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Synthesis and characterization of monomeric palladium(II) pyridine-2-chalcogenolate complexes

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Abstract

Mononuclear palladium(II) complexes of the type $[Pd(Epy)(S^{\frown}S)(PPh_3)]$ [E=S or Se; $S^{\frown}S=S_2CNEt_2$, $S_2P(OR)_2$ (R=Et, Pr^n, Pr^i)] have been prepared. All the complexes have been characterized by elemental analysis and NMR (^1H, $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$) spectral data. The NMR data indicate that there are two species in solution, i.e. one with chelating $S^{\frown}S$ ligand predominates (~95%) while the other with chelating Epy and monodentate $S^{\frown}S$ existing in ~5% concentration. The X-ray crystal structure of $[Pd(Spy)\{S_2P(OPr^i)_2\}(PPh_3)]$ has been determined. The square planar palladium atom is coordinated to asymmetrically chelated $(Pr^iO)_2PS_2^-$ ligand, PPh_3 and pyS^- groups.

Keywords: Palladium; Pyridine-2-thiolate; Pyridine-2-selenolate; Dialkyldithiophosphates; NMR; X-ray

1. Introduction

The chemistry of transition metal chalcogenolates (RE^-) has received considerable attention in recent years. The high propensity of organochalcogenide ligands (RE^-, E= S, Se, Te) to bridge two metal atoms normally makes them unsuitable for isolation of monomeric complexes [1,2]. The latter have been attractive owing to their utility as mononuclear precursors for semiconductor materials [3–5], and in many catalytic organic transformations [6,7] as well as in desulfurization of organosulfur compounds [8–10]. Several strategies have been adopted to stabilize the monomeric framework. These strategies include use of chelating phosphine ligands [11] and $^-S(CH_2)_nS^-$ [12]. Recently we have isolated a number of palladium(II) and platinum(II) organochalcogenolates employing chelating phosphine ligands [13,14]. Herein we report the synthesis of some monomeric palladium(II) complexes stabilized with internally functionalized chalcogenolates, i.e. pyS/pySe.

2. Experimental

$[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ [15], $[PdCl(S^{\frown}S)(PPh_3)]$ [$S^{\frown}S=S_2CNEt_2$, $S_2P(OR)_2$ (R=Et, Pr^n, Pr^i)] [16] and py_2Se_2 [17] were prepared according to literature methods. Triphenylphosphine (Strem Chemicals Inc) and pySH (Aldrich) were obtained from commercial sources. All reactions were carried out in anhydrous solvents under a nitrogen atmosphere. ^1H, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR were recorded on a Bruker DPX-300 NMR spectrometer in $CDCl_3$ solvent. Spectra were referenced with internal chloroform peak (δ 7.26 ppm for ^1H), external H_3PO_4 for $^{31}P\{^1H\}$ and Me_2Se [secondary reference Ph_2Se_2 in C_6D_6 (δ +463 ppm)]. Microanalyses were performed by the Analytical Chemistry Division of this research centre.

2.1. Preparation of [Pd(Spy){S_2CNEt_2}(PPh_3)]

To a methanolic solution of NaSpy [prepared from pySH (51 mg, 0.46 mmol) in methanol (5 cm^3) and sodium hydroxide solution (0.9 cm^3, 0.55 mmol, 0.61 M)] was added a dichloromethane solution (5 cm^3) of $[PdCl\{S_2CNEt_2\}(PPh_3)]$ (255 mg, 0.46 mmol) with vigorous stirring, which was continued for 5 h. The solvents were evaporated in vacuo and the residue was extracted with dichloromethane (20 cm^3) and filtered. The filtrate was concentrated to 3 cm^3 and hexane (5 cm^3) was added,

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which on slow evaporation gave red crystals (204 mg, 71%).

2.2. Preparation of [Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)]

To a dichloromethane solution (15 cm^3) of [PdCl{$S_2P(OPr^i)_2$}(PPh_3)] (193 mg, 0.31 mmol) was added solid NaSpy (41 mg, 0.31 mmol) with vigorous stirring and the whole mixture was stirred for 3 h. This was filtered and the filtrate was concentrated in vacuo. The residue was recrystallized from CH_2Cl_2–hexane mixture to give a red crystalline solid (172 mg, 80%). Similarly other Spy containing complexes were prepared and pertinent data are given in Table 1.

2.3. Preparation of [Pd(Sepy){S_2CNEt_2}(PPh_3)]

To a methanolic solution of py_2Se_2 (42 mg, 0.13 mmol), a dilute methanolic solution of $NaBH_4$ (10 mg, 0.26 mmol) was added under a nitrogen atmosphere. After 5 min a dichloromethane solution (5 cm^3) of [PdCl{S_2CNEt_2}(PPh_3)] (145 mg, 0.26 mmol) was added and the whole mixture was stirred for 5 h. The solvents were evaporated in vacuo and the residue was extracted with dichloromethane and filtered. The filtrate was concen-

Table 1
Physical, analytical and NMR spectroscopic data for palladium complexes containing Spy or Sepy ligand

Complex	Recrystallization solvent (% yield)	m.p. °C	% Analysis found (calcd.)			NMR spectroscopic data in $CDCl_3$	
			C	H	N	$^{31}P\{^1H\}$ NMR	^1H NMR
[Pd(Spy)(S_2CNEt_2)(PPh_3)]	CH_2Cl_2–hexane (71)	184–185	54.0 (53.6)	4.8 (4.7)	5.0 (4.5)	30.2 (s, *P*Ph_3) 33.2[c] (s, *P*Ph_3)	1.16 (t), 1.19 (t) (7.3 Hz each, NCH_2*Me*); 1.27 (t, 7.2 Hz, NCH_2*Me*)[c]; 3.65 (m, NCH_2); 6.70 (t)[c], 6.75 (t, 5.5 Hz, 1 H, *py*); 7.15–7.49 (m), 7.65–7.71 (m) (*Ph*+2 H, *py*); 8.26 (d, 3.7 Hz 1 H, *py*).
[Pd(Spy){$S_2P(OEt)_2$}(PPh_3)]	CH_2Cl_2–hexane (67)	89–90	48.8 48.8	4.1 (4.4)	2.5 (2.1)	32.6 (s, *P*Ph_3) 100.7 (s, dithio) 33.0[c] (s, *P*Ph_3) 104.1[c] (s, dithio)	1.33 (t, 7.0 Hz, OCH_2Me); 4.15 (m, OCH_2); 6.70 (br)[c]; 6.72 (t, 5.8 Hz, 1H, *py*); 7.13–7.39 (m), 7.52–7.72 (m) (*Ph*+1 H, *py*); 8.19 (br, 1 H, *py*).
[Pd(Spy){$S_2P(OPr^n)_2$}(PPh_3)]	acetone–diethyl ether (85)	114–115	49.7 (50.3)	4.6 (4.8)	1.4 (2.0)	32.6 (s, *P*Ph_3) 100.8 (s, dithio) 33.2[c] (s, *P*Ph_3) 104.5[c] (s, dithio)	0.86 (t, 7.4 Hz, OCH_2CH_2*Me*); 0.92 (t, 7.4 Hz, OCH_2CH_2*Me*)[c], 1.62 (m, OCH_2*CH*$_2$); 3.95 (m, O*CH*$_2$); 4.15 (br, O*CH*$_2$)[c]; 6.60 (br, *py*)[c]; 6.65 (t, 5.7 Hz, 1 H, *py*); 7.08 (d, 7.6 Hz, 1 H, *py*); 7.29–7.37 (m), 7.57–7.63 (m) (*Ph*+1 H, *py*); 8.20 (br, 1 H, *py*).
[Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)]	CH_2Cl_2–hexane (80)	125–127	50.8 (50.3)	4.8 (4.8)	2.2 (2.0)	32.6 (s, *P*Ph_3) 96.7 (s, dithio) 33.2[c] (s, *P*Ph_3) 100.6[c] (s, dithio)	1.25 (d, 6.2 Hz, OCH*Me*$_2$); 1.31 (d, 5.8 Hz, OCH*Me*$_2$)[c]; 4.73 (m, O*CH*); 6.60 (br, *py*)[c]; 6.65 (t, 6.0 Hz, 1 H, *py*); 7.08 (t, 7.0 Hz, 1 H, *py*); 7.28–7.35 (m), 7.58–7.64 (m) (*Ph*+1 H, *py*); 7.75 (br, *py*)[c]; 8.10 (d, 4 Hz, 1 H, *py*).
[Pd(Sepy)(S_2CNEt_2)(PPh_3)][a]	CH_2Cl_2–hexane (60)	185–186	48.4 (49.9)	4.1 (4.3)	4.5 (4.2)	30.5 (s, *P*Ph_3) 33.5[c] (s, *P*Ph_3)	1.14 (t), 1.19 (t) (each 7.0 Hz, OCH_2*Me*); 1.26 (t, 7.2 Hz, OCH_2*Me*)[c]; 3.55–3.68 (m, O*CH*$_2$); 3.72 (q, O*CH*$_2$)[c]; 6.80 (t, *py*)[c]; 6.86 (t, 5.0 Hz 1 H, *py*); 7.18–7.41 (m), 7.64–7.71 (m) (*Ph*+2 H, *py*); 8.32 (d, 3.1 Hz, 1 H, *py*).
[Pd(Sepy){$S_2P(OEt)_2$}(PPh_3)][b]	ether–hexane (84)	99–101	45.9 (45.6)	3.9 (4.1)	2.4 (2.0)	32.0 (s, *P*Ph_3) 101.1 (s, dithio) 33.6[c] (s, *P*Ph_3) 104.2[c] (s, dithio)	1.30 (t, 7.0 Hz, OCH_2*Me*); 1.39 (t, 7.0 Hz, OCH_2*Me*)[c]; 4.05–4.15 (m, O*CH*$_2$); 4.20 (m, O*CH*$_2$)[c]; 6.90 (br, 1 H, *py*); 7.19–7.72 (m, *Ph*+1 H, *py*); 8.29 (br, 1 H, *py*).
[Pd(Sepy){$S_2P(OPr^n)_2$}(PPh_3)]	ether–hexane (52)	110–115	46.8 (47.1)	4.6 (4.5)	1.8 (1.9)	32.1 (s, *P*Ph_3) 101.5 (s, dithio) 33.6[c] (s, *P*Ph_3) 104.7[c] (s, dithio)	0.85 (t, 7.4 Hz, OCH_2CH_2*Me*); 0.90 (t, 7.5 Hz, OCH_2CH_2*Me*)[c]; 1.64 (m, OCH_2*CH*$_2$); 3.90 (td, 7 Hz (t); 9 Hz (d), O*CH*$_2$); 4.10 (br, O*CH*$_2$); 6.65 (m)[c]; 6.80 (m, 1 H, *py*); 7.12 (m, 1 H, *py*); 7.29–7.40 (m), 7.51–7.65 (m) (*Ph*+1 H, *py*); 8.00 (m)[c], 8.22 (m, 1 H, *py*).
[Pd(Sepy){$S_2P(OPr^i)_2$}(PPh_3)]	ether–hexane (78)	115–118	46.7 (47.1)	4.7 (4.5)	1.7 (1.9)	32.1 (s, *P*Ph_3) 97.5 (s, dithio)	1.21 (d, 6.2 Hz, OCH*Me*$_2$); 4.67 (m, O*CH*); 6.80 (m, 1 H, *py*); 7.12 (m, 1 H, *py*); 7.28–7.36 (m), 7.51–7.62 (m) (*Ph*+1 H, *py*); 8.22 (m, 1 H, *py*).

[a] $^{77}Se\{^1H\}$ NMR in $CDCl_3$: 286 ppm relative to Me_2Se.
[b] $^{77}Se\{^1H\}$ NMR in $CDCl_3$: 316 ppm relative to Me_2Se.
[c] Due to chelated Epy complex containing monodentate S$^{\cap}$S ligand (~5% by integration of ^1H NMR spectra). In ^1H NMR spectra all the resonances due to the species ([c]) were not resolved because of the overlapping with the signals of the major species.

trated to 3 cm^3 and hexane 5 cm^3 was added, which on slow evaporation gave a red crystalline solid (105 mg, 60%).

2.4. Preparation of [Pd(Sepy){$S_2P(OEt)_2$}(PPh_3)]

To a methanolic solution of NaSepy [prepared from py_2Se_2 (41 mg, 0.13 mmol) and $NaBH_4$ (11 mg, 0.27 mmol) in (10 cm^3) methanol] was added a dichloromethane solution (10 cm^3) of [PdCl{$S_2P(OEt)_2$}(PPh_3)] (133 mg, 0.23 mmol) with stirring which was continued for 3 h. The solvents were evaporated in vacuo and the residue was extracted with dichloromethane and passed through a Florisil column. The solution was dried in vacuo and the residue recrystallized from a diethyl ether–hexane mixture as a red crystalline solid (134 mg, 84%). Similarly other Sepy containing complexes were prepared. Pertinent data are given in Table 1.

2.5. Attempted preparation of [Pd(Spy){$S_2P(OR)_2$}]

To a dichloromethane suspension of [{PdCl(Spy)}$_n$] (94 mg, 0.37 mmol), solid $NH_4[S_2P(OEt)_2]$ (76 mg, 0.37 mmol) was added and the whole mixture was stirred for 3 h. Reactants were filtered and the filtrate was concentrated in vacuo. The residue was first extracted with ether, filtered, dried in vacuo and recrystallized from hexane as yellow crystals (yield 65 mg, 73%) identified as [Pd{$S_2P(OEt)_2$}$_2$] (m.p. 114–116°C) from analysis [C, 20.1 (20.2); H, 4.2 (3.4)] and NMR data. After diethyl ether extraction, the residue was dissolved in CH_2Cl_2 and filtered, dried in vacuo (yield 25 mg, 41%) identified as [{Pd(Spy)$_2$}$_2$] m.p. 210° (d) [C, 30.8 (30.6); H, 2.1 (2.5); N, 7.2 (8.6) %].

The reaction of [{PdCl(Spy)}$_n$] with $NH_4S_2P(OPr^n)_2$, $NH_4S_2P(OPr^i)_2$, or $NaS_2CNEt_2.3H_2O$ proceeds similarly.

2.6. X-ray crystallography

X-ray diffraction data (Table 2) for the complex [Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)] were collected at room temperature with an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation (λ= 0.71073 Å). The unit cell parameters were determined from least-squares refinement of the setting angle of 25 reflections with 2θ in the range 6.05 to 13.76°. The data were corrected for Lorentz-polarization effects and for linear decay. Experimental absorption corrections based on psi-scans of three reflections were carried out for the structure [18]. The structure was solved by heavy atom methods using the SHELX-86 program [19] and successive difference Fourier Synthesis. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined with the riding model. The final full matrix least squares refinements on I minimizing $\Sigma_w(|F_o|-|F_c|)^2$, including 3643 reflections with $I>2\sigma(I)$, adjusting 343 parameters converged at R and R_w indices of 0.0464 and 0.1067, respectively. All calculations were carried out using the NRCVAX [20] and SHELXL-93 [21]. Neutral atom scattering factors were used [22] and anomalous scattering terms were included in F_c [23].

Table 2
Crystal data and structure refinement details for [Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)]

Empirical formula	$C_{29}H_{33}NO_2P_2S_3Pd$
MW	692.1
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	14.867(4)
b (Å)	10.160(1)
c (Å)	21.136(4)
β (°)	93.18(1)
V (Å^3)	3187.7(11)
Z	4
T (K)	293(2)
λ (Å)	0.71073
Crystal size (mm)	0.203×0.219×0.252
Density (mg/m^3)	1.442
No. reflections collected	5591
No. unique reflections $>2\sigma(I)$	3643
No. parameters	343
R_w	0.1067
R_1	0.0464

3. Results and discussion

Reaction (Eq. (1)) of [PdCl($S^{\cap}S$)(PPh_3)] with one mole equivalent of sodium pyridine-2-thiolate or -selenolate affords complexes of the type [Pd(Epy)($S^{\cap}S$)(PPh_3)] in fairly good yield. Attempts to prepare complexes free from triphenylphosphine by the reaction of [{PdCl(Spy)}$_n$] with [$NH_4S_2P(OR)_2$] (Eq. (2)) in dichloromethane leads to disproportionation to [{Pd(Spy)$_2$}$_2$] and [Pd{$S_2P(OR)_2$}$_2$] as characterized by elemental analysis and NMR data.

$$[PdCl(S^{\cap}S)(PPh_3)] + NaEpy \rightarrow [Pd(Epy)(S^{\cap}S)(PPh_3)] + NaCl \quad (1)$$

$$Na_2PdCl_4 + NaSpy \xrightarrow{\text{aqueous MeOH}} [\{PdCl(Spy)\}_n] \downarrow NH_4[S_2P(OR)_2]$$
$$\tfrac{1}{2}[Pd(Spy)_2] + \tfrac{1}{2}[Pd\{S_2P(OR)_2\}_2] + NH_4Cl \quad (2)$$

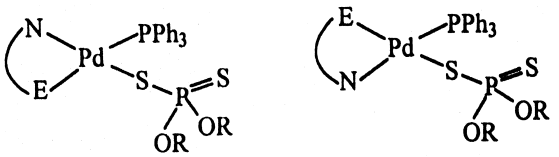
[$S^{\cap}S = S_2P(OR)_2$ (R = Et, Pr^n, Pr^i), S_2CNEt_2; E = S or Se].

All the [Pd(Epy)($S^{\cap}S$)(PPh_3)] complexes are wine red–maroon in colour, soluble in common organic solvents except petroleum ether or hexane. The IR spectra of dialkyldithiophosphate complexes showed absorptions in the regions 960–1155 and 720–855 cm^{-1} which may be

attributed to υ(P)–O–C and υP–O–(C) stretching modes, respectively.

The $^{31}P\{^{1}H\}$ NMR spectra (Table 1) exhibited two sharp singlets attributable to PPh_3 and $[S_2P(OR)_2]^-$ ligands. The resonance due to the former is deshielded (~2 ppm) on substituting chloride in $[PdCl(S^{\cap}S)(PPh_3)]$ by an Epy ligand while the signal due to $[S_2P(OR)_2]^-$ was little affected. The resonance due to $[S_2P(OR)_2]^-$ in palladium complexes appears to be little influenced by X substitutents in $[PdX(S^{\cap}S)(PR_3)]$ (X = Cl, SR, SeR, Me) [24]. The ^{1}H NMR spectra exhibited characteristic peak multiplicity and integration. As reported in other cases [25–27], the ethyl groups on the diethyldithiocarbamate ligand are non-equivalent. Unlike other organoplatinum–palladium complexes containing the $[S_2P(OPr^i)_2]^-$ ligand [24–26,28], the methyl groups in the present case are isochronous as only one doublet was observed in the ^{1}H NMR spectra.

The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of these complexes showed additional peaks integrating to ~5% and were deshielded from the main resonances. These signals may be attributed to a species containing a chelated Epy ligand. Structure I may tentatively be proposed. For II (PPh_3 *trans* to N) one would expect ^{31}P resonances at ~29 ppm, e.g. in the case of $[PdCl(Spy)(PPh_3)]$ [32].



The structure of $[Pd(Spy)\{S_2P(OPr^i)_2\}(PPh_3)]$ was established unambiguously by X-ray diffraction analysis. An ORTEP [29] view of the molecule $[Pd(Spy)\{S_2P(OPr^i)_2\}(PPh_3)]$ together with the atomic numbering scheme is shown in Fig. 1. Selected bond lengths and angles are listed in Table 3. The structure consists of a discrete molecule with a square planar configuration around palladium which is coordinated to an asymmetrically chelated $(Pr^iO)_2PS_2^-$ ligand, PPh_3 and pyS^- groups. The palladium atom is slightly away [0.035(1) Å] from its coordination plane defined by P(1)–S(1)–S(2)–S(3). Various angles around palladium are deviated from their ideal values because of the strain in the four-membered chelate ring and can be compared with the values reported in $[PdCl\{S_2P(OPr^i)_2\}(PPh_3)]$ [30].

Although all the Pd–S bond distances are within the normal Pd–S bonding values [30–34], the Pd–S bonds *trans* to PPh_3 and Spy ligands are different. Both thiolate and tertiary phosphines are known to have a strong *trans* influence [35]. Slight lengthening of the Pd(1)–S(2) bond (0.04 Å) than that of the Pd(1)–S(1) indicates that PPh_3 has a stronger *trans* influence than Spy ligand. The Pd–P bond length is, as usual, less than the radius sum. The P–S bond lengths are intermediate between double bond and

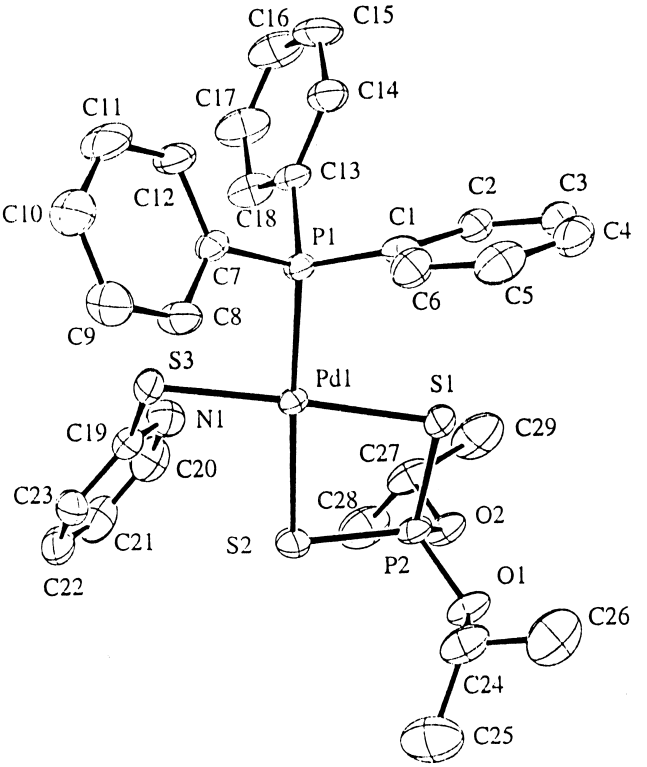


Fig. 1. Molecular structure with numbering scheme for $[Pd(Spy)\{S_2P(OPr^i)_2\}(PPh_3)]$.

single bond values confirming partial double bond character. The Pd(1)–S(3) bond distance in the present case can be compared with the values reported for the thiolate linkage in $[Pd(SMe)\{S_2CNEt_2\}(PEt_3)]$ [33]. The pyridine plane of the Spy ligand is nearly perpendicular to the coordination plane of palladium as reported in $[PdEt(SPh)(PMe_3)_2]$ [35].

In order to evaluate whether the complexes reported here can serve as precursors for the synthesis of palladium chalcogenides, thermolysis of two representative complexes was studied. Thus thermogravimetric analysis (TGA) of

Table 3
Selected bond lengths (Å) and angles (°) for $[Pd(Spy)\{S_2P(OPr^i)_2\}(PPh_3)]$

Bond lengths			
Pd(1)–P(1)	2.2582(13)	S(1)–P(2)	1.997(2)
Pd(1)–S(1)	2.3523(14)	S(2)–P(2)	1.986(2)
Pd(1)–S(2)	2.3946(14)	S(3)–C(19)	1.773(6)
Pd(1)–S(3)	2.3111(15)	N(1)–C(19)	1.331(7)
		N(1)–C(20)	1.336(8)
Bond angles (°)			
P(1)–Pd(1)–S(1)	94.40(5)	C(19)–S(3)–Pd(1)	103.3(2)
P(1)–Pd(1)–S(2)	174.32(6)	S(1)–P(2)–S(2)	104.44(8)
P(1)–Pd(1)–S(3)	88.69(5)	O(1)–P(2)–O(2)	96.6(2)
S(1)–Pd(1)–S(3)	176.59(5)	O(1)–P(2)–S(2)	116.4(2)
S(2)–Pd(1)–S(3)	93.97(5)	O(1)–P(2)–S(1)	112.4(2)
S(1)–Pd(1)–S(2)	83.09(5)	O(2)–P(2)–S(1)	113.9(2)
P(2)–S(1)–Pd(1)	86.21(7)	O(2)–P(2)–S(2)	113.6(2)
P(2)–S(2)–Pd(1)	85.31(6)		

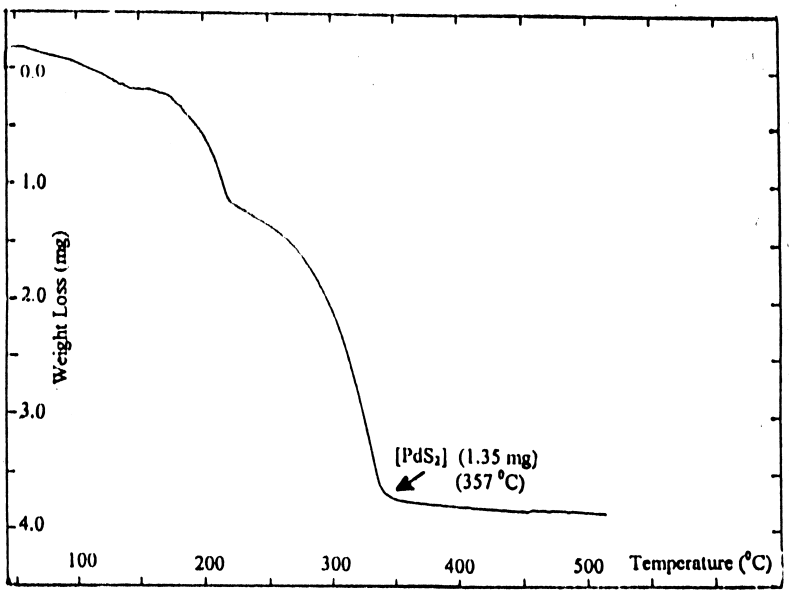


Fig. 2. Thermogravimetric curve for [Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)] (initial weight 5.1 mg).

[Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)] and [Pd(Sepy){$S_2P(OPr^i)_2$}(PPh_3)] were carried out. Both complexes underwent three stage decomposition paths. The first two stages showed elimination of organic residues, with one sulfur from the dithiophosphate. In the third stage it appears from the weight loss and the residual weight of the material that PdS_2 in the case of [Pd(Spy){$S_2P(OPr^i)_2$}(PPh_3)] and PdSeS in the case of [Pd(Sepy){$S_2P(OPr^i)_2$}(PPh_3)] are formed (Figs. 2 and 3).

Supplementary data

Crystallographic supplementary data have been deposited with the CCDC, No 102639. They are available from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK on request.

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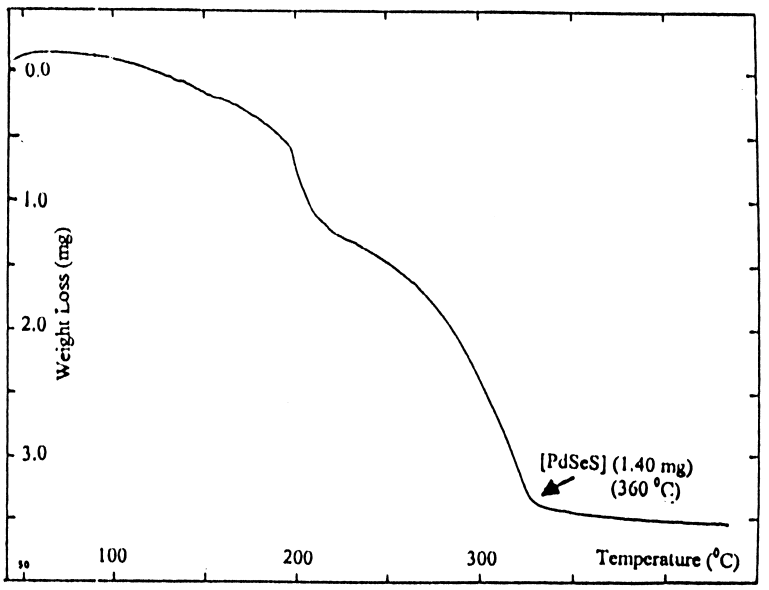

Fig. 3. Thermogravimetric curve for [Pd(Sepy){$S_2P(OPr^i)_2$}(PPh_3)] (initial weight 4.9 mg).

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References

[1] I.G. Dance, Polyhedron 5 (1986) 1037.
[2] P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121.
[3] J.G. Brennan, T. Siegrist, R.J. Carroll, S.M. Stuczynski, L.E. Brus, M.L. Steigerwald, J. Am. Chem. Soc. 111 (1989) 4141.
[4] J. Arnold, Prog. Inorg. Chem. 43 (1995) 353.
[5] W. Hirpo, S. Dhingra, M.G. Kanatzidis, J. Chem. Soc. Chem. Commun. (1992) 557.
[6] M. Rakowski Du Bois, M.C. Van Derveer, D.L. DuBois, R.C. Haltiwanger, W.K. Miller, J. Am. Chem. Soc. 102 (1980) 7456.
[7] K. Osakada, Y. Ozawa, Y. Yamamoto, J. Chem. Soc. Dalton Trans. (1991) 759.
[8] R.J. Angelici, Acc. Chem. Res. 21 (1988) 387.
[9] M.R. Dubois, Chem. Rev. 89 (1989) 1.
[10] W.D. Jones, R.M. Chin, J, Am. Chem. Soc. 116 (1994) 198.
[11] T.B. Rauchfuss, J.S. Shu, D.M. Roundhill, Inorg. Chem. 15 (1976) 2096.
[12] A.K. Fazlur-Rahman, J.G. Veskade, Inorg. Chem. 31 (1992) 5331.
[13] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Chem. Soc. Dalton Trans. (1993) 1509.
[14] A. Singhal, V.K. Jain, B. Varghese, E.R.T. Tiekink, Inorg. Chim. Acta, in press.
[15] F.R. Hartley, The chemistry of platinum and palladium, New York: John Wiley, 1973.
[16] M.C. Cornock, T.A. Stephenson, J. Chem. Soc. Dalton Trans. (1977) 501.
[17] Y. Cheng, T.J. Emge, J.G. Brennan, Inorg. Chem. 35 (1996) 342.
[18] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Cryst. A24 (1968) 351.
[19] G.M. Sheldrick, Acta Cryst. 40A (1990) 467.
[20] E.J. Gabe, Y. Le Page, J.P. Charland, F.L. Lee, P.S. White, J. Appl. Cryst. 22 (1989) 384.
[21] G.M. Sheldrick, SHELXL-93, Program for the refinement of crystal structures, University of Gottingen, Germany.
[22] D.T. Cromer, J.T. Waber, International tables for X-ray crystallography, vol. 4. Birmingham: Kynoch Press, 1974. Table 2.2B.
[23] D.T. Cromer, International tables for X-ray crystallography, vol. 4. Birmingham: Kynoch Press, 1974. Table 2.3.1.
[24] S. Narayan, V.K. Jain, S. Chaudhury, J. Organomet. Chem. 530 (1997) 101.
[25] S. Narayan, V.K. Jain, R.J. Butcher, J. Organomet. Chem. 549 (1997) 73.
[26] V.K. Jain, S. Chaudhury, J. Organomet. Chem. 468 (1994) 279.
[27] D.L. Reger, Y. Ding, D.G. Garza, L. Lebida, Organometallics 11 (1992) 4285.
[28] V.K. Jain, S. Chaudhury, A. Vyas, R. Bohra, J. Chem. Soc. Dalton Trans. (1994) 1207.
[29] C.K. Johnson, ORTEP II 1976, A Fortran Thermal Ellipsoid Plot Program for crystal structure illustrations ORNL-5138.
[30] K. Panneerselvam, T.H. Lu, S.F. Tung, V.K. Jain, S. Narayan, Unpublished results.
[31] K. Panneerselvam, T.H. Lu, S.F. Tung, V.K. Jain, S. Narayan, Unpublished results.
[32] Y. Nakatsu, Y. Nakamura, K. Matsumoto, S. Ooi, Inorg. Chim. Acta 196 (1992) 81.
[33] D.L. Reger, J. Collins, Inorg. Chem. 34 (1995) 2473.
[34] J.P. Fackler Jr., L.D. Thompson, I.J.B. Lin, T.A. Stephenson, R.O. Gould, J.M.C. Alison, A.J.F. Fraser, Inorg. Chem. 21 (1982) 2397.
[35] K. Osakada, Y. Ozawa, A. Yamamoto, Bull. Chem. Soc. Japan 64 (1991) 2002.