105.3$ Hz, $^1J(PtP^2) = 3613.4$ Hz, $^2J(P^1P^2) = -5.6$ Hz, $^2J(P^3P^4) = -25.3$ Hz, $^2J(P^3P^5) = 0.0$ Hz, $^2J(PtP^4) = -535.0$ Hz, $^3J(P^1P^3) = 34.7$ Hz, $^3J(P^1P^4) = 221.5$ Hz, $^3J(P^2P^3) = -0.2$ Hz, $^3J(P^2P^4) = 1.9$ Hz. The assignment is based on the analogous homonuclear complex $[Pt_2(\mu\text{-}SPPh_2)_2(PPh_3)_2]$ [15]. Noteworthy is the zero coupling between P^2 and P^3. This coupling is in the range of 200–600 Hz for the diplatinum(I) complexes [15] but is zero for the dipalladium(I) complexes. The palladium atom in **7** obviously prevents this coupling.

Crystal Structure

The molecular structure of $[Pd_2(\mu\text{-}SPBu^t_2)_2(\eta^2\text{-}SPBu^t_2)_2]$ (**3**) is shown in Figs. 1 and 2. Selected bond lengths, angles and torsion angles are given in Table 4. **3** represents a dinuclear complex with a centrosymmetric structure. It consists of two bis(di-t-butylthiophosphinito)palladium(II) units connected by two sharing sulfur atoms. Thus, a six-membered $(Pd\text{–}P\text{–}S)_2$ ring forms the core of the molecule. Each palladium atom is four-coordinated by two phosphorus and two sulfur atoms belonging to three ligand molecules. One of these $Bu^t_2PS^-$ ligands is coordinated in the dihapto mode forming a three-membered ring, whereas the two others act as bridging ligands and are attached to the same Pd atom by only one P or S atom, respectively. The coordination geometry around the Pd atom is nearly planar (none of the five atoms building up the PdS_2P_2 moiety is displaced by more than 0.1 Å from the l.s. plane defined by them) but very far from a square arrangement of the ligator atoms (cf. Table 4). The *trans* arrangement of the latter confirms the validity of the interpretation of the ^{31}P NMR spectra (see above). As can clearly be seen from Fig. 2 the central six-membered ring adopts a somewhat

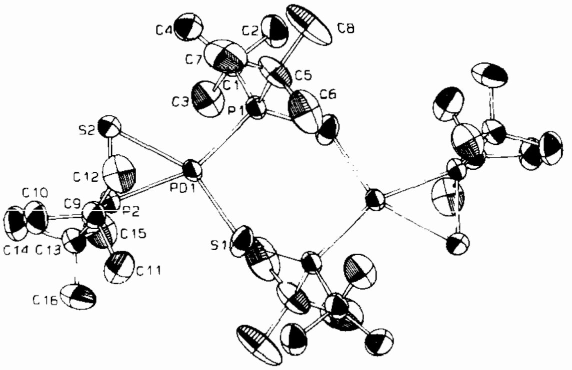


Fig. 1. ORTEP plot [18] of the molecular structure of **3** with atom labelling scheme. The thermal ellipsoids are drawn at the 50% probability level.

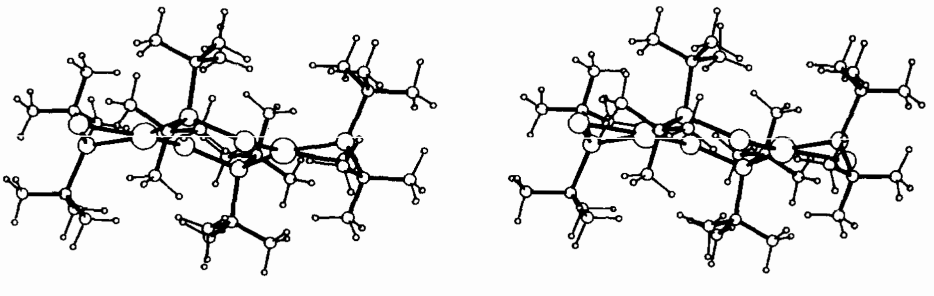


Fig. 2. Stereoscopic PLUTO plot [19] of the molecular structure of **3**.

TABLE 4. Selected bond lengths (Å), bond angles (°) and torsion angles (°) in 3

Pd1–P1	2.360(2)	P1–C1	1.906(7)
Pd1–P2	2.272(1)	P1–C5	1.893(10)
Pd1–S1	2.319(2)	P2–C9	1.875(8)
Pd1–S2	2.393(2)	P2–C13	1.881(8)
P1–S1′	2.064(2)	P2–S2	2.004(2)
P1–Pd1–P2	156.32(6)	C1–P1–S1′	98.6(2)
P1–Pd1–S1	105.00(7)	C5–P1–S1′	106.0(3)
P1–Pd1–S2	105.53(6)	C1–P1–C5	111.9(3)
P2–Pd1–S1	98.16(7)	Pd1–P2–S2	67.71(8)
P2–Pd1–S2	50.80(6)	Pd1–P2–C9	117.9(2)
S1–Pd1–S2	147.71(9)	Pd1–P2–C13	120.5(3)
Pd1–P1–S1′	120.64(7)	S1–P2–C13	110.0(2)
Pd1–P1–C1	111.8(2)	C9–P2–C13	116.0(3)
Pd1–P1–C5	107.7(3)	Pd1–S1–P1′	122.38(8)
		Pd1–S2–P2	61.49(7)
P1–Pd1–P2–S2	2.2(2)	Pd1–P1–S1′–Pd1′	−43.0(1)
P1–Pd1–S2–P2	−179.1(1)	P1–S1′–Pd1′–P1′	37.4(1)
S1–Pd1–P2–S2	170.1(1)	S1′–Pd1′–P1′–S1	−36.6(1)
S1–Pd1–S2–P2	−18.6(2)		

Symmetry operation relating primed atoms to reference atoms at x, y, z: $2 - x, -y, -z$.

flattened chair conformation with a displacement of ±0.7300(4) Å for the Pd atoms from the P_2S_2 plane. The bond angles at phosphorus atom P1, being a link of the six-membered ring, deviate markedly but not dramatically from the ideal value (range 98.6(2)–120.64(7)°), while P2 at the corner of the PPdS triangle has a very irregular four-coordination (angle Pd–P–S compressed to 67.71(7)°).

At first sight, the Pd–P, Pd–S and P–S bond lengths observed in 3 seem to have no peculiarities: they are all in the ranges of values reported for related compounds in the literature. But a more detailed inspection reveals the fact that the individual values for distances between atoms of the same kind, but belonging to different ligands, depend significantly on the coordination mode of the ligand. When compared to the dihapto-bonded ligand, the Pd–P and P–S bonds of the bridging ligand are longer (2.360(2) versus 2.272(1) Å and 2.064(2) versus 2.004(2) Å, respectively) while the Pd–S bond is shorter (2.319(2) versus 2.393(2) Å). All other bond lengths and angles are normal and unremarkable.

There are no unusually short intermolecular contacts in the crystal structure.

Supplementary Material

The data of the elemental analysis (B.W.) and further details of the crystal structure investigation are available from the authors (H.H.) on request.

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