Brief Communications

Hypercoordinated gold(1) compounds 3.* Simulation of intramolecular aurophilic Au...Au interactions in binuclear organogold compounds

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Cyclic organogold Au(o-C₆H₄)CH₂(C₆H₄-o)Au(μ -PPh₂CH₂CH₂PPh₂) complex, containing an Au...Au bond, was prepared by reaction of Ph₃PAu(o-C₆H₄)CH₂(C₆H₄-o)AuPPh₃ with dppe. The length of the carbon bridge of the diphosphine ligand, optimal for formation of the Au...Au bond, was preliminarily determined using molecular simulation. The structure of the complex obtained was determined by X-ray diffraction analysis and by MS, ¹H NMR, and ³¹P NMR.

Key words: synthesis, hypercoordinated organogold(I) compound, secondary bonds, diphenylmethane, X-ray diffraction analysis.

The occurrence of secondary (additional) bonds of gold atoms of Au...X (X is a heteroatom), Au...H-C (an aghostic bond), Au...Au, *etc.* types in covalent complexes of gold(1) results in hypercoordinated gold compounds, which have, as a rule, unusual structures and properties.^{1,2} At the same time, formation of a particular type of secondary bonds of gold atoms still cannot be predicted.

In a continuation of our investigations of the nature of secondary bonds of gold atoms in type A phosphine-containing 2,2'-diaurated derivatives of the biaryl series,³⁻⁵ in the present work, on the basis

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of molecular simulation of 2,2'-diaurated diphenylmethane derivatives, we synthesized a new complex with bis(diphenylphosphine)ethane (dppe), Au(o-C₆H₄)CH₂(C₆H₄-o)Au(μ -PPh₂CH₂CH₂PPh₂) (2), and studied its structure by X-ray diffraction.



X is a heteroatom or $(CH_2)_n$ (n = 0, 1)L = PPh₃, Ph₂(CH₂)_mPPh₂ (m = 1, 2)

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 2032-2034, October, 1995. 1066-5285/95/4410-1952\$12.50 © 1995 Plenum Publishing Corporation It was found that treatment of 2,2'-bis(triphenylphosphineaurio)diphenylmethane (1),⁵ which contains gold atoms far removed from one another and not interacting with one another (and aghostically bound to the hydrogen atoms of the bridging CH₂ group), with dppe results in easy replacement of two PPh₃ ligands by a diphosphine ligand. The reaction affords a new complex (2) in a high yield. Complex 2 incorporates a metal-containing macro ring with two interacting gold atoms, one of which is aghostically bound to one of the hydrogen atoms of the bridging CH₂ group of the organic ligand. The optimal (as regards formation of the Au...Au bond) length of the carbon bridge of the bis(diphenylphosphine) ligand was preliminarily determined by molecular simulation.

The X-ray structural study proved the presence of a metal-containing macro ring in the synthesized compound 2 (Fig. 1). The intramolecular Au...Au distance (3.012(3) Å) corresponds to the aurophilic interaction typical of Au^I compounds (see Ref. 2). The macro ring is asymmetrical and has a conformation at which the C-Au-P linear fragments are crossed; according to quantum-chemical calculations,⁶ this is a necessary condition for aurophilic interaction to occur. The C(1)-Au(2)...Au(1)-C(13) and P(1)-Au(1)...Au(2)-P(2) pseudotorsion angles are 55.6 and 52.3°, respectively.

The Au(1)-C(13) and Au(2)-C(1) bond lengths, which are 2.06(3) Å and 2.05(3) Å, respectively, and



also the Au(1)–P(1) and Au(2)–P(2) bond lengths, which are both 2.30(1) Å, are in agreement with normal values.⁷

The Au(1) atom has almost exactly linear coordination; the P(1)-Au(1)-C(13) angle is equal to $178.8(9)^{\circ}$. The collinear arrangement of the bonds at the Au(2) atom is noticeably disrupted; the P(2)-Au(2)-C(1)



Fig. 1. Molecular structure of $Au(o-C_6H_4)CH_2(C_6H_4-o)Au(\mu-PPh_2CH_2CH_2PPh_2)$ (2).

angle is $168.7(9)^{\circ}$. It is significant that the distortion of the coordination geometry of Au(2) reflects the tendency of this atom to move closer to the Au(1) atom (the sum of the Au-Au-C and Au-Au-P angles at the Au(2) atom (191.0°) is larger than 180°). The absence of similar tendency in the case of the Au(1) atom is probably caused by the fact that this atom is involved in a more complex system of secondary interactions. In the asymmetrical conformation found for the macro ring, one of the hydrogen atoms of the methylene bridge of the diphenylmethane ligand, which is directed toward the macro ring, participates in aghostic interaction with the Au(1) atom (the Au(1)-H(72) distance is 2.63 Å) and is located at a distance, excluding an aghostic bond, from the Au(2) atom (the Au(2)-H(72) distance is 3.21 Å). In the diphenylmethane fragment, the dihedral angles between the plane of each phenyl ring and the plane of the methylene bridge are 67.3 and 64.8°, respectively, and the angle between the planes of the phenyl rings is 104.5°, *i.e.*, this part of the macro ring is rather symmetrical. The symmetry of the macro ring is disrupted to the greatest extent in the region of the bridging diphosphine. In fact, the Au-P-C-C torsional angle involving the Au(1) atom is 65.8°, and that involving the Au(2) atom is 80.4° ; the P-C-C-P torsional angle is -67.7° . It is likely that the overall conformation of this macro ring is caused by the trend of molecule 2 to take advantage of all of the additional possibilities for its stabilization through a system of secondary bonds. The preliminary optimization of the geometry of the molecule under consideration by molecular mechanics (at specified lengths of bonds of the Au atom) indicates, first, the conformational mobility of the macro ring (in the absence of specific interactions in it) and, second, that a symmetrical conformation of the molecule is sterically possible.

Experimental

The ¹H NMR spectrum was recorded on a Bruker WP-200 SY spectrometer (200 MHz, tetramethylsilane as the internal standard), the ³¹P NMR spectrum was obtained on a Bruker CXP 200 instrument (81 MHz, H_3PO_4 as the external standard), and the mass spectrum was obtained on a KRATOS Concept instrument with an energy of the bombarding atoms (Cs) of 8 keV; 3-nitrobenzyl alcohol was used as the matrix.

The X-ray diffraction experiment was performed using an Enraf-Nonius CAD-4 automatic diffractometer (Mo-K α -radia-

tion, graphite monochromator, $\omega/2\theta$ -scanning, $2\theta_{max} = 56^{\circ}$). A total of 3395 reflections with $I > 2\sigma(I)$ were measured.

The structure was solved by the heavy-atom method and refined by the least-squares method in the full-matrix anisotropic approximation to R = 0.0564, $R_w = 0.0598$ over 3165 reflections with $F > 5\sigma(F)$.

Complex 2 was synthesized in an atmosphere of dry argon using anhydrous solvents.

Preparation of the

Au($o-C_6H_4$)CH₂(C_6H_4-o)Au(μ -PPh₂CH₂CH₂CH₂PPh₂) complex (2). A solution of dppe (0.17 g, 0.43 mmol) in 10 mL of benzene was added to a solution of complex 1 (0.48 g, 0.43 mmol) in 20 mL of benzene. The crystalline precipitate was separated, washed with pentane, and dried to give 0.39 g (95 %) of μ -diphenylphosphinoethane-bis-aurio(2,2'-diphenylmethane) (2), m.p. 218–219 °C (dec.). Found (%): C, 48.75; H, 3.30. C₃₉H₃₄Au₂P₂. Calculated (%): C, 48.86; H, 3.57. ¹H NMR (CD₂Cl₂), δ : 2.80 (d, 4 H, dppe, ²J_{P-H} = 12 Hz); 4.45 (s, 2 H); 7.05–7.08 (m, 28 H). ³¹P NMR (CD₂Cl₂), δ : 35.34 (s). MS (8 keV), m/z: 959 [M]⁺.

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