Compounds of hypercoordinated gold(I)
2. Synthesis and molecular structure of 2,2'-bis(triphenylphosphinegold)diphenylmethane

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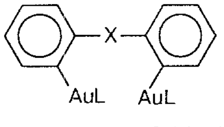
A binuclear organic derivative of gold(I) with diphenylmethane $CH_2(C_6H_4)_2(AuPPh_3)_2$ has been prepared by the reaction of 2,2'-dilithiumdiphenylmethane with $ClAuPPh_3$. X-ray analysis of this compound revealed a transoid conformation of the molecule with agostic bonds between the gold atoms and methylene hydrogens. The complex was characterized by IR, ^1H and ^{31}P NMR, and mass spectral data.

Key words: hypercoordinated gold(I), organic derivatives; agostic interactions; synthesis; diphenylmethane; X-ray diffraction study.

A specific feature of Au^I atoms in various complexes is their ability to form secondary Au...Au bonds.[1,2] The possible nature of these unusual attracting interactions between metal atoms with a d^{10} electronic configuration has been discussed from different points of view. Such interactions has been described in the framework of the consept of spd-hybridization.[3,4] Later and more accurate molecular orbital calculations revealed that electronic correlation effects, intensified by relativistic effects, are the basis of these interactions.[5—7] However, up to now no study has addressed the factors that favor or hinder the formation of the above-mentioned secondary bonds, in particular, the competitive effect on the molecular structure of the secondary hypercoordinated bonds between the Au^I atoms and other atoms or groups of atoms in the molecule, for example, such agostic bonds as Au...X (X — heteroatom), Au...H—C, and others.

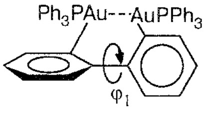
The present work is a continuation of our study of hypercoordinated interactions in binuclear σ-gold(I) organic derivatives of the diaryl series.[8,9]



X = geteroatom or $(CH_2)_m$ (m = 0, 1)
L = PPh_3, $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2)

Potentially, this type of molecule can adopt conformations in which the Au atoms are sterically forced to draw either towards each other or towards the X group. Depending on which interaction proves to be dominant, one or another molecular structure may take place. We have attempted to follow the effect of the geometrical changes in the model molecules that arise when X is changed on the character of the hypercoordinated interactions of the Au atoms.

Earlier, X-ray analysis of 2,2'-bis(triphenylphosphinegold)diphenyl (**1**) showed the cisoid conformation of the complex with the aurophilic interaction (Au...Au 3.0246(6) Å),[8] whereas 2,2'-bis(triphenylphosphinegold)diphenyloxide (**2**) proved to prefer the conformation in which the gold atoms are removed from each other.[9] In this case, the stabilization of complex **2** is



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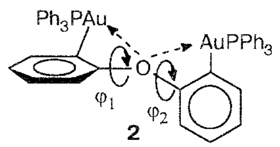

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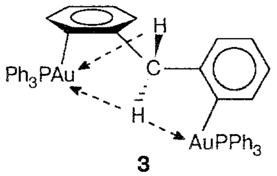

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* For Report 1 see *Russ. Chem. Bull.*, 1994, **43**, 681.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1125—1130, June, 1994.

caused by the interactions between both gold atoms and two unshared electron pairs of the O atom.

This stabilization takes place regardless of the fact that molecule **2** has a greater number of conformational degrees of freedom (the torsion angles φ_1 and φ_2) than molecule **1** (the torsion angle φ_1) to realize the aurophilic interaction. The absence of this interaction in molecule **2** suggests that two Au...O interactions provide better stabilization of the complex than one Au...Au interaction.

We were interested in knowing how the substitution of a CH_2 group for the O atom in complex **2** would affect the conformation and the mode of additional stabilization of the molecule. With this in view, we for the first time synthesized 2,2'-bis(triphenylphosphinegold)diphenylmethane (**3**) and investigated its structure.

Complex **3** was obtained in 64 % yield by the reaction of 2,2'-dilithiumdiphenylmethane[10] (prepared by metallation of 2,2'-diiododiphenylmethane with *n*-butyllithium) with $ClAuPPh_3$ in an ether—THF medium.

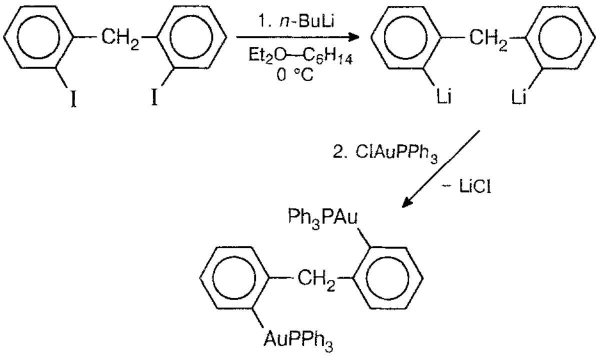

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Figure 1 shows a general view of molecule **3**; its bond lengths and bond angles are given in Tables 1 and 2. The Au—P and Au—C bond lengths are similar to the known values within the bounds of experimental accuracy (2.27—2.29 and 2.01—2.10 Å, respectively).[11] The dihedral angle between the benzene rings of the ligand is 67.6°, and the benzene ring C(8)...C(13) is almost coplanar with the C(8)—C(7)—C(6) plane of the methylene bridge, while the C(1)...C(6) ring is bent 71.5° relative to this plane.

We calculated the conformation of an isolated unsubstituted diphenylmethane molecule by the method of molecular mechanics using the MMX program, which confirmed that the most favorable conformation for this molecule is the one, where the plane of one phenyl ring is coplanar with the C—C—C plane of the methylene bridge, while the plane of the other phenyl ring is

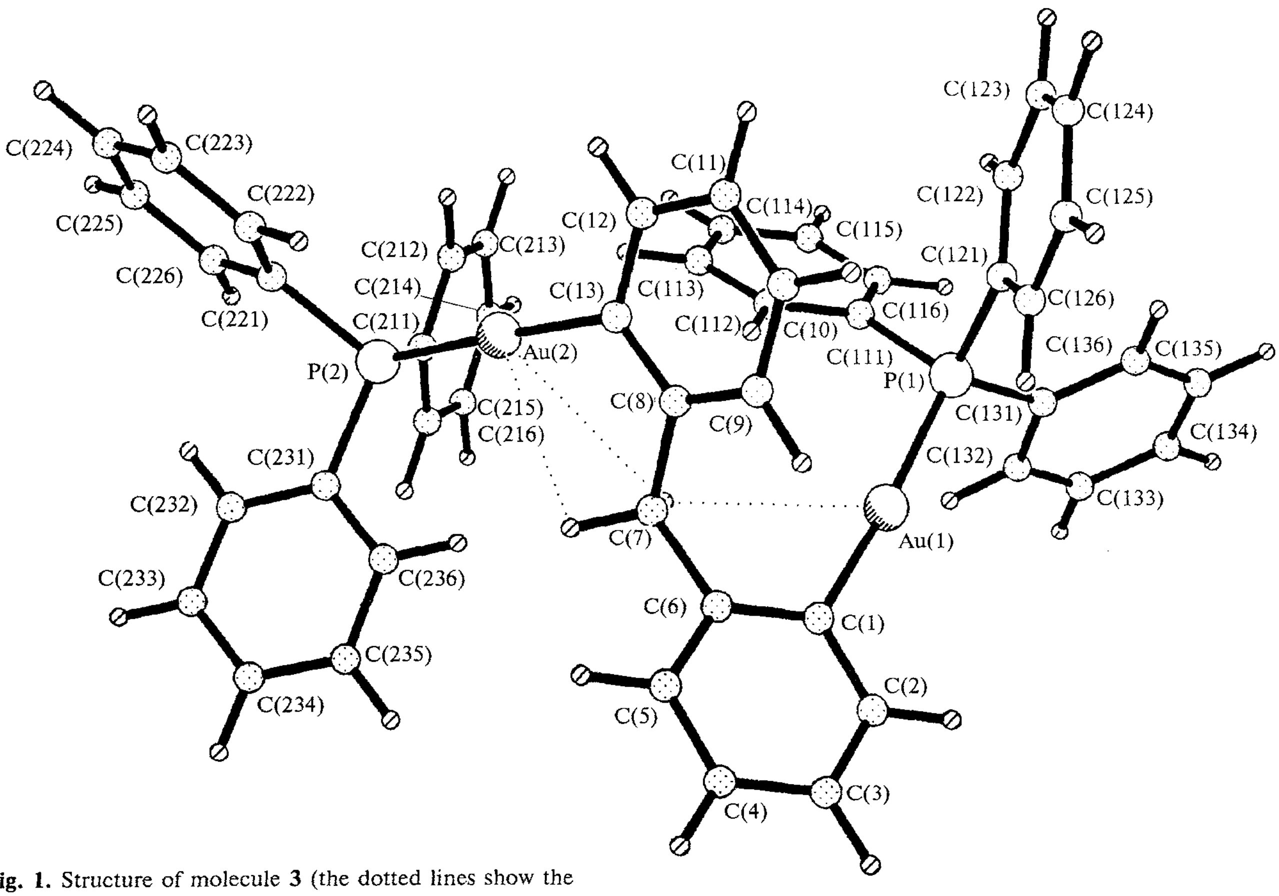
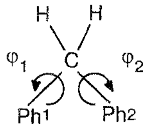


Fig. 1. Structure of molecule **3** (the dotted lines show the short Au...H distances).

Table 1. Bond lengths (*d*) in molecule **3**

Bond	*d*/ Å	Bond	*d*/ Å
Au(1)—P(1)	2.291(3)	Au(1)—C(1)	2.05(1)
Au(2)—P(2)	2.297(3)	Au(2)—C(13)	2.11(1)
P(1)—C(111)	1.82(1)	P(1)—C(121)	1.83(1)
P(1)—C(131)	1.81(1)	P(2)—C(211)	1.84(1)
P(2)—C(221)	1.83(1)	P(2)—C(231)	1.83(1)
C(1)—C(2)	1.35(2)	C(1)—C(6)	1.38(2)
C(2)—C(3)	1.39(2)	C(3)—C(4)	1.38(2)
C(4)—C(5)	1.38(2)	C(5)—C(6)	1.42(2)
C(6)—C(7)	1.55(2)	C(7)—C(8)	1.57(2)
C(8)—C(9)	1.38(2)	C(8)—C(13)	1.35(2)
C(9)—C(10)	1.37(2)	C(10)—C(11)	1.37(2)
C(11)—C(12)	1.36(2)	C(12)—C(13)	1.38(2)
C(111)—C(112)	1.39(2)	C(111)—C(116)	1.39(2)
C(112)—C(113)	1.39(2)	C(113)—C(114)	1.39(2)
C(114)—C(115)	1.32(2)	C(115)—C(116)	1.38(2)
C(121)—C(122)	1.43(2)	C(122)—C(123)	1.42(2)
C(123)—C(124)	1.36(2)	C(124)—C(125)	1.39(2)
C(125)—C(126)	1.39(2)	C(126)—C(121)	1.39(2)
C(131)—C(132)	1.38(2)	C(131)—C(136)	1.41(2)
C(132)—C(133)	1.36(2)	C(133)—C(134)	1.36(2)
C(134)—C(135)	1.35(2)	C(135)—C(136)	1.40(2)
C(211)—C(212)	1.38(2)	C(211)—C(216)	1.39(2)
C(212)—C(213)	1.37(2)	C(213)—C(214)	1.34(2)
C(214)—C(215)	1.40(2)	C(215)—C(216)	1.36(2)
C(221)—C(222)	1.39(2)	C(221)—C(226)	1.37(2)
C(222)—C(223)	1.36(2)	C(223)—C(224)	1.48(2)
C(224)—C(225)	1.38(2)	C(225)—C(226)	1.38(2)
C(231)—C(232)	1.36(2)	C(231)—C(236)	1.37(2)
C(232)—C(233)	1.38(2)	C(233)—C(234)	1.37(2)
C(234)—C(235)	1.34(2)	C(235)—C(236)	1.43(2)

perpendicular to this plane (the φ_1 and φ_2 angles are 0 and 90°, respectively).



On the other hand, the above-mentioned calculations attest that, when $\varphi_1 = 0°$ is constant, the angle φ_2 can easily vary within 90±40° with a very small change in the conformation energy:

φ_2/deg	90	80	70	60	50	48	46	44
ΔE/kcal mol^{-1}	0	0.1	0.5	1.6	4.7	5.8	7.1	8.8

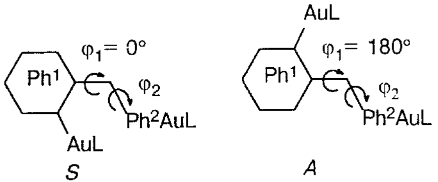
Thus, the ligand conformation in the crystal form of **3** is close to the conformation that sterically is most favorable for unsubstituted diphenylamine. In this conformation the *pseudo*-torsional angle Au(1)—C(1)...C(13)—Au(2) is 101.3°, and the gold atoms are at a distance of 5.631 Å from each other, which excludes any Au...Au interaction.

To find out whether the Au...Au interaction can be realized in molecule **3** in the bounds of sterically possible conformations of the PhOPh diphenylmethane ligand, we calculated the dependence of the Au...Au distance on the φ_2 torsional angle assuming constant $\varphi_1 = 0$ (or 180° for the model molecule). The model molecule contains PH_3 as a neutral ligand; the Au—C and Au—P bond lengths were fixed to be 2.08 and

Table 2. Bond angles (ω) in molecule **3**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
P(1)—Au(1)—C(1)	174.7(4)	C(133)—C(134)—C(135)	120(1)	C(9)—C(10)—C(11)	120(1)
Au(1)—P(1)—C(111)	112.1(4)	C(131)—C(136)—C(135)	120(1)	C(11)—C(12)—C(13)	119(1)
Au(1)—P(1)—C(131)	118.9(4)	P(2)—C(211)—C(216)	122(1)	Au(2)—C(13)—C(12)	119.4(9)
C(111)—P(1)—C(131)	102.3(6)	C(211)—C(212)—C(213)	120(1)	P(1)—C(111)—C(112)	116.7(9)
Au(2)—P(2)—C(211)	112.4(4)	C(213)—C(214)—C(215)	119(1)	C(112)—C(111)—C(116)	119(1)
Au(2)—P(2)—C(231)	111.3(4)	C(211)—C(216)—C(215)	117(1)	C(112)—C(113)—C(114)	119(1)
C(211)—P(2)—C(231)	108.1(6)	P(2)—C(221)—C(226)	121.7(9)	C(114)—C(115)—C(116)	119(1)
Au(1)—C(1)—C(2)	121.9(9)	C(221)—C(222)—C(223)	122(1)	C(123)—C(122)—C(121)	117(1)
C(2)—C(1)—C(6)	118(1)	C(223)—C(224)—C(225)	117(1)	C(123)—C(124)—C(125)	120(1)
C(2)—C(3)—C(4)	122(1)	C(221)—C(226)—C(225)	119(1)	C(125)—C(126)—C(121)	120(1)
C(4)—C(5)—C(6)	120(1)	P(2)—C(231)—C(236)	118(1)	P(1)—C(121)—C(126)	120.5(9)
C(1)—C(6)—C(7)	124(1)	C(231)—C(232)—C(233)	124(1)	P(1)—C(131)—C(132)	119(1)
C(6)—C(7)—C(8)	119(1)	C(233)—C(234)—C(235)	122(1)	C(132)—C(131)—C(136)	118(1)
C(7)—C(8)—C(13)	119(1)	C(231)—C(236)—C(235)	120(1)	C(132)—C(133)—C(134)	121(1)
C(8)—C(9)—C(10)	119(1)	P(2)—Au(2)—C(13)	178.2(4)	C(134)—C(135)—C(136)	120(1)
C(10)—C(11)—C(12)	121(1)	Au(1)—P(1)—C(121)	109.8(4)	P(2)—C(211)—C(212)	116.4(9)
Au(2)—C(13)—C(8)	121.0(9)	C(111)—P(1)—C(121)	105.3(5)	C(212)—C(211)—C(216)	121(1)
C(8)—C(13)—C(12)	120(1)	C(121)—P(1)—C(131)	107.5(6)	C(212)—C(213)—C(214)	121(1)
P(1)—C(111)—C(116)	124.7(9)	Au(2)—P(2)—C(221)	114.2(4)	C(214)—C(215)—C(216)	122(2)
C(111)—C(112)—C(113)	120(1)	C(211)—P(2)—C(221)	105.4(5)	P(2)—C(221)—C(222)	117.8(9)
C(113)—C(114)—C(115)	123(1)	C(221)—P(2)—C(231)	104.8(6)	C(222)—C(221)—C(226)	121(1)
C(111)—C(116)—C(115)	121(1)	Au(1)—C(1)—C(6)	119.8(9)	C(222)—C(223)—C(224)	118(1)
C(122)—C(123)—C(124)	122(1)	C(1)—C(2)—C(3)	121(1)	C(224)—C(225)—C(226)	123(1)
C(124)—C(125)—C(126)	121(1)	C(3)—C(4)—C(5)	118(1)	P(2)—C(231)—C(232)	124(1)
P(1)—C(121)—C(122)	119.5(9)	C(1)—C(6)—C(5)	121(1)	C(232)—C(231)—C(236)	118(1)
C(122)—C(121)—C(126)	120(1)	C(5)—C(6)—C(7)	115(1)	C(232)—C(233)—C(234)	117(1)
P(1)—C(131)—C(136)	123(1)	C(7)—C(8)—C(9)	119(1)	C(234)—C(235)—C(236)	119(1)
C(131)—C(132)—C(133)	121(1)	C(9)—C(8)—C(13)	122(1)		

2.28 Å, respectively, the angle at the gold atom was 180°, and intramolecular steric effects of the phosphine ligands were neglected. In the diaurated molecule of diphenylmethane, the two *ortho*-positions of the Ph^1 benzene ring become non-equivalent, and therefore the angles φ_1, which are 0 or 180°, correspond to two different sterically favorable configurations: *syn* (*S*) and *anti* (*A*):



3a (L = PH$_3$)

The calculation showed that only the *S*-configuration makes it possible to draw the gold atoms to each other so that the intervals between them (2.8—3.3 Å)[2] correspond to aurophilic interaction within the bounds of the sterically possible values of the angle φ_2. The dependence of the Au...Au distance (*d*), in the fixed *S*-configuration of the model molecule **3a** (φ_1 = 0°), on the dihedral angle (φ_2) is given below:

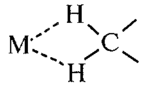
φ_2/deg	90	80	70	60	50
d/ Å	4.0	3.7	3.4	3.0	2.7

These distances can be even smaller, if it is assumed that there is a possibility of some distortion of collinearity of the P—Au—C fragment and deviation of the Au atom from the Ph^1 plane, which is characteristic for Au complexes.

Another situation takes place when the *A*-configuration is realized (in general, the latter is sterically more advantageous than the *S*-configuration, and it is the *A*-configuration that is observed in the investigated diaurated complex). Changing the φ_2 angle does not result in pulling the Au atoms together, and the shortest distance between these atoms (4.0 Å) is achieved only when φ_2 = 90°.

One cannot exclude the possible existence of other conformations in which the Au atoms approach one another due to the mutual rotation of both benzene rings (at some intermediate φ_1 and φ_2). However, it was not our intention to elucidate all of the possible conformations of **3a**, where the Au atoms are in proximity to one another. To achieve our purposes, we only needed to conclude that such conformations are in principle possible for the molecule **3a**.

Many works have been devoted to the study of the Au...Au interaction in complexes of Au^{I}.[2,5—7,12] In some of them,[2,7,13] the energy of such interaction is estimated to be 6—8 kcal mol^{-1}, which is a little higher than the value of the excess conformational energy for molecule **3a** in conformations with the shortest Au...Au distances. However, regardless of the conformational possibilities existing for the realization of aurophilic interaction in molecule **3a**, no interaction takes place in practice.

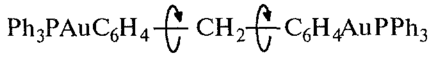
In molecule **2**, which we investigated earlier,[9] the absence of Au...Au interaction was due to the competitive formation of intramolecular secondary Au...O bonds. Apparently, the absence of Au...Au interaction in molecule **3** is also caused by the existence of competing interaction of some other kind. In fact, in the conformation of molecule **3** that was determined for the crystal, both Au atoms appear to be near the H atoms of the central methylene bridge. The Au(1) atom is 3.01 Å from the H(72) atom, and the distances between the Au(2) atom and the H(71) and H(72) atoms are 2.95 and 3.06 Å, respectively. Such distances are quite appropriate for weak agostic interactions.[2] The possible formation of an agostic bond involving the participation of two H atoms of the  kind has been studied earlier.[14] The existence of such agostic interaction in the studied molecule is confirmed by the NMR and IR spectral data and by the specific chemical behavior of compound **3**.

In the IR spectrum of complex **3**, the absorption bands for the CH bond valent vibrations are notably shifted (by ~100 cm^{-1}) downfield (ν(CH) 2820 and 2700 cm^{-1}) relative to those values in diphenylmethane and 2,2'-diiododiphenylmethane, which is characteristic of the agostic M...H—C interactions.[15]

The ^{31}P NMR spectrum of complex **3** contains one signal for two equivalent phosphorus atoms (δ = 43.68 ppm) in the temperature range +25 to −65 °C.

At room temperature, the ^{1}H NMR spectrum of **3** shows a complex multiplet for the aromatic protons within the 6.82—7.58 ppm interval and a sharp singlet for the methylene protons (at 4.65 ppm), and the ratio between the integral intensities agrees with the proposed formula. The signal of the CH$_2$-group is significantly shifted downfield relative to the signal of this group in diphenylmethane (4.00 ppm) and 2,2'-diiododiphenylmethane (4.19 ppm).

The study of the temperature dependence of the ^{1}H NMR spectrum of **3** (in CD$_2$Cl$_2$) showed that stereochemical flexibility of the molecule, due to the rotation of the gold-containing phenyl rings around the ordinal C—C bonds in solutions of



$Ph_3PAuC_6H_4-CH_2-C_6H_4AuPPh_3$ (**3**), leads, assuming fast exchange (at 25 to −4 °C), to the averaged pattern for the signals of the two equivalent protons of the CH$_2$-bridge to give one sharp signal. However, decreasing the temperature to −95 °C * leads to considerable slowing of the reversible exchange process and to

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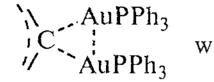
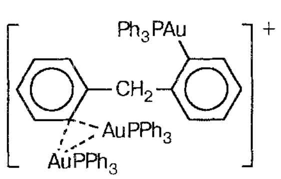
* Deeper cooling of the investigated sample in CD$_2$Cl$_2$ was impossible.

the appearance of magnetic non-equivalence of these protons. This is accompanied by a strong broadening of the signal of the CH_2-group and its shifting upfield (to 4.55 ppm).

The FAB MS spectrum of **3** exhibits a peak with $m/z = 1084$ corresponding to the molecular ion,as well as peaks for the products of its fragmentation. In addition, the MS spectrum of this compound shows a peak of high intensity with $m/z = 1543.9$ for the adduct of complex **3** with cation $AuPPh_3^+$. We believe that the appearance of this ion in the spectrum of **3** is due to the fact that cationic complex **4** is readily formed in the gas phase (as well as in condensed phase)*. This complex contains the structural fragment  with a bridging carbon atom, which is characteristic of cationic complexes of the arylgold series:[16]



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Complex **3** cannot be metallated (in benzene — THF media) either by *n*-butyllithium in the presence of *t*-BuOK, or by the *n*-BuLi·TMEDA complex (**3** is isolated from the reaction mixture in unchanged), although it is known that diphenylmethane is very easily lithiated at the methylene group by *n*-butyllithium in the presence of *t*-BuOK to give (in a high yield) an organolithium derivative $C_6H_5CH(Li)C_6H_5$, which was isolated after carboxylation as the corresponding carbonic acid.[17]

Thus, in the case of complex **3**, the agostic Au...H interactions stabilize molecule **3** to a greater extent than realization of the Au...Au interaction.

Experimental

The IR spectra were recorded on a UR-20 spectrophotometer (KBr). The ^{31}P NMR spectra (in CD_2Cl_2) were obtained on a Bruker CXP 200 instrument (81 MHz) with 85 % H_3PO_4 as the external standard; ^1H NMR spectra were recorded on a Bruker WP-200SY spectrometer (200, 13 MHz). Mass spectra were obtained on a Kratos Consept spectrometer using the energy of bombarding atoms (Cs) 8 keV and 3-nitrobenzyl alcohol as the matrix.

Synthesis of complex **3** was carried out in an atmosphere of dry argon in solvents that had been distilled prior to use over sodium benzophenone ketyl in an argon atmosphere.

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

Table 3. Coordinates for the atoms and isotropic equivalent temperature parameters (B_{iso}^{eq})

Atom	*x*	*y*	*z*	B_{iso}^{eq} */ Å^2
Au(1)	0.2096(1)	0.0840(0)	0.1439(0)	3.10(2)
Au(2)	0.1893(1)	0.2741(0)	0.4548(0)	3.06(2)
P(1)	0.0731(4)	−0.0573(2)	0.1658(2)	3.0(3)
P(2)	0.3419(3)	0.2686(2)	0.5768(2)	3.1(3)
C(1)	0.318(1)	0.2186(9)	0.1287(8)	2.5(8)
C(2)	0.373(1)	0.236(1)	0.0589(8)	3.3(9)
C(3)	0.448(1)	0.327(1)	0.0502(9)	4.6(9)
C(4)	0.463(2)	0.407(1)	0.109(1)	5.3(8)
C(5)	0.405(2)	0.391(1)	0.1801(9)	5.0(8)
C(6)	0.329(1)	0.297(1)	0.1884(8)	3.6(8)
C(7)	0.271(1)	0.288(1)	0.2709(8)	3.8(8)
C(8)	0.106(1)	0.2910(9)	0.2698(8)	2.8(7)
C(9)	0.019(1)	0.2997(9)	0.1954(8)	4.0(8)
C(10)	−0.124(2)	0.295(1)	0.1942(9)	4.4(9)
C(11)	−0.178(1)	0.284(1)	0.267(1)	4.5(9)
C(12)	−0.090(2)	0.2778(9)	0.3399(8)	3.8(9)
C(13)	0.054(1)	0.2819(9)	0.3412(8)	3.3(8)
C(111)	0.086(1)	−0.0847(9)	0.2748(7)	2.6(8)
C(112)	0.099(1)	0.001(1)	0.3293(8)	3.7(8)
C(113)	0.111(1)	−0.015(1)	0.4136(8)	4.1(9)
C(114)	0.109(1)	−0.117(1)	0.4408(8)	3.6(8)
C(115)	0.095(1)	−0.199(1)	0.3899(8)	3.2(8)
C(116)	0.086(1)	−0.1842(9)	0.3065(8)	3.3(8)
C(122)	−0.220(1)	−0.083(1)	0.1683(8)	4.4(9)
C(121)	−0.114(1)	−0.0304(9)	0.1313(7)	3.4(9)
C(123)	−0.362(2)	−0.051(1)	0.1459(9)	5.4(9)
C(124)	−0.397(1)	0.025(1)	0.0915(8)	4.6(9)
C(125)	−0.293(1)	0.073(1)	0.0547(9)	5.4(9)
C(126)	−0.152(1)	0.047(1)	0.0758(8)	4.7(9)
C(131)	0.109(1)	−0.1824(9)	0.1215(7)	3.0(8)
C(132)	0.243(1)	−0.223(1)	0.1411(8)	4.2(8)
C(133)	0.272(2)	−0.319(1)	0.1109(9)	5.0(8)
C(134)	0.174(2)	−0.375(1)	0.057(1)	6.0(9)
C(135)	0.043(2)	−0.338(1)	0.0358(9)	6.0(9)
C(136)	0.009(1)	−0.240(1)	0.0657(8)	4.0(9)
C(211)	0.383(1)	0.1344(9)	0.6077(8)	3.7(8)
C(212)	0.272(1)	0.0752(9)	0.6277(8)	3.7(8)
C(213)	0.294(1)	−0.027(1)	0.6479(8)	4.3(8)
C(214)	0.422(2)	−0.068(1)	0.653(1)	6.8(9)
C(215)	0.534(2)	−0.007(1)	0.633(1)	1.0(11)
C(216)	0.518(2)	0.094(1)	0.612(1)	8.2(9)
C(221)	0.276(1)	0.3308(8)	0.6647(8)	2.8(8)
C(222)	0.172(1)	0.4046(9)	0.6485(7)	3.1(8)
C(223)	0.116(2)	0.454(1)	0.710(1)	5.3(9)
C(224)	0.167(2)	0.428(1)	0.7958(9)	6.0(9)
C(225)	0.271(2)	0.355(1)	0.8082(8)	5.0(9)
C(226)	0.326(1)	0.306(1)	0.7442(9)	3.8(8)
C(231)	0.509(1)	0.3373(9)	0.5704(8)	3.2(8)
C(232)	0.596(1)	0.379(1)	0.6367(8)	4.4(8)
C(233)	0.718(1)	0.435(1)	0.631(1)	4.8(8)
C(234)	0.754(2)	0.445(1)	0.554(1)	6.0(9)
C(235)	0.675(2)	0.403(1)	0.486(1)	7.0(12)
C(236)	0.548(1)	0.348(1)	0.4939(9)	4.7(8)

* $B_{iso}^{eq} = (4/3) \sum_i \sum_j B_{ij} a_i a_j$.

Synthesis of 2,2'-bis(triphenylphosphinegold)diphenylmethane (3). A solution of 6 mL (17.10 mmol) of a 2.85 *N* hexane solution of *n*-BuLi in 15 ml of ether was added dropwise to a solution of 3.30 g (7.68 mmol) of 2,2'-diiododiphenylmethane[10] in 60 mL of ether at 0 °C with vigorous stirring. The obtained solution was stirred for 4 h at room temperature, and then it was added to a suspension of 2.63 g (5.31 mmol) of $ClAuPPh_3$ in 60 mL of THF in small portions over 2 h with stirring. When the halide gold complexes

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* Synthesis of complex **4** will be reported separately

($ClAuPPh_3$ and $IAuPPh_3$ generated in the course of the reaction) disappeared from the reaction mixture, the latter was decomposed with water. The organic layer was isolated, dried with annealed K_2CO_3, and concentrated to a volume of ~5 ml by evaporation. An excess of ether was added to the solution to precipitate 1.84 g (64 %) of **3**. M.p. is 186—187 °C (with decomposition) after reprecipitation by an ether—petrol ether mixture (1:1) from a benzene solution. Found (%): C, 54.26; H, 3.73; P, 5.81. $C_{49}H_{40}Au_2P_2$. Calculated (%): C, 54.25; H, 3.71; P, 5.71.

Compound **3** is a colorless crystalline substance, stable in the air (in a contrast to complex **2**),[9] and soluble in benzene and polar solvents.

X-ray diffraction analysis. Crystals of $(Ph_3PAuC_6H_4)_2CH_2$ **3** are triclinic, a = 9.579(3), b = 12.851(4), c = 16.425(4), α = 91.59(2), β = 98.75(2), γ = 90.82(2)°, V = 1997.3(7) Å^3, Z = 2, $C_{49}H_{40}Au_2P_2$ spatial group $P\bar{1}$, d_{calc} = 1.804 g cm^{-3}.

The parameters of an elementary cell and the intensities of 5292 reflections with $I > 2\sigma(I)$ were measured on an automatic four-circle κ-diffractometer ENRAF-NONIUS CAD4 (Mo-Kα-irradiation, graphite monochromator, ω/2θ-scanning, $2\theta_{max}$ = 54°). Absorption was empirically calculated using seven curves of azimuth scanning (μ(Mo-$K\alpha$) = 74.4 cm^{-1}).

The structure was deciphered by the heavy atom method and refined using the whole-matrix least squares method in anisotropic approximation for the non-hydrogen atoms. The positions of the H atoms were calculated geometrically and taken into account in the specification with the fixed values of the positional and isotropic temperature (B_{iso} = 6 E^2) parameters. The final values of the deviation factors were R = 0.0325, R_w = 0.0327. All calculations were performed on an IBM PC-AT using the SHELX programs. The coordinates of the atoms and their isotropic equivalent temperature parameters are given in Table 3.

The authors are grateful to P. V. Petrovskii and M. V. Galakhov for registration of the NMR spectra, and to D. V. Zagorevsky and K. V. Kazakov for the mass spectra.

This work was performed with partial financial support from the International Science Foundation (Project No.MDV 000).

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Received December 14, 1993