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Synthesis and characterization of cyclometallated palladium(II) dithiolate complexes of the type [Pd(E^C)(S^S)]

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Abstract

Cyclometallated palladium(II) dithiolate complexes of the type [Pd(E^C)(S^S)] (where E^CH *N,N'*-dimethylbenzylamine, azobenzene, 4-$MeOC_6H_4CH{=}NC_6H_4Me$-4, 2-phenylpyridine or tris-*o*-tolylphosphine; S^S = S_2CNEt_2 or $S_2P(OR)_2$, R = Et, Pr^n, Pr^i, Bu^n or Bu^s) have been synthesized by the reaction of $[Pd(E^C)(\mu\text{-}X)]_2$ (X = Cl, OAc) with sodium or ammonium salts of dithio acids. These complexes were characterized by elemental analysis, IR, NMR (^1H and ^{31}P) and mass spectral data. Treatment of [Pd(N^C){$S_2P(OPr^n)_2$}] [N^C = NC_5H_4–C_6H_4 or N(Ph)=NC_6H_4] with anhydrous HCl in diethyl ether afforded $[Pd(E^C)(\mu\text{-}Cl)]_2$ and the free dithio acid. When reaction was carried out with triphenylphosphine, a dynamic equilibrium was established between [Pd(N^C){$S_2P(OPr^n)_2$}] and [$Pd(PPh_3)(\eta^1\text{-}C\text{-}N)\{S_2P(OPr^n)_2\}$]. The crystal structure of [$Pd\{N(Me)_2CH_2C_6H_4\}\{S_2P(OPr^n)_2\}$] (**3**) has been determined by X-ray diffraction. The compound exhibits distorted square-planar geometry around palladium atom. © 1997 Elsevier Science S.A.

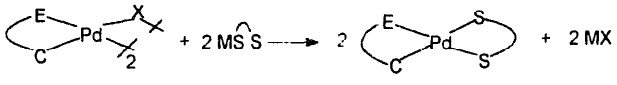
Keywords: Palladium; Orthometallated; Dithiophosphate; Crystal structure

1. Introduction

Both cyclometallated compounds [1–4] and classical coordination complexes [5–9] of palladium have been extensively studied due to their potential applications in organic synthesis [10,11], and also due to their interesting structural features and rich reaction chemistry. Of late, both series of complexes (cyclometallated and dithiolate) have shown important mesomorphic properties that lead to enhanced current interest in these molecules [12–16]. An intriguing idea is that the combination of two kinds of metallomesogens in a single molecule may give rise to a material with improved physical properties. In view of this, and in pursuance of our interest in organo-palladium–platinum dithiolate complexes [17–20], we have synthesized a series of palladium complexes of general formula [Pd(E^C)(S^S)]. The results of this work are reported herein.

2. Results and discussion

Treatment of $[Pd_2(E^C)_2(\mu\text{-}X)_2]$ with two mole equivalents of sodium diethyldithiocarbamate or ammonium dialkyldithiophosphates at room temperature gave mononuclear complexes of the type [Pd(E^C)(S^S)] (Eq. (1)).



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	E^C	S^S	X	M
1	$C_6H_4CH_2NMe_2$	S_2CNEt_2	Cl	Na
2	$C_6H_4CH_2NMe_2$	$S_2P(OEt)_2$	Cl	NH_4
3	$C_6H_4CH_2NMe_2$	$S_2P(OPr^n)_2$	Cl	NH_4
4	C_6H_4–C_5H_4N	$S_2P(OEt)_2$	Cl	NH_4
5	C_6H_4–C_5H_4N	$S_2P(OPr^n)_2$	Cl	NH_4
6	C_6H_4–C_5H_4N	$S_2P(OBu^n)_2$	Cl	NH_4
7	C_6H_4–C_5H_4N	$S_2P(OBu^s)_2$	Cl	NH_4
8	C_6H_4N=NPh	$S_2P(OEt)_2$	Cl	NH_4
9	C_6H_4N=NPh	$S_2P(OPr^n)_2$	Cl	NH_4
10	4-$MeOC_6H_3CH$=NC_6H_4Me-4	S_2CNEt_2	OAc	Na
11	4-$MeOC_6H_3CH$=NC_6H_4Me-4	$S_2P(OEt)_2$	OAc	NH_4
12	4-$MeOC_6H_3CH$=NC_6H_4Me-4	$S_2P(OPr^i)_2$	OAc	NH_4
13	2-$CH_2C_6H_4P(C_6H_4Me$-2$)_2$	S_2CNEt_2	OAc	Na
14	2-$CH_2C_6H_4P(C_6H_4Me$-2$)_2$	$S_2P(OEt)_2$	OAc	NH_4
15	2-$CH_2C_6H_4P(C_6H_4Me$-2$)_2$	$S_2P(OPr^n)_2$	OAc	NH_4
16	2-$CH_2C_6H_4P(C_6H_4Me$-2$)_2$	$S_2P(OPr^i)_2$	OAc	NH_4

All these complexes are yellow crystalline solids soluble in common organic solvents. The IR spectra of dialkyldithiophosphate complexes showed absorptions in the regions 950–1115 and 726.890 cm^{-1} attributable to ν (P)–O–C and ν P–O–(C) stretching modes, respectively [21]. The presence of several absorptions in the region 200–500 cm^{-1} due to aromatic ring and the dithio ligand thwarted unambiguous assignment of ν Pd–C, ν Pd–S stretchings. The mass spectra of these complexes showed molecular ion peaks indicating their monomeric nature. Molecular ion peaks had an expected isotopic pattern. The spectra also showed peaks assignable to $[Pd(E^C)]^+$, $[Pd(S^S)]^+$, (E^C) and $(RO)_2PS_2$ in addition to other peaks.

The ^{31}P NMR spectra of these complexes exhibited singlets for the dialkyldithiophosphate group and metallated tris-*o*-tolyphosphine (Table 1). The signal due to dialkyldithiophosphate group is deshielded as compared to that of the corresponding resonance for $[PdMe\{S_2P(OR)_2\}(PR_3)]$ complexes [20]. The ^1H NMR spectra showed expected peak multiplicities and integrations. Protons attached to the α-carbon atom of the alkoxy group attached to phosphorous appeared as multiplets due to $^3J(H-H)$ and $^3J(P-H)$ couplings. As reported in other cases [17,22,23], the ethyl groups on diethyldithiocarbamate ligands are nonequivalent. Thus, two separate resonances were observed for NEt_2 protons. However, in the case of **1** and **13**, the methyl protons quartets could not be resolved.

The structure of one of the complexes, $[\overline{Pd\{N(Me)_2CH_2C_6H_4\}\{S_2P(OPr^n)_2\}}]$ (**3**) was established by single crystal X-ray diffraction analysis. The molecular structure of the complex, together with atomic numbering scheme is shown in Fig. 1. Selected bond lengths and distances are given in Table 2. The molecular structure consists of discrete monomeric molecules with distorted square-planar geometry around the palladium atom. The metal atom is ligated to a nitrogen atom, an *ortho* carbon atom of the phenyl ring, and two sulphur atoms of the dithio ligand. The metallated *N,N'*-dimethylbenzylamine ligand forms a nonplanar five-membered ring with 'bite' angle 81.70°, which is

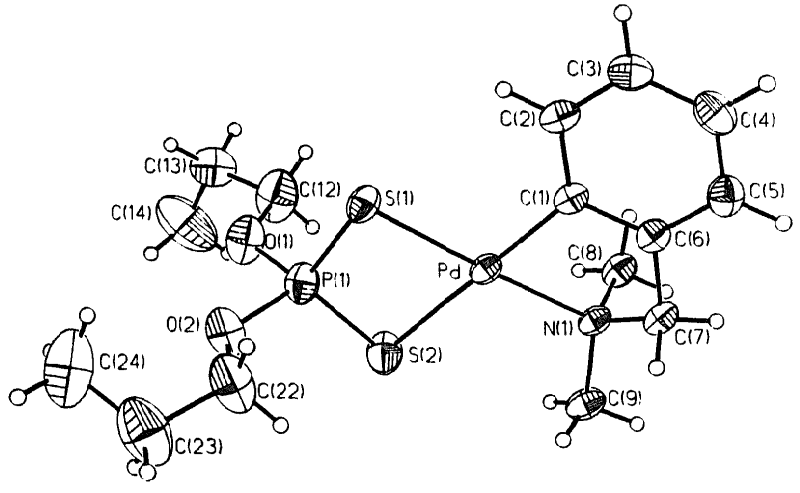
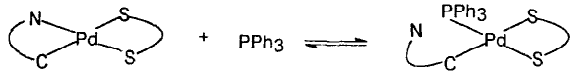


Fig. 1. Molecular structure of $[\overline{Pd\{N(Me)_2CH_2C_6H_4\}\{S_2P(OPr^n)_2\}}]$ with crystallographic numbering scheme.

comparable to the angle reported for *ortho*metallated palladium complexes [24–27]. The strain imposed by a nonplanar four-membered chelate 'PdS$_2$P' ring is also reflected in the S(1)–Pd–S(2) angle which has compressed to 83.24(5)°, while the adjacent angles C(1)–Pd–S(1) and N(1)–Pd–S(2) have opened to 95.15(12)° and 99.89(11)° respectively.

The Pd–C(1) [24–27], Pd–N [27] and Pd–S [22,23,28] distances are in good agreement with reported values. The Pd–S distance *trans* to the carbon atom of the cyclometallated ligand is slightly longer (2.458(2) Å) than that *trans* to the Pd–N bond (2.3303(12) Å), attributable to the differing *trans* influence of the phenyl carbon and nitrogen atom. The P–S bond lengths of 1.969(2) and 2.000(2) are intermediate between double bond (1.94 Å) and single bond (2.09 Å) values, confirming the partial double bond character.

A few reactions of these complexes were also investigated. The treatment of **5** or **9** with anhydrous HCl in diethyl ether readily gave sparingly soluble chloro-bridged dimer [Pd$_2$(N^C)$_2$(μ-Cl)$_2$] (N^C = NC$_5$H$_4$–C$_6$H$_4$, PhN=NC$_6$H$_4$) as characterized by microanalysis and IR data. The cleavage of a chelating dialkyldithiophosphate group, [28,29] and coordinated nitrogen atom of a metallated ligand [30,31] with tertiary phosphines, is well documented. To evaluate reactivity of [Pd(E^C)(S^S)] with neutral donor ligands, the reaction of **3** or **5** with 1 to 5 equivalents of triphenylphosphine in CDCl$_3$ was monitored by ^{31}P NMR spectroscopy. No change either in the half-line width or in the chemical shift value for the S$_2$P(OPr^n) resonance was noticed. However, the resonance due to triphenylphosphine was broadened considerably. Organoplatinum dialkyldithiophosphate complexes, [Pt{S$_2$P(OR')$_2$}R(PR''$_3$)] are inert to neutral donor ligands [27]. The observed ^{31}P NMR spectra in the present case may be interpreted in terms of a following dynamic equilibrium between the parent complex and the species formed by the cleavage of coordinated Pd–N bond (Eq. (2)).



(2)

3. Experimental

All preparations were carried out under a nitrogen atmosphere. Solvents were dried, degassed and distilled prior to use. Azobenzene, 2-phenylpyridine, *N,N*-dimethylbenzyleamine, tris-*o*-tolylphosphine, PPh$_3$, NaS$_2$CNEt$_2$ · 2H$_2$O, *p*-methoxybenzaldehyde, *p*-toludine were obtained from commercial sources. Ammonium dialkyldithiophosphates [32], [Pd{N(Me)$_2$CH$_2$C$_6$H$_4$}{μ-Cl)]$_2$ [33] [Pd(NC$_5$H$_4$-C$_6$H$_4$)(μ-Cl)]$_2$ [34], [Pd{N(C$_6$H$_4$Me-4)=C$_6$H$_3$OMe-4)}(μ-OAc)]$_2$ [35], [Pd{N(Ph)=NC$_6$H$_4$}(μ-Cl)]$_2$ [36], [Pd{P(tol-o)$_2$C$_6$H$_4$CH$_2$-o}(μ-OAc)]$_2$ [36], [37] were prepared by the reported methods. The IR spectra were recorded as Nujol mulls between CsI plates on a Bomem MB 102 FT-IR spectrometer. NMR spectra were recorded on a Bruker AMX-500 or DPX-300 spectrometer in 5 mm thin-walled tubes. Chemical shifts are referred to internal chloroform peak (δ 7.26) for proton and external 85% H$_3$PO$_4$ for ^{31}P{^{1}H}. Mass spectra were recorded on a VG micromass 7070 F or Shimadzu GCMS QP 1000A instruments with EI source at 70 eV. Microanalysis of compounds were carried out by the Analytical Chemistry Division of this research centre.

3.1. Preparation of [Pd{N(Me)$_2$CH$_2$C$_6$H$_4$}{S$_2$P(OEt)$_2$}] (2)

To a dichloromethane solution (25 ml) of [Pd$_2${N(Me)$_2$CH$_2$C$_6$H$_4$}$_2$(μ-Cl)$_2$] (338 mg, 0.614 mmol), solid NH$_4$S$_2$P(OEt)$_2$ (253 mg, 1.246 mmol) was added with vigorous stirring under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 5 h. The solvent was evaporated in vacuo. The residue was extracted with acetone (10 ml) and filtered. The filtrate was concentrated in vacuo, and the solid thus obtained was recrystallized from a dichloromethane–hexane mixture cooled in a freezer (−10°C) for 24 h. Yellow crystals were separated, washed with hexane, and dried in vacuum (yield 352 mg, 67%). Similarly, complexes **1** and **3–9** were prepared. Pertinent data are given in Table 1.

3.2. Preparation of [Pd{P(tol-o)$_2$C$_6$H$_4$CH$_2$-o}{S$_2$P(OPr^n)$_2$}] (15)

Solid NH$_4$S$_2$P(OPr^n)$_2$ (90 mg, 0.39 mmol) was added to a vigorously stirred dicloromethane (15 ml) of [Pd$_2${P(tol-o)$_2$C$_6$H$_4$CH$_2$-o}$_2$(μ-OAc$_2$)] (176 mg, 0.19 mmol). The reaction mixture was stirred at room temperature for 4 h. The solvent was removed under a reduced pressure, and the residue was extracted with benzene and filtered. The

Table 1
Physical, analytical and NMR (^{1}H and ^{31}P) data for [Pd(E⁻C(S⁻S)] complexes

Complex	Recrystallization solvent (% yield)	MP °C	Analysis found (calculated)			NMR Data in $CDCl_3$		Mass spectra molecular ion peak m/e
			%C	%H	%N	$^{31}P\{^1H\}\delta$	H δ^a	
1	CH_2Cl_2–Hexane (30)	105–108	42.6 (43.2)	5.5 (5.7)	7.1 (7.2)	–	1.28 (t), 1.32 (t)(each 7.2 Hz; S_2CNCH_2Me); 2.90 (s, NMe_2); 3.81 (q, 7.2 Hz, S_2CNCH_2–); 3.99 (s, $C_6H_4CH_2$–); 6.94–7.00 (m, C_6H_4).	–
2	CH_2Cl_2–Hexane (67)	103–105	36.4 (36.7)	5.2 (5.2)	3.6 (3.3)	104.1	1.39 (t, 7.0 Hz, OCH_2Me); 2.90 (s, NMe_2); 3.99 (s, $C_6H_4CH_2$–); 4.22 (m, OCH_2–); 6.99–7.06 (m, C_6H_4).	–
3	CH_2Cl_2–Hexane (41)	95–99	39.9 (39.7)	5.8 (5.8)	3.5 (3.1)	104.3	0.99 (t, 7.2 Hz, OCH_2CH_2Me); 1.77 (m, OCH_2CH_2–); 2.91 (s, NMe_2); 4.00 (s, $C_6H_4CH_2$); 4.10 (m, OCH_2–); 6.95–7.05 (m, C_6H_4).	454
4	Ether–Hexane (50)	77–79	40.6 (40.4)	4.3 (4.1)	3.5 (3.1)	104.6	1.40 (t, 7.0 Hz, OCH_2Me); 4.26 (m, OCH_2–); 7.31 (m, br), 7.52 (m), 8.54 (d, 5.4 Hz) (1:1:1, py); 7.13 (m, br) 7.81 (m) [Ph + 1H py].	446
5	Ether–Hexane (45)	86–89	43.0 (43.1)	4.8 (4.7)	3.1 (2.9)	104.2	0.99 (t, 7.2 Hz, OCH_2CH_2Me); 1.78 (m, OCH_2CH_2–); 4.13 (m, OCH_2–); 7.29 (br), 7.53 (m), 7.75 (d, 8 Hz), 8.54 (d, 5.3 Hz) (each equivalent to 1H) (py); 7.13 (m, 3H), 7.84 (1H) (C_6H_4).	474
6	Ether Hexane (20)	60–62	46.4 (45.5)	5.5 (5.2)	2.8 (2.8)	104.1	0.94 (t, 7.2 Hz, $OCH_2CH_2CH_2Me$); 1.44 (m, 7.2 Hz, $OCH_2CH_2CH_2$–); 1.73 (d, t, 6.6 Hz (t), 7.8 Hz (d) CH_2CH_2–; 4.18 (m, OCH_2–); 7.30 (m), 7.53 (m), 7.75 (d, 8.0 Hz), 8.55 (d, 5.4 Hz, py); 7.13 (m, 3H), 7.84 (m) (C_6H_4).	502
7	Benzene–Hexane (24)	86–89	46.1 (45.5)	5.0 (5.2)	3.8 (2.8)	101.2	0.97 (t), 0.98 (t) (each 7.4 Hz, OCH–CH_2Me); 1.40 (d), 1.41 (d) (each 6.2 Hz, $OCHMe$); 1.66 (m), 1.76 (m) ($OCHCH_2$–); 4.67 (m, OCH–); 7.30 (m), 7.53 (m), 7.76 (d, 8.0 Hz), 8.55 (d, 4.0 Hz) (py); 7.14 (m, 3H), 7.84 (br, 1H)(C_6H_4).	502
8	Ether–Hexane (31)	108–110	40.2 (40.6)	4.2 (4.1)	7.0 (5.9)	102.0	1.38 (t, 7.2 Hz, OCH_2Me); 4.20 (m, OCH_2–); 7.28–7.50 (m), 7.82 (d, 7.0 Hz); 8.05 (d, 7.0 Hz) (C_6H_4).	473

9	Ether–Hexane (32)	73–75	43.0 (43.2)	4.5 (4.6)	5.8 (5.6)	102.4	0.98 (t, 7.2 Hz, OCH_2CH_2*Me*); 1.74 (m, OCH_2CH_2–); 4.08 (m, OCH_2–); 7.26–7.48 (m), 7.82 (d, 7.0 Hz); 8.05 (d, 7.0 Hz) (Ph + C_6H_4).	501
10	Benzene–Hexane (56)	152–155	50.4 (50.1)	5.0 (5.1)	5.7 (5.8)	–	1.26(t), 1.34 (t) (each 7.2 Hz; $CNCH_2$*Me*); 2.36 (s, C_6H_4*Me*); 3.80 (q), 3.83 (q) (each 7.2 Hz, $CNCH_2$–); 3.87 (s, C_6H_4OMe); 6.62 (d, d, 2.3, 9 Hz), 6.70 (d, 2.3 Hz), 7.17–7.24 (br), 7.43 (d, 8.3 Hz) (C_6H_4 + C_6H_3); 8.14 (s, *N*=CH–).	479
11	Benzene–Hexane (45)	82–85	44.4 (44.2)	4.8 (4.7)	– (2.7)	104.8	1.36 (t, 7.0 Hz, OCH_2*Me*); 2.36 (s, C_6H_4Me); 3.85 (s, C_6H_4OMe); 4.20 (m, OCH_2–); 6.62 (d), 6.80 (d), 7.20, 7.40 (d, 8.3 Hz) (C_6H_4 + C_6H_3), 8.05 (s, *N*=CH–).	516
12	Benzene–Hexane (39)	135–137	46.2 (46.4)	5.0 (4.4)	–	98.9	1.34 (d), 1.38 (d) (each 6.2 Hz, $OCHMe_2$); 2.36 (s, C_6H_4Me); 3.86 (s, C_6H_4OMe); 4.81 (m, OCH–); 6.63 (d, d, 8.4, 2.3 Hz), 6.83 (d, d, 2.3 Hz each), 7.20 (br), 7.41 (d, 8.2 Hz) C_6H_4 + C_6H_3); 8.07 (s, N=CH–).	544
13	CH_2Cl_2–Hexane (59)	203–206	55.9 (56.0)	5.5 (5.4)	2.7 (2.5)	35.5[b]	1.25 (t), 1.30 (t) (each 7.2 Hz; $CNCH_2$*Me*); 2.47 (br) 2.79 (br) (1:1 each, 3H, tol–*Me*); 3.36 (s), 3.39 (s) (CH_2–Pd); 3.80 (br, NCH_2); 6.82–7.40 (m, C_6H_4).	558
14	CH_2Cl_2–Hexane (46)	136–137	51.5 (50.5)	4.8 (5.1)	–	102.7, 38.9[b]	1.35 (t, 7.0 Hz, OCH_2*Me*); 2.61 (br, 2Me, tol); 3.57 (s, CH_2–Pd); 4.14 (br, OCH_2–); 6.78–7.39 (m, C_6H_4).	–
15	CH_2Cl_2–Hexane (39)	93–95	52.2 (52.1)	5.3 (5.5)	–	102.9, 38.7[b]	0.95 (t, 7.2 Hz, OCH_2CH_2*Me*); 1.73 (m, OCH_2CH_2–); 2.62 (br, 2*Me*, tol); 3.57 (s, CH_2–Pd); 4.02 (br, OCH_2–); 6.78–7.39 (m, C_6H_4).	–
16	CH_2Cl_2–Hexane (70)	172–174	52.5 (52.1)	5.5 (5.5)	–	99.5, 38.7[b]	1.35 (d), 1.37 (d) (each 6.1 Hz, $OCHMe_2$); 2.18 (br, 2Me, tol); 3.57 (s, CH_2–Pd); 4.82 (br, OCH–); 6.82–7.37 (m, C_6H_4 + C_6H_3).	623

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad.
[b] *ortho*metallated tri–*o*–tolylphosphine.

Table 2
Selected bond lengths (Å) and angles (°) for **3**

Pd–C(1)	1.992(4)	Pd–N(1)	2.101(3)
Pd–S(1)	2.3303(12)	Pd–S(2)	2.458(2)
S(2)–P(1)	1.969(2)	S(1)–P(1)	2.000(2)
P(1)–O(2)	1.583(5)	P(1)–O(1)	1.573(5)
N(1)–C(8)	1.487(6)	N(1)–C(9)	1.479(6)
N(1)–C(7)	1.498(6)		
C(1)–Pd–N(1)	81.7(2)	C(1)–Pd–S(1)	95.15(12)
N(1)–Pd–S(1)	176.86(11)	C(1)–Pd–S(2)	176.66(12)
N(1)–Pd–S(2)	99.89(11)	S(1)–Pd–S(2)	83.24(5)
P(1)–S(1)–Pd	86.40(6)	P(1)–S(2)–Pd	83.64(7)
O(1)–P(1)–O(2)	93.7(3)	O(1)–P(1)–S(2)	114.3(2)
O(2)–P(1)–S(2)	114.4(2)	O(1)–P(1)–S(1)	114.5(2)
O(2)–P(1)–S(1)	113.3(2)	S(2)–P(1)–S(1)	106.59(9)
C(9)–N(1)–C(8)	107.5(4)	C(9)–N(1)–C(7)	109.8(4)
C(8)–N(1)–C(7)	109.7(4)	C(9)–N(1)–Pd	114.9(3)
C(8)–N(1)–Pd	109.2(3)	C(7)–N(1)–Pd	105.6(2)
C(6)–C(1)–Pd	113.1(3)	C(1)–C(6)–C(7)	116.5(4))
C(6)–C(7)–N(1)	109.0(3)		

filtrate was concentrated in vacuo and the residue was recrystallized from benzene–hexane (0°C) to give yellow crystals, separated by decanting the supernatant, washed with hexane and dried in vacuo (yield 165 mg, 71%).

3.3. Reaction between 5 and HCl

To a diethyl ether solution of **5** (47 mg, 0.099 mmol) was added an ethereal solution of HCl (0.04 ml, 2.44N, 0.099 mmol). Within a few minutes a cream colored solid was separated. After 10 min, additional 1 ml HCl was added. The cream-colored precipitate was filtered, washed with hexane, and dried in vacuo. Found: C, 44.4; H, 2.3; N, 4.8. Calculated for $C_{22}H_{16}N_2Cl_2Pd_2$: C, 44.6; H, 2.7; N, 4.7. IR spectra of the product was comparable to that of the authentic sample $[Pd_2(NC_6H_4\text{-}C_6H_4)_2(\mu\text{-}Cl)_2]$. The product in the filtrate (after drying in vacuum) was identified as dithiophosphoric acid by NMR spectroscopy.

Similarly, the reaction of **9** with HCl was carried out. Insoluble product isolated from the reaction showed IR spectrum and melting point (278–279°C dec.) comparable to $[Pd_2\{N(Ph)=NC_6H_4\}_2(\mu\text{-}Cl)_2]$. Found: C 44.5; H, 2.8; N, 10.0. Calculated for $C_{24}H_{18}N_4Cl_2Pd_2$: C, 45.6; H, 2.9; N, 6.6.

3.4. Reaction of 5 with PPh_3

To a $CDCl_3$ solution of 5 (22 mg, 0.046 mmol) in 5 mm NMR tube was added triphenylphosphine (12.3 mg, 0.047 mmol), shaken well, and ^1H and ^{31}P NMR were recorded. To this 1 and 3 equivalents of PPh_3 was added, and the reaction mixture was monitored by ^{31}P NMR spectroscopy. Similarly, the reaction of **3** with PPh_3 was monitored by ^{31}P NMR spectroscopy.

3.5. X-ray structure determination for 3

All measurements were made at 20 ± 2°C on a Rigaku AFC 6S diffractometer using graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). The crystallographic data together with data collection and structure refinement details are given in Table 3. The numbering scheme employed is shown in Fig. 1 drawn with the ORTEP programme [38]. All the data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterrson method and direct method [39,40], and refined by full-matrix least square on F^2. The refinement on 229 parameters coverage with $R = 0.044$ and $R' = 0.0989$ for unit weights. The maximum and minimum excursions in the final difference map were 0.912 and -0.527 e Å^3, respectively. Neutral atom factors were taken from Cromer and Waber [41]. Anomalous dispersion effects were included in F_{calc} [42]. The values of $\Delta f'$ and $\Delta f''$ were those of

Table 3
Crystal data and structure refinement for **3**

Empirical formula	$C_{15}H_{26}NO_2PPdS_2$
Formula weight	453.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 15.037(2)$ Å
	$b = 10.2637(10)$ Å
	$c = 14.460(2)$ Å
	$\beta = 114.771(7)°$
Volume	2026.4(4) Å^3
z	4
Density (calculated)	1.488 mg/m^3
Absorption coefficient	1.206 mm^{-1}
$F(000)$	928
Crystal size	0.24×0.52×0.48 mm
θ range for data collection	2.48–27.50°
Index ranges	$-17 \le h \le 19$, $0 \le k \le 13$, $-18 \le m \le 0$
Reflections collected	4842
Independent reflections	4655 ($R_{int} = 0.0204$)
Absorption correction	Semiempirical from ψ-scans
Maximum and minimum transmission	0.4122 and 0.3390
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	4654/0/229
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0440$, $wR_2 = 0.0989$
R indices (all data)	$R1 = 0.0690$ $wR_2 = 0.1139$
Largest diff. peak and hole	0.912 and −0.527 e Å^3

Cromer [43]. All calculation were performed using the TEXSAN [44] crystallographic software package of Molecular Structure.

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