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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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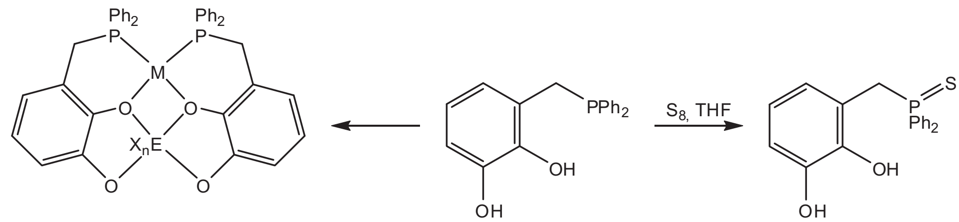

2 1 3

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, $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 7.8 Hz, $^2J_{HH}$ = 12.7 Hz, 4H, *o*-Ph); 7.51–7.46 (m, 6H, *p*-, *m*-Ph); 6.56 (td, $^4J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-cat.); 6.48 (td, $^4J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, *m*-cat.); 6.37 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *o*-cat.); 4.03 (d, $^2J_{HH}$ = 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, $^4J_{CP}$ = 3.4 Hz, C–OH); 142.2 (d, $^3J_{CP}$ = 4.8 Hz, C–OH); 132.0 (d, $^4J_{CP}$ = 3.0 Hz, *p*-Ph); 131.4 (d, $^2J_{CP}$ = 10 Hz, *o*-Ph); 130.0 (s, *i*-cat.); 129.7 (d, $^3J_{CP}$ = 12.2 Hz, *m*-Ph); 122.3 (d, $^3J_{CP}$ = 5.5 Hz, *o*-cat.); 122.8 (d, $^4J_{CP}$ = 3.1 Hz, *m*-cat.); 120.2 (d, $^2J_{CP}$ = 8.5 Hz, *i*-Ph); 114.2 (d, $^5J_{CP}$ = 3.7 Hz, *p*-cat.); 38.6 (d, $^1J_{CP}$ = 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 $C_{39}H_{33}RhO_5P_2$···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, $^4J_{HH}$ = 1.6 Hz, $^3J_{HH}$ = 8.1 Hz, $^2J_{HH}$ = 12.9 Hz, 4H, *o*-Ph); 7.58–7.41 (m, 6H, *p*-, *m*-Ph); 6.75 (td, $^4J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 8.1 Hz, 1H, *p*-cat.); 6.51 (dt, $^4J_{HH}$ = 0.9 Hz, $^3J_{HH}$ = 3.9 Hz, 1H, *m*-cat.); 5.97 (td, $^4J_{HH}$ = 2 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, *o*-cat.); 5.94 (s broad, 1H, OH); 3.97 (d, $^2J_{HH}$ = 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, $^2J_{PP}$ = 315 Hz, $^1J_{RhP}$ = 142 Hz); 27.2 (dd, $^2J_{PP}$ = 315 Hz, $^1J_{RhP}$ = 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 $C_{38}H_{34}AuO_4P_2Cl$··· DMF···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, $^4J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, C_6H_3), 6.37 (t, $^3J_{HH}$ = 7.3 Hz, 2H, C_6H_3), 6.34 (d, $^3J_{HH}$ = 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, $^4J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 8.0 Hz, $^2J_{PH}$ = 12.8 Hz, 4H, *o*-Ph); 7.57–7.44 (m, 6H, *p*-, *m*-Ph); 6.57 (dt, $^4J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, *o*-cat.); 6.48–6.33 (m, 2H, *p*-, *m*-cat.); 4.09 (d, $^2J_{PH}$ = 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 $C_{35}H_{39}Rh_2O_2PS$···1 acetone: C, 55.75; H, 5.54. Found: C, 56.26; H, 5.61%. (+)-ESI-MS: