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Intramolecular d^{10} – d^{10} interactions in neutral, dinuclear Au(I) complexes supported by amino-thiazoline- and -thiazole-based P,N-phosphine ligands

Corinna Voß, Roberto Pattacini, Pierre Braunstein*

Laboratoire de chimie de coordination, UMR 7177 CNRS, université de Strasbourg, institut Le Bel, 4, rue Blaise-Pascal, CS 90032, 67081 Strasbourg cedex, France

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Dedicated to the memory of our friend and colleague Marie-adeleine Rohmer.

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ABSTRACT

The ligands *N*-(diphenylphosphino)-thiazoline-2-amine (**1**), *N*-(diphenylphosphino)thiazol-2-amine (**2**) and *N*-(diphenylphosphino)-1,3,4-thiadiazol-2-amine **3**, readily reacted with [AuCl(THT)] in dichloromethane to form the linearly coordinated complexes [AuCl(**1**-κP)] (**5**), [AuCl(**2**-κP)] (**6**) and [AuCl(**3**-κP)] (**7**), respectively. Facile deprotonation with *t*-BuOK or Na₂CO₃ of **5–7** afforded the stable, neutral dinuclear complexes [AuCl(**1**-κP,κN)]₂ (**8**), [AuCl(**2**-κP,κN)]₂ (**9**) and [AuCl(**3**-κP,κN)]₂ (**10**), respectively. The crystal structures of the mononuclear complexes **5**, **6** and **7** and of the dinuclear complexes **8**, **9** and **10** have been determined by X-ray diffraction. The latter represent rare examples of neutral complexes supported by bridging P,N-ligands which display intramolecular Au(I)–Au(I) d^{10} – d^{10} interactions, in the range 2.8592(4)–2.8831(4) Å.

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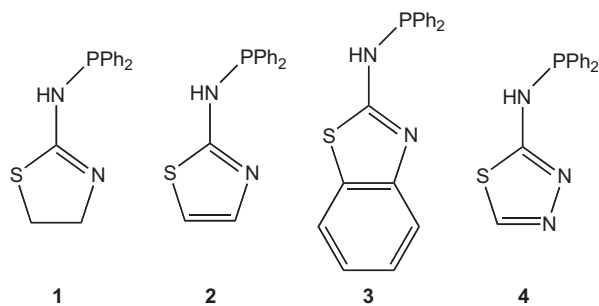
1. Introduction

It is now well established that Au(I) centres are prone to display d^{10} – d^{10} metal–metal interactions [1]. The term “aurophilicity” is commonly used to refer to such interactions in the structural chemistry of gold complexes. Although positively charged Au^I ([Xe]4f¹⁴5d¹⁰) ions could be expected to repel each other on the basis of electrostatics, the attractive interactions between these closed valence shell ions result in interatomic distances typically in the range between 2.7 and 3.3 Å, often shorter than the sum of the van der Waals radii [1]. This phenomenon could not be explained by conventional descriptions of chemical bonding [2], but is now well described as dispersion-driven and enhanced by relativistic effects [1,2]. However, the conditions for the

occurrence of aurophilicity and its structural, physical and chemical consequences remain difficult to predict, hence further experimental and theoretical studies on d^{10} – d^{10} interactions are needed, whether in homo- or in heterometallic systems [1–3]. One way to promote the generation of Au(I)–Au(I) interactions is to use assembling ligands to stabilize dinuclear complexes, the simplest candidates for such a bonding type. Slight modifications in the structural and/or electronic properties of the assembling ligand could allow a fine-tuning of the metal–metal bond length. Thus, we selected the phosphinoaminothiazoles reported in Scheme 1, namely *N*-(diphenylphosphino)-thiazoline-2-amine (**1**) [4], *N*-(diphenylphosphino)thiazol-2-amine (**2**) [5,6], *N*-(diphenylphosphino)benzo[*d*]thiazol-2-amine (**3**) [5], *N*-(diphenylphosphino)-1,3,4-thiadiazol-2-amine (**4**) [5], which readily form 5-membered ring chelates with, e.g., d⁸-metal ions, as potential bridging ligands in gold chemistry for the generation of d^{10} – d^{10} interactions because of their stereoelectronic features, the commercial availability of their precursors and their

* Corresponding author.

E-mail address: braunstein@unistra.fr (P. Braunstein).



Scheme 1.

stability when deprotonated [4,5]. Owing to their good bridging properties, we have recently used the deprotonated ligands **1_{-H}** and **4_{-H}** for the formation of, respectively, heterobimetallic coordination polymers and complexes, utilizing the free P-bound N donor [7], or homo- and heterobimetallic complexes, the latter by taking advantage of the endo-cyclic N=CH nitrogen [8]. The complex [Pt(**1_{-H}-κP,κN**)₂] showed interesting vapoluminescent properties, its emission in the visible region, when excited by UV radiation, being dramatically enhanced upon exposure to alcohols [5]. The non-coordinated N function of the latter complex is also reactive towards organic nucleophiles, e.g. leading to the formation of [Pt(**1_{-H}-κP,κN**)(**1_{-H}-EtNCS-κP,κS**)] by reaction with EtN=C=S [7]. We expected that deprotonated ligands **1_{-H}** – **4_{-H}** could form stable dinuclear gold complexes displaying Au...Au interactions, efficiently supported by a P–N bridging mode of these heteroditopic ligands.

2. Experimental

2.1. General considerations

All manipulations were carried out under inert atmosphere, using standard Schlenk-line techniques and dried and freshly distilled solvents. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded at 298 K by using the instruments Bruker Avance 300 at 300.13, 75.47 and 121.49 MHz, respectively, or Bruker Avance 400 at 400.13, 100.61, 161.98 MHz and Bruker Avance 500 at 500.13, 125.76, 202.46 MHz, respectively, using TMS or H₃PO₄ (85% in D₂O) as external standard with downfield shifts reported as positive. All spectra were measured at 298 K. The assignments of the signals were made by ¹H, ¹H-COSY, ¹H, ¹³C-HMBC and ¹H, ¹³C, HMQC experiments. Elemental C, H, N and S analyses were performed by the “Service central d’analyses”, Centre national de la recherche scientifique, Lyon or by the “Service de microanalyses”, université de Strasbourg. IR spectra were recorded in the region 4000–150 cm⁻¹ on a Nicolet 6700 FTIR equipped with the ATR accessory Smart Orbit with diamond crystal. The following compounds were prepared according to literature procedures: [AuCl(THT)] [9], **1** [4] **2** and **3** [5]. PPh₂Cl was freshly distilled before use. Other chemicals were commercially available and used as received.

2.2. Synthesis of [AuCl(**1-κP**)] (**5**)

Solid ligand **1** (0.300 g, 1.05 mmol) was dissolved in dichloromethane (50 mL) and [AuCl(THT)] (0.340 g, 1.06 mmol) was added. This solution was stirred under N₂ at room temperature for 1 h. The volatiles were removed under reduced pressure. A colourless powder was obtained and washed twice with 20 mL of diethylether, giving **5**. The precipitate was collected by filtration and dried under vacuum. Yield: 0.523 g (96% based on ligand **1**). Elemental analysis (%) calcd for C₁₅H₁₅AuClN₂PS; M = 518.75: C, 34.73; H, 2.91; N, 5.40. Found: C, 34.74; H, 3.15; N, 5.46. ¹H NMR (CDCl₃, 300 MHz) [ppm]: δ = 7.73 (m, 4H, *o*-phenyl), 7.42–7.39 (m, 6H, *m,p*-phenyl), 6.25 (s, br, 1H, NH), 3.63 (t, ³J(H,H) = 7.2 Hz, 2H, CH₂-N) and 3.41 (t, ³J(H,H) = 7.2 Hz, 2H, CH₂-S). The poor solubility of (**5**) in common organic solvents prevented the recording of a good quality ¹³C NMR spectrum. ³¹P{H} NMR (CDCl₃, 121 MHz) [ppm]: δ = 60.8. FTIR (solid, cm⁻¹): 1599 [s, ν(C=N)], Far-IR (solid, cm⁻¹): ν = 320 [s, ν(AuCl)].

2.3. Synthesis of [AuCl(**2-κP**)] (**6**)

Solid ligand **2** (0.100 g, 0.35 mmol) was dissolved in dry dichloromethane (15 mL) and solid [AuCl(THT)] (0.113 g, 0.35 mmol) was added to the solution. This mixture was stirred under N₂ for 1 h. The solvent was evaporated under reduced pressure. Complex **6** was obtained as a colourless solid, washed twice with diethyl ether (5 mL) and dried under vacuum. Single crystals suitable for X-ray analysis were obtained by layering a CH₂Cl₂ solution with pentane. Yield: 0.128 g (71% based on ligand **2**). Elemental analysis (%) calcd for C₁₅H₁₃AuClN₂PS; M = 516.74: C, 34.87; H, 2.54; N, 5.42 Found: C, 34.39; H, 2.69; N, 5.34. ¹H NMR (CDCl₃, 300 MHz) [ppm]: δ = 7.73 (ddd, 4H, ³J(PH) = 14 Hz, ³J(HH) = 7.1 Hz, ⁴J(HH) = 1.9 Hz; *o*-Ph), 7.4–7.6 (m, 6H; *m,p*-Ph), 6.19 (dd, ³J(H,H) = 4.5 Hz, ⁵J(P,H) = 1.5 Hz, 1H; N-CH), 5.88 (dd, ³J(H,H) = 4.5 Hz, ⁵J(P,H) = 3.3 Hz, 1H; S-CH). ¹³C{H} NMR (CDCl₃, 300 MHz) [ppm]: δ = 169.9 (s, N-C=N), 132.5 (d, partly masked; *i*-phenyl) 132.5 (d, ²J(C,P) = 15 Hz; *o*-Ph), 132.2 (s; *p*-Ph), 129.1, (d, ³J(C,P) = 12 Hz; *m*-phenyl), 129.17 (d, J = 14 Hz; *i*-Ph), 125.7 (s; S-CH=C), 107.3 (s; N-CH=C). ³¹P{H} NMR (CDCl₃, 121 MHz) [ppm]: δ = 60.2. FTIR (solid, cm⁻¹): 1580 [s, ν(C=N)]. Far-IR (solid, cm⁻¹): 321 [s, ν(Au-Cl)].

2.4. Synthesis of [AuCl(**3-κP**)] (**7**)

Solid [AuCl(THT)] (0.150 g, 0.47 mmol) was dissolved in dichloromethane (20 mL) and a solution of ligand **3** (0.157 g, 0.47 mmol) in dichloromethane (20 mL) was added. The mixture was stirred under N₂ for 1 h. The volatiles were removed under reduced pressure. A colourless precipitate was obtained. The solid was washed three times with 20 mL diethylether and dried under vacuum to give complex **7** which was recrystallized by layering pentane on a saturated CHCl₃ solution. Yield: 0.126 g (48% based on [AuCl(THT)]). Elemental analysis (%) calcd for C₁₉H₁₅AuClN₂PS; M = 566.79: C, 40.26; H, 2.67; N, 4.94; S, 5.66. Found: C, 39.91; H, 2.79; N, 4.81; S, 5.63. ¹H NMR (CDCl₃, 300 MHz) [ppm]: δ = 7.78 (ddd, 4H,

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