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Chemistry of 2-thienyl derivatives of arsenic and antimony: synthesis and characterization; X-ray structure of $[PdCl_2\{(C_4H_3S)_3As\}_2]$

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Abstract

Tri-(2-thienyl)-arsine and -stibine, Th_3E (E = As; Sb), were prepared by the reaction of 2-thienylmagnesium bromide and the appropriate metal trichloride. Several derivatives of the general formulae $E(C_4H_3S)_3X_2$ (X = Cl, Br, OAc; E = As, Sb) have been prepared. So as to explore the coordination behaviour of Th_3E, a series of complexes of the type $MCl_2(AsTh_3)_2$, $[PdX_2(\mu\text{-}Y)_2(AsTh_3)_2]$, $[PdCl(S{^\wedge}S)(AsTh_3)]$ [M = Pd, Pt; X = Cl, Me; Y = Cl, dmpz, pz, $S{^\wedge}S = S_2P(OEt)_2$, $S_2P(OPr^i)_2$] have also been prepared. All complexes have been characterized by elemental analysis, IR and NMR spectroscopy, and show that these ligands coordinate to palladium(II) and platinum(II) through E (As or Sb) exclusively. The molecular structure of $[PdCl_2(AsTh_3)_2]$ has been established by X-ray structural analysis and reveals a square planar geometry for palladium defined by an As_2Cl_2 donor set.

Keywords: 2-Thienyl derivatives; Arsenic; Antimony; X-ray structures; $[PdCl_2\{(C_4H_3S)_3As\}_2]$

1. Introduction

Organometallic compounds of the Group V elements find extensive applications as molecular precursors in chemical vapour deposition processess (MOCVD) for the deposition of a wide variety of semiconductors. The search for better precursors with desirable properties has been a driving force for the continued current interest in the organometallic chemistry of these elements.

The V–VI compound semiconductors differ greatly from their III–V derivatives in their extrinsic properties which are influenced by non-stoichiometry. For example, incorporation of copper can convert p-type Bi_2Te_3 to n-type. The V–VI compound Bi_2Te_3 is one of the best room temperature thermocouple materials for thermoelectric cooling [1]. Thin films of As_2S_3 (band gap 2.36 eV) are used for holographic recording [2], optical memories [3], relief imaging [4], high resolution microlithography [5], etc.

Metal complexes containing chelating ditholates (such as xanthates, dithiocarbamates, dithiophosphates) have been employed as single source precursors to deposit metal sulphide films [6]. Group V organometallic complexes derived from such ligands have been investigated quite extensively [7]. In this connection, a family of new single source precursors of Group V elements containing a thienyl group may be conceived.

Interestingly synthesis, spectroscopy [8–11] and coordination chemistry [12–15] of several 2-thienylphosphines have been reported, but the thienyl derivatives of heavier Group V congenors are conspicously missing. With this perspective it was considered worthwhile to synthesize 2-thienyl derivatives of arsenic and antimony, and to study some of their chemical and physical properties.

2. Experimental

2.1. Materials and instrumentation

All the reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade sol-

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vents. 2-Bromothiophene was purchased from Fluka and distilled prior to use. $AsCl_3$ and $SbCl_3$ were obtained from commercial sources and distilled before use. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300, 75.46 and 121.5 MHz, respectively. Chemical shifts are relative to internal $CHCl_3$ peak (δ: 7.26 ppm for ^1H and 77.0 for $^{13}C\{^1H\}$) and external 85% H_3PO_4 for $^{31}P\{^1H\}$. IR spectra were recorded as Nujol mulls on a CsI plates on a Bomen MB-102 FT IR spectrophotometer in the range 4000–200 cm^{-1}. Microanalysis of the complexes was carried out in the Analytical Chemistry Division of BARC.

2.2. Preparations

2.2.1. $[(C_4H_3S)_3As]$ (Th_3As)

To an ethereal solution of 2-thienylmagnesium bromide, C_4H_3SMgBr [prepared from Mg turnings (4.7 g, 0.19 mol) and C_4H_3SBr (31.90 g, 19.0 ml, 0.19 mol) in 300 ml ether], a solution of $AsCl_3$ (9.0 g, 0.05 mol) in Et_2O at 0 °C was added over a period of 2 h [16]. The reaction mixture was stirred at room temperature (r.t.) for 3 h followed by refluxing for 1 h. The reactants were cooled to 0 °C and treated with deoxygenated aqueous NH_4Cl solution (80–100 ml). The ether layer was separated, dried over $CaCl_2$ and passed through a Florisil column. The solvent was evaporated in vacuo leaving a yellow liquid, which was distilled under vacuum to give a pale-yellow oil in 98% yield. b.p. 150–160/0.4 mm. Pertinent data are given in Table 1.

2.2.2. $[(C_4H_3S)_3Sb]$

To an ethereal solution of 2-thienylmagnesium bromide, C_4H_3SMgBr [prepared from Mg turnings (4.2 g, 0.17 mol) and C_4H_3SBr (28.2 g, 16.7 ml, 0.17 mol) in 300 ml ether], a solution of $SbCl_3$ (9.61 g, 0.042 mol) in Et_2O at 0 °C was added over a period of 2 h. The reaction mixture was stirred at r.t. for 3 h followed by refluxing for 1 h. The reactants were cooled to 0 °C and treated with deoxygenated aqueous NH_4Cl solution (80–100 ml). The ether layer was separated, dried over $CaCl_2$ and passed through a Florisil column. The solvent was evaporated in vacuo leaving behind a yellow liquid which was recrystallized from C_6H_{14} to yield $[(C_4H_3S)_3Sb]$ as an off-white crystalline solid in 65% yield (10.2 g).

2.2.3. $[(C_4H_3S)_3AsCl_2]$

To an ice cooled C_6H_{14} solution (30 ml) of $[(C_4H_3S)_3As]$ (4.0 g, 12.3 mmol), chlorine gas was bubbled until precipitation of a white solid. This was accompanied by a colour change of the solution from pale-yellow to orange, to light-pink and finally, the solution turned yellow. The supernatent was decanted and solid washed with C_6H_{14} and recrystallized from C_6H_6–C_6H_{14} to yield $[(C_4H_3S)_3AsCl_2]$ as an off-white solid (4.17 g, 85%).

2.2.4. $[(C_4H_3S)_3SbBr_2]$

To an ice cooled C_6H_6–C_6H_{14} (2:1) solution (30 ml) of $[(C_4H_3S)_3Sb]$ (3.2 g, 8.75 mmol), a CCl_4 solution of bromine (1.40 g, 8.76 mmol) was added dropwise with continuous stirring until the brown colour of bromine

Table 1
Analytical data of tri-(2-thienyl)arsine and -stibine and their complexes

Compound	Recrystallization solvent (% yield)	M.p. (°C)	Analysis Found (Calc.)		
			C	H	N
$[(C_4H_3S)_3As]$	liquid (98)		43.8 (44.4)	2.4 (2.8)	
$[(C_4H_3S)_3Sb]$	hexane (65)	45	38.7 (38.8)	2.4 (2.4)	
$[(C_4H_3S)_3AsCl_2]$	benzene–hexane (85)	123–124	34.9 (36.5)	1.9 (2.3)	
$[(C_4H_3S)_3SbBr_2]$	benzene–hexane (50)	175–176	27.0 (27.1)	1.7 (1.7)	
$[(C_4H_3S)_3Sb(OAc)_2]$	benzene–CH_2Cl_2–hexane (39)	174–176	39.8 (39.3)	2.7 (3.1)	
$[PdCl_2(Th_3As)_2]$	CH_2Cl_2–hexane (70)	222 [a]	35.2 (34.9)	2.0 (2.2)	
$[PtCl_2(Th_3As)_2]$	CH_2Cl_2–hexane (42)	230 [a]	30.8 (31.5)	1.7 (2.0)	
$[PtCl_2(PPr^n_3)(Th_3As)]$	CH_2Cl_2–hexane (22)	142–143	32.6 (33.6)	3.6 (4.0)	
$[PtCl_2(PMe_2Ph)(Th_3As)]$	CH_2Cl_2–hexane (82)	215	33.1 (33.0)	2.5 (2.8)	
$[PtCl_2(PMePh_2)(Th_3As)]$	CH_2Cl_2–hexane (70)	197	37.3 (38.0)	2.5 (2.8)	
$[PtCl(P^\wedge C)(Th_3As)]$	CH_2Cl_2–hexane (40)	185	36.8 (38.1)	4.1 (4.7)	
$[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$	CH_2Cl_2 (75)	210 [a]	29.3 (28.7)	1.5 (1.8)	
$[Pd_2Me_2(\mu\text{-}Cl)_2(Th_3As)_2]$	CH_2Cl_2–hexane (55)	158–159 [a]	32.1 (32.5)	2.3 (2.5)	
$[PdCl(\mu\text{-dmpz})(Th_3As)]_2$	CH_2Cl_2–hexane (53)	236 [a]	35.7 (36.4)	2.3 (2.8)	4.4 (4.9)
$[PdMe\ (\mu\text{-dmpz})(Th_3As)]_2$	CH_2Cl_2–hexane (57)	182 [a]	39.5 (40.0)	3.2 (3.5)	5.2 (5.2)
$[PdMe\ (\mu\text{-pz})(Th_3As)]_2$	CH_2Cl_2–hexane (40)	120	38.1 (37.5)	2.9 (2.9)	5.0 (5.5)
$[PdCl\{S_2P(OPr^i)_2\}(Th_3As)]$	CH_2Cl_2–hexane (51)	162 [a]	31.3 (31.7)	2.9 (3.4)	
$[PdCl\{S_2P(OEt)_2\}(Th_3As)]$	benzene–hexane (42)	167 [a]	28.9 (29.5)	2.4 (2.9)	

[a] Melts with decomposition.

persisted with a concomitant formation of a white solid. The supernatent was decanted and solid washed with C_6H_{14} and recrystallized from C_6H_6–C_6H_{14} to yield $[(C_4H_3S)_3SbBr_2]$ as an off-white crystalline solid (2.32 g, 50%).

2.2.5. $[(C_4H_3S)_3Sb(OAc)_2]$

To a C_6H_6 solution of $[(C_4H_3S)_3SbBr_2]$ (422 mg, 0.79 mmol), solid AgOAc (265 mg, 1.59 mmol) was added with stirring which was continued for 6 h. Precipitated AgBr was removed by filtration and the solvent was evaporated in vacuo to give a white solid which on recrystallization from C_6H_6–CH_2Cl_2–C_6H_{14} yielded a colourless crystalline solid in 39% yield (150 mg).

2.2.6. $[PdCl_2(Th_3As)_2]$

To a C_6H_6 solution of Th_3As (1.75 g, 5.4 mmol), solid $[PdCl_2(PhCN)_2]$ (1.03 g, 2.7 mmol) was added and the reactants were stirred at r.t. for 6 h. The solvent was removed under vacuum leaving behind an orange–brown solid which was washed with C_6H_{14} (3 × 10 ml) and recrystallized from CH_2Cl_2–C_6H_{14} as an orange crystalline solid in 70% yield (1.5 g).

$[PtCl_2(Th_3As)_2]$ was prepared similarly from Th_3As and $[PtCl_2(PhCN)_2]$ as a yellow solid in 42% yield.

2.2.7. $[PtCl_2(PPr^n_3)(Th_3As)]$

To a CH_2Cl_2 solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PPr^n_3)_2]$ (48 mg, 0.056 mmol), a solution of Th_3As (36 mg, 0.11 mmol) was added with stirring. A clear pale-yellow solution was obtained almost immediately. The reactants were stirred at r.t. for 4 h after which the solvent was removed in vacuo to yield a white solid which was washed with C_6H_{14} (3 × 5 ml) and recrystallized from CH_2Cl_2–C_6H_{14} as a white crystalline solid in 22% yield (18 mg).

$[PtCl_2(PMe_2Ph)(Th_3As)]$, $[PtCl_2(PMePh_2)(Th_3As)]$ and $[PtCl(P^\wedge C)(Th_3As)]$ $(P^\wedge C = Bu^t_2PCCH_2(Me)_2)$ were prepared in a similar manner.

2.2.8. $[PdCl_2(PMePh_2)(Th_3Sb)]$

To a $CDCl_3$ solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (26 mg, 0.028 mmol), solid Th_3Sb (21 mg, 0.057 mmol) was added. A clear solution was obtained almost immediately. This solution was then studied by ^1H and ^{31}P NMR spectroscopy.

Attempted preparation of $[PdCl_2(PMePh_2)(Th_3Sb)]$.

To a $CDCl_3$ solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (27 mg, 0.036 mmol), solid Th_3Sb (28 mg, 0.075 mmol) was added. A clear solution was obtained almost immediately, although the solution turned black within a few minutes. This solution was monitored by ^{31}P NMR spectroscopy.

2.2.9. $[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$

To a MeOH solution (20 ml) of Na_2PdCl_4 (294 mg, 1.0 mmol), solid $[PdCl_2(Th_3As)_2]$ (820 mg, 0.99 mmol) was added and the reaction mixture was stirred under reflux for 4 h whereupon a brown precipitate formed. After cooling to r.t., the solid was filtered through a sintered disc, washed well with MeOH, water and finally with a small amount of absolute EtOH. It was recrystallized from CH_2Cl_2 as a brown solid in 75% yield (747 mg).

2.2.10. $[Pd_2Me_2(\mu\text{-}Cl)_2(Th_3As)_2]$

To a CH_2Cl_2 solution (15 ml) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$ (442 mg, 0.44 mmol), Me_4Sn (158 mg, 0.13 ml, 0.88 mmol) was added with stirring. An immediate colour change from dark-brown to pale-yellow and finally colourless was observed. The reaction mixture was stirred at r.t. for 4 h. The solvent was evaporated in vacuo to give a pale-yellow solid which was washed well with C_6H_{14} and recrystallized from CH_2Cl_2–C_6H_{14} to give a pale-yellow solid (233 mg, 55%).

2.2.11. $[PdCl(\mu\text{-}dmpz)(Th_3As)]_2$

To a CH_2Cl_2 solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$ (60 mg, 0.06 mmol), Nadmpz [prepared from a MeOH solution (5 ml) of dmpzH (11 mg, 0.12 mmol) and NaOH (0.005 g, 0.24 ml, 0.49 N)] was added dropwise with constant stirring. An immediate colour change from brown to pale-yellow was observed. The reactants were stirred at r.t. for 4 h after which the solvent was dried thoroughly in vacuo and extracted with CH_2Cl_2 and filtered. The solvent was evaporated under vacuum to obtain a yellow solid that was recrystallized from CH_2Cl_2–C_6H_{14} in 53% yield (35 mg).

$[PdMe(\mu\text{-}dmpz)(Th_3As)]_2$ and $[PdMe(\mu\text{-}pz)(Th_3As)]_2$ were prepared in a similar manner.

2.2.12. $[PdCl\{S_2P(OEt)_2\}(Th_3As)]$

To a C_6H_6 solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$ (63 mg, 0.063 mmol), solid $NH_4[S_2P(OEt)_2]$ (26 mg, 0.128 mmol) was added with stirring which was continued at r.t. for 4 h. It was filtered and the filtrate was concentrated in vacuo to obtain an orange oil which on recrystallization from C_6H_6–C_6H_{14} yielded an orange crystalline solid (34 mg, 42%).

$[PdCl\{S_2P(OPr^i)_2\}(Th_3As)]$ was prepared in a similar manner from $[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$ and $NH_4[S_2P(O\text{-}Pr^i)_2]$ in 51% yield.

2.3. Crystallography

Intensity data for an orange crystal of $[PdCl_2(Th_3As)_2]$ (0.18 × 0.29 × 0.29 mm) were measured at 183 K on a Bruker AXS SMART CCD diffractometer fitted with Mo Kα radiation using ω scans such that θ_{max} was 30.0°. Data were corrected for Lp as well as for absorption employing an empirical procedure [17a]. The structure was solved by heavy-atom methods [17b] and refined (anisotropic displacement parameters, H atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + 0.0508P^2 + 1.4976P]$ where $P = (F_o^2 + 2F_c^2)/3)$ by a full-matrix least-squares procedure based on F^2 [17c]. Disorder was evident for two of the thienyl groups and this was resolved by refining each of the affected thienyl groups over two positions. In effect, this meant splitting the S2/C8 and S3/C12 positions, respectively. For isotropic refinement, the site occupancy factors for the major components were 0.638(5) and 0.548(5), respectively. The atomic numbering scheme (50% probability level) is shown in Fig. 1 that was drawn with ORTEP [17d]. Calculations were performed with the teXsan package [17e].

Crystal data for $[PdCl_2(Th_3As)_2]$: $C_{24}H_{18}As_2Cl_2PdS_6$, $M = 825.9$, monoclinic, space group $P2_1/n$, $a = 8.6185(5)$, $b = 18.5077(10)$, $c = 9.4670(5)$ Å, $\beta = 108.972(1)°$, $V = 1428.04(14)$, $Z = 4$, $T = 183(2)$ K, D_{calcd}, 1.921 g cm^{-3}, μ 3.590 mm^{-1}, 4147 unique reflections, 3659 reflections with $I \geq 2\sigma(I)$, $R_1(F_o)$ and $wR_2(F_o)$ $(I \geq 2s(I))$: 0.035 and 0.093, $R_1(F_o)$ and $wR_2(F_o)$ (all data) 0.040, 0.0.095, ρ_{max} 0.97 e Å^{-3}.

3. Results and discussion

Tri-(2-thienyl)-arsine and -stibine, Th_3E (Th = C_4H_3S; E = As, Sb), were prepared by the reaction of the metal trichloride MCl_3 with 2-thienylmagnesium bromide in dry ether. The arsine is a yellow liquid while the stibine is a crystalline solid. Selected spectroscopic data for the above and their complexes are collected in Table 2. The IR spectra displayed a band of medium to strong intensity at 476 ν(As–C) and 473 ν(Sb–C) cm^{-1}, respectively attributable to ν(M–C) stretchings. The ^{1}H NMR spectra displayed characteristic resonances of the thienyl group. In the ^{13}C NMR spectra, the C-2 resonance of the stibine is shielded compared with the arsine derivative (approximately 6 ppm) while the C-5 resonance of Th_3Sb was slightly deshielded (approximately 3 ppm) compared with that for the arsine analogue. The C-3 and C-4 resonances show very little change on increasing the size of the metal atom.

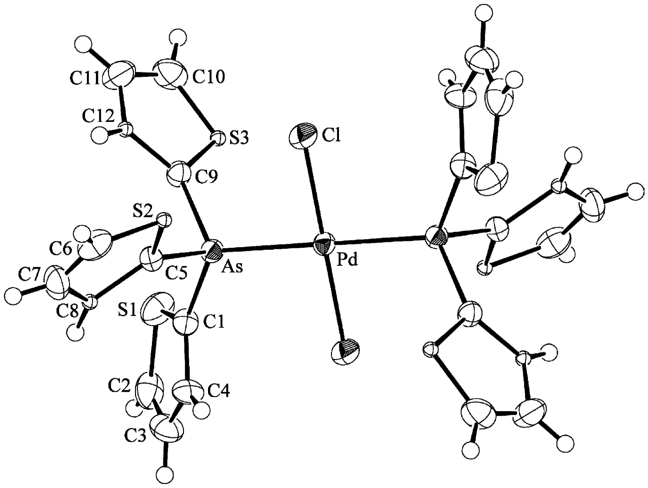

Fig. 1. Molecular structure and crystallographic numbering scheme for $[PdCl_2(Th_3As)_2]$. Selected geometric parameters (Å; °): Pd–As 2.4091(3); Pd–Cl 2.2865(7); Cl–Pd–As 88.08(2), Pd–As–C1 120.95(9), Pd–As–C5 109.72(8), Pd–As–C9 116.09(9).

Oxidation of Th_3M with halogens readily afforded the dihalides Th_3MX_2 (X = Cl; Br) in fairly good yields. Th_3AsCl_2 was highly hygroscopic while Th_3SbBr_2 was obtained as an off-white crystalline solid. The IR spectrum of Th_3AsCl_2 showed a band at 350 cm^{-1}, absent in the spectrum of Th_3As, that was assigned to ν(As–Cl). Similarly, a strong band at 289 cm^{-1} in the spectra of Th_3SbBr_2 may be assigned to ν(Sb–Br). Medium to strong bands at 463 and 454 cm^{-1} were assigned to ν(As–C) and ν(Sb–C), respectively. In the ^{1}H NMR spectra, the H-3 and H-5 proton resonances of the 2-thienyl group are considerably deshielded on oxidation. In the ^{13}C{^{1}H} NMR spectra of these dihalides, C-2, C-3 and C-5 resonances are slightly shifted (3–4 ppm) than those of the corresponding signals for Th_3E. The C-4 resonance was little affected on oxidation with halogens.

The reaction of Th_3SbBr_2 with 2 equiv. of AgOAc in benzene solution yielded $[Th_3Sb(OAc)_2]$ as a white crystalline solid. A medium intensity band at 1569 cm^{-1}, absent in the spectrum of Th_3SbBr_2 may be assigned to ν(C=O). The ^{1}H NMR spectrum displayed a single resonance at δ 2.09 ppm for the acetate protons. In the ^{13}C{^{1}H} NMR spectrum, a singlet at δ 175.7 ppm has been attributed to carbonyl carbon of the acetate.

The coordination chemistry of thienyl phosphines has been explored to some extent [12–15]. These ligands in general coordinate to metal centres via the phosphorus atom only. However, recently it has been demonstrated that Ph_2ThP can also act as a bidentate ligand in $[Re_2(CO)_8\{\mu\text{-}PPh_2(C_4H_3S)\}]$, coordinating to rhenium through both the phosphorous and sulphur atoms of the Ph_2ThP ligand [13f]. In view of the various possible bonding modes of this family of ligands it was thought of interest to examine coordination chemistry of Th_3E ligands (E = As or Sb).

Reaction of $[MCl_2(PhCN)_2]$ (M = Pd or Pt) with 2 mol equiv. of Th_3As yielded $[MCl_2(Th_3As)_2]$ as yellow crystalline solids. The palladium complex displayed only one ν(Pd–Cl) stretching band at 328 cm^{-1} indicating a *trans* configuration. Only one set of resonances are observed in the ^{1}H NMR spectrum. By contrast, the ^{1}H NMR spectrum of the platinum complex exhibited two sets of resonances; the minor set in approximately 10%

Table 2
IR and NMR data of tri-(2-thienyl)arsine and -stibine and their complexes

Compound	^{1}H NMR data (δ)	^{13}C{^{1}H} NMR data (δ)	^{31}P{^{1}H} NMR data (δ)	IR (cm^{-1})
$[(C_4H_3S)_3As]$	7.24 (dd, 3.3, 4 Hz, H-4); 7.45 (d, 3.3 Hz, H-3); 7.66 (d, 3.8 Hz, H-5)	127.7 (C-4); 131.0 (C-3); 134.3 (C-5); 138.3 (C-2)		476 νAs–C
$[(C_4H_3S)_3Sb]$	7.23 (dd, 3.3, 4.8 Hz, H-4); 7.40 (dd, 0.8, 3.3 Hz, H-3); 7.69 (dd, 0.8, 4.8 Hz, H-5)	128.1 (C-4); 132.5 (C-3); 132.7 (C-2); 137.1 (C-5)		473 νSb–C
$[(C_4H_3S)_3AsCl_2]$	7.19 (t, 4.3 Hz, H-4); 7.74 (d, 4.3 Hz, H-3); 8.28 (d, 3.0 Hz, H-5)	127.3 (C-4); 134.3 (C-3); 137.9 (C-5/C-2)		463 νAs–C 350 νAs–Cl
$[(C_4H_3S)_3SbBr_2]$	7.33 (dd, 3.8, 4.8 Hz, H-4); 7.85 (dd, 0.8, 4.8 Hz, H-3); 8.40 (dd, 0.8, 4.0 Hz, H-5)	128.0 (C-4); 135.4 (C-3); 136.2 (C-2); 140.0 (C-5)		454 νSb–C 289 νSb–Br
$[(C_4H_3S)_3Sb(OAc)_2]$	2.09 (s, CH_3CO_2); 7.14 (m); 7.35 (m); 7.66 (m)	20.2 (CH_3CO_2); 125.1, 126.8 (each singlet, for all 4 carbon atoms); 175.5 ($-CO$)		473 νSb–C 1569 νC=O
$[PdCl_2(Th_3As)_2]$	7.18 (t, 4 Hz, H-4); 7.65–7.70 (m, H-3, H-5)			472 νAs–C 328 νPd–Cl
$[PtCl_2(Th_3As)_2]$	7.04 (t, H-4); 7.37 (dd, H-3, H-5) [a]; 7.19 (t, 4.3 Hz, H-4); 7.56–7.67 (m, H-3, H-5) [b]			472 νAs–C 279, 328 νPt–Cl
$[PtCl_2(PPr^n_3)(Th_3As)]$	0.93 (t, 7 Hz, PCH_2CH_2Me); 1.48–1.67 (m, PCH_2CH_2); 7.20 (t, 5 Hz, H-4); 7.65 (d, 4 Hz); 7.70 (d, 4 Hz)		−2.1 ^{1}J(Pt–P) = 3288 Hz	325, 317 νPt–Cl
$[PtCl_2(PMe_2Ph)(Th_3As)]$	1.67 (d, 11 Hz, ^{3}J(Pt–H) = 32 Hz, PMe_2); 1.89 (d, 11 Hz, small 5%); 7.07 (t, 3.6 Hz, H-4); 7.16–7.65 (m, Ph, H-3, H-5)		−15.4 ^{1}J(Pt–P) = 3425 Hz −10.9 small% ^{1}J(Pt–P) = 3245 Hz	325 νPt–Cl
$[PtCl_2(PMePh_2)(Th_3As)]$	1.67 (d, 11 Hz, P*Me*); 7.03 (dd, 3.6 Hz, 4 Hz, H-4); 7.23–7.61 (m, Ph, H-3, H-5)		−2.2 ^{1}J(Pt–P) = 3491 Hz	325 νPt–Cl
$[PtCl(P^\wedge C)(Th_3As)]$	1.64 (d, 13.5 Hz, PBu^t_2); 1.48 (d, 13.8 Hz, $PCMe_2$); 1.26 (d, 13.6 Hz, PC–CH_2); 7.15 (t, 4.0 Hz, H-4); 7.60 (d, 4 Hz, H-3, H-5)		−7.3 ^{1}J(Pt–P) = 3038 Hz	325 νPt–Cl
$[PtCl_2(PMePh_2)(Th_3Sb)]$	2.11 (d, 11 Hz, ^{3}J(Pt–H) = 42 Hz, P*Me*); 7.09–7.79 (m, Ph + Th)		−3.3 ^{1}J(Pt–P) = 3516 Hz	487 νSb–C 325 νPt–Cl
$[PdCl_2(PMePh_2)(Th_3Sb)]$				
$[Pd_2Cl_2(\mu\text{-}Cl)_2(Th_3As)_2]$	7.18 (d, 3.7 Hz, 4 Hz, H-4); 7.67 (d, 5 Hz), 7.69 (d, 4 Hz) (H-3, H-5)			268, 328, 352 νPd–Cl
$[Pd_2Me_2(\mu\text{-}Cl)_2(Th_3As)_2]$	0.86 (s, Pd–Me); 7.15 (m, H-4); 7.66 (m, H-3, H-5)			330 νPd–Cl
$[PdCl(\mu\text{-}dmpz)(Th_3As)]_2$	1.87 (s, 3-*Me*, pz); 2.47 (s, 5-*Me*, pz); 5.37 (s, 4-H, pz); 7.03 (m, H-4); 7.56 (m, H-3, H-5)			
$[PdMe\ (\mu\text{-}dmpz)(Th_3As)]_2$	0.48 (s, Pd–*Me*); 1.70 (s, 3-*Me*, pz); 2.38 (s, 5-*Me*, pz); 5.52 (s, 4-H, pz); 7.02–7.16 (m, H-4); 7.55 (d, H-3, H-5)			
$[PdMe\ (\mu\text{-}pz)(Th_3As)]_2$	0.54 (s, Pd–*Me*); 5.92 (s, H-4, pz); 6.78 (s, H-3, 5, pz); 7.01–7.11 (m, H-4); 7.3–7.6 (m, H-3, H-5)			
$[PdCl\{S_2P(OPr^i)_2\}(Th_3As)]$	1.35, 1.39 (each d, 6.2 Hz, OCH_2Me_2); 4.83 (septet, 6.2 Hz, $OCH_2<$); 7.19 (t, 8.5 Hz, H-4); 7.66 (dd, H-3, H-5)		97.5	317, 333 νPd–Cl
$[PdCl\{S_2P(OEt)_2\}(Th_3As)]$	1.37 (t, 7.0 Hz, OCH_2Me); 4.20 (q, 7.0 Hz, $OCH_2<$); 7.19 (m, H-4); 7.66 (d, 3.7 Hz, H-3, H-5)		101.5	327 νPd–Cl

[a] Present in small % (approximately 10%) concentration, may be due to *trans* isomer.

[b] These are major peaks due to *cis* isomer.

concentration. The IR spectrum of the complex displayed two ν(Pt–Cl) stretching bands (328 and 279 cm^{-1}) indicating that the complex exists in a *cis* configuration, as is usually the case. The species in approximately 10% concentration in solution may be the trans isomer of [PtCl$_2$(Th$_3$As)$_2$]. Crystals suitable for X-ray diffraction analysis were obtained for [PdCl$_2$(Th$_3$As)$_2$] and hence, a full molecular structure determination was conducted.

The molecular structure of [PdCl$_2$(Th$_3$As)$_2$] is shown in Fig. 1 and selected geometric parameters are collected in the caption to the Figure. The molecule is centrosymmetric so that the configuration of the As$_2$Cl$_2$ donor set is *trans*. This also implies that the configuration of the Th$_3$As ligands, as viewed down the As–Pd–As axis, is staggered. The Pd–As bond distance is as found in related systems [18]. The As–C distances in Th$_3$As ligand fall in the narrow range of 1.904(3)–1.913(3) Å and the C–As–C angles lie between 101.25(12) and 103.81(13)°. These are approximately the same (1.893(3)–1.895(3) Å) and significantly smaller (107.73(8)–109.00(13)°), respectively compared to those found in the structure of the As(V) species, Th$_3$As=O [19].

The reaction of PdCl$_2$(PhCN)$_2$ or Na$_2$PdCl$_4$ with Th$_3$Sb in 1:2 molar ratio always resulted in decomposition leading to black insoluble powder (Found: C, 0.5; H, 0.3%) (possibly Pd metal). No reaction is observed when [PtCl$_2$(RCN)$_2$] (R = Me or Ph) is treated with Th$_3$Sb.

Cleavage of chloro-bridged platinum complexes [Pt$_2$Cl$_2$(μ-Cl)$_2$(PR$_3$)$_2$] or [Pt$_2$(μ-Cl)$_2$(P$^\wedge$C)$_2$] (P$^\wedge$C = Bu$^t_2$ PCCH$_2$Me$_2$) with Th$_3$As or Th$_3$Sb in dichloromethane readily afforded mononuclear complexes [PtCl$_2$(PR$_3$)(Th$_3$E)] or [PtCl(P$^\wedge$C)(Th$_3$As)] as colourless crystalline solids. Except [PtCl$_2$(PMe$_2$Ph)(Th$_3$As)], they were isolated as the cis products as revealed by the magnitude of ^1J(Pt–P) which agrees well with the reported *cis* derivatives [20]. In the former, resonances attributable to another species (approximately 5% in concentration) have been observed. They can be assigned to the trans product. The ^1J(Pt–P) (3038 Hz) for [PtCl(P$^\wedge$C)(Th$_3$As)] may be attributed the arsine trans to the orthometallated phosphorous atom. The magnitude of ^1J(Pt–P) can be compared with other complexes [PtCl(P$^\wedge$C)(L)] (L = neutral donor ligand) for which a *trans* configuration has been assigned [21]. Although Th$_3$Sb cleaves the chloro bridge in platinum complex to give [PtCl$_2$(PMePh$_2$)(Th$_3$Sb)], a similar reaction with the palladium complex [Pd$_2$Cl$_2$(μ-Cl)$_2$(PMePh$_2$)] results in decomposition. This is in contrast to the bridge cleavage reactions with phosphine or amine ligands.

Reaction of [PdCl$_2$(Th$_3$As)$_2$] with Na$_2$PdCl$_4$ afforded the chloro bridge complex [Pd$_2$Cl$_2$(μ-Cl)$_2$(Th$_3$As)$_2$]. The IR spectrum displayed three absorptions at 268, 328 and 352 cm^{-1} which are assigned to ν(Pd–Cl) absorptions. The absorption at 352 cm^{-1} is assigned to ν(Pd–Cl$_{\text{terminal}}$) while those at lower wavenumbers are assigned to the bridging ν(Pd–Cl) stretching absorptions. These assignments are in agreement to those obtained for similar arsine complexes [22]. A preliminary X-ray structural analysis of [Pd$_2$Cl$_2$(μ-Cl)$_2$(PEt$_2$Th)$_2$] shows that the phosphine is coordinated through P atom with no sulphur palladium interactions [23].

Treatment of [Pd$_2$Cl$_2$(μ-Cl)$_2$(Th$_3$As)$_2$] with Me$_4$Sn readily gave a binuclear methyl palladium complex [Pd$_2$Me$_2$(μ-Cl)$_2$(Th$_3$As)$_2$]. The IR spectrum showed a band at 330 cm^{-1} which may be assigned to ν(Pd–Cl). The ^{1}H NMR spectra showed a single resonance at 0.86 ppm attributable to Pd–Me protons.

Reactions of chloro-bridged binuclear palladium complexes [Pd$_2$X$_2$(μ-Cl)$_2$(Th$_3$As)$_2$] (X = Cl, Me) with dimethylpyrazole (dmpzH) in 1:2 stoichiometry in the presence of 2 equiv. of NaOH afforded the dimethyl pyrazolate bridged complexes [Pd$_2$X$_2$(μ-dmpz)$_2$(Th$_3$As)$_2$]. The ^{1}H NMR spectrum of the Pd–Me dimethyl pyrazolate bridged complex exhibited a singlet at 0.48 ppm for Pd–Me protons; the signal is shielded compared to the parent complex. The appearence of only one singlet for C4–H of the pyrazolate group (δ 5.52 in PdMe and 5.37 in Pd–Cl) indicates that only *trans* isomer is formed as has been observed for the analogous phosphine derivatives [24,25].

Reactions of chloro-bridged binuclear Pd complexes [Pd$_2$Me$_2$(μ-Cl)$_2$(Th$_3$As)$_2$] with pyrazole (pzH) in 1:2 stoichiometry in the presence of 2 equiv. of NaOH afforded the pyrazolate bridged complexes [Pd$_2$Me$_2$(pz)$_2$(Th$_3$As)$_2$].

Reaction of [Pd$_2$Cl$_2$(μ-Cl)$_2$(Th$_3$As)$_2$] with 2 equiv. of ammonium salt of dialkyldithiophosphate NH$_4$[S$_2$P(OR)$_2$] (R = Et, Pr^i) easily afforded dithiophosphate complexes [PdCl(S$_2$P(OR)$_2$)(Th$_3$As)]. The ^{1}H NMR spectra of both the complexes showed the expected resonances. The ^{31}P NMR also displayed single resonances (δ 97.5 ppm for Et and δ 101.5 ppm for Pr^i). These resonances are more shielded than the parent ligand. The IR spectra of both the complexes showed a band of medium to strong intensity at approximately 330 cm^{-1} assignable to ν(Pd–Cl). Structures of several [PdCl(S$^\wedge$S)(PR$_3$)] complexes have been established which show a chelated dithio ligand [26]. A similar structure is likely for the complexes reported here.

From the foregoing, it appears that the Th$_3$E (As, Sb) ligands function exclusively as monodentate donors in the systems investigated, as was usually the case for the phosphorus analogue.

4. Supplementary material

Crystallographic data for the structural analysis of [PdCl$_2$(Th$_3$As)$_2$] have been deposited at the Cambridge

Crystallographic Data Centre, CCDC No. 192486. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www. http://www.ccdc.cam.ac.uk).

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References

[1] (a) P. Lostak, C. Drasar, A. Krejcova, L. Benes, J.S. Dyck, W. Chen, C. Uher, J. Cryst. Growth 222 (2001) 565;
(b) A.L. Prieto, M.S. Sauder, M.S. Martin-Gonzalez, R. Gronsky, T. Sands, A.M. Stacy, J. Am. Chem. Soc. 123 (2001) 7160.
[2] (a) O. Salminen, A. Ozols, P. Riihola, P. Moenkkoenn, J. Appl. Phys. 78 (1993) 718;
(b) M.S. Lovu, E.G. Khanchevskaya, Phys. Status Solidi A, 156 (1996) 375 [Chem Abst., 125 (1996) 312301].
[3] K. Nagano, Y. Watanabe, B. Huybrechts, M. Tanaka, Chem. Abst, 123 (1997) 325628].
[4] R.R. Gerke, USSR Pat SU 1833502 A3/1993 [Chem. Abst., 123 (1997) 183704].
[5] (a) B.D. Mednikarov, Bulg. Chem. Commun. 26 (1993) 502;
(b) M.N. Kozieki, S.W. Hsia, US Pat 531477 A/1994 [Chem. Abst., 121 (1997) 96058].
[6] M. Bochmann, Chem. Vap. Deposition 2 (1996) 85 (and references therein).
[7] S.S. Garje, V.K. Jain, Coord. Chem. Rev., in press.
[8] (a) D.W. Allen, J. Chem. Soc., Sect. B (1970) 1490;
(b) D.W. Allen, J.R. Charlton, B.G. Hutley, Phosphorous 6 (1976) 191;
(c) D.W. Allen, P. Heatley, B.G. Hutley, M.T.J. Mellor, J. Chem. Soc., Perkin Trans. I (1976) 2529.
[9] L.H. Horner, J. Roder, Phosphorous 6 (1976) 147.
[10] (a) R.H. Kemp, W.A. Thomas, M. Gordon, C.E. Griffin, J. Chem. Soc., Sect. B (1969) 527;
(b) K. Issleib, H. Bruchlos, Z. Anorg. Allg. Chem. 316 (1962) 1;
(c) H.J. Jakobsen, J.A. Nielsen, J. Molec. Spectrosc. 31 (1969) 230;
(d) H.J. Jakobsen, J.A. Nielsen, J. Molec. Spectrosc. 33 (1970) 474;
(e) H.J. Jakobsen, M. Begtrup, J. Molec. Spectrosc. 35 (1970) 158;
(f) H.J. Jacobsen, O. Manscher, Acta Chem. Scand. 25 (1971) 680;
(g) J.P. Lampin, F. Mathey, J. Organomet. Chem. 71 (1974) 239;
(h) S.E. Tunney, J.K. Stille, J. Org. Chem. 52 (1987) 748.
[11] (a) G.E. Ivanov, V.P. Yur'ev, Khim Vysokomol Soedin Neftekhim (1973) 46; [Chem Abst., 80 (1973) 132879];
(b) E.A. Krasil'nikova, E.S. Sharafieva, A.I. Razumov, Zh. Obsch. Khim, 52 (1982) 2638; [Chem Abst., 98 (1983) 72281];
(c) E.A. Krasil'nikova, E.S. Sharafieva, A.I. Razumov, N. Yu. Zaslonova, Zh. Obsch. Khim, 52 (1982) 2793; [Chem Abst., 98 (1983) 89518].
[12] (a) Ya. L. Goldazb, A.A. Dudinov, V.P. Litvinov, D.S. Yufit, Yu. T. Struchkov, Khim Geterosikl Soedin, (1982) 1326; [Chem Abst., 98 (1983) 89625];
(b) V.K. Polovnyak, E.S. Sharafieva, V.Sh. Slobodina, E.A. Krailnikova, Zh. Obsch. Khim 53 (1983) 2148;
(c) V.K. Polovnyak, V.Sh. Slobodina, V.V. Kormachev, N.S.Akhmetov, Zh. Neorg. Khim, 28 (1983) 168; [Chem Abst., 98 (1983) 118509].
[13] (a) D.W. Allen, D.F. Ashford, J. Inorg. Nucl. Chem. 38 (1976) 1953;
(b) D.W. Allen, B.F. Taylor, J. Chem. Soc., Dalton Trans. (1982) 51;
(c) D.W. Allen, N.A. Bell, S.T. Fong, L.A. March, I.W. Newell, Inorg. Chim. Acta 99 (1985) 157;
(d) D.G. Dick, D.W. Stephan, Can. J. Chem. 64 (1986) 1870;
(e) M.C. Barral, R. Jimenez-Aparicio, R. Kramolowsky, I. Wagner, Polyhedron 12 (1993) 903;
(f) A.J. Deeming, S.N. Jayasuriya, A.J. Arce, Y.D. Sanctis, Organometallics 15 (1996) 786;
(g) J. Chantson, H. Gorls, S. Lotz, Inorg. Chim. Acta 305 (2000) 32;
(h) J.D. King, M. Monari, E.N. Nordlander, J. Organomet. Chem. 573 (1999) 272;
(i) A. Varshney, G.M. Gray, Inorg. Chim. Acta 148 (1988) 215.
[14] V.K. Jain, V.S. Sagoria, M.S. Gill, Indian J. Chem. 28A (1989) 164.
[15] V.K. Jain, H.C. Clark, L. Jain, Indian J. Chem. 40A (2001) 135.
[16] (a) A. Etienne, Mem. Services Chim. Etat (Paris), 33 (1947) 405 [Chem Abst., 43 (1949) 6102];
(b) H.E. Ramsden, Brit; 824, 944 (1959) [Chem Abst., 54 (1960) 17238].
[17] (a) SADABS (Version 2.01). Bruker AXS Inc., Madison, WI, USA, 2000;
(b) P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, J.M.M. Smits, C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994;
(c) G.M. Sheldrick, SHELX-97, Program for the refinement of crystal structures, University of Göttingen, Germany, 1997;
(d) C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976;
(e) TEXSAN, Structure analysis package, Molecular Structure Corporation, Woodlands, TX, USA, 1992.
[18] S.S. Garje, V.K. Jain, B. Varghese, Appl. Organomet. Chem. 13 (1999) 47 (and references therein).
[19] H. Mahalakshmi, V.K. Jain, E.R.T. Tiekink, Acta Crystallogr., Sect. E 57 (2001) o1222.
[20] H.C. Clark, A.B. Goel, V.K. Jain, K.G. Tyers, C.S. Wong, J. Organomet. Chem. 321 (1987) 123.
[21] H.C. Clark, A.B. Goel, R.G. Goel, S. Goel, Inorg. Chem. 19 (1980) 3220.
[22] R.J. Goodfellow, P.L. Goggin, L.M. Venanzi, J. Chem. Soc. (1967) 1897.
[23] V.K. Jain, K. Venkatasubramanium, Unpublished results.
[24] V.K. Jain, S. Kannan, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (1992) 2231.
[25] A. Singhal, V.K. Jain, J. Chem. Soc., Dalton Trans. (1993) 1515.
[26] K. Panneerselvam, T.H. Lu, S.F. Tung, S. Narayan, V.K. Jain, Acta Crystallogr., Sect. C 55 (1999) 541.