ORGANOMETALLICS

Synthesis and Structure of[Au4(C6F5)2{(PPh2)2CH}2(PPh3)2](ClO4)2.cntdot.4CH2Cl2, a Complex with Two Direct Gold-Gold Bonds

M. Concepcion Gimeno, Josefina Jimenez, Peter G. Jones, Antonio Laguna, and Mariano Laguna

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Synthesis and Structure of $[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2(PPh_3)_2](ClO_4)_2{\cdot}4CH_2Cl_2$, a Complex with Two Direct Gold–Gold Bonds[†]

M. Concepción Gimeno,[‡] Josefina Jiménez,[‡] Peter G. Jones,[§]
Antonio Laguna,[*,‡] and Mariano Laguna[‡]

*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain, and Institut für Anorganische und
Analytische Chemie, Technische Universität Braunschweig, Postfach 3329,
D-38023 Braunschweig, Germany*

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Summary: The oxidative addition of chlorine or bromine to $[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2]$ *leads to* $[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2X_2]$ *(X = Cl, Br). Displacement of chlorine by reaction with* $[Ag(OClO_3)L]$ *gives the cationic complexes* $[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2L_2](ClO_4)_2$ *(L = tht,* PPh_3, PPh_2Me, $P(tol)_3$*). The structure of the* PPh_3 *derivative has been determined by single-crystal diffraction. It crystallizes with crystallographic 2-fold symmetry in the monoclinic space group C2/c:* $a = 17.670(3)$ Å, $b = 25.484(5)$ Å, $c = 22.651(5)$ Å, $\beta = 93.86(2)^\circ$, $Z = 4$, $T = -100$ °C. *Its backbone is a linear chain of three four-coordinated gold atoms, in which the central gold atom is bonded to the others with an Au–Au distance of 2.7305(11) Å. The formal charge of the* Au_3 *unit is +5, but integral oxidation states consistent with normal coordination geometry cannot be assigned.*

Introduction

The oxidative addition of halogens to the corresponding binuclear gold(I) derivatives has been exploited as a general synthesis of binuclear gold(II) complexes, the metal centers of which display square-planar coordination geometry including the newly formed gold–gold bond.[1–3] Occasionally mixed-valent isomers of gold(I)–gold(III) without metal–metal bonds[4,5] are obtained. Here we report an oxidative addition that proceeds differently, forming new types of neutral or cationic tetranuclear gold complexes, $[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2X_2]$ (X = Cl, Br) or $[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2L_2](ClO_4)_2$ (L = tetrahydrothiophene, PPh_3, PPh_2Me, $P(tol)_3$) with a linear Au_3 group.

Results and Discussion

The reaction of the tetranuclear complex 1 (previously described by us[6]) with chlorine or bromine does not oxidize the two gold(I) centers of the diauracycle to give the usual gold(II) derivatives with an X–Au–Au–X backbone; instead, a new type of reaction occurs. The colorless solution of 1 in dichloromethane turns orange-red (X = Cl) or deep red (X = Br) on addition of a CCl_4 solution of the halogen X_2 in the molar ratio 1:1, and complex 2 or 3 is obtained (see Scheme 1).

The reaction of 2 with the silver complex $[Ag(OClO_3)(tht)]$ (tht = tetrahydrothiophene) in dichloromethane leads to the cationic complex 4. The ready displacement of tht from complex 4 facilitates the preparation of a variety of complexes. Addition of $[N(PPh_3)_2]Cl$ or neutral ligands (PR_3 = PPh_3, PPh_2Me, $P(tol)_3$) to dichloromethane solutions of 4 (molar ratio 1:2) leads to the neutral 2 or the cationic complexes 5–7, respectively. Compounds 5–7 can also be obtained from 2 and $[Ag(OClO_3)(PR_3)]$ in dichloromethane.

Complexes 2–7 were isolated as orange-red (2), deep red (3), red (4), or blue solids (5–7), the last a hitherto unknown color for gold complexes. They are unstable in the solid state or in solution at room temperature, but they can be stored for several weeks at −20 °C. The $^{31}P\{^1H\}$ NMR spectra for the four PPh_2 groups show two broad signals corresponding to a poorly resolved AA′XX′ system (see Table 1). The phosphorus atoms of the phosphine appear as a singlet for complexes 5–7. The CH protons appear as a multiplet in the ^1H NMR spectra. The ^{19}F NMR spectra indicate that the pentafluorophenyl rings cannot rotate and the *ortho* and *meta* fluorine atoms are not equivalent (see Experimental Section).

Crystals of 5 suitable for X-ray studies were obtained from dichloromethane/petroleum ether at −20 °C as blue plates. The cation of 5 is shown in Figure 1; it displays crystallographic 2-fold symmetry, the atoms Au(2) and Au(3) lying on the special positions 0.5, *y*, 0.25. Its backbone is the linear chain of three gold atoms Au(1)–Au(3)–Au(1′) (bond angle 178.68(4)°). The independent gold–gold distances are Au(1)–Au(3) = 2.7305(11) Å and Au(2)–Au(3) = 2.909(2) Å. The latter is similar to that in 1 (2.918 Å), where there is no formal gold–gold bond; furthermore, the geometry at Au(2) is essentially linear (P(2)–Au(2)–P(2′) = 176.6(2)°), so that Au(2) may reasonably be assigned the oxidation state +I.

The assignment of oxidation states to the three gold atoms in the linear chain is less straightforward. The sum must equal +5, so the only two possibilities with integral oxidation states are (a) Au^{II}–Au^{I}–Au^{II} and (b) Au^{I}–Au^{III}–Au^{I}. Au^{I} is usually linear but may be trigonal planar or tetrahedral with varying degrees of distortion, whereas Au^{II} (dinuclear) and Au^{III} are almost exclusively square planar. However, square-planar Au^{I} has been postulated in some other oligogold systems ($[\{C_6F_5Au(CH_2PPh_2CH_2)_2$-

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[‡] Universidad de Zaragoza-CSIC.

[§] Technische Universität Braunschweig.

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Scheme 1. Synthesis and Reactions of the Tetranuclear Complex 2

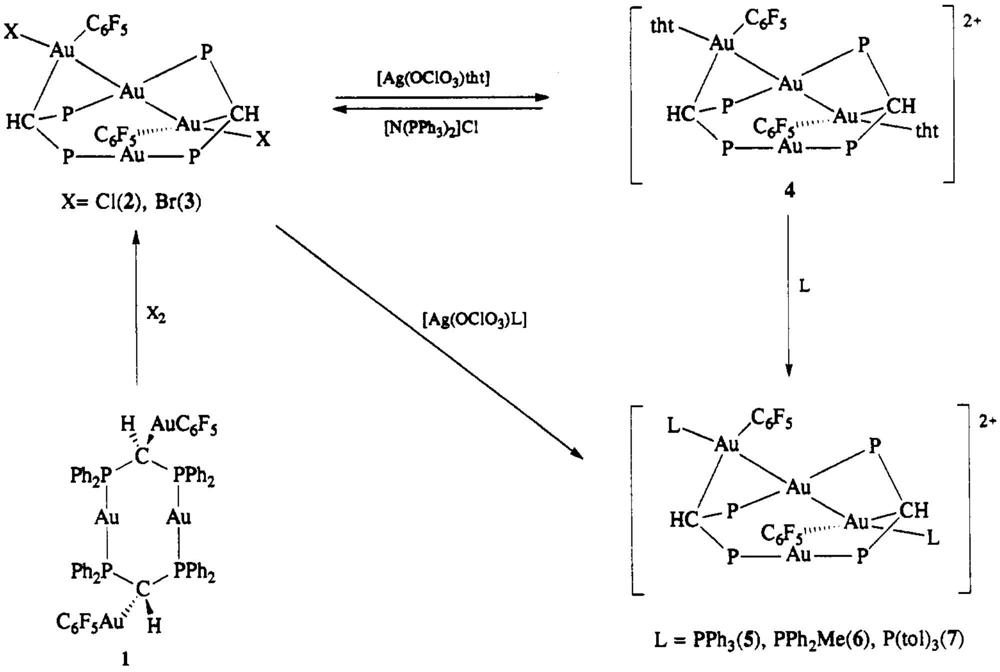

Table 1. Analytical and Spectroscopic Data for the Products

complex	yield (%)	anal. (%)[a]		$^{31}P\{^1H\}$		^{1}H NMR[b]
		C	H	δ(PPh$_2$) [*N*][c]	δ(PR$_3$)	δ(CH)
$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2Cl_2]$ (**2**)	85	37.65 (38.0)	2.1 (2.15)	41.3 ("t"), 12.7 ("t") [19.5]		4.58 (m)
$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2Br_2]$ (**3**)	84	36.45 (36.35)	2.05 (2.05)	38.4 (m), 8.3 (m)		4.69 (m)
$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2(tht)_2](ClO_4)_2$ (**4**)	74	37.05 (37.15)	2.5 (2.6)	38.9 (m), 4.6 (m)		4.71 (m)
$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2(PPh_3)_2](ClO_4)_2$ (**5**)	80	44.9 (45.05)	2.85 (2.8)	36.3 (m), 6.7 (m)	27.5 (s)	4.0 (m)
$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2(PPh_2Me)_2](ClO_4)_2$ (**6**)	75	42.65 (42.5)	2.8 (2.75)	30.9 (m), 5.5 (m)	21.7 (s)	3.87 (m)
$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2(P(tol)_3)_2](ClO_4)_2$ (**7**)	75	46.55 (46.35)	3.0 (3.15)	36.7 (m), 8.3 (m)	28.5 (s)	3.46 (m)

[a] Calculated values are given in parentheses. [b] In CDCl$_3$ (−40 °C), with values in ppm. Other data are in the Experimental Section. [c] *N* is the splitting between two consecutive lines, with values in hertz.

$Au\}_2Au(C_6F_5)_2]^+$,[7] $[\{C_6F_3H_2Au(CH_2PPh_2CH_2)_2Au\}_2\{Au(CH_2)_2PPh_2\}_2]^{2+}$ [8]) and also in $[\{Au(CH_2)_2PPh_2\}_2(SO_2)_2]$,[9] in which, however, the SO$_2$ ligands are disordered and the Au centers may be at least partially oxidized. In **5**, the geometry at Au(3) is planar (Au(3) lies only 0.05 Å out of the plane formed by its four bonding partners) but obviously distorted; however, the distortion arises mainly from the steric requirements of the four-membered ring (the transannular distance P(3)···Au(1′) is only 2.871 Å, with P(3)–Au(3)–Au(1′) = 68.49(11)°). Au(1) is also in a distorted-planar environment, with Au(3)–Au(1)–C(1) = 77.5(5)°, P(1)–Au(1)–Au(3) = 163.04(15)°, and C(81)–Au(1)–C(1) = 169.6(7)°; it lies 0.15 Å out of the plane of its four neighbors. Au(1), C(1), P(1), and C(81) are coplanar to within 0.001 Å, with Au(3) 0.69 Å out of this plane. We therefore tentatively describe Au(3) as square-planar Au^{I} and Au(1) as Au^{II}, but we cannot rule out other possibilities[10] and a delocalized model with nonintegral oxidation states may be also possible, particularly in view of the unusual color. The Au–Au bond length lies within the

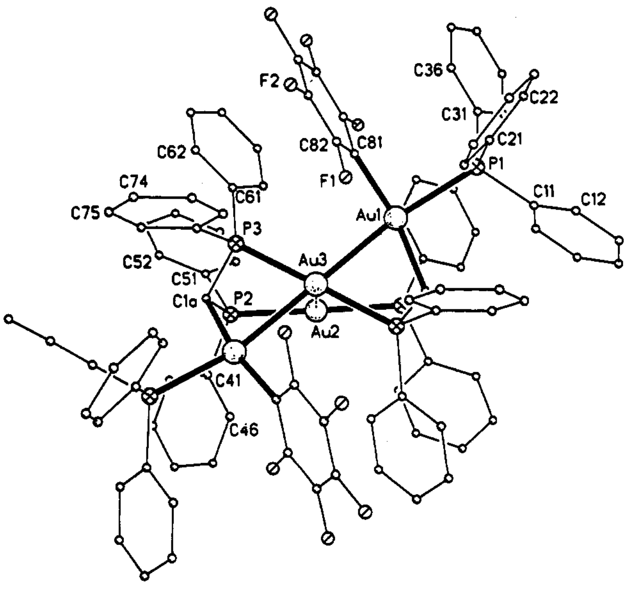

Figure 1. Cation of complex **5** in the crystal. Radii are arbitrary; H atoms are omitted for clarity.

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Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Complex 5[a]

	x	*y*	*z*	*U*(eq)
Au(1)	6389.4(4)	6580.7(3)	2040.5(3)	32.7(4)
Au(2)	5000	5451.7(4)	2500	32.9(6)
Au(3)	5000	6593.1(3)	2500	28.4(5)
P(1)	7707(3)	6758(2)	1810(3)	53(3)
P(2)	3708(3)	5479(2)	2232(2)	33(2)
P(3)	4019(3)	6564(2)	1754(2)	33(3)
C(1)	6594(11)	6148(7)	2855(8)	38(4)
C(11)	8410(11)	6577(9)	2395(9)	80(8)
C(12)	8873(14)	6939(7)	2704(11)	98(10)
C(13)	9405(13)	6769(11)	3143(11)	152(16)
C(14)	9474(14)	6237(12)	3272(11)	168(19)
C(15)	9011(16)	5875(8)	2963(12)	142(15)
C(16)	8479(13)	6045(8)	2525(10)	103(10)
C(21)	7818(10)	7473(5)	1784(7)	57(6)
C(22)	8401(9)	7704(7)	1494(8)	85(8)
C(23)	8472(10)	8248(7)	1486(9)	100(10)
C(24)	7960(12)	8559(5)	1767(10)	109(11)
C(25)	7377(10)	8327(6)	2057(8)	89(9)
C(26)	7306(8)	7784(6)	2066(7)	67(6)
C(31)	8003(10)	6545(6)	1101(6)	52(5)
C(32)	8475(11)	6111(7)	1069(7)	95(9)
C(33)	8687(11)	5936(7)	523(9)	108(11)
C(34)	8426(12)	6195(8)	8(7)	102(10)
C(35)	7953(11)	6629(8)	41(6)	100(10)
C(36)	7742(9)	6804(6)	587(8)	72(7)
C(41)	3140(7)	5176(5)	2783(5)	40(4)
C(42)	2534(8)	4848(6)	2619(5)	60(6)
C(43)	2105(7)	4630(6)	3048(7)	79(8)
C(44)	2282(8)	4739(6)	3643(6)	67(7)
C(45)	2888(8)	5068(6)	3807(4)	62(6)
C(46)	3317(7)	5286(5)	3377(5)	47(5)
C(51)	3489(7)	5121(5)	1551(5)	39(4)
C(52)	2851(7)	5223(5)	1176(6)	63(6)
C(53)	2729(7)	4943(6)	651(6)	68(7)
C(54)	3245(8)	4562(5)	502(5)	63(6)
C(55)	3883(7)	4460(5)	877(6)	52(5)
C(56)	4005(6)	4739(5)	1401(5)	44(5)
C(61)	4181(8)	6318(5)	1015(4)	44(5)
C(62)	3778(8)	6523(5)	519(6)	59(6)
C(63)	3851(8)	6298(5)	–34(5)	66(6)
C(64)	4327(8)	5870(5)	–91(4)	55(5)
C(65)	4730(7)	5665(4)	405(5)	46(5)
C(66)	4657(7)	5890(5)	958(4)	41(4)
C(71)	3514(7)	7180(4)	1643(6)	43(5)
C(72)	3909(6)	7648(5)	1732(6)	51(5)
C(73)	3543(9)	8124(4)	1622(7)	71(7)
C(74)	2782(9)	8133(5)	1423(8)	80(8)
C(75)	2387(6)	7665(6)	1333(7)	75(7)
C(76)	2752(7)	7188(5)	1443(7)	58(6)
C(81)	5991(9)	6968(4)	1292(7)	34(4)
C(82)	5717(8)	7480(6)	1274(6)	44(5)
C(83)	5469(10)	7730(6)	753(7)	57(6)
C(84)	5489(13)	7480(5)	220(9)	57(6)
C(85)	5761(11)	6977(6)	217(7)	44(5)
C(86)	6009(10)	6731(6)	741(6)	40(4)
F(1)	5678(7)	7750(4)	1784(4)	57(9)
F(2)	5214(9)	8228(4)	778(6)	83(14)
F(3)	5250(10)	7721(5)	–284(5)	84(14)
F(4)	5776(9)	6710(5)	–296(4)	70(12)
F(5)	6267(6)	6233(3)	705(4)	45(7)
Cl(1)	5829(5)	3886(3)	1812(4)	104(3)
Q(1)	5711(17)	4216(12)	2290(12)	201(15)
O(2)	6544(16)	3967(12)	1610(15)	224(17)
O(3)	5745(20)	3361(10)	1985(16)	240(19)
O(4)	5272(19)	3994(16)	1352(14)	532(60)
Cl(2)	6732(12)	1206(8)	107(9)	244(8)
Cl(3)	5732(14)	405(9)	377(10)	137(7)
Cl(3′)	6522(14)	2092(10)	39(11)	145(8)
Cl(4)	204(13)	4370(9)	1739(10)	134(7)
Cl(4′)	1180(14)	4308(10)	1494(11)	142(8)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

range found in gold clusters[11] and is similar to the values observed for formal Au^I–Au^{II} bonds in $[\{C_6F_5Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_5)_2]^+$[7] (2.755(1) Å) and $[\{C_6F_3H_2Au(CH_2PPh_2CH_2)_2Au\}_2\{Au(CH_2)_2PPh_2\}_2]^{2+}$[8] (2.7368(7) Å) yet much longer than the formal Au^I–Au^{III} bond in $[\{Au(CH_2)_2PPh_2\}_2Au(C_6F_5)_3]$[12] (2.572(1) Å).

The Au–P bonds to the phosphorus atoms of the diphosphine (2.338(5), 2.323(5) Å) are somewhat longer than in **1** (2.309(5), 2.303(5) Å), but the difference may not be highly significant. The Au(1)–P(1) bond length of 2.462(5) Å is similar to those in the four-coordinate Au^I complexes $[AuCl(PPh_3)_3]$[13] (2.395–2.431(2) Å) and $[Au(PPh_3)_4]BPh_4$[14] (2.392–2.408(4) Å).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 5[a]

Au(1)–C(81)	2.046(17)	Au(1)–C(1)	2.159(18)
Au(1)–P(1)	2.462(5)	Au(1)–Au(3)	2.7305(11)
Au(2)–P(2)	2.323(5)	Au(2)–Au(3)	2.909(2)
Au(3)–P(3)	2.338(5)	P(1)–C(31)	1.805(14)
P(1)–C(11)	1.816(18)	P(1)–C(21)	1.832(14)
P(2)–C(1i)	1.795(18)	P(2)–C(51)	1.812(10)
P(2)–C(41)	1.823(11)	P(3)–C(1i)	1.792(18)
P(3)–C(71)	1.815(11)	P(3)–C(61)	1.829(10)
C(81)–Au(1)–C(1)	169.6(7)	C(81)–Au(1)–P(1)	90.7(5)
C(1)–Au(1)–P(1)	99.7(5)	C(81)–Au(1)–Au(3)	92.4(4)
C(1)–Au(1)–Au(3)	77.5(5)	P(1)–Au(1)–Au(3)	165.04(15)
P(2)–Au(2)–P(2i)	176.6(2)	P(2)–Au(2)–Au(3)	88.30(11)
P(3)–Au(3)–P(3i)	176.4(2)	P(3)–Au(3)–Au(1i)	68.49(11)
P(3)–Au(3)–Au(1)	111.46(11)	Au(1)–Au(3)–Au(1i)	178.68(4)
P(3)–Au(3)–Au(2)	88.18(11)	Au(1)–Au(3)–Au(2)	89.34(3)
C(31)–P(1)–C(11)	110.3(9)	C(31)–P(1)–C(21)	103.5(8)
C(11)–P(1)–C(21)	102.0(9)	C(31)–P(1)–Au(1)	117.9(6)
C(11)–P(1)–Au(1)	114.1(7)	C(21)–P(1)–Au(1)	107.1(6)
C(1i)–P(2)–C(51)	109.8(7)	C(1i)–P(2)–C(41)	107.7(8)
C(51)–P(2)–C(41)	105.9(6)	C(1i)–P(2)–Au(2)	109.7(6)
C(51)–P(2)–Au(2)	110.9(5)	C(41)–P(2)–Au(2)	112.7(5)
C(1i)–P(3)–C(71)	105.8(8)	C(1i)–P(3)–C(61)	112.8(8)
C(71)–P(3)–C(61)	105.9(6)	C(1i)–P(3)–Au(3)	96.1(6)
C(71)–P(3)–Au(3)	114.0(5)	C(61)–P(3)–Au(3)	121.3(5)
P(3i)–C(1)–P(2i)	115.5(10)	P(3i)–C(1)–Au(1)	92.7(8)
P(2i)–C(1)–Au(1)	111.1(9)	C(86)–C(81)–C(82)	114.2(16)

[a] Symmetry operator: (i) 1 – *x*, *y*, 0.5 – *z*.

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer. NMR spectra were recorded on Varian XL200 and Varian XL300 Unity spectrometers in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external, ^{31}P), and $CFCl_3$ (external, ^{19}F). The yields, C and H analyses, and proton and $^{31}P\{^1H\}$ NMR data are listed in Table 1.

$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2X_2]$ (X = Cl (2), Br (3)). To a colorless solution of $[Au_4(C_6F_5)_2\{Ph_2P)_2CH\}_2]$[6] (0.1889 g, 0.1 mmol) in dichloromethane (20 mL) was added 0.1 mmol of X_2 (CCl_4 solution, X = Cl (0.15 M), X = Br (0.2 M)). The orange-red (**2**) or deep red (**3**) solution was stirred for 1 min and vacuum-evaporated to *ca.* 5 mL. Addition of *n*-hexane (20 mL) yielded complex **2** or **3**. ^1H NMR: **2**, δ 8.3–6.8 (m, 40H, Ph); **3**, δ 8.3–6.6 (m, 40H, Ph). ^{19}F NMR: **2**, δ –111.2 (m, 2F, *o*-F), –117.8 (m, 2F, *o*-F), –159.5 (t, 2F, *p*-F), –160.3 (m, 2F, *m*-F), –161.8 (m, 2F,

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m-F); **3**, δ −111.3 (m, 2F, *o*-F), −115.7 (m, 2F, *o*-F), −159.7 (*t*, 2F, *p*-F), −161.1 (m, 2F, *m*-F), −161.9 (m, 2F, *m*-F).

$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2(tht)_2](ClO_4)_2$ (4). To a solution of **2** (0.196 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Ag(OClO_3)tht]$[15] (0.059 g, 0.2 mmol). The mixture was stirred for 2 min, and then the precipitate of AgCl was filtered off. The solvent was evaporated to *ca.* 5 mL, and addition of diethyl ether (20 mL) led to the precipitation of **4** as a red solid. ^1H NMR: δ 8.24–7.06 (m, 40H, Ph), 2.28 (m, 8H, SCH_2), 1.38 (m, 8H, CH_2). ^{19}F NMR: δ −109.3 (m, 2F, *o*-F), −113.3 (m, 2F, *o*-F), −155.3 (t, 2F, *p*-F), −157.4 (m, 2F, *m*-F), −160.1 (m, 2F, *m*-F).

$[Au_4(C_6F_5)_2\{(Ph_2P)_2CH\}_2(PR_3)_2](ClO_4)_2$ (PR_3 = PPh_3 (5), PPh_2Me (6), $P(tol)_3$ (7)). (a) To a dichloromethane (20 mL) solution of **2** (0.147 g, 0.075 mmol) was added 0.15 mmol of $[Ag(OClO_3)L]$[16] (L = PPh_3 (0.0704 g), PPh_2Me (0.0611 g), $P(tol)_3$ (0.0768 g)). The mixture was stirred for 2 min, and then the precipitate of AgCl was filtered off. Concentration of the solution to *ca.* 5 mL and addition of diethyl ether (20 mL) led to the precipitation of complexes **5**–**7** as blue solids.

(b) To a solution of **4** (0.1698 g, 0.075 mmol) in dichloromethane (20 mL) was added 0.15 mmol of PPh_3 (0.0393 g), PPh_2Me (1 mL of a solution 0.1 M in hexane), or $P(tol)_3$ (0.0457 g). The mixture was stirred for 2 min and evaporated to *ca.* 5 mL. Addition of diethyl ether (20 mL) led to the precipitation of complexes **5**–**7**.

^1H NMR: **5**, δ 7.75–6.88 (m, 70H, Ph); **6**, δ 8.1–6.85 (m, 60H, Ph), 1.47 (m, 6H, CH_3); **7**, δ 8.1–6.6 (m, 64H, Ph), 2.39 (s, 18H, CH_3). ^{19}F NMR: **5**, δ −106.6 (m, 2F, *o*-F), −111.5 (m, 2F, *o*-F), −155.3 (t, 2F, *p*-F), −157.6 (m, 2F, *m*-F), −160.1 (m, 2F, *m*-F); **6**, δ −107.6 (m, 2F, *o*-F), −114.4 (m, 2F, *o*-F), −155.9 (t, 2F, *p*-F), −157.3 (m, 2F, *m*-F), −160.1 (m, 2F, *m*-F); **7**, δ −107.6 (m, 2F, *o*-F), −111.1 (m, 2F, *o*-F), −156.4 (t, 2F, *p*-F), −158.6 (m, 2F, *m*-F), −160.3 (m, 2F, *m*-F).

Crystal Structure Determination of Compound 5. Crystal data: $5\cdot 4CH_2Cl_2$, $C_{102}H_{80}Au_4Cl_{10}F_{10}O_8P_6$, M_r = 2951.85, monoclinic, space group *C*2/*c*, *a* = 17.670(3) Å, *b* = 25.484(5) Å, *c* = 22.651(5) Å, β = 93.86(2)°, *V* = 10 177(4) Å^3, *Z* = 4, D_{calcd} = 1.927 Mg m^{-3}, *F*(000) 5688, λ(Mo Kα) = 0.710 73 Å, μ = 6.2 mm^{-1}, *T* = −100 °C.

Data Collection and Reduction. A blue plate of dimensions 0.8 × 0.3 × 0.08 mm was mounted in inert oil (type RS3000, donated by Fa. Riedel de Haën). Using Mo Kα radiation on a Siemens R3 diffractometer, 9274 intensities were measured to $2\Theta_{max}$ = 50°. An absorption correction based on ψ scans was applied, with transmission factors 0.61–0.99. Merging equivalents gave 8974 unique reflections (R_{int} = 0.053), of which 8944 were used for all calculations (program SHELXL-92).[17] Cell constants were refined from setting angles of 48 reflections in the range 2Θ = 20–22°.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and refined on F^2 with Au, P, and F anisotropic and idealized hexagons for the phenyl (but not pentafluorophenyl) rings. H atoms were included using a riding model. The final $R_w(F^2)$ value was 0.237, with conventional $R(F)$ = 0.066 for 245 parameters and 40 restraints (*S* = 1.084). Both the perchlorate anion and the solvent molecules were badly resolved, with residual electron density up to 5.8 e Å^{-3}.

Atomic positional parameters for **5** are listed in Table 2, and Table 3 contains selected bond lengths and angles.

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Supplementary Material Available: A description of the crystal structure determination, including tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates of the H atoms, additional bond distances and angles, and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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