Copper(I) and Gold(I) Complexes with *N*,*N*'-Bis(diphenylphosphino)-2,6diaminopyridine as Ligand: Synthesis and Molecular Structures

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Dedicated to Professor Kurt Dehnicke on the Occasion of his 75th Birthday

Abstract. Reaction of CuI with 1 or 2 equivalent(s) N,N'-Bis(diphenylphosphino)-2,6-diaminopyridine (BDDP) gives two different complexes, [Cu(I)µ-(BDDP- $\kappa P, N_{py}$)]₂ (1) and [Cu(BDDP- $\kappa P, N_{py}$)₂]I (2), in high yields. The determination of the molecular structure show that both Cu^I atoms are tetrahedrally coordinated, rather than a square-planar geometry reported for Cr⁰, Ni^{II}-BDDP complexes before, which contains a planar tridentate chelate ring

system. The introduction of AuCl(tht) (tht = tetrahydrothiophene) into [Cu(BDDP- $\kappa P, N_{py}$)₂]I leads unexpectedly to the formation of a digold complex 2,6-[(ClAuPh₂P)HN]₂C₅H₃N and dimeric [Cu(I) μ -(BDDP- $\kappa P, N_{py}$)]₂.

Keywords: Phosphinoamine; N,P Ligand; Copper; Gold

Introduction

In principal, the central metal atoms of different soft and hard Lewis acidity usually need to be satisfied in a most suitable fashion, in hence heterodentate ligands have the most possibility to form multinuclear complexes [1]. Among these, phosphinoamine ligands are of increasing interest in synthetic inorganic and organometallic chemistry [2], due to its significantly high flexibility in coordination, both N,P elements are extensively used as 'docking spot', and the steric and electronic effects of electron-donating atoms as well as the bridging unit could be tuned over wide limits [3].

Recently there have been many research efforts by us and others in developing phosphinoamide chemistry of the transition metals, such as monophosphanylamides (R_2PNR') (**A**) [4, 5, 6, 7], diphosphanylamides ((Ph_2P_2N) (**B**) [5, 8, 9], phosphoraneiminato (R_3PN) (**C**) [10], phosphiniminomethanides (($RNPR'_2$)CH) (**D**) [11, 12, 13, 14, 15, 16]. *N*,*N'*-Bis(diphenylphosphino)-2,6-diaminopyridine (**BDDP**) (**E**) was first introduced by *Haupt* et al. with the neutral carbonyl compounds of chromium family, and also MCl₂ (M= Ni, Pd, Pt) in 1987 [17, 18]. Some lanthanide complexes have been prepared [19], however its coordination behaviour with late transition metals is still far beyond understand. The d¹⁰ ions of the coinage metals demonstrate variable coordination geometry, for example, Cu^I and Ag^I are

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Scheme 1 Some selected aminophosphane ligands

predominantly found as tetrahedral species, while Au^I appears essentially in a linear molecule with coordination number 2, even if the ligand is ideal to form a trigonal planar or tetrahedral species [20]. In this paper we describe the synthesis of copper(I) complexes with BDDP and the unexpected results when trying to introduce a second metal, gold(I) or cobalt(II), into the molecular frame.

Results and Discussion

The rigid N,N'-bis(diphenylphosphino)-2,6-diaminopyridine (**BDDP**) was studied as a multifunctional ligand in co-





Scheme 2 Synthesis of $[Cu(I)BDDP]_2$ (1) and $[Cu(BDDP-\kappa P, N_{py})_2]I$ (2)



Fig. 1 Solid-state structure of 1 showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths/pm and bond angles/° include:

Cu1-P1 225.53(10), Cu1-P4 225.56(10), Cu1-N1 216.2(3), Cu1-I1 260.10(5), Cu2-P2 224.87(10), Cu2-P3 226.06(11), Cu2-N4 214.9(3), Cu2-I2 260.84(5), I1-Cu1-P1 120.52(3), I1-Cu1-P4 109.60(3), I1-Cu1-N1 102.49(8), P1-Cu1-N1 84.66(8), P1-Cu1-P4 123.84(4), P4-Cu1-N1 108.60(8), N2-P1-Cu1 97.59(11), I2-Cu2-P3 115.76(3), I2-Cu2-P2 112.47(3), I2-Cu2-N4 98.53(8), P3-Cu2-N4 83.90(8), P3-Cu2-P2 125.84(4), P2-Cu2-N4 111.97(8), N5-P3-Cu2 98.49(12).

ordination chemistry with $[M(CO)_3(CH_3CN)_3]$ (M=Cr, Mo, W) and MCl₂ (M = Ni, Pd and K₂PtCl₄ as the source of Pt) [17]. In both cases, the determined molecular structures show a nearly planar tridentate chelating ring system, namely two fused five-member rings docking by phosphorus atoms and pyridine nitrogen. We were interested to study the BDDP ligand in the coordination chemistry of the coinage metals. One goal was to obtain with the heterodentate phosphanylamine multinuclear complexes, which tend to contain some metal-metal interactions.

The treatment of CuI with equal molar BDDP in THF afforded the dimer $[Cu(I)\mu-(BDDP-\kappa P, N_{pv})]_2$ (1) in good yield. The solid state structure of compound 1 was established by single crystal X-ray diffraction (Figure 1). Compound 1 crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. In compound 1 each copper atom is tetrahedrally coordinated by the pyridine nitrogen and one chelating phosphorus atom from one ligand, a phosphorus atom from another ligand, and one iodine atom to balance the charge. The corresponding ³¹P{¹H} NMR spectrum shows a sharp singlet at $\delta = 27.3$ indicating that all of the phosphorus atoms are chemically equivalent. An ESI -MS spectrum recorded from 1 dissolved in DMSO does not show any sign of decomposition in solution. The peak with the highest intensity could be assigned to the fragment $[Cu_2(I)(BDDP-\kappa P, N_{pv})_2]^+$. The bond lengths of Cu1-P1 and Cu1-P4 are very similar, 225.53(10) pm and 225.56(10) pm, respectively, while the distances of Cu2-P2 and Cu2-P3 are slightly different, 224.87(10) pm and 226.06(11) pm. The other bond lengths, such as Cu-N and Cu-I are symmetrically equal and fall well in the expected regions [21]. Both of the amine nitrogen atoms have not taken part in the coordination.

Since all phosphorus atoms are already chemically bonded in 1, a new compound containing two BDDP ligands, [Cu(BDDP- $\kappa P, N_{py}$)₂]I (2), have been prepared, in order to obtain more vacant coordinating sites. Compound 2 crystallizes in the monoclinic space group $P2_1/n$ having four molecules of 2 in the unit cell. The structure of compound 2 was solved but as a result of the poor quality of the crystal could not be fully refined. Since the quality of the refinement is low only the lattice constants but no detailed discussion is presented. The central metal in 2 is like in 1 tetrahedrally coordinated by the two pyridine nitrogens



Fig. 2 Solid-state structure of 2 showing the atom labeling scheme, omitting hydrogen atoms.

and two chelating phosphorus atoms from each ligand (Figure 2). Slightly different from 1, the iodine acts as a noncoordinating counter anion and the structure suggests there is a possible hydrogen bond interaction between the iodine and one close amino group.

An ESI-MS spectrum recorded from 2 dissolved in DMSO does not show any sign of decomposition in solution. The molecular peak of the $[Cu(BDDP-\kappa P, N_{py})_2]^+$ could be clearly detected. The ³¹P{¹H} NMR spectrum in d₆-DMSO shows two very close singlets at 16.3 and 17.2 ppm, respectively, the chemical shifts move towards a higher field than 1 (27.3 ppm). There is no obvious signal for the two non-coordinating phosphorus atoms and the nearly identical chemical shifts on the ³¹P{¹H} spectrum could possibly explained by a fast coordinating equilibrium between these four phosphorous atoms in the solution. As a result of the high melting point of DMSO low temperature VT NMR spectra cannot be recorded. Compared with 1, the ¹H spectrum of 2 shows a broad aromatic proton signal with a few splitting fine structures.

Next we tried to coordinate another kind of metal to the non coordinating phosphorus atoms of **2**. After the addition of two equivalents of AuCl(tht) (tht = tetrahydrothiophene), the solution turned into yellow immediately. Xray suitable single crystals were grown from the mother solution directly after the following filtration and concentration. To our surprise, it forms a digold(I) complex, [2,6-{(ClAuPh₂P)NH}₂C₅H₃N] (**3**), rather than a heterometallic compound as expected (Figure 3). The crystal data of **3** revealed the structure reported by *Dyson* et al. in 2004 [22], which contains only different solvent molecules. The molecule has slight shorter distances between gold and phosphorus, namely 222(3) pm for Au1-P1 and 222(3) pm for Au2-P2; and longer Au-Cl bonds, 237(3) pm for Au1-Cl1 and 239(3) pm for Au2-Cl(2). Both the fragments of P-Au-



Fig. 3 Solid-state structure of 3 showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths/pm and bond angles/° include:

Au1-P1 222(3), Au1-Cl1 237(3), P1-N1 168(4), Au2-P2 222(3), Au2-Cl2 239(3), P2-N3 170(4), P1-Au1-Cl1 176.78(2), P2-Au2-Cl2 177.81(2).

Cl are nearly linear with angles of 176.78(2) and 177.81(2). ${}^{31}P{}^{1}H{}$ NMR spectrum of **3** in d₈-THF shows a sharp singlet with chemical shift at 56.3 ppm.

Because of the fast coordinating equilibrium between the four phosphorus donors, it is reasonable to have two AuCl lunched on the same ligand simultaneously. However, so far it could not be explained the 'driving force' to reach the final product. Au^I complex usually adopts linear coordination geometry, and apparently there is no steric problem for the heterometallic intermediate. A NMR tube-scale reaction of **2** and AuCl(tht) in 1:2 ratio in d₆-DMSO does not lead to clear results of the mechanism.

Experimental

All manipulations of air- and moisture-sensitive complexes were carried out under an atmosphere of Argon using standard Schlenk-lines or glove box techniques. Solvents were dried according to standard methods and collected by distillation. BDDP was prepared according to literature method [17], purified by recrystallization from toluene/pentane (1:7) and checked by NMR measurements. AuCl(tht) was prepared according to a similar synthetic route for AuCl(PPh₃) [23]. ¹H and ³¹P{¹H} NMR spectra were recorded on JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to tetramethylsilane and 85 % phosphoric acid (³¹P{¹H} NMR). Elemental analysis was conducted on an Elementar vario EL. Mass spectra were taken on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, APEX II) equipped with a 7T magnet and an electrospray ionization source (Analytica of Branford) with a home-built rf ion optics for improved sensitivity. Solutions from 1 and 2 in DMSO were prepared and sprayed using nitrogen as nebulizing gas at a flow rate of 300 µl/h. The desolvation capillary was typically heated to about 80 °C.

Synthesis of $[Cu(I)\mu$ -(BDDP- $\kappa P, N_{py})]_2$ (1):

20 ml THF was condensed at -196 °C into a mixture of 0.06 g CuI (0.315 mmol) and 0.15 g BDDP (0.315 mmol). The reaction

mixture was allowed to warm to room temperature and kept stirring until the dust of CuI disappeared gradually. After filtration, the pale green solution was concentrated to 10 ml under vaccum, and the product was obtained as white block crystalline after days, 0.206 g (77 % in yield). Elemental analysis for $C_{58}H_{50}N_6P_4Cu_2I_2$ ·4THF (1624.29), calcd. C,54.71, H,5.09, N,5.17; found C,54.06, H,4.63, N,5.12 %.

IR (KBr/cm⁻¹): 3187 (s), 3050 (m), 1599 (s), 1576 (vs), 1454 (vs), 1433 (m), 1323 (m), 1231 (m), 1162 (m), 1097 (s), 1047 (m), 1033 (s), 998 (m), 971 (s), 819 (m), 781 (m), 737 (s), 694 (s), 512 (m). ¹H NMR (d₆-DMSO, 400 MHz, 25 °C): δ = 7.20-8.52 (multi and broad, 23H, aromatic H), 6.18 (s, NH), 174, 3.59 ppm (s, THF). ³¹P{¹H} NMR (d₆-DMSO, 161.7 MHz, 25 °C): δ = 27.3 (s). **ESUMS:** *mlz* (%): 1874 ([M + [Cu(BDDP- $\kappa P, N_{py})_2$]⁺, rel. int. 4), 1207 ([M–1]⁺, 100), 1017 (5), 833 ([Cu(BDDP- $\kappa P, N_{py})_2$]⁺, 43), 540 ([Cu(BDDP- $\kappa P, N_{py})_2$]⁺, 40).

Synthesis of $[Cu(BDDP-\kappa P, N_{py})_2]I(2)$:

20 ml THF was condensed at -196 °C into a mixture of 0.06 g CuI (0.315 mmol) and 0.3 g BDDP (0.629 mmol). The mixture was stirred for 2 hours at room temperature, and the suspension of CuI disappeared gradually during this period. After filtration, the pale green solution was concentrated to 10 ml under vaccum, and the product was obtained as white block crystalline after days, 0.283 g (79 % in yield). Elemental analysis for C₅₈H₅₀N₆P₄CuI (1145.42), calcd. C,60.82, H,4.40, N,7.34; found C,60.17, H,4.09, N,7.25 %.

IR (KBr/cm⁻¹): 3343 (w), 3321 (w), 3314 (m), 3068 (m), 1602 (s), 1573 (vs), 1476 (vs), 1344 (m), 1317 (vs), 1228 (w), 1170 (m), 1161 (s), 1097 (s), 1068 (s), 1032 (s), 998 (m), 971 (s), 913 (s), 867 (m), 781 (m), 737 (s), 696 (s), 690 (s) 518 (s), 504 (s). **¹H NMR** (d₆-DMSO, 400 MHz, 25 °C): δ = 6.80-7.70 (b, 23H, aromatic H), 6.05-6.40 (m, 2H, NH). ³¹P{¹H} NMR (d₆-DMSO, 161.7 MHz, 25 °C): δ = 16.3, 17.2 (s). **ESI/MS:** m/z (%): 1017 ([Cu(BDDP- $\kappa P, N_{py})_2$]⁺, rel. int. 60), 833 ([Cu(BDDP- $\kappa P, N_{py})_2$]⁺, 43), 540 ([Cu(BDDP- $\kappa P, N_{py})_2$]⁺, 100).

Synthesis of $[2,6-\{(ClAuPh_2P)HN\}_2C_5H_3N]$ (3):

0.2 g AuCl(tht) (0.625 mmol) was added to the THF solution of $[Cu(I)\mu$ -(BDDP- $\kappa P, N_{pv})]_2$ (0.315 mmol) prepared above without any further isolation. The reaction mixture was shielded with aluminium foil and stirred overnight. After filtration, the yellow solution was concentrated to 10 ml, and the digold complex, **3** was obtained as colourless block crystalline after days, 0.081 g (48 % in yield). Elemental analysis for C₂₉H₂₅N₃P₂Au₂Cl₂·1.5THF (2100.97), calcd. C,40.02, H,3.55, N,4.00; found C,40.33, H,3.50, N,3.74 %. (AuCl)₂BDDP is also possibly prepared by the direct reaction of AuCl(tht) and BDDP in a 2:1 molar ratio in THF.

¹H NMR (d₈-THF, 400 MHz, 25 °C): δ = 6.50-8.20 (m, aromatic H), 6.50 (br. NH). ³¹P{¹H} NMR (d₈-THF, 161.7 MHz, 25 °C): δ = 56.3 (s).

X-ray Crystallographic Studies of 1, 2 and 3.

Crystals of **1** were obtained from THF/ *n*-pentane (1:4). Crystals of **2** and **3** were grown from THF. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the -100 °C cold N₂ stream of a Stoe IPDS2T diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

Data collection and refinement: SHELXS-97 [24], SHELXL-97; [25] 1: $C_{70}H_{74}N_6O_3P_4Cu_2I_2$, monoclinic space group $P2_1/n$ (no.14); lattice constants a = 2409.14(9), b = 1256.86(4), c = 2487.44(10) pm, $\beta = 117.07(0)^\circ$, V = 6706.74(10) 10⁶ pm³, Z = 4; μ (Mo-K $_{\alpha}$) = 1.701 mm⁻¹; θ_{max} = 29.29°; 18094 ($R_{int} = 0.0741$) independent reflections measured, of which 12752 were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.022 and -0.829 e/A^{-3} ; 713 parameters (all non hydrogen atoms were calculated anisotropic; the positions of the H atoms were calculated for idealised positions) R1 = 0.0528; wR2 = 0.1024 (all data). GOOF = 1.043.

2: $C_{58}H_{39}N_6P_4CuI$, monoclinic space group $P2_1/n$ (no.14); lattice constants a = 1953.47(3), b = 1220.02(2), c = 2318.48(4) pm, $\beta = 106.14(1)^\circ$, V = 5307.7(2) 10⁶ pm³.

3: $C_{70}H_{74}N_6O_3P_4Cl_4Au_4$, triclinic, $P\overline{1}$ (no.2), a = 1003.7(2), b = 1282.2(2), c = 1530.7(3) pm, $\alpha = 65.90(3)$, $\beta = 78.04(3)$, $\gamma = 83.15(3)^\circ$; $V = 1757.84(25) \ 10^6$ pm³, Z = 1, μ (Mo-K_{α}) = 8.614 mm⁻¹; $\theta_{max} = 29.24^\circ$; 9389 ($R_{int} = 0.0392$) independent reflections measured, of which 6594 were considered observed with $I > 2\sigma(I)$; max. residual electron density 2.895 and -2.519 e/A^{-3} ; 380 parameters (all non hydrogen atoms were calculated anisotropic; the positions of the H atoms were calculated for idealised positions) R1 = 0.0364, wR2 = 0.0938(all data), GOOF = 0.899.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-275264 (1) and 275265 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: mailto:deposit@ccdc.cam.ac.uk).

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References

- a) R. Kempe, H. Noss, T. Irrgang, J. Organomet. Chem. 2002, 647, 12. b) N. Wheatley, P. Kalck, Chem. Rev. 1999, 99, 3379.
 c) R. Fandos, C. Hermández, A. Otero, A. Rodríguez, M. J. Ruiz, P. Terreros, Chem. Eur. J. 2003, 9, 671.
- [2] a) M. Knorr, C. Strohmann, *Eur. J. Inorg. Chem.* 1998, 495.
 b) S.Wingerter, M. Pfeiffer, A. Murso, C. Lustig, T. Stey, V. Chandrasekhar, D. Stalke, *J. Am. Chem. Soc.* 2001, *123*, 1381.
- [3] M. S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. C. T. R. Burckett St. Laurent, *Coord. Chem. Rev.* 1994, 129, 1–90.
- [4] D. Fenske, B. Maczek, K. Maczek, Z. Anorg. Allg. Chem. 1997, 623, 1113.
- [5] O. Kühl, T. Koch, F. B. Somoza, P. C. Junk, E. Hey-Hawkins, D. Plat, M. S. Eisen, *J. Organomet. Chem.* **2000**, 604, 116.
- [6] O. Kühl, P. C. Junk, E. Hey-Hawkins, Z. Anorg. Allg. Chem. 2000, 626, 1591.
- [7] a) T. G. Wetzel, S. Dehnen, P. W. Roesky, Angew. Chem. 1999, 111, 1155; Angew. Chem., Int. Ed. 1999, 38, 1086. b) S.
 Wingerter, M. Pfeiffer, F. Baier, T. Stey, D. Stalke, Z. Anorg. Allg. Chem. 2000, 626, 1121.
- [8] P. W. Roesky, M. T. Gamer, M. Puchner, A. Greiner, *Chem. Eur. J.* 2002, 8, 5265.
- [9] a) P. Braunstein, J. Durand, G. Kickelbick, M. Knorr, X. Morise, R. Pugin, A. Tiripicchio, F. Ugozzoli, *Dalton Trans.* 1999, 4175. b) M. Knorr, C. Strohmann, *Organometallics*

1999, *18*, 248. c) P. Braunstein, J. Cossy, M. Knorr, C. Strohmann, P. Vogel, *New J. Chem.* **1999**, *23*, 1215.

- [10] For reviews see: a) K. Dehnicke, F. Weller, *Coord. Chem. Rev.* 1997, 158, 103. b) K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* 1999, 182, 19.
- [11] P. Imhoff, J. H. Guelpen, K. Vrieze, W. J. J. Smeets, A. L. Spek, C. J. Elsevier, *Inorg. Chim. Acta* **1995**, 235, 77.
- [12] a) M. W. Avis, M. E. van der Boom, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, J. Organomet. Chem. 1997, 527, 263. b) M. W. Avis, C. J. Elsevier, J. M. Ernsting, K. Vrieze, N. Veldman, A. L. Spek, K. V. Katti, C. L. Barnes, Organometallics 1996, 15, 2376. c) M. W. Avis, K. Vrieze, H. Kooijman, N. Veldman, A. L. Spek, C. J. Elsevier, Inorg. Chem. 1995, 34, 4092. d) P. Imhoff, R. van Asselt, J. M. Ernsting, K. Vrieze, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, A. P. M. Kentgens, Organometallics 1993, 12, 1523.
- [13] C. M. Ong, P. McKarns, D. W. Stephan, *Organometallics* 1999, 18, 4197.
- [14] M. T. Gamer, S. Dehnen, P. W. Roesky, *Organometallics* 2001, 20, 4230.

- [15] G. Aharonian, K. Feghali, S. Gambarotta, G. P. A. Yap, Organometallics 2001, 20, 2616.
- [16] M. T. Gamer, P. W. Roesky, Z. Anorg. Allg. Chem. 2001, 627, 877.
- [17] W. Shirmer, U. Flörke, H. J. Haupt, Z. Anorg. Allg. Chem. 1987, 545, 83.
- [18] W. Shirmer, U. Flörke, H. J. Haupt, Z. Anorg. Allg. Chem. 1989, 574, 239.
- [19] M. Rastätter, P. W. Roesky unpublished work.
- [20] M. A. Carvajal, J. J. Novoa, S. Alvarez, J. Am. Chem. Soc. 2004, 126, 1465.
- [21] M. L. Engelhardt, P. C. Healy, J. D. Kildea, A. H. White, Aust. J. Chem. 1989, 42, 913.
- [22] N. Biricik, Z. F. Fei, R. Scopelliti, P. J. Dyson, *Eur. J. Inorg. Chem.* 2004, 4232.
- [23] B. J. Gregory, C. K. Ingold, J. Chem. Soc. B 1969, 276.
- [24] G. M. Sheldrick SHELXS-97, Program of Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [25] G. M. Sheldrick, SHELXL-97 Program of Crystal Structure Solution, University of Göttingen, Germany, 1997.