

Synthesis and characterization of methylpalladium(II) dithiolate complexes of the type $[\text{PdMe}(\widehat{\text{S}}\widehat{\text{S}})(\text{ER}_3)]$ ($\widehat{\text{S}}\widehat{\text{S}} = \text{S}_2\text{CNR}_2$, S_2COEt , $\text{S}_2\text{P}(\text{OR})_2$, S_2PPh_2 ; $\text{ER}_3 = \text{PMePh}_2$, PPh_3 , AsPh_3)

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Abstract

Methylpalladium(II) dithiolate complexes of the type $[\text{PdMe}(\widehat{\text{S}}\widehat{\text{S}})(\text{ER}_3)]$ ($\widehat{\text{S}}\widehat{\text{S}} = \text{S}_2\text{CNR}_2$ ($\text{R} = \text{Me}$ or Et), S_2COEt , $\text{S}_2\text{P}(\text{OR})_2$ ($\text{R} = \text{Et}$, ^iPr , ^tPr), S_2PPh_2 ; $\text{ER}_3 = \text{PMePh}_2$, PPh_3 , AsPh_3) have been synthesized by the reaction of $[\text{Pd}_2\text{Me}_2(\mu\text{-Cl})_2(\text{PMePh}_2)_2]$ with sodium/potassium/ammonium salts of the dithio acid or by treatment of $[\text{PdMeCl}(\text{cod})]$ with ER_3 followed by sodium/potassium/ammonium salts of the dithio ligand. All the complexes were characterized by elemental analysis, IR and nuclear magnetic resonance (^1H , ^{31}P) data.

Keywords: Palladium; Methylpalladium(II); Xanthate; Dithiocarbamate; Dithiophosphate

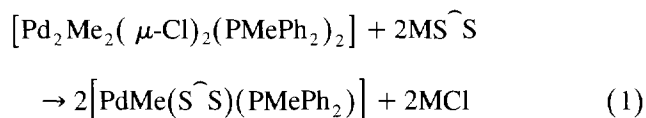
1. Introduction

During the last two decades or so the synthesis and reaction chemistry of the classical coordination complexes of palladium(II) and platinum(II) with anionic dithio ligands, $\widehat{\text{S}}\widehat{\text{S}}$ (where $\widehat{\text{S}}\widehat{\text{S}} = \text{S}_2\text{CR}$, S_2COR , S_2CNR_2 , S_2PR_2) have attracted much attention [1–5]. The dithiolate ligand in these complexes acts in a bidentate chelating, monodentate or ionic fashion. Despite extensive studies on classical coordination complexes of these elements with dithio ligands, organometallic chemistry remained unexplored until recently. A number of organoplatinum complexes have been reported by us [6–8] and Reger and coworkers [9]. Unlike classical coordination complexes, such as $[\text{Pt}(\widehat{\text{S}}\widehat{\text{S}})_2]$, $[\text{Pt}(\widehat{\text{S}}\widehat{\text{S}})\text{Cl}(\text{PR}_3)]$, etc., on the one hand organoplatinum complexes $[\text{PtR}(\widehat{\text{S}}\widehat{\text{S}})(\text{L})]$ are inert to excess of triphenylphosphine [6], while on the other hand they show unusually high thermal stability even for

alkyls containing β -hydrogen atoms [9]. However, there is a paucity of data on analogous organopalladium complexes with anionic dithio ligands, except for some dithiocarbamate complexes [10]. In this paper we describe the synthesis and characterization of methylpalladium complexes with a variety of anionic dithio ligands.

2. Results and discussion

Reaction of $[\text{Pd}_2\text{Me}_2(\mu\text{-Cl})_2(\text{PMePh}_2)_2]$ with two mole equivalents of sodium/potassium/ammonium salt of a dithio acid gave mononuclear complexes of the type $[\text{PdMe}(\widehat{\text{S}}\widehat{\text{S}})(\text{PMePh}_2)]$ (Eq. (1)). Complexes of this type can also be obtained by the reaction of $[\text{PdMeCl}(\text{cod})]$ with a neutral donor ligand followed by treatment with sodium/potassium/ammonium salt of a dithio ligand (Eq. (2)).

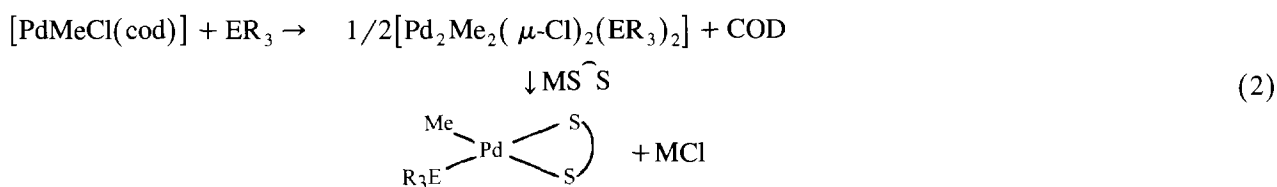


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Table 1
Physical, analytical and NMR (^1H , ^{31}P) data for $[\text{PdMe}(\text{S}^{\wedge}\text{XER}_3)]$

Complex	Recrystallization solvent (yield (%))	Melting point ($^{\circ}\text{C}$)	Analysis: found (calc.)		NMR data in CDCl_3^a	
			C	H	$\delta^{31}\text{P}$	$\delta^1\text{H}$
$[\text{PdMe}(\text{S}_2\text{CNEt}_2)(\text{PMePh}_2)]$	Benzene–hexane (35)	77–79	47.8 (48.6)	5.4 (5.6)	18.2(s)	0.41 (d, 4.9 Hz, PdMe); 1.21 (t); 1.28 (t) (each 7.2 Hz, NCMe); 1.96 (d, 8.8 Hz, PMe); 3.75 (q); 3.82 (q) (each 7.2 Hz, NCH_2 –); 7.40 (m), 7.62 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{COEt})(\text{PMePh}_2)]$	Ether–hexane (61)	97–99	46.1 (46.1)	4.5 (4.8)	18.9(s)	0.56 (d, 4.4 Hz, PdMe); 1.43 (t, 7.1 Hz, OC-CH_3); 2.01 (d, 9.1 Hz, PMe); 4.58 (q, 7.1 Hz, OCH_2 –); 7.42 (m), 7.61 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{OEt})_2)(\text{PMePh}_2)]$	Ether–hexane (59)	54–55	42.8 (42.7)	5.0 (5.2)	20.1 (s) (PMePh_2) 101.2 (s, $\text{S}^{\wedge}\text{S}$)	0.59 (d, 4.4 Hz, PdMe); 1.36 (t, 7.2 Hz, OC-CH_3); 2.01 (d, 9.3 Hz, PMe); 4.15 (m, OCH_2 –); 7.41 (m), 7.60 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)(\text{PMePh}_2)]$	Hexane (62)	89–91	44.0 (44.9)	5.0 (5.6)	18.9 (s) (PMePh_2) 96.7 (s, $\text{S}^{\wedge}\text{S}$)	0.58 (d, 4.5 Hz, PdMe); 1.34 (d), 1.37 (d) (each 6.2 Hz, Me_2CHO); 2.00 (d, 9.4 Hz, PMe); 4.81 (m, OCH –); 7.39–7.44 (m), 7.58–7.62 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{CNMe}_2)(\text{PPh}_3)]$	Benzene–hexane (44)	142–147	51.7 (52.4)	4.7 (4.8)	36.5(s)	0.44 (d, 4.6 Hz, PdMe); 3.28 (s), 3.38 (s) (NMe_2); 7.40 (m), 7.58 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{CNEt}_2)(\text{PPh}_3)]$	Benzene–hexane (71)	143–145	54.6 (54.2)	5.2 (5.3)	35.2 (s)	0.42 (d, 4.6 Hz, PdMe); 1.21 (t), 1.29 (t) (each 7.1 Hz, N-C-Me); 3.76 (q), 3.83 (q) (each 7.1 Hz, NCH_2 –); 7.40 (m), 7.56 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{COEt})(\text{PPh}_3)]$	Benzene–hexane (58)	138–142	52.7 (52.3)	4.5 (4.6)	35.6 (s)	0.58 (br, PdMe); 1.44 (t, 7.1 Hz, OC-Me); 4.62 (q, 7.1 Hz, OCH_2 –); 7.43 (m), 7.56 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{OEt})_2)(\text{PPh}_3)]$	Benzene–hexane (43)	135–138	48.2 (48.6)	4.7 (5.0)	37.4 (s, PPh_3) 99.9 (s, $\text{S}^{\wedge}\text{S}$)	0.61 (d, 4.2 Hz, PdMe); 1.36 (t, 7.1 Hz, OCCH_3); 4.15 (m, OCH_2 –); 7.40 (m), 7.58 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{O}^n\text{Pr})_2)(\text{PPh}_3)]$	Ether–hexane (53)	92–94	50.3 (50.3)	5.3 (5.4)	38.4 (s, PPh_3) 101.1 (s, $\text{S}^{\wedge}\text{S}$)	0.61 (d, 4.4 Hz, PdMe); 0.95 (t, 7.1 Hz, OCCCH_3); 1.73 (sextet, 7.1 Hz, OCCH_2 –); 4.04 (m, OCH_2 –); 7.41 (m), 7.60 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)(\text{PPh}_3)]$	Benzene–hexane (40)	145–146	50.1 (50.3)	5.3 (5.4)	38.2 (s, PPh_3) 97.4 (s, $\text{S}^{\wedge}\text{S}$)	0.59 (d, 4.4 Hz, PdMe); 1.33 (d), 1.38 (d) (each 6.2 Hz, OCMe_2); 4.82 (m, OCH –); 7.40 (m), 7.59 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{PPh}_2)(\text{PPh}_3)]$	Benzene–hexane (45)	189–191	58.2 (58.8)	4.5 (4.5)	37.2 (s, PPh_3) 76.9 (s, $\text{S}^{\wedge}\text{S}$)	0.59 (d, 4.1 Hz, PdMe); 7.40 (m), 7.60 (m), 7.87 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{CNMe}_2)(\text{AsPh}_3)]$	Benzene–hexane (50)	158–162	48.6 (48.2)	4.4 (4.4)	—	0.44 (s, PdMe); 3.31 (s), 3.38 (s), (NMe_2); 7.40 (m), 7.58 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{CNEt}_2)(\text{AsPh}_3)]$	CH_2Cl_2 –hexane (31)	120–122	51.0 (50.0)	4.9 (4.9)	—	0.43 (s, PdMe); 1.23 (t), 1.30 (t) (each 7.1 Hz, NCMe); 3.77 (q), 3.82 (q) (each 7.1 Hz, NCH_2 –); 7.40 (m), 7.53 (br) [Ph].
$[\text{PdMe}(\text{S}_2\text{COEt})(\text{AsPh}_3)]$	Benzene–hexane (22)	95–97	48.0 (48.1)	4.0 (4.2)	—	0.59 (s, PdMe); 1.46 (t, 7.1 Hz, OCCH_3); 4.64 (q, 7.1 Hz, OCH_2 –); 7.40 (m), 7.52 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{OEt})_2)(\text{AsPh}_3)]$	Benzene–hexane (55)	117–118	45.4 (45.1)	4.4 (4.6)	99.9 (s)	0.64 (s, PdMe); 1.38 (t, 7.1 Hz, OCCCH_3); 4.21 (m, OCCH_2 –); 7.42 (m), 7.54 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{P}(\text{O}^n\text{Pr})_2)(\text{AsPh}_3)]$	Ether–hexane (46)	87–89	47.0 (46.8)	5.2 (5.0)	101.1 (s)	0.64 (s, PdMe); 0.98 (t, 7.1 Hz, OCCCH_3); 1.74 (m, OCCH_2 –); 4.08 (m, POCH_2 –); 7.41 (m), 7.54 (m) [Ph].
$[\text{PdMe}(\text{S}_2\text{PPh}_2)(\text{AsPh}_3)]$	Acetone–hexane (53)	165–167	54.3 (55.0)	4.0 (4.2)	80.3 (s)	0.60 (s, PdMe); 7.42 (m), 7.55 (m), 7.90 (m) [Ph].

^a s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.



M = Na, K, NH₄; $\widehat{\text{S}} = \text{S}_2\text{CNR}_2$ (R = Me, Et); S₂COEt; S₂P(OR)₂ (R = Et, ⁿPr, ⁱPr); S₂PPh₂; E = P, As

All these complexes are cream-coloured crystalline solids, soluble in common organic solvents. The IR spectra of these complexes exhibited bands in the region 470–515 cm⁻¹ and 275–350 cm⁻¹ attributable to $\nu\text{Pd-C}$ [11] and $\nu\text{Pd-S}$ [12] respectively. The mass spectra of [PdMe(S₂CNEt₂)(PMePh₂)], [PdMe(S₂P(OEt)₂)(ER₃)] (ER₃ = PMePh₂, PPh₃, AsPh₃) did not show molecular ion peaks; however, peaks attributable to a demethylated species [Pd(S $\widehat{\text{S}}$)(ER₃)⁺ (m/e 455, 491, 554, 598 respectively) were observed. Spectra also showed peaks due to ER₃ and R₃ES in addition to several other peaks.

The ³¹P NMR spectra exhibited singlets for the S₂PR₂ and tertiaryphosphine ligands. However, for analogous platinum complexes ³J(³¹P–³¹P) of 5–10 Hz has been reported [6–8]. The ¹H NMR spectra showed the expected peak multiplicity and integration (Table 1). The complexes containing tertiaryphosphines displayed a doublet for palladium–methyl protons due to phosphorus coupling ³J(³¹P–¹H) ~ 4.5 Hz. As is evident from Table 1, the chemical shift of the palladium–methyl resonance is influenced by the type of dithiolate ligand. The signal is deshielded in the following order of the dithiolate ligand: S₂CNR₂ < S₂COR < S₂PR₂. As reported in other cases [6,9,10] the R groups on dialkyldithiocarbamate ligands are non-equivalent. Thus two separate sets of resonances were observed for NR₂ protons. The methyl groups of the OⁱPr moiety of S₂P(OⁱPr)₂ are anisochronous, as two doublets were observed in the ¹H NMR spectra of [PdMe(S₂P(OⁱPr)₂)(PR₃)].

3. Experimental details

All preparation were carried out under a nitrogen atmosphere. Solvents were dried, degassed and distilled prior to use. NaS₂CNR₂ (R = Me, Et), PMePh₂, PPh₃, AsPh₃ were obtained from commercial sources. K[S₂COEt] [13], NaS₂PPh₂ [14] NH₄S₂P(OR)₂ [15], [Pd₂Me₂(μ-Cl)₂(PMePh₂)₂] [16] [PdMeCl(cod)] [17] were prepared according to literature methods. IR spectra were recorded as Nujol mulls between CsI plates on

a Perkin–Elmer-783 spectrometer. NMR spectra (¹H and ³¹P{¹H}) were recorded in 5 mm NMR tubes in CDCl₃ on a Varian XL-300 NMR spectrometer. Chemical shifts were referenced to internal TMS (Me₄Si) for ¹H and external 85% H₃PO₄ for ³¹P. Mass spectra of some of the respective complexes were recorded on a VG Micromass 7070F instrument. Microanalyses of the compounds were carried out by the Analytical Chemistry Division of this research centre.

3.1. Preparation of [PdMe(S₂COEt)(PMePh₂)]

To a benzene solution of [Pd₂Me₂(μ-Cl)₂(PMePh₂)₂] (103 mg, 0.144 mmol), an ethanolic solution (5 ml) of KS₂COEt (46 mg, 0.288 mmol) was added with vigorous stirring at room temperature. The reaction mixture was stirred at room temperature for 4 h. The solvents were removed in vacuo and the residue was extracted with diethyl ether (3 × 10 ml) and filtered. The filtrate was concentrated to 1 ml and hexane (2 ml) was added, which on cooling in a freezer gave pale yellow crystals (78 mg, 61%). Other complexes were prepared similarly.

3.2. Preparation of [PdMe(S₂P(OEt)₂)(AsPh₃)]

To a benzene solution of [PdMeCl(cod)] (99 mg, 0.373 mmol), solid triphenylarsine (118 mg, 0.386 mmol) was added with stirring, which was continued for 30 min. To this, a solution of NH₄S₂P(OEt)₂ (78 mg, 0.384 mmol) in ethanol (5 ml) was added and the whole was stirred for 4 h at room temperature. (If the sequence of addition of ligands is reversed, i.e. first dithio ligand followed by neutral ligand, considerable decomposition was noticed. However, this sequence of addition of ligands was adopted for the preparation of analogous platinum complexes [7,8].) The solvents were removed in vacuo and the residue was extracted with benzene and filtered. This was passed through a short Florisil column. The volume was reduced to 2 ml and hexane added. This solution on cooling gave a cream-coloured solid (126 mg, 55%).

The complexes with triphenylphosphine and triphenylarsine were prepared in a similar fashion. Ammonium salts of the dialkyldithiophosphates were dissolved in an alcohol corresponding to the alkoxy group on phosphorus. Analytical data for these complexes are given in Table 1.

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