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Different coordination behavior of a catechol phosphine and its sulfide: Formation of an unprecedented dinuclear rhodium complex with a non-coordinated P═S unit

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Dedicated to Professor Wolfgang Kaim on the occasion of his 60th birthday.

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ABSTRACT

Sulfurization of 3-[(diphenylphosphinyl)methyl]benzene-1,2-diol **1** produced phosphine sulfide **3**. Both ligands reacted easily to form gold(I) and rhodium(I) complexes which were characterized by analytical and spectroscopic data, and single-crystal X-ray diffraction studies. Whereas the phosphine prefers to form complexes with a metal-to-ligand ratio of 1:2 with both metals, the phosphine sulfide exhibits a reduced donor power and yields only a 1:1 complex with AuCl. With rhodium(I), formation of a homobimetallic complex with a metal-to-ligand ratio of 2:1 was found. This complex displays an unusual coordination of both metal atoms to the catechol moiety whereas the phosphine sulfide moiety remains inactive.

1. Introduction

During the last three decades, bidentate phosphine ligands have become a powerful instrument for applications in coordination chemistry and catalysis [1]. In spite of the tremendous evolution of the field, the design and synthesis of tailored bisphosphine ligands still remains a time consuming and complex task. Recent developments have focused in particular on modular syntheses which permit to assemble bidentate ligands from smaller building blocks. This task can either be achieved by employing conventional coupling reactions allowing the introduction of two phosphine units into an organic substrate [2], or by connecting two building blocks by non-covalent interactions such as hydrogen bonds, electrostatic attraction, or Lewis-donor–acceptor interactions [3], following a supramolecular "aufbau principle" [3].

The challenge in this approach is to control geometrical constraints of the ligand, which are often categorized in terms of descriptors like the cone angle or the "natural bite angle" [4]. We have recently established a method for template-controlled synthesis of heterobimetallic chelate complexes **2** [5] from the flexible, ditopic phosphine ligand **1** which exhibits binding sites at the phosphorus atom and the catechol unit (Scheme 1). Complexes **2** can be put together either in a stepwise manner, introducing each metal in a separate reaction [6], or in a single step via a self-assembly process, and it has been shown that variation of the template gives rise to a series of compounds featuring controlled variation of P–Pd–P bite angles [5].

As an alternative to controlling the geometrical constraints by using different templates, one can also conceive to modify the ligand backbone. Converting the phosphine into the corresponding sulfide (Scheme 1) is easy to implement and would seem an obvious choice since the P═S-moiety exhibits a similar preference to coordinate to "soft" lewis acids as the phosphine functionality of **2**, and is known to form stable complexes with late transition metals [7]. In the following, we report the synthesis of phosphine sulfide **3**, and compare the reactivity of phosphine **1** and phosphine sulfide **3** toward some gold(I) and rhodium(I) compounds.

2. Experimental

2.1. General information

All manipulations were carried out under dry argon using standard Schlenk techniques. Solvents and triethylamine were dried by standard procedures [8] unless otherwise mentioned. Catechol phosphine **1** was prepared as reported earlier [9]. (Tetrahydrothiophene)–gold(I) chloride was prepared as described in the literature [10], [Rh(CO)$_2$(acac)] is commercially available and was used without further purification. Solution NMR spectra were recorded on Bruker Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz, ^{103}Rh: 12.74 MHz), Avance 250 (^{1}H: 250 MHz, ^{13}C:

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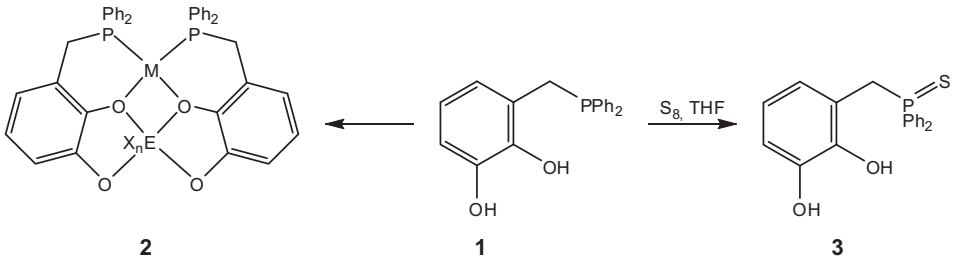


Scheme 1. Synthesis of phosphine **1**, heterobimetallic complexes **2**, and phosphine sulfide **3** (M = Pd, Pt, Cu, Ag, Au; EXn = B, $SnCl_2$, $SnMe_2$, GaCl, BiCl).

62.8 MHz, ^{31}P: 101.2 MHz) or Avance 600 spectrometers (^{1}H: 600.1 MHz, ^{103}Rh: 18.97 MHz) at 303 K unless mentioned otherwise; ^{103}Rh NMR data were collected from ^{1}H-detected ^{1}H,^{103}Rh gs-HMQC experiments. Chemical shifts are referenced to external TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), or a virtual reference frequency of Ξ = 3.160000 MHz (^{103}Rh). Coupling constants are given as absolute values; prefixes *i*, *o*, *m*, *p*-Ph denote atoms of P–C_6H_5 substituents, *i*, *o*, *m*, *p*-cat represents atoms in the catechol rings. EI-MS: Varian MAT 711, 70 eV. ESI-MS: Bruker Daltonics-micrOTOF-Q. Given *m*/*e*-numbers refer to the mass of the most abundant isotopomer. The suggested elemental composition was in all cases confirmed by comparison of observed and simulated isotope patterns. IR: Nicolet 6700 FT-IR with ATR unit, spectral range 4000–600 cm^{-1}; Elemental analyses: Perkin–Elmer 2400CHSN/O Analyser. Deviations from calculated values are in the case of solvates attributable to nonstoichiometric amounts of solvent; complex **6** is light sensitive and presumably underwent some decomposition during sample preparation.

*2.1.1. 3-[(Diphenylphosphorothioyl)-methyl]-benzene-1,2-diole (**3**)*

Sulfur (255 mg, 7.95 mmol) was added to a solution of 3-[(diphenylphosphanyl)-methyl]-benzene-1,2-diole **1** (2.24 g, 7.27 mmol) in 100 ml anhydrous THF. The mixture was stirred for 6 h at room temperature. The solvent was then evaporated and the residue recrystallized from MeOH to give colorless crystals, suitable for X-ray analysis (2.14 g, yield 86%, m.p. 137 °C). *Anal.* Calc. for $C_{19}H_{17}O_2PS$: C, 67.05; H, 5.03. Found: C, 66.58; H, 4.97%. EI-MS: *m*/*e* = 340.0 [M$^+$], 324, 308 [M$^+$−S], 217 [$SPPh_2^+$], 139 [$SPPh^+$], 123 [$C_7H_7O_2^+$], 107 [$C_6H_3O_2^+$]. ^{1}H NMR (DMSO-d_6): δ = 9.11 (s, 1H, OH); 8.24 (s, 1H, OH); 7.87 (ddd, $^{4}J_{HH}$ = 1.7 Hz, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{HH}$ = 12.7 Hz, 4H, *o*-Ph); 7.51–7.46 (m, 6H, *p*-, *m*-Ph); 6.56 (td, $^{4}J_{HH}$ = 1.8 Hz, $^{3}J_{HH}$ = 7.7 Hz, 1H, *p*-cat.); 6.48 (td, $^{4}J_{HH}$ = 1.9 Hz, $^{3}J_{HH}$ = 7.7 Hz, 1H, *m*-cat.); 6.37 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, *o*-cat.); 4.03 (d, $^{2}J_{HH}$ = 13.7 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 42.8; (DMSO-d_6): δ = 42.1. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 148.8 (d, $^{4}J_{CP}$ = 3.4 Hz, C–OH); 142.2 (d, $^{3}J_{CP}$ = 4.8 Hz, C–OH); 132.0 (d, $^{4}J_{CP}$ = 3.0 Hz, *p*-Ph); 131.4 (d, $^{2}J_{CP}$ = 10 Hz, *o*-Ph); 130.0 (s, *i*-cat.); 129.7 (d, $^{3}J_{CP}$ = 12.2 Hz, *m*-Ph); 122.3 (d, $^{3}J_{CP}$ = 5.5 Hz, *o*-cat.); 122.8 (d, $^{4}J_{CP}$ = 3.1 Hz, *m*-cat.); 120.2 (d, $^{2}J_{CP}$ = 8.5 Hz, *i*-Ph); 114.2 (d, $^{5}J_{CP}$ = 3.7 Hz, *p*-cat.); 38.6 (d, $^{1}J_{CP}$ = 52.9 Hz, CH_2). IR: 3476, 3389, 3273, 3170 (OH).

*2.2. Complex **4***

Solid [$Rh(CO)_2$(acac)] (82 mg, 0.32 mmol) was added to a solution of **1** (200 mg, 0.64 mmol) in anhydrous EtOH (20 mL). The resulting mixture was stirred for 1 h at room temperature. The formed precipitate was filtered off and dried in vacuum. Recrystallisation from acetone afforded pale yellow cubic crystals, suitable for X-ray diffraction analysis (172 mg, 72%, m.p. 227 °C). *Anal.* Calc. for $C_{39}H_{33}RhO_5P_2\cdots$2 acetone: C, 62.65; H, 5.26. Found: C, 62.67; H, 5.25%. (+)-ESI-MS: *m*/*e*: 747.09 [MH$^+$]. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.07 (s broad, 1H, OH); 7.78 (ddd, $^{4}J_{HH}$ = 1.6 Hz, $^{3}J_{HH}$ = 8.1 Hz, $^{2}J_{HH}$ = 12.9 Hz, 4H, *o*-Ph); 7.58–7.41 (m, 6H, *p*-, *m*-Ph); 6.75 (td, $^{4}J_{HH}$ = 1.9 Hz, $^{3}J_{HH}$ = 8.1 Hz, 1H, *p*-cat.); 6.51 (dt, $^{4}J_{HH}$ = 0.9 Hz, $^{3}J_{HH}$ = 3.9 Hz, 1H, *m*-cat.); 5.97 (td, $^{4}J_{HH}$ = 2 Hz, $^{3}J_{HH}$ = 7.7 Hz, 1H, *o*-cat.); 5.94 (s broad, 1H, OH); 3.97 (d, $^{2}J_{HH}$ = 12.9 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 48.5 (s, broad); 30.5 (s, broad). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ = 53.1 (dd, $^{2}J_{PP}$ = 315 Hz, $^{1}J_{RhP}$ = 142 Hz); 27.2 (dd, $^{2}J_{PP}$ = 315 Hz, $^{1}J_{RhP}$ = 135 Hz). IR: 3470, 3388 cm^{-1} (OH), 1968 cm^{-1} (CO).

*2.3. Complex **5***

Solid [Au(tetrahydrothiophene)Cl] (103 mg, 0.32 mmol) was added to a solution of **1** (200 mg, 0.64 mmol) in anhydrous THF (20 mL). The resulting mixture was stirred for 1 h at room temperature. A few drops of DMF were added until the formed precipitate had dissolved, and the clear solution was stored overnight at 4 °C to give colorless crystals suitable for X-ray diffraction analysis (260 mg, 84%, m.p. 190 °C). Anal. Calc. for $C_{38}H_{34}AuO_4P_2Cl\cdots$ DMF$\cdots$THF: C, 53.61; H, 4.90; N, 2.78. Found: C, 53.07; H, 4.82; N, 2.59%. (+)-ESI-MS: *m*/*e*: 813.16 [M$^+$]. ^{1}H NMR (250 MHZ, DMSO-d_6): δ = 9.43 (s, 1H, o-OH), 8.96 (s, 1H, *m*-OH), 7.80–7.65 (m, 8H, Ph), 7.60–7.45 (m, 12H, Ph), 6.67 (dd, $^{4}J_{HH}$ = 2.5 Hz, $^{3}J_{HH}$ = 6.8 Hz, 2H, C_6H_3), 6.37 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, C_6H_3), 6.34 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, C_6H_3), 4.15 (s broad, 4H, CH_2). ^{31}P{^{1}H} NMR (DMSO-d_6): δ = 40.2 (s broad).

*2.4. Complex **6***

Solid [Au(tetrahydrothiophene)Cl] (112 mg, 0.35 mmol) was added to a solution of **3** (236 mg, 0.70 mmol) in anhydrous dichloromethane (20 mL). The mixture was stirred for 30 min at room temperature. The resulting precipitate was filtered off, washed with dichloromethane, and dried in vacuum. Recrystallization from acetone gave colorless crystals, suitable for X-ray diffraction analysis (152 mg, 76%, m.p. 123 °C). *Anal.* Calc. for $C_{19}H_{17}AuClO_2PS$: C, 39.84; H, 2.99. Found: C, 39.15; H, 2.97%. (−)-ESI-MS: *m*/*e*: 571.00 [M$^+$]. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 9.1 (s broad, OH); 8.1 (s broad, OH); 7.86 (ddd, $^{4}J_{HH}$ = 1.4 Hz, $^{3}J_{HH}$ = 8.0 Hz, $^{2}J_{PH}$ = 12.8 Hz, 4H, *o*-Ph); 7.57–7.44 (m, 6H, *p*-, *m*-Ph); 6.57 (dt, $^{4}J_{HH}$ = 2.0 Hz, $^{3}J_{HH}$ = 7.5 Hz, 1H, *o*-cat.); 6.48–6.33 (m, 2H, *p*-, *m*-cat.); 4.09 (d, $^{2}J_{PH}$ = 13.8 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR (DMSO-d_6): δ = 42.6. IR: 3442, 3371 cm^{-1} (OH).

*2.5. Complex **7***

Solid [Rh(cyclooctadiene)Cl]$_2$ (83 mg, 0.168 mmol) was added to a solution of **3** (120 mg, 0.35 mmol) in dry EtOH (5 mL). Triethylamine (0.06 mL, 0.9 mmol) was added and the mixture was stirred for 1 h at room temperature. The formed precipitate was filtered off and dried in vacuum. Recrystallisation from acetone gave yellow crystals, suitable for X-ray diffraction analysis (129 mg, 76%, m.p. 139 °C). *Anal.* Calc. for $C_{35}H_{39}Rh_2O_2PS\cdots$1 acetone: C, 55.75; H, 5.54. Found: C, 56.26; H, 5.61%. (+)-ESI-MS:

m/*e*: 761.06 [MH^+]. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.87 (dd, $^3J_{HH}$ = 7.7 Hz, $^2J_{HH}$ = 12.9 Hz, 2H, *o*-Ph); 7.81 (dd, $^3J_{HH}$ = 7.7 Hz, $^2J_{HH}$ = 13.2 Hz, 2H, *o*-Ph); 7.49–7.33 (m, 6H, *p*-, *m*-Ph); 6.01 (d, $^3J_{HH}$ = 6.7 Hz, 1H, *p*-cat.); 5.64 (d, $^3J_{HH}$ = 5.5 Hz, 1H, *m*-cat.); 5.01 (t, $^3J_{HH}$ = 6.1 Hz, 1H, *o*-cat.); 4.68 (dd, $^2J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 13.9 Hz, 1H, CH_2); 3.91–3.69 (m, 8H, *cod*); 3.21 (t, $^2J_{PH}$ = 15.0 Hz, 1H, CH_2); 2.41–2.09 (m, 8H, *cod*); 1.99–1.88 (m, 4H, *cod*); 1.75–1.55 (m, 4H, *cod*). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.00 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.3 Hz, $^2J_{PH}$ = 12.7 Hz, 2H, *o*-Ph); 7.81 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz, $^2J_{PH}$ = 13.2 Hz, 2H, *o*-Ph); 7.61–7.57 (m, 2H, *p*-Ph); 7.56–7.53 (m, 2H, *m*-Ph); 7.52–7.48 (m, 2H, *m*-Ph); 6.14 (dt, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, *o*-cat.); 5.77 (d, $^3J_{HH}$ = 5.0 Hz, 1H, *p*-cat.); 5.14 (t, $^3J_{HH}$ = 6.2 Hz, 1H, *m*-cat.); 4.80 (dd, $^2J_{HH}$ = 11.0 Hz, $^2J_{PH}$ = 14.1 Hz, 1H, CH_2); 4.03–3.97 (m, 2H, *cod*); 3.94–3.89 (m, 3H, *cod*); 3.87–3.83 (m, 3H, *cod*); 3.34 (t, $^2J_{PH}$ = 14.6 Hz, 1H, CH_2); 2.43–2.27 (m, 8H, *cod*); 2.10–2.04 (m, 4H, *cod*); 1.86–1.78 (m, 2H, *cod*); 1.77–1.70 (m, 2H, *cod*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 43.7 (d, *J* = 3 Hz). ^{103}Rh NMR (CD_2Cl_2): δ = 1118, −422.

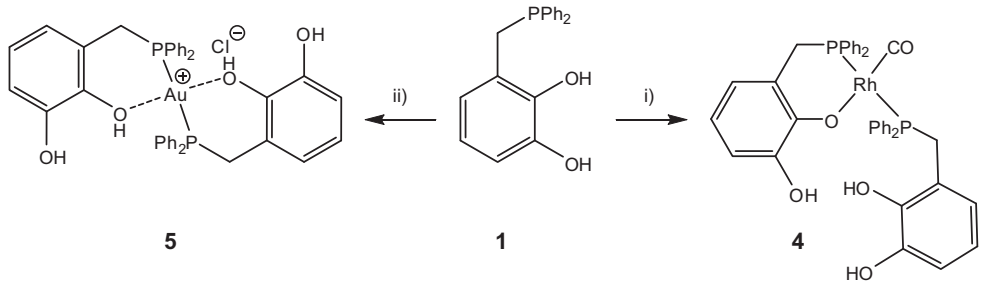
2.6. Crystal structure determinations

Crystallographic data were collected on a Bruker Nonius Kappa CCD diffractometer at 123(2) K (**3**–**5**, **7**) or on a Nonius Kappa CCD diffractometer at 100(2) K (**6**) using Mo Kα radiation (λ = 0.71073). Direct methods (SHELXS-97 [11]) were used for structure solution and refinement (SHELXL-97, [12] full-matrix, least-squares on F^2). Hydrogen atoms were refined using a riding model (H(O) free). *Complex* ***3***. Colorless crystals, $C_{19}H_{17}O_2PS$, M = 340.36 g mol^{-1}, crystal size 0.35 × 0.30 × 0.25 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 9.493(2) Å, b = 13.293(3) Å, c = 13.863(3) Å, α = 89.55(2)°, β = 72.32(2)°, γ = 81.28(2)°, V = 1646.1(6) Å^3, Z = 4, ρ_{calcd} = 1.373 Mg m^{-3}, F(0 0 0) = 712, μ = 0.300 mm^{-1}, absorption correction: none, 16 589 reflections (2θmax = 55°), 7394 unique [R_{int} = 0.040], 427 parameters, 4 restraints, goodness-of-fit on F^2: 1.20, R_1 ($I > 2\sigma(I)$) = 0.054, wR_2 (all data) = 0.130, largest diff. peak and hole 0.571 and −0.383 e A^{-3}. *Complex* ***4-acetone***. Pale yellow cubic crystals, $C_{39}H_{33}O_5P_2Rh \times 2C_3H_6O$, M = 862.66 g mol^{-1}, crystal size 0.30 × 0.15 × 0.10 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 10.593(1) Å, b = 16.620(2) Å, c = 23.179(3), β = 93.03(1)°, V = 4075.1(8) Å^3, Z = 4, ρ_{calcd} = 1.406 Mg m^{-3}, F(0 0 0) = 1784, μ = 0.548 mm^{-1}, semi-empirical absorption correction from equivalents, min/max. transm. 0.7068/0.9472, 61 872 reflections (2θmax = 55°), 9325 unique [R_{int} = 0.068], 509 parameters, 9 restraints, goodness-of-fit on F^2: 1.05, R_1 ($I > 2\sigma(I)$) = 0.040, wR_2 (all data) = 0.081, largest diff. peak and hole 0.607 and −0.418 e A^{-3}. *Complex* ***4-acetonitrile***. Orange crystals, $C_{39}H_{33}O_5P_2Rh \times 2CH_3CN$, M = 828.61 g mol^{-1}, crystal size 0.24 × 0.08 × 0.04 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 10.624(1) Å, b = 15.477(2) Å, c = 23.849(4) Å, β = 95.53(1)°, V = 3903.2(9) Å^3, Z = 4, ρ_{calcd} = 1.410 Mg m^{-3}, F(0 0 0) = 1704, μ = 0.567 mm^{-1}, semi-empirical absorption correction from equivalents, min/max. transm. 0.7118/0.9703, 58 886 reflections (2θmax = 55°), 8934 unique [R_{int} = 0.099], 489 parameters, 3 restraints, goodness-of-fit on F^2: 1.07, R_1 ($I > 2\sigma(I)$) = 0.064, wR_2 (all data) = 0.164, largest diff. peak and hole 2.563 (near Rh1) and −1.051 e A^{-3}. *Complex* ***5***×*2DMF*×*THF*. Colorless crystals, $C_{38}H_{34}O_4P_2AuCl \times 2C_3H_7NO \times C_4H_8O$, M = 1067.30 g mol^{-1}, crystal size 0.25 × 0.20 × 0.15 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 9.2132(1) Å, b = 13.2035(2) Å, c = 20.6659(3) Å, α = 92.041(1)°, β = 99.654(1)°, γ = 109.079(1)°, V = 2331.13(6) Å^3, Z = 2 (4 × 0.5), ρ_{calcd} = 1.521 Mg m^{-3}, F(0 0 0) = 1080, μ = 3.333 mm^{-1}, semi-empirical absorption correction from equivalents, min/max. transm. 0.5059/0.6143, 46 657 reflections (2θmax = 55°), 10 666 unique [R_{int} = 0.042], 564 parameters, 74 restraints, goodness-of-fit on F^2: 1.09, R_1 ($I > 2\sigma(I)$) = 0.031, wR_2 (all data) = 0.075, largest diff. peak and hole 1.180 and −0.986 e A^{-3}. *Complex* ***6***. Colorless crystals, $C_{19}H_{17}O_2PSAuCl$, M = 572.77 g mol^{-1}, crystal size 0.20 × 0.15 × 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 9.4738(3) Å, b = 10.0651(3) Å, c = 10.8564(3) Å, α = 108.527(2)°, β = 105.608(2)°, γ = 98.982(2)°, V = 911.67(5) Å^3, Z = 2, ρ_{calcd} = 2.087 Mg m^{-3}, F(0 0 0) = 548, μ = 8.427 mm^{-1}, semi-empirical absorption correction from equivalents, min/max. transm. 0.2870/0.4853, 16 429 reflections (2θmax = 55°), 4131 unique [R_{int} = 0.061], 242 parameters, 5 restraints, goodness-of-fit on F^2: 1.06, R_1 ($I > 2\sigma(I)$) = 0.038, wR_2 (all data) = 0.098, largest diff. peak and hole 3.905 (near Au1) and −3.174 e A^{-3}. The AuCl group is disordered (ration 0.954(1):0.046(1)). *Complex* ***7***. Orange plates, $C_{35}H_{39}O_2PSRh_2$, M = 760.51 g mol^{-1}, crystal size 0.40 × 0.30 × 0.25 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.482(1) Å, b = 12.689(1) Å, c = 13.314(1) Å, α = 110.91(1)°, β = 111.70(1)°, γ = 90.77(1)°, V = 1515.3(2) Å^3, Z = 2, ρ_{calcd} = 1.667 Mg m^{-3}, F(0 0 0) = 772, μ = 1.243 mm^{-1}, semi-empirical absorption correction from equivalents, min/max. transm. 0.6403/0.7456, 22,746 reflections (2θmax = 55°), 6923 unique [R_{int} = 0.031], 370 parameters, goodness-of-fit on F^2: 1.08, R_1 ($I > 2\sigma(I)$) = 0.031, wR_2 (all data) = 0.078, largest diff. peak and hole 0.890 and −0.680 e A^{-3}. *Complex* ***7-acetone***. Orange crystals, $C_{35}H_{39}O_2PSRh_2 \times C_3H_6O$, M = 818.59 g mol^{-1}, crystal size 0.40 × 0.16 × 0.08 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 11.383(1) Å, b = 12.220(1) Å, c = 13.029(1) Å, α = 72.45(1)°, β = 89.12(1)°, γ = 82.82(1)°, V = 1714.0(2) Å^3, Z = 2, ρ_{calcd} = 1.586 Mg m^{-3}, F(0 0 0) = 836, μ = 1.107 mm^{-1}, semi-empirical absorption correction from equivalents, min/max. transm. 0.7262/0.9144, 41,778 reflections (2θmax = 55°), 7843 unique [R_{int} = 0.028], 408 parameters, goodness-of-fit on F^2: 1.05, R_1 ($I > 2\sigma(I)$) = 0.0207, wR_2 (all data) = 0.050, largest diff. peak and hole 0.516 and −0.529 e A^{-3}.

3. Results and discussion

Phosphine **1** was synthesized as previously described [9]. Reaction with [Rh(CO)$_2$(acac)] in anhydrous ethanol or with [Au(tetrahydrothiophene)Cl] in THF produced the complexes **4** and **5** (Scheme 2), respectively. Reaction of **1** with [Rh(cyclooctadiene)Cl]$_2$ was messy and produced according to a ^{31}P NMR assay a mixture of several products none of which was unambiguously identified or isolated. Crystals of **4** and **5** suitable for a single-crystal X-ray diffraction study were obtained as pale yellow cubes by recrystallisation of the crude samples from acetone or THF/DMF, respectively. Crystals of **5** withered and crumbled within a few days under loss of solvent.

The rhodium complex **4** crystallizes as solvate in the monoclinic space group $P2_1/c$ with four molecules per unit cell and two molecules of acetone per complex. The molecular structure of **4** is shown in Fig. 1 together with the most important distances and angles. One solvent molecule connects via a hydrogen bond to one of the phenolic OH-groups. In addition, there are intramolecular O–H···O hydrogen bonds connecting the two hydroxyl groups in the same catechol ring, and a further one connecting the metal bound oxygen of the chelate ligand with the closest OH-group of the other phosphine moiety (O(1)···O(21) 2.614(2) Å). In contrast to other monometallic complexes derived from **1** [6,13], the two catechol phosphine units exhibit different coordination modes. One ligand unit is deprotonated and features a P,O-chelating coordination, whereas the other one remains neutral and acts as a monodentate, P-coordinated ligand. Both Phosphorus atoms occupy *trans*-positions at the square-planar coordinated metal. The two distances between rhodium and phosphorus are different; The Rh(1)–P(1) distance to the chelating ligand is noticeably shorter (2.285(1) Å) than the opposite one (Rh(1)–P(2) 2.3320(7) Å). The other distances in both ligands do not vary significantly from each other or the free ligand **1** [9] and fall into known ranges of similar compounds.



Scheme 2. Synthesis of the phosphine complexes **4** and **5**. (i) $Rh(CO)_2(acac)$, NEt_3, EtOH; (ii) (tht)AuCl, THF.

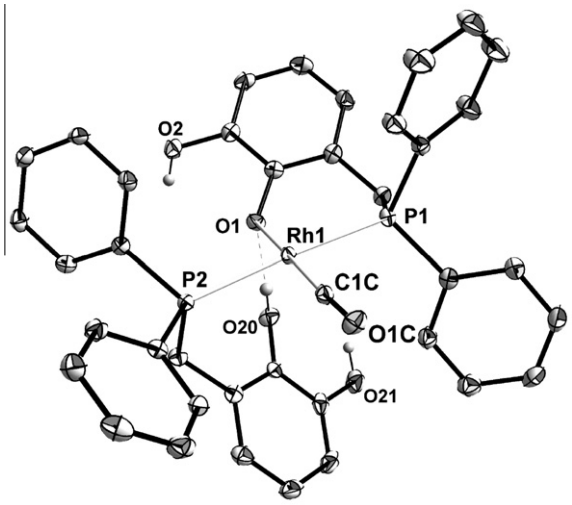


Fig. 1. Molecular structure of **4** (H-atoms omitted for clarity, except H on O20; 50% probability thermal ellipsoids); selected bond lengths (Å) and angles (°): Rh(1)–P(1) 2.285(1), Rh(1)–P(2) 2.332(1), Rh(1)–C(1C) 1.802(3), Rh(1)–O(1) 2.082(2), C(1C)–O(1C) 1.149(3), C(1)–O(1) 1.363(3), C(20)–O(20) 1.365(3), P(1)–C(7) 1.824(2), P(2)–C(26) 1.850(2), P(2)–Rh(1)–P(1) 172.62(2), C(1C)–Rh(1)–O(1) 174.61(9), Rh(1)–C(1C)–O(1C) 174.7(2).

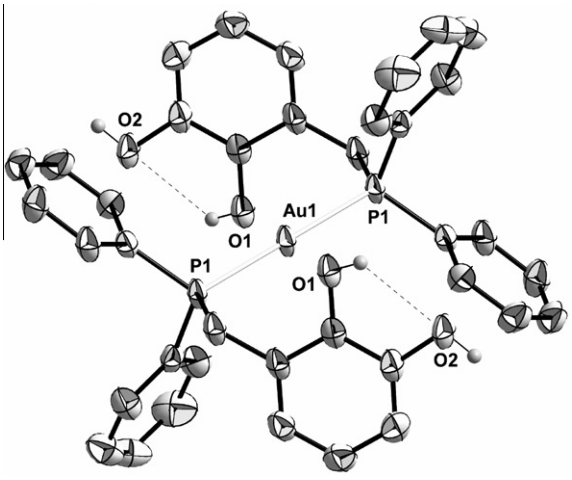


Fig. 2. Molecular structure of one of the two crystallographically independent complex cations of **5** (H-atoms, except those of OH-groups, omitted for clarity; 50% probability thermal ellipsoids; dashed lines denote intramolecular hydrogen bonds); selected bond lengths (Å) and angles (°) (values in brackets denote data for the second crystallographically independent complex): Au(1)–P(1) 2.3092(8) [2.3085(8)], Au(1)–O(1) 3.420(3) [3.269(2)], O(2′)-Cl(1) 2.988(2), O(2′)–H(2′)–Cl(1) 173(4).

The solution NMR spectra of **4** show a marked temperature dependence. The $^{31}P\{^1H\}$ NMR spectrum displays at −20 °C two sharp multiplets which form the AB-part of an ABX (X = ^{103}Rh) spin system and broaden into two unstructured singlets at 48.5 ppm and 30.5 ppm at ambient temperature. The ^1H NMR spectrum contains at −20 °C broad signals which could not be interpreted in detail, and displays at ambient temperature a single set of resonances for both catechol phosphine units. All changes are fully reversible. We interpret these findings by assuming that the molecular structure is fluxional and the chelating and non-chelating ligands undergo mutual dynamic exchange. The magnitude of $^2J_{PP}$ of 315 Hz suggests that the *trans*-alignment of the phosphine units persists in solution.

The triclinic crystals (space group $P\bar{1}$) of the gold complex **5** are composed of an array of chloride anions and complex cations $[Au(\mathbf{1})_2]$ which are evenly distributed between two crystallographically independent sites, and contain further three solvent molecules (two DMF and one THF) per formula unit. The gold atoms of both types of cations are situated on inversion centers, so that the whole cationic complexes display thus crystallographic C_i-symmetry. Fig. 2 shows one of the two crystallographically independent cations together with the most important distances and angles. The chloride anions exhibit a O–H···Cl hydrogen bond to one of the "outer" OH-groups in one complex (O(2′)–H···Cl(1) 2.988(2) Å), and additional weak C–H···Cl hydrogen bridging interactions to carbon-bound hydrogens of further adjacent molecules. The remaining OH-groups feature hydrogen bonds to solvent molecules (DMF and THF). The gold atom displays a linear coordination by the two phosphorus atoms and features additional secondary interactions to the oxygen atoms of the "inner" OH-groups (Au1–O1 3.420(3) Å, Au1′–O1′ 3.269(2) Å). The Au–P distances (Au1–P1/Au1′–P1′ 2.309(1) Å) compare well to the average Au–P distance of 2.303 ± 0.0043 Å in gold complexes of PPh_3 [14].

Once isolated, crystalline **5** is only soluble in polar solvents like DMSO or acetonitrile. The $^{31}P\{^1H\}$ NMR spectra of these solutions show slightly broadened signals (δ = 40.2 in DMSO-d_6). A positive-mode electrospray ionization mass spectrum (ESI-MS) of an acetonitrile solution of **5** displays a peak attributable to the cation $[(\mathbf{1})_2Au]^+$ (m/z: 813.16) as the only detectable species, and corroborates thus that the cationic bis-phosphine complex persists in solution.

Sulfurization of **1** was accomplished by stirring a mixture of the free phosphine with elemental sulfur in anhydrous THF. Recrystallisation from dry methanol gave the desired product **3** (Scheme 1) as analytical pure, colorless crystals, that were soluble in most organic solvents except hydrocarbons. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 42.8 ppm in $CDCl_3$, and 42.1 ppm in DMSO-d_6, respectively, which matches reported values for similar compounds [15]. The compound crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent molecules in the unit cell, one of which is displayed together with a listing of the most important distances and angles in Fig. 3. The P–S-distances

of 1.960(1)/1.963(1) Å correspond to the standard bond length of 1.954 ± 0.005 Å in tertiary phosphine sulfides [16]; other distances and angles are unpeculiar and similar to those in **1**. The crystallographically independent molecules are distinguished by different hydrogen bond patterns. Two molecules of one type form a centrosymmetric dimer via intermolecular O–H···S hydrogen bonds (O(2)···S(1)#2 3.174(2) Å). The remaining OH-group in each molecule binds via a further intermolecular O–H···O hydrogen bond (O(1)···O(2′) 2.838(3) Å) to one OH-group of one molecule of the second type, whereas the second OH-group of this molecule is saturated by an intramolecular O–H···S hydrogen bond (O(1′)···S(1′) 3.163(3) Å). The hydrogen bond network is completed by intramolecular O–H···O hydrogen bonds connecting the adjacent OH-groups in all catechol rings. On the whole, the hydrogen bonding interactions lead thus to the formation of centrosymmetric supramolecular tetramers which display an overall rod-like shape and contain one pair of each type of crystallographically independent molecules.

In order to survey the coordination ability of the phosphine sulfide **3** we studied its reactivity, as in the case of phosphine **1** [6], towards soft Lewis acids like gold(I), rhodium(I), silver(I), and palladium(II), respectively. Attempts to synthesize silver and palladium complexes remained yet unsuccessful and produced only black or brown, intractable materials. In contrast, reaction with [Au(tetrahydrothiophene)Cl] under similar conditions as had been employed for **1** gave good yields of neutral complex **6** (Scheme 3). It should be noted that despite the presence of an excess of ligand **3**, no evidence for the formation of a 2:1 complex with similar structure as **5** was obtained. The $^{31}P\{^{1}H\}$ NMR spectrum of **6** shows a broad singlet at 42.6 ppm in DMSO-d_6, which does not differ much from the free ligand, as expected.

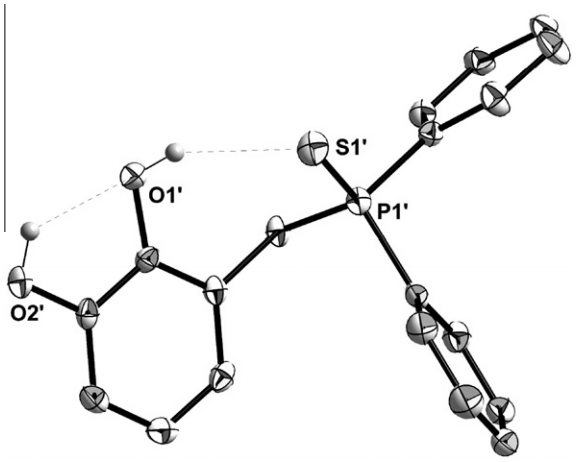
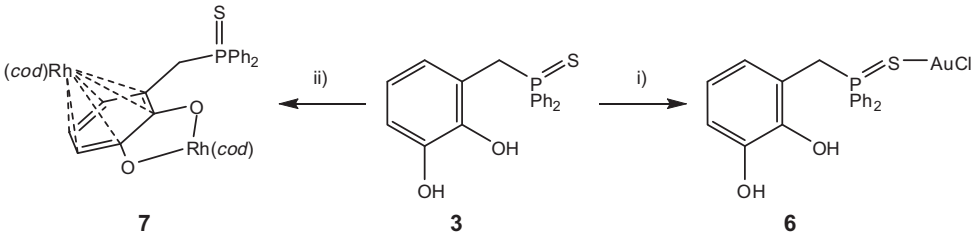


Fig. 3. Molecular structure of one of the crystallographically independent molecules of **3** (H-atoms omitted for clarity; 50% probability thermal ellipsoids; dashed lines denote intramolecular hydrogen bonds); selected bond length (Å): P(1)–S(1) 1.960(1).

Complex **6** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell which show a pairwise arrangement with a parallel alignment of S–Au–Cl units. Molecules in different pairs are connected by weak intermolecular O–H···Cl hydrogen bonds (O···Cl 3.15–3.42 Å). The molecular structure is shown in Fig. 4 together with significant distances and angles. The AuCl-group is disordered between two positions with relative site occupancies of 95:5. The distances and angles in the two disordered instances of the S–Au–Cl-units differ to some extent, which is presumably explained by different patterns of close contacts to hydrogen atoms in phenyl or methylene groups. The gold atom exhibits a quasilinear coordination geometry and the Au–Cl is similar and the Au–S-distance somewhat shorter than a standard bond length (Au–Cl 2.301 ± 0.094 Å, Au–S 2.324 Å [14]). The size of the Au–Au distance between two paired molecules (Au(1)–Au(1)#2 4.16 [4.36] Å) excludes the presence of aurophilic interactions. The PS-distance is by some 5 pm longer than in the free ligand and matches normal bond distances of 2.000 ± 0.021 Å in coordinated phosphine sulfides [14].

Following the same procedure as in the preparation of rhodium phosphine complex **4**, we expected that reaction of **3** with [Rh(CO)$_2$(acac)] should yield a similar chelate complex. Surprisingly, no reaction at all occurred in this case, and only starting materials were recovered. Successful formation of a rhodium complex was, however, accomplished by reacting **3** with [Rh(cyclooctadiene)Cl]$_2$ in ethanol in the presence of triethyl amine as proton scavenger. The product precipitated from the reaction mixture and was isolated in pure form after recrystallization from acetone. The excess ligand present in the reaction mixture did not undergo any reaction and remained unchanged after separation of the complex. Characterization by analytical, spectroscopic, and X-ray diffraction studies allowed us to identify the product as complex **7** whose molecular structure differs significantly from that of an anticipated S-coordinated phosphine–sulfide complex.

The $^{31}P\{^{1}H\}$ NMR spectrum in CD_2Cl_2 shows a sharp doublet at 43.8 ppm with a coupling constant of $J_{Rh,P}$ = 3 Hz. The data give no clue to the coordination mode since coordinated phosphine sulfides show only small coordination shifts and are thus hard to distinguish from the free ligands. Crucial structural information was derived from the ^{1}H NMR spectrum where the signal of the benzylic protons does not show up as a simple doublet as in the spectra of free **3** and complex **6** but forms the AB part of an ABX spin system (X = ^{31}P), thus indicating that both geminal protons are anisochronic. The signals associated with the three protons in the catechol ring are shifted to notably higher field, which is characteristic for protons in an aromatic ring that is π-bound to a metal. The signals of cyclooctadiene protons appear as a highly complex pattern which could not be analyzed in detail; however, evaluation of the number of individual signals and their relative integrals permits to derive the presence of two cyclooctadiene ligands with different chemical environment. This assignment was further



Scheme 3. Synthesis of complexes **6** and **7**. (i) (tht)AuCl, CH_2Cl_2; (ii) [(cod)RhCl]$_2$, NEt_3, EtOH.

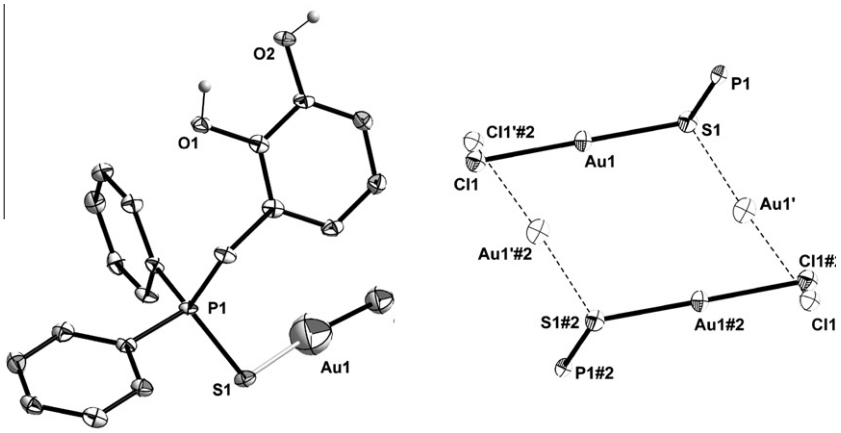


Fig. 4. Molecular structure of complex **6** in the crystal (left) and reduced plot showing the disorder scheme in the AuCl-units of a centrosymmetric supramolecular pair (right); 50% probability thermal ellipsoids; H-atoms except those on O1 and O2 omitted for clarity; Au(1)/Au(1′) and Cl(1)/Cl(1′) denote disordered atomic positions with site occupancy factors of 0.954(1) and 0.046(1); atoms labeled #2 belong to the second molecule in a supramolecular pair). Selected bond distances (Å) and angles (°): Au(1)–S(1) 2.266(1), Au(1′)–S(1) 2.221(4), Au(1)–Cl(1) 2.300(1), Au(1′)–Cl(1′) 2.327(9), P(1)–S(1)–Au(1) 105.2(1), P(1)–S(1)–Au(1′) 99.5(1), S(1)–Au(1)–Cl(1) 173.71(4), S(1)–Au(1′)–Cl(1′) 176.1(8), S(1)–P(1) 2.023(2).

substantiated by measurement of a ^{1}H, ^{103}Rh HMQC spectrum which revealed the presence of two ^{103}Rh signals with chemical shifts of 1118 and −422 ppm, respectively. Comparison with literature data suggests that the two ^{103}Rh signals are located in the ranges characteristic for (cyclooctadiene)rhodium(I)diketonates and (cyclooctadiene)rhodium(π-arene) complexes, respectively [17]. Putting all information together led us to formulate the product as a dinuclear complex **7** featuring binding of one metal to the oxygen atoms and the second one to the electron rich π-system of the catecholate moiety. This hypothesis was further backed by a positive-mode ESI-MS which displayed signals of pseudomolecular ions of the composition $[Rh_2(cyclooctadiene)_2(\mathbf{3})Na]^+$ (*m*/*e*: 783.0, 20%) and $[Rh_2(cyclooctadiene)_2(\mathbf{3})H]^+$ (*m*/*e*: 761.0, 100%) beside additional signals arising from loss or addition of a (cyclooctadiene)Rh-fragment (*m*/*e* 551.0, 50%, $[Rh(cyclooctadiene)\ (\mathbf{3})H_2]^+$; m/e: 971.0, 50%, $[Rh_3(cyclooctadiene)_3(\mathbf{3})]^+$).

The final confirmation for the proposed structure came from the results of a single-crystal X-ray diffraction study of crystalline samples obtained by repeated recrystallization from acetone. The resulting crystals were either isolated as solvates with one co-crystallized acetone molecule per complex, or without solvent. Both pseudo-polymorphs crystallize in the triclinic space group $P\bar{1}$, and incorporation of solvent into the crystal induces no significant structural changes. Fig. 5 shows the molecular structure of **7** as determined from the solvent free crystal, together with the most important distances and angles.

Each complex consists of one ligand **3** and two (cyclooctadiene)Rh-units one of which binds, as expected, in a doubly O,O-chelating fashion to form a planar five-membered chelate ring, whereas the other one is η^6-attached to the aromatic ring of the catecholate moiety. A similar asymmetrically μ-bridging coordination mode for a catecholate group is known for a few Ru(II)-complexes [18] but to the best of our knowledge unprecedented for rhodium. As a result of the special coordination in **7**, the two rhodium atoms have different electronic environments with formal electron counts of 16 (O,O-chelating metal) and 18 (π-arene coordinated metal) valence electrons. The η^6-bound metal atom sits nearly above the center of the aromatic ring (the angle between a line connecting the Rh1 atom and the center of the six-membered ring (Ar1) with the normal of the ring is 3.3 [3.0]°). As a consequence of the π-coordination, the mean aromatic CC-bond length is much larger (1.423(1) [1.412(1)] Å) than in the free ligand (1.390(1) Å). On the other hand, the C–O-bond lengths, which have been established as an indicator for the evaluation of a formal

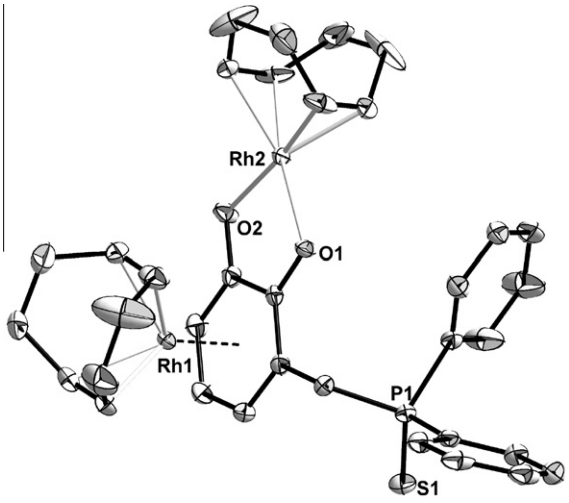


Fig. 5. Molecular structure of **7** (H-atoms omitted for clarity; 50% probability thermal ellipsoids); selected bond lengths (Å) and angles (°) (values in brackets denote data for the acetone solvate; Ar(1) denotes the centroid of the catechol ring): Rh(1)–Ar(1) 1.837(3) [1.836(1)], Rh(2)–O(1) 2.068(2) [2.052(1)], Rh(2)–O(2) 2.048(2) [2.047(1)], C(1)–O(1) 1.308(3) [1.303(2)], C(2)–O(2) 1.308(4) [1.308(2)], P(1)–S(1) 1.953(1) [1.957(1)], O(2)–Rh(2)–O(1) 81.6(1) [81.9(1)], O(1)–C(1)–C(2)–O(2) −0.9(4) [−0.9(2)].

oxidation state of the catechol unit [19], are remarkably short (mean distance 1.308(2) [1.305(2)] Å; cf. distances between 1.369 and 1.375 Å for **3** and **6**) and correspond more closely to a semiquinone than a catecholate moiety. Nevertheless, a molecular structure containing a semiquinone radical would hardly be compatible with the diamagnetic nature of complex **7**, and we prefer to explain the bond shortening as a consequence of increased conjugation between the oxygen lone-pairs and the aromatic π-electron system which is triggered by the net π-electron withdrawal associated with the metal coordination. The P(1)–S(1) bond (1.953(1) [1.957(1)] Å) is slightly shorter than in **3** (1.960(1) Å).

4. Conclusion

In summary, we have demonstrated that the catechol phosphine sulfide **3** can act in a similar way as the catechol phosphine **1** as multifunctional ligand toward soft Lewis acids like Rh(I) or

Au(I). In contrast to **1**, however, **3** exhibits a somewhat lower donor power that impedes the coordination of two ligands to the same metal center. Furthermore, the structural modification of the ligand backbone seems to reduce the tendency to form P═S,O-chelate complexes at the expense of O,O-chelates. This behavior became evident in the syntheses of a dinuclear rhodium complex **7** featuring an unusual coordination with O,O-attachment to one and η^6-π-coordination of the catecholate unit to the second metal atom, but no coordination of the phosphine sulfide moiety. The unsymmetrically μ-bridging coordination mode of a catecholate unit had previously been known for a few other metals but is unprecedented for rhodium. As a result of this unusual coordination, the CO-distances in the catecholate are remarkably short and match CO-distances that are usually found in semiquinone complexes. A prospective chemical reactivity associated with this feature will be subject of future investigations.

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Appendix A. Supplementary material

CCDC 807000, 807001, 807852, 807002, 807003, 807004 and 807005 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.076.

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