Hypercoordinated gold(I) compounds

4.* Synthesis and structure of an *ortho*-diaurated 4-*tert*-butylbiphenyl derivative

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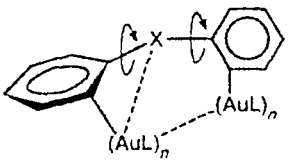
A hypercoordinated 2,2′-diaurated 4-*tert*-butylbiphenyl derivative, which contains an intramolecular Au...Au secondary bond, was first synthesized by the reaction of 2,2′-dilithio-4-*tert*-butylbiphenyl with $ClAuPPh_3$. The structure of the complex was established by X-ray structural analysis, ^1H and ^{31}P NMR spectroscopy, and fast-atom bombardment mass spectrometry.

Key words: synthesis, 4-*tert*-butylbiphenyl, hypercoordinated organogold(I) compounds, secondary bonds, X-ray structural analysis.

In 14-electron σ-organic R—Au—L complexes (where R is an organic ligand and L is the stabilizing phosphine ligand), the gold(I) atom is characterized by a tendency to form additional, weaker attractive secondary coordination bonds with other atoms, for example, Au...Au, Au...X (X is a heteroatom), Au...H—C, or Au...π system bonds.[2–5] As a result of this bonding, hypercoordinated gold(I) compounds, which have unusual structures and properties, are formed.[4,5] Nonbonded "aurophilic" Au...Au interactions between monovalent gold d^{10} atoms, which formally have no electrons to form this bond, are of most interest. Attempts to relate the nature of the Au...Au interaction to any known type of chemical bonding have not met with success.[5–7] The factors that favor or prevent the formation of secondary coordination bonds between gold atoms remain unclear.

This work was undertaken as part of our continuing systematic studies of the chemistry of hypercoordinated organogold(I) compounds, in particular, polynuclear phosphine-containing complexes of the diaryl series **A**. These compounds are convenient models for studying various nonbonded interactions of the Au^I atom because their molecules can adopt conformations in which the Au atoms are in spatial proximity either to each other or to the X group to form secondary coordination bonds, for example, Au...X (X is a heteroatom), Au...H—C (agostic bonds), Au...Au, *etc.*, under conditions of their competition.

Previously, we have prepared and studied new hypercoordinated diaurated organogold(I) *ortho*-derivatives of this class for biphenyl,[8] diphenyl oxide,[9] and diphenylmethane.[1,10] Using these compounds as examples, we studied for the first time the effect of the nature of the bridging group of organic and phosphine ligands as well as of the number of gold-containing fragments in model compounds on the character of secondary hypercoordination bonds with the participation of Au atoms. In addition, the effect of the secondary coordination bonds on the structure, reactivity, and dynamic behavior of the molecules has been assessed.[11]



A

X = O or $(CH_2)_m$ (m = 0, 1); L = PPh_3 or $Ph_2P(CH_2)_2PPh_2$; n = 1, 2

In this work, we synthesized a new representative of organogold(I) compounds, namely, 2,2′-diaurated 4-*tert*-butylbiphenyl, $(2\text{-}Ph_3PAu\text{—}C_6H_4)\text{—}C_6H_3\text{-}4\text{-}Bu^t\text{-}2\text{-}AuPPh_3$ (**1**), and elucidated its structure (including its crystal structure). This complex was synthesized by the reaction of the 2,2′-dilithio-4-*tert*-butylbiphenyl with $ClAuPPh_3$ according to Scheme 1.

Note that 2,2′-dilithiation of 4-*tert*-butylbiphenyl was carried out for the first time. A Bu^nLi/TMEDA complex in hexane was used as the lithiating agent. To obtain organogold compound **1**, it is necessary to use the crystalline 2,2′-dilithio-4-*tert*-butylbiphenyl that has been thoroughly washed off from admixtures and toluene as the solvent.

In addition to the 2,2′-organodigold derivative of 4-*tert*-butylbiphenyl **1**, the reaction yielded a second

* For Part 3, see Ref. 1.

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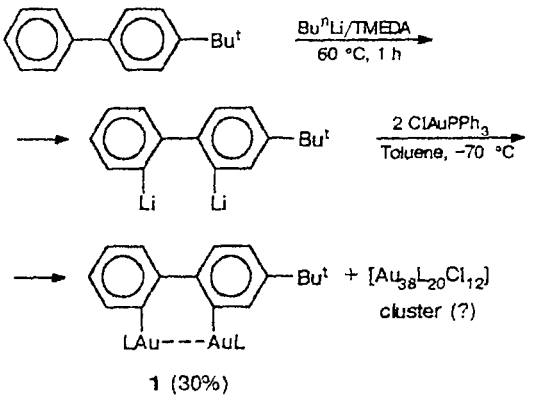
Scheme 1



1 (30%)

L = PPh_3

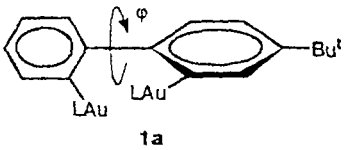
gold-containing reaction product in low yield. The second product is a finely crystalline bright-red compound insoluble in most organic solvents. It reacts rapidly with chloroform and dichloromethane to form the chloride, $ClAuPPh_3$. Based on the data of elemental analysis and the results of IR spectroscopy, EXAFS (extended X-ray absorption fine structure) spectroscopy, and mass spectrometry, it can be suggested that the compound isolated is an inorganic gold cluster, which contains triphenylphosphine ligands and chlorine atoms at gold atoms. The mass spectrum of the compound has ion peaks $[AuPPh_3]^+$ at m/z 459. According to the data of EXAFS spectroscopy, three types of interatomic Au...Au distances [2.65, 3.00 (which correspond to aurophilic interactions), and 4.00 Å] are observed in this complex.

Organodigold complex **1**, which was obtained as the major reaction product, is a colorless crystalline compound soluble in benzene, toluene, and THF. The compound is moderately stable in solutions at room temperature and decomposes readily in $CHCl_3$ and CH_2Cl_2 to form $ClAuPPh_3$.

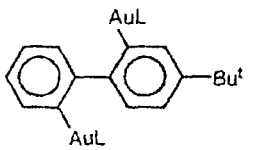
The ^1H NMR spectrum of compound **1** (in C_6D_6) shows a singlet of methyl protons of the Bu^t substituent at δ 1.47 and a complex multiplet of aromatic protons at δ 6.90—8.32. The ^{31}P NMR spectrum (in C_6D_6) has one signal of phosphorus nuclei at δ 42.26.

In the FAB (fast-atom bombardment) mass spectrum of complex **1**, the molecular ion $[M+H]^+$ (at m/z 1115) and a heavier $[M+AuPPh_3]^+$ ion (at m/z 1573), which corresponds to the molecular ion and an additional gold-containing group, are observed. This indicates that in the gaseous phase clusterization occurs, which is typical of gold(I) complexes.[4]

In the crystal of complex **1**, one of two possible molecular conformations, namely, cisoid (or *gauche*) (**1a**) and transoid (**1b**), which is close to planar, conformations might occur.



1a



1b

L = PPh_3

A priori, it cannot be asserted what conformation is preferable. The *gauche* structure of *o,o'*-diaurated biphenyl (conformation **1a**) is favorable to the formation of secondary Au...Au coordination bonds, which additionally stabilize the molecule.[8] In the case of transoid conformation **1b**, the molecule can be additionally stabilized through π-conjugation between two aurated phenyl rings of the organic ligand. However, the contribution of this effect should be apparently insignificant, because in the gaseous phase the biphenyl molecule is nonplanar. The angle φ between the planes of the rings is 42°.[12] The *ortho*-substituted biphenyl molecules adopt a cisoid conformation as well. The angles φ between the planes of the Ph rings are 30° and larger.[13]

X-ray structural analysis of complex **1** demonstrated* that its molecule adopts *gauche* conformation **1a** (Fig. 1) with the distance between the Au atoms of 3.1691(6) Å, which is smaller than twice the van der Waals radius of the Au atom (3.32 Å).[14] The observed Au...Au distance lies in the 2.7—3.5 Å range, which is typical of this type of aurophilic interactions in other complexes of monovalent

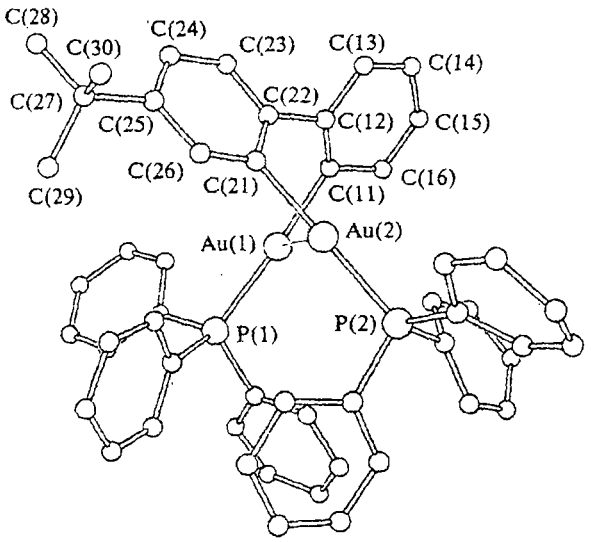


Fig. 1. Molecular structure of the (2-Ph_3PAu—C_6H_4)—C_6H_3-4-Bu^t-2-$AuPPh_3$ complex (**1**).

* The details of X-ray structural analysis of complex **1** will be reported elsewhere.

gold[3,8,15] and corresponds to the Au...Au interaction. The dihedral angle between the planes of the *ortho*-aurated phenyl rings of the biphenyl fragment is 54.8°. In this molecular conformation, the linear C—Au—P fragments have the mutual twist arrangement, which is typical of aurophilic Au...Au interactions.[16]

The Au—C bond lengths in complex **1** correspond to the normal values of the Au—C(sp^2) bond lengths. The Au—P bond lengths are within the range (2.272—2.301 Å) typical of the structures with the linear C—Au—PPh_3 fragment.

Experimental

The ^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200 MHz, Me_4Si as the internal standard). The ^{31}P NMR spectrum was obtained on a Bruker CXP 200 instrument (81 MHz, H_3PO_4 as the internal standard). The mass spectrum was measured on a KRATOS CONCEPT instrument; 3-nitrobenzyl alcohol was used as the matrix; the energy of bombarding atoms (Cs) was 8 keV.

Synthesis of complex **1** was carried out under an atmosphere of dry argon. The solvents were distilled immediately before use over sodium benzophenone ketyl under an atmosphere of argon.

The course of the reaction was monitored by TLC on Silufol UV-254 plates in benzene. The spots were developed by heating.

Synthesis of 4-*tert*-butyl-2,2′-bis(triphenylphosphineaurio)biphenyl, (2-Ph_3PAu—C_6H_4)—C_6H_3-4-Bu^t-2-$AuPPh_3$ (1). TMEDA (3.7 mL, 26 mmol) was added with stirring to a 2.3 *M* hexane solution (12 mL) of Bu^nLi (27 mmol) in anhydrous hexane (15 mL). After 10 min, 4-*tert*-butylbiphenyl (2.00 g, 10 mmol), which was prepared according to a procedure reported previously,[17] was added. The reaction mixture was stirred at 60 °C for 3 h (a virtually colorless crystalline precipitate was gradually formed). The reaction mixture was cooled to ~20 °C and kept for 1 h. The precipitate was separated by decantation and washed with anhydrous hexane (2×10 mL). Then a suspension of the precipitate of 4-*tert*-butyl-2,2′-dilithiobiphenyl in anhydrous hexane (10 mL) was added portionwise to a stirred suspension of $ClAuPPh_3$ (1.48 g, 3 mmol) in anhydrous toluene (35 mL) at −70 °C for 1 h. The reaction mixture was stirred at −60 °C for 1 h and then at −70 °C for 1 h (the amount of the precipitate decreased substantially, and it turned brown). According to the TLC data, $ClAuPPh_3$ reacted completely.

The solution was separated from the precipitate by decantation and treated with water. The organic layer was dried with calcined K_2CO_3 and concentrated to dryness *in vacuo*. The residue was triturated with ether (~3 mL), dried *in vacuo*, and repricipitated from the benzene solution with petroleum ether. Complex **1** was obtained in a yield of 1.00 g (30% with respect to Au added), m.p. 127—129 °C.

Found (%): C, 55.26; H, 4.21; P, 5.68. $C_{52}H_{46}Au_2P_2$. Calculated (%): C, 54.94; H, 4.16; P, 5.56.

^1H NMR (C_6D_6), δ: 1.47 (s, 9 H, CMe_3); 6.99—8.30 (m, 27 H, H arom.). ^{31}P NMR (C_6D_6), δ: 42.26 (s). FAB mass spectrum, *m/z*: 1115 $[M+H]^+$, 1573 $[M+AuPPh_3]^+$.

The brown residue (separated from the reaction solution) was washed with a cooled 1 : 1 toluene—hexane mixture and water and dissolved in benzene (10 mL). A finely crystalline red precipitate formed. The precipitate was separated, washed with pentane, and dried. A gold-containing compound, whose structure was not established, was obtained, yield 0.19 g, decomposition temperature >150 °C. Found (%): C, 33.39; H, 3.13. The $Au_{38}(PPh_3)_{20}Cl_{12}$ cluster, $C_{360}H_{300}Cl_{12}P_{20}Au_{38}$. Calculated (%): C, 32.86; H, 2.29.

The compound does not burn in open flame, and it is insoluble in most organic solvents.

After separation of this compound, $ClAuPPh_3$ was isolated in a yield of 0.12 g from the mother liquor, m.p. 242—243 °C (see Ref. 18).

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