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Coinage metal complexes of 2-diphenylphosphino-3-methylindole[†]

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Coordination of P,N indolyl-phosphine ligands to Au¹, Ag¹ and Cu¹ metal ions under weakly basic conditions results in easy deprotonation of the indolyl N–H function and effective formation of a family of homo- and heterobimetallic complexes $MM'(PPh_2C_9H_7N)_2$ (M = M' = Au (2), Ag (5); M = Au, M' = Cu (3), Ag (4)). The latter (4) exists as an inseparable mixture of four different complexes, which are in equilibrium driven by slow dynamics. The reaction of silver(I) and copper(I) ions with $PPh_2(C_9H_8N)$ affords a rare tetranuclear Z-shaped cluster $Ag_2Cu_2(PPh_2C_9H_7N)_4$ (6), which exhibits red luminescence in solid state (650 nm) and a weak dual emission in solution with the main component in the near-IR region (746 nm).

Introduction

Coordination chemistry of d¹⁰ coinage metals in general and of gold(I) in particular, is significantly diversified by the effective secondary metal-metal interactions which may lead to the formation of various polymetallic assemblies¹ demonstrating attractive photophysical properties. It has been shown that luminescence of these compounds often originates or considerably depends on the metallophilic contacts both in the solid state and in solution.²⁻⁴ Therefore different types of bridging ligands, which could bring two metal ions in close proximity, have been successfully employed in preparative chemistry of the copper subgroup metal complexes. As Au^I demonstrates much higher affinity toward phosphorus ligands in comparison to hard donors such as nitrogen and oxygen, the preference has been given to the bidentate phosphines with a short bite angle e.g., P,P diphosphine ligands PR_2-X-PR_2 (X = CH₂, CH⁻, NR', C=PMe₃, ferrocenyl, various aromatic spacers *etc.*),^{3,5} and some mixed-donor phosphines with $P_{c}C^{-}(PR_{2}C_{6}X_{4}^{-})$,⁶ P,S (PhP₂CH₂SPh),⁷ or P,N (PPh₂-pyridine, 2-PPh₂-1-X-imidazole X = methyl, benzyl *etc.*)^{8,9} coordinating functions (Scheme 1).

Additionally, these heterophosphines having N or S donor atoms allowed for the successful assembly of the mixed-metal systems,^{7,9,10} some of which exhibit very intense and tunable photoluminescence.^{4,11}



Scheme 1 Examples of bidentate phosphine bridging coordination.

However, the chemistry of P,NH heterodentate ligands, where NH represents pyrrolyl or indolyl groups, to the best of our knowledge, has never been investigated with respect to the coinage metal ions and very poorly studied in general. The reason for this lack of attention probably resides in the rather ineffective synthetic approach to 2-diphenylphosphino-pyrrole,¹² as well as in the limited ligand stability, manifested by a tendency to break the P-C bond upon coordination to transition metals.¹³ Closely related 2-diphenylphosphino-3-methylindole was reported in 2005 as an easy to make and stable phosphine.14 Subsequent synthesis of its Pd(II) dinuclear compounds,15 where both P and deprotonated N donor atoms participate in metal binding, prompted us to explore the related chemistry of d¹⁰ copper subgroup metal compounds. Herein we report the preparation of a series of the novel homo- and heterometallic Au^I, Ag^I and Cu^I complexes with 2-diphenylphosphino-3-methylindole and the study luminescent properties of the tetranuclear Ag^I-Cu^I cluster.

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Experimental

General comments

Au(tht)Cl (tht = tetrahydrothiophene),¹⁶ 2-diphenylphosphino-3methylindole¹⁴ were obtained according to the literature methods. Other reagents and solvents were used as received. The solution 1D ¹H, ³¹P NMR and ¹H–¹H COSY spectra were recorded on Bruker Avance 400 and Bruker DPX 300 spectrometers. Microanalyses were carried out in the analytical laboratory of the University of Eastern Finland.

[Au(PPh₂C₉H₈N)₂]PF₆ (1). Au(tht)Cl (100 mg, 0.312 mmol) was dissolved in CH_2Cl_2 (7 cm³) and crystalline $PPh_2(C_9H_8N)$ (200 mg, 0.635 mmol) was added. The colorless transparent mixture was stirred for 15 min and then treated with a solution of $AgPF_6$ (79 mg, 0.312 mmol) in acetone (3 cm³). The stirring was continued for an additional 15 min, the precipitate of AgCl was removed by filtration and the colorless filtrate was evaporated. The amorphous solid was washed with diethyl ether $(3 \times 5 \text{ cm}^3)$ and recrystallized by gas-phase diffusion of diethyl ether into a CH₂Cl₂ solution of 1 at 5 °C to give a colorless crystalline material (279 mg, 92%). ³¹P{¹H} NMR $(CDCl_3; \delta)$: 24.6 (s, 2P), -143 (sept, 1P). ¹H NMR $(CDCl_3; \delta)$ δ): 2.33 (s, 6H, CH₃ of indole), 7.17 (dd, 2H, aromatic H of indole, J(HH) 8.4, 7.1 Hz), 7.30 (dd, 2H, aromatic H of indole, J(HH) ca. 8, 7.1 Hz), 7.52 (d, 2H, aromatic H of indole, J(HH) 8.4 Hz), 7.59 (d, 2H, aromatic H of indole, J(HH) ca. 8 Hz), 7.55-7.66 (m, 20H, phenyl H), 8.61 (s, 2H, NH of indole). Anal. Calc. for AuC₄₂H₃₆F₆N₂P₃: C, 51.87; H, 3.73; N, 2.88. Found: C, 51.58; H 3.98; N 2.89.

Au₂(PPh₂C₉H₇N)₂ (2). Method A. 1 (50 mg, 0.051 mmol) was dissolved in CH₂Cl₂ (10 cm³) and a solution of Au(tht)Cl (17.0 mg, 0.053 mmol) in CH₂Cl₂ (3 cm³) was added, followed by NEt₃ (1 drop). The colorless solution was stirred for 30 min, evaporated, washed with methanol (2×5 cm³), diethyl ether (2×5 cm³) and recrystallized by slow evaporation of the CHCl₃–heptane solution of **2** at room temperature to give a colorless crystalline material (48 mg, 92%).

Method B. Au(tht)Cl (100 mg, 0.312 mmol) was dissolved in CH_2Cl_2 (10 cm³) and crystalline $PPh_2(C_9H_8N)$ (100 mg, 0.317 mmol) was added. The colorless transparent mixture was stirred for 15 min and then treated with NEt₃ (8 drops, slight excess). The stirring was continued for an additional 30 min, then the colorless solution was filtered and evaporated. The white solid was washed with methanol $(2 \times 5 \text{ cm}^3)$ and diethyl ether $(2 \times 5 \text{ cm}^3)$, and then recrystallized by slow evaporation of the CHCl3-heptane solution of 2 at room temperature to give a colorless crystalline material (150 mg, 94%). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃; δ): 15.8 (s). ${}^{1}H{}$ NMR (CDCl₃; δ): 1.89 (d, 6H, CH₃ of indole, J(HP) 1.4 Hz), 7.02 (dd, 2H, aromatic H of indole, J(HH) 8.0, 7.0 Hz), 7.16 (dd, 2H, aromatic H of indole, J(HH) 8.1, 7.0 Hz), 7.41–7.49 (m, 12H, phenyl H), 7.58 (d, 2H, aromatic H of indole, J(HH) 8.0 Hz), 7.62-7.69 (m, 8H, phenyl H), 7.76 (d, 2H, aromatic H of indole, J(HH) 8.1 Hz). Anal. Calc. for Au₂C₄₂H₃₄N₂P₂: C, 49.33; H, 3.35; N, 2.74. Found: C, 49.16; H 3.34; N 2.74.

AuCu(PPh₂C₉H₇N)₂ (3). Method A. 1 (50 mg, 0.051 mmol) was dissolved in CH_2Cl_2 (10 cm³) and a solution of $[Cu(NCMe)_4]PF_6$ (19.5 mg, 0.054 mmol) in CH_2Cl_2 (3 cm³) was

added, followed by NEt₃ (1 drop). The pale yellow solution was stirred for 30 min, evaporated, washed with methanol (2×5 cm³) and diethyl ether (2×5 cm³) and recrystallized by gas-phase diffusion of diethyl ether into the CHCl₃-ethanol solution of **3** at +5 °C to give very pale yellow crystals (81 mg, 93%).

Method B. **2** (50 mg, 0.049 mmol) was dissolved in CH_2Cl_2 (15 cm³) and a solution of [Cu(NCMe)₄]PF₆ (37.0 mg, 0.099 mmol) and PPh₂(C₉H₈N) (31 mg, 0.098 mmol) in CH₂Cl₂ (5 cm³) was added, followed by NEt₃ (2 drop). The pale yellow solution was treated as above (method A) to give pale yellow crystals of **3** (81 mg, 93%).

³¹P{¹H} NMR (CDCl₃; δ): 28.5 (s). ¹H NMR (CDCl₃; δ): 1.93 (s, 6H, C<u>H</u>₃ of indole), 7.05 (dd, 2H, aromatic H of indole, *J*(HH) *ca.* 8.0, 6.8 Hz), 7.25 (dd, 2H, aromatic H of indole, *J*(HH) 8.3, 6.8 Hz), 7.42–7.51 (m, 12H, phenyl H), 7.57–7.63 (m, 8H, phenyl H), 7.59 (d, 2H, aromatic H of indole, *J*(HH) *ca.* 8.0 Hz), 7.97 (d, 2H, aromatic H of indole, *J*(HH) 8.3 Hz). Anal. Calc. for AuC₄₂CuH₃₄N₂P₂: C, 56.73; H, 3.85; N, 3.15. Found: C, 56.47; H 4.09; N 3.17.

{AuAg(PPh₂C₉H₇N)₂} (4). Method A. 1 (50 mg, 0.051 mmol) was dissolved in CH₂Cl₂ (10 cm³) and a solution of AgCF₃SO₃ (13.5 mg, 0.053 mmol) in methanol (2 cm³) was added, followed by NEt₃ (1 drop). The reaction mixture was treated analogously to that of **2** to give colorless crystalline material (44 mg, 91%).

Method B. AgCF₃SO₃ (51 mg, 0.198 mmol) was dissolved in methanol (2 cm³) and a solution of PPh₂(C₉H₈N) (62 mg, 0.197 mmol) in CH₂Cl₂ (3 cm³) was added. This mixture was added to a solution of **2** (100 mg, 0.098 mmol) in CH₂Cl₂ (15 cm³), followed by NEt₃ (5 drops). The colorless solution darkened to brownish and was stirred for 1.5 h. Then it was treated analogously to **2** to give 168 mg (92%) of white crystalline material.

³¹P{¹H} NMR (CDCl₃; δ): the spectrum corresponds to the mixture of 4 complexes, see discussion; 4.5 (two d, $J(^{107}Ag-P)$ 555 Hz and $J(^{109}Ag-P)$ 641 Hz, ³J(PP) 4.6 Hz), 8.3 (two d, $J(^{107}Ag-P)$ 543 Hz and $J(^{109}Ag-P)$ 629 Hz), 15.8 (s), 19.9 (d, ³J(PP) 4.6 Hz), 28.8 (s). Anal. Calc. for AgAuC₄₂H₃₄N₂P₂: C, 54.04; H, 3.67; N, 3.00. Found: C, 53.71; H 3.86; N 3.02.

Ag₂(PPh₂C₉H₇N)₂ (5). AgCF₃SO₃ (40 mg, 0.156 mmol) was dissolved in methanol (3 cm³) and added to a solution of $PPh_2(C_9H_8N)$ (50 mg, 0.159 mmol) in CH_2Cl_2 (20 cm³), followed by NEt₃ (2 drops). The colorless solution was filtered and placed into a refrigerator at 5 °C. Small block colorless crystals formed within 2–3 days, washed with methanol $(3 \times 5 \text{ cm}^3)$ and diethyl ether $(2 \times 5 \text{ cm}^3)$, and vacuum dried (60 mg, 91%). The crystalline samples are very poorly soluble in common organic solvents. ³¹P{¹H} NMR (CDCl₃; δ): 8.3 (two d, $J(^{107}Ag-P)$ 545 Hz and $J(^{109}\text{Ag-P})$ 629 Hz). ¹H NMR (CDCl₃; δ): 1.94 (s, 6H, CH₃ of indole), 7.01 (dd, 2H, aromatic H of indole, J(HH) 8.2, 7.8 Hz), 7.13 (dd, 2H, aromatic H of indole, J(HH) ca. 8.0, 7.8 Hz), 7.40-7.48 (m, 12H, phenyl H), 7.52 (d, 2H, aromatic H of indole, J(HH) 8.2 Hz), 7.55–7.61 (m, 10H, phenyl H and aromatic H of indole). Anal. Calc. for Ag₂C₄₂H₃₄N₂P₂: C, 59.74; H, 4.06; N, 3.32. Found: C, 59.32; H 4.19; N 3.27.

 $Ag_2Cu_2(PPh_2C_9H_7N)_4$ (6). $AgCF_3SO_3$ (50 mg, 0.195 mmol) was dissolved in methanol (3 cm³) and added to a solution of $PPh_2(C_9H_8N)$ (125 mg, 0.397 mmol) and Cu(NCMe)_4PF_6 (73 mg, 0.196 mmol) in CH₂Cl₂ (20 cm³), followed by NEt₃ (2 drops).

The resulting orange solution was stirred for 30 min, filtered and evaporated. The orange solid was washed with methanol $(2 \times 5 \text{ cm}^3)$ and diethyl ether $(2 \times 5 \text{ cm}^3)$ and recrystallized by slow evaporation of the CHCl₃-heptane solution of **4** at room temperature to give an orange-red crystalline material (136 mg, 87%). ³¹P{¹H} NMR (CDCl₃; -50 °C δ): 3.0 (two d, 1P (J(¹⁰⁷Ag–P) 441 Hz and J(¹⁰⁹Ag–P) 509 Hz)); 2.6 (two d, 1P (J(¹⁰⁷Ag–P) 479 Hz and J(¹⁰⁹Ag–P) 551 Hz)). Anal. Calc. for Ag₂C₈₄Cu₂H₆₈N₄P₄: C, 63.05; H, 4.28; N, 3.50. Found: C, 62.90; H 4.24; N 3.52.

Photophysical measurements

The photophysical measurements for 6 were carried out in solid state and in CH₂Cl₂, which was distilled immediately prior to use. The solutions were carefully degassed before taking lifetime measurements. The light-emitting diodes (LEDs, maximum emission at 390 and 532 nm) were used to pump luminescence. The LEDs were used in the continuous and pulse modes (pulse width, 1–20 µs; duty of edge, ~90 ns; repetition rate, 100 Hz to 10 kHz). A digital oscilloscope Tektronix TDS3014B (Tektronix, bandwidth 100 MHz), monochromator MUM (LOMO, interval of wavelengths 10 nm) and photomultiplier tube Hamamatsu were used for life-time measurements. Emission spectra were recorded using an HR2000 spectrometer (Ocean Optics). A halogen lamp, LS-1-CAL (Ocean Optics), and deuterium lamp, DH2000 (Ocean Optics), were used to calibrate the absolute spectral response of the spectral system in the 200-1100 nm range. Excitation spectra were measured on a Varian Cary Eclipse spectrofluorimeter.

X-ray structure determinations

The crystals of 3, 5 and 6 were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected on a Bruker AXS Smart ApexII diffractometer using Mo-K α radiation ($\lambda = 0.710$ 73 Å). The APEX217 program package was used for cell refinements and data reductions. The structures were solved by direct methods using the SHELXS-9718 program with the WinGX19 graphical user interface. Multi-scan absorption corrections based on equivalent reflections (SADABS)²⁰ were applied to all data. Structural refinements were carried out using SHELXL-97.18 In 3 a chlorine atom in one of the chloroform of crystallization was disordered over three sites with occupancies of 0.4/0.4/0.2. One of the disordered chlorines was restrained so that its U_{ij} components approximate to isotropic behavior. Furthermore, the hydrogen atom of CHCl₃ was refined with a fixed C-H distance (1.00(4) Å) and $U_{iso} = 1.2 U_{ex}$ (parent carbon atom). In 5 the solvent of crystallization (CH_2Cl_2) was disordered over two sites with equal occupancies. The carbon and chlorine atoms of the solvent molecules were restrained so that their U_{ii} components approximate to isotropic behavior. In 6 the chlorine atoms in one of the CHCl₃ solvent molecules were disordered over two sites with occupancies of 0.74 and 0.26. Also, the carbon atom C85 of the second CHCl₃ solvent molecule was disordered over two sites with occupancies 0.63 and 0.37. The C-Cl and Cl-Cl distances in both chloroform molecules were restrained to be similar. The hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.950.99 Å, and $U_{iso} = 1.2-1.5 U_{eq}$ (parent atom). The crystallographic details are summarized in the corresponding footnote.[‡]

Results and discussion

Synthesis and characterization

The reaction of Au(tht)Cl with PPh₂(C_9H_8N) in a 2 : 1 stoichiometric ratio and consequent treatment with AgPF₆ resulted in nearly quantitative formation of the complex [Au(PPh₂C₉H₈N)₂]PF₆ (1), Scheme 2. The composition of 1 has been established on the basis of ¹H, ³¹P NMR spectroscopic studies and elemental analysis. Thus, its ³¹P spectrum displays a singlet resonance at 24.6 ppm along with septet of PF₆⁻ counterions (-143 ppm), indicating the equivalence of the phosphine ligands. The ¹H spectrum consists of a set of resonances of aromatic protons together with the high-field singlet of the methyl group and a broad low-field resonance of the N–H proton of the indolyl moiety, relative intensity and multiplicity of the signals are also completely compatible with equivalence of the phosphine ligands. (Experimental and Fig. S1, ESI[†]).

Addition of 1 equivalent of Au(tht)Cl to 1 in the presence of base (NEt₃, to deprotonate indolyl nitrogen atoms) gave a dimeric digold complex formulated as Au₂(PPh₂C₉H₇N)₂ (2). Alternatively, 2 can be obtained in the one-step reaction of Au(tht)Cl with PPh₂(C₉H₈N) (1:1 ratio) upon treatment with NEt₃. Dimer 2 didn't give crystals suitable for X-ray diffraction studies and was characterized by ¹H, ³¹P NMR spectroscopy. The ³¹P{¹H} spectrum displays a singlet at 15.8 ppm, while the ¹H NMR data fit well the structure shown in Scheme 2 (Experimental and Fig. S1, ESI[†]). The position of the ³¹P signal is considerably shifted into high field in comparison with that of 1, which points to the head-to-tail coordination of the phosphines in 2. Analysis of the spectral patterns of other complexes (see below) also confirms this hypothesis.

Similar to the synthesis of **2**, the reaction of **1** with $[Cu(NCMe)_4]PF_6$ and NEt₃ led to high yield formation of the heterometallic dimer AuCu(PPh₂C₉H₇N)₂ (**3**). Treatment of **2** with 2 equivalents of $[Cu(NCMe)_4]PF_6$, PPh₂(C₉H₈N) and NEt₃ allowed for the selective preparation of **3**. The crystal structure

 $[\]ddagger$ Crystal data for 3: C₄₄H₃₆AuCl₆CuN₂P₂, M = 1127.89, colourless block, $0.28 \times 0.16 \times 0.14 \text{ mm}^3$, triclinic, space group P1, a = 10.8076(3), 0.28 × 0.16 × 0.14 mm, trennic, space group 11, *a* = 10.0076(3), *b* = 13.5369(4), *c* = 16.5304(5) Å, *α* = 68.8140(10), *β* = 82.764(2), *γ* = 72.5220(10)°, *V* = 2150.45(11) Å³, *Z* = 2, *D_c* = 1.742 g cm⁻³, *F*₀₀₀ = 1108, Mo-Kα radiation, λ = 0.71073 Å, *T* = 100(2)K, 2*θ*_{max} = 72.9°, 76139 reflections collected, 20526 unique ($R_{int} = 0.0560$). Final GooF = 1.022, R1 = 0.0315, wR2 = 0.0652, R indices based on 20526 reflections with $I > 2\sigma(I)$ (refinement on F^2), 529 parameters, 7 restraints; wR2 = 0.0691 (all data). Crystal data for 5: $C_{44}H_{38}Ag_2Cl_4N_2P_2$, M = 1014.24, colourless needle, $0.14 \times 0.08 \times 0.06$ mm³, monoclinic, space group C2/c, a = 26.223(2), b = 8.9783(8), c = 18.0291(16) Å, $\alpha = 90, \beta = 107.870(5), \gamma = 90^{\circ}, V = 100$ 4040.0(6) Å³, Z = 4, $D_c = 1.668$ g cm⁻³, $F_{000} = 2032$, Mo-K α radiation, $\lambda =$ 0.71073 Å, T = 100(2)K, $2\theta_{max} = 52.0^{\circ}$, 15701 reflections collected, 3935 unique ($R_{int} = 0.0480$). Final GooF = 1.052, R1 = 0.0454, wR2 = 0.1119, *R* indices based on 3935 reflections with $I > 2\sigma(I)$ (refinement on F^2), 269 parameters, 36 restraints; wR2 = 0.1193 (all data). Crystal data for 6: $C_{86}H_{70}Ag_2Cl_6Cu_2N_4P_4$, M = 1838.86, orange block, $0.20 \times 0.10 \times 0.07$ mm³, triclinic, space group $P\bar{1}$, a = 12.8508(5), b = 16.2521(6), c = 18.9675(7) Å, $\alpha = 98.284(2), \beta = 92.794(2), \gamma = 95.373(2)^{\circ}, V = 3895.1(3) \text{ Å}^3, Z = 2,$ $D_{\rm c} = 1.568 \text{ g cm}^{-3}, F_{000} = 1856, \text{ Mo-K}\alpha \text{ radiation}, \lambda = 0.71073 \text{ Å}, T =$ 100(2)K, $2\theta_{\text{max}} = 55.3^{\circ}$, 61774 reflections collected, 17947 unique ($R_{\text{int}} =$ 0.0639). Final GooF = 1.005, R1 = 0.0510, wR2 = 0.1058, R indices based on 17947 reflections with $I > 2\sigma(I)$ (refinement on F^2), 979 parameters, 58 restraints; wR2 = 0.1231 (all data).



Scheme 2 Reaction conditions: (*a*) 0.5 Au(tht)Cl, 0.5 AgPF₆; (*b*) Au(tht)Cl, NEt₃; (*c*) Au(tht)Cl, NEt₃; (*d*) $[Cu(NCMe)_4]PF_6$, NEt₃; (*e*) 2 $[Cu(NCMe)_4]PF_6$, 2 PPh₂(C₉H₈N), NEt₃; (*f*) AgCF₃SO₃, NEt₃; (*g*) 2 AgCF₃SO₃, 2 PPh₂(C₉H₈N), NEt₃.



Fig. 1 Structural plot of $AuCu(PPh_2C_9H_7N)_2$ (3). Selected bond distances (Å): Au(1)-P(2) 2.3061(5), Au(1)-P(1) 2.3132(5), Au(1)-Cu(1) 2.7054(2), Cu(1)-N(1) 1.8594(17), Cu(1)-N(2) 1.8660(17); angles (deg): P(2)-Au(1)-P(1) 166.989(18), N(1)-Cu(1)-N(2) 173.87(7).

of **3** is shown in Fig. 1. Complex **3** adopts a head-to-head coordination mode of the heterodentate PN phosphines, where the gold and copper ions are bound to phosphorus and nitrogen atoms, respectively. Hard-to-hard and soft-to-soft metal–ligand interaction is evidently the driving force in the formation of the structural pattern found in **3**. A visible distortion of the linear geometry at gold(1) center (167°) is probably determined by a rather short intermetallic distance (2.7054(2) Å) that is considerably less than the sum of Au and Cu van der Waals radii (3.06 Å) and falls in the range found for other Au¹–Cu¹ bonds reported in the literature.^{10,21} The solution NMR spectral data for **3** are consistent with the solid-state structure. The ³¹P spectrum displays one singlet at 28.5 ppm and the proton NMR pattern consists of the resolved set of signals, which correspond to the aromatic protons together with a high field singlet of the CH₃

group of indolyl substituent (Experimental and Fig. S1, ESI[†]). The number of signals and their relative intensities confirm the equivalence of the phosphine ligands.

In an attempt to synthesize the silver analogue of 3, we investigated the reaction of 1 with AgCF₃SO₃ and NEt₃. Instead of the expected dinuclear complex AuAg(PPh₂C₉H₇N)₂, a mixture of compounds 4 were generated according to ${}^{31}P{H}$ NMR spectrum (Fig. 2). Numerous attempts to recrystallize the mixture in order to separate the constituents were not successful and even didn't change the relative intensities of the ${}^{31}P{H}$ NMR signals. Moreover, variation of the synthetic method (Scheme 2(f,g) and Experimental) also led to the formation of the mixture of exactly the same composition that points to a dynamic equilibrium of the molecular species presented in solution. The VT NMR experiments in the -50 - +45 °C temperature interval (Figure S2, ESI[†]) showed only slight broadening of the minor signal (8.3 ppm) at +50 °C and small variations in relative intensities of all resonances. This is an indication of a relatively slow (in the NMR time scale) intermolecular dynamics which start to affect the spectroscopic pattern only at the temperature close to the solvent boiling point. Comparative analysis of the room temperature spectrum, which can be considered as a low temperature dynamics limit, allowed for a tentative assignment of the observed signals to the species shown in Fig. 2. Thus, the signal at 15.8 ppm exactly matches that of complex 2 (species c). The low field singlet at 28.8 ppm very probably originates from the head-tohead AuAg(PPh₂C₉H₇N)₂ complex, with the phosphorus atom coordinated to gold (species a), as its position is very close to the resonance of the Au-Cu relative 3 (28.5 ppm). The multiplicity and the coupling constants of the dominant signals at 19.9 (d, ³J(PP) 4.6 Hz) and 4.5 (dm, J(¹⁰⁷Ag- P) 555 Hz and J(¹⁰⁹Ag-P) 641 Hz, ${}^{3}J(PP)$ 4.6 Hz) ppm indicate that the corresponding phosphorus atoms are bound to the Au^I and Ag^I ions, respectively. This spectral pattern most probably stems from the nonsymmetric head-to-tail AuAg(PPh₂C₉H₇N)₂ complex (Fig. 2, b). A typical "silver" multiplet-two doublets at 8.3 ppm (J(107 Ag-P) 543 Hz and $J(^{109}\text{Ag-P})$ 629 Hz) is indicative of the phosphorus coordination to the silver(I) ions, very probably in the head-to-tail mode of the phosphine ligands in the homometallic $Ag_2(PPh_2C_9H_7N)_2$ complex (species d).



Fig. 2 ${}^{31}P{}^{1}H$ NMR spectrum of the mixture **4**, 400 MHz, CDCl₃, 25 °C. The relative molar ratio of the forms *a:b:c:d* is *ca.* 1:7.5:1.8:1.4.

In order to prove this structural hypothesis we have probed a direct reaction of AgCF₃SO₃ with the diphosphine under study. Indeed, mixing the stoichiometric amounts of the reagents and the addition of NEt₃ (Scheme 3*a*) led to fast crystallization of colorless $Ag_2(PPh_2C_9H_7N)_2$ (5), which was characterized by an X-ray diffraction study (Fig. 3) and by NMR spectroscopy.



Fig. 3 Structural plot of $Ag_2(PPh_2C_9H_7N)_2$ (5). Selected bond distances (Å): Ag(1)-N(1) 2.101(4), Ag(1)-P(1) 2.3507(13), Ag(1)-Ag(1') 2.8577(7); angles (deg): N(1)-Ag(1)-P(1) 174.86(12).



Scheme 3 Reaction conditions: (*a*) AgCF₃SO₃, NEt₃; (*b*) 0.5 AgCF₃SO₃, 0.5 [Cu(NCMe)₄]PF₆, NEt₃.

Complex **5** expectedly shows the symmetrical head-to-tail bonding mode of the PN ligands. Both silver(I) ions have the linear two-coordinate environment. The intermetallic distance is 2.8577(7) Å, which is much less than the sum of van der Waals radii (3.44 Å) and is consistent with the previously reported values for Ag–Ag separations in phosphine-containing compounds,^{9,22} testifying to a presence of the metal–metal interaction. The ³¹P{¹H} NMR spectrum displays two doublets centered at 8.3 ppm which is characteristic for P–Ag coordination. The values of the chemical shift and coupling constants for the ¹⁰⁷Ag and ¹⁰⁹Ag containing isotopomers ($J(^{107}Ag-P)$ 545 Hz and $J(^{109}Ag-P)$ 629 Hz) are exactly the same as the corresponding parameters of the *d* species revealed in the mixture **4** (Fig. 2, *d*). The proton NMR data of dimer **5** are in complete agreement with the solid state structure.

The observed non-selective formation of different homo- and heterometallic species in the presence of gold(I) and silver(I) ions is most probably a consequence of similar "softness" of these coordination centers in contrast to the formation a single isomer in the case of related gold–copper chemistry with essentially different properties of the coordinating metal ions. Solid state ³¹P{¹H} CP-MAS NMR spectrum of the crystalline bulk sample

The synthetic approach, which gave the homometallic Au¹, Ag¹ complexes **2** and **5**, respectively (see Scheme 2*c*, Scheme 3*a*), did not allow for isolation of any stable product in the case of Cu¹ ions, though some interaction occurred judging by the appearance of yellow color upon adding NEt₃ to the solution containing $[Cu(NCMe)_4]PF_6$ and $PPh_2(C_9H_8N)$. The ¹H and ³¹P{¹H} NMR spectra of the reaction mixture showed non-informative patterns of broad signals. However, when two metal ions, Cu¹ and Ag¹, were combined together followed by treatment with 2 equivalents of the PN ligand and NEt₃, a bright orange solution was formed, from which a red-orange crystalline sample of the tetranuclear cluster Ag₂Cu₂(PPh₂C₉H₇N)₄ (**6**) was obtained in high yield (Scheme 3*b*). Its crystal structure is shown in Fig. 4.



Fig. 4 Structural plot of $Ag_2Cu_2(PPh_2C_9H_7N)_4$ (6). Selected bond distances (Å): Ag(1)-P(4) 2.3953(12), Ag(1)-P(1) 2.4263(13), Ag(1)-Cu(1) 2.7335(7), Ag(1)-Ag(2) 3.0745(5), Ag(2)-P(2) 2.4071(12), Ag(2)-P(3) 2.4327(12), Ag(2)-Cu(2) 2.7492(7), Cu(1)-N(1) 1.838(4), Cu(1)-N(2) 1.845(4), Cu(2)-N(3) 1.842(4), Cu(2)-N(4) 1.847(4); angles (deg): P(4)-Ag(1)-P(1) 140.72(4), Cu(1)-Ag(1)-Ag(2)74.665(17), P(2)-Ag(2)-P(3) 140.22(4), Cu(2)-Ag(2)-Ag(1) 69.427(16), N(1)-Cu(1)-N(2) 174.09(18), N(3)-Cu(2)-N(4) 172.58(17).

The metal core of complex 6 has a rare Z-shaped planar geometry, in which the spatially separated copper ions are bound to the central di-silver unit in an asymmetric way. This structural pattern gives only two effective Ag-Cu contacts (Ag(1)-Cu(1) 2.7335(7) and Ag(2)-Cu(2) 2.7492(7) Å), which fits well the literature data,23,24 while two other silver-copper distances are considerably elongated (3.327 and 3.533 Å) and exceed the sum of Ag and Cu van der Waals radii (3.12 Å). The non-bridged Ag-Ag bond (3.0745(5) Å) is longer than that in 5 (2.8577(7) Å) but is still within the reported range of this type of contacts.^{9,22} The phosphine ligands are coordinated in a bridging mode providing N,N and P,P environment for the copper and silver centers, respectively. The geometry at the copper ions is almost linear, while the P-Ag-P angles are only ca. 140 °C. To the best of our knowledge the tetranuclear Ag¹₂Cu¹₂ metal core has been previously found only in one structurally characterized complex, $(PPh_3)_2Ag_2Cu_2(C_3H_4NS_2)_4,$ which has a "butterfly" arrangement of the metal ions.^{23}

The ³¹P and ¹H NMR spectra of **6** display intramolecular dynamics in the temperature range above -30 °C, Fig. 5 and S2–S4, ESI.† However, the limiting low temperature ³¹P{¹H} spectrum was obtained at -50° C.



Fig. 5 VT ³¹P{¹H} NMR spectra of the complex 6, CDCl₃, 300 MHz.

The structure of 6, revealed in the solid state, belongs to the C₂ symmetry group with the two-fold axis through (perpendicular to) the center Ag(1)-Ag(2) bond. In this symmetry group, four phosphine ligands are grouped into two couples: $P(1) \leftrightarrow P(3)$ and $P(2) \leftrightarrow P(4)$, bound to each other by the symmetry element. In accord with this structural pattern, the ³¹P{¹H} NMR spectrum displays two slightly different pairs of doublets at 2.6 ppm (J(107Ag-P) 479 Hz, J(109Ag-P) 551 Hz) and 3.0 ppm (J(107Ag-P) 441 Hz, J(¹⁰⁹Ag–P) 509 Hz), respectively (Fig. 5, top spectrum). Analysis of the spectroscopic variations observed in the ³¹P spectrum upon warming the $CDCl_3$ solution of **6** shows that the high-field resonance starts to broaden first, which is evidently related to local dynamics of the organic substituents at this phosphorus center. This low temperature dynamics eventually results in the fast symmetry exchange of the phosphine ligands, causing the signal to split into a broad doublet due to the coupling to the silver nuclei. The proton VT NMR spectra (Fig. S3, ESI[†]) show more complicated behavior to reveal the presence of major and minor conformations of the organic environment around the phosphorus centers at -40 °C. The proton signals corresponding to these conformations can be distinguished in the ¹H-¹H COSY spectrum of 6, Fig. S4, ESI[†], but they are particularly visible in the high field part of the 1D spectrum where two major singlets of the methyl groups at 1.71 and 1.89 ppm, associated with the different phosphorus ligands, are in dynamic equilibrium with the minor signals of conformationally different indole fragments. Thus the spectroscopic data obtained are compatible with the structure shown in Fig. 4 and also point to its fluxionality in solution.

	λ_{abs}, nm	$\lambda_{\rm em},{\rm nm}$	λ_{ex}, nm	<i>τ</i> , μs	$arPsi_{ m em}$
Solution (CH ₂ Cl ₂)	294, 450	746 w	452	а	$(8 \pm 2) \cdot 10^{-4}$
Solid state		650		0.76 ± 0.05	

"Lifetime in solution couldn't be accurately determined due to low intensity of emission.

Photophysical characteristics of the $Ag_2Cu_2(PPh_2C_9H_7N)_4$ cluster (6)

None of the bimetallic complexes 1-5 show appreciable photoemission in the solid state or fluid medium at room temperature, while the tetrametallic cluster **6** is moderately emissive in the solid state and exhibits a weak luminescence in degassed dichloromethane solution. The characteristics of absorption, emission and excitation spectra are given in Table 1 below.

The solid state emission band (Fig. S5, ESI[†]) is centered at 650 nm to show substantial Stokes shift, single exponential decay and excited state lifetime in microsecond domain that is indicative of triplet origin of the emission. The previous works on the Ag–Cu heterometallic cluster complexes²⁵ showed that the metal cluster-centered orbitals make a considerable contribution to both the ground and emissive excited states of these compounds. The emission in this case is very probably associated with the MLCT or (d \rightarrow s) excitations modified by metal–metal contacts, which is characteristic of the polynuclear d¹⁰ complexes with metallophilic interactions in the coordination core.²⁶

In dichloromethane solution, complex **6** displays weak dual emission at 746 and 520 nm, the latter being too weak to determine its parameters. Substantial differences in emission characteristics of the solid sample and solution is probably determined by "dissociative" equilibria in fluid media which were detected by the NMR measurements. Relatively weak metallophilic Ag-Ag bonding in the Z-shaped Ag_2Cu_2 cluster may be broken upon transfer of the tetranuclear aggregate in solution, which in turn results in changes in the nature of emission responsible excited state, making it similar to those of non-emissive binuclear heterometallic complexes **3** and **4**.

Conclusions

We have investigated coordination chemistry of the heterobidentate P,N indolyl-phosphine ligand with respect to Cu^I, Ag^I and Au^I metal ions. The phosphine demonstrated an ability to serve as bridging P,N- group upon deprotonation of the indolyl nitrogen atom under mild conditions. The homometallic complexes of Ag and Au were found in dimeric head-to-tail forms $M_2(PPh_2C_9H_7N)_2$ (M = Au (2), Ag (5)). The heterobimetallic compound AuCu(PPh₂C₉H₇N)₂ (3) demonstrated a head-to-head ligand arrangement and preferential binding of P and N donor atoms to Au and Cu, respectively. Interestingly, its Au-Ag analogue 4 doesn't exist in a single molecular form, but appears to be an inseparable mixture of four different bimetallic complexes, which present in slow dynamic equilibrium. Coupling of the Ag^I and Cu^I metal ions in the presence of the indolyl-functionalized phosphine unexpectedly gave a tetranuclear Z-shaped cluster $Ag_2Cu_2(PPh_2C_9H_7N)_4$ (6), which exhibits red luminescence in solid and dual emission in solution with main component in near-IR region (746 nm).

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