

The preparation, properties and X-ray structures of gold(I) trithiophosphite complexes

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Abstract

The first gold(I) trithiophosphite complexes were synthesised and fully characterised. Reaction of (tht)AuX (X = Cl, C₆F₅; tht = tetrahydrothiophene) with trithiophosphites (RS)₃P (R = Me, Ph) and the bicyclic [(SCH₂CH₂S)P(SCH₂)₂]²(L) afforded the corresponding molecular complexes (RS)₃PAuX [R = Me, X = Cl (**1**); R = Me, X = C₆F₅ (**2**); R = Ph, X = Cl (**3**); R = Ph, X = C₆F₅ (**4**)], and ²L(AuX)₂ [X = Cl (**5**), X = C₆F₅ (**6**)]. Reacting (tht)AuCl consecutively with two mole equivalents of (MeS)₃P and then AgOTf, gave the ionic compound {[MeS)₃P]₂Au}OTf (**7**). The compounds were characterised by multinuclear NMR spectroscopy, IR measurements and mass spectrometry, and the crystal and molecular structures of **1**, **3**, **6**, two polymorphs of **2** as well as the known (MeO)₃PAuCl (**8**) were determined by X-ray diffraction. The halide complexes **1** and **8** are isostructural and exhibit infinite chains of “crossed-sword”-type aurophilic interactions with Au···Au contact distances of 3.2942(3) and 3.1635(4) Å, respectively. Complex **6** exhibits a long Au···Au contact of 3.4671(9) Å. Au···S interactions between 3.3455(7) and 3.520(2) Å are present in the structures of **1** and one polymorph of **2**. © 2006 Elsevier B.V. All rights reserved.

Keywords: Gold(I) complexes; Trithiophosphite; X-ray crystal structure; Aurophilic interaction; Gold–sulphur interaction; Phosphorus–sulphur heterocycle

1. Introduction

Even though trithiophosphites were reported for the first time in 1872 [1], relatively little coordination chemistry with these ligands is known. This may be in part owing to the properties of trithiophosphites whose odour and toxicity render them unattractive substrates of study. A recent paper by Kataeva et al. summarises trithiophosphite coordination chemistry [2]. A limited number of crystal structures have been published for a series of trithiophosphite (L) complexes of copper(I) halides and pseudohalides [2,3], two CpMn(CO)₂L-type compounds [4], an (arene)Cr(CO)₂L [5] and one each of di- and trinuclear iron carbonyl complexes [6].

Addition compounds of AuCl₃ with trithiophosphites have been mentioned but have only been identified by their melting points [7]. No other gold–trithiophosphite interactions have been investigated.

In this study, we set out to further expand the knowledge of the ligand properties of trithiophosphites by preparing a series of gold(I) complexes with the three ligands trimethyltrithiophosphite, triphenyltrithiophosphite and 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane. To our knowledge, no coordination compounds of the latter ligand are known.

The trithiophosphite complexes prepared by us were fully characterised by elemental analysis as well as NMR, IR, FAB- and ESI-MS measurements, and, for several compounds, X-ray structure determination. While this work was in progress, we also noticed that the crystal structure of chloro(trimethylphosphite)gold(I) (**8**) is not known so this compound was prepared and its crystal and molecular structures determined for comparison.

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2. Experimental

2.1. General

Solvents were freshly distilled from sodium (toluene, pentane), sodium benzophenone ketyl radical (diethyl ether, thf) or CaH₂ (dichloromethane) under an atmosphere of dry dinitrogen. All operations were conducted in oven-dry Schlenk-type glassware under an atmosphere of dry argon. (MeS)₃P and (PhS)₃P [8], (tth)AuCl [9,10] and (tth)AuC₆F₅ [10] were synthesised following published procedures. Melting points were determined in sealed capillary on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Elemental analyses and FAB mass spectra (nitrobenzyl alcohol matrices) were performed by the University of the Witwatersrand. Standard infrared spectra were recorded at 4 cm⁻¹ resolution on a Nicolet Avatar 300 FT-IR instrument equipped with a Smart Performer ZnSe disk ATR accessory. The spectra were corrected for ATR effects using Omnic software. Far-IR spectra were recorded in polyethylene discs at 4 or 2 cm⁻¹ resolution on a Nicolet Nexus FT-IR spectrometer using a solid substrate beam splitter and a DTGS polyethylene detector. The ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra (δ in ppm) were recorded on a Varian VXR 300 or a Varian Unity INOVA 400 spectrometer at the indicated frequencies. Solvent residual peaks were used to reference ¹H and ¹³C spectra. For ¹⁹F and ³¹P spectra, CFCl₃ and 85% H₃PO₄, respectively, were used as external references. Values for coupling constants are given in Hz, ¹J_{CH} coupling constants were obtained from ¹³C satellites in the ¹H spectra. ESI mass spectra were recorded on a Waters API Quattro Micro instrument at 50 V cone voltage in thf/acetonitrile solutions. Thermal gravimetric analysis was conducted on a TA Instruments TGA Q500 device.

2.2. Preparation of the compounds

2.2.1. 1,2-Bis(1,3,2-dithiaphospholan-2-ylthio)ethane

A diethyl ether solution (40 mL) of ethane-1,2-dithiol (2.25 g, 24 mmol) was added dropwise to a stirred solution of freshly distilled phosphorus trichloride (2.05 g, 15 mmol) and pyridine (4.07 g, 52 mmol) in diethyl ether (60 mL) at 0 °C. After 2 h pyridine hydrochloride was removed by filtration and washed with dichloromethane (60 mL). The solvents were removed in vacuo and the remaining colourless solid extracted with toluene (100 mL) and again filtered. Toluene was removed in vacuo affording a colourless microcrystalline solid (0.789 g, 31%); m.p. 123 °C.

2.2.2. Chloro(trimethyltrithiophosphite)gold(I) (I)

(MeS)₃P (0.146 g, 0.85 mmol) was dissolved in thf (15 mL) and (tth)AuCl (0.272 g, 0.85 mmol) was added. The resulting homogeneous slightly yellowish solution was stirred for 1 h. All volatiles were removed in vacuo during which the compound started to precipitate from

the solution. The obtained solid was again dissolved in thf (15 mL), filtered through Celite and stripped of solvent affording the target compound as a colourless microcrystalline solid in quantitative yield (0.342 g). Crystals suitable for X-ray diffraction measurement were grown by layering a deuteriochloroform solution with pentane, m.p. 114 °C (dec.) Anal. Calc. for C₃H₉AuCIPS₃: C, 8.90; H, 2.24. Found: C, 8.7; H, 2.3%. IR (cm⁻¹): 2920 (CH₃, s), 1415 (CH₃, vs), 694 (s), 566 (vs), 512 (vs), 503 (vs), 315 (Au³⁵Cl, s), 308 (Au³⁷Cl, m). ¹H NMR (300 MHz, CDCl₃): δ 2.43 (d, ³J_{PH} 17.6, ¹J_{CH} 144). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 16.1 (s). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 123.4 (s). MS (ESI): *m/z* 613 [62%, (LAu · AuSMe)⁺]; 567 (40), 541 (15, L₂Au⁺), 369 (30, LAu⁺).

2.2.3. (Pentafluorophenyl)(trimethyltrithiophosphite)-gold(I) (2)

A solution of (MeS)₃P (0.107 g, 0.62 mmol) in diethyl ether (30 mL) was cooled to 0 °C and transferred via a teflon cannula to a second Schlenk tube charged with (tth)AuC₆F₅ (0.273 g, 0.60 mmol). The mixture was stirred for 45 min at 0 °C followed by filtration of the purplish solution through Celite previously washed with diethyl ether. After removal of the volatiles in vacuo a crude purple product was obtained. The filtration procedure was repeated to afford a colourless microcrystalline solid (0.283 g, 87%). Crystals of polymorph A suitable for X-ray diffraction measurement were grown by diffusing pentane vapour into a diethyl ether solution. Polymorph B crystallised from a thf solution layered with pentane, m.p. 92 °C (dec.) Anal. Calc. for C₉H₉AuF₅PS₃: C, 20.16; H, 1.69. Found: C, 20.1; H, 1.7%. IR (cm⁻¹): 2917 (CH₃, s), 1634 (m), 1501 (s), 1454 (vs), 1419 (CH₃, vs), 1061 (s), 952 (vs), 790 (s) 693 (m). ¹H NMR (400 MHz, CDCl₃): δ 2.51 (d, ³J_{PH} 16.4, ¹J_{CH} 143). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 149.3 (dm, ¹J_{FC} 229, *ortho*-C), 140.0 (dm, ¹J_{FC} 248, *meta*-C), 137.6 (dm, ¹J_{FC} 253, *para*-C), 15.4 (s, CH₃). ¹⁹F NMR (376 MHz, CDCl₃): δ -116.7 (2F, m, *ortho*-F), -157.4 (1F, m, *para*-F), -162.2 (2F, m, *meta*-F). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 144.3 (s). MS (FAB): *m/z* 536 (9%, M⁺), 522 [10, (M-C₆F₅ + C₇H₇NO₃)⁺], 369 [18, (M-C₆F₅)⁺].

2.2.4. Chloro(triphenyltrithiophosphite)gold(I) (3)

The complex was prepared in an analogous manner to **I** employing (PhS)₃P (0.346 g, 0.97 mmol) and (tth)AuCl (0.315 g, 0.98 mmol) affording a viscous colourless oil which slowly crystallised over several days at -16 °C yielding a colourless solid (0.539 g, 95%). A crystal suitable for X-ray structure determination was grown from a thf solution layered with diethyl ether at -16 °C, dec. 63 °C without melting. Anal. Calc. for C₁₈H₁₅AuCIPS₃: C, 36.59; H, 2.56. Found: C, 36.4; H, 2.7%. IR (cm⁻¹): 3044 (CH, m), 1572 (m), 1470 (vs), 1436 (vs), 1082 (s), 1023 (s), 745 (vs), 687 (vs), 461 (vs), 339 (AuCl, s), 318 (s), 262 (m), 235 (m). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.64 (6H, m, *ortho*-H), 7.54 (3H, m, *para*-H), 7.46 (6H, m, *meta*-H). ¹³C{¹H}

NMR (75.4 MHz, CD₂Cl₂): δ 136.9 (d, ²J_{PC} 5.0, *ipso*-C), 131.5 (d, ³J_{PC} 3.6, *ortho*-C), 130.6 (d, ⁴J_{PC} 2.8, *meta*-C), 129.0 (br s, *para*-C). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ 142.1 (s). MS (ESI): *m/z* 1167 [30%, (LAu · 2AuSPh)⁺], 1123 (30), 913 (30, L₂Au⁺), 861 [100, (LAu · AuSPh)⁺], 817 (70), 665 [30, (LAu · PhSH)⁺].

2.2.5. (Pentafluorophenyl)(triphenyltrithiophosphite)-gold(I) (**4**)

The compound was prepared in an analogous manner to **2** employing (PhS)₃P (0.145 g, 0.40 mmol) and (tth)AuC₆F₅ (0.189 g, 0.42 mmol). After evaporation of all volatiles a colourless crystalline solid was obtained (0.283 g, 97%), m.p. 86 °C (dec.) Anal. Calc. for C₂₄H₁₅AuF₅PS₃: C, 39.90; H, 2.09. Found: C, 40.0; H, 2.1%. IR (cm⁻¹): 3054 (CH, m), 1638 (m), 1609 (m), 1503 (s), 1456 (vs), 1438 (vs), 1355 (s), 1060 (s), 952 (vs), 741 (s), 683 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.60 (6H, m, *ortho*-H), 7.43 (3H, m, *para*-H), 7.37 (6H, m, *meta*-H). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 148.6 (dm, ¹J_{FC} 230, *ortho*-C₆F₅), 139.4 (dm, ¹J_{FC} 248, *meta*-C₆F₅), 137.0 (dm, ¹J_{FC} 253, *para*-C₆F₅), 136.6 (d, ²J_{PC} 3.7, *ipso*-C₆H₅), 130.7 (d, ³J_{PC} 3.3, *ortho*-C₆H₅), 130.0 (d, ⁴J_{PC} 2.8, *meta*-C₆H₅), 128.5 (br s, *para*-C₆H₅). ¹⁹F NMR (376 MHz, CDCl₃): δ -115.9 (2F, m, *ortho*-C₆F₅), -158.2 (1F, t, ³J_{FF} 20.0, *para*-C₆F₅), -162.7 (2F, m, *meta*-C₆F₅). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 161.3 (s). MS (FAB): *m/z* 722 (15%, M⁺), 613 [5, (M-SPh)⁺], 555 [20, (M-C₆F₅)⁺], 446 [8, (M-C₆F₅-SPh)⁺], 249 [58, [P(SPh)₂]⁺].

2.2.6. Dichloro{ μ -[1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane]}digold(I) (**5**)

A solution of (tth)AuCl (0.218 g, 0.68 mmol) and 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane (0.115 g, 0.34 mmol) in thf (15 mL) was stirred at r.t. A precipitate was observed and after 1.5 h the volatiles were removed in vacuo affording a yellowish solid (0.263 g, 96%). Only limited analytical data could be obtained due to the insolubility of the material, m.p. dec. 95 °C without melting. Anal. Calc. for C₆H₁₂Au₂Cl₂P₂S₆: C, 8.97; H, 1.51. Found: C, 8.9; H, 1.5%. IR (cm⁻¹): 2958 (CH₂, s), 2922 (CH₂, s), 1416/1411 (CH₂, vs), 1288 (m), 1202 (vs), 938 (s), 837 (vs), 728 (m), 673 (s), 433 (m), 371 (m), 323 (AuCl, s).

2.2.7. Bis(pentafluorophenyl){ μ -[1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane]}digold(I) (**6**)

A solution of 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane (0.077 g, 0.23 mmol) in thf (10 mL) was cooled to 0 °C and (tth)AuC₆F₅ (0.210 g, 0.46 mmol) was added. After stirring the homogeneous solution for 30 min the volatiles were removed in vacuo during which the product started to precipitate. The dry solid was again dissolved in thf (30 mL), filtered through Celite and stripped of solvent to afford a colourless crystalline product (0.216 g, 87%). Crystals suitable for X-ray diffraction were obtained by layering a thf solution with pentane, m.p. dec. 158 °C without melting. Anal. Calc. for C₁₈H₁₂Au₂F₁₀P₂S₆: C, 20.27; H,

1.13. Found: C, 20.4; H, 1.2%. IR (cm⁻¹): 2924 (CH₂, w), 1638/1632 (m), 1502 (vs), 1452 (vs), 1357 (s), 1199 (m), 1061 (s), 952 (s), 789 (s). ¹H NMR (400 MHz, thf-*d*₈): δ 3.65 (8H, m, ring-CH₂), 3.46 (4H, m, bridge-CH₂). ¹³C{¹H} NMR (101 MHz, thf-*d*₈): δ 41.3 (s, ring-CH₂), 36.6 (s br, bridge-CH₂). ¹⁹F NMR (376 MHz, thf-*d*₈): δ -115.4 (4F, m, *ortho*-F), -159.6 (2F, t, ³J_{FF} 19.6, *para*-F), -163.7 (4F, m, *meta*-F). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 134 (br s). MS (FAB): *m/z* 899 [1%, (M-C₆F₅)⁺], 595 (1), 535 [1, (M-AuC₆F₅-C₆F₅)⁺], 164 (15), 162 (24).

2.2.8. Bis(trimethyltrithiophosphite)gold(I) triflate (**7**)

(MeS)₃P (0.139 g, 0.81 mmol) was dissolved in acetonitrile (10 mL) and (tth)AuCl (0.130 g, 0.41 mmol) was added which yielded a yellow precipitate. After 1 h thf (10 mL) was added which dissolved the precipitate affording a hazy yellowish solution. A solution of silver triflate (0.102 g, 0.40 mmol) in acetonitrile (5 mL) was added causing immediate precipitation of AgCl. The suspension was stirred for another hour and then filtered through Celite. The filter was washed with thf (20 mL) and the filtrate evaporated in vacuo affording a yellow oil which slowly crystallised at -16 °C. Treatment of the raw product with diethyl ether (40 mL), inverse filtration and drying in vacuo afforded a hygroscopic yellow solid (0.153 g, 56%) which is very sensitive to moisture, m.p. 60 °C with evolution of gas. Anal. Calc. for C₇H₁₈AuF₃O₃P₂S₇: C, 12.17; H, 2.63. Found: C, 12.5; H, 2.9%. IR (cm⁻¹): 2916 (CH₃, m), 2847 (CH₃, m), 1422/1418 (CH₃, s), 1253 (CF₃SO₃, s), 1219 (CF₃SO₃, vs), 1155 (s), 1140 (s), 1026 (s), 955 (m). ¹H NMR (300 MHz, CDCl₃): δ 2.40 (d, ³J_{PH} 14.7, ¹J_{CH} 144). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 15.2 (d, ²J_{PC} 4.0). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 128.1 (s). MS (ESI): *m/z* 785 {7%, [(MeS)₃P]₂Au⁺ · AuSMe}, 583 (12), 541 {90, [(MeS)₃P]₂Au⁺}.
 2.2.9. Chloro(trimethylphosphite)gold(I) (**8**)

2.2.9. Chloro(trimethylphosphite)gold(I) (**8**)

In an analogous manner to the preparation of **1** the reaction of trimethylphosphite (0.041 g, 0.33 mmol) and (tth)AuCl (0.108 g, 0.34 mmol) afforded a crystalline powder after evaporation of all volatiles. It was redissolved in thf (7 mL), the solution layered with pentane and stored at -16 °C whereupon the target compound crystallised as colourless needles (0.104 g, 90%). A suitable crystal was mounted for X-ray diffraction; m.p. 101 °C. ¹H NMR (300 MHz, CDCl₃): δ 3.74 (d, ³J_{PH} 14.0, ¹J_{CH} 150). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 53.1 (br s). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 121.0 (s).

2.3. Crystal structure determinations

Intensity data were collected at *T* = 100 K with a Bruker SMART Apex diffractometer [11] with graphite monochromated Mo K α radiation (λ = 0.71073 Å). Intensities were measured using the ω -scan mode and were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and refined by full-matrix least-squares

on F^2 using the SHELXL-97 software package and X-SEED [12]. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogens were placed in calculated positions. Figures were created using POV-RAY 3.5 with thermal displacement ellipsoids at the 50% probability level, all hydrogen atoms were omitted for clarity. Data and parameters of the crystal structure determinations are shown in Table 1.

3. Results and discussion

The preparation of the complexes is outlined in Scheme 1. Syntheses of **1–6** were readily achieved in high yields by replacing tetrahydrothiophene from either chloro(tetrahydrothiophene)gold(I) or (pentafluorophenyl)(tetrahydrothiophene)gold(I) with the respective trithiophosphite. The substitutions were carried out in thf at room temperature for the chloro complexes or in diethyl ether solution at 0 °C for the pentafluorophenyl compounds. Evaporation of all volatile matter afforded microcrystalline product mixtures that were, especially in the case of the pentafluorophenyl derivatives, contaminated with metallic gold. Filtration over Celite yielded the complexes as colourless microcrystalline compounds after stripping of solvent. Preparation of (**7**) was effected by reacting two equivalents of (MeS)₃P with (tth)AuCl and AgOTf in acetonitrile/thf. The known [13,14] phosphite complex **8** was prepared analogously to **1**.

Compounds **1–4** are stable for months without any signs of decomposition when stored at –16 °C. Stability at room

temperature however is lower and slow deterioration with deposition of metallic gold occurs within days. Complexes of the bicyclic ligand, **5** and **6**, as well as the homoleptic **7** are more sensitive and turn yellow within weeks upon storage in the freezer. This might be caused by P–S bond cleavage which was observed in the synthesis of iron carbonyl complexes of trithiophosphites [6]. While **1** and **3** are soluble in polar, aprotic solvents, complexes **2** and **4** are also soluble in diethyl ether; all compounds are insoluble in aliphatic hydrocarbons. The solubility of the binuclear complexes is poor; **5** does not dissolve at all and **6** only dissolves in thf when freshly prepared but after prolonged storage becomes insoluble. The complexes exhibit a faint odour of the parent thiol and are decomposed slowly by moisture. Protic solvents like methanol effect fast decomposition indicating a destabilising effect of the coordinated gold moiety on the ligand. This pathway has been used to convert coordinated trithiophosphites into phosphonates by hydrolysis of copper(I) halide complexes [15].

3.1. Thermal gravimetric analysis

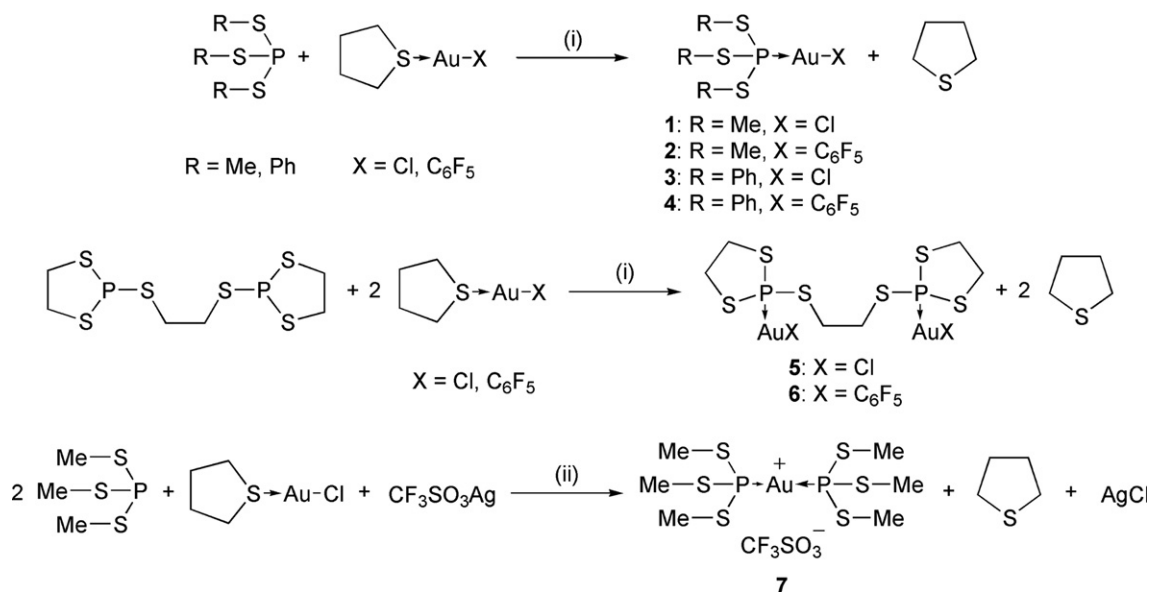
A crystalline sample of **1** (4.0 mg) was heated at a rate of 10 °C min⁻¹ to 400 °C. The sample mass was constant up to the melting point (114 °C) when rapid loss (44.3%) of weight set in until 176 °C was reached. Thereafter the mass stayed fairly constant up to 400 °C when a final loss of 45.7% occurred. A yellow solid remained in the pan. The observed weight loss falls between the theoretical loss to

Table 1
Crystallographic and data collection parameters for compounds **1**, **2A**, **2B**, **3**, **6** and **8**

Compound	(MeS) ₃ PAuCl (1)	(MeO) ₃ PAuCl (8)	(MeS) ₃ PAuCl (2A)	(MeS) ₃ PAuCl (2B)	(PhS) ₃ PAuCl (3)	² L(AuClF ₅) ₂ ³ (6)
Empirical formula	C ₃ H ₉ AuClPS ₃	C ₃ H ₉ AuClO ₃ P	C ₉ H ₉ AuF ₅ PS ₃	C ₉ H ₉ AuF ₅ PS ₃	C ₁₈ H ₁₅ AuClPS ₃	C ₁₈ H ₁₂ Au ₂ F ₁₀ P ₂ S ₆
<i>M_r</i>	404.69	356.49	536.30	536.30	590.90	1066.5
Crystal habit	Needle	Needle	Block	Block	Block	Block
Crystal dimensions (mm)	0.2 × 0.1 × 0.05	0.5 × 0.1 × 0.1	0.05 × 0.04 × 0.03	0.1 × 0.1 × 0.05	0.2 × 0.2 × 0.15	0.1 × 0.08 × 0.04
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)	<i>P1̄</i> (No. 2)	<i>P1̄</i> (No. 2)	<i>P2₁/c</i> (No. 14)	<i>I2/a</i> (No. 15)
<i>a</i> (Å)	6.5671(6)	6.2810(8)	11.7392(16)	7.7052(13)	15.156(2)	9.0659(15)
<i>b</i> (Å)	15.6506(15)	14.5070(18)	11.7574(16)	10.0602(17)	13.1192(18)	17.155(3)
<i>c</i> (Å)	18.3143(17)	17.324(2)	12.6724(17)	11.0138(19)	10.1472(14)	17.061(3)
α (°)	90	90	103.971(2)	65.077(2)	90	90
β (°)	90	90	105.090(2)	82.579(3)	100.834(2)	94.020(4)
γ (°)	90	90	110.925(2)	69.830(3)	90	90
<i>V</i> (Å ³)	1882.3(3)	1578.6(3)	1464.9(3)	726.6(2)	1981.7(5)	2646.8(8)
<i>Z</i> , <i>D_c</i> (Mg m ⁻³)	8, 2.856	8, 3.000	4, 2.432	2, 2.451	4, 1.980	4, 2.676
μ (Mo K α) (mm ⁻¹)	16.670	19.119	10.614	10.699	7.953	11.749
Number of reflections, unique	10206, 2007	8198, 1604	8780, 6057	7786, 2963	11766, 4510	7592, 2726
<i>R_{int}</i>	0.0259	0.0268	0.0201	0.0282	0.0443	0.0510
Data/restraints/parameters	1924/0/85	1514/0/85	5267/0/349	2770/0/175	3815/0/217	2308/0/172
<i>F</i> (000)	1488	1296	1000	500	1128	1976
<i>R₁</i> , <i>wR₂</i> ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0163, 0.0395	0.0218, 0.0446	0.0341, 0.0813	0.0279, 0.0632	0.0462, 0.0856	0.0531, 0.1002
<i>R₁</i> , <i>wR₂</i> (all data)	0.0173, 0.0399	0.0239, 0.0453	0.0407, 0.0845	0.0310, 0.0644	0.0588, 0.0890	0.0666, 0.1047
Goodness-of-fit	1.101	1.188	1.029	1.079	1.130	1.139

^a ²L = 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane.

^b $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 1. Preparation of the compounds: (i) thf, r.t. for X = Cl; diethyl ether, 0 °C for X = C₆F₅. (ii) acetonitrile/thf, r.t.

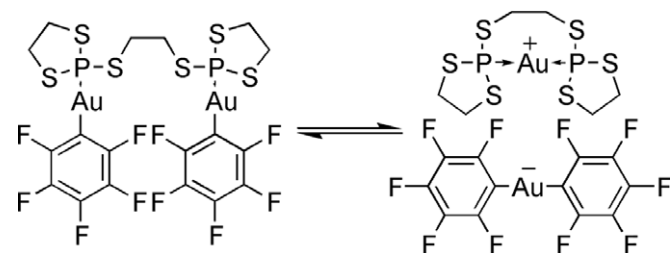
afford the possible decomposition products Au₂S (47.4%) and AuCl (42.6%).

3.2. Spectroscopic analyses

3.2.1. Nuclear magnetic resonance

The coordination of the trithiophosphite ligands to the gold(I) centre could be verified by comparison of the ¹H and ³¹P NMR spectra of the free ligands and complexes. Coordination to the AuCl moiety does not greatly affect the ³¹P shift, Δδ being −2.3 for **1** and +2.2 for **3**, in contrast to the large Δδ (+38 to +48) observed for gold(I) chloride adducts of simple tertiary phosphanes [16,17], and with the ³¹P upfield shift (Δδ, −20) associated with normal phosphite coordination to AuCl [16]. Upon coordination to the AuC₆F₅ fragment, however, a pronounced Δδ, averaging +20 for the trithiophosphite ligands, is observed. All ³¹P signals are sharp singlets except for complex **6**, which shows a broad peak; see Scheme 2.

The proton spectra for **1**, **2** and **7** show a downfield shift of the methyl signal by 0.2–0.3 ppm. The ¹J_{CH} coupling constants obtained from the ¹³C satellites remain essentially unchanged at an average value of 143 Hz upon coordination of (MeS)₃P. The aromatic protons in **3** and **4** are shifted to lower field by ca. 0.1–0.2 ppm vs. free ligand thus allowing the discrimination of *meta*- and *para*-signals that overlap in the spectrum of (PhS)₃P.



Scheme 2. Possible dynamic homoleptic rearrangement of compound **6** to an ionic species giving rise to the broad resonance in the ³¹P NMR spectrum.

In the ¹³C spectra of **2** and **4** the *ipso*-carbon atoms of the pentafluorophenyl group and the CF₃-carbon in **7** were not observed due to low intensity, **6** was not soluble enough to detect any carbon resonances of the C₆F₅ groups. Unexpectedly, the J_{PC} coupling constants of all ligands decrease upon coordination, again showing dissimilarity to the simple phosphanes [17]. Though the protons of the trimethyltrithiophosphite complexes **1**, **2** and **7** all indicate coupling with the ³¹P nucleus, a substantial ²J_{PC} in the ¹³C spectra is only observed for the free ligand (18 Hz); the complexes with the exception of **7** (²J_{PC} 4 Hz) only exhibit a sometimes broadened singlet for the methyl carbon atoms, similar to the methyl resonance of **8**. This could be due to fast ligand exchange in the complexes as was observed earlier for phosphine and phosphite complexes [13].

For the triphenyltrithiophosphite ligand the ¹³C signals are split into doublets up to the *meta* carbon atoms. The *para* carbons appear as broad singlets and the values of the J_{PC} coupling constants especially for the *ipso* carbon (²J_{PC} 5–6 Hz), are lower than for the free ligand (13 Hz). With the bicyclic ligand, 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane, the doublet of doublets of the two bridging carbon atoms at higher field in the free ligand spectrum [18] is again reduced to a broad singlet in **6**.

In addition, the pentafluorophenyl groups of **2**, **4** and **6** were examined by ¹⁹F NMR spectroscopy and the usual pattern of shifts and multiplicities for the AuC₆F₅ moiety is observed [19].

3.2.2. Infrared spectroscopy

Routine IR spectra essentially show the absorptions of the ligand groups for complexes **1**, **3** and **5**. Compounds

2, **4** and **7**, additionally, exhibit the characteristic vibrations of the C_6F_5 or CF_3SO_3 groups.

In addition to these standard spectra, far-IR spectra in the frequency range $600\text{--}200\text{ cm}^{-1}$ of compounds **1**, **3** and **5** were recorded in polyethylene discs to locate Au–Cl vibrations. Compound **1** exhibits a sharp $\nu(Au^{35}Cl)$ band at 315 cm^{-1} with a $\nu(Au^{37}Cl)$ satellite at 308 cm^{-1} consistent with theory; $\nu(AuCl)$ for the phosphite complex **8** has been reported at 326 cm^{-1} [20]. Combined with the crystallographic findings (see below) this suggests that the Au \cdots S contacts in **1** could weaken both Au–P and Au–Cl bonds compared to **8**.

The spectrum of **3** shows two vibrations at 339 and 318 cm^{-1} , but only the band at higher wavenumber has a shoulder indicative of a non-resolved $\nu(Au^{37}Cl)$ vibration. The Au–Cl stretching band for $(PhO)_3PAuCl$ was reported at 340 cm^{-1} [20], suggesting that both ligands induce a similar electronic effect since no close intermolecular contacts are observed in the molecular structures of these compounds (see below).

Compound **5** shows a broad $\nu(AuCl)$ band at 323 cm^{-1} suggesting that Au \cdots Au interactions are present as would be expected from the insolubility of the compound and the effect of intermolecular contacts in **1**.

3.2.3. Mass spectrometry

The FAB mass spectra of compounds **2**, **4** and **6** show the loss of a pentafluorophenyl unit but the molecular ion was observed for **2** and **4**. For compounds **1** and **3** FAB-MS measurements failed to give interpretable patterns and ESI-MS in thf/acetonitrile solution was employed. Fragmentation of the trithiophosphite ligand was observed leading to strong signals for $[(RS)_3PAu \cdot AuSR]^+$ clusters along with other ions. However, due to the insolubility of **5** no mass spectrum could be obtained with any of above ionisation methods.

It is noteworthy that **1** does lose the ligand on heating but rather loses the chloride in ionising conditions.

3.2.4. Crystallography

Compounds **1**, **2**, **3**, **6** and **8** furnished crystals suitable for X-ray diffraction. For compound **2** two polymorphs both in the space group $P\bar{1}$ were discovered. First, a modification with two independent molecules in the asymmetric unit (referred to in the following discussion as polymorph **A** with

molecules **2A-1** and **2A-2**) was found by diffusing pentane vapour into an diethyl ether solution of **2**; later, crystals of the more symmetric polymorph, **B**, with only one molecule in the asymmetric unit (**2B**) were obtained by layering a thf solution of **2** with pentane. Complex **1**, the isostructural **8** as well as **6**, exhibit Au \cdots Au interactions. Important bond lengths and angles are reported in Table 2.

In general, it was noted that even though it is potentially possible for trithiophosphite ligands to adopt local C_3 symmetry in the crystal, in agreement with gold(I) complexes of tertiary phosphanes like chloro(triethylphosphane)gold(I) [21], it was not observed. Two of the SMe or SPh moieties are bent more or less towards the gold while the S–C axis of the third group points away from the metal centre. This observation is also echoed by the Au–P–S angles which are in the order of $116\text{--}118^\circ$ for the former and 108° for the latter moieties.

The crystal structures of **1** (Fig. 1), and **8** (Fig. 2), in the orthorhombic space group $Pbca$ are isostructural and exhibit infinite, slightly bent chains owing to Au \cdots Au interactions. Au(1)–Au(1')–Au(1'') angles are $170.783(8)^\circ$ for **1** and $166.166(12)^\circ$ for **8** along the *a*-axis, with the P–Au–Cl axes oriented in the “crossed sword” motif (Fig. 3). The Cl(1)–Au(1) \cdots Au(1')–Cl(1') torsion angles are $103.88(4)^\circ$ and $100.96(6)^\circ$, respectively. It is clear from Au–P bond lengths that the trimethylphosphite ligand is both more strongly bonded to the gold(I) centre and causes stronger aurophilic interactions between the molecules. The differences in bond lengths are more pronounced than for the triphenyltrithiophosphite and triphenylphosphite ligands (see below). One sulphur atom of **1** is also involved in an intermolecular sub van der Waals contact [Au(1) \cdots S(3') $0.5 + x, y, 0.5 - z$] “supporting” the Au chain and may in part be responsible for weakening the Au–P bond and affording longer aurophilic interactions in **1**. Au \cdots S contacts have previously been found to play a role in the packing of other gold(I) complexes [22]. The compounds chloro(trimethylphosphane)gold(I) [23] [Au \cdots Au distances 3.271, 3.386 and 3.356 Å] and chloro(triethylphosphane)gold(I) [21] [Au \cdots Au distance 3.568 Å] which have tertiary phosphane ligands of similar or less steric requirement than $(MeS)_3P$ or $(MeO)_3P$, crystallise in space groups of lower symmetry suggesting that the sulphur and oxygen lone pairs could be involved in directing the crystallisation of compounds **1** and **8**.

Table 2
Selected bond angles ($^\circ$) and distances (Å) for compounds **1**, **2A**, **2B**, **3**, **6** and **8**

	1 (X = Cl)	2A (2A-1/2A-2) (X = C_6F_5)	2B (X = C_6F_5)	3 (X = Cl)	6 (X = C_6F_5)	8 (X = Cl)
Au–P	2.2352(8)	2.2662(14)/2.2724(16)	2.2704(14)	2.2184(16)	2.271(3)	2.2110(12)
Au–X	2.3100(8)	2.043(5)/2.049(6)	2.041(5)	2.2816(16)	2.063(10)	2.3106(11)
Au \cdots Au/Au \cdots S	3.2942(3)/3.3455(7)	–/–	–/3.5201(15)	–/–	3.4671(9)/–	3.1635(4)/–
P–Au–X	178.55(3)	178.89(16)/174.21(17)	178.61(15)	176.99(6)	171.7(3)	175.90(4)
Au–P–S(1,2,3)	118.59(4)	116.16(8)/112.87(8)	117.37(7)	115.13(8)	118.78(14)	117.00(14) ^a
	119.37(4)	107.47(8)/121.42(8)	107.06(7)	114.64(9)	114.72(13)	108.66(13)
	106.57(4)	116.83(8)/108.08(8)	118.34(7)	108.53(8)	113.63(13)	118.98(14)

^a Values for Au–P–O angles.

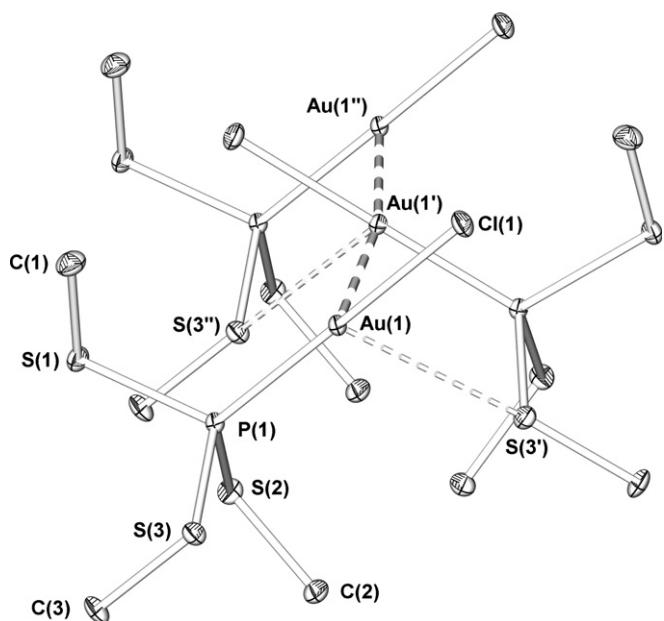


Fig. 1. Molecular structure of **1**. Au...Au and Au...S interactions are indicated with dashed lines.

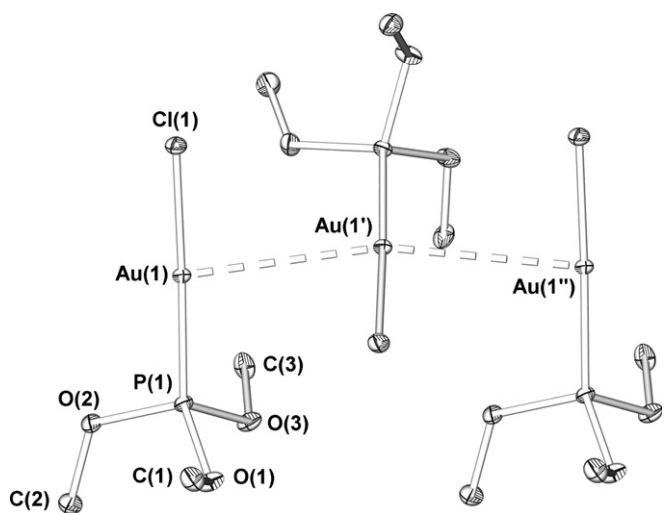


Fig. 2. Molecular structure of **8**. Au...Au interactions are shown with dashed lines.

Triphenyltrithiophosphite crystallises in the space group $R\bar{3}$ and the molecules exhibit local C_3 symmetry at the phosphorus atom [24]. The P–S bond length is 2.126 Å and the P–S–C angle 99.6°. Upon coordination to AuCl, the P–S bonds undergo a significant shortening to 2.094(2) [P(1)–S(1)], 2.090(2) [P(1)–S(2)] and 2.084(2) Å [P(1)–S(3)] for the three independent PhS groups in **3** (Fig. 4). The P–S–C angles are not greatly affected by coordination and remain at 99.1(2)° [P(1)–S(1)–C(11)] to 103.8(2)° [P(1)–S(3)–C(31)]. In contrast to the isostructural **1** and **8**, monoclinic **3** (space group $P2_1/c$) is not isostructural with triclinic chloro(triphenylphosphite)gold(I) (space group $P\bar{1}$) [25]. This may be due to the absence of Au...Au and Au...S interactions in these structures. Thus, classical forces pre-

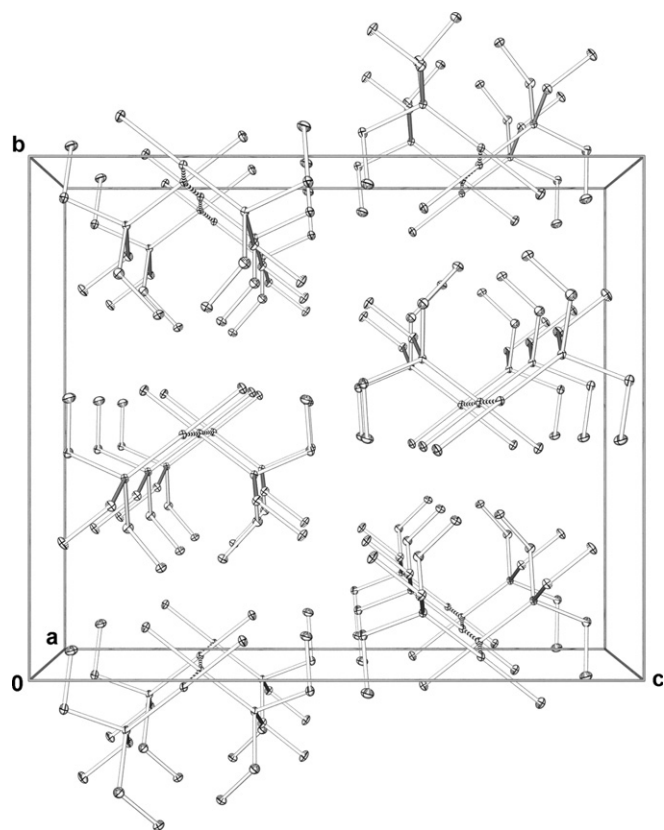


Fig. 3. Packing of **1** in the unit cell shown along the *a*-axis. Compound **8** has the same structure with slightly different cell dimensions.

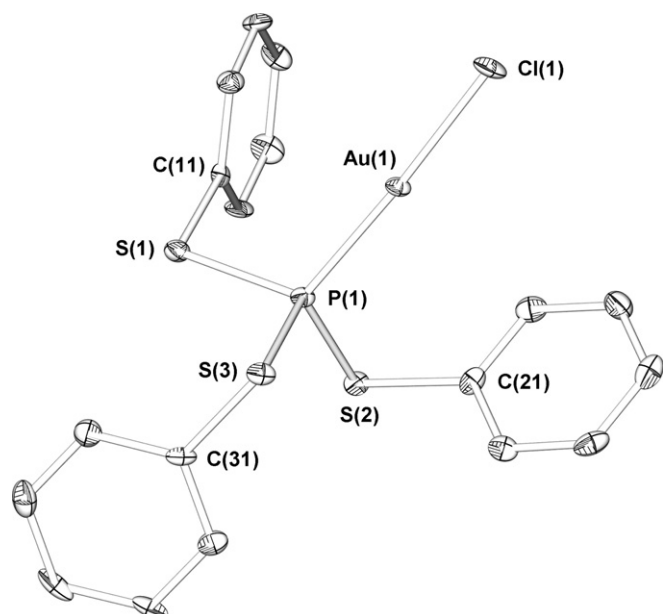


Fig. 4. Molecular structure of **3**.

vail in the crystals and lead to different structures. The Au–Cl and Au–P distances and the P–Au–Cl angles are comparable at 2.2816(16), 2.2184(16) Å and 176.99(6)° for **3** and 2.273(5), 2.192(5) Å and 178.5(2)° for the oxo-analogue.

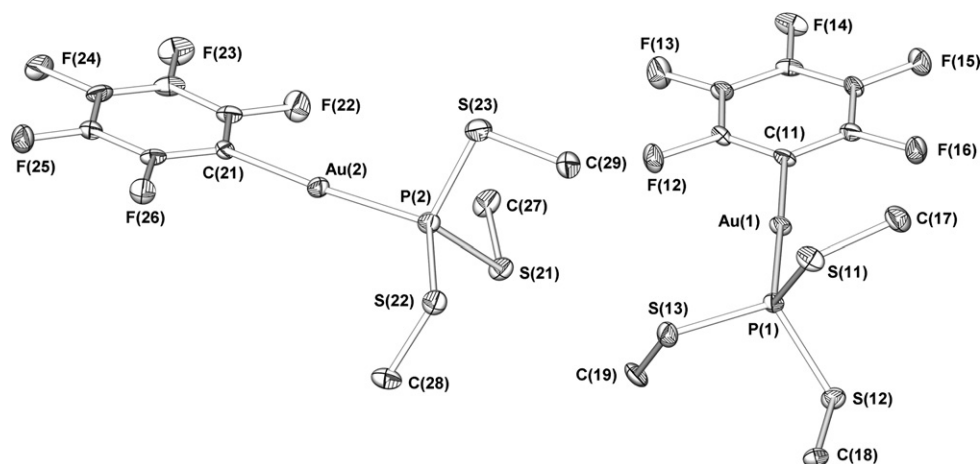


Fig. 5. Molecular structure of **2A**. Both crystallographically independent molecules of the asymmetric unit are shown (**2A-1** on the right, **2A-2** on the left).

In contrast to **1**, polymorphs **A** and **B** (both in space group $P\bar{1}$, $Z=4$ for **A** and $Z=2$ for **B**) of **2** (Figs. 5 and 6) do not exhibit aurophilic interactions, which may be due to the prevalence of other association phenomena discussed below as steric factors are not likely to contribute. Instead, **A** exhibits infinite $AA'BB'$ stacks of pentafluorophenyl groups (distances between the phenyl- C_6 centroids $AA' = BB'$ 3.668, $A'B$ 3.534, and $B'A$ 3.541 Å) for both crystallographically independent molecules running in the direction of the spatial vector defined by the cell axes. The pentafluorophenyl groups of **2B** on the other hand exhibit no $\pi \cdots \pi$ interaction, but $Au \cdots S$ contacts between the molecules related by an inversion centre are observed which are in the range of the sum of the van der Waals radii [$Au(1) \cdots S(3')$ $-x, 1-y, 1-z$]. Even though the packing of the molecules in both polymorphs is governed by different modes of interaction, the normalised cell volumes differ by less than 1%. **2A-2** exhibits significantly distorted geometry at the gold centre compared

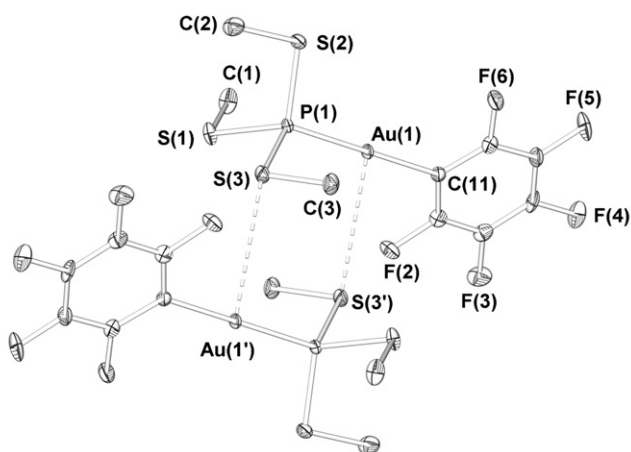


Fig. 6. Molecular structure of **2B**; $Au \cdots S$ interactions are indicated by dashed lines.

to the other molecule **2A-1** whose angle is close to the expected 180° , as it is the case in **2B**. The plane of the C_6F_5 ring in **2A-1** is nearly eclipsed with the $P(1)-S(13)$ bond while the C_6F_5 ring in **2A-2** adopts a staggered conformation also found in polymorph **B**.

The bond lengths in both polymorphs are the same within experimental error, with only the $Au(1)-P(1)$ bond of **2A-1** somewhat shorter than in the other molecules **2A-2** and **2B**. The $Au-P$ distances in both polymorphs of **2** are longer than the $Au-P$ distances of **1**, resembling the situation in chloro(triphenylphosphane)gold(I) ($Au-P$ 2.233 Å) [26] and (pentafluorophenyl)(triphenylphosphane)gold(I) ($Au-P$ 2.273 Å) [27].

The crystal structure of 1,2-bis(1,3,2-dithiaphospholan-2-ylthio)ethane has been reported [28]. It crystallises in the space group $P2_1/c$ with two molecules in the unit cell. Only half of the molecule is unique and an inversion centre is located at the bridging $C-C$ bond. Two $P-S$ distances [2.120(3) and 2.126(3) Å] and the exocyclic $P-S-C$ angle [$98.7(3)^\circ$] are comparable to the values in $(PhS)_3P$. In the five-membered ring one $P-S$ bond is shorter than expected [2.102(3) Å] and the $P-S-C$ angles [$96.9(3)^\circ$ and $101.8(3)^\circ$] are slightly distorted. In the molecular structure of compound **6** (Fig. 7), the conformation of the ligand has changed: instead of the arrangement with an inversion centre, a structure with a C_2 axis through the $C(1)-C(1')$ and $Au(1) \cdots Au(1')$ bonds is observed which allows intramolecular aurophilic bonding. The $P(1)-Au(1) \cdots Au(1')-P(1')$ torsion angle is $110.19(13)^\circ$. Again, coordination causes the $P-S$ bonds to shorten to 2.067(4), 2.081(3) and 2.086(4) Å; the situation found in the free ligand, i.e., that one of the cyclic $P-S$ bonds is shorter than the other two, is retained. The $Au-P-S$ angles do not follow the trend of the other compounds with two angles at 117° and one at 108° but have intermediate values, probably caused by restraints associated with the five-membered ring. The $P(1)-Au(1)-C(11)$ angle deviates from linearity, a result of the intramolecular aurophilic attraction of the gold atoms.

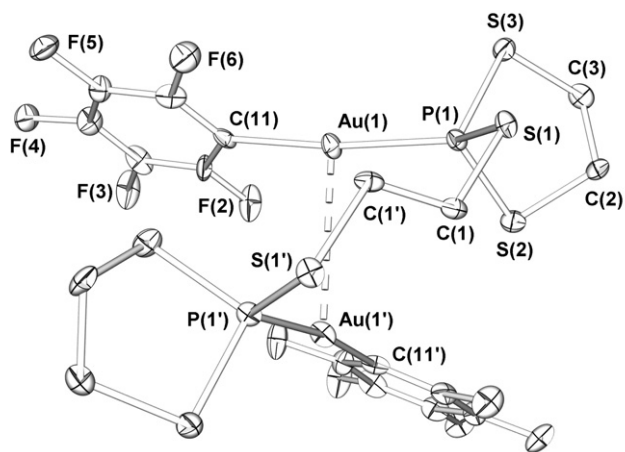


Fig. 7. Molecular structure of **6**.

4. Conclusion

The present study expands the scope of trithiophosphite coordination chemistry and shows that gold(I) trithiophosphite complexes are stable compounds and easily accessible from common starting materials. The ligands only being coordinated via their phosphorus atoms and the gold(I) centres exhibiting the standard linear dicoordinate geometry, though weak inter- and intramolecular Au...S contacts are also observed. The simplest complex chloro(trimethyltrithiophosphite)gold(I) and the isostructural chloro(trimethylphosphite)gold(I) aggregate in infinite chains via Au...Au interactions.

Appendix. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 609872–609877 for compounds **1**, **2A**, **2B**, **3**, **6**, and **8**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.034.

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