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Novel Gold(I) and Silver(I) Complexes of Phosphorus-1,1,-dithiolates and Molecular Structure of [O,O'-(Bornyl)₂PS₂]H₃NC(CH₃)₃

Samet Solak¹, Cemal Aydemir¹, Mehmet Karakus^{1*} and Peter Lönnecke²

Abstract

Background: The novel chiral phosphorus-1,1-dithiolates [4-CH₃OC₆H₄P(S)(OR)S]⁻[H₃NC(CH₃)₃]⁺ were synthesized by the reaction of [RPS₂]₂ (R = 4-MeOC₆H₄) or P₂S₅ and the respective alcohol ROH (R = myrtanyl, 2-naphthylethyl, myrtenyl, borneol) in toluene. The reaction of phosphorus-1,1-dithiolates **1–4** and Au(tht)Cl, AuClPPh₃ or AgNO₃ and PPh₃ gave rise to gold(I)- and silver(I)-complexes in THF. All compounds have been characterised by elemental analyses, IR, NMR (¹H-, ¹³C- and ³¹P-) spectroscopy as well as MS measurements. Optical rotation values confirmed the chirality of the compounds. The Compound **4** has been characterized structurally by X-ray crystallography.

Results: Phosphorus-1,1-dithiolate compounds were formed as liquids and were treated with suitable amine in order to convert them to their salts **1–4**. They have been successfully characterized spectroscopically (IR, ¹H, ¹³C, ³¹P NMR) as well as mass spectra. The compound **4** has been also structurally by X-ray crystallography. The compound **4** crystallizes in the orthorhombic space group P2(1)2(1)2(1) with Z = 4. Compounds containing phosphorus and sulfur donor atoms are excellent ligands due to offering many metal complexes especially group 11–12 metals. The synthesis of gold(I) and silver(I) complexes with chiral phosphorus-1,1-dithiolate and triphenylphosphine have been described and investigated.

Conclusions: In the present work, we report the synthesis, characterization of the chiral phosphorus-1,1-dithiolate ligands and preparing the gold(I) and silver(I) phosphorus-1,1-dithiolate or S-donor with phosphine complexes. The molecular structure of the Compound **4** was determined by X-ray diffraction. Due to an easy synthesis method of phosphorus-1,1-dithiolate compounds and a good complexing reagent, it is possible the improvement of the collecting metallic gold or silver from the minerals. When the more ionic salt of phosphorus-1,1-dithiolate compounds were prepared in this way, the water can be used as a cheap solvent. As a result, it can be an alternative method for the collecting metallic gold or silver from the minerals in future.

Keywords: Phosphorus-1,1-dithiolate, Chiral, Silver(I) and gold(I) complexes

Background

Phosphorus-1,1'-dithiolate ligands are an important class in organophosphorus chemistry [1,2]. To date, many phosphorus-1,1'-dithiolate have been synthesized and widely utilised in agricultural, medicinal and technological fields [1-4]. Since the discovery of Lawesson reagent's and its analogue, they have been used a thionation reagent in organic chemistry and also considerable number of dithiophosphonates and their metal complexes have been

synthesized [5-29]. For example, dithiophosphonates which are derivatives of phosphorus-1,1'-dithiolate ligands are not commercially available but they can be easily synthesized by the reaction of Lawesson's reagent or Ferrocenyl Lawesson's reagent and the respective alcohols or amines due to a ring opening reaction by nucleophilic attack. The application of metal complexes in the field of medicinal, bioinorganic and bioorganic chemistry has become important in recent decades. For example, some complexes of gold(I), such as Auranofin and some related complexes have been used in the treatment of severe rheumatoid arthritis [30]. Although there are many gold(I), silver(I) and copper(I) complexes of dithiophosphonates

* Correspondence: mkarakus@pau.edu.tr

¹Department of Chemistry, Faculty of Arts & Sciences, Pamukkale University, Kinikli 20075, Denizli, Turkey

Full list of author information is available at the end of the article

[8-12,22,24], chiral dithiophosphonates and their metal complexes are rare. Recently, a few gold(I) complexes with chiral dithiophosphonates have been reported in our laboratory [5,6].

In the present work, we report mono and dinuclear metal complexes with chiral dithiophosphonates and also triphenylphosphine complexes. All compounds were characterized by elemental analyses, IR, NMR (^1H -, ^{13}C -, ^{31}P -) spectroscopy as well as MS measurements.

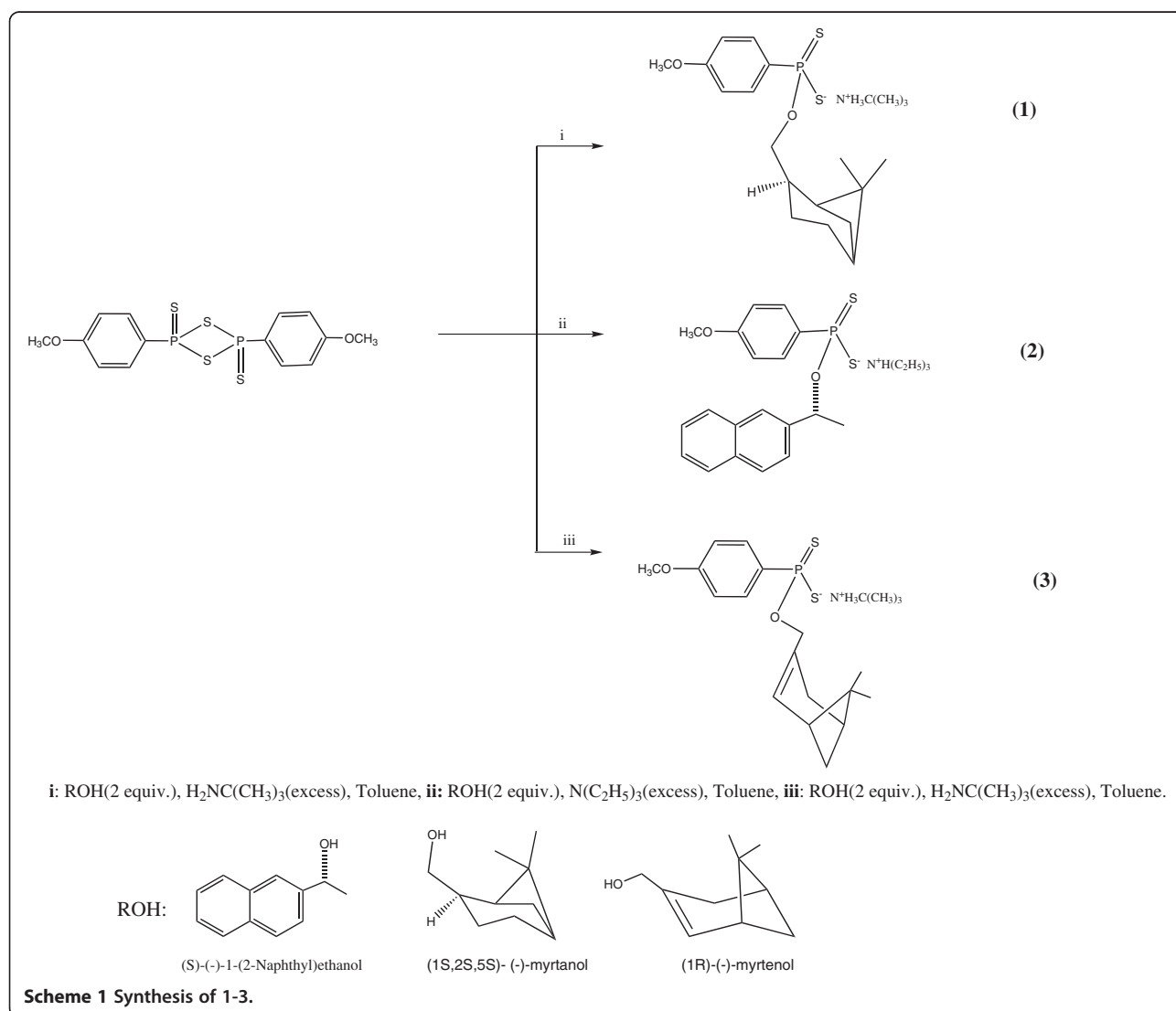
Results and discussion

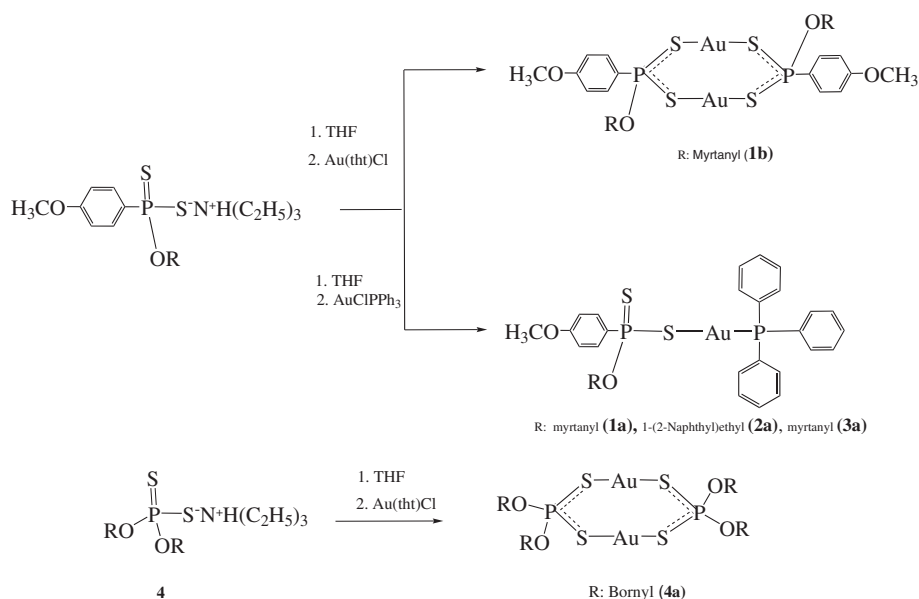
Chiral phosphorus-1,1-dithiolate ligands have been synthesized from Lawesson's reagent and chiral hydroxyl compounds (Scheme 1).

O-dithiophosphonic acid derivatives of phosphorus-1,1-dithiolate were formed as liquids and were treated with suitable amine in order to convert them to their salts **1-4**. The ^{31}P NMR spectra of the ligands **1-4** were measured

in $[\text{D}_6]\text{DMSO}$ and showed one signal as expected. The synthesis and X-ray determination of the compound **2** was reported by Solak et al. [7] but the spectral studies of the compound **2** were not. All ligands **1-4** and gold(I) complexes reported here have been characterized by elemental analysis, IR, NMR and mass spectroscopies. An analogue (triethyl ammonium -O,O'-diborneildithiophosphate) of the compound **4** was synthesized by Ohta et al. [31]. In this study, a single crystal structural and full spectroscopically studies of the compound **4**, *tert*-butylammonium -O,O'-diborneildithiophosphate, also performed here.

The synthesis of gold(I) and silver(I) complexes with chiral phosphorus-1,1-dithiolate and triphenylphosphine have been described and also characterized by elemental analyses, IR, NMR and MS spectroscopies (Additional file 1). The synthesis mononuclear and dinuclear gold(I) complexes were summarized in the Scheme 2. The ligands **1**, **2** and **3** were reacted with $\text{AuCl}(\text{PPh}_3)$ in order





Scheme 2 Synthesis of dinuclear and mononuclear gold(I) complexes 1a-4a.

to obtain gold(I)-phosphino complexes with phosphorus-1,1,-dithiolate (Scheme 2). The ³¹P NMR spectrum of **1a** exhibits two signals at 100.33 ppm (PS₂) and 37.30 ppm (PPh₃). The complexes **2a** and **3a** also showed two signals in the ³¹P NMR spectrum as expected and other spectroscopic data confirm their structure (Additional file 1). The reaction of the ligands **1** and **4** with Au(tht)Cl gave rise to dinuclear gold(I) complex **1b** and **4a**. The spectra of the complexes **1b** and **4a** were suitable and agree with reported similar structures by Van Zyl et al. [8-10,22]. To obtain dinuclear gold(I) complexes with amido derivatives of phosphoro-1,1-dithiolate, all attempts were unsuccessful. The complex **1b** displayed two signals as expected in its ³¹P NMR spectrum. One signal is assigned to the trans isomer and the other is assigned to cis isomer. Both signals in the ³¹P NMR spectrum for dinuclear and mononuclear gold(I) complexes are slightly upfield when compared to the free ligands.

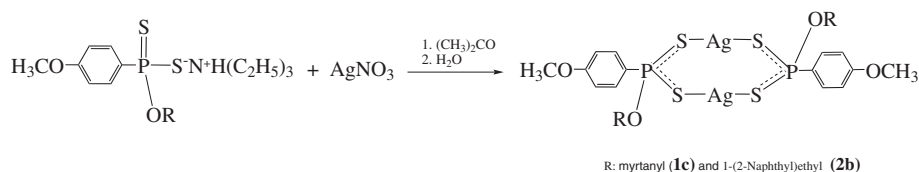
In the case of dinuclear silver(I) complexes, the ligands were reacted with AgNO₃ in acetone-water(1:1) at room temperature (Scheme 3). The ³¹P NMR spectra of the dinuclear silver(I) complexes are similar to the dinuclear gold(I) complexes. The expected cis and trans isomer

were observed at 107.35 and 105.49 ppm (for **1c**) and 107.2 and 105.8 ppm (for **2b**) (Additional file 1).

The IR spectrum of the ligands and their complexes showed two characteristic bands at around 692–642 cm⁻¹ and 582 – 515 cm⁻¹ which are assigned to ν_{as}(PS₂) and ν_s(PS₂), respectively (Additional file 1). The molecular ion peak of the ligands **2** and **4**, the complexes **1b** and **2a** were observed at m/z = 430 (for [M + 1]⁺), 476 [for M]⁺, 832 (for [M]⁺), 1104 (for [M]⁺), respectively, in their mass spectra whereas the other ligands and the complexes exhibited m/z-values for identifiable certain fragments (Additional file 1). Specific rotations of all compounds showed that only one optical isomer was formed.

Molecular structure of 4

Single crystals of **4** suitable for X-ray diffraction studies were obtained from acetone/*n*-hexane. Compound **4** crystallizes in the orthorhombic space group P2(1)2(1)2(1) with Z = 4. The molecular structure of **4** is depicted in Figure 1. Selected bond lengths and angles are given Table 1 and Crystal and structure-refinement data in Table 2. The P1-S1 and P1-S2 bond lengths are 197.56(5) and 198.13(5) pm, respectively. Those values are very



Scheme 3 Synthesis of dinuclear silver(I) complexes (1c and 2c).

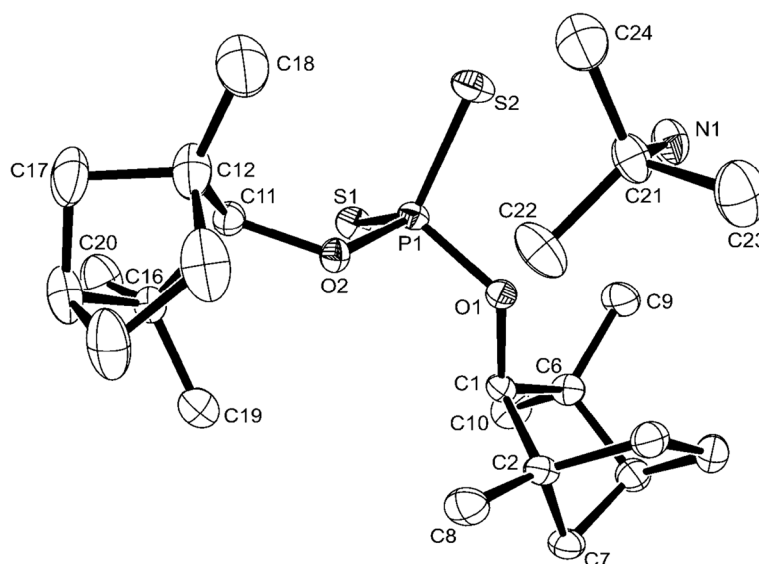


Figure 1 Molecular structure of **4** (ORTEP, 50% probability).

close to each other due to a delocalized PS_2 fragments. Bond lengths and angles are in a good agreement with those of related previously reported compounds [7,9]. Figure 1 shows that the phosphorus atom has a tetrahedral coordination environment with [O1-P1-S1 113.30(4)°, O2-P1-S1 110.12(4)°, O(1)-P(1)-S(2) 105.02(4)°, O2-P1-S2 110.05(4)°] and the O1-P1-O2 [99.61(6)°] having a deviation from the ideal value (109.5°).

Experimental

Materials

When necessary, the reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All other chemicals were purchased from commercial sources and used directly without further purification.

Measurements

Elemental analyses were determined with a GmbH varioMICRO CHNS apparatus. Melting points were

determined by using Electrothermal apparatus. NMR spectra were recorded on a Bruker AVANCE DRX 400 NMR spectrometer and Jeol GSX 270 in $CDCl_3$ and d_6 -DMSO. IR spectra was measured on a Perkin-Elmer 2000 FTIR spectrophotometer (4000 – 400 cm^{-1}). Mass spectra were recorded with an AGILENT 1100 MSD and Waters machines. Optical rotation values were determined with an automatic digital ADP 440+ polarimeter.

X-ray crystallography

Data were collected on an Xcalibur-S diffractometer (Agilent Technologies) using Mo- K_α radiation ($\lambda = 71.073$ pm) and ω -scan rotation (see Table 2). Data reduction was performed with CrysAlis Pro [32] including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by direct methods and the refinement of all non-hydrogen atoms was performed with SHELX97 [33]. All non-hydrogen atoms were refined with anisotropic thermal parameters. With the exception of one borneol molecule (C(11) to C(20)) all hydrogen atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. The structure figure was generated with DIAMOND-3 [34]. Crystallographic details are given in the Additional file 2. CCDC (4) 921954 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of compounds

Synthesis of ^tbutyl ammonium salt of (1S,2S,5S)-(-)-myrtanyl-4-methoxyphenyl dithiophosphonate 1

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's reagent: LR) (0.50 g, 1.23 mmol) was

Table 1 Bond lengths [pm] and angles [°] for **4**

| | |
|----------------|------------|
| S(1)-P(1) | 197.56(5) |
| S(2)-P(1) | 198.13(5) |
| P(1)-O(1) | 159.14(11) |
| P(1)-O(2) | 160.96(11) |
| O(1)-P(1)-O(2) | 99.61(6) |
| O(1)-P(1)-S(1) | 113.30(4) |
| O(2)-P(1)-S(1) | 110.12(4) |
| O(1)-P(1)-S(2) | 105.02(4) |
| O(2)-P(1)-S(2) | 110.05(4) |
| S(1)-P(1)-S(2) | 117.23(2) |

Table 2 Crystal data and structure refinement for 4

| | | |
|-----------------------------------|---|---------|
| Empirical formula | C ₂₄ H ₄₆ N O ₂ P S ₂ | |
| Formula weight | 475.71 | |
| Temperature | 130(2) K | |
| Wavelength | 71.073 pm | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 1029.440(10) pm | α = 90° |
| | b = 1366.64(2) pm | β = 90° |
| | c = 1949.83(2) pm | δ = 90° |
| Volume | 2.74316(6) nm ³ | |
| Z | 4 | |
| Density (calculated) | 1.152 Mg/m ³ | |
| Absorption coefficient | 0.272 mm ⁻¹ | |
| F(000) | 1040 | |
| Crystal size | 0.5 × 0.4 × 0.3 mm ³ | |
| Theta range for data collection | 2.98 to 30.51° | |
| Index ranges | -14 < h < 14, -19 < k < 19, -27 < l < 27 | |
| Reflections collected | 56268 | |
| Independent reflections | 8360 [R(int) = 0.0375] | |
| Completeness to theta = 30.51° | 99.8% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1 and 0.98374 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 8360 / 0 / 390 | |
| Goodness-of-fit on F ² | 0.997 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0348, wR2 = 0.0909 | |
| R indices (all data) | R1 = 0.0403, wR2 = 0.0925 | |
| Absolute structure parameter | 0.01(5) | |
| Largest diff. peak and hole | 0.626 and -0.309 e.Å ⁻³ | |

reacted with 1S,2S,5S)-(-)-myrtanol (0.39g, 2.4693 mmol) in toluene (20 mL). The mixture was refluxed until all solids had dissolved. The colourless solution was cooled to rt, filtered and treated with excess tert-butyl amine. The product precipitated at -18°C from toluene as a white solid, which was isolated by filtration, washed with toluene and n-hexane and then dried in air. Yield: 0.76 g (72%), m. p.: 161-163°C. $[\alpha]_{589}^{25} = 57.14$ (c = 0.105 in THF). Elemental analysis calculated for C₂₁H₃₆NO₂PS₂ (429.63 g.mol⁻¹): C, 58.71; H, 8.45; N, 3.26; S, 14.93, Found: C, 59.18; H, 8.51; N, 3.18; S, 14.69. IR(cm⁻¹): 670 (ν_{asym} PS₂) and 556(ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 8.07 (dd, 2H, ³J_{P,H} = 13.65 Hz, ³J_{H,H} = 8.80 Hz), 6.9 (dd, 2H, ⁴J_{P,H} = 2.57 Hz, ³J_{H,H} = 8.75 Hz), 3.85 (s, 3H, OCH₃), 3.48 (m, 2H, OCH₂), 1.88 (m, 7H, myrtanyl), 1.37 (s, 9H, 3×CH₃), 1.17 (d, 3H, CH₃),

0.79(d, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 161.32 (d, ⁴J_{PC} = 2.91 Hz), 133.16(d, ¹J_{PC} = 109.49 Hz), 132.32 (d, ²J_{PC} = 13.43 Hz), 112.91(d, ³J_{PC} = 14.83 Hz), 68.78(d, ²J_{PC} = 8.55), 55.36, 54.00, 35.45(d, ³J_{PC} = 8.40 Hz) 28.22, 42.10, 40.86, 39.02, 26.63, 24.09, 23.36, 20.12, 18.12 ppm. ³¹P NMR (CDCl₃): δ = 105.24 ppm. MS: m/z = 430[M + 1]⁺. 357[M-NH₂C(CH₃)₃]⁺.

Triethyl ammonium salt of (S)-(-)-O-(2-naphthyl)ethyl-4-methoxyphenyl dithiophosphonate 2

Compound 2 was prepared as described in the literature [7]. $[\alpha]_{589}^{25} = -37.74$ (c = 0.053 in THF). Elemental analysis calculated for C₂₅H₃₄NO₂PS₂ (475.66 g.mol⁻¹): C, 63.13; H, 7.21; N, 2.95; S, 13.48 %, Found: C, 63.59; H, 7.32; N, 2.92; S, 12.74 %. IR(cm⁻¹): 667 (ν_{asym} PS₂) and 569 (ν_{sym} PS₂). ¹H-NMR (CDCl₃): δ = 9.89 (br, H, HN), 8.1 (dd, 2H, ³J_{P,H} = 13.58 Hz, ³J_{H,H} = 8.81 Hz), 7.21 (m, 4H.), 7.53 (dd, 1H), 7.40 (m, 2H), 6.7 (dd, 2H, ⁴J_{P,H} = 2.62 Hz, ³J_{H,H} = 8.87 Hz), 5.7 (m, 1H, OCH, ³J_{P,H} = 13.07, ²J_{H,H} = 6.53 Hz), 3.69 (s, 3H, OCH₃), 3.07 (q, 6H, 3×NCH₂), 1.56 (d, 3H, CH₃), 1.18 (t, 9H, 3×CH₃) ppm. ¹³C NMR (CDCl₃): δ = 160.75(d, ⁴J_{PC} = 3.03 Hz), 141.64(d, ³J_{PC} = 4.32 Hz), 135.54(d, ¹J_{PC} = 111.36 Hz), 133.11, 132.10, 132.03(d, ²J_{PC} = 13.48 Hz), 127.97, 127.50, 125.70, 125.45, 124.99(d, ⁴J_{PC} = 5.01 Hz), 112.52(d, ³J_{PC} = 14.88 Hz), 73.84(d, ²J_{PC} = 7.41), 55.23, 45.90, 24.66(d, ³J_{PC} = 4.19 Hz), 8.48 ppm. ³¹P NMR (CDCl₃): δ = 105.35 ppm.

Synthesis of ^tButyl ammonium salt of (1R)-(-)-O-myrtanyl-4-methoxyphenyl dithiophosphonate 3

Compound 3 was prepared in the same way as compound 1, from LR (0.50 g, 1.23 mmol) and (1R)-(-)-myrtenol (0.38 mL, 2.4693 mmol) in toluene (20 mL). Yield: 0.73 g (69%), m.p.: 110-113°C. $[\alpha]_{589}^{25} = 159.1$ (c = 0.044 in THF). Elemental analysis calculated for C₂₁H₃₄NO₂PS₂ (427.61 g.mol⁻¹): C, 58.99; H, 8.01; N, 3.28; S, 15.00; Found: C, 59.18; H, 8.51; N, 3.18; S, 14.69. IR(cm⁻¹): 669 (ν_{asym} PS₂) and 556 (ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 8.07 (dd, ³J_{P,H} = 13.59 Hz, ³J_{H,H} = 8.83 Hz), 6.9 (dd, 2H, ⁴J_{P,H} = 2.66 Hz, ³J_{H,H} = 8.88 Hz), 4.1 (m, 2H, OCH₂), 5.46 (t, H, CH), 3.84 (s, 3H, OCH₃), 2.2 (m, 5H, myrtenyl), 1.38 (s, 9H, 3×CH₃), 1.27 (d, 3H, CH₃) 1.09 (d, 1H, CH) 0.74 (d, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 161.33(d, ⁴J_{PC} = 3.03 Hz), 144.20(d, ³J_{PC} = 9.68 Hz), 133.25 (d, ¹J_{PC} = 109.67 Hz), 132.29 (d, ²J_{PC} = 13.50 Hz), 119.69, 112.92 (d, ³J_{PC} = 14.91 Hz), 67.70 (d, ²J_{PC} = 7.62), 55.36, 53.17, 43.25, 40.76, 37.98, 31.35, 28.19, 26.16, 20.97 ppm. ³¹P NMR (CDCl₃): δ = 104.88 ppm.

Synthesis of ^tButyl ammonium salt of O,O'-dibornyl-4-methoxyphenyl dithiophosphonate (4)

P₄S₁₀ (1g, 2.25 mmol) was reacted with (-) borneol (2.77 g, 9 mmol) in a 1:4 ratio in 50 mL hot toluene to give the crude dithiophosphoric acid. The reactions were refluxed until all solids dissolved and the yellow

solutions were obtained. The solution was filtered and then was treated with excess *tert*-butyl amine at r.t. The *tert*-butyl ammonium salt of O,O'-dibornyl-dithiophosphoric acids resulted in as a precipitated white solid product. The product was filtrated, washed with pentane several times, dried under vacuum and recrystallized from acetone/hexane. Yield: 3.89g (91%), m.p.: 188°C. Elemental analysis calculated for C₂₄H₄₆NOPS₂(475.73 g/mol): C, 60.79; H, 9.26; N, 2.89; S, 13.18; Found: C, 60.59; H, 9.74; N, 2.94; S 13.48. IR(cm⁻¹): 665 (ν_{asym} PS₂) and 560 (ν_{sym} PS₂). ¹H-NMR (CDCl₃): δ = 4.64 (t, 2H), 2.28 (br, 4H), 2.00 (br, 2H), 1.71-1.79(br, m, 4H), 1.23(br, m, 4H), 0.91(s, 6H, 2×CH₃), 0.86(s, 6H, 2×CH₃), 0.85(s, 6H, 2×CH₃). ¹³C-NMR (CDCl₃): δ = 53.83, 49.52(d, ²J_{PC} = 6.74 Hz), 47.31, 44.93, 37.44, 28.30, 27.00, 19.94, 18.69, 13.67. ³¹P-NMR (CDCl₃): δ = 106.53(d). MS (FAB): m/z 476 [M]⁺.

Synthesis of complexes

[Au(PPh₃)(R¹PS₂(OR²))] (R¹: 4-methoxyphenyl and R²: ((1S,2S,5S)-(-)-myrtanyl) 1a

A solution of the compound **1** (0.044 g, 0.102 mmol) in THF (10 mL) was added dropwise to a solution of AuClPPh₃ (0.05 g, 0.102 mmol) in THF (10 mL) and stirred at r.t. for 2 h. A colourless solution was observed and then a solid, *t*-butylammonium chloride, was immediately precipitated. The reaction mixture was filtered and the solvent was removed under reduced pressure. The reaction mixture was filtered and 10 mL of *n*-hexane was added to the solution. The solvent was removed at room temperature and a white crystalline product was isolated. The white crystalline product was dried in air. Yield: 0.042 g (51%), m.p.: 72–74°C. [α]₅₈₉²⁵ = 37.97 (c = 0.079 in THF). Elemental analysis calculated for C₃₅H₃₉O₂SP₂Au (814.78 g.mol⁻¹); calcd: C, 51.60; H, 4.82; S, 7.87; Found: C, 49.78; H, 4.52; S, 10.61. IR(cm⁻¹): 668(ν_{asym} PS₂) and 536(ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 7.89(dd, 2H, ³J_{BH} = 13.77 Hz, ³J_{H,H} = 8.61 Hz), 7.50(m, 15H), 6.77 (dd, 2H, ³J_{H,H} = 8.31 Hz, ³J_{BH} = 2.18 Hz), 3.95 (q, H, OCH₂), 3.73 (s, 3H, OCH₃) 1.80 - 0.78 (br, 15H, myrtanyl) ppm. ³¹P NMR (CDCl₃): δ = 100.33 (PS₂), 37.31(PPh₃) ppm.

[Au(R¹PS₂(OR²))]₂ (R¹: 4-methoxyphenyl and R²: ((1S,2S,5S)-(-)-myrtanyl) 1b

A solution of **1** (0.15 g, 0.35 mmol) in THF (10 mL) was added dropwise to a solution of Au(tht)Cl (tht = tetrahydrothiophene) (0.11 g, 0.35 mmol) in THF (10 mL) and stirred for 2 h. A solid, *t*-butylammonium chloride, was immediately observed. The reaction mixture was filtered and 10 mL of *n*-hexane was added to the mixture. The solvent was removed at room temperature and orange crystals were isolated. Yield: 0.097 g (50%), m.p.: 123–125°C. [α]₅₈₉²⁵ = 29.85 (c = 0.067 in THF). Elemental analysis calculated for C₃₄H₄₈O₄S₄P₂Au₂ (1104.90 g.mol⁻¹): C, 36.96; H, 4.38; S, 11.61; Found: C, 36.76; H, 4.51; S,

11.75. IR(cm⁻¹): 640(ν_{asym} PS₂) and 542(ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 7.91 (br, 4H), 6.90 (dd, 4H, ³J_{H,H} = 8.63 Hz, ³J_{BH} = 2.41 Hz), 4.40 (br, 4H, OCH₂), 3.79 (s, 6H, OCH₃), 1.81-1.29 (m, 18H, myrtanyl), 1.17 (s, 6H, 2×CH₃), 0.79 (s, 6H, 2×CH₃) ppm. ¹³C NMR (CDCl₃): δ = 163.06 (d, ⁴J_{PC} = 3.12 Hz), 133.87 (d, ¹J_{PC} = 118.49 Hz), 132.46 (d, ²J_{PC} = 13.25 Hz), 113.95 (d, ³J_{PC} = 15.43 Hz), 71.31 (d, ²J_{PC} = 5.33), 55.51, 35.68 (d, ³J_{PC} = 7.70 Hz), 42.23, 40.84, 39.36, 28.20, 26.71, 24.03, 23.75, 20.28, 18.09 ppm. ³¹P NMR (CDCl₃): (cis, trans isomer) δ = 104.12, 100.95. MS(ESI): m/z = 1104[M]⁺, 907[M-Au]⁺.

[Ag(R¹PS₂(OR²))]₂ (R¹: 4-methoxyphenyl and R²: ((1S,2S,5S)-(-)-myrtanyl) 1c

The compound **1** (0.20 g, 0.41 mmol) was dissolved in acetone (10 mL). A solution of AgNO₃ (0.08 g, 0.41 mmol) in a mixture (10 mL) of acetone-water (1:1) was added dropwise to the solution and stirred for 2 h. A white powder solid was obtained, filtered and recrystallized in CHCl₃. The solvent was removed at room temperature and white powder were isolated. Yield: 0.14g (73%), m.p.: 124–126°C. [α]₅₈₉²⁵ = 27.39 (c = 0.073 in CHCl₃). Elemental analysis calculated for C₃₄H₄₈O₄S₄P₂Ag₂ (926.70 g.mol⁻¹): C, 44.07; H, 5.22; S, 13.84; Found: C, 43.62; H, 5.32; S, 13.37. IR(cm⁻¹): 656 (ν_{asym} PS₂) and 543 (ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 7.90 (dd, 4H, ³J_{BH} = 13.15 Hz, ³J_{H,H} = 8.54 Hz), 6.84 (br, 4H), 3.76 (s, 6H, 2×OCH₃), 1.9 (m, 18H, myrtanyl), 1.11 (d, 6H, CH₃) 0.73 (d, 6H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 162.24, 132.50 (d, ²J_{PC} = 13.24 Hz), 129.83 (d, ¹J_{PC} = 119.83 Hz), 113.54 (d, ³J_{PC} = 15.06 Hz), 70.25 (d, ²J_{PC} = 7.03), 55.42, 35.57 (d, ³J_{PC} = 8.40 Hz), 42.19, 40.87, 39.22, 26.69, 24.11, 23.66, 20.54, 18.14 ppm. ³¹P NMR (CDCl₃) (cis, trans isomer) δ = 107.35 and 105.49 ppm.

[Au(PPh₃)(R¹PS₂(OR²))] (R¹: 4-methoxyphenyl, R²: ((S)-(-)-O-(2-naphthyl)ethyl) 2a

2a was prepared in a similar manner to **1a** using AuClPPh₃ (0.049 g, 0.10 mmol) and *t*-butyl ammonium ((S)-(-)-O-(2-naphthyl)ethyl 4-methoxyphenyldithiophosphonate **2** (0.049 g, 0.10 mmol). Yield: 0.04g (48%), m.p.: 62–64 °C. [α]₅₈₉²⁵ = 51.94 (c = 0.077 in THF). Elemental analysis calculated for C₃₇H₃₃O₂S₂P₂Au (832.72 g.mol⁻¹): C, 53.37; H, 3.99; S, 7.70; Found: C, 52.50; H, 4.12; S, 7.12 %. IR(cm⁻¹): 674 (ν_{asym} PS₂) and 537 (ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 8.09(dd, 2H, ³J_{BH} = 13.94 Hz, ³J_{H,H} = 8.86 Hz), 7.5(br, 15H), 6.79 (dd, 2H, ³J_{H,H} = 8.86, ³J_{BH} = 3.06 Hz), 6.10(q, H, OCH), 3.78 (s, 3H, OCH₃), 1.78 (m, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 161.52 (d, ⁴J_{PC} = 4.42 Hz), 135.21(d, ¹J_{PC} = 134.60 Hz), 134.23(d, ²J_{PC} = 13.94 Hz), 132.07, 131.93, 131.70, 129.15, 128.14, 127.88, 127.56, 127.45, 125.84, 125.66, 125.01, 124.77, 124.66, 113.14 (d, ³J_{PC} = 15.63 Hz), 74.66(d, ²J_{PC} = 6.61 Hz), 55.30, 24.82(d) ppm. ³¹P NMR (CDCl₃): δ = 100.43 (PS₂), 37.20 (PPh₃). MS(ESI) = m/z: 832[M]⁺.

[Ag(R¹PS₂(OR²))]₂ (R¹: 4-methoxyphenyl and R²: (2-naphthyl) ethyl) **2b**

2b was prepared in a similar manner to **1b** using AgNO₃ (0.07 g, 0.41 mmol) and triethyl ammonium(S)-(–)-O-(2-naphthyl)ethyl-4-methoxyphenyl dithiophosphonate, (0.20 g, 0.41 mmol). Yield: 0.13 g (64%), m.p.: 114–115°C. [α]₅₈₉²⁵ = –36.14 (c = 0.083 in CHCl₃). Elemental analysis calculated for C₃₈H₃₆O₄P₂S₄Ag₂ (962.65 g.mol^{–1}): C, 47.41; H, 3.77; S, 13.32; Found: C, 46.15; H, 3.99; S, 12.29. IR(cm^{–1}): 655 (ν_{asym} PS₂) and 569 (ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 7.60 (br, 18H), 6.55 (br, 4H), 5.62 (br, 2H, OCH), 3.55 (s, 6H, OCH₃), 1.50 (d, 6H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 162.06 (d, ⁴J_{P,C} = 2.26 Hz), 139.78 (d, ⁴J_{P,C} = 4.27 Hz), 133.01 (d, ²J_{P,C} = 11.68 Hz), 129.94 (d, ¹J_{P,C} = 117.92 Hz), 128.26, 128.16, 127.03, 125.89, 124.69, 124.99 (d, ⁴J_{P,C} = 5.01 Hz), 113.22 (d, ³J_{P,C} = 12.57 Hz), 55.27, 24.66 (d) ppm. ³¹P NMR (CDCl₃) (cis, trans isomer): δ = 107.21, 105.84 ppm. MS (ESI) = m/z: 855[M-Ag]⁺.

2.3.6. [Au(PPh₃)(R¹PS₂(OR²))] (R¹: 4-methoxyphenyl and R²: (1R-(–)-myrtenyl) **3a**

3a was prepared in a similar manner to **1a** using AuClPPh₃ (0.05 g, 0.10 mmol) and t-butyl ammonium-(1R)-(–)-myrtenyl-4-methoxyphenyldithiophosphonate **3** (0.048 g, 0.10 mmol). Yield: 0.036 g (43%), m.p.: 76–78°C. [α]₅₈₉²⁵ = 30.76 (c = 0.065 in THF). C₃₅H₃₇O₂SP₂Au (812.73 g.mol^{–1}); calcd: C, 51.72; H, 4.59; S, 7.89%, found: C, 51.01; H, 5.22; S, 6.69%. IR(cm^{–1}): 691 (ν_{asym} PS₂) and 565 (ν_{sym} PS₂). ¹H NMR (CDCl₃): δ = 7.99 (dd, 2H, ³J_{P,H} = 13.84 Hz, ³J_{H,H} = 8.76 Hz), 7.41-7.19(br, 15H,), 6.75 (dd, 2H, ³J_{H,H} = 8.79 Hz, ³J_{P,H} = 2.96 Hz), 5.49 (t, H, CH), 4.52 (q, H, OCH₂), 3.71 (s, 3H, OCH₃), 2.25 - 0.78 (br, 12H, myrtenyl) ppm. ¹³C NMR (CDCl₃): δ = 161.56 (s, ⁴J_{P,C} = 3.32 Hz), 144.22 (d, ³J_{P,C} = 9.87 Hz), 134.37(d, ¹J_{P,C} = 121.39 Hz), 132.29 (d, ²J_{P,C} = 13.50 Hz), 131.75, 129.52, 128.94, 120.26, 113.25 (d, ³J_{P,C} = 15.47 Hz), 66.96 (d, ²J_{P,C} = 6.27 Hz), 55.34, 43.32, 40.86, 38.10, 31.20, 26.19, 21.20 ppm. ³¹P NMR (CDCl₃): δ = 100.60 (PS₂), 37.29 (PPh₃) ppm.

Synthesis of [O,O'-(Bornyl)₂PS₂]₂Au₂ **4a**

Compound **4a** was prepared in a similar manner to **1b** using **4** (0.075 g, 0.155 mmol) and Au(tht)Cl (tht = tetrahydrothiophene) (0.05 g, 0.155 mmol) in THF(20 mL). Yield: 0.065 g (% 70), m.p. 212°C. Elemental analysis calculated for C₄₀H₆₈O₄P₂S₄Au₂(1197.10 g/mol): C, 40.67; H, 5.68; S, 10.68; Found C, 40.13; H, 5.72; S, 10.71. IR(cm^{–1}): 644(ν_{asym} PS₂) and 543(ν_{sym} PS₂). ¹H-NMR (CDCl₃): δ = 4.95 (br, t, 2H), 2.43 (br, t, 2H), 1.79(br, s, 4H), 1.44(t, 4H, ³J_{H,H} = Hz), 1.30(br, t, 4H), 0.99(s, 6H, 2xCH₃), 0.93(s, 6H, 2xCH₃), 0.89(s, 6H, 2xCH₃). ¹³C-NMR (CDCl₃): δ = 49.94, 47.55, 47.95, 37.35, 30.05, 27.96, 26.86, 19.91, 18.93, 13.71. ³¹P-NMR (CDCl₃): δ = 102.19(s). MS (ESI): m/z 999.5 [M-Au]⁺, 967.5[M-AuS]⁺.

Conclusion

The new chiral phosphorus-1,1-dithiolate ligands were synthesized and were then utilised in the preparation of gold(I) and silver(I) phosphorus-1,1-dithiolate or S-donor with phosphine complexes. If the phosphorus-1,1-dithiolate ligands carefully utilised in the preparation of gold(I) complexes, those type compounds can be improvement of the collecting metallic gold or silver from the minerals. We hope that this study will extend the unexplored area in phosphoro-1,1-dithiolate chemistry.

Additional files

Additional file 1: Spectra of the compounds.

Additional file 2: Cif file of compound 4.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MK has coordinated the experimental work, characterized the structure of the all compounds and wrote the manuscript. SS synthesized the compounds and measured the IR spectra. CA synthesized and obtained the single crystals of the compound **4**. PL carried out X-ray studies. All authors have read and approved the final manuscript.

Authors' information

Part of M.Sc. of S. Solak.

Acknowledgments

This study was supported by Turkish Council of Research and Technology, TUBITAK (Grant no: 107T817) and Pamukkale University (Grant nos: 2009FBE020 and 2010FBE043).

Author details

¹Department of Chemistry, Faculty of Arts & Sciences, Pamukkale University, Kinikli 20075, Denizli, Turkey. ²Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103, Leipzig, Germany.

Received: 12 February 2013 Accepted: 6 May 2013

Published: 20 May 2013

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doi:10.1186/1752-153X-7-89

Cite this article as: Solak et al.: Novel Gold(I) and Silver(I) Complexes of Phosphorus 1,1,-dithiolates and Molecular Structure of $[\text{O},\text{O}'\text{-}(\text{Bornyl})_2\text{PS}_2]\text{H}_3\text{NC}(\text{CH}_3)_3$. *Chemistry Central Journal* 2013 **7**:89.

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