# Further Evidence for Attractive Interactions between Gold(I) Centers in Binuclear Complexes

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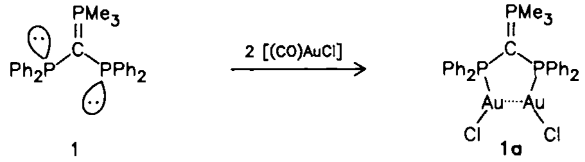
**Another example of the conformation-determining attractive interaction between gold(I) centers is presented, based on changes in the conformation of the butadiene skeleton. The *s-trans* ground state geometry of 2,3-bis(diphenylphosphino)-1,3-butadiene (2) is abandoned in the gold complex 3, and the two gold atoms are brought into contact at a distance of 3.023(1) Å. The conformational change of the ligand also occurs at a single metal atom, where the bisphosphine acts as a difunctional chelating ligand, as demonstrated in the rhodium complex 4.**

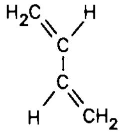
Structural[1,2] and spectroscopic studies[3,4] on mono- and polynuclear gold(I) compounds have provided indirect evidence of an attractive interaction between the gold atoms. This weak bonding appears to be operative perpendicular to the linear X–Au–L axes and leads either to a catenated or layered aggregation of the molecules by Au···Au contacts, which are ca. 3.0 Å in length, or to the intramolecular pairing of the gold atoms with similar equilibrium distances. It can be described as a $5d^{10}-5d^{10}$ interaction based on a mixing with the $6s^2$ states[5], whose energy difference is lowered by relativistic effects[6,7]. In the case of the neighbour element mercury these effects are less obvious and restricted to only a few examples[8]. However, recent work has shown that Au···Hg interactions can also be detected in complexes tailored after the Au···Au precedents[9].

In our search for further experimental evidence and for means to determine directly or indirectly the strength of this force quantitatively, initially doubly phosphino-substituted *ylides* 1 where chosen as model system. These compounds change their ground state *syn/anti* orientation to a symmetrical *syn/syn* conformation upon double complexation with AuCl[2c]. In the complex the two gold(I) centres are seperated by 3.000(1) Å. From temperature-dependent NMR studies the energy of the Au···Au interaction can be estimated to be in the order of 7–8 kcal/mol.

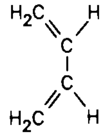


We report in this paper another example of the conformation-determining attractive interaction between gold(I) centers, based on changes in the conformation of the *butadiene* skeleton. The ground state geometry of butadiene is determined by the conjugation of the two π systems, and only two conformers represent energy minima in the energy profile of C2–C3 rotation.

At room temperature the *s-trans* form is clearly favoured over the *s-cis* form (*s-cis/s-trans* ratio 1:99[10]). As a consequence of the preferred *s-trans* conformation butadiene shows low reactivity in Diels-Alder [4 + 2] cycloadditions, which require the *s-cis* arrangement. According to electron diffraction[11], microwave[12], NMR[13], UV[14], infrared and Raman[15] data, and the results of force-field and ab initio calculations[16] the *s-trans* form of the unsubstituted butadiene is about 3 kcal/mol more stable than the *s-cis* isomer, and rotation requires an activation energy of 6–8 kcal/mol. The *s-cis* conformation shows a *gauche* arrangement with a torsion angle of 23° as the ground state.



*s-trans*-butadiene

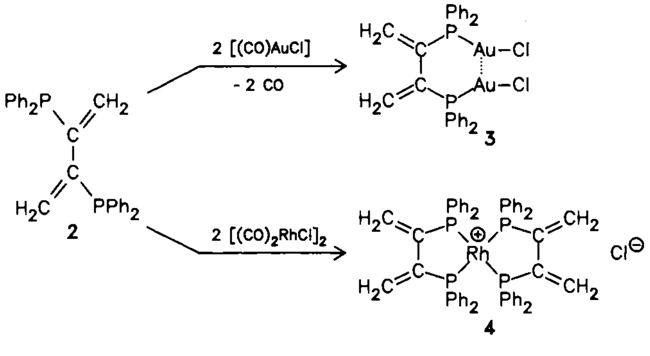


*s-cis*-butadiene

Experimental observations indicate that the *s-cis/s-trans* ratio can be affected by bulky ligands: Single substitution at C-2 thus favours the (nonplanar) *s-cis* isomer, whereas a 2,3-dibsubstitution induces the (planar) *s-trans* form even more strongly. An example is 2,3-bis[bis(dimethylamino)phosphinyl]-1,3-butadiene, which shows an almost perfectly planar *s-trans*-butadiene skeleton[17].

A similar situation is also encountered in the case of 2,3-bis(diphenylphosphino)-1,3-butadiene (2), which is readily accessible[18]. Due to its *s-trans* conformation 2 shows no affinity for a Diels-Alder [4 + 2] cycloaddition.

Reaction of 2 with two equivalents of [(CO)AuCl] affords – with CO evolution – the 2:1 complex 3 in high yields, whose composition is confirmed by spectroscopic and analytical data.



In order to determine the solid-state configuration of the butadiene skeleton, an X-ray analysis of the complex was performed (see Experimental). This study showed that the *s-trans* conformation of 2 is abandoned during formation of the complex 3. The product adopts a *gauche* conformation with torsion angles P1–C1–C2–

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*) X-ray crystal structure analysis.

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P2 and C11–C1–C2–C21 of 99.9 and 106.2°, respectively, as expected for the distortion in a crowded *s-cis* structure. The gold(I) atoms are brought into contact at a distance of 3.023(1) Å. With this Au···Au interaction taken into account, the structure corresponds to a six-membered ring in a twist configuration. The overall molecular symmetry is approximately $C_2$ (Figure 1). The two chlorine atoms are located on different sides of the ring, thus reducing steric interactions. Consequently, the linearity of the P–Au–Cl axes is almost unaffected, as compared to the marked deformation of these angles in complex **1a**, where the Au–Cl axes are almost parallel, placing the Cl atoms close to each other[2c].

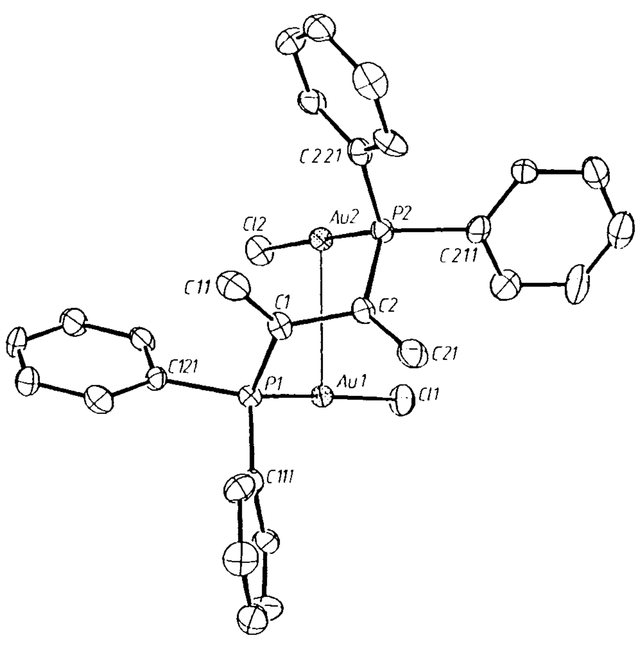

Figure 1. Perspective view of the molecular structure of **3** as seen approximately down the noncrystallographic twofold axis (ORTEP, displacement ellipsoids at the 50% probability level; H atoms omitted for clarity)

If it is assumed that the *s-trans* → *s-cis* reorientation is caused by Au···Au attraction, the bond energy can again be estimated from the above mentioned energy values. The difference of the energies of the two conformers in the order of 7 kcal/mol is in satisfactory agreement with the value derived for compound **1a**.

Much less surprisingly, C–C rotation of the 2,3-bisphosphino-substituted butadiene skeleton also occurs at a metal center, where the bisphosphine can act as a difunctional chelating ligand, as observed in the reaction of **2** with $[(CO)_2RhCl]_2$ with formation of **4**.

Compound **4** is isolated as a yellow microcrystalline solid and is easily identified by standard analytical and spectroscopic techniques. The *s-cis* conformation of **4** is also demonstrated in the affinity of the complex for ethyl vinyl ether in a [4 + 2] cycloaddition[24], which does not occur with the free ligand.

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## Experimental

*μ-[2,3-Bis(diphenylphosphino)-1,3-butadiene-P,P′]-dichlorodigold(I)(Au–Au)* (**3**): A suspension of 0.85 g of [(CO)AuCl] (3.26 mmol) in toluene (15 ml) was treated with a solution of 0.69 g of **2**[18] (1.63 mmol) in toluene (10 ml). Evolution of CO was observed. After stirring for 16 h at room temp. the mixture was filtered and the white precipitate washed several times with pentane, dried under reduced pressure, and recrystallized from chloroform: Yield 1.36 g (88%), m. p. 260°C (decomp.). – $^1$H NMR ($CDCl_3$, 20°C): $\delta$ = 5.3 (d, AA′BB′XX′, $N$ = 15 Hz, 2H, *cis*-CH); 6.0 (d, AA′BB′XX′, $N$ = 30 Hz, 2H, *trans*-CH); 7.4–8.0 (m, 20H, Ph). – $^{31}$P NMR ($CDCl_3$, 20°C): $\delta$ = 33.58 (s). – $^{13}$C NMR ($CDCl_3/F_3CCO_2H$, 20°C): $\delta$ = 125.4 (centered dd, AXX′, $N$ = 69.5 Hz, C-1); 129.6 (t, AXX′, $N$ = 11.7 Hz, C-2); 132.9 (s, C-4); 134.7 (t, AXX′, $N$ = 14.7 Hz, C-3); 140.0 (centered dd, AXX′, $N$ = 63.5 Hz, CP); $CH_2$: obscured by C-3.

| | | | |
|---|---|---|---|
| $C_{28}H_{24}Au_2Cl_2P_2$ (887.3) | Calcd. | C 37.90 | H 2.73 |
| | Found | C 38.43 | H 2.87 |

*Bis[2,3-bis(diphenylphosphino)-1,3-butadiene-P,P′]rhodium Chloride* (**4**): A solution of 0.11 g of $[(CO)_2RhCl]_2$ (0.283 mmol) in benzene (10 ml) was treated with a solution of 0.50 g of **2** (1.18 mmol) in the same solvent (15 ml). The reaction mixture was stirred for ca. 12 h. The yellow precipitate was filtered, washed with benzene and dried under reduced pressure. Yield 0.50 g (90%), m. p. 250°C (decomp.). – $^1$H NMR ($CDCl_3$, 20°C): $\delta$ = 5.17 (t, $N$ = 12 Hz, 2C, *cis*-CH); 6.07 (centered dd, $N$ = 26.6 Hz, 2H, *trans*-CH); 6.9–7.6 (m, 20H, Ph). – $^{31}$P NMR ($CDCl_3$, 20°C): $\delta$ = 44.2 [d, $^1J$(Rh–P) = 131.2 Hz]. – $^{13}$C NMR ($CDCl_3$, 20°C): $\delta$ = 125.5 (broad s, $CH_2$); 128.1 (broad s, C-2); 128.8 ("quint", $N$ = 46.86 Hz, C-1); 130.7 (s, C-4); 133.3 ("quint", $N$ = 13.7 Hz, C-3); 145.2 ("quint", $N$ = 84 Hz, CP); $^1$H coupled: $^1J$(CH) = 160.1 Hz ($CH_2$).

| | | | | |
|---|---|---|---|---|
| $C_{56}H_{48}ClP_4Rh$ (983.3) | Calcd. | C 68.41 | H 4.97 | Cl 3.61 |
| | Found | C 66.85 | H 4.96 | Cl 4.11 |

*X-Ray Structure Analysis of* **3**: Syntex $P2_1$ diffractometer, Mo-$K_\alpha$ radiation, $\lambda$ = 0.71069 Å, graphite monochromator, $T$ = –50°C. Crystal data: $C_{28}H_{24}Au_2Cl_2P_2$, $M_r$ = 887.29, monoclinic, space group $P2_1$ (No. 4), $a$ = 9.099(1), $b$ = 11.509(1), $c$ = 12.920(2) Å, $\beta$ = 99.13(1)°, $V$ = 1335.8 Å, $d_{calcd.}$ = 2.206 g/cm$^3$ for $Z$ = 2, $\mu$(Mo-$K_\alpha$) = 112.7 cm$^{-1}$, $F(000)$ = 828. The integrated intensities of 5596 reflexions were measured up to $(\sin \Theta/\lambda)_{max}$ = 0.617 Å$^{-1}$ (*hkl*: +11, ±14, ±15; ω scan, $\Delta\omega$ = 0.8°). Lp and empirical absorption corrections (rel. transmission: 0.64–1.00) were applied to the data. After merging of equivalent data ($R_{int}$ = 0.026) 5230 independent structure factors remained, 5081 of which with $F_o \geq 4.0\ \sigma(F_o)$ were deemed "observed" and used for all further calculations. $P2_1$ was assumed as space group and confirmed by the successful refinement of the structure. The centrosymmetric alternative $P2_1/m$ can be excluded, because the molecule does not contain an inversion center or a plane of symmetry as required by $P2_1/m$ for $Z$ = 2. Reduced cell calculations did not indicate any higher symmetry (DELOS[19], LEPAGE[20]). The structure was solved by automated Patterson methods (SHELXS-86[21]). 14H atoms out of a total of 24 could be located in difference syntheses, the remainder was calculated at idealized geometrical positions. Full-matrix least-squares refinement of 306 parameters converged at $R$ ($R_w$) = 0.025 (0.032), $w = 1/\sigma^2(F_o)$ (function minimized: $\Sigma w(|F_o| - |F_c|)^2$; SHELX-76[22]). All non-H atoms were refined anisotropically, the H atoms were included as fixed atom contributions in the structure factor calculations ($U_{iso}$ = 0.05 Å$^2$). Refinement of the inverse data set yielded $R$ ($R_w$) = 0.053 (0.067). The residual electron densitiy showed no anomalies [$\Delta\varrho_{fin}$ (max/min) = 1.08/–2.02 $e$/Å$^3$]. Table 1 contains the atomic coordinates, Table 2 selected distances and angles. Figure 1 shows the molecular structure. Complete tables of atomic parameters and observed and calculated structure factor amplitudes have been deposited[23].

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **3** [$U_{eq} = (U_1U_2U_3)^{1/3}$, where $U_i$ are the eigenvalues of the $U_{ij}$ matrix]

| ATOM | X/A | Y/B | Z/C | U(eq.) |
|---|---|---|---|---|
| AU1 | 0.21000(3) | 0.00000 | 0.85067(2) | 0.018 |
| AU2 | 0.04654(3) | 0.12100(3) | 0.65864(2) | 0.019 |
| CL1 | 0.3359(3) | -0.1207(2) | 0.7536(2) | 0.030 |
| CL2 | -0.1031(3) | -0.0407(2) | 0.6319(2) | 0.028 |
| P1 | 0.1160(2) | 0.1302(2) | 0.9515(1) | 0.018 |
| P2 | 0.1901(2) | 0.2785(2) | 0.6921(2) | 0.019 |
| C1 | 0.1243(9) | 0.2757(6) | 0.8949(6) | 0.019 |
| C11 | 0.023(1) | 0.3558(7) | 0.9002(7) | 0.029 |
| C2 | 0.2541(9) | 0.2923(6) | 0.8334(6) | 0.018 |
| C21 | 0.392(1) | 0.3107(8) | 0.8796(7) | 0.030 |
| C111 | 0.2256(8) | 0.1383(7) | 1.0831(6) | 0.021 |
| C112 | 0.295(1) | 0.0358(8) | 1.1251(7) | 0.025 |
| C113 | 0.370(1) | 0.0367(8) | 1.2263(7) | 0.033 |
| C114 | 0.384(1) | 0.1380(9) | 1.2837(6) | 0.031 |
| C115 | 0.319(1) | 0.2413(8) | 1.2428(7) | 0.031 |
| C116 | 0.237(1) | 0.2397(9) | 1.1417(7) | 0.029 |
| C121 | -0.0773(8) | 0.1112(7) | 0.9685(6) | 0.020 |
| C122 | -0.172(1) | 0.0525(8) | 0.8896(6) | 0.025 |
| C123 | -0.321(1) | 0.0401(9) | 0.8969(7) | 0.031 |
| C124 | -0.3782(9) | 0.0886(8) | 0.9822(8) | 0.027 |
| C125 | -0.284(1) | 0.1483(8) | 1.0603(7) | 0.029 |
| C126 | -0.133(1) | 0.1609(8) | 1.0541(6) | 0.026 |
| C211 | 0.3565(9) | 0.2735(7) | 0.6318(6) | 0.022 |
| C212 | 0.449(1) | 0.1778(8) | 0.6534(7) | 0.031 |
| C213 | 0.575(1) | 0.1652(9) | 0.6030(9) | 0.034 |
| C214 | 0.606(1) | 0.245(1) | 0.5335(7) | 0.037 |
| C215 | 0.513(1) | 0.339(1) | 0.5091(7) | 0.033 |
| C216 | 0.389(1) | 0.3556(7) | 0.5583(6) | 0.026 |
| C221 | 0.097(1) | 0.4157(8) | 0.6564(6) | 0.024 |
| C222 | 0.170(1) | 0.5219(7) | 0.6856(7) | 0.026 |
| C223 | 0.096(1) | 0.620(1) | 0.6594(7) | 0.034 |
| C224 | -0.051(1) | 0.6252(9) | 0.6048(7) | 0.030 |
| C225 | -0.121(1) | 0.5195(9) | 0.5783(7) | 0.033 |
| C226 | -0.046(1) | 0.4148(7) | 0.6039(7) | 0.025 |

Table 2. Selected distances [Å] and angles [°] for **3** (estimated standard deviations in units of the last significant figure are given in parentheses)

| | | | |
|---|---|---|---|
| P1-C1 | 1.834(8) | P1-C1-C2 | 113.8(5) |
| P2-C2 | 1.833(8) | P1-C1-C11 | 123.1(6) |
| | | P2-C2-C1 | 110.8(5) |
| C11-C1 | 1.31(1) | P2-C2-C21 | 126.5(7) |
| C1-C2 | 1.54(1) | C11-C1-C2 | 123.0(7) |
| C21-C2 | 1.32(1) | C21-C2-C1 | 122.7(7) |
| P1-Au1 | 2.242(2) | Au2-P2-C2 | 110.3(2) |
| P2-Au2 | 2.236(2) | Au1-P1-C1 | 109.6(2) |
| Au1-Au2 | 3.023(1) | P2-Au2-Cl2 | 177.4(1) |
| | | P1-Au1-Cl1 | 172.4(1) |
| Au1-Cl1 | 2.295(2) | P1-C1-C2-P2 | 99.9 |
| Au2-Cl2 | 2.299(2) | C11-C1-C2-C21 | 106.2 |

## CAS Registry Numbers

**2**: 116011-74-6 / **3**: 119620-41-6 / **4**: 119638-25-4 / [(CO)AuCl]: 50960-82-2 / [$(CO)_2RhCl]_2$: 14523-22-9 / ethyl vinyl ether: 109-92-2

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