# **2-(Diphenylphosphino)-pyridine as an Ambidentate Ligand in Homo- and Hetero-binuclear Complexes of Copper, Silver, and Gold**

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Copper(I), Silver(I), Gold(I) Coordination, 2-(Diphenylphosphino)-pyridine, 1-Pyridyl-diphenylphosphine, Ambidentate Ligand

The reaction of 2-diphenylphosphino-pyridine (1) with AgBF<sub>4</sub> in an equimolar ratio affords the cyclic, dinuclear complex 2 with mixed P,N-coordination of the metal atoms. With two equivalents of 1 the 2:1 complexes 4a,b are formed which have the metal atoms solely Pcoordinated. The previously reported gold complex (3), an analogue of 2, or  $[Au(tht)_2]ClO_4$  (tht = tetrahydrothiophen) also give the 2:1 complexes (5a,b) when treated with an excess of ligand 1. Addition of AgClO<sub>4</sub> to a solution of 5a in acetone, or treatment of 4a with  $[Au(tht)_2]ClO_4$  in dichloromethane, give the same mixed-metal complex 6, where the Au atoms are exclusively P-coordinated, while the Ag atoms are coordinated by the two pyridine nitrogen atoms. In the crystal there are also weak interactions of the perchlorate counterions with the silver atom. Addition of  $[Cu(MeCN)_4]BF_4$  to compound 5b gives the Cu/Au-complex with P,P-coordinated gold and N,N-bonded copper centers. All products were characterized by standard analytical and spectroscopic techniques; the crystal structure of complex 6 was determined in a single crystal X-ray diffraction study.

## Introduction

2-Diphenylphosphino-pyridine(1-pyridyl-diphenylphosphine, 1) is an ambidentate ligand system widely employed in the coordination chemistry of Transition Metals. The 1,3-stereochemistry of the two donor centers (N,P) in compound 1 is not suitable for metal chelation, which would lead to highly strained four-membered rings, but is rather in favour of metal bridging in homo- or heteropolynuclear systems (M,M; M,M') with our without metal-metal bonding (M-M; M-M') [1 - 4].

The coinage (group 11) metals in their low oxydation state +I have a strong affinity for phosphine and pyridine donor centers and can be expected to form a wide variety of strong complexes with ligand **1**, in which the metal atoms are held in close proximity thus allowing direct metal-metal interactions. This concept was used in the synthesis of a dinuclear dicationic 1:1 complex of ligand **1** with Au<sup>+</sup>  $BF_4^-$ , where one of the shortest Au–Au contacts between the two d<sup>10</sup> metal centers has been observed [5]. Preparative and structural studies of analogous complexes of Cu(I) and Ag(I) salts with the same ligand were also successful [6 - 9], but no mixedmetal systems have been considered to-date. In the work presented in this report we have therefore become engaged in the synthesis and stereochemistry of Cu/Au and Ag/Au compounds containing ligand **1**, which were expected to show interesting isomerism depending either on the donor preferences of these metals for N or P donor sites, or on effects of metal-metal bonding. It should be noted that the metal-metal bonding referred to here is of the non-classical type between seemingly closedshell atoms, which is now recognized to contribute significantly to the overall stability of compounds of this type [10].

### **Results and Discussion**

The reaction of silver tetrafluoroborate with ligand **1** (pyPh<sub>2</sub>P) in a molar ratio 1:1 in acetone in the dark gives high yields of a binuclear complex {[(pyPh<sub>2</sub>P)<sub>2</sub>Ag<sub>2</sub>]<sup>2+</sup> (BF<sub>4</sub><sup>-</sup>)<sub>2</sub>}, **2**, as a colourless microcrystalline solid (Scheme 1). The product has been identified by microanalysis, mass spectrometry and NMR spectroscopy (Exp. Part). The <sup>31</sup>P NMR spectrum is proof for a structure with

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equivalent phosphorus atoms, and therefore a socalled "head-to-tail" structure **2** is proposed for this compound in solution. This result is in agreement with the data available for the gold(I) analogue (**3**, Scheme 1), the structure of which was confirmed by an X-ray structure analysis [5]. The structure is somewhat fluxional in CDCl<sub>3</sub> solution at ambient temperature as suggested by significant line broadening, but at -60°C ( $\delta$  20.4 ppm) the sharp lines of a well-resolved AA'XX'/YY'/XY spin system are observed (A: <sup>31</sup>P; X: <sup>109</sup>Ag; Y: <sup>107</sup>Ag).

The reaction of the same components in the ratio 1:2, or treatment of complex **2** with two mole equivalents of ligand **1**, afford the 1:2 complex salt **4b**, which is also available as the perchlorate **4a** (Scheme 1). The two products, colourless air-stable salts, are also readily identified through their analytical and spectroscopic data. The <sup>31</sup>P NMR spectra are identical and obviously independent of the nature of the anion. The <sup>31</sup>P signals ( $\delta$  10.8 ppm) show P,Ag coupling at -60 °C, but there is again line broadening at +20°C. The large coupling constants *J*(Ag,P) leave no doubt that the metal atoms are exclusively P-bonded (**4**, Scheme 1). Treatment of the dinuclear 1:1 complex of gold(I) (3) with two equivalents of ligand 1 gives the 1:2 complex **5b**, and the perchlorate **5a** is accessible from  $[Au(tht)_2]^+ CIO_4^-$ , (tht = tetrahydrothiophen) and the ligand (Scheme 1). The analytical and spectroscopic data are indicative of a structure closely related to that of the silver salts (above), although in the absence of diagnostic P,Au spin-spin coupling there is no direct evidence for this structure.

Compounds **4a** and **5a** were used as the precursors for the synthesis of a mixed-metal cluster (Ag/Au: **6**): Treatment of the gold complex **5a** with AgClO<sub>4</sub> in acetone, or of the silver complex **4a** with  $[Au(tht)_2]^+$  ClO<sub>4</sub><sup>-</sup> in dichloromethane, lead to identical colourless crystalline products, as readily demonstrated through standard analytical and spectroscopic fingerprint techniques (Exp. Part). These results suggest a non-centrosymmetrical "head-tohead" structure in solution (CDCl<sub>3</sub>), with the gold atom coordinated only to the P-donor sites, and the silver atoms exclusively engaged in bonding to the N-donor ends.

The solid state structure of compound 6 has been determined by a single crystal X-ray diffraction

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Crystal data	
Formula	C <sub>35</sub> H <sub>30</sub> AgAuCl <sub>4</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub>
Mr	1115.19
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n [No. 14]
a (Å)	10.537(1)
$b(\mathbf{A})$	23.989(1)
<i>c</i> (Å)	15.530(1)
$\beta$ (°)	95.69(1)
$V(A^3)$	3906.2(5)
$\rho_{\rm calc} ({\rm gcm}^{-3})$	1.896
Z	4
F(000)(e)	2168
$\mu$ (Mo K <sub><math>\alpha</math></sub> ) (cm <sup>-1</sup> )	46.61
Data collection	
Diffractometer	Enraf Nonius CAD4
Radiation	Mo K <sub>a</sub> , 0.71073 Å
T (°C)	-68
Scan mode	$\omega$ - $\theta$
hkl Range	$-13 \rightarrow +13 / 0 \rightarrow +30 /$
e	$0 \rightarrow +19$
$\theta$ -Range for data collection (°)	3-27
Measured refl.	8769
Unique refl.	8459
Observed refl.	8440
I >	$2 \sigma I$
Absorption correction	psi-scans
$T_{min}/T_{max}$	0.575/0.999
Refinement	
Refined parameters	444
H atoms (found/calcd.)	0/28. solvent H atoms
	neglected
R1 <sup>[a]</sup>	0.0563
wR2 <sup>[b]</sup>	0.1469
GOOF	1.091
(shift/error)max	< 0.001
$\rho_{\rm fin}({\rm max/min}) ({\rm e}{\rm \AA}^{-3})$	+4.15/-1.46 <sup>[c]</sup>
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Table I. Crystal data, data collection, and structure refinement for compound  $6 \times CH_2Cl_2$ .

 $[a] R1 = \sum ||F_0| - |F_c|| / \sum |F_0|;$ 

<sup>10]</sup> 
$$wR2 = \{ [\sum_{w} (F_o^2 - F_c^2)^2] / \sum_{w} [w(F_o^2)^2] \}^{1/2}; w = 1/2\sigma^2 (F_o^2) + (ap)^2 + bp; p = (F_o^2 + F_c^2)/3; a = 0.0720; b = 35.31.$$

<sup>[c]</sup> for the residual electron density see Experimental Part.

study (Table I, Fig. 1). **6** crystallizes together with one molecule of solvent  $CH_2Cl_2$  in the monoclinic space group  $P2_1/n$  without any crystallographically imposed molecular symmetry. The lattice is composed of dinuclear mixed metal dications associated with two perchlorate anions. The gold atom is P,Pcoordinated, whereas the silver atom is bound to the nitrogen atoms of the pyridine rings and carries the two perchlorate counterions. Due to the



Fig. 1. Molecular structure of compound **6** with atom numbering (ORTEP plot with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au-P1 2.296(2), Au-P2 2.297(2), Au...Ag 2.820(1), Ag-N1 2.289(8), Ag-N2 2.310(9), Ag-O1 2.52(2), Ag-O5 2.47(2); P1-Au-P2 171.77(7), N1-Ag-N2 142.3(3).



silver-perchlorate interactions, the N-Ag-N moiety deviates strongly from linearity [142.3(3) Å], while the linear P-Au-P arrangement within the eightmembered metalla-heterocycle remains almost unaffected [171.77(7)°]. This structure is of considerabe interest because 1) it demonstrates the strong preference of Au(I) for P-coordination, clearly overruling any similar preference of the Ag(I) competitor; thus, out of three possible isomers (Scheme 2) only one is experimentally observed; 2) it shows the residual acceptor properties of two-coordinate silver(I), which leads to weak, but obvious perchlorate contacts, overruling such tendencies, if any, of twocoordinate gold(I); 3) the short transannular Au–Ag contact is suggesting attractive forces between the two metals, reminiscent of such interactions in the homonuclear complex [5].

The reaction of complex **5b** with  $[Cu(MeCN)_4]^+$ BF<sub>4</sub><sup>-</sup> also gives a mixed metal complex (Cu/Au: 7), but the pale-yellow product could not be crystallized. All analytical and spectroscopic data are consistent with a structure related to that of compound **6** in solution, but details of the solid state structure regarding e.g. cation/anion packing cannot be predicted.

#### Experimental

*General:* All experiments were carried out at room temperature without special precautions against moisture, except for complex **7**. The complexes of silver must be protected against daylight. Warning: Perchlorate salts may be explosive. 2-(Diphenylphosphino)pyridine was purchased from Aldrich.  $[Au_2(PPh_2py)_2][BF_4]_2[5]$ ,  $[Au(tht)_2]ClO_4[11]$  and  $[Cu(NCMe)_4]BF_4[12]$  were prepared following the literature procedures. MS: Varian MAT 311A spectrometer; NMR: JEOL GX 400 spectrometer, CDCl<sub>3</sub> or (CD<sub>3</sub>)\_2CO (**7**) as solvents with TMS as internal standard for <sup>1</sup>H, and H<sub>3</sub>PO<sub>4</sub> (85%) as external standard for <sup>31</sup>P{<sup>1</sup>H}.

[ $Ag_2(PPh_2py)_2$ ][ $BF_4$ ]<sub>2</sub> (**2**): To a solution of silver tetrafluoroborate (0.4 mmol, 0.078 g) in acetone (20 ml) was added ligand **1** (0.4 mmol, 0.106 g). After 1h of stirring in the dark the solution was concentrated in a vacuum. Addition of diethylether gave complex **2** as a white solid, yield 0.163 g (89%). - <sup>1</sup>H NMR:  $\delta$  = 7.19-7.57 (m, Ph, 20H + py, 2H), 7.68 (m, py, 2H), 7.91 (m, py, 2H), 9.22 (m, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR (22°C):  $\delta$  = 21.5 (broad); -60°C:  $\delta$  = 20.4 (AA'XX'/YY'/XY, N(<sup>109</sup>Ag) = 699.8 Hz, N(<sup>107</sup>Ag) = 608.2 Hz. - MS (FD): m/z (%) = 829.2 (100) [M-BF<sub>4</sub>]<sup>+</sup>. -

C<sub>34</sub>H<sub>28</sub>Ag<sub>2</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>P<sub>2</sub> (915.90):

Calcd. C 44.59, H 3.08, N 3.06%, Found C 44.83, H 3.48, N 2.85%.

[*Ag*(*PPh*<sub>2</sub>*py*)<sub>2</sub>]*ClO*<sub>4</sub> (**4a**): To a solution of silver perchlorate (0.2 mmol, 0.041 g) in 20 ml of acetone was added ligand **1** (0.4 mmol, 0.106 g). After 1h of stirring in the dark the solution was concentrated in a vacuum. Addition of 15 ml of diethylether lead to the precipitation of **4a** as a white solid, yield 0.123 g (84%). - <sup>1</sup>H NMR:  $\delta$ = 6.86 (m, py, 2H), 7.01-7.33 (m, Ph, 20H), 7.48 (m, py, 2H), 7.66 (m, py, 2H), 9.30 (m, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR (22°C):  $\delta$  = 11.4 (broad); -60°C:  $\delta$  = 10.8 (dd, <sup>1</sup>*J*(<sup>109</sup>AgP) = 374.9, <sup>1</sup>*J*(<sup>107</sup>AgP) = 324.8 Hz). - MS (FAB): *m/z* (%) = 633.2 (66.32) [M-ClO<sub>4</sub>]<sup>+</sup>, 370.2 (100) [AgPPh<sub>2</sub>py<sup>+</sup>]. - C<sub>34</sub>H<sub>28</sub>AgClN<sub>2</sub>O<sub>4</sub>P<sub>2</sub> (733.88): Calcd. C 55.65, H 3.85, N 3.82%, Found C 54.81, H 3.96, N 3.57%.

 $[Ag(PPh_2py)_2]BF_4$  (4b): Method 1: A solution of 2 (0.1 mmol, 0.091 g) in 20 ml of acetone was treated with ligand 1 (0.2 mmol, 0.053 g) and the solution was stirred for 1h in the dark. The solvent was then removed in a vacuum. Addition of diethylether gave complex 4b as a white solid, yield 0.128 g (89%).

Method 2: To a solution of silver tetrafluoroborate (0.2 mmol, 0.039 g) in 20 ml of acetone was added ligand **1** (0.4 mmol, 0.106 g). After 1h of stirring in the dark the solvent was evaporated and 15 ml of diethylether was added to precipitate complex **4b** as a white solid, yield 0.133 g (92%). - <sup>1</sup>H NMR:  $\delta = 6.97$  (m, py, 2H), 7.05-7.41 (m, Ph, 20H + py, 2H), 7.66 (m, py, 2H), 9.10 (m, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR (22°C):  $\delta = 12.0$  (m); -60°C:  $\delta = 10.8$  (dd, <sup>1</sup>J(<sup>109</sup>AgP) = 374.9, <sup>1</sup>J(<sup>107</sup>AgP) = 324.8 Hz). -

C<sub>34</sub>H<sub>28</sub>AgBF<sub>4</sub>N<sub>2</sub>P<sub>2</sub> (721.23):

Calcd. C 56.62, H 3.91, N 3.88%, Found C 55.79, H 4.08, N 3.69%.

[*Au*(*PPh*<sub>2</sub>*py*)<sub>2</sub>]*ClO*<sub>4</sub> (**5a**): To a solution of ligand **1** (0.4 mmol, 0.106 g) in dichloromethane (20 ml) was added [Au(tht)<sub>2</sub>]ClO<sub>4</sub> (0.2 mmol, 0.095 g). After 1h of stirring at room temperature the solution was concentrated in a vacuum. Addition of diethylether lead to the precipitation of **4** as a white solid. Yield 0.145 g (88%). - <sup>1</sup>H NMR:  $\delta$  = 7.52-7.65 (m, Ph, 20H + py, 4 H), 7.96 (m, py, 2H), 8.85 (d, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  = 44.4 (s). - MS (FAB): m/z (%) = 723.3 (100) [M-ClO<sub>4</sub>]<sup>+</sup>, 460.4 (50.86) [AuPPh<sub>2</sub>py<sup>+</sup>]. -

 $C_{34}H_{28}AuClN_2O_4P_2$  (822.98):

Calcd. C 49.62, H 3.43, N 3.40%, Found C 49.12, H 3.45, N 3.24%.

[*Au*(*PPh 2py*)<sub>2</sub>]*BF*<sub>4</sub> (**5b**): To a solution of ligand **1** (0.2 mmol, 0.053 g) in 20 ml of dichloromethane was added [Au<sub>2</sub>(*PPh*<sub>2</sub>py)<sub>2</sub>][*BF*<sub>4</sub>]<sub>2</sub> (0.1 mmol, 0.109 g), and the solution was stirred for 1h. The solvent was then removed in a vacuum and 15 ml of diethylether was added to precipitate complex **5b** as a white solid, yield 0.144 g (89%). - <sup>1</sup>H NMR:  $\delta$  = 7.52-7.65 (m, Ph, 20H + py, 4 H), 7.98 (m, py, 2H), 8.85 (d, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  = 44.3 (s). -

C<sub>34</sub>H<sub>28</sub>AuBF<sub>4</sub>N<sub>2</sub>P<sub>2</sub>(810.33):

Calcd. C 50.40, H 3.48, N 3.46%, Found C 49.72, H 3.48, N 3.30%.

 $[(O_3ClO)_2Ag(\mu-PPh_2py)_2Au]$  (6): Method 1: To a solution of silver perchlorate (0.2 mmol, 0.041 g) in acetone was added **5a** (0.2 mmol, 0.165 g), and the mixture was stirred in the dark for 1h. The solvent was evaporated and diethylether was added to give **6** as a white solid, yield 0.175 g (85%).

Method 2: To a solution of **4a** (0.2 mmol, 0.147 g) in 20 ml of dichloromethane was added [Au(tht)<sub>2</sub>]ClO<sub>4</sub> (0.2 mmol, 0.095 g). The solution was stirred for 1h in the dark and the solution was then concentrated in a vacuum. The addition of diethylether (15 ml) gave complex **6** as a white solid. The product was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane at room temperature, yield 0.165 g (80%). - <sup>1</sup>H NMR:  $\delta$  = 7.29-7.60 (m, Ph, 20H + py, 4 H), 7.98 (m, py, 2H), 9.33 (m, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR (22°C):  $\delta$  = 47.8 (s); -60°C:  $\delta$  = 47.4 (d, <sup>2</sup>J<sub>AgP</sub> = 4.4 Hz). - MS (FD): m/z (%) = 931.1 (100) [M-ClO<sub>4</sub>]<sup>+</sup>, 947.1 (48.73) [M-ClO<sub>3</sub>]<sup>+</sup>. -

 $\begin{array}{c} C_{34}H_{28}AgAuCl_2N_2O_2P_2\cdot CH_2Cl_2\ (115.19):\\ Calcd.\ C\ 37.70,\ H\ 2.71,\ N\ 2.51\%,\\ Found\ C\ 37.75,\ H\ 2.82,\ N\ 2.51\%. \end{array}$ 

[ $AuCu(\mu$ - $PPh_2py)_2$ ][ $BF_4$ ]<sub>2</sub> (7): To a solution of [Cu(NCMe)\_4]BF<sub>4</sub> (0.2 mmol, 0.063 g) in dichloromethane (15 ml) **5b** was added (0.2 mmol, 0.162 g) and the reaction mixture was stirred for 1h under nitrogen. The solvent was evaporated in a vacuum and diethylether was added to precipitate complex **7** as a pale-yellow solid, yield 0.152 g (79%). - <sup>1</sup>H NMR:  $\delta$  = 8.55-8.74 (m, Ph, 20H + py, 2 H), 8.83 (m, py, 2H), 9.20 (m, py, 2H), 10.40 (m, py, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR (22°C):  $\delta$  = 48.6 (broad); -60°C:  $\delta$  = 47.4 (s). - MS (FD): m/z (%) = 873.0 (100) [M-BF<sub>4</sub>]<sup>+</sup>. -

C<sub>34</sub>H<sub>28</sub>AuBCuF<sub>2</sub>N<sub>2</sub>P<sub>2</sub> (960.68): Calcd. C 42.51, H 2.94, N 2.92%,

Found C 41.14, H 3.30, N 3.01%.

#### Crystallographic structure determination

A specimen of suitable quality was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Lp correction was applied and intensity data were corrected for absorption effects (psi-scans). The structure was solved by Patterson methods and completed by full-matrix least-squares techniques against  $F^2$ . The oxygen atoms of the perchlorates as well as the chlorine atoms of the solvent molecule were strongly disordered. The latter were refined isotropically in split positions, whereas the oxygen atoms were included with fixed isotropic contributions ( $U_{iso(fix)} = 0.15$ ). All remaining non-H atoms were refined with anisotropic displacement parameters. All H-atoms except for those of the disordered solvent molecule were placed in idealized calculated positions and allowed to ride on their carbon atoms with  $U_{iso(fix)} = 1.5 \times U_{eq}(C)$ . The solvent H atoms were neglected. The residual electron density of about 4  $e^{A^{-3}}$  was located between the carbon atoms C226 and C132, with distances and angles comparable to those of the N1-Ag-N2 moiety. This observation together with the relatively large U values of the Ag atom (compared to Au) indicate another slight disorder in the molecule. Attempts to resolve this were not made.

Details on crystal data, data collection and structure refinement are summarized in Table 1, selected bond lengths and angles are given in the figure caption. Further information on the X-ray structure determination can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-406500, the names of the authors, and the journal citation.

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