

# 1,1'-Bis(diphenylphosphino)bicyclopropyl: Synthesis, Properties, Precursors, Derivatives, and Metal Complexes

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The title compound **4** has been prepared from readily available 2,3-bis(diphenylphosphinyl)-1,3-butadiene (**1**) through double cyclopropanation using  $\text{Me}_2\text{S}(\text{CH}_2)\text{O}$  to give 1,1'-bis(diphenylphosphinyl)bicyclopropyl (**2**), followed by reduction using  $\text{HSiCl}_3/\text{NEt}_3$ . Addition of sulfur to compound **4** yields the disulfide **5**, and reaction with tetrahydrofuran – borane affords the 1:2 adduct with  $\text{BH}_3$  (**6**). Quaternization reactions with  $\text{MeI}$  or  $\text{CH}_2\text{I}_2$  give the double quaternary salts **7** and **8**, respectively. Single dehydrohalogenation employing  $n\text{BuLi}$  converts **8** into the cyclic semiylide salt **9**. **4** is an excellent ligand for low-valent late transition-metal cations. With  $\text{PdI}_2$  the 1:1 complex  $\text{LPdI}_2$  (**10**, with  $\text{L} = \mathbf{4}$ ), and with  $[(\text{CO})_2\text{RhCl}]_2$  the ionic 2:1 complex  $\text{L}_2\text{Rh}^+\text{Cl}^-$  (**11**) are obtained. Experiments with  $(\text{CO})\text{AuCl}$  yield the 1:2 complex  $\text{L}(\text{AuCl})_2$  (**12**). X-ray structure

analyses were performed with single crystals of the disulfide **5**, as well as the rhodium(I) and gold(I) complexes **11** and **12**. **5** has a conformation between *s-cis* and *s-trans* with the PS functions pointing away from each other at opposite ends of the molecule. By contrast, in the gold(I) complex the ligand approaches an *s-cis* conformation, and through rotations about P–C and C–C bonds – as referred to the conformation of **5** – the metal atoms are brought into close contact:  $\text{Au}\cdots\text{Au} = 3.085 \text{ \AA}$ . Through temperature-dependent NMR investigations of compounds **5** and **12**, and by comparison with values calculated or experimentally determined for related bicyclopropyl compounds (available in the literature), the energy of the  $\text{Au}\cdots\text{Au}$  attraction has been estimated to be ca. 6 kcal/mol. Compound **11** features a square-planar, double-chelate cation.

Ditertiary phosphines are an important class of compounds for a number of reasons: 1) As ligands, they are extremely powerful chelating systems for low-valent metals<sup>1,2</sup>. Through steric or electronic substituent effects, their geometry can be tailored such that access to a reactive center is only possible from certain directions or that one substrate molecule is favoured over the other. Through this strategy, stereo- and regioselectivity in reactions with a variety of compounds, stoichiometrically or catalytically, has been accomplished<sup>3</sup>. In other cases, a special selection of substituents and their anchoring at support materials can be used for inducing either solubility in specific solvents or complete insolubility. – 2) Ditertiary phosphines are precursors for the corresponding open-chain or cyclic phosphonium salts, phosphine – boranes, oxides, sulfides etc., which can be transformed further, e.g. into phosphonium ylides, carbodiphosphoranes, and related compounds<sup>4,5</sup>.  $\alpha,\omega$ -Ditertiary phosphines like bis(diphenylphosphino)methane (“dppm”) or -ethane (“dppe”, “diphos”) based on an *alkane* skeleton are particularly prominent examples, which have also been used extensively in this laboratory, e.g. as ligands to gold and other coinage metals<sup>6–8</sup>.

In contrast, the chemistry of poly(phosphino)-functional alkenes and alkynes is less well developed, and even simple representatives have appeared only recently. Owing to the rigidity of their *alkene/alkyne* skeleton, these ligands have special features and were quickly recognized as very valuable alternatives.

Consequently, the chemistry of species like 1,1-bis(diphenylphosphino)ethene or 2,3-bis(diphenylphosphino)butadiene is presently attracting considerable attention<sup>9–13</sup>. Due to the well known similarities in chemical reactivity and structural rigidity of *alkene* and *cyclopropane* functions, the chemistry of *phosphinocyclopropanes* has likewise become the subject of current studies. We report here

our results on the title compound, which are an extension of our previous findings on phosphonium cyclopropylides<sup>14</sup> and 1,1-bis-(diphenylphosphino)cyclopropane<sup>15,16</sup>, as well as on 2,3-bis-(diphenylphosphino)-1,3-butadiene<sup>12,17</sup>.

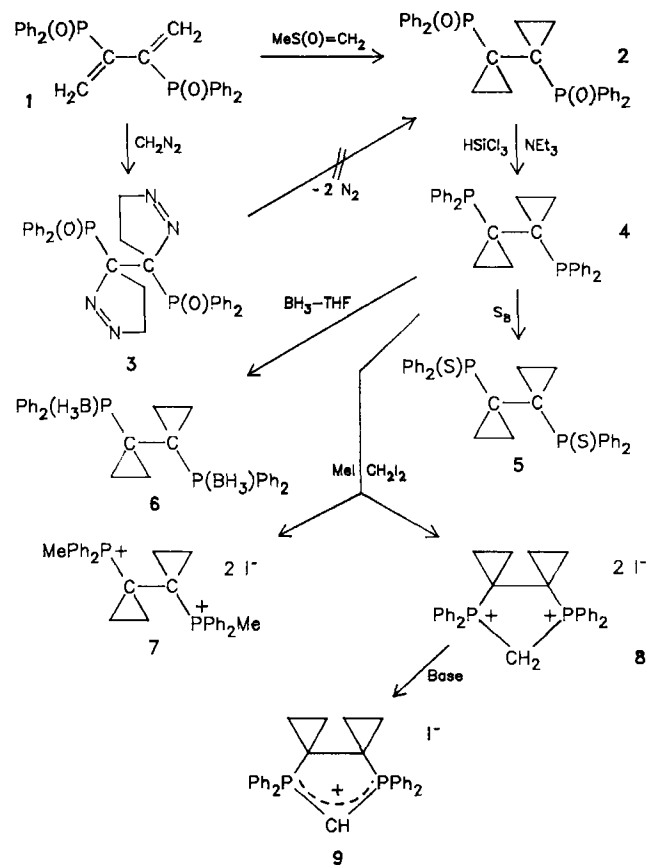
## Synthesis of 1,1'-Bis(diphenylphosphino)bicyclopropyl

A careful reinvestigation of the reaction between 2-butyne-1,4-diol and chlorodiphenylphosphine<sup>13</sup> has made 2,3-bis(diphenylphosphinyl)-1,3-butadiene (**1**) a readily available starting material. Treatment of this compound with dimethylsulfoxonium methylide in dimethyl sulfoxide led to double cyclopropanation affording 1,1'-bis(diphenylphosphinyl)bicyclopropyl (**2**) in moderate yield (ca. 40%). Attempted cyclopropanation through double [2 + 3]-cycloaddition of diazomethane (followed by nitrogen elimination: **3** → **2**) failed owing to difficulties in the second step. While **3** could be isolated in pure form (ca. 40% yield), its decomposition was difficult to control and gave only a multicomponent mixture of products.

Reduction of compound **2** was accomplished by treatment with trichlorosilane in the presence of triethylamine in toluene. After hydrolytic workup, the title compound **4** could be isolated in ca. 45% yield (Scheme 1).

Characterization of compounds **2**, **3**, and **4** by analytical and spectroscopic techniques was straightforward (see Experimental). According to the NMR data, compounds **2** and **4** in solution have (at least time-averaged) mirror symmetry

Scheme 1



rendering the phenyl and methylene groups equivalent. Compound 3, for which owing to its two chiral centers diastereomers could be expected, was isolated as only one isomer according to the  $^{31}\text{P}$ -NMR singlet and the corresponding set of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR signals. No attempt has been made to identify this isomer.

#### Derivatives of 1,1'-Bis(diphenylphosphino)bicyclopropyl (4)

Addition of elemental sulfur to solutions of 4 in tetrahydrofuran at room temperature leads to the formation of the disulfide 5, the thio analogue of the oxide 2. This compound is easily obtained as large single crystals, the structure of which could be determined by X-ray diffraction (below). As expected, the NMR and IR data show close parallels with those of the oxide 2. The  $^1\text{H}$ -NMR spectrum is independent of temperature in the range from  $-90$  to  $+50^\circ\text{C}$ . The spectra are in agreement with either free internal rotations about all bonds, or with a fixed symmetrical conformation (all Ph and all  $\text{CH}_2$  groups equivalent).

A bis(borane) adduct 6 is obtained on treatment of 4 with two equivalents of the tetrahydrofuran–borane adduct. The analytical data are consistent with a symmetrical addition, i.e. of one  $\text{BH}_3$  group at each phosphorus atom. Ionic forms based on the introduction of the moieties  $\text{BH}_2^+$  and  $\text{BH}_4^-$  can be excluded.

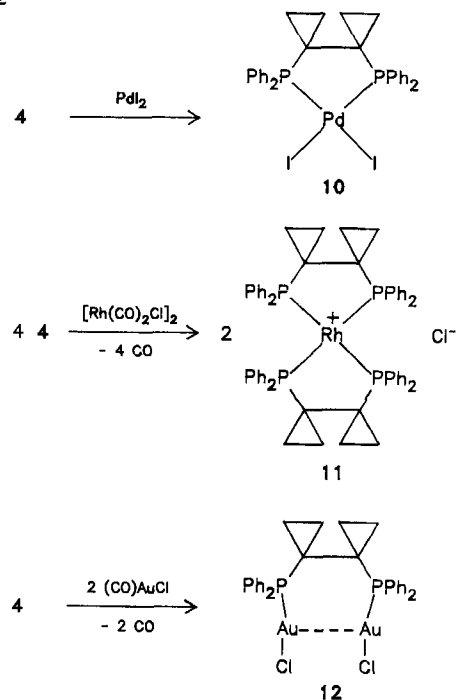
Excess iodomethane converts compound 4 into the bis-(phosphonium) salt 7. The cation of this diiodide is isoelectronic with the bis(phosphine–borane) 6. Diiodomethane

affords the cyclic bis(phosphonium) salt 8, containing a five-membered ring with the onium centers in 1,3-position. As observed previously for analogous cyclic phosphonium salts<sup>18</sup>, the  $\text{CH}_2$  bridge between the P atoms is readily deprotonated on reaction with one equivalent of *n*-butyllithium in pentane to give the semiylide salt 9. The  $^{13}\text{C}$ -NMR signals of the new semiylide function show the characteristic large triplet splitting [ $J(\text{PC}) = 113.8 \text{ Hz}$ ]<sup>18</sup>. No attempts have been made to generate a highly strained cyclic carbodiphosphorane<sup>19</sup>.

#### Metal Complexes of 1,1'-Bis(diphenylphosphino)-bicyclopropyl (4)

Compound 4 is a strong bidentate ligand for low-valent second- and third-row transition metals. A typical example is furnished in the reaction with palladium diiodide in dichloromethane, which produces an almost quantitative yield of the extremely stable neutral 1:1 complex 10 (m.p.  $345^\circ\text{C}$ ).

Scheme 2



The ionic 2:1 rhodium(I) complex 11 is formed on reaction with the chloro(dicarbonyl)rhodium(I) dimer in benzene solution. After the evolution of carbon monoxide gas has ceased, high yields of a yellow product can be isolated, which is forming single crystals containing disordered solvent molecules upon slow crystallization from dimethyl sulfoxide. The crystal structure has been determined by X-ray diffraction, and the complex cation of the salt has been observed in the field-desorption mass spectrum (below).

Finally, the crystalline 1:2 complex 12 is formed in high yield in the reaction of the ligand 4 with two equivalents of carbonyl(chloro)gold(I) in tetrahydrofuran. The molecular structure of this dinuclear species could be determined by X-ray diffraction analysis. A complete set of analytical and

## 1,1'-Bis(diphenylphosphino)bicyclopropyl

spectroscopic data is also available (see below and Experimental).

In the present context it is an important finding that the NMR spectra of complex **12** show a temperature dependence in solution. While at ambient temperature the spectra suggest equivalent CH<sub>2</sub> and Ph groups, at low temperature two sets of signals are observed for these moieties. This indicates a fixed *gauche* conformation of C<sub>2</sub> symmetry in solution at low temperature (in agreement with the crystal structure, below), but at least a free oscillating motion about the central C—C bond at higher temperatures rendering the CH<sub>2</sub> and Ph groups equivalent on the NMR time scale by conformation averaging to give pseudo C<sub>s</sub> symmetry. It must remain an open question at this stage if the intramolecular Au...Au contact detected in the crystal is lost in the rotation about the central C—C bond, since a simple *gauche/gauche* conformational change through a 120° C—C rotation is fully sufficient to account for the spectroscopic data. From the coalescence temperatures of the CH<sub>2</sub> and Ph signals free activation energies of the equilibration process can be calculated. The values obtained are 13.1 and 12.7 kcal/mol, respectively. This energy, averaged at 12.9 kcal/mol, can either be taken as the barrier for the C—C bond "oscillation" (*gauche/gauche*), or as the barrier to full rotation about this bond (*gauche-trans-gauche*) including the rupture of the Au...Au linkage (see Discussion and Conclusions).

### The Structure and Conformation of the 1,1'-Bis(diphenylphosphino)bicyclopropyl Ligand and Its Complexes

We have become particularly interested in the structural and conformational details of the ligand **4**, since a more profound knowledge of these could allow yet another approach to the question of weak intramolecular forces between third-row transition-metal centers with a closed-shell electronic configuration in their complexes<sup>20</sup>. For this purpose it was considered more appropriate to determine the structure of the disulfide **5**, rather than that of the "free" ligand, where the phosphorus atoms are uncoordinated. With the sulfur atoms in positions otherwise occupied by metal atoms, the geometry at the phosphorus atoms should be similar to that in the complexes, and no specific conformational changes are to be expected from attractive or repulsive S...S contacts.

Moreover, there appears to be a general interest in the structure of bicyclopropyl compounds, since the few investigations on such systems reported to-date do not yet provide a consistent picture of the relative stabilities of the various possible conformations<sup>21–23</sup>.

### 1,1'-Bis(diphenylthiophosphinyl)bicyclopropyl (**5**)

The structure of compound **5** is shown in Figure 1. The molecule has no crystallographic symmetry, but a structural relation to a configuration with point group C<sub>i</sub> can nevertheless be recognized. The projection chosen for Figure 1 shows, that the two cyclopropyl rings are not in a standard conformation (*s-trans*, *s-cis*, or *gauche*). Most importantly,

it is also obvious, that the two phosphorus—sulfur vectors are pointing away from each other on different sides of the molecular skeleton. Since the P—S vectors in **4**, clearly with this conformation neither could the ligand **4** chelate one metal atom nor could two metals in a dinuclear complex (one at each phosphorus atom) be in close contact. Extensive rotation about the P—C bonds (P1—C13 and P2—C23) and about the central C—C bond (C13—C23) would be necessary to allow these types of coordination interaction.

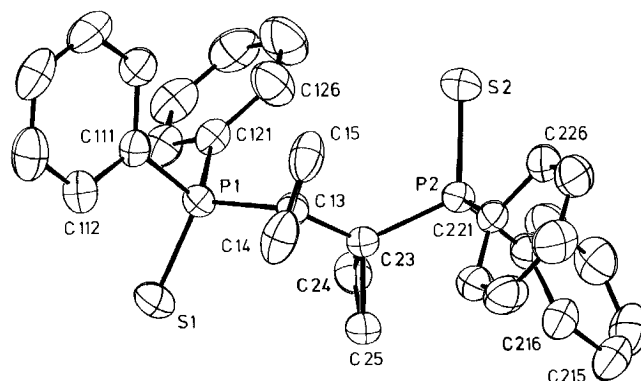


Figure 1. Molecular structure of compound **5** (ORTEP, 50% probability ellipsoids, with atomic numbering; H atoms omitted for clarity)

The bond lengths and angles of molecule **5** are normal and comparable to those reported by Dunitz et al.<sup>23</sup> for other bicyclopropyl compounds. The torsion angle P1—C13—C23—P2 of 139.39° indicates an intermediate conformation between *s-trans* and *s-cis* (*gauche*), probably determined by the steric bulk of the two Ph<sub>2</sub>PS groups. This is in contrast to the geometry encountered with 1,1'-dinitrobicyclopropyl, where the planes of the NO<sub>2</sub> substituents are bisecting the cyclopropyl rings<sup>23</sup>, probably for electronic reasons as suggested by the orientation of the Walsh orbitals of the strained ring systems.

### 1,1'-Bis[chloroaurio(I)diphenylphosphino]bicyclopropyl (**12**)

Complex **12** crystallizes from chloroform with two solvent molecules in the unit cell. Again, the molecule has no crystallographic symmetry, but the molecular geometry is close to point group C<sub>2</sub> (Figure 3). With the torsion angle P1—C13—C23—P2 at only 94.93°, the ligand conformation in **12** is approaching the *gauche* orientation, and through this change, together with rotations about the P1—C13 and P2—C23 bonds (as compared to **5**), the gold atoms have been brought into close proximity. The resulting Au...Au contact of 3.085(1) Å is reminiscent of the many other cases in the structural chemistry of gold, where it is becoming obvious that an attractive force is operative between the d<sup>10</sup> metal centers.

The remainder geometry of the ligand and the almost linear P—Au—Cl axes (which form an angle of 56.18°) are by no means exceptional. It thus appears that replacement

of the sulfur atoms in **5** by the AuCl groups (to give **12**) induces major conformational changes. Since the steric requirements of the two "substituents" (S, AuCl) are comparable, and since polarities should not be grossly different (associated with similar packing forces), the reason for the changes must be attributed to Au...Au attraction. This is even more compelling since the sub-van-der-Waals Au...Au contact of ca. 3.00 Å is in excellent agreement with findings for related systems<sup>7–9,17</sup>.

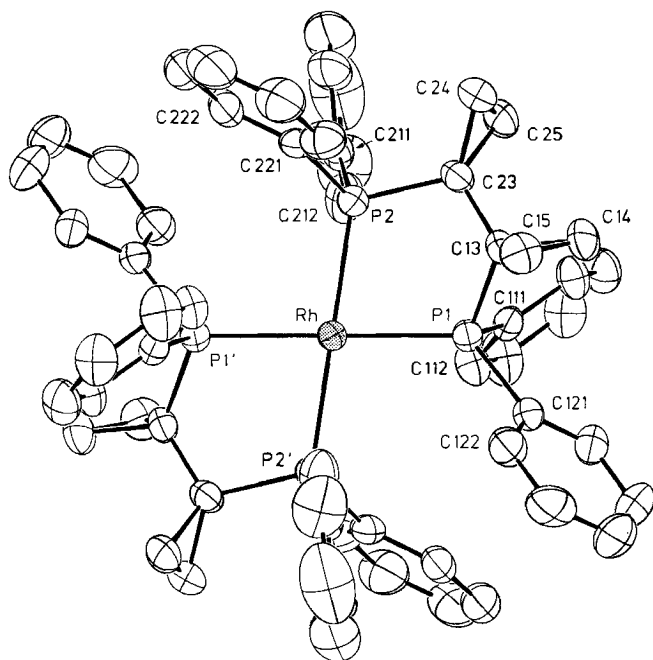


Figure 2. Molecular structure of the cation A in complex **11** (ORTEP, 50% probability ellipsoids, with atomic numbering; H atoms omitted for clarity). The structure of cation B is very similar. Both cations have a crystallographic center of inversion, occupied by a rhodium atom

It is tempting to try to complement this qualitative confirmation of previous evidence by an estimate of the energy gain associated with the Au...Au contact. Theoretical studies<sup>21,22</sup> and NMR investigations<sup>23</sup> suggest activation barriers for the C–C bond rotation in bicyclopopyl and its derivatives to be not in excess of 3.5 kcal/mol. These estimates are of course subject to major corrections for steric and electronic effects of substituents and of the environment (solvent, gas phase). As judged from the known effects of methyl crowding, another 2–3 kcal/mol may be a realistic estimate for the 1,1'-bis(diphenylphosphino) substituents. These effects should be similar for **5** and **12** (above), and it is therefore justified to assume that the Au...Au attraction is stronger than the sum of ca. 6 kcal/mol from the two contributions mentioned above.

It is gratifying that this result is in good agreement with those arrived at for other systems<sup>17,20</sup>. The ligand **4** thus proved to be a very useful system for the elucidation of parameters which are difficult to obtain otherwise. The given energetics of its internal motions are ideal for a determination of weak attractive forces between metal atoms.

### Bis[1,1'-bis(diphenylphosphino)bicyclopopyl]rhodium(I) Chloride (**11**)

Crystals of this compound, grown in dimethyl sulfoxide, contain two crystallographically independent molecules (complex cations and chloride anions) and two molecules of solvent in the unit cell with the rhodium atoms positioned on inversion centers. The two independent cations differ only slightly, mainly due to variations in the orientation of the phenyl groups (Figure 3). To a first approximation, the rhodium coordination sphere can be described as square planar as expected for a metal with a  $d^8$  low-spin electronic configuration in a strong ligand field. The ligands are fixed in a staggered conformation (torsion angle P–C–C–P is 37.7°). This configuration reduces steric interference of cyclopropyl and phenyl moieties. The five-membered rings adopt envelope configurations<sup>24</sup>.

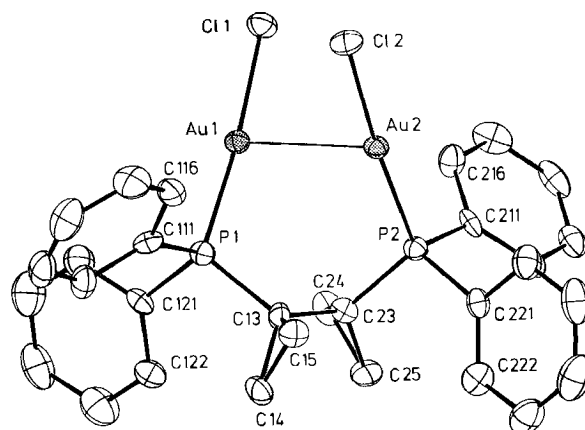


Figure 3. Molecular structure of complex **12** (ORTEP, 50% probability ellipsoids, with atomic numbering; H atoms omitted for clarity)

### Discussion and Conclusions

The present studies have shown, that 1,1'-diphosphino-bicyclopopyls are readily available from convenient starting materials. They form numerous derivatives, including metal complexes where the metal atoms are either chelated or ligand-bridged. As judged from the crystal structure of the disulfide, the free ligand's ground state conformation is close to the *trans* orientation of the cyclopropyl rings, similar to those observed previously for the parent hydrocarbon and its simple derivatives.

In the dinuclear complex with two AuCl equivalents a conformation close to the *cis* (*gauche*) form is encountered in the crystal, probably owing to a weak Au...Au attraction.

According to low-temperature NMR spectra, this structure is also present in solution, but at ambient temperature the complex becomes flexible, and equilibration leads to a loss of the diastereotopic nature of the diagnostic groups in the ligand (CH<sub>2</sub>, Ph<sub>2</sub>). The activation barrier determined for this structural relaxation is 12.9 ± 0.5 kcal/mol. This energy difference may be composed of both the C–C rotation barrier and the Au...Au bond rupture. The former is expected to be quite small for bicyclopopyl and some of its derivatives (ca. 3 kcal/mol) according to theoretical calculations,

though an experimental value of as much as 12.5 kcal/mol has been measured for the 1,1'-dinitrobicyclopropyl. However, the situation is a very special one in the latter case, since electronic interactions between the  $\pi$  systems of the nitro groups and the Walsh orbitals of the cyclopropyl groups induce a quite rigid perpendicular orientation of the planes of these groups (with the  $\text{NO}_2$  plane bisecting the C—C—C angle of the neighbouring cyclopropyl group). For the disulfide **5** no pertinent energy value is available, probably due to the (pseudo) symmetrical near-*trans* conformation in the solid and in solution, and the resulting temperature independence of the NMR spectra. It appears likely, however, that the C—C bond rotation is not strongly hindered.

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## Experimental

**General:** All experiments were carried out under an atmosphere of dry, purified nitrogen. Solvents and glassware were dried and saturated/filled with nitrogen. — NMR: Jeol FX 60, GX 270, and GX 400. — IR: Perkin-Elmer 577. — MS: Varian MAT CH 7. — The preparation of compound **1** had been described previously<sup>12</sup>. All other reagents were obtained commercially or by standard literature procedures.

**1,1'-Bis(diphenylphosphinyl)bicyclopropyl (2):** 125 ml of dry dimethyl sulfoxide are slowly added at room temp. to a mixture of powdered sodium hydride (2.11 g, 88.0 mmol) and trimethylsulfoxonium iodide (19.4 g, 88.2 mmol). Hydrogen gas is evolved. After 1 h of vigorous stirring, this reaction mixture is introduced into a hot solution (70°C) of 2,3-bis(diphenylphosphinyl)-1,3-butadiene (**1**, 20.0 g, 44.0 mmol) in 100 ml of dimethyl sulfoxide. Stirring is continued for 2 h at 70°C. After cooling to room temp., 200 ml of chloroform is added, and the mixture is extracted four times with 50 ml of water. The organic phase is dried with magnesium sulfate, the solvent is evaporated, and the residue is crystallized from tetrahydrofuran; yield 8.20 g (39%), m.p. 219°C. — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.85 and 1.60 (A,A' and BB' of AA'BB'XX' system,  $N$  = 16 and 8 Hz, 4H each,  $\text{CH}_2$ ), 7.3–8.1 (m, 20H, Ph). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  = 12.4 (br. s,  $\text{CH}_2$ ), 18.0 (AXX',  $N$  = 105.6 Hz, PC), 127.8 [t (AXX'),  $N$  = 11.5 Hz, C-3], 131.3 (s, C-4), 131.6 (AXX',  $N$  = 101.9 Hz, C-1), 131.7 [t (AXX'),  $N$  = 8.5 Hz, C-2]; <sup>1</sup>H-coupled:  $J(\text{CH})$  = 165 Hz for  $\text{CH}_2$ . — <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  = 38.11 (s). — MS (EI, 70 eV):  $m/e$  (%) = 482 (40) [ $\text{M}^+$ ].

$\text{C}_{30}\text{H}_{28}\text{O}_2\text{P}_2$  (482.49) Calcd. C 74.68 H 5.85  
Found C 74.11 H 5.81

**3,3'-Bis(diphenylphosphinyl)-4,4',5,5'-tetrahydro-3,3'-bi(3H-pyr-azolyl) (3):** Compound **1** (12.5 g, 5.5 mmol) is dissolved in 50 ml of chloroform, treated with a solution of two equivalents of diazomethane in diethyl ether at room temp., and stirred for ca. 12 h. The solvent is then evaporated and the residue crystallized from toluene/hexane mixtures; yield 1.20 g (41%), m.p. 183°C. — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.86–2.05, 2.14–2.27, 2.88–3.07, and 4.15–4.22 (m each, 2H each,  $\text{CH}_2$ ), 7.0–7.9 (m, 20H, Ph). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  = 24.04 [t (AXX'),  $N$  = 6.7 Hz,  $\text{CH}_2$ ], 78.64 (s,  $\text{CH}_2$ ), 104.43 [dd (AXX'),  $N$  = 76.3 Hz, PC], 127.65, 127.86 [t

(AXX') each,  $N$  = 11.0 and 12.2 Hz, C-3], 129.83 [dd (AXX'),  $N$  = 105.0 Hz, C-1], 131.46 and 131.70 (s each, C-4), 132.08 and 132.15 [t (AXX') each,  $N$  = 10.4 Hz, C-2 (2 diastereotopic Ph)]; <sup>1</sup>H-coupled:  $J(\text{CH})$  = 137.2 and 142.6 Hz for  $\text{CH}_2$ . — <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  = 29.98 (s). — MS (EI, 70 eV):  $m/e$  (%) = 538 (0.1) [ $\text{M}^+$ ], 510 (1.2) [ $\text{M}^+ - \text{N}_2$ ], 482 (61) [ $2^+$ ].

$\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_2\text{P}_2$  (538.53) Calcd. C 66.91 H 5.24 N 10.40  
Found C 65.12 H 5.01 N 9.64

**1,1'-Bis(diphenylphosphino)bicyclopropyl (4):** Compound **2** (12.1 g, 25.1 mmol) is dissolved in 400 ml of toluene and treated with trichlorosilane (30 ml, excess) and triethylamine (12 ml, excess). The mixture is heated at reflux for 3 h, cooled to room temp., and extracted twice with aqueous sodium hydroxide (25%) and twice with water. The organic layer is dried with magnesium sulfate and the solvent evaporated. The residue is crystallized from methanol; yield 4.90 g (43%), m.p. 145°C. — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.33 and 0.75 (AA'BB'XX' each,  $N$  = 18 and 16 Hz, 4H each,  $\text{CH}_2$ ), 7.35 (br. s, 20H, Ph). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  = 10.5 [t (AXX'),  $N$  = 9.8 Hz,  $\text{CH}_2$ ], 19.6 [t (AXX'),  $N$  = 5.9 Hz, PC], 128.3 (s, C-4), 127.6, 134.4, and 137.0 [t (AXX') each,  $N$  = 6.8, 21.5, and 12.7 Hz for C-3, C-2, and C-1, respectively]; <sup>1</sup>H-coupled:  $J(\text{CH})$  = 162.1 Hz for  $\text{CH}_2$ . — <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.84 (s). — MS (EI, 70 eV):  $m/e$  (%) = 450 (100) [ $\text{M}^+$ ].

$\text{C}_{30}\text{H}_{28}\text{P}_2$  (450.50) Calcd. C 79.98 H 6.26  
Found C 79.11 H 6.30

**1,1'-Bis(diphenylthiophosphinyl)bicyclopropyl (5):** Compound **4** (500 mg, 1.11 mmol) and elemental sulfur (71.7 mg, 2.22 mmol) are dissolved in 10 ml of tetrahydrofuran. The mixture is stirred for 1 d at room temp., the solvent evaporated to a small volume, and the product precipitated by the addition of methanol; yield 420 mg (74%), m.p. 190°C. — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.9 and 1.8 (AA'BB'XX' each,  $N$  = 16 and 7 Hz, 4H each,  $\text{CH}_2$ ), 7.45 and 8.1 (m, 20H, Ph). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  = 15.1 (br. s,  $\text{CH}_2$ ), 20.0 (AXX',  $N$  = 83 Hz, PC), 131.4 (s, C-4); 127.9, 131.1, and 132.7 (AXX' each,  $N$  = 11.7, 84.0, and 8.8 Hz for C-3, C-1, and C-2, respectively); <sup>1</sup>H-coupled:  $J(\text{CH})$  = 165 Hz for  $\text{CH}_2$ . — <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  = 54.36 (s).

$\text{C}_{30}\text{H}_{28}\text{P}_2\text{S}_2$  (514.62) Calcd. C 70.02 H 5.48 S 12.46  
Found C 69.27 H 5.37 S 13.00

**1,1'-Bis(boranatodiphenylphosphino)bicyclopropyl (6):** Compound **4** (500 mg, 1.11 mmol) is dissolved in 10 ml of tetrahydrofuran and treated with 4.5 ml of a 1 M solution of  $\text{THF}-\text{BH}_3$  in tetrahydrofuran for 1 h at room temp. The solution is concentrated in vacuo and the product precipitated by addition of *n*-hexane; yield 350 mg (66%), m.p. 182°C. — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.95 and 1.40 (AA'BB'XX' each, 4H each,  $\text{CH}_2$ ), 7.6 (m, 20H, Ph);  $\text{BH}_3$  not located. — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  = 14.2 (br. s,  $\text{CH}_2$ ), 131.0 (s, C-4), 128.2, 128.3, and 133.4 (AXX' each,  $N$  = 9.8, 54.7, and 7.8 Hz for C-3, C-1, and C-2, respectively); PC not located. — <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  = 31.2 (s).

$\text{C}_{30}\text{H}_{34}\text{B}_2\text{P}_2$  (478.16) Calcd. C 75.36 H 7.17  
Found C 75.74 H 7.00

**1,1'-Bis(methyldiphenylphosphonio)bicyclopropyl Diiodide (7):** Compound **4** (460 mg, 1.02 mmol) is dissolved in 5 ml of chloroform and treated with 2 ml (excess) of iodomethane at room temp. for 3 d in the dark. The solvent is evaporated, the residue extracted with hot toluene, filtered, and dried in vacuo; yield 690 mg (91%), m.p. 205°C. — <sup>1</sup>H NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ ):  $\delta$  = 1.49 and 1.88 (AA'BB'XX' each,  $N$  = 15.1 and 7.8 Hz, 4H each,  $\text{CH}_2$ ), 2.51 ( $\text{A}_3\text{A}'_3\text{XX}'$ ,  $N$  = 12.2 Hz, 6H, Me), 7.75 (m, 20H, Ph). — <sup>13</sup>C NMR ( $\text{CDCl}_3/\text{CF}_3\text{CO}_2\text{H}$ ):  $\delta$  = 8.78 (AXX',  $N$  = 58.0 Hz, PC), 13.42

(AXX',  $N = 89.1$ , Me), 16.20 (br. s, CH<sub>2</sub>), 117.6, 130.9, and 132.5 (AXX' each,  $N = 86.7$ , 12.8, and 9.8 Hz for C-1, C-2, and C-3, respectively); 135.9 (s, C-4). — <sup>31</sup>P NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H):  $\delta = 32.5$  (s). C<sub>32</sub>H<sub>34</sub>I<sub>2</sub>P<sub>2</sub> (734.38) Calcd. C 52.34 H 4.67 Found C 51.28 H 4.76

*1',3'-Dihydro-1',1',3',3'-tetraphenyldispiro[cyclopropane-1,4'-[2H][1,3]diphosphole-5',1'-cyclopropane]-1',3'-diium Diiodide (8)*: Compound **4** (760 mg, 1.69 mmol) is dissolved in 15 ml of chloroform and treated with diiodomethane (0.136 ml, 1.69 mmol) at room temp. for 1 month in the dark. The product is precipitated by addition of *n*-pentane, filtered, and dried in vacuo; yield 880 mg (73%), m.p. 239 °C. — <sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H):  $\delta = 1.14$  and 1.72 (AA'BB'XX' each,  $N = 4.0$  and 7.3 Hz, 4H each, CH<sub>2</sub>), 5.28 (t,  $J = 12.2$  Hz, 2H, PCH<sub>2</sub>P), 7.76 (m, 20H, Ph). — <sup>13</sup>C NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H):  $\delta = 12.84$  (br. s, CH<sub>2</sub>), 19.54 (AXX',  $N = 81.7$  Hz, PC), 21.81 (t,  $J = 48.2$  Hz, PCH<sub>2</sub>P), 113.30, 131.09, and 133.68 (AXX' each,  $N = 87.1$ , 6.8, and 11.2 Hz for C-1, C-2, and C-3, respectively), 136.85 (s, C-4). — <sup>31</sup>P NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H):  $\delta = 41.43$  (s).

C<sub>31</sub>H<sub>30</sub>I<sub>2</sub>P<sub>2</sub> (718.37) Calcd. C 51.83 H 4.21 Found C 51.45 H 4.18

*1',1',3',3'-Tetraphenyldispiro[cyclopropane-1,4'-[1H][1,3λ<sup>5</sup>]-diphosphole-5',1'-cyclopropan]-1'-ium Iodide (9)*: Compound **8** (1.55 g, 2.16 mmol) is dispersed in 30 ml of tetrahydrofuran and treated, at -70 °C, with 1.5 ml of a 1.5 M solution of *n*BuLi in pentane (2.25 mmol). The mixture is allowed to warm to room temp. and stirred for ca. 12 h. The solid is filtered, dissolved in chloroform, the solution extracted twice with water, dried with magnesium sulfate and evaporated to dryness; yield 1.00 g (79%), m.p. 270 °C (dec.). — <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.75$  and 1.15 (AA'BB'XX' each, 4H each, CH<sub>2</sub>), 2.00 (t,  $J = 6.6$  Hz, 1H, CH), 7.60 (m, 20H, Ph). — <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 3.4$  (t,  $J = 113.8$  Hz, CH), 10.1 (br. s, CH<sub>2</sub>), 21.5 (AXX',  $N = 131.8$  Hz, PC), 125.9, 129.4, and 131.7 (AXX' each,  $N = 139.6$ , 12.7, and 10.7 Hz for C-1, C-2, and C-3, respectively), 133.2 (s, C-4). — <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta = 41.33$  (s).

C<sub>31</sub>H<sub>29</sub>IP<sub>2</sub> (590.46) Calcd. C 63.06 H 4.95 Found C 63.74 H 4.96

*[1,1'-Bis(diphenylphosphino)bicyclopropyl]diiodopalladium(II) (10)*: A suspension of PdI<sub>2</sub> (544 mg, 1.51 mmol) in 30 ml of dichloromethane is treated at room temp. with a solution of compound **4** (680 mg, 1.51 mmol) in 20 ml of the same solvent. A colourless precipitate is first formed, which redissolved completely after 2 h. The solution is passed through silica gel, and the solvent is evaporated; yield 1100 mg (90%) of a curry-coloured powder, m.p. 345 °C. — <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 0.45$  and 0.60 (AA'BB'XX' each, 4H each, CH<sub>2</sub>), 7.9 (m, 12H, *m*-, *p*-H), 8.25 (m, 8H, *o*-H). — <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 9.4$  (br. s, CH<sub>2</sub>), 24.5 (AXX',  $N = 82.0$  Hz, PC), 127.2, 127.6, and 134.4 (AXX' each,  $N = 51.8$ , 11.7, and 11.7 for C-1, C-3, and C-2, respectively), 131.2 (s, C-4). — <sup>31</sup>P NMR ([D<sub>6</sub>]DMSO):  $\delta = 78.0$  (s).

C<sub>30</sub>H<sub>28</sub>I<sub>2</sub>P<sub>2</sub>Pd (810.71) Calcd. C 44.45 H 3.48 Found C 44.02 H 3.48

*Bis[1,1'-bis(diphenylphosphino)bicyclopropyl]rhodium(I) Chloride (11)*: Compound **4** (500 mg, 1.11 mmol) is dissolved in 15 ml of benzene and this solution added at room temp. to a solution of [(CO)<sub>2</sub>RhCl]<sub>2</sub> (105 mg, 0.27 mmol) in 10 ml of the same solvent. The mixture is stirred for ca. 12 h, the yellow precipitate filtered, extracted with warm *n*-hexane, and dried; yield 560 mg (87%), dec. at 263 °C. — <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 0.30$  and 0.66 (br. s each, 8H each, CH<sub>2</sub>), 7.50 (m, 40H, Ph). — <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 12.7$  [(AXX')<sub>2</sub>Y,  $N = 19$  Hz, CH<sub>2</sub>], 25.63 [(AXX')<sub>2</sub>Y,  $N = 82$  Hz,

PC]; 129.15, 131.31, 131.73, and 134.72 (br. s each for C-3, C-1, C-4, and C-2, respectively); <sup>1</sup>H-coupled:  $J(\text{CH}) = 164$  Hz for CH<sub>2</sub>. — <sup>31</sup>P NMR ([D<sub>6</sub>]DMSO):  $\delta = 65.29$  [d,  $J(\text{RhP}) = 130.0$  Hz]. — MS (EI, 70 eV):  $m/e$  (%) = 1003 (100) [M<sup>+</sup> - Cl].

C<sub>60</sub>H<sub>56</sub>ClP<sub>4</sub>Rh (1039.36) Calcd. C 69.34 H 5.43 Found C 68.58 H 5.44

Table 1. Crystal-data collection and structure-refinement parameters for compounds **5**, **11**, and **12**

	<b>5</b>	<b>11</b>	<b>12</b>
Formula	C <sub>30</sub> H <sub>28</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>60</sub> H <sub>56</sub> ClP <sub>4</sub> Rh × 2.5 DMSO	C <sub>30</sub> H <sub>28</sub> Au <sub>2</sub> Cl <sub>2</sub> P <sub>2</sub> × 2 CHCl <sub>3</sub>
<i>M<sub>r</sub></i>	514.633	1234.702	1154.102
Space group	<i>P</i> 2 <sub>1</sub> (Nr. 4)	<i>P</i> $\bar{1}$ (Nr. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (Nr. 14)
<i>a</i> [Å]	9.452(1)	12.044(1)	13.152(1)
<i>b</i> [Å]	14.866(1)	13.153(1)	17.133(2)
<i>c</i> [Å]	9.846(1)	20.720(2)	16.522(2)
$\alpha$ [°]	90.0	80.20(1)	90.0
$\beta$ [°]	104.79(1)	79.74(1)	95.16(1)
$\gamma$ [°]	90.0	86.53(1)	90.0
<i>V</i> [Å <sup>3</sup> ]	1337.7	3181.2	3707.9
<i>Z</i>	2	2	4
$\rho_{\text{calcd.}}$ [g cm <sup>-3</sup> ]	1.278	1.289	2.067
$\mu$ (Mo-K $\alpha$ ) [cm <sup>-1</sup> ]	3.2	5.2	85.7
<i>T</i> [°C]	23	23	-55
(sin $\Theta$ / $\lambda$ ) <sub>max</sub> [Å <sup>-1</sup> ]	0.593	0.594	0.572
<i>hkl</i> range	±12, ±17, ±12	+16, ±16, ±25	+15, +19, ±18
Number of reflections			
measured	4975	11168	7986
unique	4681	11147	5727
observed	4299	9468	4851
Refined parameters	306	665	397
<i>R</i> <sup>a</sup>	0.028	0.080	0.034
<i>R<sub>w</sub></i> <sup>b</sup>	0.026	0.101	0.033
$\Delta\rho_{\text{min}}$ [e · Å <sup>-3</sup> ]	+0.30/-0.29	+3.27/-2.08	+0.80/-1.44

<sup>a</sup>)  $R = \Sigma (F_o - F_c) / \Sigma F_o$ . — <sup>b</sup>)  $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$ ,  $w = 1/\sigma^2(F_o)$ .

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **5**

ATOM	X/A	Y/B	Z/C	U(eq.)
P1	0.91406(6)	0.95844(6)	0.52786(6)	0.035
P2	0.64132(6)	0.84636(6)	0.12385(6)	0.035
S1	0.87744(8)	0.90632	0.69829(7)	0.048
S2	0.65960(7)	0.95866(6)	0.02656(6)	0.049
C111	1.1072(2)	0.9861(2)	0.5549(2)	0.036
C112	1.2086(3)	0.9416(2)	0.6617(3)	0.049
C113	1.3575(3)	0.9607(2)	0.6860(7)	0.067
C114	1.4045(3)	1.0211(2)	0.6006(4)	0.054
C115	1.3053(3)	1.0647(2)	0.4948(3)	0.050
C116	1.1570(3)	1.0493(2)	0.4723(3)	0.045
C121	0.8137(2)	1.0630(2)	0.4775(2)	0.037
C122	0.7813(3)	1.1153(2)	0.5828(3)	0.047
C123	0.6983(3)	1.1924(2)	0.5469(3)	0.057
C124	0.6460(3)	1.2168(2)	0.4106(4)	0.073
C125	0.6788(4)	1.1656(2)	0.3063(3)	0.095
C126	0.7634(3)	1.0884(2)	0.3396(3)	0.070
C13	0.8707(2)	0.8813(2)	0.3768(2)	0.034
C14	0.9855(3)	0.8079(2)	0.3942(3)	0.066
C15	0.9764(3)	0.8769(2)	0.2844(3)	0.046
C211	0.4505(2)	0.8104(2)	0.0906(2)	0.039
C212	0.3407(3)	0.8759(2)	0.0603(3)	0.056
C213	0.1961(3)	0.8528(2)	0.0351(3)	0.070
C214	0.1574(3)	0.7622(2)	0.0393(3)	0.060
C215	0.2641(3)	0.6969(2)	0.0675(3)	0.049
C216	0.4115(3)	0.7202(2)	0.0923(3)	0.045
C221	0.7272(2)	0.7519(2)	0.0566(2)	0.031
C222	0.7714(3)	0.6727(2)	0.1317(3)	0.042
C223	0.8307(3)	0.6029(2)	0.0708(3)	0.054
C224	0.8425(3)	0.6109(2)	-0.0646(3)	0.060
C225	0.7966(3)	0.6881(2)	-0.1402(3)	0.050
C226	0.7391(3)	0.7586(2)	-0.0813(3)	0.040
C23	0.7106(2)	0.8533(2)	0.3160(2)	0.033
C24	0.5941(2)	0.8824(2)	0.3882(3)	0.047
C25	0.6453(3)	0.7876(2)	0.4020(3)	0.038

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for complex 11

ATOM	X/A	Y/B	Z/C	U(eq.)
Rh1	0.00000	1.00000	0.00000	0.043
P1	0.0562(2)	0.8618(1)	-0.05501(9)	0.049
P2	0.1935(2)	1.0243(2)	-0.0207(1)	0.052
C111	0.0775(6)	0.8993(5)	-0.1448(4)	0.050
C112	0.0005(7)	0.9689(6)	-0.1724(4)	0.076
C113	0.0114(9)	0.9985(7)	-0.2404(5)	0.103
C114	0.0994(9)	0.9610(7)	-0.2826(4)	0.083
C115	0.1791(8)	0.8903(7)	-0.2549(4)	0.079
C116	0.1662(7)	0.8595(6)	-0.1869(4)	0.068
C121	-0.0208(6)	0.7420(6)	-0.0423(4)	0.071
C122	-0.0642(7)	0.6967(6)	0.0233(4)	0.078
C123	-0.1228(8)	0.6077(7)	0.0354(5)	0.113
C124	-0.1413(9)	0.5643(7)	-0.0189(7)	0.143
C125	-0.1001(9)	0.6086(7)	-0.0826(5)	0.106
C126	-0.0395(7)	0.6966(6)	-0.0939(4)	0.077
C13	0.1971(6)	0.8191(6)	-0.0387(4)	0.057
C14	0.2459(7)	0.7154(6)	-0.0533(5)	0.098
C15	0.2078(7)	0.7299(7)	0.0176(4)	0.085
C211	0.2433(7)	1.1275(6)	-0.0882(4)	0.067
C212	0.1748(9)	1.1569(7)	-0.1372(4)	0.080
C213	0.210(1)	1.2215(9)	-0.1924(6)	0.114
C214	0.310(2)	1.261(1)	-0.2028(7)	0.176
C215	0.386(1)	1.2367(9)	-0.1575(8)	0.172
C216	0.3493(8)	1.1679(7)	-0.0986(5)	0.112
C221	0.2572(6)	1.0448(6)	0.0501(4)	0.067
C222	0.2738(7)	1.1421(7)	0.0622(5)	0.098
C223	0.3158(9)	1.154(1)	0.1180(6)	0.142
C224	0.3397(9)	1.068(1)	0.1627(6)	0.127
C225	0.3251(9)	0.9735(9)	0.1512(5)	0.097
C226	0.2819(8)	0.9606(7)	0.0957(4)	0.078
C23	0.2724(6)	0.9102(6)	-0.0498(4)	0.059
C24	0.3954(7)	0.8938(7)	-0.0436(5)	0.115
C25	0.3630(7)	0.9236(7)	-0.1106(5)	0.082
Rh2	0.00000	0.50000	0.039	0.039
P3	-0.0150(2)	0.6439(2)	0.42080(9)	0.050
P4	-0.1578(2)	0.5771(2)	0.55614(9)	0.048
C311	0.0556(7)	0.7539(6)	0.4372(4)	0.063
C312	0.0251(9)	0.8558(7)	0.4150(5)	0.103
C313	0.079(1)	0.9370(7)	0.4293(6)	0.146
C314	0.168(1)	0.9152(9)	0.4633(7)	0.160
C315	0.1975(9)	0.8170(9)	0.4836(7)	0.156
C316	0.1422(7)	0.7377(7)	0.4714(5)	0.108
C321	0.0295(7)	0.6438(6)	0.3317(4)	0.063
C322	-0.0042(8)	0.5611(7)	0.3052(4)	0.078
C323	0.030(1)	0.5537(8)	0.2391(5)	0.092
C324	0.097(1)	0.626(1)	0.1991(5)	0.118
C325	0.130(1)	0.7104(9)	0.2228(5)	0.113
C326	0.0955(8)	0.7190(7)	0.2903(4)	0.083
C33	-0.1644(6)	0.6847(6)	0.4286(4)	0.058
C34	-0.2384(7)	0.6521(7)	0.3846(4)	0.077
C35	-0.2068(7)	0.7616(7)	0.3735(4)	0.092
C411	-0.2747(6)	0.4899(6)	0.5826(4)	0.068
C412	-0.2950(7)	0.4330(7)	0.6462(4)	0.081
C413	-0.3757(9)	0.3572(8)	0.6621(5)	0.117
C414	-0.4359(8)	0.3355(8)	0.6153(7)	0.134
C415	-0.4159(8)	0.3920(8)	0.5524(6)	0.113
C416	-0.3370(7)	0.4688(7)	0.5356(4)	0.076
C421	-0.1484(6)	0.6362(6)	0.6281(4)	0.057
C422	-0.0445(7)	0.6770(7)	0.6298(4)	0.073
C423	-0.0362(9)	0.7369(8)	0.6774(5)	0.100
C424	-0.130(1)	0.7584(8)	0.7222(5)	0.095
C425	-0.2316(8)	0.7181(8)	0.7213(5)	0.092
C426	-0.2414(7)	0.6569(6)	0.6748(4)	0.066
C43	-0.2106(6)	0.6872(6)	0.5005(4)	0.065
C44	-0.3290(7)	0.7317(7)	0.5211(5)	0.106
C45	-0.2274(9)	0.7937(7)	0.5220(4)	0.100
C11	0.5346(2)	0.2562(2)	0.2229(2)	0.151
S1	0.2856(3)	0.6469(3)	0.6629(2)	0.215
O1	0.2252(3)	0.5935(3)	0.6206(2)	0.240
C11	0.4216(3)	0.5794(3)	0.6598(2)	0.237
C12	0.2278(3)	0.5954(3)	0.7480(2)	0.161
S2	0.4528(5)	0.0152(4)	0.6231(3)	0.192
O2A	0.4771(9)	0.1128(7)	0.5737(5)	0.066
C21A	0.484(2)	0.041(2)	0.7011(6)	0.133
C22A	0.571(2)	-0.073(1)	0.602(1)	0.192
O2B	0.446(3)	-0.094(1)	0.609(1)	0.232
C21B	0.427(2)	0.008(2)	0.7120(5)	0.084
C22B	0.603(1)	0.039(4)	0.607(2)	0.634
S3	-0.4358(9)	-0.5531(8)	0.8605(4)	0.160
O3	-0.4048(9)	-0.6537(8)	0.9018(4)	0.133
C31	-0.5733(9)	-0.5179(8)	0.9038(4)	0.097
C32	-0.3569(9)	-0.4557(8)	0.8829(4)	0.140

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters for complex 12

ATOM	X/A	Y/B	Z/C	U(eq.)
Au1	-0.17846(2)	0.21279(2)	0.23468(2)	0.024
Au2	0.03786(2)	0.24712(2)	0.31484(2)	0.023
C11	-0.2156(1)	0.3423(1)	0.2098(1)	0.035
C12	-0.0184(1)	0.3295(1)	0.4099(1)	0.037
P1	-0.1576(1)	0.0852(1)	0.2595(1)	0.024
P2	0.1076(1)	0.1715(1)	0.2247(1)	0.024
C111	-0.1951(5)	0.0638(5)	0.3604(5)	0.033
C112	-0.2538(6)	-0.0010(5)	0.3764(5)	0.039
C113	-0.2839(6)	-0.0126(6)	0.4540(6)	0.047
C114	-0.2535(7)	0.0378(7)	0.5153(6)	0.051
C115	-0.1940(7)	0.1006(6)	0.4995(5)	0.046
C116	-0.1662(6)	0.1142(5)	0.4234(5)	0.039
C121	-0.2414(6)	0.0236(5)	0.1918(5)	0.024
C122	-0.2077(6)	-0.0403(5)	0.1502(5)	0.037
C123	-0.2773(8)	-0.0846(6)	0.1004(6)	0.048
C124	-0.3800(8)	-0.0655(7)	0.0947(6)	0.039
C125	-0.4130(7)	-0.0009(7)	0.1339(6)	0.051
C126	-0.3440(6)	0.0429(5)	0.1836(5)	0.039
C13	-0.0271(5)	0.0507(5)	0.2553(5)	0.025
C14	-0.0068(6)	-0.0349(5)	0.2796(5)	0.033
C15	0.0314(6)	0.0280(5)	0.3364(5)	0.035
C211	0.1333(5)	0.2286(4)	0.1365(4)	0.017
C212	0.2193(6)	0.2169(5)	0.0947(5)	0.028
C213	0.2361(6)	0.2621(5)	0.0275(5)	0.029
C214	0.1692(7)	0.3202(5)	0.0031(5)	0.024
C215	0.0815(7)	0.3334(5)	0.0429(5)	0.042
C216	0.0649(5)	0.2874(5)	0.1090(5)	0.035
C221	0.2330(5)	0.1351(5)	0.2652(5)	0.023
C222	0.2666(6)	0.0602(5)	0.2520(5)	0.041
C223	0.3633(7)	0.0367(6)	0.2854(6)	0.059
C224	0.4248(7)	0.0873(8)	0.3313(6)	0.065
C225	0.3919(7)	0.1629(7)	0.3425(6)	0.044
C226	0.2952(6)	0.1875(6)	0.3112(5)	0.039
C23	0.0297(5)	0.0883(5)	0.1895(4)	0.024
C24	-0.0259(6)	0.0954(5)	0.1037(5)	0.025
C25	0.0632(6)	0.0420(5)	0.1181(5)	0.036
C1	0.7199(6)	0.1651(6)	-0.0714(6)	0.050
C111	0.7443(2)	0.1971(2)	0.0281(2)	0.070
C112	0.6209(2)	0.2205(3)	-0.1219(2)	0.133
C113	0.6908(3)	0.0666(2)	-0.0743(3)	0.113
C2	0.5254(7)	0.1941(7)	0.6465(7)	0.070
C121	0.5223(2)	0.1464(2)	0.5527(2)	0.079
C122	0.4960(2)	0.2935(2)	0.6325(3)	0.112
C123	0.4422(2)	0.1497(2)	0.7090(2)	0.070

Table 5. Selected interatomic distances [Å] and angles [°] for compound 5 (for atomic numbering see Figure 1)

P1 -- S1	1.958(1)	P1 -- C111	1.823(2)
P1 -- C121	1.822(2)	P1 -- C13	1.840(2)
P2 -- S2	1.954(1)	P2 -- C211	1.829(2)
P2 -- C221	1.829(2)	P2 -- C23	1.840(2)
C13 -- C14	1.517(3)	C13 -- C15	1.515(3)
C13 -- C23	1.536(3)	C14 -- C15	1.476(4)
C23 -- C24	1.517(3)	C23 -- C25	1.522(3)
C24 -- C25	1.485(3)		
S1 -- P1 -- C111	110.7(1)	S1 -- P1 -- C121	112.1(1)
C111 -- P1 -- C121	106.3(1)	S1 -- P1 -- C13	113.2(1)
C111 -- P1 -- C13	105.5(1)	C121 -- P1 -- C13	108.6(1)
S2 -- P2 -- C211	111.6(1)	S2 -- P2 -- C221	112.1(1)
C211 -- P2 -- C221	102.7(1)	S2 -- P2 -- C23	113.8(1)
C211 -- P2 -- C23	106.0(1)	C221 -- P2 -- C23	109.9(1)
P1 -- C13 -- C14	110.6(2)	P1 -- C13 -- C15	117.9(2)
C14 -- C13 -- C15	58.3(2)	P1 -- C13 -- C23	118.5(1)
C14 -- C13 -- C23	117.1(2)	C15 -- C13 -- C23	119.3(2)
C13 -- C14 -- C15	60.8(2)	C13 -- C15 -- C14	60.9(2)
P2 -- C23 -- C13	118.2(1)	P2 -- C23 -- C24	112.8(1)
C13 -- C23 -- C24	120.1(2)	P2 -- C23 -- C25	116.6(2)
C13 -- C23 -- C25	117.1(2)	C24 -- C23 -- C25	58.5(2)
C23 -- C24 -- C25	60.9(2)	C23 -- C25 -- C24	60.6(1)

*Bis*[chloroaurio(*I*)diphenylphosphino]bicyclopropyl (12): Compound 4 (675 mg, 1.50 mmol), dissolved in 15 ml of tetrahydrofuran, is added dropwise with stirring at room temp. to a solution of (CO)AuCl (780 mg, 3.00 mmol) in 15 ml of the same solvent. CO gas is evolved, and a colourless precipitate is formed which is filtered and dried in vacuo; yield 1140 mg (83%), dec. at 270°C. — <sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H): δ = 0.75 and 1.30 (br. each, 4H each,

CH<sub>2</sub>), 7.6 (m, 20H, Ph). — <sup>13</sup>C NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H): δ = 14.2 (br., CH<sub>2</sub>), 19.5 (AXX', N = 69.3 Hz, PC), 126.0 (s, C-1), 129.4 (AXX', N = 11.7, C-3), 132.5 (s, C-4), 134.0 (AXX', N = 12.7 Hz, C-2). — <sup>31</sup>P NMR (CDCl<sub>3</sub>/CF<sub>3</sub>CO<sub>2</sub>H): δ = 40.91 (s).

C<sub>30</sub>H<sub>28</sub>Au<sub>2</sub>Cl<sub>2</sub>P<sub>2</sub> (915.34) Calcd. C 39.37 H 3.08  
Found C 38.83 H 3.13

**X-ray Structure Determinations:** A summary of the data collection and structure refinement parameters is given in Table 1. Further details of the individual determinations are described below. The final coordinates are presented in Tables 2–4, Tables 5–7 contain selected distances and angles.

**Compound 5:** Enraf-Nonius CAD4 diffractometer, Mo-K<sub>α</sub> radiation, λ = 0.71069 Å, graphite monochromator, Θ-2Θ scan. Lp and decay corrections were applied. After merging of equivalent data (R<sub>int</sub> = 0.012) the remaining independent structure factors with F<sub>o</sub> ≥ 4.0σ(F<sub>o</sub>) were deemed "observed" and used for all calculations. P2<sub>1</sub> was assumed as the space group and confirmed by suc-

cessful refinement of the structure. The centrosymmetrical alternative P2<sub>1</sub>/m can be excluded, because the molecule does not contain an inversion center nor a plane of symmetry as required by this space group for Z = 2. Reduced-cell calculations did not indicate any higher symmetry (DELOS, LEPAGE). The structure was solved by direct methods (SHELXS-86) and completed by difference Fourier syntheses. 26 H atoms could be located in difference syntheses. The two remaining ones were calculated at idealized geometrical positions. All non-H atoms were refined anisotropically, the H atoms were included as fixed atom contributions in the structure factor calculations (U<sub>iso</sub> = 0.05 Å<sup>2</sup>). Refinement of the inverse data yielded R(R<sub>w</sub>) = 0.028 (0.026). The molecular structure is shown in Figure 1.

**Compound 11:** Enraf Nonius CAD4 diffractometer, Θ-2Θ scan. Lp and empirical absorption corrections (relative transmission 0.95–1.00) were applied. After merging of equivalent data (R<sub>int</sub> = 0.01), the independent structure factors with F<sub>o</sub> < 4.0σ(F<sub>o</sub>) were deemed "unobserved" and not used in all further calculations. The centrosymmetrical space group P1̄ was assumed and confirmed by the successful refinement of the structure. Reduced-cell calculations did not indicate any higher symmetry. The structure was solved by Patterson methods (SHELXS-86) and completed by difference Fourier syntheses. All H atoms were calculated at idealized geometrical positions. The non-H atoms were refined anisotropically with the exception of the crystal solvent molecule atoms. The H atoms were included as fixed atom contributions in the structure factor calculations (U<sub>iso</sub> = 0.05 Å<sup>2</sup>). The structure of the cation is shown in Figure 2. Two DMSO molecules were refined as rigid groups, one with anisotropic displacement parameters, the second one with isotropic parameters (occupancy 0.5). The remaining DMSO was refined isotropically with the O/C atoms in split positions (0.4/0.6). All solvent H atoms were neglected, except for those at the anisotropically refined DMSO.

**Compound 12:** Syntex P2<sub>1</sub> diffractometer, ω scan, Δω = 0.8°. Lp and empirical absorption corrections (relative transmission

Table 6. Selected interatomic distances [Å] and angles [°] for complex 11 (for atomic numbering see Figure 2)

Rh1 -- P1	2.312(2)	Rh1 -- P2	2.325(2)
P1 -- C111	1.818(7)	P1 -- C121	1.832(8)
P1 -- C13	1.826(8)	P2 -- C211	1.819(7)
P2 -- C221	1.837(9)	P2 -- C23	1.858(8)
C13 -- C14	1.51(1)	C13 -- C15	1.52(1)
C13 -- C23	1.51(1)	C14 -- C15	1.50(1)
C23 -- C24	1.51(1)	C23 -- C25	1.50(1)
C24 -- C25	1.49(1)	Rh2 -- P3	2.306(2)
Rh2 -- P4	2.318(2)	P3 -- C311	1.830(9)
P3 -- C321	1.829(8)	P3 -- C33	1.834(8)
P4 -- C411	1.818(8)	P4 -- C421	1.818(8)
P4 -- C43	1.848(8)	C33 -- C34	1.51(1)
C33 -- C35	1.53(1)	C33 -- C43	1.50(1)
C34 -- C35	1.48(1)	C43 -- C44	1.52(1)
C43 -- C45	1.53(1)	C44 -- C45	1.51(1)
S1 -- O1	1.513(6)	S1 -- C11	1.811(5)
S1 -- C12	1.808(6)	S2 -- O2A	1.51(1)
S2 -- C21A	1.81(2)	S2 -- C22A	1.82(2)
S2 -- O2B	1.52(2)	S2 -- C21B	1.80(1)
S2 -- C22B	1.81(2)	O2A -- C22B	1.92(3)
C21A -- C21B	0.81(4)	C22A -- O2B	1.53(4)
C22A -- C22B	1.57(6)	S3 -- O3	1.51(1)
S3 -- C31	1.81(1)	S3 -- C32	1.81(2)

P1 -- Rh1 -- P2	81.6(1)	Rh1 -- P1 -- C111	112.2(2)
Rh1 -- P1 -- C121	124.8(3)	C111 -- P1 -- C121	102.5(4)
Rh1 -- P1 -- C13	107.6(3)	C111 -- P1 -- C13	103.4(3)
C121 -- P1 -- C13	104.3(3)	P1 -- Rh1 -- P1	180.0(1)
Rh1 -- P2 -- C211	115.7(3)	Rh1 -- P2 -- C221	116.5(2)
C211 -- P2 -- C221	105.8(4)	Rh1 -- P2 -- C23	111.1(3)
C211 -- P2 -- C23	101.7(3)	C221 -- P2 -- C23	104.4(4)
P2 -- Rh1 -- P2	180.0(1)	P1 -- C13 -- C14	120.4(6)
P1 -- C13 -- C15	118.5(5)	C14 -- C13 -- C15	59.2(5)
P1 -- C13 -- C23	110.3(5)	C14 -- C13 -- C23	120.2(6)
C15 -- C13 -- C23	119.9(7)	C13 -- C14 -- C15	60.8(5)
C13 -- C15 -- C14	59.9(5)	P2 -- C23 -- C13	111.2(5)
P2 -- C23 -- C24	119.0(6)	C13 -- C23 -- C24	120.2(7)
P2 -- C23 -- C25	120.4(5)	C13 -- C23 -- C25	118.1(7)
C24 -- C23 -- C25	59.2(6)	C23 -- C24 -- C25	60.3(6)
C23 -- C25 -- C24	60.5(5)	P3 -- Rh2 -- P4	82.1(1)
Rh2 -- P3 -- C311	111.6(3)	Rh2 -- P3 -- C321	123.1(3)
C311 -- P3 -- C321	104.4(4)	Rh2 -- P3 -- C33	107.7(2)
C311 -- P3 -- C33	104.6(4)	C321 -- P3 -- C33	103.9(4)
P3 -- Rh2 -- P3	180.0(1)	Rh2 -- P4 -- C411	112.1(3)
Rh2 -- P4 -- C421	120.8(3)	C411 -- P4 -- C421	105.6(4)
Rh2 -- P4 -- C43	110.2(2)	C411 -- P4 -- C43	105.3(4)
C421 -- P4 -- C43	101.3(4)	P4 -- Rh2 -- P4	180.0(1)
P3 -- C33 -- C34	120.8(6)	P3 -- C33 -- C35	120.5(5)
C34 -- C33 -- C35	58.4(6)	P3 -- C33 -- C43	108.6(5)
C34 -- C33 -- C43	119.8(6)	C35 -- C33 -- C43	121.3(6)
C33 -- C34 -- C35	61.5(6)	C33 -- C35 -- C34	60.1(6)
P4 -- C43 -- C33	112.5(5)	P4 -- C43 -- C44	118.6(5)
C33 -- C43 -- C44	120.4(7)	P4 -- C43 -- C45	119.6(6)
C33 -- C43 -- C45	116.8(6)	C44 -- C43 -- C45	59.4(6)
C43 -- C44 -- C45	60.5(6)	C43 -- C45 -- C44	60.1(6)
O1 -- S1 -- C11	103.7(3)	O1 -- S1 -- C12	105.6(3)
C11 -- S1 -- C12	97.3(3)	O3 -- S3 -- C31	103.7(7)
O3 -- S3 -- C32	105.6(8)	C31 -- S3 -- C32	97.3(7)

Table 7. Selected interatomic distances [Å] and angles [°] for complex 12 (for atomic numbering see Figure 3)

Au1 -- Au2	3.085(1)	Au1 -- C11	2.301(2)
Au1 -- P1	2.237(2)	Au2 -- C12	2.284(2)
Au2 -- P2	2.233(2)	P1 -- C111	1.817(8)
P1 -- C121	1.833(8)	P1 -- C13	1.823(7)
P2 -- C211	1.813(7)	P2 -- C221	1.832(7)
P2 -- C23	1.819(8)	C13 -- C14	1.54(1)
C13 -- C15	1.53(1)	C13 -- C23	1.52(1)
C14 -- C15	1.49(1)	C23 -- C24	1.54(1)
C23 -- C25	1.52(1)	C24 -- C25	1.49(1)
C1 -- C111	1.737(9)	C1 -- C112	1.759(9)
C1 -- C113	1.73(1)	C2 -- C121	1.75(1)
C2 -- C122	1.76(1)	C2 -- C123	1.75(1)
Au2 -- Au1 -- C11	93.8(1)	Au2 -- Au1 -- P1	90.8(1)
C11 -- Au1 -- P1	174.8(1)	Au1 -- Au2 -- C12	94.0(1)
Au1 -- Au2 -- P2	91.2(1)	C12 -- Au2 -- P2	174.6(1)
Au1 -- P1 -- C111	109.0(3)	Au1 -- P1 -- C121	113.2(3)
C111 -- P1 -- C121	104.3(4)	Au1 -- P1 -- C13	114.2(3)
C111 -- P1 -- C13	107.7(3)	C121 -- P1 -- C13	107.8(4)
Au2 -- P2 -- C211	109.9(3)	Au2 -- P2 -- C221	111.4(3)
C211 -- P2 -- C221	104.5(3)	Au2 -- P2 -- C23	114.5(2)
C211 -- P2 -- C23	107.8(3)	C221 -- P2 -- C23	108.2(4)
P1 -- C13 -- C14	116.2(5)	P1 -- C13 -- C15	116.7(5)
C14 -- C13 -- C15	57.9(5)	P1 -- C13 -- C23	114.5(5)
C14 -- C13 -- C23	120.5(6)	C15 -- C13 -- C23	119.5(6)
C13 -- C14 -- C15	60.9(5)	C13 -- C15 -- C14	61.2(5)
P2 -- C23 -- C13	113.8(5)	P2 -- C23 -- C24	116.1(5)
C13 -- C23 -- C24	118.0(6)	P2 -- C23 -- C25	117.6(5)
C13 -- C23 -- C25	122.0(7)	C24 -- C23 -- C25	58.3(5)
C23 -- C24 -- C25	60.1(5)	C23 -- C25 -- C24	61.6(5)
C111 -- C1 -- C112	110.1(5)	C111 -- C1 -- C113	110.9(6)
C112 -- C1 -- C113	111.2(5)	C121 -- C2 -- C122	110.4(6)
C121 -- C2 -- C123	110.8(6)	C122 -- C2 -- C123	110.9(6)



0.58–1.00) were applied to the data. Merging of equivalent data ( $R_{\text{int}} = 0.02$ ) led to the independent structure factors, those of which with  $F_o \geq 4.0 \sigma(F_o)$  were treated as "observed" and used for further calculations. Reduced-cell calculations did not indicate any higher symmetry. The structure was solved by Patterson methods (SHELXS-86) and difference Fourier syntheses. 10H atoms out of a total of 28 could be located in difference syntheses, the remainder were calculated at idealized geometrical positions. All non-H atoms were refined anisotropically except for the H atoms which were included as fixed atom contributions in the structure factor calculations ( $U_{\text{iso}} = 0.05 \text{ \AA}^2$ ). Solvent H atoms were neglected. The structure is shown in Figure 3.

Further details of the crystal structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2. Requests should be accompanied by the depository number CSD-54222, the names of the authors, and the full literature citation.

#### CAS Registry Numbers

1: 113017-77-9 / 2: 123542-05-2 / 3: 123565-78-6 / 4: 123542-06-3 / 5: 123565-79-7 / 6: 123542-10-9 / 7: 123542-07-4 / 8: 123542-08-5 / 9: 123542-09-6 / 10: 123542-11-0 / 11: 123542-12-1 / 11 · 2.5 DMSO: 123542-14-3 / 12: 123542-13-2 / 12 · 2 CHCl<sub>3</sub>: 123542-15-4 / HSiCl<sub>3</sub>: 10025-78-2 / PdI<sub>2</sub>: 7790-38-7 / [(CO)<sub>2</sub>RhCl]<sub>2</sub>: 14523-22-9 / (CO)AuCl: 50960-82-2 / trimethylsulfoxonium iodide: 1774-47-6

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