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NEW ORGANOGOLD COMPLEXES: TETRAPHENYLCYCLOPENTADIENE DERIVATIVES

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Summary

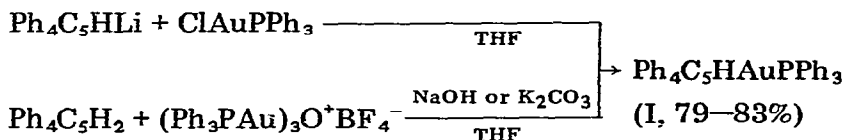
Mono- and diaurated derivatives of tetraphenylcyclopentadiene, $\text{Ph}_4\text{C}_5\text{HAuPPh}_3$ and $\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_2$, have been obtained by auration of tetraphenylcyclopentadiene with tris(triphenylphosphinegold)oxonium tetrafluoroborate. Under the action of $[\text{Ph}_3\text{PAu}]^+\text{BF}_4^-$ both mono- and diaurated derivatives form the trinuclear cationic complex $[\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_3]^+\text{BF}_4^-$, which is converted into $\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_2$ when treated with nucleophiles.

The structure of $\text{Ph}_4\text{C}_5\text{HAuPPh}_3$ and $[\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_3]^+\text{BF}_4^-$ was established by IR, UV, PMR spectral and X-ray structural studies. $\text{Ph}_4\text{C}_5\text{HAuPPh}_3$ has a C—Au bond and additional coordination of Au with two neighboring carbon atoms of the five-membered ring; the structure is non-fluxional. The complex $[\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_3]^+\text{BF}_4^-$ includes rather rare structural moieties: a three-membered carbometal cycle Au—C—Au , three gold atoms linked to each other, Au—Au—Au , and univalent gold coordinated with three carbon atoms of the Ph_4C_5 ring.

Cyclopentadienyl metal complexes in which the cyclopentadienyl group is bonded to the metal by either one or five carbon atoms are quite numerous and have been well studied, whereas cyclopentadienyl complexes with the metal coordinated with three carbon atoms are rather rare. In this paper we report on organogold derivatives of tetraphenylcyclopentadiene in which univalent gold is coordinated to three carbon atoms of the cyclopentadienyl ring. Organogold derivatives of tetraphenylcyclopentadiene containing one, two and three AuPPh_3 groups were obtained. In the trinuclear organogold complex the three gold atoms are bonded with each other and with carbon atoms. This is a new type of organogold clusters, since previously only clusters containing more than

five Au atoms without Au—C bonds and binuclear complexes $[R(AuPPh_3)_2]^+X^-$ [1,2] incorporating the Au—C—Au fragment have been reported.

Two methods were used to prepare tetraphenylcyclopentadienyl(triphenylphosphine)gold (I): interaction of lithium tetraphenylcyclopentadienide with Ph_3PAuCl and auration of tetraphenylcyclopentadiene (II) in the presence of NaH or K_2CO_3 with tris(triphenylphosphine)gold oxonium tetrafluoroborate (III) which, as has been shown earlier [1], readily aurates various organic compounds.



Complex I is not very stable in air, slowly decomposing with formation of tetraphenylcyclopentadienone, but its thermal stability is much higher than that of $C_5H_5AuPPh_3$ [3].

The PMR spectrum of I displays two groups of signals: a complex multiplet of phenyl protons ($\delta = 7.36$ ppm) and a doublet from the cyclopentadienyl proton centered at $\delta = 5.36$ ppm, $^3J(^1H-^{31}P) = 12$ Hz. The value of the splitting constant is typical of organogold compounds with a fixed H—C—AuPR₃ fragment containing an Au—C σ -bond [4–7]. Complex I is non-fluxional, unlike $C_5H_5AuPPh_3$ ($^3J(^1H-^{31}P) = 2.8$ Hz) and $CH_3C_5H_4AuPPh_3$ [8].

The geometry of I with the most important bond lengths (X-ray data, diffractometer, 3913 reflections, $R = 0.049$) is shown in Fig. 1*. The tetraphenylcyclopentadienyl ring is planar (within 0.02 Å) and the value and distribution of carbon—carbon bond lengths in the cyclopentadienyl ring correspond to a diene system. The Au—C(1) bond (2.15 Å) is slightly shorter than the sum of covalent radii of a gold atom (in the metal) and a sp^3 -hybridized carbon atom (2.20 Å). The bond angles C(1)—Au—C(2) and C(1)—Au—C(5) are 99° and 93°, respectively, and the distance Au—C(2) 2.67 Å and Au—C(5) 2.76 Å.

The X-ray structural data suggest that the Au atom in tetraphenylcyclopentadienyl(triphenylphosphine)gold (I) is bonded to three carbon atoms, but the bonds are non-equivalent: the Au—C(1) distance is much shorter than Au—C(2) and Au—C(5). The coordination of the gold atom in I is unusually high for univalent gold. Complex I may be considered as a σ -derivative of gold with additional weak coordination with C(2) and C(5).

Thermolysis of I (mass spectrometer, 150°C) yields II, triphenylphosphine and metallic gold.

Complex I, like other organogold compounds in which gold is coordinated with an sp^3 -hybridized carbon atom [9,10], is resistant towards the action of HBF_4 . The reaction only proceeds in the presence of a nucleophilic agent. Thus in the presence of triphenylphosphine the Au—C bond in I is ruptured to form

* The X-ray structural study was carried out by Yu.T. Struchkov and Yu.L. Slovokhotov. Full X-ray data will be published separately [18].

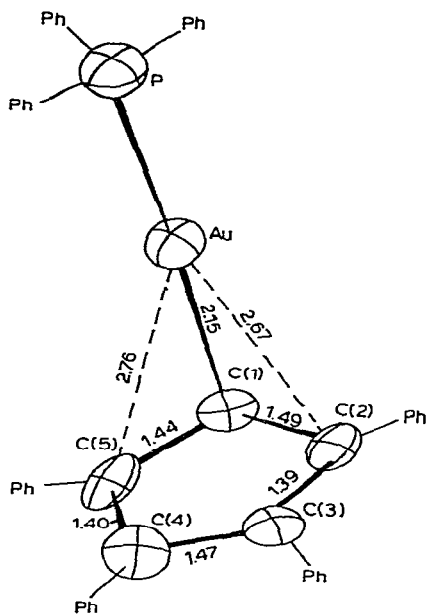
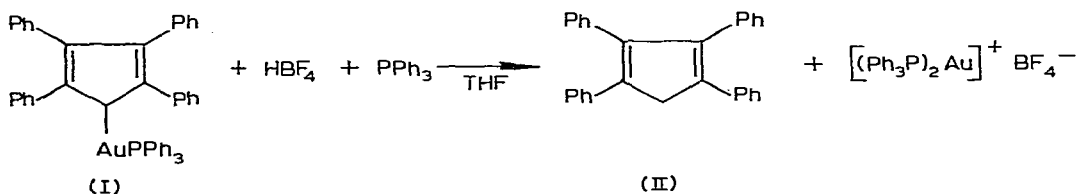
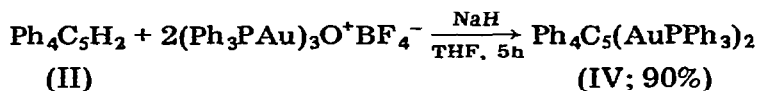


Fig. 1. The structure of $\text{Ph}_4\text{C}_5\text{HAuPPh}_3$ (I).

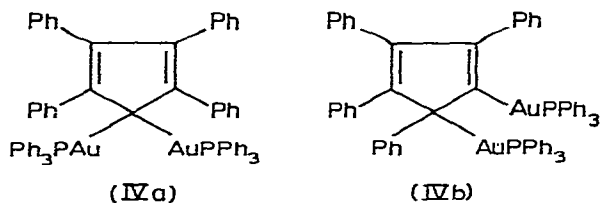
II and bis(triphenylphosphine)gold tetrafluoroborate.



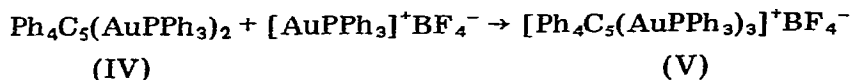
Upon prolonged interaction of tetraphenylcyclopentadiene with a larger quantity of tris(triphenylphosphinegold)oxonium tetrafluoroborate III than in the synthesis of monoaurated compound I, a diaurated derivative, IV, is formed.



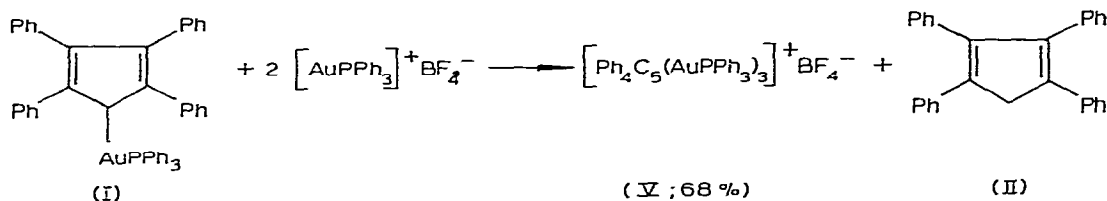
Complex IV is quite stable in air, practically insoluble in organic solvents, and reacts slowly with CHCl_3 , forming II and Ph_3PAuCl . In the presence of HCl IV is quantitatively converted into II and Ph_3PAuCl . The structure of the diaurated tetraphenylcyclopentadiene has not yet been determined. Available data do not allow one to ascertain whether the gold atoms are bonded with the same carbon atom (IVa) or with different (IVb) atoms.



Interaction of IV with Ph_3PAu^+ cation gives the cationic complex V in quantitative yield.



Complex V is also obtained from the monoaurated compound under the action of Ph_3PAu^+ .



Complex V is stable in the absence of moisture (quenching with water gives $(\text{Ph}_3\text{PAu})_3\text{O}^+\text{BF}_4^-$ and tetraphenylcyclopentadiene) and forms a solvate with two benzene molecules $[\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_3]^+\text{BF}_4^- \cdot 2\text{C}_6\text{H}_6$ (Va). The solvate Va is diamagnetic (EPR data and negative magnetic susceptibility).

The structure of Va was determined by X-ray structural analysis (diffractometer, 9494 reflections, $R = 0.054$)*. Parameters of the main skeleton of Va are shown in Fig. 2. The tetraphenylcyclopentadienyl ligand is practically planar (within 0.04 Å) and occupies a bridging position between the atoms Au(2) and Au(3). The plane of the triangle C(2)Au(2)Au(3) is approximately normal to the cyclopentadienyl plane. The distances Au(2)—C(2) and Au(3)—C(2) are about equal to the sum of covalent radii of these atoms (C—Au 2.2 Å) and length of the Au(2)—Au(3) bond (1.82 Å) is less than the distance between gold atoms in the metal (2.88 Å) [11]. The angle Au(2)C(2)Au(3) (76°) is significantly smaller than tetrahedral. These data indicate strong bonding of the Au(2)C(2)Au(3) atoms and considerable strain in this triangle. The Au(1)—Au(2) distance (3.021 Å) slightly exceeds the Au—Au distance in the metal, however, it definitely indicates Au(1)—Au(2) bonding.

In complex Va the same type of coordination of the tetraphenylcyclopentadienyl ligand with Au atom (η^3 -coordination with unequal Au—C bonds) as in the mononuclear complex $\text{Ph}_4\text{C}_5\text{HAuPPh}_3$ (I) (see Fig. 1) is observed. The length of the Au(1)—C(1) bond is 2.21 Å and it is directed practically normal to the cyclopentadienyl plane, the bond angles Au(1)C(1)C(2) and Au(1)C(1)—C(5) are 91° and 88°, respectively. The Au(1)—C(2) and Au(1)—C(5) bond lengths are 2.71 and 2.60 Å, respectively. The values of the bond angles C(2)-

* See footnote on page 404.

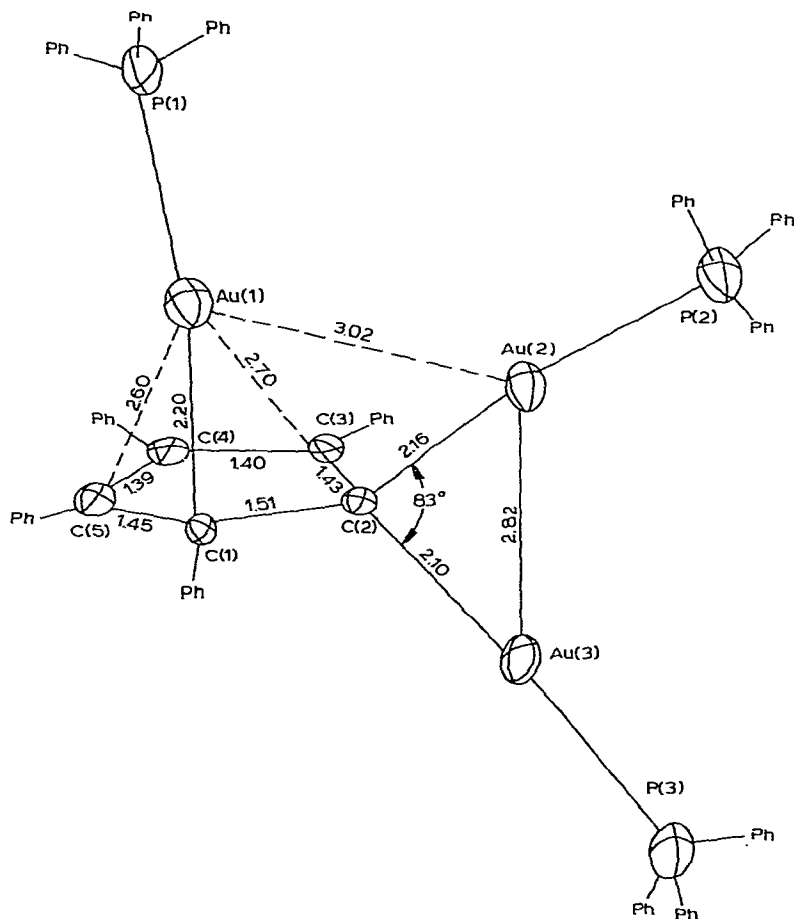


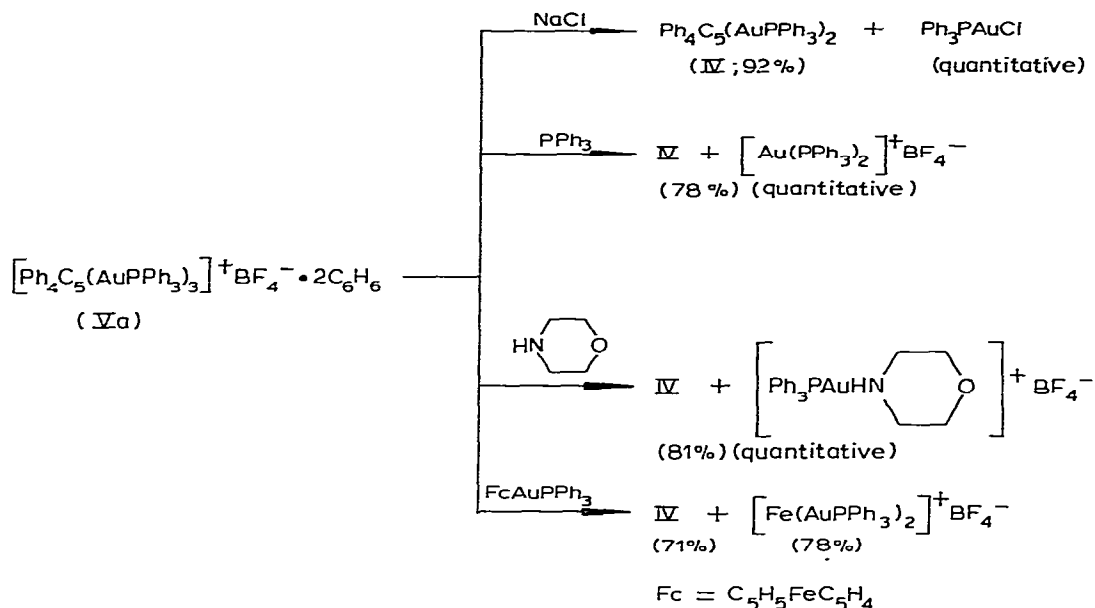
Fig. 2. The structure of the $[\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_3]^+$ cation.

$\text{C}(1)\text{Ph}$ (121°) and $\text{C}(5)\text{C}(1)\text{Ph}$ (129°) indicate considerable deviation of the $\text{C}(1)$ atoms from tetrahedral (sp^3) to planar-trigonal (sp^2) configuration.

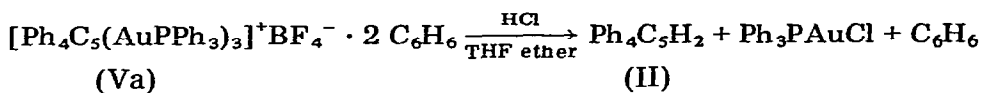
Comparison of bond lengths and angles of the $\text{C}(1)\text{Au}(1)\text{C}(2)\text{C}(5)$ fragment in complexes Va and I suggests that coordination of $\text{Au}(1)$ with $\text{C}(2)$ and $\text{C}(5)$ in Va is somewhat stronger than in Ia and that the distortion of the diene system in the tetraphenylcyclopentadienyl ring is stronger in Va.

The structure of complex Va is unique. It combines such rare structural fragments as the three-membered carbometalloycycle $\text{Au}-\text{C}-\text{Au}$, a chain of three gold atoms and tetracoordinated univalent gold bonded with three C atoms of the Ph_4C_5 ring.

The trinuclear cationic complex Va reacts with nucleophiles like the previously studied binuclear cationic complexes of gold do [1], the cation Ph_3PAu^+ being removed. The reaction of Va with various nucleophiles (NaCl, PPh_3 , morpholine, ferrocenyl derivative of gold) is shown below. In all cases a binuclear compound IV and a complex of the nucleophile with Ph_3PAu^+ is formed.



Phenyl(triphenylphosphine)gold, unlike ferrocenyl(triphenylphosphine)gold, is not nucleophilic enough to react with Va. Under the action of HCl all three Ph₃PAu groups are abstracted from Va and II is formed:



Experimental

IR spectra were recorded on an IKS-29 instrument as Nujol mulls; UV spectra on a Specord UV-VIS instrument in chloroform, PMR spectra were obtained with T-60 (working frequency 60 MHz) and XL-100 (working frequency 100 MHz) instruments; internal reference TMS; ³¹P NMR spectra with a C-60 HL instrument; working frequency 24.3 MHz, external reference H₃PO₄.

Mass spectra were obtained with a MS-30 instrument with a DS-50 data processing system; ion source temperature 250°C, injection temperature 120°C, ionization voltage 70 V.

GLC data were obtained on a TSVET chromatograph; 3 m × 4 mm column; Silicone SE 30, 5% on Chesasorb AW, HMDS, nitrogen as gas carrier, flame-ionization detector at 20 mm/min*.

Tetraphenylcyclopentadiene (II)

Synthesis of II was carried out according to a modified technique [13]. 200 ml of absolute ether was carefully added, while stirring and cooling with ice-water, to a mixture of 4.0 g (0.11 mol) of lithium aluminum hydride and 7.5 g

* O.A. Vasil'ev took part in this experiment.

(0.06 mol) of anhydrous aluminum chloride. The mixture was stirred for 5 min, cooling was stopped and, while stirring, 10.0 g (0.03 mol) of tetracyclone (m.p. 218°C) [12] and then 100 ml of abs. ether were added. The tetracyclone color rapidly disappeared and the mixture acquired a yellow-green color. Stirring was continued for 10 min at 20°C and then for 2 h at the boiling point of ether. The yellow-green color disappeared over this period and the mixture was refluxed for another hour while stirring. The excess of lithium aluminum hydride was quenched by careful addition of 175 ml of diluted (1 : 1) hydrochloric acid. 250 ml of benzene was then added and the mixture was stirred for 10 min. The organic layer was separated, washed with water and with two portions of saturated NaHCO₃ solution (200 ml) and then again with water and dried by Na₂SO₄. The filtered solution was evaporated under reduced pressure to dryness to yield 8.0 g (84%) of II. The product was dissolved in 80 ml of boiling benzene, the solution filtered, the filtrate diluted with 160 ml of ethanol and cooled to 5–6°C. The crystals of II formed were filtered, washed with 80 ml of petroleum ether and dried under vacuum to yield 7.0 g of II, m.p. 177–178°C (lit. [13]. m.p. 178°C).

Synthesis of tetraphenylcyclopentadienyl(triphenylphosphine)gold (I)

(a) *Auration of II in the presence of NaH.* A mixture of II (1.00 g, 2.8 mmol), III (1.00 g, 0.68 mmol) and NaH (0.02 g, 1.0 mmol) in 40 ml of abs. THF was stirred for 45 min. The oxonium salt was dissolved completely over this period. The solution obtained was filtered and evaporated to dryness under reduced pressure. The solid residue was dissolved in benzene, the solution obtained was added to 60 ml of ether/hexane (1/1) and stored for 1.5 h at 0°C for crystallization. The yellow crystals of I which formed were separated, washed with pentane and dried in air to give 1.40 g (83%) of I, m.p. 159–160°C, decomp. (after reprecipitation from solution in benzene with an ether/hexane mixture). Found: C, 68.06; H, 4.26; Au, 25.40. C₄₇H₃₆AuP calcd.: C, 68.10; H, 4.38; Au, 23.77%.

Compound I is a yellow crystalline substance readily soluble in chloroform, THF, benzene and insoluble in hexane. PMR spectrum (CDCl₃) δ: 7.36 m (35 H), 5.36 ppm d (1 H, ³J(¹H–³¹P) = 12 Hz). Decoupling of spin–spin interaction of the proton with ³¹P (double resonance) results in coalescence of the doublet into a singlet. IR spectrum: 1600w, 1550w, 1318w, 1245w, 1190w, 1165w, 1108w, 1065w, 1035w, 1006w, 918w, 850w, 820m, 795s, 766s, 740w, 700s cm⁻¹. The UV spectrum displays two maxima at 224 nm (ε = 4583 cm⁻¹ mol⁻¹) and 313 nm (ε = 671 cm⁻¹ mol⁻¹).

(b) *Auration of II in the presence of K₂CO₃.* A mixture of K₂CO₃ (0.15 g, 1.8 mmol), II (1.00 g, 2.7 mmol), water (1 ml) and 40 ml of THF was stirred for 5 min and then 1.00 g (0.68 mmol) of III was added. Stirring was continued for 4.5 h until the oxonium salt was completely dissolved. The solution was filtered and then treated as described in the previous experiment. Yield 1.30 g (79%) of I, m.p. 158–160°C (dec.).

(c) *From lithium tetraphenylcyclopentadienide and Ph₃PAuCl.* To 7.5 ml of a solution of butyllithium (8.5 mmol) in hexane 10 ml of THF was added, then were added dropwise at 0–5°C a suspension of 2.10 g (5.5 mmol) of II in 50 ml of abs. THF and after 30 min a suspension of 2.50 g (5.0 mmol) of Ph₃-

PAuCl in 40 ml of abs. THF were added. The reaction mixture was stirred at 10–15°C for 1.5 h and 20 ml of water was then added. The organic layer was separated, dried with K₂CO₃ for 15 min and evaporated to dryness under reduced pressure. Reprecipitation of the solid residue from a benzene/petroleum ether mixture afforded 3.30 g (81%) of I, m.p. 159–160°C (dec.). The IR, UV and PMR spectra of complex I obtained in experiments a, b and c are identical.

Synthesis of bis(triphenylphosphinegold)tetraphenylcyclopentadiene (IV)

A mixture of II (0.50 g, 1.4 mmol), tris(triphenylphosphinegold)oxonium tetrafluoroborate (1.00 g, 0.68 mmol) and NaH (0.05 g, 2.1 mmol) in 40 ml of abs. THF was stirred for 5 h. The white oxonium salts gradually dissolved and a bright yellow, finely crystalline precipitate of complex IV was formed which was separated from the solution. After evaporation of the solvent under reduced pressure, 0.05 g (10% in gold) of I was obtained, m.p. 158–160°C (dec.) (recipitated from a benzene/hexane mixture). Washing with alcohol, THF and ether gave 1.20 g (90%) of IV, decomp. above 200°C. Found: C, 60.07; H, 4.08; Au, 29.90. C₆₅H₅₀Au₂P₂ calcd.: C, 60.64; H, 3.94; Au, 30.61%. IR spectrum (cm⁻¹): 1593m, 1223w, 1098m, 1057w, 1025w, 998w, 792w, 774m, 761m, 745m, 695s.

Interaction of I with HBF₄ in the presence of triphenylphosphine

A solution of HBF₄ in ether was added dropwise to a solution of 0.20 g (0.24 mmol) of I and 0.07 g (0.26 mmol) of triphenylphosphine in 20 ml of THF until the solution became weakly acidic. The solution became colorless and a white crystalline precipitate of bis(triphenylphosphine)gold tetrafluoroborate was formed. It was filtered, and washed with benzene and ether to yield 0.20 g (98%) of [(Ph₃P)₂Au]⁺BF₄⁻, m.p. 224–226°C (dec.) (from methanol-hexane/ether), lit. [14]: m.p. 224–225°C (dec.). The filtrate was evaporated to dryness under reduced pressure, and the residue dissolved in benzene. Precipitation with petroleum ether afforded 0.10 g (quantitative yield) of II, which is identical in m.p. and IR and PMR spectra to an authentic sample.

Interaction of IV with hydrogen chloride

A suspension of 1.00 g (0.76 mmol) of IV in 25 ml of abs. CH₂Cl₂ was shaken for 15 min with 100 ml of 0.02 N HCl aqueous solution (2.0 mmol). IV was completely dissolved, the aqueous layer was removed, and the organic layer was thrice washed with 10 ml of water. 0.42 mmol of excess HCl was found in the combined aqueous extracts (titration with NaOH solution, phenolphthalein indicator). Therefore, IV and HCl react in a 1 : 2 molar ratio.

The CH₂Cl₂ solution was dried with anhydrous Na₂SO₄ and filtered. Evaporation to dryness of the filtrate under reduced pressure gave 1.10 g of a mixture of II and Ph₃PAuCl, which was extracted with 40 ml of benzene: II and part of the Ph₃PAuCl were dissolved. The undissolved residue was washed with a small amount of ether to give 0.35 g (61%) of Ph₃PAuCl, m.p. 242–243°C (lit. [15] m.p. 243–244°C).

The benzene solution was treated with excess aqueous silver trifluoroacetate in order to separate II from Ph₃PAuCl (Ph₃PAuCl is thus converted to the

oxonium salt $(\text{Ph}_3\text{PAu})_3\text{O}^+\text{CF}_3\text{COO}^-$ which is insoluble in benzene [16]). The precipitate consisting of silver chloride and the gold-containing oxonium salt was separated, and the benzene solution was dried with Na_2SO_4 and evaporated to dryness at reduced pressure. The residue was extracted with a ether/hexane mixture (1/2) and the extract evaporated to dryness, yielding 0.19 g (90%) of II which was identical in m.p., IR and PMR spectra to an authentic sample.

Synthesis of tris(triphenylphosphinegold)tetraphenylcyclopentadiene tetrafluoroborate (V)

(a) *By reaction of I with triphenylphosphinegold tetrafluoroborate.* A solution of $[\text{Ph}_3\text{PAu}]^+\text{BF}_4^-$ obtained from 0.238 g (0.48 mmol) of Ph_3PAuCl and 0.094 g (0.48 mmol) of silver tetrafluoroborate in 35 ml of abs. THF was added dropwise to a solution of 0.400 g (0.48 mmol) of I in 10 ml of abs. THF. The small amount of metallic gold formed was filtered off (0.008 g, 8%). The filtrate was added dropwise to 200 ml of ether/hexane mixture (1/1) for precipitation of V, which was then separated and washed with ether to yield 0.6 g (68%) of complex V in the form of fine yellow crystals, m.p. 210–212°C (dec.) (reprecipitated from 1/1/1 acetone/ether/hexane). Found: C, 54.58; H, 3.64. $\text{C}_{83}\text{H}_{65}\text{Au}_3\text{P}_3\text{BF}_4$ calcd.: C, 54.41; H, 3.52%.

After precipitation of V complex II (0.13 g) was obtained from the filtrate, and was identified by m.p. and IR and PMR spectra.

PMR spectrum of V (CDCl_3): δ 7.26 ppm m (C_6H_5). ^{31}P NMR spectrum (CDCl_3): one signal δ -36.02 ppm.

Reprecipitation of V from acetone/benzene/petroleum ether (1/1/1) gave a yellow crystalline solvate $[\text{Ph}_4\text{C}_5(\text{AuPPh}_3)_3]^+\text{BF}_4^- \cdot 2 \text{C}_6\text{H}_6$ (Va), m.p. 165–167°C (dec.). Found: C, 57.97; H, 3.94; Au, 28.68. $\text{C}_{95}\text{H}_{77}\text{Au}_3\text{P}_3\text{HF}_4$ calcd.: C, 57.36; H, 3.98; Au, 29.71%. Solvate Va is readily soluble in chloroform and acetone, but insoluble in benzene, ether and alkanes. IR spectrum (cm^{-1}): 1600w, 1320w, 1245w, 1195w, 1060s, 1018w, 920w, 875w, 800m, 778m, 720w, 700s. ^{31}P NMR spectrum (CHCl_3): one signal δ -36.02 ppm. The presence of C_6H_6 in Va was established by GLC after decomposition of Va with hydrogen chloride in diglyme.

(b) *By reaction of IV with triphenylphosphinegold borofluoride.* A solution of $[\text{Ph}_3\text{PAu}]^+\text{BF}_4^-$, obtained from 0.163 g (0.33 mmol) of Ph_3PAuCl and 0.064 g (0.33 mmol) of silver tetrafluoroborate in 20 ml of THF, was gradually added while stirring to a suspension of 0.141 g (0.11 mmol) of IV in 10 ml of THF. The mixture was stirred for 45 min until complete dissolution of IV. The solution was filtered and added dropwise while stirring to 200 ml of ether/petroleum ether (1/1). The precipitated yellow powder-like substance was isolated, washed with ether, dissolved in 4 ml of THF/acetone (1/3), and then 15 ml of benzene/ether/hexane (3/2/1) was added. Tris(triphenylphosphinegold)-oxonium tetrafluoroborate formed in the reaction precipitated (0.03 g). The solution was filtered, the filtrate diluted with hexane and stored for 8 h at 0° to crystallize. The yellow crystals of Va formed were washed with ether and pentane to yield 0.20 g (quantitative yield) of Va, m.p. 165–167°C (dec., in sealed capillary).

Reactions of complex Va

(a) *With sodium chloride.* A solution of 0.04 g (0.68 mmol) of NaCl in 0.5 ml of water was added to a solution of 0.07 g (0.04 mmol) of Va in 5 ml of acetone/THF (1/1). The yellow precipitate of IV formed was filtered off, washed with water, THF and ether to give 0.05 g (92%) of complex IV, which has an identical IR spectrum to complex IV obtained by auration of II. The filtrate was dried over sodium sulfate, and evaporated to dryness under reduced pressure to give 0.02 g (quantitative yield) of Ph_3PAuCl , m.p. 242–243°C (lit. [15]: 243–244°C).

(b) *With triphenyl phosphine.* A solution of 0.05 g (0.20 mmol) of triphenylphosphine in 5 ml of acetone was added to 0.20 g (0.10 mmol) of Va in 10 ml of acetone. A yellow crystalline precipitate of IV was gradually formed. An hour after beginning the reaction the precipitate was filtered off and washed with acetone and ether to give 0.15 g (78%) of complex IV. The filtrate was evaporated to 5 ml and cooled to 0°C. The white crystals formed were washed with benzene and ether giving 0.08 g (quantitative yield) of bis(triphenylphosphine)gold tetrafluoroborate, m.p. 224–226°C (from methanol/ether/hexane) (lit. [14]. m.p. 224–226°C).

(c) *With morpholine.* Several drops of morpholine were added to 1.00 g (0.05 mmol) of Va in 20 ml of acetone. After an hour the precipitate of IV was filtered off, washed with acetone and ether. 0.075 g (81%) of IV was obtained. Addition of petroleum ether to the filtrate gave 0.03 g (quantitative yield) of the solvate $[\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NHAuPPh}_3]^+\text{BF}_4^- \cdot (\text{CH}_3)_2\text{CO}$, m.p. 166–168°C (dec.) (from acetone/petroleum ether) (lit. [14]: 166–168°C, dec.).

(d) *With ferrocenyl(triphenylphosphine)gold.* A solution of 0.20 g (0.10 mmol) of Va in 5 ml of acetone was added to 0.06 g (0.09 mmol) of ferrocenyl(triphenylphosphine)gold in 5 ml of acetone. The solution gradually turned red and yellow crystalline IV precipitated. 40 min after beginning the reaction the precipitate was filtered off and washed with THF, acetone and ether, yielding 0.13 g (71%) of IV. The filtrate was diluted with petroleum ether until cloudy and stored for 10 h at 0°C. Crystallization yielded 0.13 g (78%) of bis(triphenylphosphinegold)ferrocene tetrafluoroborate, m.p. 160–161°C (dec.) (lit. [17]. m.p. 160–161°C, dec.).

Acknowledgement

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References

- 1 E.G. Perevalova, E.I. Grandberg, D.A. Lemenovskii and V.P. Dyadchenko, *Vestnik Mosk. Univ.*, Ser. II, 20 (1979) 299.
- 2 A.N. Nesmeyanov, E.G. Perevalova, D.A. Lemenovskii, T.V. Baikova and O.B. Afanasova, *J. Organometal. Chem.*, 65 (1974) 131.
- 3 R. Huttel, U. Raffay and H. Reinheimer, *Angew. Chem.*, 79 (1967) 859.
- 4 H. Schmidbeur and A. Shiotani, *Chem. Ber.*, 104 (1971) 2821.
- 5 A.N. Nesmeyanov, K.I. Grandberg, E.I. Smyslova and E.G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1972) 2375.
- 6 A.N. Nesmeyanov, E.G. Perevalova, V.V. Krivkykh, A.N. Kosina, E.I. Smyslova and K.I. Grandberg,

- Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 653.
- 7 H. Schmidbaur and R. Franke, Chem. Ber., 105 (1972) 2985.
 - 8 C.H. Campbell and M.L.H. Green, J. Chem. Soc. (A), (1971) 3282.
 - 9 A.N. Nesmeyanov, E.G. Perevalova, O.B. Afanasova, M.V. Tolstaya and K.I. Grandberg, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1118.
 - 10 A.N. Nesmeyanov, E.G. Perevalova, O.B. Afanasova and K.I. Grandberg, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1122.
 - 11 W.B. Pearson, Lattice Spacing and Structure of Metals and Alloys, Pergamon Press, London, 1957.
 - 12 B. Eistert and A. Langbein, Justus Liebigs Ann. Chem., 678 (1964) 88.
 - 13 H.M.N. Bandars, N.D.S. Rajasekera and S. Sotheeswaren, Tetrahedron, 30 (1974) 2587.
 - 14 K.I. Grandberg, T.V. Baukova, E.G. Perevalova and A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 206 (1972) 1355.
 - 15 C. Cowals and J.M. Swan, Austral. J. Chem., 19 (1966) 547.
 - 16 A.N. Nesmeyanov, E.G. Perevalova, Yu.T. Struchkov, M.Yu. Antipin, K.I. Grandberg and V.P. Dyadchenko, J. Organometal. Chem., 201 (1980) 343.
 - 17 E.G. Perevalova, D.A. Lemenovskii, K.I. Grandberg and A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 202 (1972) 93.
 - 18 T.V. Baukova, Yu.L. Slovokhotov and Yu.T. Struchkov, J. Organometal. Chem., in press.