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Rearrangement of two 8-membered 1,5-diaza-3,7-diphosphacyclooctane rings into 16-membered P_4N_4 ligand on the gold(I) template

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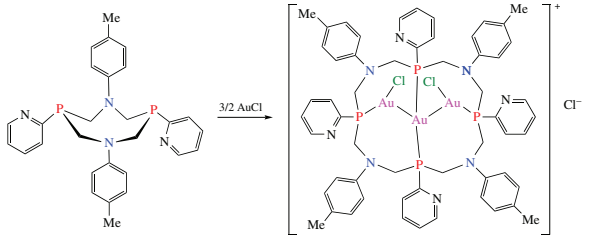
The reaction of gold(I) chloride with two molecules of 1,5-diaza-3,7-diphosphacyclooctane derivative causes their reorganization into 16-membered macrocyclic tetraphosphine ligand. The structure of the trinuclear gold(I) complex obtained was confirmed by X-ray analysis. The dynamic equilibrium between dinuclear gold(I) complexes with eight-membered cyclic ligands and the trinuclear gold(I) complex with 16-membered ones has been revealed.



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Cyclic aminomethylphosphines such as 1,5-diaza-3,7-diphosphacyclooctanes find an application as ligands for the design of catalysts in the electrochemical oxidation/reduction of hydrogen/proton[1–7] or other catalytic processes,[4,8,9] and for the design of luminescent complexes of d^{10} metals.[10–12] *P*-Pyridyl-substituted aminomethylphosphines represent a group of P,N-hybrid ligands capable of stabilizing the d^{10}-subgroup metals by the coordination with both phosphine and *N*-pyridyl donor centers.[13,14] Recent works describing pyridyl-containing 1,5-diaza-3,7-diphosphacyclooctanes demonstrate wide perspectives for their use in the construction of dinuclear gold(I)[10,15,16] and copper(I) complexes including unique hexanuclear copper(I) clusters.[17–20] All such complexes exhibit moderate luminescence in the solid state and promising luminescent sensory properties (vapochromism, solvatochromism, thermochromism and the sensory properties towards biothiols).

One of the intriguing properties of cyclic aminomethylphosphines is the lability of the P–CH_2–N moiety, which in particular leads to the transformation of medium cycles to macrocycles and *vice versa* in solution,[21] interconversion of P-stereoisomers as well as intercycle exchange of amino groups.[22] The reorganization of 14- or 16-membered P_4N_2-macrocycles in solutions proceeds spontaneously with the formation of P_2N-stereoisomer mixtures of 1-aza-3,6-diphosphacycloheptanes or 1-aza-3,7-diphosphacyclooctanes,[22] with the more dynamically preferable product prevailing in the equilibrium mixture. The rate of the equilibrium attainment increases in the presence of H^+. It was shown that the lability of the P–CH_2–N moiety is also possible for stable 1,5-diaza-3,7-diphosphacyclotanes, containing phenyl substituents at phosphorus atoms, on the Cr^{III} template.[23,24] The reaction of 1,5-diaza-3,7-diphosphacyclooctane with $CrCl_2$(THF) in THF solution led to the complex with 16-membered $P_4^{Ph}N_4^{Ph}$ macrocyclic ligand, whose structure was confirmed by the X-ray crystallography.

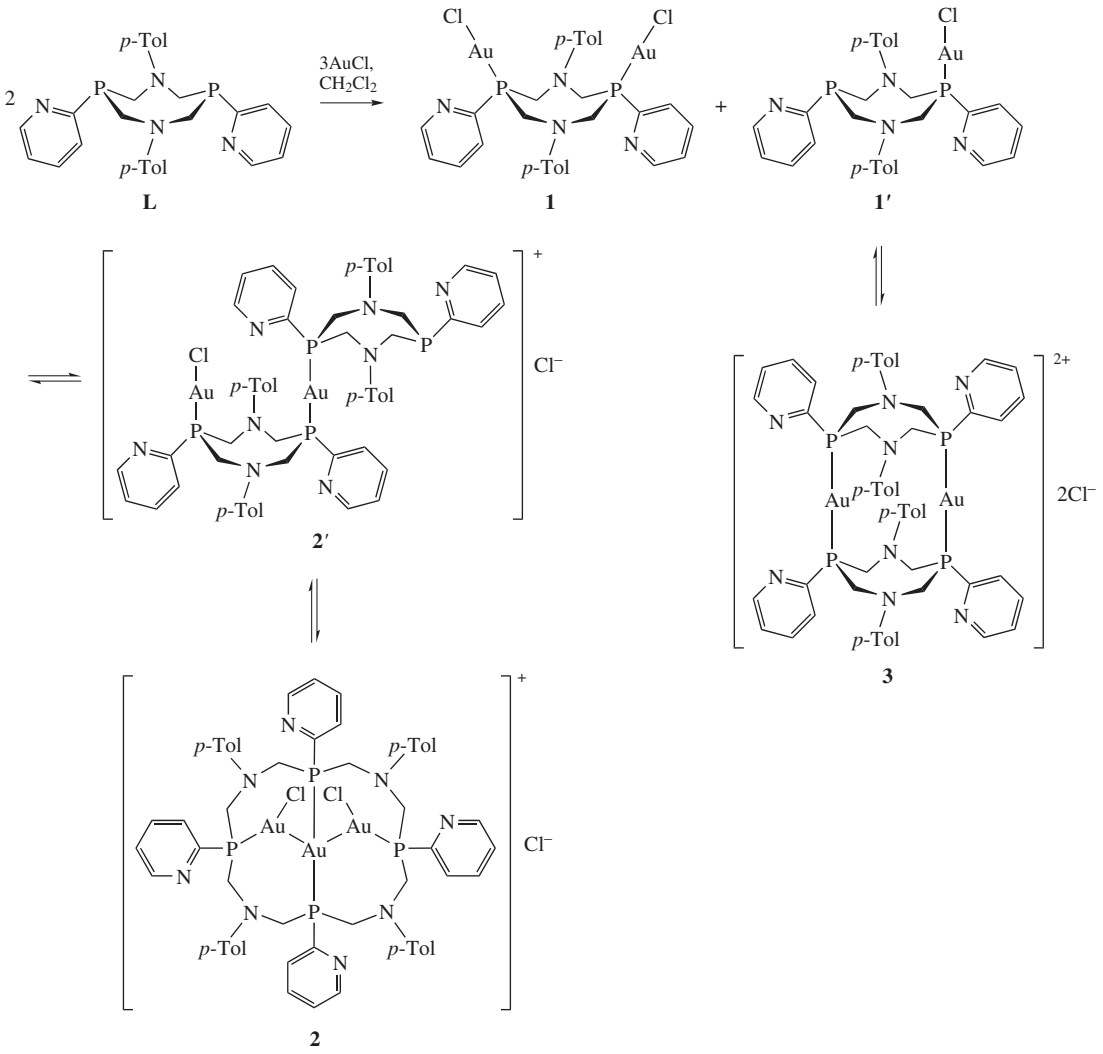
Herein, we report on the synthesis and characterization of the product of spontaneous association of two eight-mebered cyclic ligands into 16-membered macrocyclic one in the course of the reaction with gold(I) chloride.

It has been recently shown that the reaction of pyridyl-containing 1,5-diaza-3,7-diphosphacyclooctanes and (tetrahydrothiophene)gold(I) chloride with the ligand/metal molar ratios of 1 : 1 and 1 : 2 leads to binuclear cationic[16] or neutral[10,15] luminescent complexes. In all cases, the eight-membered cyclic ligands retained their structure. Unexpectedly, the reaction of 3,7-di(pyridin-2-yl)-1,5-di(*p*-tolyl)-1,5-diaza-3,7-diphosphacyclooctane **L** (Scheme 1) with 1.5 equivalents of gold(I) chloride in dichloromethane resulted in a mixture of complexes **1**–**3**. Broad peaks in the range from 5 to 27 ppm in the ^{31}P NMR spectrum of the reaction mixture were observed. MALDI mass spectrum of the mixture indicated the presence of major peaks with the masses of 1629.0 and 2403.6 Da, which corresponded to compounds with $L_2Au_3Cl_2$ and $L_4Au_2Cl_2$ compositions, respectively.

The evaporation of the solvent from the reaction mixture *in vacuo* afforded a yellowish powder. Crystallization of the obtained powder from DMSO gave dinuclear complex **1**, while the crystallization of the same powder from ethanol solution gave complex **2** (see Scheme 1).

The broad signals in the NMR spectra and the crystallization of two different compounds from the reaction mixture indicate a possible dynamic equilibrium, which occurs in solution (see Scheme 1).

The above assumption of the equilibrium is also supported by Lin,[25] who has observed an analogous behavior of the gold(I) chloride complexes with bis(diphenylphosphino)methane (dppm) ligands in solution. The driving force of such type of dynamic process was the coordination ability of chlorine ion. As for complexes **1**–**3**, chlorine ion would form Au–Cl coordination bond in a trinuclear complexes **2** and **2′** with the following dissociation of the Au–P bond and formation of complexes **1** and **1′**. Complex **1′** undergoes reversible dimerization leading to compex **3**. The analogous transformations were also found for



Scheme 1

the gold(I) alkynyl complexes containing the strong electron-withdrawing groups at gold(I) cations.[26] Those works[25,26] as well as our experiments demonstrate that the electron properties and the coordination lability of the counter ion can play a crucial role in the formation of the complex core. According to quantum chemical computations, complex **2** is more stable than compound **2′** by 29 kcal mol^{-1}. This energy difference is more pronounced than the energy gain produced by macrocyclization of free ligands, *i.e.* macrocyclic ligand P_4N_4 is by 24 kcal mol^{-1} more stable compared with two P_2N_2 ligands. This leads us to suggestion that the formation of macroheterocycle is promoted by metal.

Crystals of complex **2** suitable for the X-ray analysis were grown from ethanol solution and its molecular structure is shown in Figure 1.[†] According to XRD analysis, compound **2** is a trinuclear gold(I) complex with *cis–cis–cis*-configuration of the 16-membered macrocycle as a coupling product of two molecules of initial 1,5-diaza-3,7-diphosphacyclooctane. The 16-membered cyclic ligand in complex **2** has a C_2-symmetrical 'crown-type' conformation with an axis passing through the central gold(I) ion. All substituents at heteroatoms occupy positions in the plane formed by the N- and P-atoms or deviate from it towards the trinuclear gold(I) core. The strongest deviation from the plane is observed for the substituents at two phosphorus atoms of the P–Au–P moiety. Two peripheric gold(I) atoms in the Au_3 core have a trigonal environment formed by the coordination of phosphorus atom, chloride ion and Au···Au interaction. The central gold(I) atom has a tetragonal environment, which is formed by the bonding of two phosphorus atoms and by two aurophilic interactions with the

[†] *Crystallographic data for* $[C_{56}H_{60}Au_3Cl_2N_8P_4^+]Cl^-$ **2**, C_2H_5OH (molecular formula $C_{58}H_{66}Au_3OCl_3N_8P_4$), M = 1712.33, monoclinic, *C2/c* (no. 15), a = 23.94(2), b = 13.913(14) and c = 21.35(2) Å, β = 113.454(12)°, V = 6524(11) Å^3, Z = 4, Z' = 1/2 (complex in the special position on axis 2), d_{calc} = 1.743 g cm^{-3}, μ(Mo) = 6.994 mm^{-1}, F(000) = 3304, $T_{max/min}$ = 0.5518/0.7457; 37459 reflections were collected (2.4° ⩽ θ ⩽ 26.0°), 6360 of which were unique, R_{int} = 0.404, completeness to θ of 26.0° was 99.3%. The refinement of 352 parameters with no restraints converged to R_1 = 0.0849, wR_2 = 0.1295 for 2380 reflections with $I > 2\sigma(I)$ and R_1 = 0.2565, wR_2 = 0.1857 for all data with S = 0.98 and residual electron density, peak/hole 1.14/–1.85 e Å^{-3}.

The measurements were performed on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα (λ = 0.71073 Å) radiation and ω-scan rotation at room temperature. Data collection images were indexed, integrated and scaled using the APEX2 data reduction package[28] and corrected for absorption using SADABS.[29] The structure was solved by direct methods and refined using SHELX[30] program. The solvated complex molecule was solved and three strong peaks in difference Fourier map, which was interpreted as a molecule of ethanol disordered by axis 2. All non-hydrogen atoms were refined anisotropically, H atoms were calculated on idealized positions and refined as riding ones.

CCDC 1939086 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

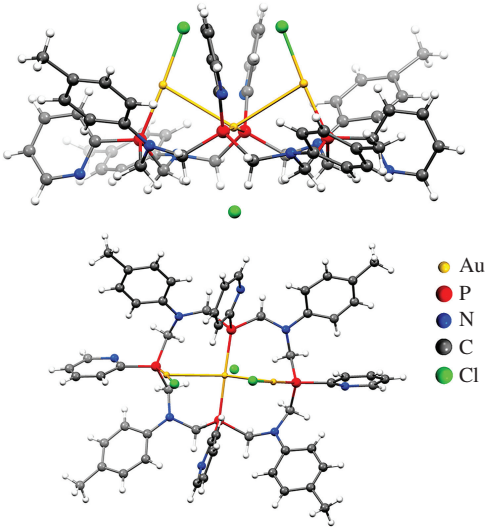


Figure 1 Molecular structure of complex **2** in two different projections.

neighboring gold(I) atoms. Thus, all metals of the Au_3 core are involved in aurophilic interactions. The Au–Au distances are about 3.18 Å, that is less than the sum of van der Waals radii (3.32 Å according to Bondi[27]).

In the summary, the reorganization of 1,5-diaza-3,7-diphosphacyclooctanes in the course of their reaction with gold(I) chloride, leading to the formation of 16-membered macrocyclic ligands, has been observed. The obtained trinuclear gold(I) complex of the 16-membered cyclic aminomethylphosphine ligand has been characterized by X-ray crystallography. Our finding additionally confirms the high lability of the P–CH_2–N moiety in aminomethylphosphines, which can result in the formation of new compounds.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.013.

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