

## CHARACTERISTIC STRUCTURAL FEATURES OF POST-TRANSITION METAL CYCLOPENTADIENYL DERIVATIVES

### I. TETRAPHENYLCYCLOPENTADIENYL(TRIPHENYLPHOSPHINE)-GOLD(I) ( $\text{Ph}_4\text{HC}_5\text{AuPPh}_3$ )

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#### Summary

The gold(I) complex of tetraphenylcyclopentadiene,  $\text{Ph}_4\text{C}_5\text{HAuPPh}_3$  (I), has been obtained for the first time by interaction both between  $\text{Ph}_4\text{C}_5\text{H}_2$  and  $[(\text{AuPPh}_3)_3\text{O}]^+\text{BF}_4^-$  and between  $\text{Ph}_4\text{HC}_5\text{Li}$  and  $\text{Ph}_3\text{PAuCl}$ . The structure of I was determined by an X-ray crystal analysis (3913 reflections,  $R = 0.049$ ). Crystals of I are monoclinic, at  $-120^\circ\text{C}$   $a = 13.303(2)$ ,  $b = 12.951(2)$ ,  $c = 21.117(4)$  Å,  $\beta = 96.60(1)^\circ$ ,  $Z = 4$ , space group  $P2_1/c$ . An unusual feature was found in the interaction of the Au atom with the Cp ring, viz. a coordination intermediate between  $\eta^1(\sigma)$  and  $\eta^3$ . In accordance with PMR spectroscopy data, complex I, unlike other  $\eta^1$ -cyclopentadienyl compounds of monovalent gold, is a stereochemically rigid system with a fixed  $\text{H}-\overset{\text{C}}{\underset{\text{AuPPh}_3}{\text{C}}}$  fragment.

#### Introduction

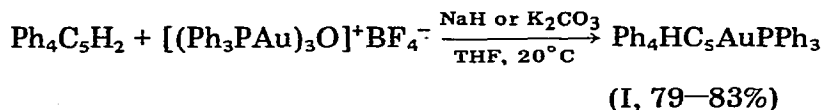
The stereochemistry of cyclopentadienyl derivatives of Au and Hg has for some years attracted the attention of scientists who have used IR and NMR spectroscopy to elucidate their structure [1]. However, X-ray structural data on cyclopentadienyl derivatives of elements at the end of the long periods and, especially, of post-transition elements are rather limited. The structurally studied Cp complexes of metals in the Cu, Zn and Ga subgroups are represented by a few examples, unlike derivatives of the Sc–Co sub-groups. At the present time structures of  $(\text{C}_5\text{H}_5)\text{CuPPh}_3$  (II), with a symmetrical  $\eta^5$  coordination of the Cp ligand [2], the ylide complex of divalent mercury  $\{[\text{Ph}_3\text{PC}_5\text{H}_4\text{Hg}]\text{I}_2\}_2$  (III) [3] and the polymeric complex  $(\text{C}_5\text{H}_5)_3\text{In}$  (IV) [4] have been determined. In the last two compounds the metal atom is bonded to the Cp ligand predominantly in the  $\eta^1$  mode. Since complexes of monovalent gold have features in

common with both  $\text{Cu}^{\text{I}}$  complexes and  $\text{Hg}^{\text{II}}$  compounds, the mode of coordination of Au in Cp complexes is of great interest.

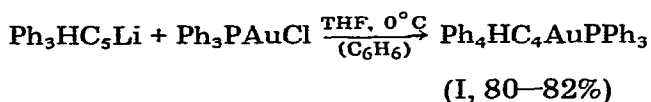
In the present paper the synthesis of a tetraphenylcyclopentadienyl-Au<sup>I</sup> complex,  $\text{Ph}_4\text{HC}_5\text{AuPPh}_3$ , is described for the first time, and its structure as determined by an X-ray crystal analysis.

## Results and discussion

We obtained tetraphenylcyclopentadienyl(triphenylphosphine)gold(I) by two ways: by auration of tetraphenylcyclopentadiene with tris(triphenylphosphine)gold(oxonium tetrafluoroborate) in the presence of an alkaline agent (NaH or  $\text{K}_2\text{CO}_3$ ):



and by reaction of  $\text{Ph}_4\text{HC}_5\text{Li}$  with the triphenylphosphine complex of monovalent gold chloride:



Complex I is moderately stable in air and gradually decomposes with formation of tetraphenylcyclopentadienone, but the thermal stability of I is much higher than that of  $\text{C}_5\text{H}_5\text{AuPPh}_3$  [6].

The PMR spectrum of I in  $\text{CDCl}_3$  contains a complex multiplet from the phenyl protons ( $\delta = 7.36$  ppm) and a doublet from the cyclopentadienyl proton centred at  $\delta = 5.36$  ppm with  ${}^3J(^1\text{H}-{}^{31}\text{P}) = 12$  Hz. Proton- ${}^{31}\text{P}$  spin decoupling results in coalescence of the doublet into a singlet ( $\delta = 5.35$  ppm). The value of  ${}^3J(^1\text{H}-{}^{31}\text{P})$  found for I is typical for the organogold complexes  $\text{RAuPPh}_3$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{Ph}, \text{CH}_2\text{COCH}_3$ ) containing a fixed  $\text{H}-\overset{\text{C}}{\underset{\text{P}}{\text{C}}}-\text{AuPPh}_3$  fragment with a Au-C  $\sigma$ -bond [7–10]. Thus, complex I is stereochemically rigid, unlike the Cp derivatives of monovalent gold  $\text{RH}_4\text{C}_5\text{AuPPh}_3$  ( $\text{R} = \text{H}, \text{CH}_3$ ), in which a rapid metallotropic isomerization is observed ( ${}^3J(^1\text{H}-{}^{31}\text{P})$  constants are 2.8 and 4.8 Hz respectively [11]).

As shown earlier, addition of small quantities of free phosphine  $\text{PR}'_3$  to monovalent gold phosphine complexes  $\text{RAuPR}'_3$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{Ph}, \text{CH}_2\text{COCH}_3$ ;  $\text{R}' = \text{Alk}, \text{Ar}$ ) leads to the coalescence of the proton doublet of the  $\text{H}-\overset{\text{C}}{\underset{\text{P}}{\text{C}}}-\text{AuPR}'_3$  fragment in the NMR spectra into a narrow singlet as a consequence of fast exchange of phosphine ligands through intermediate formation of the bis-phosphine complex  $\text{RAu}(\text{PR}'_3)_2$  [9,12].

Addition of free  $\text{PPh}_3$  to a solution of I in  $\text{CDCl}_3$  (molar ratio  $\text{PPh}_3$  : I of 1 : 2) results only in a significant broadening of the Cp proton signal ( $\delta = 5.36$  ppm) in the PMR spectrum of I, but the coalescence of the doublet components into a narrow singlet is not observed. Thus, in the case of I formation of an intermediate biphosphine complex seems to be hindered, which leads to significant slowing down (on the NMR time scale) of exchange processes between phosphine ligands.

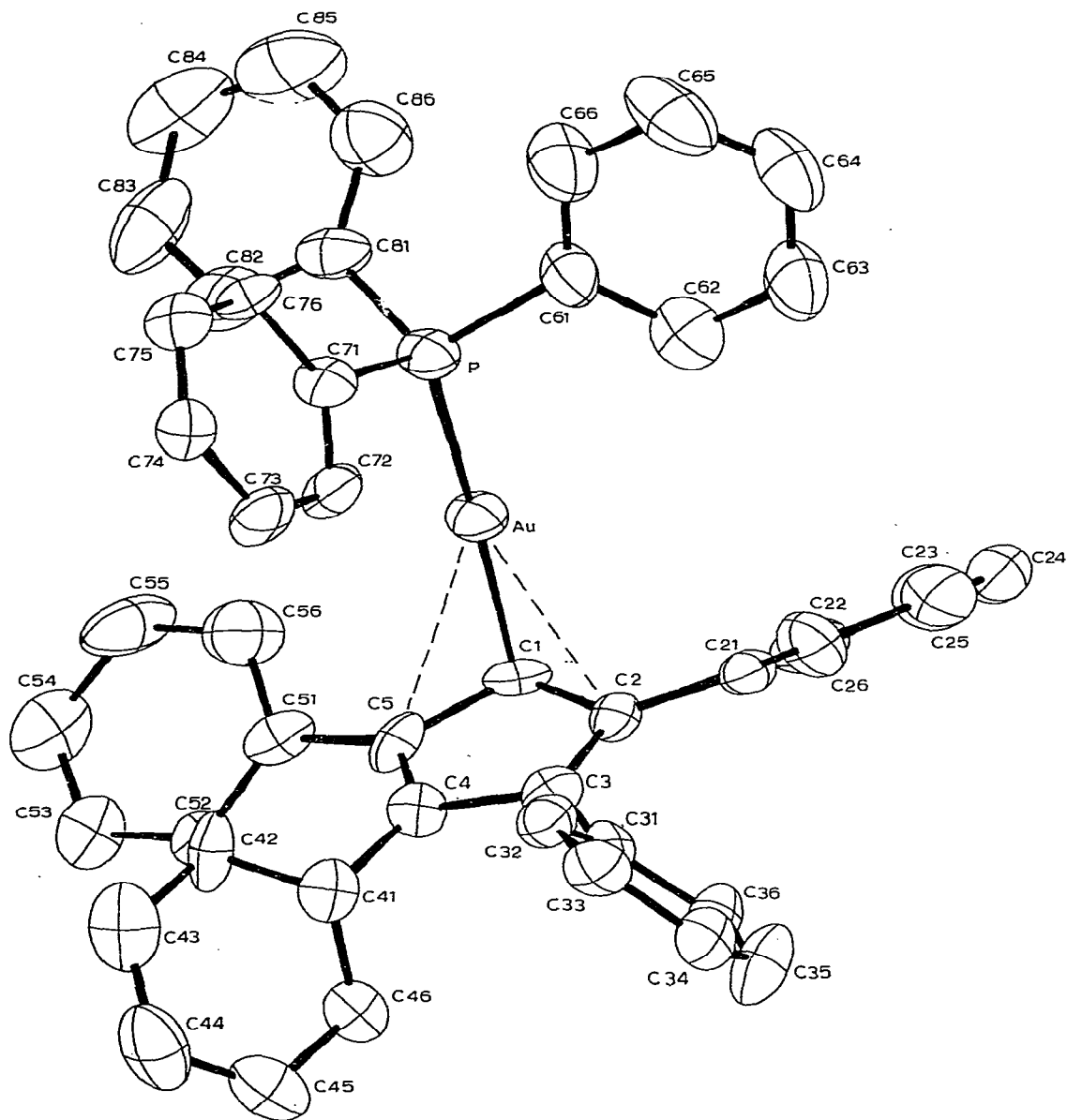


Fig. 1. An ORTEP drawing of a molecule of compound I.

To elucidate the mode of coordination of the Au atom by the tetraphenylcyclopentadienyl ligand in complex I we carried out its X-ray structure study.

Crystals of I are built up of discrete  $\text{Ph}_4\text{HC}_5\text{AuPPh}_3$  molecules at normal Van der Waals distances from each other. The molecular structure of I is shown in Fig. 1, bond lengths are presented in Table 1 and bond angles in Table 2. The molecule I represents a monocyclopentadienyl compound of Au(1+) (with a formal  $d^{10}$  electron configuration). The Au atom is linearly coordinated to P and C(1) atoms, the bond length Au—P of 2.239(3) and Au—C(1) of 2.15(1)

(Continued on p. 130)

TABLE 1  
BOND LENGTHS  $d$  (Å)

Bond	$d$	Bond	$d$	Bond	$d$
Au—P	2.239(3)	C(24)—C(25)	1.39(3)	C(55)—C(56)	1.40(2)
Au—C(1)	2.15(1)	C(25)—C(26)	1.41(2)	C(61)—C(62)	1.41(2)
Au—C(2)	2.67(1)	C(31)—C(32)	1.36(2)	C(61)—C(66)	1.36(2)
Au—C(5)	2.76(1)	C(31)—C(36)	1.38(2)	C(62)—C(63)	1.39(2)
P—C(61)	1.84(1)	C(32)—C(33)	1.40(2)	C(63)—C(64)	1.37(2)
P—C(71)	1.82(1)	C(33)—C(34)	1.39(2)	C(64)—C(65)	1.34(3)
P—C(81)	1.82(1)	C(34)—C(35)	1.37(2)	C(65)—C(66)	1.36(3)
C(1)—C(2)	1.47(2)	C(35)—C(36)	1.39(2)	C(71)—C(72)	1.39(2)
C(1)—C(5)	1.46(2)	C(41)—C(42)	1.39(2)	C(71)—C(76)	1.37(2)
C(2)—C(3)	1.39(2)	C(41)—C(46)	1.39(2)	C(72)—C(73)	1.38(2)
C(2)—C(21)	1.47(2)	C(42)—C(43)	1.40(2)	C(73)—C(74)	1.38(2)
C(3)—C(4)	1.45(2)	C(43)—C(44)	1.39(3)	C(74)—C(75)	1.36(2)
C(3)—C(31)	1.51(2)	C(44)—C(45)	1.36(3)	C(75)—C(76)	1.39(2)
C(4)—C(5)	1.38(2)	C(45)—C(46)	1.37(2)	C(81)—C(82)	1.36(2)
C(4)—C(41)	1.47(2)	C(51)—C(52)	1.40(2)	C(81)—C(86)	1.35(2)
C(5)—C(51)	1.48(2)	C(51)—C(56)	1.39(2)	C(82)—C(83)	1.39(3)
C(21)—C(22)	1.38(2)	C(52)—C(53)	1.42(2)	C(83)—C(84)	1.39(3)
C(21)—C(26)	1.40(2)	C(53)—C(54)	1.35(2)	C(84)—C(85)	1.39(3)
C(22)—C(23)	1.40(2)	C(54)—C(55)	1.42(3)	C(85)—C(86)	1.40(3)
C(23)—C(24)	1.36(3)				

TABLE 2  
BOND ANGLES  $\omega$  (DEGREES)

Angle	$\omega$	Angle	$\omega$	Angle	$\omega$
PAuC(1)	178.6(3)	C(1)C(5)C(4)	109(1)	C(51)C(52)C(53)	120(1)
PAuC(2)	147.7(3)	C(1)C(5)C(51)	124(1)	C(52)C(53)C(54)	122(1)
PAuC(5)	147.2(3)	C(4)C(5)C(51)	127(1)	C(53)C(54)C(55)	118(2)
C(1)AuC(2)	33.3(4)	C(2)C(21)C(22)	121(1)	C(54)C(55)C(56)	121(2)
C(1)AuC(5)	31.7(4)	C(2)C(21)C(26)	122(1)	C(51)C(56)C(55)	120(1)
C(2)AuC(5)	51.1(4)	C(22)C(21)C(26)	117(1)	PC(61)C(62)	118(1)
AuPC(61)	114.0(5)	C(21)C(22)C(23)	122(1)	PC(61)C(66)	123(1)
AuPC(71)	112.5(4)	C(22)C(23)C(24)	121(2)	C(62)C(61)C(66)	119(1)
AuPC(81)	110.8(5)	C(23)C(24)C(25)	120(2)	C(61)C(62)C(63)	120(1)
C(61)PC(71)	105.3(6)	C(24)C(25)C(26)	119(2)	C(62)C(63)C(64)	119(2)
C(61)PC(81)	109.7(6)	C(21)C(26)C(25)	121(1)	C(63)C(64)C(65)	118(2)
C(71)PC(81)	104.0(6)	C(3)C(31)C(32)	119(1)	C(64)C(65)C(66)	125(2)
AuC(1)C(2)	93.4(8)	C(3)C(31)C(36)	122(1)	C(61)C(66)C(65)	118(2)
AuC(1)C(5)	97.8(8)	C(32)C(31)C(36)	119(1)	PC(71)C(72)	117.6(9)
C(2)C(1)C(5)	106(1)	C(31)C(32)C(33)	120(1)	PC(71)C(76)	122.1(9)
AuC(2)C(1)	53.3(6)	C(32)C(33)C(34)	120(1)	C(72)C(71)C(76)	120(1)
AuC(2)C(3)	104.0(8)	C(33)C(34)C(35)	119(1)	C(71)C(72)C(73)	120(1)
AuC(2)C(21)	102.6(8)	C(34)C(35)C(36)	120(1)	C(72)C(73)C(74)	120(1)
C(1)C(2)C(3)	107(1)	C(31)C(36)C(35)	121(1)	C(73)C(74)C(75)	119(1)
C(1)C(2)C(21)	123(1)	C(4)C(41)C(42)	121(1)	C(74)C(75)C(76)	122(1)
C(3)C(2)C(21)	130(1)	C(4)C(41)C(46)	120(1)	C(71)C(76)C(75)	119(1)
C(2)C(3)C(4)	110(1)	C(42)C(41)C(46)	119(1)	PC(81)C(82)	116(1)
C(2)C(3)C(31)	127(1)	C(41)C(42)C(43)	121(1)	PC(81)C(86)	123(1)
C(4)C(3)C(31)	122(1)	C(42)C(43)C(44)	118(1)	C(82)C(81)C(86)	121(1)
C(3)C(4)C(5)	108(1)	C(43)C(44)C(45)	121(2)	C(81)C(82)C(83)	119(2)
C(3)C(4)C(41)	124(1)	C(44)C(45)C(46)	120(1)	C(82)C(83)C(84)	123(2)
C(5)C(4)C(41)	128(1)	C(41)C(46)C(45)	121(1)	C(83)C(84)C(85)	115(2)
AuC(5)C(1)	50.4(6)	C(5)C(51)C(52)	121(1)	C(84)C(85)C(86)	123(2)
AuC(5)C(4)	103.5(8)	C(5)C(51)C(56)	120(1)	C(81)C(86)C(85)	119(2)
AuC(5)C(51)	111.3(8)	C(52)C(51)C(56)	119(1)		

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TABLE 3  
LEAST-SQUARES PLANES IN THE MOLECULE OF I

Plane <sup>a</sup>	Coefficients of plane equations $Ax + By + Cz + D = 0$				Deviations of atoms from mean planes (Å)
	A	B	C	D	
I	0.2542	-0.1919	-0.9479	6.4129	C(1) (-0.02), C(2) (0.02), C(3) (-0.01), C(4) (-0.01), C(5) (0.02), C(21) <sup>b</sup> (-0.01), C(31) <sup>b</sup> (-0.15), C(41) <sup>b</sup> 0.05, C(51) <sup>b</sup> (0.14), Au <sup>b</sup> (-2.15)
II	0.3894	0.4017	-0.8289	3.1914	C(21) (0.01), C(22) (0.09), C(23) (-0.02), C(24) (0.02), C(25) (-0.01), C(26) (-0.01), C(2) <sup>b</sup> (-0.03)
III	0.9508	-0.1646	-0.2624	0.4194	C(31) (0.00), C(32) (0.01), C(33) (0.00), C(34) (-0.01), C(35) (0.01), C(36) (-0.01), C(3) <sup>b</sup> (0.00)
IV	0.2534	-0.9215	-0.2944	-4.2487	C(41) (-0.01), C(42) (0.01), C(43) (-0.01), C(44) (0.01), C(45) (0.09), C(46) (0.00), C(4) <sup>b</sup> (0.01)
V	-0.3434	-0.4168	-0.6416	-8.1445	C(51) (-0.01), C(52) (0.00), C(53) (0.01), C(54) (-0.01), C(55) (0.00), C(56) (0.01), C(5) <sup>b</sup> (-0.04)

<sup>a</sup> Dihedral angles between planes (degrees): I/II 36.1, I/III 58.5, I/IV 58.7, I/V 37.8, II/III 58.6, II/IV 91.6 II/V 66.6, III/IV 62.0, III/V 92.1, IV/V 57.0.

<sup>b</sup> These atoms are not included in the calculation of plane equations.

Å having the usual values [13]. The five-membered cycle C(1)—C(5) is planar to within 0.02 Å (Table 3), its bond length distribution is characteristic of a diene structure: two bonds, C(2)—C(3) of 1.39(2) and C(4)—C(5) of 1.38(2) Å, are shortened significantly as compared with the other three bonds, C(1)—C(2) of 1.47(2), C(1)—C(5) of 1.46(2) and C(3)—C(4) of 1.45(2) Å. The *ipso*-carbons of the Ph substituents are only slightly displaced from the Cp ligand plane (Table 3). In agreement with the NMR data, the above-mentioned structural features are indicative of  $\eta^1(\sigma)$  coordination of the Au atom to the tetraphenylcyclopentadienyl ligand. However, the bond angles C(2)C(1)Au of  $93.4(8)^\circ$  and C(5)C(1)Au of  $97.8(8)^\circ$  are significantly smaller than the tetrahedral value of  $109.5^\circ$ , typical of  $sp^3$  hybridization of a carbon atom, and the distances Au...C(2) of 2.67(1) and Au...C(5) of 2.76(1) Å correspond to a weak (“secondary”) coordination of the Au atom with the respective C atoms. This indicates a more complicated type of metal—cyclopentadienyl interaction in I, which seems to be described more correctly as a case of coordination intermediate between  $\eta^1(\sigma)$  and  $\eta^3(\pi\text{-allyl})$ .

The unusual nature of the Au atom coordination in I, which differs strongly from the symmetrical  $\eta^5$  bonding in the copper complex II of similar stoichiometry, gives rise to a number of questions. To explain the structure of I, it is of interest to compare structural data on Cp compounds of transition and post-transition metals. The chemistry of organic derivatives of the nickel sub-group metals and, further, the copper and zinc sub-groups is known to be characterized by a number of features distinguishing these metals from “typical” transition ones. The most important of these features are the tendency to decreasing characteristic coordination number and the stability of a not fully occupied electron shell (16e for Pt, 14e for Au). The second feature, i.e. violation of the EAN rule, is also seen in the fact that the useful Wade’s rule (“ $2n + 2$ ”) [14] which enables prediction of the geometry of cluster and polyhedral compounds, seems to be inapplicable to “framework” compounds of Pt and is completely invalid in the case of Cu and Au complexes. The inconsistency of Au cluster structures with the “ $2n + 2$ ” rule has been treated theoretically [15]: according to EHM calculations, the participation of metal *p*-orbitals in cluster bonding is negligible which, in its turn, is a result of increasing energy difference between *s*- and *p*-AO’s of the outer electron shell on moving from transition to post-transition metals in the periodic table [16]. A decrease in coordination ability of the metal atom is seen clearly in a series of polyhedral metal carbaboranes, in which a change was found in the coordination of a metal by the nido-polyhedron  $C_2B_9H_{11}$  from “symmetrical” in the case of Fe and Co derivatives through “slipped” towards B atoms (like the  $\pi$ -allyl type) in the case of Ni, Cu and Au to a rather unusual interaction in  $Ph_3PHgC_2B_9H_{11}$  with one short Hg—B bond of 2.20 Å and two “secondary” Hg...B bonds of 2.50 and 2.53 Å [17]. Apparently, the latter type of coordination is rather similar to that observed in I.

Turning from metal carbaboranes to  $\pi$ -cyclopentadienyl derivatives, which also may be considered as “framework” compounds (containing a 6-vertex nido-polyhedron  $\eta^5-C_5H_5M$  [14]), it is natural to expect analogous structural features, though it must be taken into account that the presence of different types of atoms (B and C) in a metal carbaborane framework facilitates distortion of the polyhedron geometry. Unfortunately, there are a number of gaps

in the available structural data on Cp-transition metal derivatives (for example, accurate structure investigations of Cp complexes of Pt and post-transition metals are lacking). Nevertheless, the available information allows one to draw a certain parallel between metal carbaboranes and Cp derivatives and to establish unambiguously a successive opening of the M—Cp “framework” on passing from transition to post-transition metals. As found in a series of structures of Cp-transition metal derivatives, the completely symmetrical  $\eta^5$  coordination in the M—Cp unit, which is characteristic of ferrocene (Fe—C distances of 2.018–2.048(5) Å [18]) and cobaltocene (Co—C 2.079–2.111(8) Å [19]), is violated in Rh, Ir and Pd compounds where the difference in M—C(Cp) bond lengths reaches 0.10–0.15 Å, i.e. becomes statistically significant for an accurate structural investigation and is usually specially indicated in the corresponding papers [20–23]. For example, in  $\text{Ph}_4\text{ClC}_5\text{Rh}(\text{C}_2\text{H}_4)_2$  the Rh—C(Cp) distances vary from 2.183(4) Å (for the C atom bonded to Cl) to 2.305 Å, the difference of 0.122 Å being far beyond experimental errors, and the distribution of bond lengths in the Cp ligand clearly reveals a contribution from the diene structure. It should be noted that the above-mentioned structural features are retained in  $\text{Cl}_5\text{C}_5\text{Rh}(\text{COD})$  (COD = cycloocta-1,4-diene), with a symmetrically substituted Cp ligand [20]. The structure of  $(\text{C}_5\text{H}_5)\text{Ir}(\text{CO})\text{PPh}_3$ , containing an unsubstituted Cp ligand, also reveals a difference in the Ir—C(Cp) distances of 2.23–2.30(1) Å [21]. In the binuclear  $(\text{Ph}_5\text{C}_5)_2\text{Pd}_2\text{Ph}_2\text{C}_2$  complex with symmetrically substituted Cp ligands the Pd—C(Cp) distances are 2.27–2.37 Å at one Pd atom and 2.32–2.46 Å at the other [22]. In the ylide  $\pi$ -complex  $\text{Ph}_3\text{PC}_5\text{H}_4\text{Pd}[\text{C}_4(\text{COOMe})_4]$ , which contains a chelate palladacyclopentadiene fragment, the Pd—C(Cp) distances vary from 2.334(6) to 2.447(6) Å. There are two long C—C bonds of 1.47(1) and 1.46(1) and three short bonds of 1.39(1)–1.42(2) Å in the planar Cp ligand; on the whole the distribution of bond lengths indicates a noticeable contribution from  $\eta^3$  coordination which is in agreement with NMR data [23]. A similar non-equivalence of the metal—C(Cp) distances is found in cyclopentadienylnickel derivatives [24,25]. In structures of  $(\text{C}_5\text{H}_5)\text{PtMe}_3$  [26] and  $(\text{C}_{10}\text{H}_8)\text{Pt}_2(\text{C}_5\text{H}_5)_2$  [27] the Pt—C(Cp) distances vary within 0.2–0.3 Å, but the experimental accuracy of these investigations does not justify any conclusions on the significance of the discrepancies mentioned.

Both a majority of the 12-vertex metal carbaboranes with a “slipped” framework involving  $\pi$ -allyl type M— $\text{C}_2\text{B}_9\text{H}_{11}$  bonding and the Cp complexes considered with a “distorted”  $\eta^5$  M— $\text{C}_5\text{H}_5$  coordination formally obey the EAN rule (i.e. with a normal, symmetrical coordination of  $\text{C}_2\text{B}_9\text{H}_{11}$  or  $\text{C}_5\text{H}_5$  fragments the M atom should possess an 18-electron outer shell). At present, Cp-transition metal complexes in which the M atom is bonded to  $\text{C}_5\text{H}_5$  in a “slipped”  $\pi$ -allyl mode are unknown, if with the usual  $\eta^5$  M—Cp coordination the metal atom attains an inert gas configuration. However, formally 20-electron Cp complexes of W have been studied, viz. derivatives of  $(\text{C}_5\text{H}_5)_2\text{W}(\text{CO})_2$ , wherein one of the two Cp ligands is coordinated in the  $\eta^3$  mode and bent so that the W atom actually has a stable 18-electron shell [28]. Similar distortions may be supposed for the formally 18-electron Cp derivatives of Pt and, possibly, Au, but at the present time such complexes have not been structurally characterized.

The known structures of Cp derivatives of Hg (complex III) [2] and In (complex IV) [3] involve a M—Cp fragment with its geometry being on the

whole similar to I, viz. the preferred  $\eta^1$  coordination of a 5-membered cycle, but with decreased (as compared to tetrahedral) M—C(Cp)—C(Cp) bond angles ( $98.7$  and  $101.2(7)^\circ$  in III,  $90.3$ – $101.3(6)^\circ$  in two terminal Cp ligands in IV), and a diene system of C—C bonds in the Cp ligand with shortened C—C distances (as compared with normal C—C bonds not involved in a butadiene fragment). The contribution of  $\pi$ -allyl Au—Cp coordination in I is more pronounced than in III and IV\*. As a whole, the comparison of structures I, III and IV shows that the distortion of the symmetrical  $\eta^5$  coordination of Cp derivatives of the heavy post-transition elements is displayed much more strongly than in derivatives of metals of the Co and Ni sub-groups, leading to a “nearly  $\eta^1$ ” M—Cp bond, although the symmetrical  $\eta^5$  metal—ring bonding observed in II corresponds to the attainment of a 18-electron shell (in I–IV the formal electron configuration of a metal atom is  $d^{10}$ ).

According to the data quoted, filling of the  $d$  shell in the transition metal series is accompanied in some cases by progressive “opening” of the polyhedral system both of metal carbaboranes and  $\pi$ -cyclopentadienyl complexes. In both classes of compounds maximum distortions are observed for the heavy post-transition metals ( $d^{10}$ ). Further filling of the valence shell AO's results, however, not in “pure”  $\eta^1$  coordination but again in polyhedral  $\eta^5$  structures. A relevant example among metal carbaboranes is the monovalent thallium ( $d^{10}s^2$ ) derivative, viz. the “polyhedral” anion  $[(C_2B_9H_{11})Tl]^-$  [17]. The monocyclopentadienide of monovalent indium,  $C_5H_5In$ , also has a pyramidal structure according to gas electron diffraction data [30], while in complex IV where In has the +3 oxidation state ( $d^{10}$ ), the In— $C_5H_5$  bonding is close to  $\eta^1$  coordination. Symmetrical  $\eta^5$  coordination of the Cp ligand is found in the “wedge-like sandwich”  $(C_5H_5)_2-Sn$  and in the cation  $[(C_5Me_5)Sn]^+$  [31]. In these “polyhedral” complexes of non-transition metals, with their  $d$ -AO's unable to take part in ligand bonding, the “ $2n + 2$ ” rule is followed and the M atom is to some degree an analog of the apical C atom in the dication  $C_6Me_6^{2+}$ , for which a pyramidal structure was postulated on the basis of spectral data [32]. It is not excluded that the subdivision of complexes with a similar (“polyhedral”) structure into “ $\pi$ -complexes” of transition metals and “framework” compounds of non-transition metals reflects only a lack of structural information on non-transition metal  $\pi$ -complexes, since fulfilment of the “ $2n + 2$ ” rule by both of them suggests a similar type of the metal—ring interaction, viz. a participation of  $s$ - and  $p$ -AO's of the outer shell of the metal in a delocalized polyhedral system [33].

The whole family of metal-Cp derivatives may be thus considered as a class of “framework” compounds containing a pyramidal CpM fragment which for certain M elements may undergo more or less significant distortions. Examples of symmetrical  $\eta^5$  coordination include both “classical”  $\pi$ -complexes of  $d$ -metals, such as  $(C_5H_5)_2Fe$  or  $C_5H_5Mn(CO)_3$ , and the considerably less well studied “non-classical” framework structures such as  $[(Me_5C_5)Sn]^+$ . Distortions

\* We have found [29] that in the crystal structure of diaurated derivative of I, viz.  $[Ph_3PAuC_5Ph_4(AuPPh_3)_2]^+[BF_4]^-$ , a contribution from the  $\eta^3$  coordination of one of Au atoms is displayed even more clearly than in I: the “ $\sigma$ ” bond Au(1)—C(1) is elongated to  $2.21(2)$  Å ( $2.15(1)$  Å in I) and the “secondary” bonds Au(1)···C(2) of  $2.60(2)$  and Au(1)···C(5) of  $2.71(2)$  Å are somewhat shortened ( $2.67(1)$  and  $2.76(1)$  Å in I); the Au(1)C(1)C(2) and Au(1)C(1)C(5) bond angles are  $91(1)$  and  $88(1)^\circ$ , respectively (atom numbering in the 5-membered cycle is the same as in I).



of the symmetrical  $\eta^5$  coordination of the Cp ligand occur at the end of the transition metal series and reach their maximum for Au and Hg. This fact is in agreement with an increase of the energy gap between the *s*- and *p*-sublevels of the outer shell in the series  $\text{Pt}^- \rightarrow \text{Ag}^0 \rightarrow \text{Hg}^+ \rightarrow \text{Tl}^{2+}$  [16], which must prevent the involvement of metal *p*-AO's in metal-ring bonding. A further filling of the electron shells of the Group III and IV elements decreases the polyhedron distortion and again makes possible  $\eta^5$  coordination\*.

The symmetrical Cu-Cp bonding in II (Cu-C(Cp) distances of 2.190(3)–2.232(2) Å [2]) is not easily understood on the basis of the above considerations although it may be compared with the smaller value of the energy gap between *s*- and *p*-AO's for Cu as compared with Au [16]. Introduction of various substituents into a five-membered cycle seems to favour a distortion of the M-Cp coordination: as an undirect proof of this supposition may serve the absence of  $\text{Ph}_3\text{PAu}$  group migration (on the NMR time scale) in solutions of I, while for  $\text{Ph}_3\text{PAu}(\text{C}_5\text{H}_5)$  a rapid metallotropic process is observed [11]. In this respect a determination of the crystal structure of a  $\text{Cu}^{\text{I}}$  derivative similar in composition to I, viz.  $\text{Ph}_4\text{HC}_5\text{CuPPh}_3$ , and/or the gold complex  $\text{C}_5\text{H}_5\text{AuPPh}_3$  with an unsubstituted cyclopentadienyl ligand, would be of great importance.

The symmetrical coordination of Au or Hg not realized in crystals of I and III respectively, may in principle occur as a transition state of the metallotropic rearrangement of Cp derivatives of these elements in solution [1]. The disadvantage of the mechanism consisting of H and  $\text{SiH}_3$  migration over the Cp centre in comparison to the 1;2-shift was demonstrated by CNDO calculations [34], but for heavy post-transition metals an intermediate  $\eta^5$  (or  $\eta^3$ ) state may turn out to be additionally stabilized. The various ways of Cp ligand bonding with elements similar in their chemical properties and position in the Periodic system are of undoubted interest and make further structure investigations of cyclopentadienyl derivatives of Pt, Au and Hg desirable.

## Experimental

The IR spectra were registered with an IKS-29 instrument in Nujol mulls. The UV spectrum was measured with a Specord UV-Vis instrument in  $\text{CHCl}_3$ , PMR spectra were obtained with a T-60 spectrometer at a working frequency of 60 MHz and with an XL-100 instrument at a working frequency of 100 MHz using TMS as an internal standard.

X-ray diffraction data were obtained with a four-circle Syntex  $\text{P2}_1$  automatic diffractometer at  $-120^\circ\text{C}$  ( $\lambda$  Mo- $K_\alpha$ , graphite monochromator,  $\theta/2\theta$  scan,  $2 \leq 2\theta \leq 46^\circ$ , 5069 independent reflections, including 3913 with  $I > 2\sigma$ , the absorption was neglected).

Crystals of I are monoclinic, at  $-120^\circ\text{C}$   $a = 13.303(2)$ ,  $b = 12.951(2)$ ,  $c = 21.117(4)$  Å,  $\beta = 96.60(1)^\circ$ ,  $V = 3614(1)$  Å<sup>3</sup>,  $M = 828$ ,  $d_{\text{calcd.}} = 1.530$  g/cm<sup>3</sup>,  $Z = 4$ , space group  $\text{P2}_1/c$ .

The structure was solved by the heavy atom technique and refined by least

\* In this discussion, one should distinguish between Cp derivatives of metals (both transition and post-transition) which can realize the  $\eta^5$  coordination with a Cp ligand according to the EAN or "2n + 2" rules and "true"  $\sigma$ -Cp complexes such as  $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_5$  and  $\text{C}_5\text{H}_5\text{SnR}_3$ .

TABLE 4  
 ATOMIC COORDINATES ( $\times 10^4$ ,  $\times 10^5$  for Au) <sup>a</sup>

Atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Au	17487(4)	19352(4)	42321(2)	3.90(2)	3.94(3)	1.94(2)	-0.18(3)	0.55(3)	-0.58(2)
P	1349(3)	2145(8)	5225(2)	3.3(2)	4.2(2)	2.2(1)	-0.3(1)	0.7(1)	-0.8(1)
C(1)	2162(10)	1708(9)	3289(6)	3.7(6)	3.1(7)	2.2(5)	-0.5(5)	1.4(4)	0.2(4)
C(2)	1956(9)	2788(10)	3103(5)	2.8(6)	3.9(7)	1.4(5)	-0.3(5)	-0.2(4)	0.0(4)
C(3)	2870(10)	3315(9)	3204(6)	3.6(6)	3.1(7)	2.1(5)	-0.1(5)	0.3(4)	-0.8(4)
C(4)	3680(10)	2603(10)	3422(6)	3.5(6)	2.2(6)	2.3(5)	0.2(5)	0.4(4)	-1.2(5)
C(5)	3258(10)	1636(9)	3458(5)	4.1(7)	2.5(6)	1.3(5)	0.1(5)	-0.2(4)	-0.3(4)
C(21)	933(3)	3187(11)	2901(6)	3.0(6)	4.2(7)	2.3(5)	-0.4(6)	0.4(4)	0.7(5)
C(22)	222(11)	2592(13)	2539(7)	4.4(8)	6.0(9)	3.6(7)	-2.7(7)	-0.2(6)	0.5(5)
C(23)	-187(13)	2936(18)	2367(9)	3.9(8)	9(1)	5.9(9)	-4.0(9)	-0.7(7)	0.8(9)
C(24)	-1054(12)	3894(19)	2537(9)	3.2(7)	9(1)	5.6(9)	-0.9(8)	-0.1(7)	3.2(9)
C(25)	-375(13)	4512(15)	2918(9)	5.0(9)	7(1)	6.2(9)	1.6(8)	1.9(8)	1.6(8)
C(26)	615(10)	4153(13)	3099(7)	3.1(7)	5.2(9)	5.9(8)	-0.4(6)	0.4(6)	0.3(7)
C(31)	3039(9)	4462(9)	3160(6)	2.6(5)	2.2(6)	3.0(6)	0.6(4)	0.7(4)	-0.2(5)
C(32)	3453(10)	4971(10)	3689(6)	3.5(6)	3.1(6)	2.8(6)	0.2(5)	0.6(5)	0.2(5)
C(33)	3612(10)	6035(10)	3670(7)	3.3(6)	2.9(7)	4.3(7)	-0.7(5)	0.5(5)	-0.1(6)
C(34)	3356(11)	6581(10)	3108(7)	4.1(7)	2.4(6)	4.6(8)	0.5(5)	0.6(6)	0.0(5)
C(35)	2953(12)	6061(11)	2572(7)	6.5(9)	3.3(7)	3.7(7)	1.2(6)	-0.5(6)	0.5(6)
C(36)	2774(10)	5006(10)	2605(6)	4.2(7)	3.1(6)	3.1(6)	1.1(5)	0.1(5)	-0.1(5)
C(41)	4755(9)	2896(8)	3538(6)	3.4(6)	1.5(6)	3.2(6)	0.4(4)	0.0(5)	-0.5(4)
C(42)	5316(11)	2705(10)	4122(7)	4.4(7)	2.0(5)	4.0(7)	0.6(5)	-1.7(5)	0.0(5)
C(43)	6346(12)	2960(11)	4226(9)	4.8(8)	2.9(7)	7.2(9)	-1.3(6)	-2.5(7)	-1.4(7)
C(44)	6802(11)	3360(13)	3718(10)	3.1(7)	4.4(9)	9(1)	-0.7(5)	1.1(5)	0.0(5)

C(46)	5243(9)	3397(9)	3947(6)	3.4(6)	1.9(6)	3.9(6)	-0.3(4)	0.4(5)	-0.5(5)
C(51)	3798(10)	655(10)	3608(6)	4.7(7)	2.4(6)	2.6(6)	-1.3(5)	0.3(5)	-0.3(5)
C(52)	4741(10)	461(10)	3403(6)	4.0(7)	3.2(7)	3.3(6)	-0.1(5)	0.5(5)	-0.2(6)
C(53)	5252(11)	-479(11)	3565(7)	5.5(8)	2.5(7)	4.3(7)	0.2(6)	0.3(6)	-0.8(6)
C(54)	4855(14)	-1208(11)	3916(8)	8(1)	1.8(7)	5.8(9)	0.7(7)	1.1(8)	0.0(6)
C(55)	3884(15)	-1025(12)	4116(8)	9(1)	3.2(7)	5.8(9)	0.3(8)	3.5(8)	1.3(7)
C(56)	3364(12)	-102(12)	3954(8)	5.6(8)	3.9(8)	5.9(9)	0.6(7)	2.2(7)	0.4(7)
C(61)	209(10)	2935(12)	5274(7)	3.3(6)	5.7(9)	3.2(6)	0.6(6)	0.1(5)	-0.9(6)
C(62)	-195(11)	3479(12)	4726(7)	4.0(7)	4.5(8)	4.5(8)	-0.7(6)	-0.2(6)	-1.5(6)
C(63)	-1001(12)	4150(14)	4750(8)	3.9(7)	7(1)	5.0(8)	0.7(6)	-1.0(6)	-0.6(8)
C(64)	-1445(11)	4226(14)	5304(9)	3.6(7)	7(1)	6.1(9)	0.6(7)	-0.4(7)	-2.1(9)
C(65)	-1049(13)	3673(16)	5811(10)	4.1(8)	8(1)	7(1)	0.5(8)	1.9(8)	-3.2(9)
C(66)	-237(12)	3037(15)	5820(7)	4.9(8)	10(1)	3.7(7)	2.9(9)	0.5(6)	-1.3(8)
C(71)	2851(10)	2786(10)	5744(6)	3.6(6)	3.7(7)	2.0(5)	-0.2(5)	0.8(5)	-1.2(5)
C(72)	2991(10)	3450(11)	5462(6)	4.1(7)	4.1(7)	2.6(6)	-0.9(6)	0.0(5)	0.8(6)
C(73)	3731(11)	3990(11)	5839(7)	4.6(7)	3.4(7)	3.9(7)	-0.9(6)	0.5(5)	1.6(6)
C(74)	3818(10)	3890(10)	6496(6)	3.6(6)	2.4(6)	3.8(7)	-0.2(5)	-0.2(5)	-0.2(6)
C(75)	3185(10)	3239(10)	6764(6)	4.1(6)	3.7(7)	2.6(6)	-0.6(6)	0.4(5)	-0.8(6)
C(76)	2450(10)	2672(10)	6394(6)	4.5(7)	3.5(6)	1.9(5)	-0.4(5)	0.8(5)	0.2(5)
C(81)	1206(11)	902(11)	5607(6)	4.2(7)	4.5(7)	2.4(6)	-1.3(6)	0.8(5)	-0.8(6)
C(82)	2002(14)	241(14)	5616(8)	7(1)	6(1)	4.3(8)	2.0(9)	2.3(7)	0.6(7)
C(83)	1935(18)	-733(14)	5886(9)	12(2)	4.1(9)	5.1(9)	2.0(9)	-0.1(9)	0.6(8)
C(84)	1086(19)	-1055(15)	6154(9)	10(1)	5(1)	5.8(9)	-5(1)	-0.8(9)	0.4(8)
C(85)	323(18)	-335(19)	6152(10)	9(1)	7(1)	8(1)	-4(1)	2(1)	0(1)
C(86)	353(13)	621(14)	5851(9)	4.8(8)	5.0(9)	8(1)	-0.8(7)	0.9(8)	0.2(8)

<sup>a</sup> Anisotropic temperature factors are given in the form:  $T = \exp[-1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$ .

squares in the anisotropic approximation. Positions of the hydrogen atoms of the Ph rings were calculated geometrically, and these atoms were included in the refinement with a fixed positional and isotropic thermal ( $B_{\text{iso}} = 5.0 \text{ \AA}^2$ ) parameters. Finally,  $R = 0.049$ ,  $R_w = 0.068$  for 3474 independent reflections with  $F^2 > 5\sigma$ . All calculations were performed with an Eclipse S/200 mini-computer with modified EXTL programs\*. Coordinates of non-hydrogen atoms and parameters of anisotropic temperature factors are listed in Table 4.

#### *Tetraphenylcyclopentadiene*

A mixture of 4.0 g (0.11 mol) of  $\text{LiAlH}_4$  and 7.5 g (0.06 mol) of  $\text{AlCl}_3$  at  $0^\circ\text{C}$  in 200 ml of absolute ether was stirred, and after 5 min 10.0 g (0.03 mol) of tetracyclone (m.p.  $218^\circ\text{C}$ ) [35] and 100 ml of absolute ether were added: the mixture became yellow-green in colour. The reaction mixture was stirred first at  $20^\circ\text{C}$  for 10 min and then under reflux for 3 hours (the solution became colourless). The excess of  $\text{LiAlH}_4$  was carefully decomposed with 175 ml of diluted (1 : 1)  $\text{HCl}$ , then 250 ml of benzene was added and the mixture was stirred for 10 min more. The organic layer was separated, washed with water, washed twice with saturated  $\text{NaHCO}_3$  solution, again with water and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The solution was filtered and evaporated to dryness. 7.0 g of  $\text{Ph}_4\text{C}_5\text{H}_2$  were obtained, m.p.  $177\text{--}178^\circ\text{C}$  (lit.  $178^\circ\text{C}$  [36]).

#### *Tetraphenylcyclopentadienyl(triphenylphosphine)gold(I)*

*a) Auration of  $\text{Ph}_4\text{C}_5\text{H}_2$  in the presence of  $\text{NaH}$ .* A mixture of 1.00 g (2.8 mmol) of  $\text{Ph}_4\text{C}_5\text{H}_2$ , 1.00 g (0.68 mmol) of tris(triphenylphosphine)gold oxonium tetrafluoroborate and 0.02 g (1 mmol) of  $\text{NaH}$  in 40 ml of absolute THF was stirred for 45 min. The oxonium salt dissolved completely. The solution obtained was filtered and the solvent removed in vacuo. The solid residue was dissolved in benzene, and the solution was added to 60 ml of the mixture of ether and hexane (1 : 1) and was left to stand for 1.5 hours at  $0^\circ\text{C}$ . The yellow crystalline precipitate formed was separated, washed with pentane and dried in air. 1.40 g (83%) of I were obtained, m.p.  $159\text{--}160^\circ\text{C}$  (with decomposition) (after precipitation from the benzene solution by the ether-hexane mixture). Found: C, 68.06; H, 4.26; Au, 23.40.  $\text{C}_{47}\text{H}_{36}\text{AuP}$  calcd.: C, 68.10; H, 4.38; Au, 23.77%.

Compound I is a yellow crystalline substance, well soluble in  $\text{CHCl}_3$ , THF, benzene and practically insoluble in hexane. PMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.36 (35 H), 5.36 (1 H,  $^3J(^1\text{H}\text{--}^31\text{P}) = 12 \text{ Hz}$ ). IR ( $\text{cm}^{-1}$ ): 1600m, 1350w, 1318w, 1245w, 1190w, 1165w, 1108w, 1065w, 1035w, 1006w, 918w, 850w, 820m, 795s, 766w, 700s. In the UV spectrum two absorption maxima are observed: 224 nm ( $\epsilon = 4583 \text{ cm}^{-1} \text{ mol}^{-1}$ ) and 313 nm ( $\epsilon = 671 \text{ cm}^{-1} \text{ mol}^{-1}$ ).

*b) Auration of tetraphenylcyclopentadiene in the presence of  $\text{K}_2\text{CO}_3$ .* A mixture of 0.15 g (1.8 mmol) of  $\text{K}_2\text{CO}_3$ , 1.00 g (2.7 mmol) of  $\text{Ph}_4\text{C}_5\text{H}_2$  and 1 ml of water in 40 ml of THF was stirred for 5 min, and then 1.00 g (0.68 mmol) of tris(triphenylphosphine)gold oxonium tetrafluoroborate was added. Stirring was continued for 4.5 hours until the oxonium salt was dissolved completely.

\* Modification of EXTL programs was carried out by A.I. Yanovsky and R.G. Gerr (Institute of Organo-Element Compounds of the U.S.S.R. Academy of Sciences).

The solution obtained was filtered and treated as in the previous experiment: 1.30 g (79%) of I were obtained, m.p. 158–160°C with decomposition.

c) *From lithium tetraphenylcyclopentadienide and Ph<sub>3</sub>PAuCl*. To 7.5 ml of a 1.14 N solution (8.5 mmol) of n-BuLi in hexane were added 10 ml of absolute THF. Then a suspension of 2.10 g (5.5 mmol) of Ph<sub>4</sub>C<sub>5</sub>H<sub>2</sub> in 30 ml of absolute THF was added dropwise at 0–5°C; after 30 min a suspension of 2.50 g (5.0 mmol) of Ph<sub>3</sub>PAuCl in 40 ml of absolute THF was added. The reaction mixture was stirred at 10–15°C for 1.5 hours, and then 20 ml of water was added. The organic layer was separated, dried with K<sub>2</sub>CO<sub>3</sub> for 15 min, evaporated to dryness in vacuo and the solid residue was reprecipitated from a benzene-petroleum ether mixture: 3.30 g (81%) of I were obtained as pink crystals, m.p. 159–160°C with decomposition.

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