Inorganica Chimica Acta, *144* (1988) 157–162

O,*O*-Alkylene Dithiophosphates of Palladium(II) and their Adducts with Triphenylphosphine

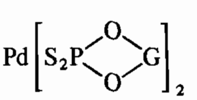
C. P. BHASIN, G. SRIVASTAVA and R. C. MEHROTRA

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

(Received June 10, 1987)

Abstract

The diamagnetic square-planar, *O*,*O*-alkylene dithiophosphates of palladium(II) with the general formula,



(where $G(OH)_2$ = 2,3-dimethylbutane-2,3-diol; butane-2,3-diol; 2-methylpentane-2,4-diol and 2,2-dimethylpropane-1,3-diol) have been synthesized by the reactions of potassium tetrachloropalladate(II) with ammonium alkylene dithiophosphates or the parent alkylene dithiophosphoric acid in 1:2 molar ratios. These compounds are orange or brown coloured solids and except for bis(neopentylene dithiophosphato)palladium(II), they are soluble in halocarbons ($CHCl_3$ and CH_2Cl_2). IR, NMR (^1H and ^{31}P) and electronic spectra along with magnetic data indicate four-coordinated planar geometry for these derivatives. With triphenylphosphine, the above derivatives form 1:1 solid halocarbon soluble adducts, the structures of which have been elucidated by low temperature ^{31}P NMR spectra.

Introduction

In contrast to considerable published work on the ligating properties of dialkyl dithiophosphoric acids to transition metals [1] including palladium and platinum [2–4], similar studies with their alkylene analogues [5] have attracted scant attention [6–8]. In continuation of our earlier work, on alkylene dithiophosphates of nickel [9–11] and platinum [12], we report in this paper the synthesis and characterization of palladium(II) alkylene dithiophosphates and their adducts with triphenylphosphine. Structural features of these derivatives have been discussed with the help of IR, ^1H NMR, ^{31}P NMR, electronic spectral and magnetic susceptibility measurements.

Experimental

In all the experiments, potassium chloropalladate was prepared *in situ* by the reaction of palladium(II) chloride and potassium chloride.

Reaction of Ammonium Tetramethylethylene Dithiophosphate with Palladium Chloride and Potassium Chloride

To an aqueous solution (~30 ml) containing palladium chloride (0.244 g; 1.37 mmol) and potassium chloride (0.235 g; 3.15 mmol) was added dropwise an aqueous solution (~15 ml) of ammonium tetramethylethylene dithiophosphate (0.968 g; 4.28 mmol) with simultaneous stirring for ~45 min. An orange precipitate was separated out which was filtered, washed with ether and crystallized from dichloromethane/acetone mixture.

Reaction of 2,3-Butylene Dithiophosphoric Acid with Palladium(II) Chloride and Potassium Chloride

Bis(2,3-butylene dithiophosphato)palladium(II) was obtained as a blackish brown precipitate by stirring a mixture of palladium chloride (0.275 g; 1.55 mmol in ~10 ml water), potassium chloride (0.280 g; 3.75 mmol in ~10 ml water) and 2,3-butylene dithiophosphoric acid (0.941 g; 5.11 mmol in ~10 ml ethanol) for ~45 min at room temperature. The product was crystallized from dichloromethane/acetone mixture.

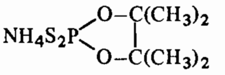
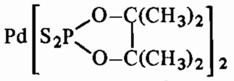
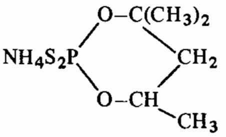
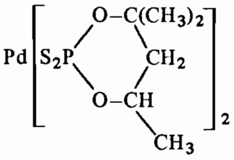
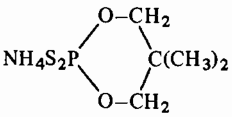
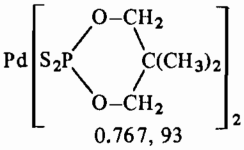
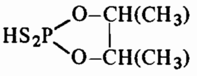
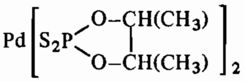
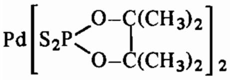
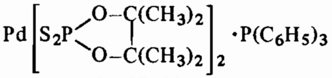
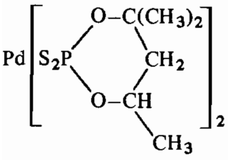
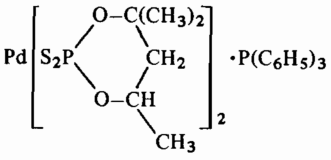
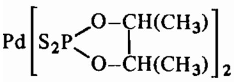
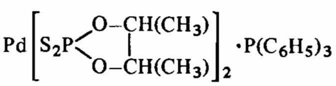
Relevant data for the similar synthesis of other compounds are given in Table I.

Reaction of Bis(tetramethylethylene Dithiophosphato)palladium(II) with Triphenylphosphine in 1:1 Molar Ratio

Triphenylphosphine (0.227 g; 0.866 mmol), dissolved in dichloromethane, was added slowly to bis(tetramethylethylene dithiophosphato)palladium(II) (0.376 g; 0.712 mmol) in hot dichloromethane. On addition the orange colour of solution became yellow. The mixture was kept at 0 °C, after addition of 10–15 ml acetone. Yellow crystals were separated.

0020-1693/88/$3.50

TABLE I. Synthesis of Palladium(II) Alkylene Dithiophosphates and Their Adducts

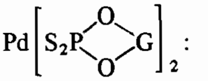
Reactants (g)			Product (g), yield (%)	Colour (melting point (°C))	Analysis (%) Found (calc.)	
					Pd	S
$PdCl_2$ 0.244	KCl 0.235	 0.968	 0.599, 83	orange (254, decomp.)	20.23 (20.12)	24.20 (24.22)
$PdCl_2$ 0.225	KCl 0.206	 0.875	 0.594, 90	brown (230, decomp.)	20.01 (20.12)	24.16 (24.22)
$PdCl_2$ 0.272	KCl 0.242	 0.995	 0.767, 93	orange (240, decomp.)	21.13 (21.24)	25.76 (25.58)
$PdCl_2$ 0.275	KCl 0.232	 0.941	 0.524, 72	blackish brown (248, decomp.)	22.00 (22.50)	27.32 (27.11)
$PdCl_2$ 0.293	KCl 0.299	$NaS_2P(OC_2H_5)_2$ 1.07	$Pd[S_2P(OC_2H_5)_2]_2$ 0.635, 81	orange (116)	22.37 (22.31)	26.62 (26.89)
 0.376		$P(C_6H_5)_3$ 0.227	 0.467, 83	light yellow (260, decomp.)	13.65 (13.45)	16.07 (16.20)
 0.185		$P(C_6H_5)_3$ 0.093	 0.205, 74	brownish yellow (240, decomp.)	13.53 (13.45)	16.08 (16.20)
 0.414		$P(C_6H_5)_3$ 0.268	 0.374, 60	dark yellow (248, decomp.)	14.38 (14.44)	17.36 (17.43)
$Pd[S_2P(OC_2H_5)_2]_2$ 0.197		$P(C_6H_5)_3$ 0.113	$Pd[(S_2P(OC_2H_5)_2]_2 \cdot P(C_6H_5)_3$ 0.217, 65	yellow (118)	14.52 (14.36)	17.30 (17.34)

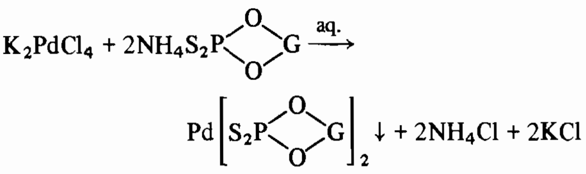
Triphenylphosphine adducts of bis(hexylene dithiophosphato)palladium(II) and bis(2,3-butylene dithiophosphato)palladium(II) were prepared by similar methods.

IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1}. ^{1}H NMR spectra were recorded in $CDCl_3$ on an X-L-100 A spectrometer, using TMS as internal standard. ^{31}P NMR spectra of bis(alkylene dithiophosphato)palladium(II) (in $CDCl_3$) and their adducts (in CH_2Cl_2) were recorded on Jeol-FX-2 100 spectrometer and Nicolet 300 MHz FT NMR spectrometer respectively, using 85% H_3PO_4 as an external standard. Electronic spectra were recorded in $CHCl_3$ with an S.P. 8-100 UV–Vis Pye Spectrophotometer.

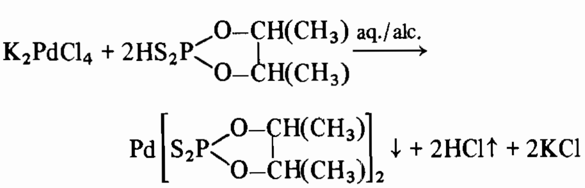
Results and Discussion

Soluble potassium tetrachloropalladate(II), obtained by mixing palladium chloride and potassium chloride in water, reacts with ammonium *O,O*-alkylene dithiophosphate or the parent alkylene dithiophosphoric acid in 1:2 molar ratio to afford orange or brown coloured complexes of the type,





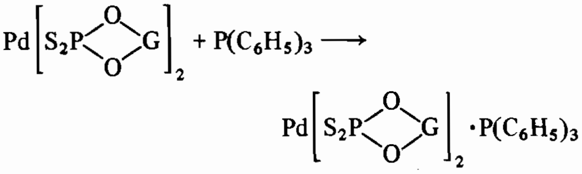
(where G = $-(CH_3)_2C{\cdot}C(CH_3)_2-$; $-(CH_3)_2{\cdot}C{\cdot}CH_2{\cdot}CH(CH_3)-$; $-CH_2{\cdot}C(CH_3)_2{\cdot}CH_2-$)



A slight excess of ligand is used to avoid the formation of bridged complexes of the type dtp-$PdCl_2Pd$dtp (dtp = alkylene dithiophosphate) [13].

Except for bis(neopentylene dithiophosphato)-palladium(II), the above compounds are soluble in halocarbons ($CHCl_3$ and CH_2Cl_2) and can be crystallized from a dichloromethane/acetone mixture.

The 1:1 adducts of bis(alkylene dithiophosphates) of palladium(II) with triphenylphosphine have been readily obtained by heating a mixture of the two components in dichloromethane and then cooling to 0 °C.



IR Spectra

IR spectra of the palladium bis(alkylene dithiophosphates) show two bands in the region 1145–1045 and 900–860 cm^{-1} which may be assigned to (P)–O–C and P–O–(C) stretching modes [14], while the band in the region 990–930 cm^{-1} is due to dioxaphospholane and dioxaphosphorinane ring vibrations [15, 16]. A strong band in the region 710–670 cm^{-1} in the spectra of *O,O*-alkylene dithiophosphoric acids and their ammonium salts which can be attributed to ν(P=S) is shifted to lower frequency by ~30 cm^{-1} in the corresponding palladium derivatives. The bands observed in the region 560–530 cm^{-1} are attributed to P–S symmetric and asymmetric vibrations (Table II).

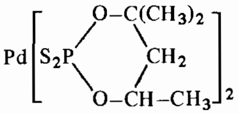
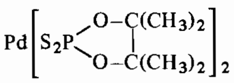
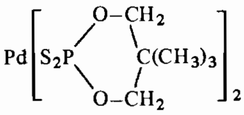
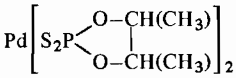
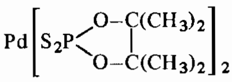
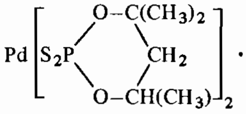
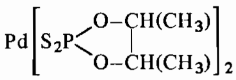
NMR Spectra

The ^{1}H NMR spectra show the characteristic resonances of the corresponding alkylene as well as those of the aryl protons. The sharp singlet present at 3.7 ppm characteristic of the S–H proton in 2,3-butylene dithiophosphoric acid is absent in the ^{1}H NMR spectrum of the corresponding palladium(II) bis(2,3-butylene dithiophosphate) indicating the formation of a Pd–S bond. The complex multiplet due to the protons of the phenyl group attached to the phosphorus atom in 1:1 adducts appears in the region δ 7.35 to 7.80 ppm (Table III).

The ^{31}P chemical shift values in the spectra of bis(alkylene dithiophosphato)palladium(II) are higher than those of the parent acids (Table IV).

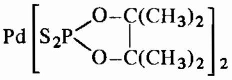
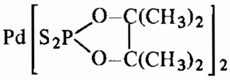
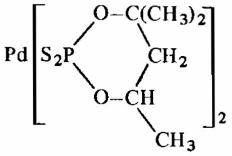
Considering the NMR evidence for cleavage of metal sulphur bond in the formation of equimolar adducts of triphenylphosphine with acyclic analogues of these complexes [4], the triphenylphosphine adducts of bis(alkylene dithiophosphato)palladium(II) have been studied by low temperature ^{31}P NMR spectra to throw light on their structure in solution. The ^{31}P NMR spectrum of the triphenylphosphine adduct of bis(2,3-butylene dithiophosphato)-palladium(II) shows two peaks at room temperature, one for the phosphorus of the dithio moiety at δ 115.62 ppm and the other for the phosphorus of triphenylphosphine at δ 31.13 ppm. At −90 °C the appearance of two peaks in the region of the dithiophosphate moiety (at δ 119.51 ppm and δ 116.04 ppm) shows two non-equivalent phosphorus (Fig. 1), which become equivalent at room temperature due to fast exchange. In the case of the triphenylphosphine adduct of bis(tetramethyl-

TABLE II. IR Spectral Data[a] of Pd(II) *O,O*-Alkylene Dithiophosphates

Compound	(P)–O–C	P–O–(C)	Ring vibrations	P=S	P–S
	1045m	890m	970s	625s 665w	530w
	1140m	880m	935s	650s	500w
	1045s	860m	990s	675s	550w
	1040m	865m	930s	640s	560w
 $\cdot P(C_6H_5)_3$	1145m	900s	930s	700s 600s	540m
 $\cdot P(C_6H_5)_3$	1050m	880m	970s	630s 660s	540w
 $\cdot P(C_6H_5)_3$	1040m	860m	935s	650s	560w

[a] m = medium, s = strong, w = weak.

TABLE III. PMR spectral Data of Pd(II) *O,O*-Alkylene Dithiophosphates

Compound	Chemical shift (δ)
	1.5(s)
 $\cdot P(C_6H_5)_3$	1.35(s), 24H(CH_3) 7.4–7.7(m), 15H(C_6H_5)
	1.38–2.05(m), 22H(CH_2, CH_3) 4.55–5.05(m), 2H(CH)

(continued)

TABLE III. *(continued)*

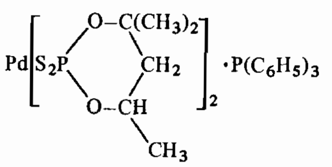
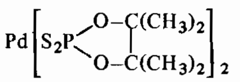
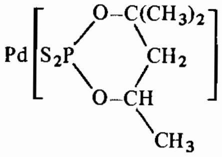
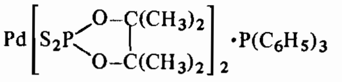
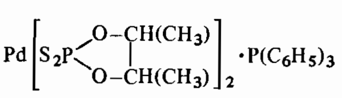
Compound	Chemical shift (δ)
	1.25–2.0(m), 22H(CH_2, CH_3) 4.60–5.0(m), 2H(CH) 7.35–7.80(m), 15H(C_6H_5)
$Pd[S_2P(OC_2H_5)_2]_2$	1.20–1.45(t), 12H(CH_3) 4.0–4.50(q), 8H(CH)

TABLE IV. ^{31}P Spectral Data of *O,O*-Alkylene Dithiophosphates and their Adducts with Triphenylphosphine

Compound	Chemical shift (δ)
	117.00
	95.00
	
Room temperature	117.09 112.69 30.29 –5.02
–90 °C	114.87 32.48
	
Room temperature	115.62 31.13
–90 °C	119.51 116.04 33.91

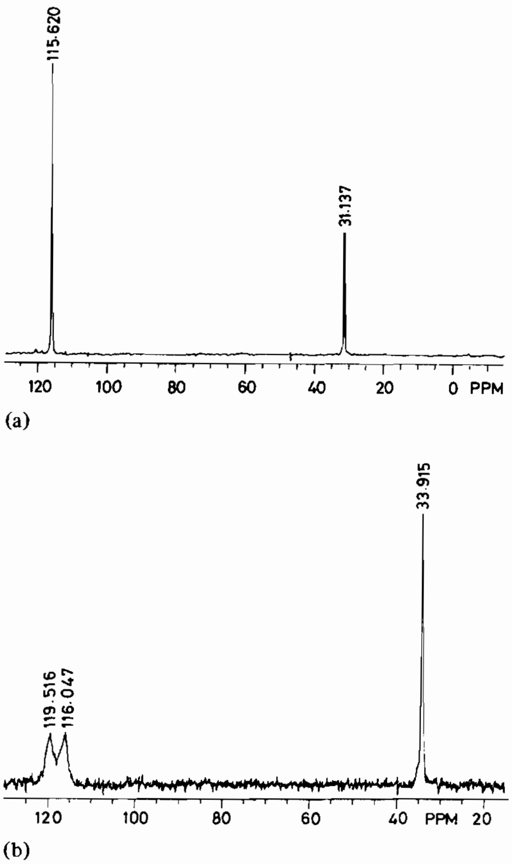


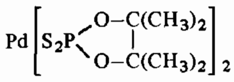
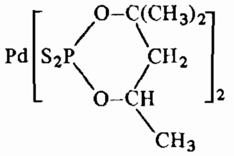
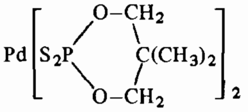
Fig. 1. ^{31}P NMR spectral data of the triphenylphosphine adduct of bis(2,3-butylene dithiophosphato)palladium(II): (a) room temperature, (b) at –90 °C.

ethylene dithiophosphato)palladium(II) at room temperature four peaks are observed which indicate the dissociation of the adduct in solution. However, at –90 °C the peaks for the free complex and the free triphenylphosphine disappear, but unlike the triphenylphosphine adduct of bis(2,3-butylenedithiophosphato) palladium(II) in the region of the dithiophosphate moiety two peaks are not observed, but the broadening of the room temperature peak indicates the presence of two different peaks which may separate on further lowering of temperature.

Electronic Spectral and Magnetic Measurements

Electronic spectra of a few representative compounds have been recorded. The transitions have been reported in Table V. The similarity of these transitions to that reported earlier for dialkyl di-

TABLE V. Electronic Spectra of Palladium(II) Bis(*O*,*O*-alkylene Dithiophosphates)

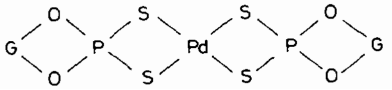
Compound	λ_{max} (nm)
	440, 322
	464, 324
	464, 328
pd[$S_2P(OC_2H_5)_2]_2$	460, 326
Pd[$S_2P(OC_2H_5)_2]_2$^{a}	460, 340

^{a}Scanned in acetone.

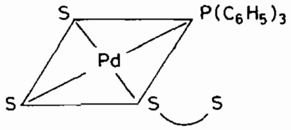
thiophosphates of palladium(II) [13] indicates the four coordination of the central palladium atom.

Magnetic measurements of bis(alkylene dithiophosphato)palladium and their adducts show the diamagnetic nature of these complexes, which confirms their planar four-coordinate structure.

The above spectral and magnetic studies indicate the following square-planar structure for palladium(II) bis(*O*,*O*-alkylene dithiophosphates):



In view of the above, the following tentative structure can be assigned for the 1:1 adducts:



References

1 J. R. Wasson, G. M. Woltermann and H. J. Stoklosa, *Top. Curr. Chem., 35,* 65 (1973).

2 J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.,* 254 (1973).

3 M. C. Cornock and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.,* 501 (1977).

4 J. P. Fackler, L. D. Thompson, J. B. Lin, T. A. Stephenson, R. O. Gould, J. M. C. Alison and A. J. F. Faser, *Inorg. Chem., 21,* 2397 (1982).

5 H. P. S. Chauhan, C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Phosphorus Sulphur, 15,* 99 (1983).

6 V. F. Toropova, R. A. Cherkasov, N. I. Savel'eva and E. I. Petrova, *Zh. Obshchei. Khim., 44,* 531 (1974); *Chem. Abstr., 81,* 6771 (1974).

7 V. V. Ovchinikov, A. R. Garifzyanov, N. I. Savel'eva, R. A. Cherkasov and V. F. Toropova, *Vses. Chugaev. Soveshch. PO Khimi Kompleks. Soedin, 1978,* 296 (1978); *Chem. Abstr., 90,* 110802 (1979).

8 V. V. Ovchinikov, A. R. Garifzyanov, N. I. Savel'eva and V. F. Toropova, *Izy. Vyssh. Uchebn. Zaved, Khim. Khim. Tekhnol, 22,* 654 (1979); *Chem. Abstr., 91,* 113225 (1979).

9 C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta, 77,* L131 (1983).

10 C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta, 128,* 69 (1987).

11 C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Indian J. Chem., 26A,* 834 (1987).

12 C. P. Bhasin, G. Srivastava and R. C. Mehrotra, *Inorg. Chim. Acta, 131,* 195 (1987).

13 C. K. Jørgensen, *J. Inorg. Nucl. Chem., 24,* 1571 (1962).

14 D. E. C. Corbridge, *Top. Phosphorus Chem., 6,* 235 (1969).

15 J. Cason, W. N. Baxter and W. DeAcetis, *J. Org. Chem., 24,* 247 (1959).

16 R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.,* 4376 (1960).