Mixed-Valent Linear Chains of Gold Atoms. X-ray Structure of [{(2,4,6-$C_6F_3H_2$)Au($CH_2PPh_2CH_2$)$_2$Au}$_2$Au($CH_2PPh_2CH_2$)$_2$Au](ClO_4)$_2$

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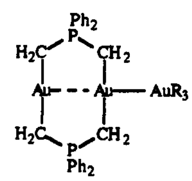
Reactions of asymmetrical gold(II) derivatives [RAu($CH_2PPh_2CH_2$)$_2$AuX] (R = C_6F_5, 2,4,6-$C_6F_3H_2$; CH_3, X = halogen) with $AgClO_4$ lead to the compounds [RAu($CH_2PPh_2CH_2$)$_2$AuOClO_3], which further react with NBu_4[AuR_2] (R = C_6F_5, $C_6F_3H_2$) or [Au($CH_2PPh_2CH_2$)$_2$Au] to give pentanuclear [{RAu($CH_2PPh_2CH_2$)$_2$Au}$_2$AuR_2]ClO_4 or hexanuclear [{RAu($CH_2PPh_2CH_2$)$_2$Au}$_2$Au($CH_2PPh_2CH_2$)$_2$Au](ClO_4)$_2$ gold complexes in different oxidation states. The same results can be achieved if the reactions are carried out with [RAu($CH_2PPh_2CH_2$)$_2$Au(tht)]ClO_4 (tht = tetrahydrothiophene). The structure of [{(2,4,6-$C_6F_3H_2$)Au($CH_2PPh_2CH_2$)$_2$Au}$_2$Au($CH_2PPh_2CH_2$)$_2$Au](ClO_4)$_2$ has been determined by a single-crystal X-ray diffraction study. It crystallizes in the monoclinic space group $P2_1/c$ with a = 12.150(1) Å, b = 15.498(2) Å, c = 24.693(2) Å, β = 95.18(1)°, Z = 2, R = 0.0404, and R_w = 0.0417 for 5132 observed reflections. The centrosymmetric cationic complex exhibits a linear hexametallic skeleton and is composed of three pairs of gold atoms, each of them doubly bridged by two bis-ylide ligands. Two σ-bonded $C_6F_3H_2$ groups complete the coordination of the external gold centers. The three "Au($CH_2PPh_2CH_2$)$_2$Au" moieties are held together through two unbridged Au–Au direct bonds (2.7370(7) Å), with the ligand-bridged Au–Au separations at 2.6540(7) and 2.8378(7) Å.

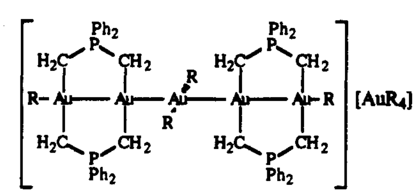
Introduction

There has been much current interest in the synthesis of gold clusters and gold complexes containing gold–gold bonds. The oxidation state of the gold atoms in these complexes is usually 0 and I in clusters[1,2] or II in dinuclear gold complexes.[3–8] These latter contain one[3] or, more frequently, two ligands bridging the two gold centers.[4–8] Another relevant Au(I)–Au(III) case with ylide metallacycles has been described.[9]

Despite the extensive work done in this area, the only two hitherto known complexes with a direct formal gold–gold bond unbridged by any other ligand have been reported recently: 1 and 2.[10,11]



R=C_6F_5(1)



R=C_6F_5(2)

Complex 1 contains a formal gold(I)–gold(III) donor–acceptor bond, but the oxidation states of the gold atoms in the Au_5 chain of 2 remain unclear.

The formation of complex 2 by the reaction of the dinuclear bis-ylide derivative [(C_6F_5)Au($CH_2PPh_2CH_2$)$_2$Au(C_6F_5)] with [Au(C_6F_5)$_3$OEt_2], although in relatively low yield, prompted the investigation of a systematic synthesis of this complex and related ones. In this paper we describe the preparation of mixed-valent gold complexes containing linear Au_5 or Au_6 chains. The molecular structure of the hexanuclear [{(2,4,6-$C_6F_3H_2$)Au($CH_2PPh_2CH_2$)$_2$Au}$_2$Au($CH_2PPh_2CH_2$)$_2$Au](ClO_4)$_2$ has been established by single-crystal X-ray analysis.

Results and Discussion

The bonding in complex 2 can be explained by taking into account that one aurate(I) moiety [Au(C_6F_5)$_2$]$^-$ may be donating electron density to the dinuclear gold(II) cation

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Table 1. Analytical Data for Products

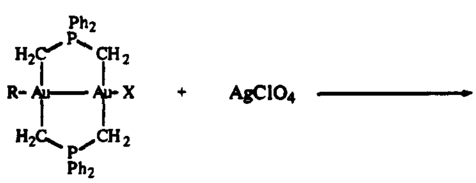
complex	anal. (%)[a] C	anal. (%)[a] H	δ(PPh₂)[b] (³¹P{¹H}) Au^II–CH₂P	δ(PPh₂)[b] (³¹P{¹H}) Au^I–CH₂P	δ(CH₂) (¹H)[b] [N][c]
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuOClO_3]$ (3)	37.2 (37.55)	1.9 (2.6)	32.3 (s)		1.36 ("d") [11.5], 1.94 ("d") [12]
$[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2AuOClO_3]$ (4)	39.1 (38.85)	3.1 (2.9)	31.7 (s)		1.36 ("d") [12.2], 1.89 ("d") [12.9]
$[(CH_3)Au(CH_2PPh_2CH_2)_2AuOClO_3]$ (5)	37.55 (37.25)	3.35 (3.35)	27.1 (s)		1.30 ("d") [10.3], 1.68 ("d") [13.4]
$[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_5)_2]ClO_4$ (6)	36.75 (36.9)	2.05 (2.15)	35.5 (s)		1.33 ("d") [11.2], 2.07 ("d") [13.2]
$[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_3H_2)_2]ClO_4$ (7)	39.1 (39.05)	2.5 (2.6)	33.4 (s)		1.28 ("d") [13.4], 2.05 ("d") [12.2]
$[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au](ClO_4)_2$ (8)	38.35 (38.5)	2.7 (2.85)	39.0 (s)	33.5 (s)	1.14 ("d") [11.6], 1.39 ("d") [9.9], 1.78 ("d") [13.3]
$[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au](ClO_4)_2$ (9)	39.75 (39.45)	3.75 (3.05)	35.7 (s)	33.9 (s)	1.09 ("d") [14.4], 1.37 ("d") [11.5], 1.80 ("d") [14.9]
$[\{(CH_3)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au](ClO_4)_2$ (10)	38.85 (38.4)	2.3 (1.8)	31.7 (s)[d]	34.5 (s)[d]	1.15 ("d") [12.2],[d] 1.3 ("d") [10.5],[d] 1.64 ("d") [12.9][d]

[a] Calculated values are given in parentheses. [b] In $CDCl_3$; values in ppm. [c] Values in Hz. [d] In CD_2Cl_2; values in ppm.

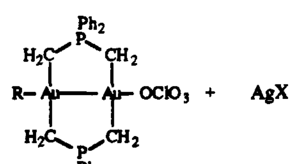
$[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au]^+$. Species of this type have been proposed for the group exchange in gold(II) derivatives by Fackler[12] and Murray and by us.[8b] Furthermore, complexes containing the organoaurates $[AuR_2]^-$ (R = C_6F_5, 2,4,6-$C_6F_3H_2$) acting as donor centers to silver atoms have also been described.[13-15]

Using this idea in a synthetic strategy, we have considered the use of the recently reported complexes[8b] $[RAu(CH_2PPh_2CH_2)_2Au(tht)]ClO_4$ (R = C_6F_5, 2,4,6-$C_6F_3H_2$) as adequate precursors for the synthesis of high-nuclearity complexes since tetrahydrothiophene, which is a poor ligand in gold chemistry, could be replaced by the $[AuR_2]^-$ donor anions.

Other candidates as starting materials could be the dinuclear gold(II) derivatives of the type $[RAu(CH_2PPh_2CH_2)_2AuX]$ containing one halogen as ligand, which can be converted into the corresponding perchlorates 3–5 by reaction with silver perchlorate (eq 1).



R= C_6F_5 or $C_6F_3H_2$, X= Cl
R= CH_3, X= I

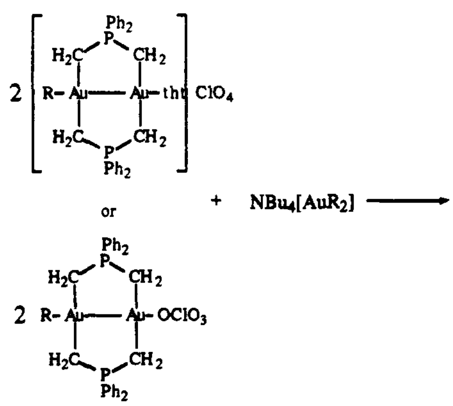


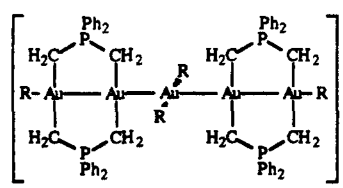
(1)

R= C_6F_5(3), 2,4,6-$C_6F_3H_2$(4), CH_3(5)

Complexes 3–5 were isolated as yellow (3 and 4) or green-brown (5) solids, air- and moisture-stable at room temperature. Their NMR spectra are in accordance with an asymmetrical formulation; only one absorption in the $^{31}P\{^1H\}$ spectra and two resonances in the methylene region in the ^1H spectra were observed (see Table 1). Addition of PPh_3 to dichloromethane solutions of 3 and 4 gives rise to the previously reported[8b] complexes $[RAu(CH_2PPh_2CH_2)_2Au(PPh_3)]ClO_4$ (R = C_6F_5, $C_6F_3H_2$).

Complexes 3–5 react with organoaurates $NBu_4[AuR_2]$ (R = C_6F_5 or $C_6F_3H_2$) in a 2:1 ratio, to give a mixture of the pentanuclear complex 6 or 7 and NBu_4ClO_4, which can be separated because of their different solubilities in ethanol/diethyl ether (1:1). Complexes 6 and 7 can also be obtained by an alternative method, *viz.* the 2:1 reaction of monocationic $[RAu(CH_2PPh_2CH_2)_2Au(tht)]ClO_4$ with a dichloromethane solution of organoaurate(I), as is shown in eq 2.





(2)

R= C_6F_5(6), $C_6F_3H_2$(7)

Complexes 6 and 7 are red solids, air- and moisture-stable at room temperature. Complex 6 shows ^1H, $^{31}P\{^1H\}$, and ^{19}F NMR spectra very similar to those previously described for 2 with the lack of the corresponding absorptions of the $[Au(C_6F_5)_4]^-$ group in the ^{19}F NMR spectra. Complex 7 shows one resonance at 33.4 ppm for $^{31}P\{^1H\}$ NMR, two pseudodoublets for the methylene protons in the ^1H NMR spectra, and four different signals (two assigned to *ortho* F and two to *para* F) corresponding to two different $C_6F_3H_2$ groups for ^{19}F NMR.

Complexes 6 and 7 are the only species containing phosphorus in process 2, as can be seen from the ^{31}P NMR of the reaction mixture, but the only slightly different

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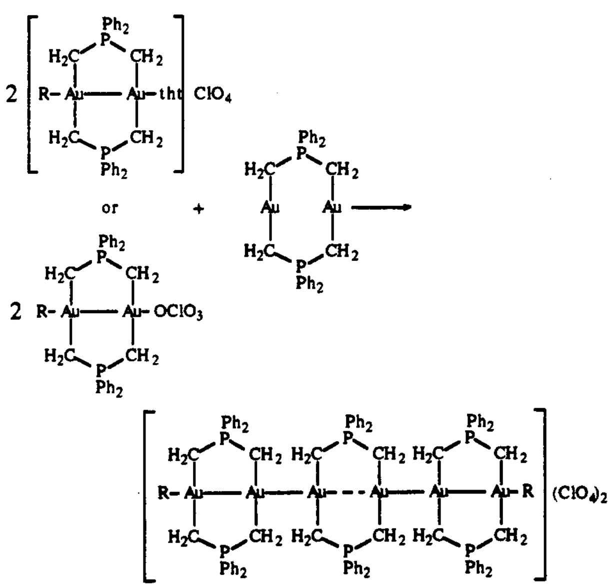
solubilities as compared to that of NBu_4ClO_4 prevent a better yield (~50%) of the pure solids 6 and 7.

The success of the synthesis of the pentanuclear cation 6 in this way indicates that it seems sensible to assume that complexes 2 and 6 are formed by a donor–acceptor interaction between the gold center of the anionic aurate(I) $[Au(C_6F_5)_2]^-$ and the dinuclear cationic gold(II) fragment, in which the central aurate(I) moiety is donating electron density to both gold(II) centers. With this in mind, attempts to synthesize other polynuclear gold complexes using other gold complexes as electron donors were successful. Therefore, similar gold(II) fragments were used as starting materials and made to react with a bis(μ-diphenylphosphonium bismethylido)digold(I) complex (2:1 ratio, dichloromethane) hexanuclear derivatives were obtained (eq 3). The bis(ylide)digold(I) complex has been used previously as an electron donor agent in gold chemistry, as is shown in the synthesis of 1.[10]



(3)

R= C_6F_5(8), $C_6F_3H_2$(9), CH_3(10)

Complexes 8–10 can be isolated as dark red solids, air and moisture stable at room temperature. Their molar conductivities in acetone solution (for complexes 8 and 9) are in agreement with the dicationic formulation. Their $^{31}P\{^1H\}$ NMR spectra show a singlet signal for the PPh_2 groups at gold(II) auracycles and a smaller one for PPh_2 groups of gold(I) centers. The ^1H NMR spectra show three pseudodoublets of equal intensities because of the three different CH_2–P groups, but the assignment is not unambiguous. A singlet, at 1.88 ppm, is observed for the CH_3 group in 10.

The structure of 9 was determined by X-ray diffraction. The molecular structure of the cationic complex is shown in Figure 1 together with the numbering scheme used. Atomic coordinates are listed in Table 2, and selected bond distances and angles in Table 3. This complex has a crystallographically imposed center of inversion located in the center of the Au(3)–Au(3′) vector. The whole dication consists of three $Au(CH_2PPh_2CH_2)_2Au$ moieties linked together through two unbridged gold–gold bonds, building up an almost linear six-atom metal chain (Au(1)–Au(2)–Au(3) = 173.87(3)° and Au(2)–Au(3)–Au(3′) = 177.11(3)°). Each of the two metal atoms at the ends of the chain is coordinated to a $C_6F_3H_2$ group.

Table 2. Atomic Coordinates (×10⁴; ×10⁵ for Au Atoms) and Equivalent or Isotropic Displacement Coefficients for Complex 9

atom	*x/a*	*y/b*	*z/b*	U_{eq},[a] Å²
Au(1)	102762(4)	7798(3)	10404(2)	433(2)
Au(2)	82600(4)	5147(3)	5618(2)	426(2)
Au(3)	61178(4)	1894(4)	1752(2)	487(2)
P(1)	9558(3)	−1233(2)	873(1)	449(11)
P(2)	8656(3)	2331(2)	1171(1)	498(12)
P(3)	5261(3)	928(2)	−995(1)	530(12)
C(1)	10684(10)	−551(8)	1013(5)	482(43)
C(2)	8653(10)	−735(8)	374(5)	514(45)
C(3)	7780(12)	1798(9)	673(6)	694(57)
C(4)	10022(10)	2129(8)	1028(5)	582(51)
C(5)	6465(9)	582(8)	−606(5)	537(46)
C(6)	5884(10)	−165(9)	963(5)	617(52)
C(7)	11810(10)	999(8)	1467(5)	505(47)
C(8)	12611(11)	1459(10)	1222(6)	638(56)
C(9)	13637(13)	1652(11)	1474(8)	874(77)
C(10)	13844(14)	1368(12)	1977(10)	960(87)
C(11)	13101(15)	908(12)	2263(8)	948(81)
C(12)	12083(13)	742(11)	1972(6)	713(61)
C(13)	9995(10)	−2277(8)	647(5)	523(47)
C(14)	9283(13)	−2777(9)	321(6)	659(58)
C(15)	9623(15)	−3574(10)	139(6)	820(71)
C(16)	10708(14)	−3833(10)	284(6)	760(64)
C(17)	11401(14)	−3352(10)	609(7)	789(68)
C(18)	11040(12)	−2572(10)	793(6)	711(58)
C(19)	8869(11)	−1416(9)	1490(5)	582(52)
C(20)	8154(14)	−2084(12)	1496(7)	908(76)
C(21)	7628(17)	−2264(14)	1950(9)	1169(100)
C(22)	7832(15)	−1756(14)	2408(8)	981(88)
C(23)	8511(14)	−1071(12)	2395(6)	839(71)
C(24)	9042(12)	−903(10)	1918(6)	680(58)
C(25)	8364(13)	3470(9)	1163(5)	627(56)
C(26)	7367(17)	3778(13)	966(8)	1067(94)
C(27)	7181(21)	4655(15)	959(9)	1290(119)
C(28)	7953(24)	5248(12)	1134(10)	1231(127)
C(29)	8856(23)	4939(13)	1299(10)	1383(132)
C(30)	9135(17)	4061(12)	1331(8)	1089(91)
C(31)	8468(11)	1933(9)	1844(5)	548(49)
C(32)	9309(14)	2059(11)	2240(6)	823(69)
C(33)	9219(16)	1784(14)	2764(7)	1063(90)
C(34)	8279(18)	1316(12)	2868(8)	973(88)
C(35)	7501(15)	1182(13)	2491(7)	931(78)
C(36)	7577(13)	1487(10)	1959(6)	760(64)
C(37)	4935(13)	1978(10)	−746(6)	683(60)
C(38)	4389(15)	2068(12)	−257(8)	960(82)
C(39)	4196(16)	2841(12)	−44(7)	1007(87)
C(40)	4561(18)	3526(14)	−287(9)	1215(110)
C(41)	4994(21)	3516(13)	−758(11)	1634(147)
C(42)	5172(17)	2700(13)	−994(8)	1076(92)
C(43)	5527(11)	1062(10)	−1697(6)	627(53)
C(44)	4779(14)	862(11)	−2111(6)	843(71)
C(45)	4977(18)	996(15)	−2645(7)	1192(103)
C(46)	5994(18)	1305(15)	−2751(8)	1166(102)
C(47)	6803(16)	1468(13)	−2350(7)	989(85)
C(48)	6562(12)	1349(11)	−1835(6)	764(65)
F(1)	12421(7)	1734(6)	709(4)	879(39)
F(2)	14813(9)	1509(8)	2273(5)	1495(62)
F(3)	11321(8)	288(6)	2227(3)	940(41)
Cl	2901(5)	4341(4)	1047(2)	986(21)
O(1)[b]	2737(11)	4599(9)	506(6)	1213(45)
O(2)[b]	3115(15)	5032(13)	1404(8)	1803(51)
O(3)[b]	2150(23)	3783(18)	1184(11)	2710(124)
O(4)[b]	3857(20)	3842(16)	1114(9)	2349(100)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] These atoms were refined isotropically.

The Au(1)–Au(2) bond length is 2.6540(7) Å, very similar to other reported Au^{II}–Au^{II} distances in dinuclear bisylide gold(II) complexes (e.g. 2.675(1) Å for $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$[16] and 2.6612(8) Å for $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)]ClO_4$[8b]) and identical with the mean value described for this type of complex.[17] The Au(3)–Au(3′) distance is significatively longer (2.8378(7) Å) and seems to be consistent with the absence of a Au–

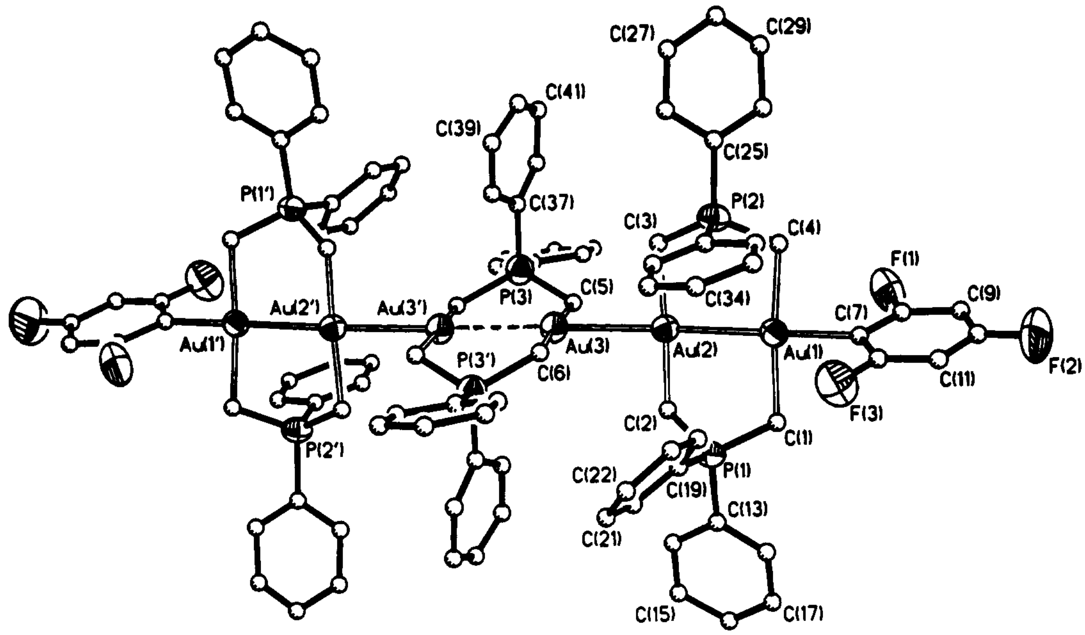


Figure 1. Molecular diagram of the cationic complex $[\{(2,4,6\text{-}C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au]^{2+}$ (cation of **9**). Primed atoms are related to the unprimed ones by the symmetry transformation $1 - x, -y, -z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 9[a]

Au(1)-Au(2)	2.6540(7)	Au(2)-C(2)	2.058(12)
Au(1)-C(1)	2.123(12)	Au(2)-C(3)	2.098(14)
Au(1)-C(4)	2.114(12)	Au(3)-C(5)	2.101(12)
Au(1)-C(7)	2.084(12)	Au(3)-C(6)	2.065(13)
Au(2)-Au(3)	2.7370(7)	Au(3)···Au(3')	2.8378(7)
P(1)-C(1)	1.738(12)	P(2)-C(25)	1.800(15)
P(1)-C(2)	1.755(12)	P(2)-C(31)	1.806(14)
P(1)-C(13)	1.807(13)	P(3)-C(5)	1.761(11)
P(1)-C(19)	1.826(14)	P(3)-C(6')	1.832(14)
P(2)-C(3)	1.757(14)	P(3)-C(37)	1.796(16)
P(2)-C(4)	1.755(13)	P(3)-C(43)	1.803(15)
Au(2)-Au(1)-C(1)	92.5(3)	Au(3)-Au(2)-C(2)	88.9(3)
Au(2)-Au(1)-C(4)	91.1(3)	Au(3)-Au(2)-C(3)	87.3(4)
Au(2)-Au(1)-C(7)	176.0(4)	C(2)-Au(2)-C(3)	174.2(5)
C(1)-Au(1)-C(4)	174.1(5)	Au(2)-Au(3)-Au(3')	177.11(3)
C(1)-Au(1)-C(7)	88.5(5)	Au(2)-Au(3)-C(5)	90.2(3)
C(4)-Au(1)-C(7)	88.2(5)	Au(2)-Au(3)-C(6)	85.9(3)
Au(1)-Au(2)-Au(3)	173.87(3)	Au(3')-Au(3)-C(5)	92.6(3)
Au(1)-Au(2)-C(2)	91.3(3)	Au(3')-Au(3)-C(6)	91.3(3)
Au(1)-Au(2)-C(3)	92.9(4)	C(5)-Au(3)-C(6)	176.0(5)
C(1)-P(1)-C(2)	107.7(6)	Au(1)-C(1)-P(1)	114.6(6)
C(1)-P(1)-C(13)	111.0(6)	Au(2)-C(2)-P(1)	113.5(6)
C(1)-P(1)-C(19)	109.9(6)	Au(2)-C(3)-P(2)	112.3(7)
C(2)-P(1)-C(13)	111.1(6)	Au(1)-C(4)-P(2)	108.3(6)
C(2)-P(1)-C(19)	110.4(6)	Au(3)-C(5)-P(3)	111.3(6)
C(3)-P(2)-C(4)	107.5(7)	Au(3)-C(6)-P(3')	112.5(6)
C(3)-P(2)-C(25)	110.3(7)	Au(1)-C(7)-C(8)	119.5(10)
C(3)-P(2)-C(31)	111.3(7)	C(8)-C(7)-C(12)	116.1(13)
C(4)-P(2)-C(25)	111.2(7)	C(4)-P(2)-C(31)	108.9(6)
C(5)-P(3)-C(6')	112.1(6)	C(5)-P(3)-C(37)	106.7(7)
C(5)-P(3)-C(43)	110.4(6)	C(6')-P(3)-C(37)	112.2(7)
C(6')-P(3)-C(43)	108.6(6)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation $1 - x, -y, -z$.

Au bond. However, this distance, which is shorter than that observed in its gold(I) precursor $[Au(CH_2PPh_2CH_2)_2Au]$ (2.977(1) Å), indicates the presence of a weak intermetallic interaction, as has been suggested for related Au(I) complexes.[18] The Au(2) atom is bonded to the proposed Au(I) center (labeled as Au(3)) of the central $[Au(CH_2PPh_2CH_2)_2Au]$ unit with a distance of 2.7368(7) Å, comparable to the unbridged bond in $[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_5)_2]^+$ (**2**), which is 2.755(1) Å.[11]

All three independent metal atoms show slightly distorted square-planar coordination (assuming that the Au(3') atom occupies the fourth coordination position of its symmetry-related Au(3) center). The coordination planes of Au(1) and Au(2) are almost coplanar (dihedral angle 14(2)°), with those planes of the Au(3) atom and of the $C_6F_3H_2$ ligand disposed nearly perpendicularly (mean dihedral angles 83(1) and 74(1)°, respectively).

Interestingly, the two external symmetry-related eight-membered rings present a clear boat conformation and are linked by another similar metallacycle exhibiting the alternative chair conformation.

Despite the differences between **2** and **9**, i.e. C_6F_5 instead of $2,4,6\text{-}C_6F_3H_2$ and $[Au(C_6F_5)_2]^-$ instead of $[Au(CH_2PPh_2CH_2)_2Au]$, all analogous Au–Au bond distances are very close. These data and the preparative methods prompt us to argue that probably complex **2** has an Au(I) atom in the center of the metal chain. Thus, complex **9** seems to be formed by a donation of electron density from the central $[Au^I(CH_2PPh_2CH_2)_2Au^I]$ unit to two $[RAu(CH_2PPh_2CH_2)_2Au]^+$ gold(II) fragments.

Experimental Section

General Data. Instrumentation and general experimental techniques were as described earlier.[8b] All the reactions were performed at room temperature.

$[RAu(CH_2PPh_2CH_2)_2Au(OClO_3)]$ (R = C_6F_5 (3), $C_6F_3H_2$ (4), CH_3 (5)). To a solution of $[RAu(CH_2PPh_2CH_2)_2AuCl]$[8b] (R = C_6F_5 (0.1023 g, 0.1 mmol), $2,4,6\text{-}C_6F_3H_2$ (0.0987 g, 0.1 mmol)) or $[CH_3Au(CH_2PPh_2CH_2)_2AuI]$[19] (0.0962 g, 0.1 mmol) in dichloromethane (20 mL) was added $AgClO_4$ (0.0207 g, 0.1 mmol). The mixture was stirred for 1 h, and the precipitated AgCl or AgI was filtered off and washed with dichloromethane (3 × 5 mL).

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Concentration of the filtrate to ca. 5 mL and addition of diethyl ether (20 mL) led to the precipitation of complexes **3–5** as yellow (**3**, **4**) or green-brown (**5**) solids. ^{19}F NMR: **3**, δ –124.02 (m, 2F, *o*-F), –157.43 (t, 1F, *p*-F), –160.77 (m, 2F, *m*-F); **4**, δ –93.83 (m, 2F, *o*-F), –113.29 (m, 1F, *p*-F). Yield: **3**, 87 mg (80%); **4**, 79 mg (75%); **5**, 42 mg (45%).

[{RAu(CH$_2$PPh$_2$CH$_2$)$_2$Au}$_2$AuR$_2$]ClO$_4$ (R = C$_6$F$_5$ (6), C$_6$F$_3$H$_2$ (7)). (a) To a solution of [RAu(CH$_2$PPh$_2$CH$_2$)$_2$Au(tht)]ClO$_4$[8b] (R = C$_6$F$_5$ (0.1175 g, 0.1 mmol), C$_6$F$_3$H$_2$ (0.1139 g, 0.1 mmol)) in dichloromethane (20 mL) was added NBu$_4$[AuR$_2$][20] (0.05 mmol, R = C$_6$F$_5$ (0.0387 g), C$_6$F$_3$H$_2$ (0.0351 g)). After the mixture was stirred for 15 min at room temperature, the solution was evaporated to ca. 5 mL. Addition of diethyl ether (20 mL) led to the precipitation of a mixture of complex **6** or **7** and NBu$_4$ClO$_4$, which was washed with methanol/diethyl ether (50%) to remove NBu$_4$ClO$_4$.

(b) To a solution of [(C$_6$F$_5$)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(OClO$_3$)] (**3**; 0.1087 g, 0.1 mmol) in dichloromethane (20 mL) was added NBu$_4$[Au(C$_6$F$_5$)$_2$][20a] (0.0387 g, 0.05 mmol), and the mixture was stirred for 30 min. The solution was evaporated to ca. 5 mL, and addition of diethyl ether (20 mL) led to the precipitation of a dark red solid (**6**), which was washed with a mixture of methanol/diethyl ether (50%) to remove the NBu$_4$ClO$_4$ also formed. Λ_M (~5 × 10^{-4} M, acetone solutions): 136 (**6**), 118 (**7**) Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR: **6**, δ –123.81 (m, 4F, *o*-F), –157.41 (t, 2F, *p*-F), –160.65 (m, 4F, *m*-F) and –117.22 (m, 4F, *o*-F), –159.62 (t, 2F, *p*-F), –162.68 (m, 4F, *m*-F); **7**, δ –93.81 (m, 4F, *o*-F), –112.98 (m, 2F, *p*-F) and –85.93 (m, 4F, *o*-F), –113.53 (m, 2F, *p*-F). Yield: **6**, 65 mg (50%); **7**, 55 mg (45%).

[{RAu(CH$_2$PPh$_2$CH$_2$)$_2$Au}$_2$Au(CH$_2$PPh$_2$CH$_2$)$_2$Au](ClO$_4$)$_2$ (R = C$_6$F$_5$ (8), C$_6$F$_3$H$_2$ (9), CH$_3$ (10)). (a) To a solution of [RAu(CH$_2$PPh$_2$CH$_2$)$_2$Au(tht)]ClO$_4$[8b] (R = C$_6$F$_5$ (0.1175 g, 0.1 mmol), C$_6$F$_3$H$_2$ (0.1139 g, 0.1 mmol)) in dichloromethane (20 mL) was added [Au(CH$_2$PPh$_2$CH$_2$)$_2$Au][5] (0.0410 g, 0.05 mmol). The mixture was stirred for 15 min. Concentration of the solution to ca. 5 mL and addition of diethyl ether (20 mL) gave complexes **8** and **9** as dark red (**8**) and red (**9**) solids.

(b) To a solution of [RAu(CH$_2$PPh$_2$CH$_2$)$_2$Au(OClO$_3$)] (R = C$_6$F$_5$ (**3**; 0.1087 g, 0.1 mmol), CH$_3$ (**5**; 0.0935 g, 0.1 mmol)) in dichloromethane (20 mL) was added [Au(CH$_2$PPh$_2$CH$_2$)$_2$Au][5] (0.0410 g, 0.05 mmol). After it was stirred for 30 min, the solution was evaporated to ca. 5 mL. Addition of diethyl ether (20 mL) led to the precipitation of complexes **8** and **9** as dark red and brown solids, respectively. Λ_M (~9 × 10^{-5} M, acetone solutions): 300 (**8**), 280 (**9**) Ω^{-1} cm^2 mol^{-1}. Complex **10** is not soluble enough. ^{19}F NMR: **8**, δ –123.51 (m, 4F, *o*-F), –157.66 (t, 2F, *p*-F), –160.66 (m, 4F, *m*-F); **9**, δ –93.65 (m, 4F, *o*-F), –113.61 (m, 2F, *p*-F). Yield: **8**, 127 mg (85%); **9**, 102 mg (70%); **10**, 100 mg (75%).

X-ray Structure Analysis of 9. Collection and Reduction of Data. Crystals of **9** suitable for the X-ray study were obtained from a dichloromethane/diethyl ether solution as red plates. A red prismatic crystal was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. A summary of crystal data, intensity collection procedures, and refinement data is reported in Table 4. Cell constants were obtained from the least-squares fit of the setting angles of 52 reflections in the range 20 ≤ 2θ ≤ 35°. The 8729 recorded reflections (±*h*,+*k*,–*l*) were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no intensity decay was observed. An empirical method was used to correct the data for absorption effects.[21]

Table 4. Crystallographic Data for 9

Crystal Data	
formula	$C_{96}H_{88}Au_6Cl_2F_6O_8P_6$
mol wt	2922.29
color, habit	red, irregular, prismatic block
cryst size, mm	0.152 × 0.175 × 0.397
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	12.150(1)
b, Å	15.498(2)
c, Å	24.693(2)
β, deg	95.18(1)
V, Å^3; *Z*	4630.7(8); 2
D_{calcd}, g cm^{-3}	2.096
Data Collection and Refinement	
diffractometer	four-circle Siemens AED
λ(Mo Kα radiation), Å; technique	0.710 69; bisecting geometry
monochromator	graphite oriented
μ, cm^{-1}	96.80
scan type	ω/2θ
2θ range, deg	3–50
no. of data collected	8729 (±*h*,+*k*,–*l*)
no. of unique data	8181
unique obsd data	5132 ($F_o \geq 6\sigma(F_o)$)
no. of params refined	540
R, R_w[a]	0.0404, 0.0417
max, min correctn factors	0.729, 1.185

[a] $w^{-1} = \sigma^2(F_o) + 0.000508F_o^2$.

Structure Solution and Refinement. The structure was solved by Patterson (Au atoms) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares, initially with isotropic thermal parameters. Further refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms (except for oxygen atoms of the perchlorate group). Hydrogen atoms were included in calculated positions and refined riding on carbon atoms with a common isotropic thermal parameter. The function minimized was $\Sigma([F_o] - [F_c])^2$ with the weight defined as $w^{-1} = \sigma^2(F_o) + 0.000508F_o^2$. Atomic scattering factors, corrected for anomalous dispersion for Au, P and Cl, were taken from ref 22. Final *R* and R_w values were 0.0404 and 0.0417, respectively. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[23]

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen coordinates, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (16 pages). Ordering information is given on any current masthead page.

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