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First Representatives of Auᴵ Complexes of *P,N*–Containing Bicyclo[7.7.5]henicosane

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Dedicated to Academician of RAS Oleg Sinyashin on the occasion of his 60ᵗʰ Anniversary

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Bi- and tetranuclear gold(I) complexes of P,N-containing cryptand have been synthesized by gradual addition of gold(I) chloride to (SSSS/RRRR)-3,7,11,15-tetramesityl-3,7,11,15-tetraphospha-1,9-(m-xylylene)-1,9-(endo,endo)-diazabicyclo[7.7.5]henicosane.

Keywords: Cryptands, gold(I) complexes, *P,N*-heterocycles.

Первые представители комплексов Auᴵ с *P,N*–содержащим бицикло[7.7.5]хеникозаном

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Синтезированы новые би- и тетраядерные комплексы золота(I) с P,N-содержащим криптандом путем последовательного добавления хлорида золота(I) к (SSSS/RRRR)-3,7,11,15-тетрамезитил-3,7,11,15-тетрафосфа-1,9-(м-ксилилен)-1,9-(эндо,эндо)-диазабицикло[7.7.5]хеникозану.

Ключевые слова: Криптанды, комплексы золота(I), *P,N*-гетероциклы.

Cryptands are a family of synthetic bi- and polycyclic multidentate ligands for a variety of cations.[1] Because of their unique and selective complexing properties[2] cryptands are of great interest to chemists worldwide. Cryptands are able to encapsulate cations of alkali and alkaline earth metals,[3] transition metals,[4] and lanthanoids;[5] they display high selectivity in such reactions and stabilize the resulting complexes due to the cryptate effect. Their unique properties are a base for development of original sensors,[6] catalysts,[7] organic electrides,[8] and luminescent materials.[9] While *O*-donor cryptands are commonly used for effective binding of alkali metals and alkaline earth metals, *N*-donor cryptands are generally applied with transition metals and lanthanoids. It is well known that the phosphorus(III) atom in phosphines

is an excellent donor center for transition metals, however, there are only a few reports on the synthesis of phosphine cryptands.[4a,10-12] The large number of stereoisomers[13] as well as homeomorphic[12] isomers can be formed in the case of polyphosphorus cryptands and there is a problem for their separation. Complexation with transition metals is one of the approach to the stabilization of the isomers and their successful separation.[12b,14]

Recently, we have reported an efficient stereoselective covalent self-assembly of the various macrocyclic polyphosphines (14-, 16-, 18-, 20-membered corands and 28-, 36- and 38-membered cyclophanes)[15] based on the condensation reactions of primary phosphines or secondary *bis*phosphines with formaldehyde and primary amines

or diamines. Later we have expanded the covalent self-assembly approach to the stereoselective synthesis of a novel phosphine cryptand **1** containing two bridgehead nitrogen and four asymmetric phosphorus atoms in the 16-membered core cycle *via* the reaction of 1,3-*bis*(mesitylphosphino)-propane, formaldehyde and *meta*-xylylenediamine.[16] It should be mentioned that only one *SSSS/RRRR* isomer was isolated in the moderate yield. Cryptand **1** represents an *endo – endo* isomer with only the lone pairs of electrons of the bridgehead nitrogen atoms pointing directly into the cavity (Scheme 1). The lone pairs of electrons of the neighbouring phosphorus atoms have an axial orientation and are located in opposite directions relative to the 16-membered ring.

In the present work we have demonstrated the synthesis of the first representatives of bi- and tetranuclear Au[I] complex of cryptand **1**.

The interaction of cryptand **1** with gold chloride in dichloromethane in the ratio 1:2 led to the formation of binuclear Au[I] complex **2** (Scheme 1).[17] Compound **2** was obtained as pale yellow precipitate after reaction mixture concentrating and addition of diethyl ether.

The structure elucidation of compound **2** was based on ^{31}P, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. In the ^{31}P NMR spectrum of complex **2** two signals

gold coordinated phosphorus atoms (Scheme 1, H-9) are noticeably upshifted to 1.63 ppm. The aromatic protons of this mesityl are registered as doublet at 7.41 ppm with spin-spin coupling $^{4}J_{PH} = 3.5$ Hz. This feature may be explained by influence of close location of metal center to methyl groups of mesityl fragment. So, we have established that compound **2** is an individual complex with uncoordinated and coordinated phosphorus atoms.

Apart from NMR spectroscopy, complex **2** has been characterized by elemental analysis, which also confirmed 1:2 ligand to gold stoichiometry. However ESI-mass-spectrometry has shown only one *m/z* pick corresponding to [L+Au]+ ion and MALDI mass-spectrum has demonstrated *m/z* picks corresponding to [L+Au]+ and [L+Au+O]+ ions. [17] This fact can be explained by gold atom elimination and uncoordinated phosphorus atom oxidation in experimental conditions.

X-Ray diffraction analysis has unambiguously established the proposed structure of complex **2** (Figure 1).[18] Indeed, only two alternating phosphorus atoms of ligand **1** are coordinated to two gold atoms, whereas two other phosphorus atoms are "free". Both P-Au-Cl fragments are in the one direction and are opposite to the xylylene spacer. The lone pairs of electrons of the uncomplexed phosphorus atoms
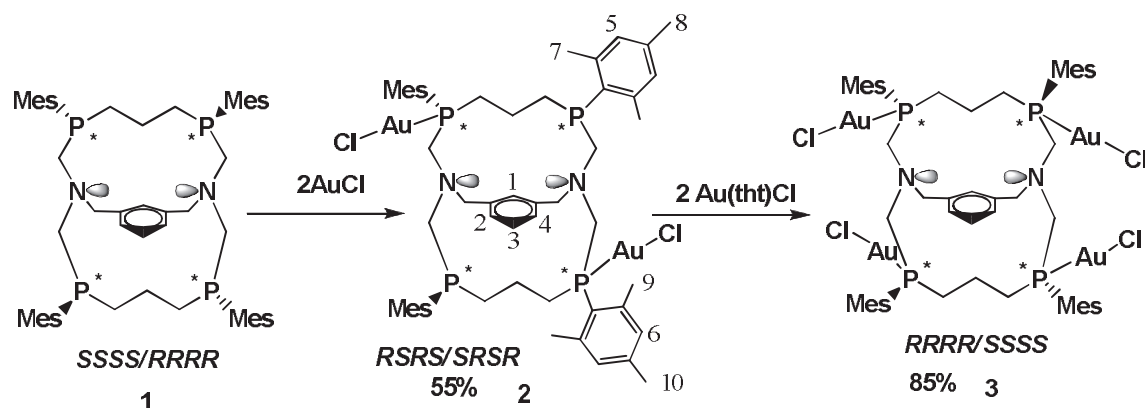
Scheme 1.

were registered: sharp at -41.3 ppm and slightly broadened at 22.0 ppm. The chemical shift at -41.3 ppm is similar to the same in initial cryptand **1**[16] and corresponds to uncomplexed phosphorus atoms, the chemical shift at 22.0 ppm is typical for linear gold aminomethylphosphine complexes (δ_P 17–22 ppm)[14] and belongs to gold bonded phosphorus atoms. In the ^{1}H NMR spectrum of **2** only one set of signals is registered. All of the cyclic alkylene protons are unequivalent, namely, signals of the cyclic propylene protons are registered at the range of 1.69–3.08 ppm as six groups of multiplets, the methylene protons of P-CH$_2$-N-fragment are observed as four overlapped multiplets in the region 3.56–3.65 ppm, the methylene protons of xylylene fragment showed two groups of low-resolved signals at 3.34–3.44 ppm and 5.15–5.24 ppm. Notably unusual picture is observed for the methyl protons of mesityl substituents. The methyl protons belonging to mesityl at uncoordinated phosphorus atom are registered as two singlets at 2.33 and 2.20 ppm for *o*- and *p*-positioned respectively. Unexpectedly *o*-methyl protons of mesityl at
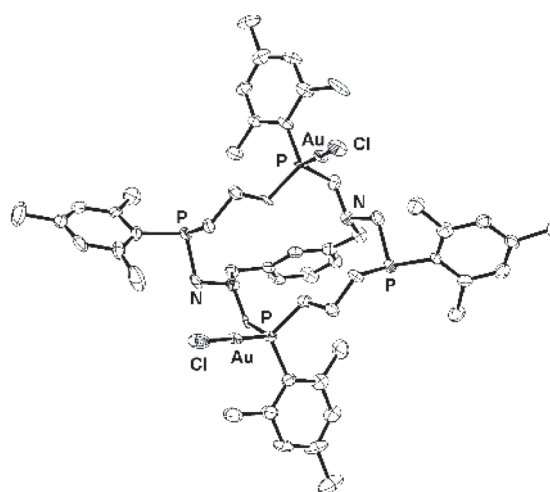

Figure 1. Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity.

P1 and P2 have an axial orientation and are located in opposite directions relative to the P-Au-Cl fragments. Compound **2** forms a true racemic mixture of two enantiomers with RSRS and SRSR configuration of four phosphorus atoms. It should be mentioned that all phosphorus atoms in complex have retained their real ligand configuration but formal signs of metal bonded phosphorus atoms are changed according to the stereochemical rule of configuration determination.[19] Ligand in the complex **2** represents an *endo–endo* isomer with the lone pairs of electrons of the bridgehead nitrogen atoms pointing directly into the cavity.

The geometry of both nitrogen atoms is tetrahedral (the sum of the bond angles is 332.00° and 335.32°). As expected, the overall geometry about each gold(I) center is essentially linear (P-Au-Cl angles are 178.78° and 175.42°) with typical Au–Cl (2.28 Å) and Au–P (2.25 Å) bond distances.[19,20] Noticeably *o*-methyl groups of mesityl substituent at coordinated phosphorus atoms are located in the close proximity to the gold atoms (the minimal distance Au…H is 2.657 Å) that probably is a reason of unusual chemical shift of their protons in the ^{1}H NMR spectrum of complex **2**. It should be mentioned that molecules of complex **2** do not form any specific supramolecular motifs such as layers of columns as it has been shown for **1** and relative 16-membered macroheterocycles.[15f,16]

The following addition of two equivalents of chloro(tetrahydrothiophene)gold to the complex **2** in dichloromethane resulted in the tetranuclear *P*-coordinated gold complex **3** (Scheme 1).[21]

In the ^{31}P NMR spectrum of complex **3** two sharp signals of equal intensity at 8.0 and 12.9 ppm were registered that evidenced the coordination of all phosphorus atoms and their unequivalence. The values of chemical shifts differ from that of the complex **2** but are common for other ditertiary nonsymmetric phosphines.[16] The ^{1}H NMR spectrum demonstrated analogous unusual picture of methyl and aromatic protons of mesityl substituents indicating the close location of metal center to methyl groups of mesityl fragments. So, the *o*-CH$_3$ protons of two pairs of unequivalent mesityl fragments are unusually upshifted and present broad singlets at 1.70 and 2.03 ppm whereas the chemical shifts of *p*-CH$_3$ protons are common. It should be noted that aromatic mesityl protons show two doublets at 7.00 and 6.94 ppm with spin–spin coupling $^4J_{PH}$=3.5 Hz as in complex **2**. The cyclic propylene protons are registered as two multiplets at 1.95–2.03 ppm and 2.62–2.72 ppm, the protons of P-CH$_2$-N-fragments are unequivalent and registered as four groups of signals, and one of them is significantly downshifted to 5.89 ppm that is probably explained by a considerable distortion of the 16-membered ring in ligand.

In conclusion, the first examples of transition metals complexes of novel *P,N*-containing cryptand, namely, two bi- and tetranuclear gold(I) complexes of (*SSSS/RRRR*)-3,7,11,15-tetramesityl-3,7,11,15-tetraphospha-1,9-(*m*-xylylene)-1,9-(*endo,endo*)-diazabicyclo[7.7.5]henicosane have been successfully synthesized by gradual addition of gold(I) chloride to cryptand **1**. It was demonstrated that firstly the phosphorus atoms with lone pair of electrons located at the site opposite to *m*-xylylene spacer are coordinated, and then two other phosphorus atoms are bound by gold atoms. Complexes **2** and **3** exist as one isomer in the both solid states and the solution despite the presence of four chiral intracyclic phosphorus atoms.

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17. All reactions and manipulations were carried out under a dry argon atmosphere by using standard vacuum-line techniques. Solvents were purified, dried, deoxygenated, and distilled before use. EI-MS (70 eV) were recorded with a DFS Thermo Electron Corporation (Germany) spectrometer with direct sample admission into the ion source (ion-source temperature =2808 °C; vaporizer temperature programmed from 50–3508 °C). The XCalibur program was used to process the mass spectrometry data. ^{1}H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were recorded with a Bruker Avance-DRX 400 spectrometer. Chemical shifts are reported in ppm relative to SiMe$_4$ (^{1}H, internal standard), and 85 % H$_3$PO$_4$ (aq) (^{31}P; external standard). Coupling constants (J) are reported in Hz. *Complex 2*. To a solution of cryptand **1** (90 mg, 0.1 mmol) in dichloromethane (7 ml) suspension of gold(I) chloride (45 mg, 0.19 mmol) was added. Reaction mixture became colorless clear liquid with small amount of unreacted components. After 12 hours of stirring no changes was observed and solvent was evaporated. Afterward complex was washed with benzene (7 ml) and precipitated with diethyl ether (5 ml). The white solid was filtered off, washed with diethyl ether (10–15 ml) and dried at 0.05 Torr. Yield: 0.07 g, 55 %. Mp = 225–227 °C. Found, %: C, 48.34; H, 5.41; Cl, 5.23; N, 2.12; P, 9.32. C$_{54}$H$_{72}$Au$_2$Cl$_2$N$_2$P$_4$ Calculated, %: C, 48.48; H, 5.42; Cl, 5.30; N, 2.09; P, 9.26. Mass spectrum (ESI) *m/z* (%): 1070 (100) [L+Au]$^+$), (MALDI):

1070 (100) [L+Au]$^+$), 1086 (52) [L+Au+O]$^+$).^{31}P NMR (162 MHz, CD$_2$Cl$_2$, 303 K) δ$_p$ ppm: 22.0; -41.3. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 303 K) δ$_H$ ppm: 8.45 (1H, br.s, H-1 in xylylene), 7.41 (1H, t $^3J_{HH}$=7.6, H-3 in xylylene), 7.18 (2H, d, $^3J_{HH}$=7.6, H-2,4 in xylylene), 7.07 (4H, s, H-5 in Mes), 6.80 (4H, d, $^4J_{PH}$=2.3, H-6 in Mes), 5.15–5.24 (2H, m, CH$_2$-B in xylylene), 3.65–3.71 (4H, m, P–CH$_2$–N), 3.56–3.63 (4H, m, P–CH$_2$–N), 3.34–3.44 (2H, m, CH$_2$-A in xylylene), 3.00–3.08 (2H, m, PCH$_2$CH$_2$CH$_2$P), 2.53–2.60 (4H, m, PCH$_2$CH$_2$CH$_2$P), 2.33 (18H, s, H-7+H-8 in Mes), 2.20 (6H, s, H-10 in Mes), 2.08–2.18 (2H, m, PCH$_2$CH$_2$CH$_2$P), 1.98–2.07 (2H, m, PCH$_2$CH$_2$CH$_2$P), 1.69–1.78 (2H, m, PCH$_2$CH$_2$CH$_2$P), 1.63 (12H, s, H-9 in Mes).

18. Crystal data of **2** were collected on a Bruker Smart Apex II diffractometer (MoKα=0.71073 Å) using ω – scans mode. Semi-empirical absorption corrections corrections were carried out with SADABS$^{[24]}$ program. The structures were solved by direct methods and refinement was carried out with SHELX program.$^{[25]}$ All non-hydrogen atoms were refined anisotropically, H atoms were calculated on idealized positions and refined as riding atoms. CCDC 1455383 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk). Crystal data, structure refinement for compound **2** at 150 K. C$_{54}$H$_{70}$N$_2$Au$_2$Cl$_2$P$_4$ (1); M=1335.83, triclinic, space group P-1, a=11.532(4), b=11.743(4), c=21.142(7) Å, α=87.855(5), β=89.300(4), γ=71.671(4)°, *V*=2716.0(16) Å^3, Z=2, D calcd=1.633 g·cm^{-3}; μ(Mo-Ka)=5.648 mm^{-1}; 12640 reflections measured, 8824 independent reflections. Final R$_1$=0.0785, R$_w$=0.2138 for 7555 reflections with I>2σ(I), and R$_1$=0.0867, R$_w$=0.2184 for all reflections.

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21. *Complex 3*. To a solution of complex **2** (30 mg, 0.02 mmol) in dichloromethane (3 ml) chloro(tetrahydrothiophene)gold(I) (13 mg, 0.04 mmol) was added. Reaction mixture became colorless clear liquid. After 12 hours of stirring no changes was observed and solvent was evaporated. Afterward complex was precipitated with diethyl ether (3 ml). The pale yellow solid was filtered off, washed with diethyl ether (5 ml) and dried at 0.05 Torr. Yield: 36 mg, 85 %. Mp>230 °C. Mass spectrum (ESI) *m/z* (%): 1533 (100, [L+3Au+2Cl]$^+$). ^{31}P NMR (162 MHz, CD$_2$Cl$_2$, 303 K) δ$_p$ ppm: 12.9; 8.0. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 303 K) δ$_H$ ppm: 7.99 (1H, br.s, H-1 in xylylene), 7.47 (1H, t, $^3J_{HH}$=7.5, H-3 in xylylene), 7.27 (2H, d, $^3J_{HH}$=7.5, H-2,4 in xylylene), 7.00 (4H, d, $^4J_{HH}$=3.5, H-5, in Mes), 6.94 (4H, d, $^4J_{HH}$=3.5, H-6 in Mes), 5.89 (2H, dd, $^2J_{HH}$=15.4, $^2J_{PH}$≈5–6, P-CH$_2$-N), 5.29–5.36 (2H, m, CH$_2$-B in xylylene, partially overlapped with the signal of solvent), 5.15 (2H, dd, $^2J_{HH}$≈$^2J_{PH}$≈14–15, P-CH$_2$-N), 4.18 (2H, ddd, $^2J_{HH}$≈$^2J_{PH}$≈14–15, $^4J_{HH}$≈5–6, P-CH$_2$-N), 3.99–4.10 (2H, m, P-CH$_2$-N in xylylene), 3.68 (2H, d, $^2J_{HH}$=15.4, P-CH$_2$-N), 2.62–2.72 (4H, m, PCH$_2$CH$_2$CH$_2$P), 2.29 (6H, s, H-8 in Mes), 2.20 (6H, s, H-10 in Mes), 2.03 (12H + 8H, br.s, H-7 in Mes + PCH$_2$CH$_2$CH$_2$P), 1.70 (12H, br.s, H-9 in Mes).

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