

Characteristic structural features of cyclopentadienyl derivatives of post-transition metals

III *. Synthesis and structure of fluorenyl (triphenylphosphine)gold(I)

Yu.T. Struchkov, Yu.L. Slovokhotov, D.N. Kravtsov*, T.V. Baukova,

A.N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, Vavilov St. 28, Moscow 117813 (U.S.S.R.)

E.G. Perevalova and K.J. Grandberg

Chemistry Department, Moscow State University, Leninskie Gory, Moscow, B-234 (U.S.S.R.)

(Received June 17th, 1987)

Abstract

The fluorenyl gold derivative $C_{13}H_9AuPPh_3$ (I) was obtained by fluorene auration with the complex $[(AuPPh_3)_3O]^+BF_4^-$ or interaction of $C_{13}H_9Li$ or $C_{13}H_9Na$ with $ClAuPPh_3$. An X-ray structure study of I ($-120^\circ C$, λ Mo, 8192 reflections, space group $P2_1/c$, $Z = 12$, $R = 0.024$) shows that the Au atom in I has η^1 coordination. Moreover, the structure of three geometrically different, crystallographically independent molecules of I in crystal indicates limited structural non-rigidity, i.e. pendular motion" of the $AuPPh_3$ group at the sp^3 -hybridized carbon atom of the fluorenyl ligand. The PMR spectral characteristics of I are typical of stereochemically rigid σ -organic gold(I) derivatives.

Introduction

At present the organic derivatives of monovalent gold of the $RAuL$ type are prepared mainly by two methods: (i) interaction of the organic derivatives of alkaline or alkaline-earth metals with complex gold salts [1] and (ii) direct auration of organic compounds with the salts of the gold-containing oxonium cation [2,3]. Tris(triphenylphosphine)gold(oxonium)borofluoride was shown to represent a fairly versatile aurating agent which can be effectively used for auration of various types

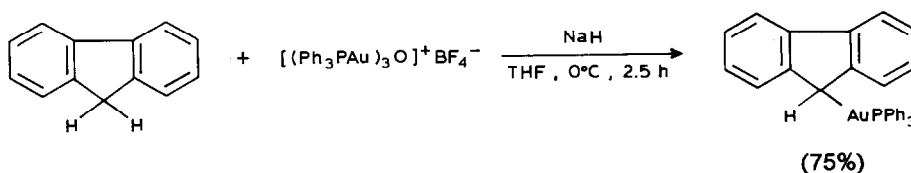
* For parts I and II see refs. 11 and 12, respectively.

of organic compounds [4,5]. On the basis of data obtained up to now it can be concluded that the tendency of a hydrocarbon to undergo auration correlates qualitatively with its C–H acidity. Weak C–H acids such as alkanes and benzene ($pK_a = 43$ [6]) * cannot be aured, and thus alkyl- and arylgold compounds are prepared by use of the first method only. Cyclopentadienyl gold derivatives (pK_a of cyclopentadiene is 16.6 [6]) can be successfully prepared by both methods [7–9]. Alkylgold derivatives with substituents displaying pronounced electron-acceptor properties were only obtained by auration of corresponding compounds with a high C–H acidity. However, applicability limits of the auration reaction remain uncertain.

We have studied the behaviour of fluorene ($pK_a = 22.8$ [6]) under auration conditions which permits setting a lower limit to the applicability of auration of organic compounds with $[O(AuPPh_3)_3]^+BF_4^-$. We also prepared the fluorenyl gold derivative by a different method, viz., by the reaction of $ClAuPPh_3$ with lithium and sodium fluorene derivatives.

Results and discussion

The auration of fluorene with tris(triphenylphosphinegold)oxonium under ordinary conditions (3/1 reactant ratio, at 20 °C, for 15–20 min) is not at all successful. Increasing the reaction time and varying the reactant ratio gives the same result. Compound I could be prepared in high yield if the reaction was carried out in tetrahydrofuran (THF) in the presence of sodium hydride, with the addition of a small excess of fluorene is at the final (and not at the initial) reaction stage.

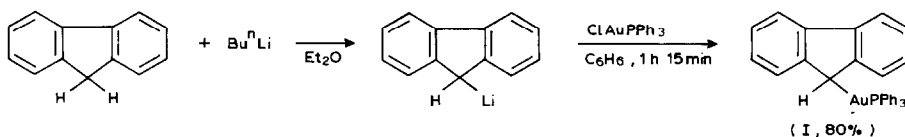


It is noteworthy that auration of fluorene occurs more slowly (over 2 h) than that of cyclopentadiene (15 min) or tetraphenylcyclopentadiene (45 min) [9], which is consistent with CH acidity decreasing in the order cyclopentadiene – $Ph_4C_5H_2$ – fluorene [6]. It is likely that the auration reaction cannot be used for the preparation of gold derivatives of hydrocarbons whose acidity is lower than that of fluorene.

In the synthesis of 9-fluorenyl(triphenylphosphine)gold (I) from fluorenyl derivatives of alkali metals and $ClAuPPh_3$ we encountered serious difficulties. In this case it is important to select right conditions; an appropriate solvent, reaction temperature, reagent ratio and order in which the reactants are mixed. It was found that in solvents such as THF the reaction does not proceed to completion despite the addition of a significant excess of fluorenyllithium and heating of the reaction mixture, and the process is accompanied by decomposition, with precipitation of metal gold.

Reaction of a large excess of 9-fluorenyllithium with $AuClPPh_3$ in benzene gives I without admixture of starting $AuClPPh_3$.

* The pK_a values of hydrocarbons are given according to the Streitwieser scale (in cyclohexylamine).



However, I thus obtained is contaminated with fluorenol and fluorenone. A comparison of literature and our data indicates that oxygen-containing by-products are obtained mainly at the first stage of the reaction, i.e. metallation of fluorene with butyllithium [10].

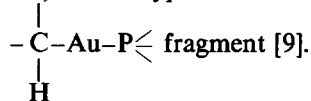
When 9-fluorenylsodium is used, the yield of I increases but the amount of oxygen-containing fluorene derivatives from side-reactions remains about the same.

Compound I is unstable and thus cannot be purified by chromatography. Most of the impurities can be removed by washing the reaction product with pentane, with subsequent recrystallizing from a toluene/petroleum ether mixture.

Compound I is a colourless crystalline substance, well soluble in benzene, acetone, chloroform and THF. In solutions it decomposes fairly rapidly with precipitation of gold metal whereas addition of small amounts of PPh_3 suppresses decomposition.

The PMR spectrum of I (in C_6H_6 and CDCl_3) shows, besides the multiplet signal of the aromatic system protons, a proton doublet due to the cyclopentadienyl moiety of the fluorene molecule at δ 4.68 ppm ($^3J(^1\text{H}-^{31}\text{P})$ 16 Hz). Thus, as expected, the introduction of an AuPPh_3 group into position 9 of the fluorene molecule results in a significant downfield shift of the proton signal from position 9 of the fluorenyl ligand compared with the position of the signals of these protons in the spectrum of fluorene itself (δ 3.71 ppm).

The coupling constant of this proton signal splitting on the phosphorus atom (16 Hz) turned out to be somewhat greater than the common value of this constant (12 Hz) and is typical of all stereochemically rigid σ -organic gold derivatives with the



Addition of a small amount of PPh_3 to the solution of I results in the coalescence of this proton doublet into a singlet. From earlier data [9] it was seen that addition of PPh_3 to a solution of the tetraphenylcyclopentadienylgold derivative only serves to broaden the cyclopentadienyl proton signal without coalescence of the doublet components, which indicates more rapid exchange processes in I.

The structure of cyclopentadienyl Au^{I} compounds is of great interest because recently an unusual type of Au^{I} -cyclopentadienyl bonding has been found. This bonding type represents an extreme case of the π -coordination distortion in cyclopentadienyl derivatives of the post-transition elements [11-14]. In the structure of aurated cyclopentadienes [11-14] an elongation of the $\text{Au}-\text{C}$ σ -bond up to 2.15-2.20 Å and short $\text{Au} \cdots \text{C}$ contacts of 2.6-2.8 Å with carbon atoms in the positions 2 and 5 of the five-membered cycle, a weak attractive interaction was found. In such compounds the Au -cyclopentadienyl coordination can be regarded as being intermediate between $\sigma(\eta^1)$ and π -allyl (η^3). Therefore it was important to undertake an X-ray structure study of an Au^{I} derivative with a fluorenyl ligand, to which the five-membered carbocycle is attached via its multiple bonds into the π -systems of phenylene fragments.

(Continued on p. 274)

Table 1
Atomic coordinates ($\times 10^4$ for C, $\times 10^5$ for Au and P, $\times 10^3$ for H) and thermal parameters a (B (\AA^2)) for the three different molecules of I

Atom	Molecule IA				Molecule IB				Molecule IC			
	x	y	z	B^a	x	y	z	B^a	x	y	z	B^a
Au	19395(3)	13219(1)	45516(1)	2.28(1)	24240(3)	62354(1)	29807(1)	2.32(1)	45865(3)	85466(1)	13171(1)	2.33(1)
P	22499(18)	2064(8)	44195(4)	2.16(4)	19545(19)	51682(8)	27749(4)	2.36(4)	40204(18)	96033(8)	11250(4)	2.24(4)
C(1)	1597(6)	2363(3)	4640(1)	2.2(2)	2786(7)	7272(3)	3095(1)	2.6(2)	4997(7)	7512(3)	1407(2)	2.7(2)
C(2)	677(6)	2462(3)	4926(1)	2.3(2)	3685(7)	7387(3)	3411(1)	2.4(2)	5428(7)	7356(3)	1756(2)	2.5(2)
C(3)	-779(7)	2286(3)	4968(2)	2.9(3)	5172(7)	7264(3)	3493(2)	2.9(2)	6753(7)	7446(3)	1943(2)	3.1(2)
C(4)	-1389(7)	2454(3)	5259(2)	3.5(2)	5771(7)	7417(3)	3812(2)	3.1(2)	6864(8)	7263(3)	2273(2)	3.8(2)
C(5)	-582(8)	2773(3)	5513(2)	3.7(2)	4875(8)	7680(3)	4048(2)	3.1(2)	5654(8)	6954(3)	2424(2)	3.7(2)
C(6)	853(7)	2960(3)	5480(2)	2.9(2)	3405(7)	7801(3)	3968(2)	2.9(2)	4324(8)	6856(3)	2246(2)	3.3(3)
C(7)	1488(7)	2807(3)	5183(2)	2.3(2)	2801(7)	7667(3)	3647(1)	2.4(2)	4205(7)	7070(3)	1910(1)	2.5(2)
C(8)	2939(6)	2966(3)	5073(1)	2.3(2)	1334(7)	7793(3)	3492(1)	2.4(2)	3012(7)	6995(3)	1660(1)	2.4(2)
C(9)	4135(7)	3302(3)	5231(2)	3.1(2)	60(7)	8073(3)	3613(2)	3.4(2)	1591(8)	6738(3)	1675(2)	3.6(2)
C(10)	5378(8)	3415(4)	5064(2)	4.0(2)	-1162(7)	8160(3)	3396(2)	3.4(2)	684(8)	6689(4)	1382(2)	4.3(2)
C(11)	5425(7)	3192(4)	4740(2)	3.7(2)	-1133(7)	7987(3)	3067(2)	3.5(2)	1230(8)	6886(3)	1079(2)	4.0(2)
C(12)	4244(7)	2861(3)	4580(2)	3.1(2)	101(7)	7697(3)	2942(2)	3.1(2)	2602(8)	7144(3)	1064(2)	3.3(2)
C(13)	2993(7)	2728(3)	4747(2)	2.5(2)	1359(7)	7591(3)	3158(2)	2.6(2)	3511(7)	7216(3)	1355(1)	2.5(2)
C(111)	3156(6)	-330(3)	4735(1)	2.2(2)	3612(7)	4730(3)	2664(1)	2.5(2)	5676(7)	10032(3)	1015(1)	2.3(2)
C(112)	2752(7)	-247(3)	5058(2)	2.8(2)	3956(7)	4077(3)	2775(2)	2.9(2)	6070(7)	10683(3)	1124(2)	2.9(2)
C(113)	3264(7)	-684(3)	5304(2)	3.1(2)	5238(7)	3765(3)	2684(2)	3.6(2)	7366(8)	10970(3)	1042(2)	3.7(2)
C(114)	4223(7)	-1201(3)	5237(1)	2.7(2)	6136(7)	4087(3)	2475(2)	3.2(2)	8285(7)	10614(3)	844(2)	3.3(2)
C(115)	4674(7)	-1269(3)	4920(2)	2.9(2)	5821(7)	4739(4)	2367(2)	3.2(2)	7907(7)	9983(3)	731(1)	2.8(2)
C(116)	4158(7)	-840(3)	4672(1)	2.5(2)	4551(7)	5061(3)	2461(2)	3.1(2)	6609(7)	9684(3)	819(2)	2.8(2)
C(121)	516(6)	-228(3)	4318(1)	2.3(2)	843(7)	5239(3)	2388(1)	2.3(2)	2902(7)	9532(3)	740(1)	2.4(2)
C(122)	56(7)	-792(3)	4485(2)	2.7(2)	958(7)	4778(3)	2128(3)	3.2(2)	1787(7)	9049(3)	711(2)	2.8(2)
C(123)	-1321(7)	-1087(3)	4398(2)	2.3(2)	32(8)	4829(3)	1845(2)	3.4(2)	947(7)	8964(4)	423(2)	3.5(2)
C(124)	-2183(7)	-831(3)	4141(2)	3.4(2)	-1032(7)	5329(3)	1816(2)	3.0(2)	1194(8)	9360(4)	150(2)	4.1(2)
C(125)	-1741(7)	-270(4)	3970(2)	3.5(2)	-1159(7)	5787(3)	2069(2)	2.9(2)	2295(8)	9846(4)	172(2)	3.9(2)

C(126)	-390(7)	33(3)	4060(2)	3.1(2)	-223(7)	5742(3)	2350(2)	2.7(2)	3119(7)	9931(3)	468(2)	2.9(2)
C(131)	3248(6)	111(3)	4048(1)	2.1(2)	982(6)	4557(3)	3014(1)	2.5(2)	3030(6)	10202(3)	1371(1)	2.2(2)
C(132)	4101(7)	633(3)	3938(1)	2.6(2)	86(8)	4062(4)	2862(2)	3.7(2)	3195(7)	10152(3)	1714(2)	3.8(2)
C(133)	4875(1)	555(3)	3659(2)	3.0(2)	-588(7)	3573(4)	3050(2)	3.6(2)	2449(8)	10607(4)	1905(2)	3.0(2)
C(134)	4844(7)	-51(3)	3487(1)	2.8(2)	-392(7)	3588(3)	3388(2)	3.4(2)	1579(7)	11105(3)	1758(2)	2.9(2)
C(135)	3981(7)	-583(3)	3593(2)	2.9(2)	472(9)	4089(4)	3541(2)	4.8(2)	1410(7)	11148(3)	1421(2)	2.9(2)
C(136)	3166(6)	-499(3)	3867(2)	2.5(2)	1168(8)	4571(4)	3355(2)	3.8(2)	2140(7)	10703(3)	1227(2)	6(2)
H(1)	126(5)	255(3)	444(1)	2(1)	312(5)	741(2)	291(1)	2(1)	558(7)	736(3)	124(2)	4(2)
H(2)	-128(5)	206(2)	481(1)	2(1)	575(6)	709(3)	335(1)	3(1)	759(6)	764(3)	182(1)	4(1)
H(3)	-231(5)	234(2)	527(1)	2(1)	698(6)	731(3)	386(1)	4(2)	782(6)	737(3)	240(1)	6(2)
H(4)	-99(6)	286(3)	569(1)	4(2)	526(6)	773(3)	428(1)	3(1)	565(7)	687(3)	266(2)	4(2)
H(5)	141(6)	318(3)	565(1)	3(1)	275(5)	798(2)	412(1)	1(1)	331(7)	675(3)	237(1)	2(1)
H(6)	403(7)	346(3)	547(1)	5(2)	8(5)	820(2)	387(1)	2(1)	126(5)	661(2)	188(1)	3(1)
H(7)	633(7)	365(3)	518(2)	5(2)	-214(6)	834(3)	349(1)	3(1)	-25(6)	652(3)	140(1)	7(2)
H(8)	631(6)	323(3)	463(1)	3(2)	-191(5)	801(2)	291(1)	1(1)	47(8)	684(4)	88(2)	5(2)
H(9)	430(7)	268(3)	435(1)	4(2)	11(7)	758(3)	269(1)	6(2)	284(7)	729(3)	85(2)	5(2)
HC(112)	220(6)	14(3)	510(1)	3(1)	331(6)	383(3)	292(1)	3(1)	554(6)	1089(3)	125(1)	5(2)
HC(113)	297(6)	-59(3)	550(1)	3(1)	552(7)	328(3)	277(2)	5(2)	763(7)	1146(3)	114(1)	4(2)
HC(114)	452(7)	-150(3)	538(2)	4(2)	702(6)	386(3)	240(1)	3(1)	913(6)	1077(3)	78(1)	3(1)
HC(115)	520(5)	-162(2)	487(1)	2(1)	638(6)	494(3)	224(1)	2(1)	841(6)	972(3)	62(1)	3(1)
HC(116)	450(5)	-90(3)	444(1)	2(1)	430(6)	549(3)	238(1)	2(1)	640(6)	928(3)	78(1)	3(1)
HC(122)	63(6)	-98(3)	464(1)	2(1)	177(5)	447(2)	214(1)	2(1)	167(6)	880(3)	89(1)	6(2)
HC(123)	-163(5)	-148(2)	454(1)	1(1)	7(8)	448(4)	168(2)	7(2)	27(8)	866(3)	39(2)	6(2)
HC(124)	-312(7)	-103(3)	408(1)	4(2)	-167(6)	541(3)	160(1)	3(1)	63(6)	930(3)	-4(1)	4(2)
HC(125)	-229(6)	-10(3)	379(1)	3(2)	-189(6)	606(3)	206(1)	2(1)	248(5)	1015(2)	-2(1)	2(1)
HC(126)	-14(6)	44(3)	393(1)	3(1)	-22(7)	605(3)	253(1)	5(2)	386(6)	1029(3)	47(1)	4(2)
HC(132)	407(5)	107(2)	404(1)	2(1)	0(7)	407(3)	259(2)	6(2)	375(6)	973(3)	179(1)	5(2)
HC(133)	537(6)	88(3)	359(1)	3(1)	-118(7)	323(3)	294(1)	4(2)	255(7)	1063(3)	213(1)	4(2)
HC(134)	538(7)	-12(3)	328(1)	4(2)	-83(6)	326(3)	350(1)	3(1)	120(6)	1147(3)	188(1)	5(2)
HC(135)	402(5)	-100(2)	347(1)	1(1)	70(7)	412(3)	379(2)	5(2)	85(5)	1155(2)	134(1)	2(1)
HC(136)	259(6)	-84(3)	393(1)	2(1)	175(6)	492(3)	346(1)	3(1)	206(7)	1068(3)	99(2)	5(2)

^a B_{iso} for nonhydrogen, B_{iso} for hydrogen atoms.

X-Ray structure study of I

The unit cell parameters and intensities of 8827 independent reflections were measured at -120°C with a Syntex P2₁ automatic four-circle diffractometer (λ Mo- K_{α} , graphite monochromator, $\theta/2\theta$ scan, $2\theta < 54^{\circ}$). The crystals of I are monoclinic, a 9.077(2), b 19.635(5), c 40.392(9) Å, β 93.90(2) $^{\circ}$, space group $P2_1/c$, $Z = 12$ (three $\text{Ph}_3\text{PAuC}_{13}\text{H}_8$ molecules in the asymmetric cell). 8192 observed reflections ($I > 2\sigma$) were used in calculations; I_{peak} and $I_{\text{background}}$ values were obtained by the analysis of peak profiles by the PROFAN program. A correction for absorption, taking into account the real crystal shape, was applied as described elsewhere [15]. The structure of I was solved by a direct method using the MULTAN program and refined by a least-squares block-diagonal technique in an anisotropic approximation. All hydrogen atoms were located in a difference synthesis and included in the refinement with isotropic temperature parameters, which converged finally to $R = 0.024$ and $R_w = 0.027$ based on 7321 reflections with $I > 5\sigma$. The calculations were carried out with an Eclipse S/200 computer using the INEXTL programs [16].

Crystal and molecular structure of I

Atomic coordinates and temperature parameters are listed in Table 1. The interatomic distances in three independent molecules of I (A, B and C in Fig. 1) are listed in Table 2 and the relevant bond angles in Table 3. The most important geometric features of the structures of the cyclopentadienyl Au^{I} derivatives are compared in Table 4.

In contrast to the previously studied monocyclic aurated cyclopentadienyl derivatives, compound I shows no intermediate " $\eta^1 \leftrightarrow \eta^3$ " coordination which is

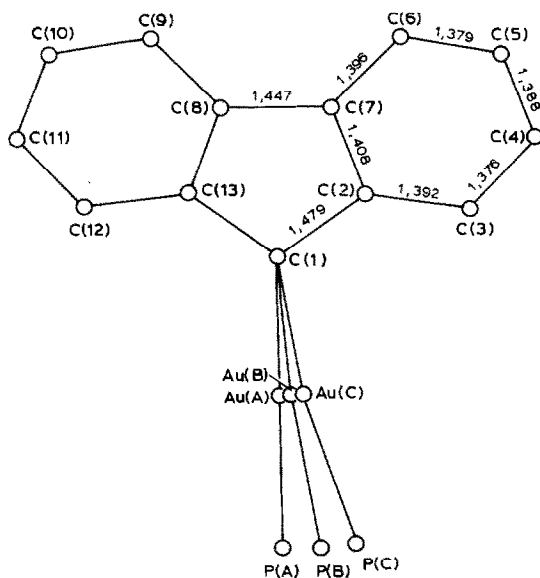


Fig. 1. Superposition of molecules IA, IB and IC with coincident fluorenyl ligands and averaged bond lengths (Å).

Table 2
Bond lengths (Å)

Bond	Molecule IA	Molecule IB	Molecule IC
Au-P	2.276(2)	2.284(2)	2.266(2)
Au-C(1)	2.103(6)	2.109(6)	2.093(6)
P-C(111)	1.807(6)	1.815(6)	1.802(6)
P-C(121)	1.812(6)	1.807(6)	1.805(6)
P-C(131)	1.816(6)	1.807(6)	1.814(6)
C(1)-C(2)	1.482(8)	1.483(9)	1.469(9)
C(1)-C(13)	1.494(8)	1.476(9)	1.471(9)
C(1)-H(1)	0.93(5)	0.85(5)	0.93(6)
C(2)-C(3)	1.388(8)	1.389(9)	1.388(9)
C(2)-C(7)	1.404(8)	1.402(8)	1.424(9)
C(3)-C(4)	1.371(9)	1.396(9)	1.378(9)
C(4)-C(5)	1.372(9)	1.394(9)	1.40(1)
C(5)-C(6)	1.368(9)	1.372(9)	1.38(1)
C(6)-C(7)	1.399(9)	1.397(9)	1.399(9)
C(7)-C(8)	1.452(8)	1.454(9)	1.436(9)
C(8)-C(9)	1.388(9)	1.399(9)	1.390(9)
C(8)-C(13)	1.401(8)	1.406(9)	1.410(8)
C(9)-C(10)	1.372(9)	1.379(9)	1.40(1)
C(10)-C(11)	1.38(1)	1.37(1)	1.41(1)
C(11)-C(12)	1.377(9)	1.383(9)	1.35(1)
C(12)-C(13)	1.385(9)	1.407(9)	1.397(9)
C(111)-C(112)	1.389(8)	1.388(9)	1.390(9)
C(111)-C(116)	1.389(8)	1.386(9)	1.381(9)
C(112)-C(113)	1.369(9)	1.387(9)	1.364(9)
C(113)-C(114)	1.377(9)	1.367(9)	1.383(9)
C(114)-C(115)	1.377(9)	1.377(9)	1.357(9)
C(115)-C(116)	1.367(9)	1.389(9)	1.384(9)
C(121)-C(122)	1.377(9)	1.397(9)	1.387(9)
C(121)-C(126)	1.382(9)	1.384(9)	1.373(9)
C(122)-C(123)	1.401(9)	1.375(9)	1.357(9)
C(123)-C(124)	1.352(9)	1.376(9)	1.38(1)
C(124)-C(125)	1.374(9)	1.374(9)	1.38(1)
C(125)-C(126)	1.389(9)	1.375(9)	1.377(9)
C(131)-C(132)	1.377(8)	1.384(9)	1.386(9)
C(131)-C(136)	1.402(8)	1.377(9)	1.379(9)
C(132)-C(133)	1.375(9)	1.390(9)	1.384(9)
C(133)-C(134)	1.378(9)	1.364(9)	1.367(9)
C(134)-C(135)	1.390(9)	1.38(1)	1.362(9)
C(135)-C(136)	1.382(9)	1.39(1)	1.373(9)

typical of these compounds and is characterized by elongation of the Au-C bond and its derivation from the idealized (for $C(sp^3)$) orientation towards the centre of the five-membered cycle, thereby approaching the normal to its mean-square plane [11-14]. In molecules IA-IC the Au-C bond lengths of 2.093(6)-2.109(6) Å are within the range of values typical of organic Au^I σ -complexes [17] and are much shorter than the Au-C bonds in monocyclic cyclopentadienyl derivatives (2.15-2.20 Å, see Table 4). The bond lengths in the fluorenyl ligands of molecules IA-IC coincide within experimental accuracy, and there are no significant differences between the two phenylene moieties of each ligand, which are related approximately

Table 3
Bond angles (deg)

Angle	Molecule IA	Molecule IB	Molecule IC
P–Au–C(1)	176.1(2)	171.2(2)	169.7(2)
Au–P–C(111)	116.9(2)	112.8(2)	109.7(2)
Au–P–C(121)	112.7(2)	108.9(2)	108.9(2)
Au–P–C(131)	111.7(2)	120.0(2)	120.9(2)
C(111)–P–C(121)	103.4(3)	104.3(3)	104.7(3)
C(111)–P–C(131)	107.1(3)	105.1(3)	106.7(3)
C(121)–P–C(131)	103.8(3)	104.4(3)	104.7(3)
Au–C(1)–C(2)	111.0(4)	113.8(4)	113.7(4)
Au–C(1)–C(13)	112.5(4)	108.8(4)	102.0(4)
Au–C(1)–H(1)	106(3)	100(3)	106(4)
C(2)–C(1)–C(3)	102.9(5)	103.0(5)	103.8(5)
C(2)–C(1)–H(1)	119(3)	119(3)	120(4)
C(13)–C(1)–H(1)	105(3)	112(3)	109(4)
C(1)–C(2)–C(3)	130.8(5)	130.4(6)	131.3(6)
C(1)–C(2)–C(7)	110.1(5)	109.8(5)	109.6(5)
C(3)–C(2)–C(7)	119.0(5)	119.8(6)	119.1(6)
C(2)–C(3)–C(4)	119.2(6)	119.6(6)	119.8(6)
C(3)–C(4)–C(5)	121.6(6)	120.2(6)	120.9(6)
C(4)–C(5)–C(6)	120.9(6)	120.4(6)	120.8(6)
C(5)–C(6)–C(7)	118.4(6)	120.0(6)	118.8(6)
C(2)–C(7)–C(6)	120.8(5)	120.0(5)	120.5(6)
C(6)–C(7)–C(8)	108.6(5)	108.8(5)	107.9(5)
C(6)–C(7)–C(8)	130.6(6)	131.2(6)	131.5(6)
C(7)–C(8)–C(9)	131.3(6)	132.0(6)	131.6(6)
C(7)–C(8)–C(13)	107.8(5)	107.0(5)	108.1(5)
C(9)–C(8)–C(13)	120.9(6)	121.0(6)	120.2(6)
C(8)–C(9)–C(10)	119.7(6)	118.2(6)	119.0(6)
C(9)–C(10)–C(11)	119.6(7)	121.2(6)	119.7(7)
C(10)–C(11)–C(12)	121.3(6)	121.8(6)	121.6(7)
C(11)–C(12)–C(13)	119.9(6)	118.4(6)	119.6(6)
C(1)–C(13)–C(8)	110.4(5)	110.9(5)	109.9(5)
C(1)–C(13)–C(12)	131.0(6)	129.8(6)	130.1(6)
C(8)–C(13)–C(12)	118.6(6)	119.3(6)	119.9(6)

by an idealized symmetry plane passing through the C(1) atom and the midpoint of the C(7)–C(8) bond. The bond lengths in Fig. 1 averaged over the IA–IC molecules correspond to a diene structure of the central five-membered cycle of the fluorenyl ligand. Thus in I the Au^I–fluorenyl bond is predominantly of the $\sigma(\eta^1)$ type.

At the same time, the bond angles at the C(1) atom bonded to the Au atom differ significantly in the three crystallographically independent molecules of I. Thus in the molecule IA the AuPPh₃ group is close to the idealized symmetry plane of the fluorenyl ligand and the angles, AuC(1)C(2) (111.0(4)°) and AuC(1)C(13) (112.5(4)°) correspond to “the classic” σ -coordination of the metal atom (the difference in these angles is small ($\Delta\varphi = 1.5^\circ$), whereas in IC, Au–C(1) bonding is significantly asymmetric ($\Delta\varphi = 11.7^\circ$), and molecule B represents an intermediate case ($\Delta\varphi = 5.0^\circ$). The difference in Au–fluorenyl coordination in the molecules IA, IB and IC are evident from Fig. 1 where the fluorenyl ligands of these molecules have been made to coincide.

In contrast to the Au^I compounds with the “ $\eta^1 \leftrightarrow \eta^3$ ” type of Au–cyclopentadienyl coordination (Table 4), molecules of IB and IC show a AuPPh₃ group that is displaced from the position corresponding to “ideal” σ -bonding, not towards the centre of the five-membered cycle, but towards its periphery. This displacement gives rise to the short Au \cdots C(2) contact of 2.798(6) Å, a feature which is not accompanied by a noticeable change in bond lengths in the molecule (Table 2). The PAuCl bond angle in IA–IC is related to the degree of distortion of the symmetric σ -coordination, which is a feature not observed in other Au^I cyclopentadienyl derivatives (Table 4). The distortion of the Au–C(1) σ -bond which increases in the series IA, IB and IC, causes a slight increase in the bending angle of the central five-membered cycle of the fluorenyl ligand along the C(2) \cdots C(13) line, for the series: IA, 4.1°, IB, 7.0° and IC, 7.7°.

The coexistence of geometrically different molecules of the same compound in crystal has been observed previously, particularly in the series of Hg^{II} organic derivatives and have been interpreted as evidence for a shallow energy minimum which corresponds to the metal–ligand interaction [18]. A shallow minimum in the potential energy surface of the molecule is a prerequisite for its stereochemical nonrigidity and presents a low-potential barrier for rearrangement, whose successive stages in fairly rare cases are frozen in the solid phase to give crystallographically independent molecules. Thus differences in the C(α)C(1)Au and PAuCl bond angles in IA–IC can be regarded as an indication of the nonrigidity of molecule I, which could lead to the various dynamic processes.

In the monocyclic cyclopentadienyl derivatives of Au^I the NMR method has revealed the dynamic rearrangements attributed to metallotropy, i.e. migration of the AuL fragment (where L is a phosphine ligand) [19]. Such migrations can be hindered on the NMR time scale by the introduction of bulky substituents into the cycle [1]. Metallotropy was also revealed by NMR spectroscopy of, and X-ray diffraction studies on the π -fluorenyl derivatives of the chromium subgroup metals ($\eta^6 \rightleftharpoons \eta^5$ transitions) [20]. In the case of the Au^I cyclopentadienyl derivatives, where the metal atom has lower coordination ability, the migration of the AuL group along the cycle periphery is expected to be assisted by the “ $\eta^1 \leftrightarrow \eta^3$ ” coordination and to involve some $sp^3 \rightleftharpoons sp^2$ rehybridization of the carbon atoms in the cycle. However, in the fluorenyl ligand such rehybridization is impossible owing to the fact that four carbon atoms of its cyclopentadienyl system are involved in the planar phenylene moieties. Thus in compound I only limited structural nonrigidity is observed, viz. pendular motion of the AuPPh₃ group at the sp^3 -hybridized C(1) atom of the fluorenyl ligand and apparently undergoes no migration to the adjacent carbon atom. In the crystal structure of I the individual stages of this swinging are fixed in geometrically different positions in crystallographically independent molecules IA, IB and IC.

Experimental

The IR spectra of the compounds investigated were recorded with an IKS-29 instrument in Nujol mulls, the PMR spectra were measured with a BS-497 instrument at a working frequency of 100 MHz and with a T-60 instrument at a working frequency of 60 MHz using HMDS as the internal standard.

Table 4
Main geometric parameters (Å and deg) of Au^I cyclopentadienyl derivatives

Compound	Au-P	Au-C	Au...C'	Au...C''	Au-C-C'	Au-C-C''	C-Au-P	Refs.
Ph ₃ PAuC ₅ HPh ₄	2.239(3)	2.15(1)	2.67(1)	2.76(1)	93.4(8)	97.8(8)	178.6(3)	[11]
[(Ph ₃ PAu) ₃ C ₅ Ph ₄] ⁺ BF ₄ ^{-a}	2.257(5)	2.21(2)	2.60(2)	2.71(2)	88(1)	91(1)	172.8(4)	[12]
(i-Pr) ₃ PAuC ₅ H ₅	2.267(2)	2.175(9)	2.688(9)	2.781(9)	94.0(5)	98.9(6)	177.0(2)	[13]
Ph ₃ PAuC ₅ (COOMe) ₅	2.253(1)	2.199(4)	2.705(4)	2.813(4)	93.3(3)	98.5(2)	169.7(1)	[14]
Ph ₃ PAuC ₁₃ H ₉ (IA)	2.276(2)	2.103(6)	2.975(6)	3.010(6)	111.0(4)	112.5(4)	176.1(2)	This work
Ph ₃ PAuC ₁₃ H ₉ (IB)	2.284(2)	2.109(6)	2.937(6)	3.028(6)	108.8(4)	113.8(4)	171.2(2)	This work
Ph ₃ PAuC ₁₃ H ₉ (IC)	2.266(2)	2.093(6)	2.798(6)	3.001(6)	102.0(4)	113.7(4)	169.7(2)	This work

^a Parameters for one of the three Au atoms in the cation coordinated by the "η¹ ↔ η³" type

The reactions were monitored by thin-layer chromatography on Al_2O_3 (the second degree of activity).

9-Fluorenyl(triphenylphosphine)gold (I) was prepared under argon using absolute solvents.

9-Fluorenyl(triphenylphosphine)gold (I)

(a) *From fluorene and $[\text{O}(\text{AuPPh}_3)_3]^+ \text{BF}_4^-$.* A suspension of 0.1 g (0.63 mmol) of fluorene, 0.31 g (0.21 mmol) of tris(triphenylphosphine)gold oxonium borofluoride and 0.01 g (0.5 mmol) of NaH in 15 ml of absolute THF was stirred at -10°C for 2 h (the amount of the precipitate that separated was seen to decrease slightly and the reaction mixture turned slightly pink). Then to the mixture was added 0.05 g (0.31 mmol) of fluorene and 5 ml of absolute THF, stirred for another 30 min, and gradually heated to 15°C , by this time nearly all the precipitate had dissolved. The solution was filtered under argon, diluted with petroleum ether to turbidity and left to stand overnight at -10°C . The precipitate, a colourless crystalline substance was separated off, washed with cooled pentane, and dried in a vacuum desiccator over P_2O_5 . Yield: 0.15 g and additionally 0.07 g from mother solutions, the total yield being 0.22 g (75%), m.p. $135\text{--}137^\circ\text{C}$ (decomp.) in a sealed capillary. Found: C, 59.90; H, 3.70; Au, 31.60. $\text{C}_{31}\text{H}_{24}\text{AuP}$ calc: C, 59.62; H, 3.87; Au, 31.54%.

IR (cm^{-1}) 3050w, 1605m, 1564m, 1320m, 1214m, 1184m, 1165w, 1148w, 1104s, 1023w, 1000m, 967w, 940m, 930m, 912s, 850m, 817w, 756s, 742s, 729m, 713m, 690s, 618m, 535s, 512s, 494m.

PMR (CHCl_3 , δ , ppm): 8.04–6.52 (m); 4.68 (d) ($^3J(^1\text{H}\text{--}^{31}\text{P})$ 16 Hz).

After addition of 0.01 g (0.02 mmol) of PPh_3 to a solution of 0.05 g (0.08 mmol) of I in 1 ml of CDCl_3 the PMR spectrum showed the coalescence of doublet components centered at δ 4.68 ppm into a singlet.

(b) *From fluorenyllithium and AuClPPh_3 .* A solution of fluorenyllithium* (obtained from 2 g (12 mmol) of fluorene and 8.3 g (13 mmol) of 1.56 N $n\text{-C}_4\text{H}_9\text{Li}$) was added dropwise to a solution of 0.05 g (1 mmol) of AuClPPh_3 in 60 ml of absolute benzene with stirring under argon. The reaction mixture was stirred at 20°C for 75 min, and then at 80°C for another 15 min, the solution turning wine-red. After cooling, the reaction mixture was decomposed with water and the water layer extracted with benzene. The combined benzene fractions were dried over K_2CO_3 for 15 min, concentrated by evaporation in vacuo to 5–7 ml, and then poured into ca. 40 ml of petroleum ether cooled to 0°C . The precipitate was filtered off, washed with cold pentane, dried, and extracted in a Soxhlet apparatus with three portions of pentane (50 ml each) for 2–3 h. The combined pentane extracts and the mother solution (after isolation of the reaction product) were chromatographed on an Al_2O_3 column (the second degree of activity) (l 25, d 2.5 cm). Fluorene and a small amount of difluorenyl were eluted with petroleum ether to yield 1.27 g of fluorene, m.p. $113\text{--}114^\circ\text{C}$ (lit. [22]: m.p. $115\text{--}116^\circ\text{C}$). A petroleum ether/benzene mixture (5/1) was used to eluate 0.16 g of fluorene, m.p. $80\text{--}81^\circ\text{C}$ (lit. [23]: m.p. $82\text{--}83^\circ\text{C}$) and methanol to eluate 0.18 g of fluorene (an additional 0.12 g was isolated from the mother solution), m.p. $154\text{--}155^\circ\text{C}$ (lit. 23: m.p. $154\text{--}156^\circ\text{C}$).

* Under the conditions used the yield of $\text{C}_{13}\text{H}_9\text{Li}$ was 78% (determined by carboxylation).

The solid product left in the Soxhlet apparatus holder was recrystallized from an ether/toluene mixture (2/1) at -70°C , washed with pentane, and dried in vacuo to give 0.5 g (80%) of the title compound, m.p. $133\text{--}135^{\circ}\text{C}$ (decomp.). IR and PMR spectra were identical to those of the sample obtained by the fluorene auration (experiment as above).

(c) *From fluorenylsodium and AuClPPh₃*. To a suspension of NaNH_2 in liquid NH_3 (obtained from 0.66 g (23 mmol) of sodium) was added 70 ml of absolute ether and a solution of 3.36 g (20 mmol) of fluorene in the same solvent. The reaction mixture was stirred at -50°C for 30 min, unchanged ammonia was removed and at -30°C a solution of 1.4 g (2.8 mmol) of AuClPPh_3 in 50 ml of absolute THF was added. The mixture was then heated to room temperature and stirred for 15 min in a water bath. After that the mixture was treated as described for the previous experiment (b). Extraction in the Soxhlet apparatus yielded 1.74 g of the title compound (97%) m.p. $133\text{--}135^{\circ}\text{C}$ (decomp.) (from an ether/toluene mixture). IR and PMR spectra were identical with those of the sample obtained in (a).

Acknowledgement

The authors wish to thank V.E. Zavodnik and Dr. V.K. Belsky for providing the PROFAN program used in the analysis of profiles of X-ray reflections.

References

- 1 K.I. Grandberg, *Usp. Khim.*, 3 (1982) 438.
- 2 A.N. Nesmeyanov, K.I. Grandberg, V.P. Dyadchenko, D.A. Lemenovsky and E.G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3 (1974) 740.
- 3 A.N. Nesmeyanov, E.G. Perevalova, D.A. Lemenovsky, V.P. Dyadchenko and K.I. Grandberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7 (1974) 1661.
- 4 E.G. Perevalova, K.I. Grandberg, D.A. Lemenovsky and V.P. Dyadchenko, *Vestn. Mosk. Univ., Khim.*, 20 (1979) 299.
- 5 K.I. Grandberg, *Koord. Khim.*, 10 (1984) 646.
- 6 O.A. Reutov, I.P. Beletskaya and K.P. Butin, *CH Acids, Moscow, "Science"*, 1980.
- 7 R. Hüttel, U. Raffay and H. Reinheimer, *Angew. Chem.*, 79 (1967) 859.
- 8 E.G. Perevalova, K.I. Grandberg, V.P. Dyadchenko and T.V. Baukova, *J. Organomet. Chem.*, 217 (1981) 403.
- 9 E.G. Perevalova, K.I. Grandberg, T.V. Baukova, V.P. Dyadchenko, Yu.L. Slovokhotov and Yu.T. Struchkov, *Koord. Khim.*, 8 (1982) 1337.
- 10 D. Bethell and R.J.E. Talbot, *J. Chem. Soc. (B)* (1968) 638.
- 11 T.V. Baukova, Yu.L. Slovokhotov and Yu.T. Struchkov, *J. Organomet. Chem.*, 220 (1981) 123.
- 12 T.V. Baukova, Yu.L. Slovokhotov and Yu.T. Struchkov, *J. Organomet. Chem.*, 221 (1981) 375.
- 13 H. Werner, H. Otto, Tri Ngo-Khac and Ch. Burschka, *J. Organomet. Chem.*, 262 (1984) 123.
- 14 M.I. Bruce, J.K. Walton, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.* (1983) 809.
- 15 R.G. Gerr, M.Yu. Antipin, N.G. Furmanova and Yu.T. Struchkov, *Kristallogr.*, 24 (1979) 951.
- 16 R.G. Gerr, A.I. Yanovsky and Yu.T. Struchkov, *Kristallogr.*, 28 (1983) 1029.
- 17 P.G. Jones, *Gold Bull.*, 14 (1981) 102.
- 18 L.G. Kuz'mina and Yu.T. Struchkov, *Croat. Chem. Acta*, 57 (1984) 701.
- 19 C.H. Campbell and L.H. Green, *J. Chem. Soc. (A)* (1971) 3282.
- 20 A.N. Nesmeyanov, N.A. Ustynyuk, L.N. Novikova, V.G. Andrianov, Yu.T. Struchkov, Yu.A. Ustynyuk, Yu.F. Oprunenko and Yu.N. Luzikov, *J. Organomet. Chem.*, 226 (1982) 239.
- 21 R.R. Buther and J.W. Cusoc, *J. Am. Chem. Soc.*, 65 (1943) 262.
- 22 N.D. Zelinsky, J. Titz and M. Gaverdowskaja, *Ber.*, 59 (1926) 2590.
- 23 E.H. Huntress, E.B. Hershberg and J.S. Gliff, *J. Am. Chem. Soc.* 53 (1931) 2720.
- 24 H. Stadinger and A. Gaule, *Ber.*, 49 (1916) 1951.