

Synthesis, Structure, and Reactivity of the Anionic Trinuclear Methanide

NBu₄[{Au(C₆F₅)₃(PPh₂CHPPh₂)₂Au}]₂Au]

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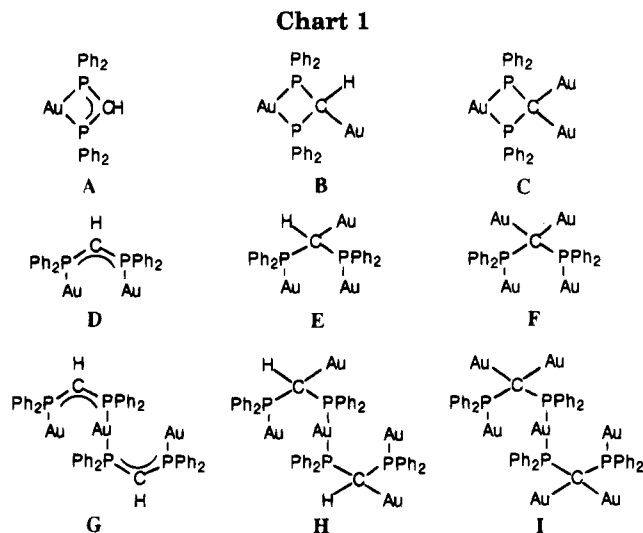
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The reaction of [Au(tht)₂]ClO₄ or NBu₄[Au(acac)₂] with 2 equiv of [Au(C₆F₅)₃PPh₂CH₂PPh₂] affords the cationic [[Au(C₆F₅)₃PPh₂CH₂PPh₂]₂Au]ClO₄ (**1**) or anionic complex NBu₄[{Au(C₆F₅)₃PPh₂CHPPh₂}]₂Au] (**2**), respectively, in high yield. The methanide complex **2** can displace tetrahydrothiophene from [AuX(tht)] to give the pentanuclear NBu₄[{Au(C₆F₅)₃PPh₂CH(AuX)PPh₂}]₂Au] (X = Cl, C₆F₅). The heptanuclear [Au(C₆F₅)₃PPh₂C(AuPPh₃)₂PPh₂]₂Au]ClO₄ is obtained by reaction of **1** with [Au(acac)PPh₃] (molar ratio 1:4). The structure of **2** has been determined by a single-crystal X-ray diffraction study. It crystallizes in the space group *P* $\bar{1}$ with *a* = 14.213(4) Å, *b* = 16.067(4) Å, *c* = 23.840(6) Å, α = 88.60(2)°, β = 89.27(2)°, γ = 71.23(2)°, *Z* = 2, and *T* = -100 °C. It does not display gold–gold interactions.

Introduction

We have reported the synthesis of methanide or methanediide complexes of gold starting from bis(diphenylphosphino)methane gold complexes, such as [Au(C₆F₅)₂{(PPh₂)₂CH₂}]ClO₄ or [CH₂{PPh₂AuPPh₂}]₂CH₂(ClO₄)₂, and by reaction with sodium hydride,¹ (acetylacetonato)gold derivatives,^{2,3} and other deprotonating agents.¹ However, in these complexes, the diphosphine acts as a chelating or bridging ligand, respectively, and after deprotonation the only possibility for further coordination is through the methanide carbon atom. The reaction of [Au(acac)PPh₃] with (PPh₂)₂CH₂ (dppm) leads to the deprotonation of the CH₂ group and formation of a dinuclear eight-membered-ring complex in which the donor atoms at gold are the phosphorus atoms of the phosphine.⁴ The different coordination forms reported^{1–4} for these ligands are in Chart 1 (A–F). There is no example of a derivative with three gold centers bonded by two methanide or methanediide ligands (forms G–I). Most of the gold methanide complexes described so far are neutral or cationic; there are very few examples of anionic complexes.

In this paper we describe the preparation of the trinuclear NBu₄[{Au(C₆F₅)₃PPh₂CHPPh₂}]₂Au] by reaction of [Au(C₆F₅)₃PPh₂CH₂PPh₂] with NBu₄[Au(acac)₂]. Its molecular structure has been established by X-ray studies and shows the presence of two PPh₂CHPPh₂



groups bridging the gold(I) and gold(III) centers. The excess electron density on the C-methanide can be used to coordinate to new gold centers.

Results and Discussion

The diphosphine in [Au(C₆F₅)₃PPh₂CH₂PPh₂] acts as a monodentate ligand,⁵ and the free phosphorus atom can be used to coordinate other gold centers. Thus, the reaction with [Au(tht)₂]ClO₄ (molar ratio 2:1) leads to the trinuclear complex [[Au(C₆F₅)₃PPh₂CH₂PPh₂]₂Au]ClO₄ (**1**) (Scheme 1).

The use of acetylacetonato (acac) complexes, such as [Au(acac)₂]⁻ or [Au(acac)PPh₃], as deprotonating agents which allow one to form Au–C bonds very easily has been previously reported.^{2,3,6,7} The reaction of NBu₄–

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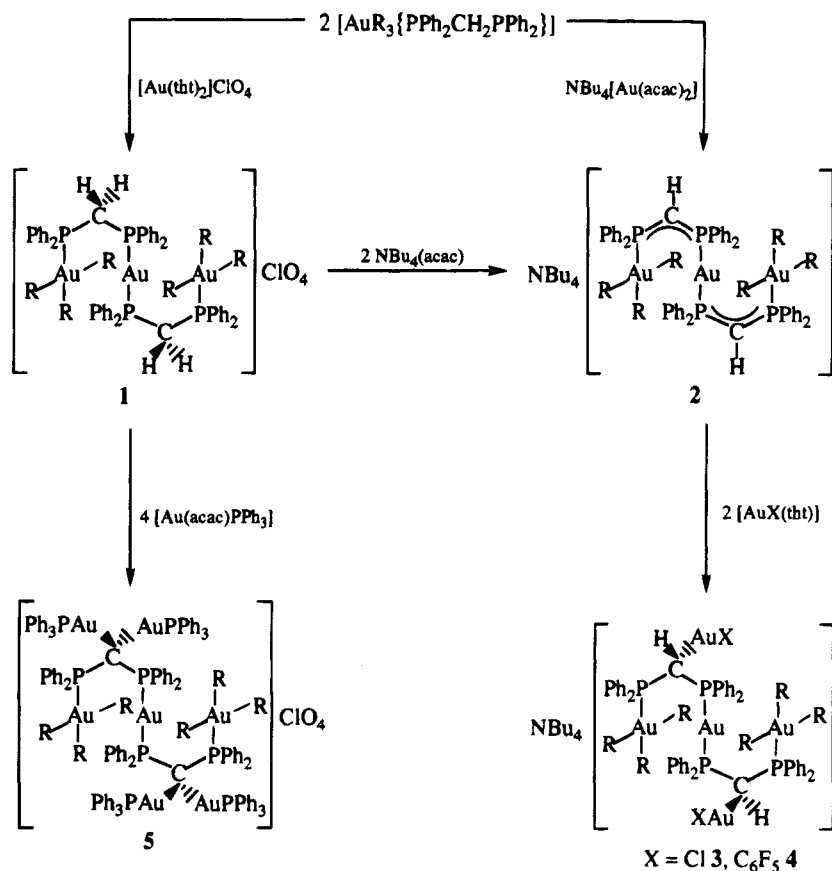
(1) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743.

(2) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Lopez-de-Luzuriaga, J. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3365.

(3) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Lopez-de-Luzuriaga, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 87.

(4) Gimeno, M. C.; Laguna, A.; Laguna, M.; Sanmartín, F.; Jones, P. G. *Organometallics* **1993**, *12*, 3984; *Organometallics* **1994**, *13*, 1538.

(5) Usón, R.; Laguna, A.; Laguna, M.; Fernández, E. J.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1971.

Scheme 1^a^a R = C₆F₅.

[Au(acac)₂] with [Au(C₆F₅)₃PPh₂CH₂PPh₂] (molar ratio 1:2) leads to the deprotonation of the CH₂ group and formation of the trinuclear complex **2** (Scheme 1). The gold(I) center is coordinated to the free phosphorus atom instead of the C-methanide, as we have observed in other complexes.^{4,8} Complex **2** can also be obtained by reaction of **1** with NBu₄(acac), in molar ratio 1:2, but in this case a mixture of **2** and NBu₄ClO₄ is obtained, and separation of these two products is difficult because of their similar solubilities in common organic solvents.

The presence of excess electron density on the methanide carbons causes them to act as C-donor nucleophiles, and they are able to displace tetrahydrothiophene (tht) from [AuX(tht)] (X = Cl or C₆F₅) to give the pentanuclear complexes **3** or **4** (Scheme 1).

The reaction of the trinuclear complex **1** with 4 equiv of [Au(acac)PPh₃] affords the heptanuclear [(Au(C₆F₅)₃PPh₂C(AuPPh₃)₂PPh₂)₂Au]ClO₄ (**5**) in which the bis(diphenylphosphino)methanediide acts as an eight-electron donor ligand bonded to four gold atoms. Only two examples are known^{3,9} in which this ligand bridges four metal centers. [Au(acac)PR₃] was previously used in the preparation of complexes with two =C{Au(PR₃)₂}₂ groups, as in the synthesis of [(PPh₃)Au]₂C(PPh₂AuPPh₂)₂C{Au(PPh₃)₂}(ClO₄)₂³ or [(Au(PMe₂Ph))₄{μ-C(PPh₃)₂CO}](ClO₄)₂.⁶

Complexes **1–5** are air- and moisture-stable white (**1**, **5**), pale yellow (**3**, **4**), or yellow (**2**) solids. They behave as 1:1 electrolytes in acetone solution [118 (**1**), 110 (**2**), 119 (**3**), 140 (**4**), or 80 (**5**) Ω⁻¹ cm² mol⁻¹ for 5 × 10⁻⁴ M solutions]. Their IR spectra show bands at *ca.* 1505 (vs), 967 (vs), and 800 (s) cm⁻¹ arising from C₆F₅ groups bonded to gold(III) centers.⁵ Furthermore, complex **2** shows a band at 1174 (m) cm⁻¹ assigned to the methanide (P–CH–P) system.¹ For complexes **3** the ν(Au–Cl) vibration appears at 320 (m) cm⁻¹.

The ¹⁹F NMR spectra of complexes **1**, **2**, and **5** are characteristic of tris(pentafluorophenyl) compounds, showing three groups of signals associated with the two different types of C₆F₅. However, for complex **3** several signals appear in the region of the *ortho*-fluorine at δ -118.1 (m) and -122.3 (m) (relative intensities 2:1, for the two mutually *trans* C₆F₅ and one *cis* C₆F₅ groups, respectively) and at -119.1 (m) and -120.8 (m) (relative intensities 2:1) indicating the presence of two diastereomers with relative abundance 1:0.58. Since complex **3** has two chiral centers, four isomers or two diastereomers are possible. The spectrum of complex **4** also shows the presence of two diastereomers; six resonances due to the *ortho*-fluorine atoms at -115.1 (m), -118.6 (m), -120.6 (m) (relative intensities 1:1:2) and -116.0 (m), -118.3 (m), -122.1 (m) (relative intensities 1:1:2) appear (relative abundance between isomers 0.7:1). In both complexes the signals corresponding to *para*- and *meta*-fluorine atoms are overlapped for the two isomers and appear as multiplets at δ -157.5 (m) and -157.8 (m) (*para*-F) and -161.3 (m) and -162.3 (m) (*meta*-F) (**3**) and at -157.8 (m), -158.3 (m), and -159.4 (m)

(6) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Jones, P. G.; Meyer-Bäse, K.; Erdbrügger, C. F. *Organometallics* **1988**, *7*, 997.

(7) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Lagunas, M. C. *J. Chem. Soc., Chem. Commun.* **1992**, 915.

(8) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *J. Chem. Soc., Dalton Trans.* **1993**, 3401.

(9) Luser, M.; Peringer, P. *Organometallics* **1984**, *3*, 1916.

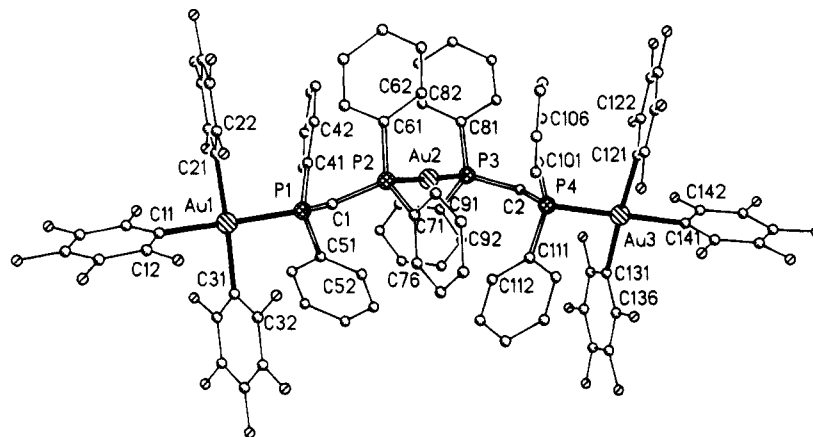


Figure 1. Anion of complex **2** in the crystal. Hydrogen atoms are omitted for clarity.

(*para*-F) and -161.8 (m), -162.7 (m), and -163.5 (m) (*meta*-F) (**4**).

The presence of two diastereomers in complex **4** can also be observed in the ^1H NMR spectrum. Thus, the resonances of the methine protons appear as two doublets of doublets (dd), one for each isomer, at 3.27 ppm [$J(\text{H}-\text{P}) = 11.3$ and 6.0 Hz] and 2.93 ppm [$J(\text{H}-\text{P}) = 14.0$ and 6.0 Hz]. In complex **3** only one resonance is observed at 3.4 ppm (dd) [$J(\text{H}-\text{P}) = 11.9$ and 5.9 Hz] probably caused by the overlapping of the other signal with one of the resonances due to the tetrabutylammonium cation [3.2(m) ppm]. For complexes **1** or **2** the resonance of the methine groups appear at 4.7 (m) or 3.55 ("t") [$J(\text{H}-\text{P}) = 11$ Hz], respectively.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1**–**5** show two broad signals corresponding to a poorly resolved AA'XX' system, even at low temperature. In complex **5** the signal due to PPh_3 appears as a singlet (see Experimental Section).

The structure of complex **2** was confirmed by an X-ray structure determination (Figure 1). Atomic coordinates are collected in Table 1, and selected bond lengths and angles, in Table 2. The gold(III) centers Au(1) and Au(3) display the expected planar coordination; the gold atoms lie 0.04 and 0.01 Å, respectively, out of their ligand planes. The Au–C bond lengths lie in the range 2.057(8)–2.080(8) Å, similar to those in other tris(pentafluorophenyl)gold(III) derivatives.¹⁰ The Au(III)–P distances are both 2.367(2) Å, longer than in $[\text{AuCl}_3(\text{PPh}_3)]$ ¹¹ (2.335(4) Å), $[\text{AuMe}_3(\text{PPh}_3)]$ ¹² [2.350(6) and 2.347(6) Å, two independent molecules], or $[\text{Au}(\text{C}_6\text{F}_5)(\text{S}_2\text{C}_6\text{H}_4)(\text{PPh}_3)]$ ¹³ (2.340(1) Å), reflecting the higher *trans* influence of the pentafluorophenyl groups. The central gold(I) atom Au(2) is linearly coordinated [Au–P = 2.311(2) and 2.314(2) Å and P–Au–P = 177.95(7)°]. There are no short gold–gold interactions; the intramolecular contacts Au(1)···Au(2) = 6.28 Å and Au(2)···Au(3) = 6.10 Å are the shortest. The P–C_{methanide} bond distances lie in the range 1.701(8)–1.722(7) Å, shorter than in the bis(diphenylphosphino)methane ligand; e.g., the P–C distance in $[\text{Au}(\text{C}_6\text{F}_5)_2\{(\text{PPh}_2)_2-$

$\text{CH}_2\}] \text{ClO}_4^{14}$ is 1.845(9) Å. This difference arises from a degree of multiple P–C bonding in the methanide ligand. The angles around the methanide carbons are P(4)–C(2)–P(3) = 123.9(5) and P(1)–C(1)–P(2) = 129.0(5)°, close to the ideal value of 120° for sp^2 hybridization.

The molecular backbone consists of two extended peripheral sections, with torsion angles C(11)···P(1)–C(1)–P(2) = -163° , P(1)–C(1)–P(2)···P(3) = -19° , P(2)···P(3)–C(2)–P(4) = -1° , and P(3)–C(2)–P(4)···C141 = -174° ; the conformation about the central gold is *gauche*, with C(1)–P(2)···P(3)–C(2) = -137° .

Experimental Section

Materials and Instrumentation. All compounds described in this report are air-stable, but reactions were performed under nitrogen atmosphere and at room temperature. Solvents were purified by standard methods and distilled under nitrogen prior to use. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured with a Jenway 4010 digital conductimeter. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. NMR spectra were recorded on Bruker ARX-300 spectrometer. Chemical shifts are cited relative to SiMe_4 (external, ^1H), 85% H_3PO_4 (external, ^{31}P), and CFCl_3 (external, ^{19}F).

Safety Note! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Synthesis. $[\text{NBu}_4][\text{Au}(\text{acac})\text{Cl}]$. To a solution of $[\text{AuCl}(\text{tbt})]^{15}$ (0.32 g, 1 mmol) in dichloromethane (30 mL) was added $[\text{NBu}_4][\text{acac}]$ (0.34 g, 1 mmol). After 30 min the solution was filtered over Celite and the solvent was concentrated to ca. 5 mL. Addition of diethyl ether (15 mL) gave $[\text{NBu}_4][\text{Au}(\text{acac})\text{Cl}]$ as a white solid. Yield: 68%. Decomposes at 42 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{43}\text{AuNO}_2\text{Cl}$: C, 44.0; H, 7.55; N, 2.45. Found: C, 44.0; H, 8.0; N, 2.45. Λ_M : 119 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR: 1654 (vs) and 1639 (vs) [$\nu(\text{CO})$], 318 (m) [$\nu(\text{AuCl})$]. ^1H NMR (CDCl_3): 4.31 (s, CH), 3.15 (m, CH_2), 2.17 [s, CH_3 (acac)], 1.59 (m, CH_2), 1.37 (m, CH_2) and 0.91 [t, CH_3 (Bu), $J(\text{HH}) = 7.3$ Hz].

$[\text{NBu}_4][\text{Au}(\text{acac})_2]$. To a solution of $[\text{NBu}_4][\text{Au}(\text{acac})\text{Cl}]$ (0.574 g, 1 mmol) in dichloromethane (30 mL) was added $\text{Ti}(\text{acac})_3$ (0.30 g, 1 mmol). After the mixture was stirred for 4 h, the precipitated TiCl_4 was filtered off. The solution was evaporated to ca. 5 mL, and addition of diethyl ether (15 mL)

(10) Usón, R.; Laguna, A.; Laguna, M.; Castilla, M. L.; Jones, P. G.; Fittschen, C. *J. Chem. Soc., Dalton Trans.* **1987**, 3017.

(11) Bandoli, G.; Clemente, D. A.; Marangoni, G.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1973**, 886.

(12) Stein, J.; Fackler, J. P., Jr.; Pappas, C.; Chen, H. W. *J. Am. Chem. Soc.* **1981**, 103, 2192.

(13) Cerrada, E.; Fernández, E. J.; Gimeno, M. C.; Laguna, A.; Laguna, M.; Terroba, R.; Villacampa, M. D. *J. Organomet. Chem.*, in press.

(14) Usón, R.; Laguna, A.; Laguna, M.; Fernández, E.; Villacampa, M. D.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1679.

(15) Usón, R.; Laguna, A. *Organomet. Synth.* **1986**, 3, 322.

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Au(1)	-906.8(2)	7470.9(2)	3735.50(12)	25.50(15)	C(93)	3126(4)	1935(4)	3529(2)	49(2)
Au(2)	1675.8(2)	4723.1(2)	2033.62(12)	24.29(15)	C(94)	2293(5)	2258(4)	3870(2)	55(3)
Au(3)	5450.7(2)	2287.4(2)	969.55(12)	24.60(15)	C(95)	1422(4)	2841(4)	3649(2)	58(3)
P(1)	80.7(14)	6262.9(13)	3213.7(8)	24.5(10)	C(96)	1384(3)	3101(4)	3087(2)	44(2)
P(2)	1104.5(14)	6241.0(12)	2052.6(8)	23.0(9)	C(101)	3276(3)	4108(3)	906(2)	25(2)
P(3)	2190.1(14)	3203.0(12)	2018.1(8)	23.2(9)	C(102)	3403(4)	4923(3)	811(2)	32(2)
P(4)	4041.8(14)	3272.3(13)	1409.2(8)	24.1(9)	C(103)	2911(4)	5464(3)	371(2)	37(2)
C(1)	566(5)	6715(5)	2674(3)	27(2)	C(104)	2292(4)	5192(3)	25(2)	40(2)
C(2)	3327(5)	2709(5)	1707(3)	26(2)	C(105)	2165(4)	4378(3)	119(2)	36(2)
C(11)	-1768(5)	8544(5)	4173(3)	35(2)	C(106)	2657(4)	3836(3)	560(2)	30(2)
C(12)	-1611(6)	9350(5)	4148(3)	42(2)	C(111)	4553(4)	3889(3)	1886(2)	27(2)
C(13)	-2154(6)	10060(5)	4451(3)	52(2)	C(112)	4260(4)	3991(4)	2446(2)	40(2)
C(14)	-2899(6)	9981(6)	4801(4)	58(3)	C(113)	4678(4)	4450(4)	2800(2)	51(2)
C(15)	-3091(6)	9196(5)	4839(3)	45(2)	C(114)	5389(4)	4806(4)	2595(2)	48(2)
C(16)	-2525(5)	8502(5)	4531(3)	35(2)	C(115)	5681(4)	4703(4)	2035(2)	39(2)
F(12)	-881(4)	9454(3)	3814(2)	51(3)	C(116)	5264(4)	4245(4)	1681(2)	35(2)
F(13)	-1970(5)	10832(3)	4424(3)	77(5)	C(121)	4817(4)	2656(3)	190(3)	27(2)
F(14)	-3435(5)	10674(4)	5109(3)	85(5)	C(122)	4313(5)	2176(5)	-75(3)	33(2)
F(15)	-3827(4)	9125(4)	5180(2)	64(3)	C(123)	3871(5)	2419(5)	-588(3)	37(2)
F(16)	-2737(4)	7739(3)	4585(2)	48(3)	C(124)	3913(6)	3184(4)	-849(4)	44(2)
C(21)	-2084(5)	7618(3)	3207(3)	31(2)	C(125)	4416(6)	3679(5)	-597(3)	43(2)
C(22)	-2269(5)	8229(5)	2775(3)	39(2)	C(126)	4857(5)	3407(4)	-86(3)	30(2)
C(23)	-3048(6)	8359(5)	2399(3)	47(2)	F(122)	4231(4)	1439(3)	178(2)	44(3)
C(24)	-3667(7)	7866(4)	2454(4)	52(2)	F(123)	3385(4)	1936(4)	-831(2)	58(3)
C(25)	-3514(6)	7257(5)	2880(3)	47(2)	F(124)	3473(4)	3442(4)	-1346(2)	65(4)
C(26)	-2727(5)	7138(5)	3249(3)	40(2)	F(125)	4457(4)	4421(3)	-848(2)	59(4)
F(22)	-1684(4)	8743(3)	2701(2)	44(3)	F(126)	5338(3)	3914(3)	149(2)	42(3)
F(23)	-3193(4)	8977(4)	1984(2)	67(4)	C(131)	6132(5)	1851(4)	1733(3)	35(2)
F(24)	-4439(4)	8002(4)	2107(3)	81(4)	C(132)	5897(6)	1237(5)	2076(3)	42(2)
F(25)	-4121(4)	6759(4)	2941(3)	72(3)	C(133)	6363(7)	937(6)	2580(4)	60(3)
F(26)	-2615(4)	6526(3)	3664(2)	50(3)	C(134)	7115(7)	1239(6)	2745(5)	74(3)
C(31)	246(5)	7431(4)	4264(3)	29(2)	C(135)	7384(7)	1844(6)	2418(4)	64(3)
C(32)	1047(5)	7706(5)	4106(3)	36(2)	C(136)	6888(6)	2143(5)	1923(3)	40(2)
C(33)	1806(6)	7678(5)	4464(3)	48(2)	F(132)	5180(4)	911(3)	1927(2)	49(3)
C(34)	1802(7)	7350(5)	4997(3)	54(2)	F(133)	6101(5)	342(4)	2901(2)	83(6)
C(35)	1036(6)	7070(5)	5178(3)	48(2)	F(134)	7594(6)	946(5)	3239(3)	120(8)
C(36)	276(5)	7124(5)	4817(3)	38(2)	F(135)	8124(5)	2138(5)	2585(3)	101(5)
F(32)	1082(4)	8028(3)	3578(2)	45(3)	F(136)	7196(4)	2711(4)	1610(2)	52(3)
F(33)	2553(4)	7961(4)	4280(3)	75(4)	C(141)	6694(5)	1475(4)	558(3)	29(2)
F(34)	2548(5)	7310(4)	5350(3)	86(5)	C(142)	6838(5)	598(4)	474(3)	33(2)
F(35)	1017(5)	6755(4)	5705(2)	74(5)	C(143)	7614(5)	72(5)	162(3)	36(2)
F(36)	-487(4)	6862(3)	5013(2)	49(3)	C(144)	8306(6)	419(4)	-66(3)	40(2)
C(41)	-653(4)	5584(3)	2961(2)	27(2)	C(145)	8197(5)	1291(5)	16(3)	39(2)
C(42)	-1120(4)	5800(3)	2444(2)	32(2)	C(146)	7402(5)	1798(4)	323(3)	31(2)
C(43)	-1722(4)	5335(4)	2255(2)	40(2)	F(142)	6191(3)	219(3)	697(2)	46(3)
C(44)	-1857(4)	4654(3)	2582(2)	39(2)	F(143)	7722(4)	-781(3)	82(2)	53(3)
C(45)	-1390(4)	4438(3)	3099(2)	39(2)	F(144)	9079(4)	-87(3)	-371(2)	59(3)
C(46)	-788(4)	4903(3)	3289(2)	35(2)	F(145)	8868(4)	1633(4)	-211(2)	59(3)
C(51)	987(3)	5494(3)	3687(2)	28(2)	F(146)	7320(3)	2657(3)	379(2)	44(3)
C(52)	1960(4)	5082(4)	3514(2)	35(2)	N	2007(5)	9871(5)	2620(3)	38(2)
C(53)	2630(3)	4500(4)	3875(2)	49(2)	C(151)	1346(6)	9414(6)	2361(4)	38(2)
C(54)	2327(4)	4330(4)	4410(2)	50(2)	C(152)	534(8)	9975(7)	1975(5)	54(3)
C(55)	1353(4)	4742(4)	4583(2)	42(2)	C(153)	-159(9)	9475(8)	1822(5)	64(3)
C(56)	684(3)	5324(3)	4222(2)	32(2)	C(154)	-1007(10)	9992(9)	1449(6)	78(4)
C(61)	262(3)	6642(3)	1456(2)	27(2)	C(155)	2471(6)	10300(6)	2170(4)	38(2)
C(62)	438(3)	6175(3)	961(2)	31(2)	C(156)	3164(7)	9660(6)	1763(4)	42(2)
C(63)	-178(4)	6485(3)	501(2)	45(2)	C(157)	3460(7)	10120(6)	1265(4)	40(2)
C(64)	-971(4)	7262(4)	537(2)	49(2)	C(158)	4230(7)	9496(6)	907(4)	44(2)
C(65)	-1147(3)	7729(3)	1032(2)	42(2)	C(159)	2802(7)	9178(6)	2949(4)	42(2)
C(66)	-531(4)	7419(3)	1491(2)	33(2)	C(160)	3590(7)	9477(6)	3225(4)	46(2)
C(71)	2111(3)	6704(4)	1898(2)	28(2)	C(161)	4293(7)	8745(6)	3563(4)	48(2)
C(72)	2198(3)	7097(4)	1382(2)	36(2)	C(162)	5131(8)	8989(7)	3819(5)	57(3)
C(73)	3006(4)	7386(4)	1275(2)	45(2)	C(1')	1395(7)	10614(6)	2999(4)	44(2)
C(74)	3728(3)	7283(4)	1682(2)	38(2)	C(2')	1099(12)	10239(9)	3561(5)	42(4)
C(75)	3641(4)	6890(4)	2198(2)	48(2)	C(3')	277(9)	11026(8)	3843(5)	74(3)
C(76)	2833(4)	6601(4)	2306(2)	42(2)	C(4')	249(22)	10734(17)	4471(7)	92(8)
C(81)	1216(4)	2871(4)	1676(2)	29(2)	C(2'')	574(12)	10373(11)	3347(6)	51(5)
C(82)	228(4)	3261(4)	1831(3)	67(3)	C(4'')	1059(17)	10691(16)	4308(9)	83(8)
C(83)	-517(3)	3041(5)	1560(3)	78(4)	C(3)	5632(23)	1901(20)	4238(7)	233(14)
C(84)	-274(4)	2432(4)	1134(3)	57(3)	C(1)	5406(7)	2689(6)	3678(4)	223(4)
C(85)	714(4)	2041(4)	979(2)	41(2)	C(12)	4790(8)	2573(7)	4750(4)	244(4)
C(86)	1459(3)	2261(3)	1250(2)	34(2)	C(4)	5466(16)	6004(21)	4372(18)	310(21)
C(91)	2217(4)	2777(4)	2746(2)	31(2)	C(13)	4348(10)	5949(8)	4055(6)	306(6)
C(92)	3088(3)	2195(4)	2967(2)	38(2)	C(14)	6226(13)	4899(11)	4220(7)	379(8)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Au(1)–C(21)	2.057(8)	Au(1)–C(11)	2.063(8)
Au(1)–C(31)	2.063(8)	Au(1)–P(1)	2.367(2)
Au(2)–P(2)	2.311(2)	Au(2)–P(3)	2.314(2)
Au(3)–C(121)	2.064(8)	Au(3)–C(131)	2.069(9)
Au(3)–C(141)	2.080(8)	Au(3)–P(4)	2.367(2)
P(1)–C(1)	1.706(8)	P(1)–C(51)	1.845(4)
P(1)–C(41)	1.849(4)	P(2)–C(1)	1.736(8)
P(2)–C(61)	1.838(4)	P(2)–C(71)	1.843(4)
P(3)–C(2)	1.722(7)	P(3)–C(81)	1.842(5)
P(3)–C(91)	1.845(4)	P(4)–C(2)	1.701(8)
P(4)–C(111)	1.828(4)	P(4)–C(101)	1.856(4)
C(21)–Au(1)–C(11)	89.1(2)	C(21)–Au(1)–C(31)	175.4(2)
C(11)–Au(1)–C(31)	87.5(2)	C(21)–Au(1)–P(1)	90.4(2)
C(11)–Au(1)–P(1)	178.56(15)	C(31)–Au(1)–P(1)	93.0(2)
P(2)–Au(2)–P(3)	177.95(7)	C(121)–Au(3)–C(131)	176.8(2)
C(121)–Au(3)–C(141)	87.5(2)	C(131)–Au(3)–C(141)	89.7(2)
C(121)–Au(3)–P(4)	90.8(2)	C(131)–Au(3)–P(4)	92.1(2)
C(141)–Au(3)–P(4)	177.08(13)	C(1)–P(1)–C(51)	116.1(3)
C(1)–P(1)–C(41)	112.1(3)	C(51)–P(1)–C(41)	102.7(2)
C(1)–P(1)–Au(1)	105.2(3)	C(51)–P(1)–Au(1)	109.0(2)
C(41)–P(1)–Au(1)	111.8(2)	C(1)–P(2)–C(61)	111.4(3)
C(1)–P(2)–C(71)	105.5(3)	C(61)–P(2)–C(71)	102.8(2)
C(1)–P(2)–Au(2)	117.0(3)	C(61)–P(2)–Au(2)	107.9(2)
C(71)–P(2)–Au(2)	111.3(2)	C(2)–P(3)–C(81)	110.5(3)
C(2)–P(3)–C(91)	109.0(3)	C(81)–P(3)–C(91)	104.4(3)
C(2)–P(3)–Au(2)	115.7(3)	C(81)–P(3)–Au(2)	108.1(2)
C(91)–P(3)–Au(2)	108.5(2)	C(2)–P(4)–C(111)	116.3(3)
C(2)–P(4)–C(101)	109.0(3)	C(111)–P(4)–C(101)	105.0(2)
C(2)–P(4)–Au(3)	110.1(3)	C(111)–P(4)–Au(3)	104.5(2)
C(101)–P(4)–Au(3)	111.8(2)	P(1)–C(1)–P(2)	129.0(5)
P(4)–C(2)–P(3)	123.9(5)	C(16)–C(11)–C(12)	114.8(8)
C(22)–C(21)–C(26)	115.5(8)	C(32)–C(31)–C(36)	114.4(7)
C(126)–C(121)–C(122)	116.5(7)	C(132)–C(131)–C(136)	115.7(8)
C(142)–C(141)–C(146)	115.7(7)		

led to $[\text{NBu}_4][\text{Au}(\text{acac})_2]$ as a white solid. Yield: 85%. Decomposes at 59 °C. Anal. Calcd for $\text{C}_{26}\text{H}_{50}\text{AuNO}_4$: C, 48.95; H, 7.9; N, 2.2. Found: C, 48.95; H, 8.5; N, 2.25. Λ_M : 98 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR: 1642 (vs) and 1633 (vs) $[\nu(\text{CO})]$. ^1H NMR (CDCl_3): 4.35 (s, CH), 3.28 (m, CH_2), 2.34 [s, CH_3 (acac)], 1.61 (m, CH_2), 1.41 (m, CH_2) and 0.98 [t, CH_3 (Bu) J(HH) = 7.3 Hz].

[Au(C₆F₅)₃PPh₂CH₂PPh₂]₂AuClO₄ (1). To a solution of $[\text{Au}(\text{C}_6\text{F}_5)_3\text{PPh}_2\text{CH}_2\text{PPh}_2]^{5+}$ (0.216 g, 0.2 mmol) in dichloromethane (20 mL) was added $[\text{Au}(\text{tbt})_2]\text{ClO}_4^{16}$ (0.047 g, 0.1 mmol). A white precipitate of **1** was formed, and the mixture was stirred for 30 min. The solvent was concentrated to ca. 5 mL. Addition of 20 mL of hexane completed the precipitation of complex **1**. Yield: 85%. Mp: 205 °C dec. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{Au}_3\text{ClF}_{30}\text{O}_4\text{P}_8$: C, 41.95; H, 1.8. Found: C, 41.45; H, 1.6. $^{31}\text{P}\{^1\text{H}\}$ NMR [$(\text{CD}_3)_2\text{CO}$]: δ 15.6 [m, P–Au(III)], 37.5 [m, P–Au(I)].

NBu₄[Au(C₆F₅)₃PPh₂CHPPH₂]₂Au (2). To a diethyl ether solution (20 mL) of $[\text{Au}(\text{C}_6\text{F}_5)_3\text{PPh}_2\text{CH}_2\text{PPh}_2]^{5+}$ (0.216 g, 0.2 mmol) was added $\text{NBu}_4[\text{Au}(\text{acac})_2]$ (0.063 g, 0.1 mmol), and the mixture was stirred for 2 h. Concentration of the solution to ca. 5 mL and addition of 20 mL of hexane led to precipitation of complex **2**. Yield: 90%. Mp: 80 °C dec. Anal. Calcd for $\text{C}_{102}\text{H}_{80}\text{Au}_3\text{F}_{30}\text{NP}_4$: C, 47.1; H, 3.0; N, 0.55. Found: C, 47.15; H, 2.95; N, 0.55. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 15.4 [m, P–Au(III)], 33.8 [m, P–Au(I)].

NBu₄[Au(C₆F₅)₃PPh₂CH(AuX)PPh₂]₂Au (X = Cl (3), C₆F₅ (4)). To a yellow solution of complex **2** (0.260 g, 0.1 mmol) in 20 mL of dichloromethane was added $[\text{AuX}(\text{tbt})]^{15}$ (0.2 mmol; X = Cl, 0.064 g; X = C₆F₅, 0.090 g), and the mixture

(16) Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Gómez, M. P.; Sáinz, A.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3457.

(17) Gibson, D.; Johnson, B. F. G.; Lewis, J.; *J. Chem. Soc. A* **1970**, 367.

(18) Sheldrick, G. M. SHELXL-93. A program for Crystal Structure Refinement. University of Göttingen, Göttingen, 1993.

Table 3. Details of Data Collection and Structure Refinement for Complex 2·2CH₂Cl₂

chem formula	$\text{C}_{104}\text{H}_{82}\text{Au}_3\text{Cl}_4\text{F}_{30}\text{NP}_4$	$2\theta_{\text{max}}/\text{deg}$	50
cryst habit	yellow prism	$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	4.53
cryst size/mm	$0.55 \times 0.25 \times 0.20$	transm	0.65–0.85
space group	P1	no. of reflcns measd	20894
<i>a</i> /Å	14.213(4)	no. of unique reflcns	18166
<i>b</i> /Å	16.067(4)	no. of reflcns used	18150
<i>c</i> /Å	23.840(6)	R_{int}	0.058
α/deg	88.60(2)	R^2 ($I > 2\sigma(I)$)	0.043
β/deg	89.27(2)	wR^2 (F^2 , all reflcns)	0.118
γ/deg	71.23(2)	no. of params	684
$V/\text{Å}^3$	5153(2)	no. of restraints	364
<i>Z</i>	2	S^c	1.065
$D_x/\text{Mg m}^{-3}$	1.787	max $\Delta\rho/e \text{ Å}^{-3}$	2.18
<i>M</i>	2772.29	max $\Delta\sigma$	0.012
<i>F</i> (000)	2696		
<i>T</i> /°C	–100		

$^a R(F) = \sum |F_o| - |F_c| / \sum |F_o|$. $^b wR(F)^2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + F_c^2]/3$ and *a* and *b* are constants adjusted by the program. $^c S = [\sum \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

was stirred for 1 h. The resulting colorless solution was evaporated to ca. 5 mL. Addition of 20 mL of hexane gave complexes **3** or **4**. **3**. Yield: 57%. Mp: 70 °C dec. Anal. Calcd for $\text{C}_{102}\text{H}_{80}\text{Au}_5\text{Cl}_2\text{F}_{30}\text{NP}_4$: C, 39.4; H, 2.55; N, 0.45. Found: C, 39.3; H, 2.55; N, 0.55. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 19.5 [m, P–Au(III)] and 27.6 [m, P–Au(I)]. **4**. Yield: 60%. Mp: 78 °C dec. Anal. Calcd for $\text{C}_{114}\text{H}_{80}\text{Au}_5\text{F}_{40}\text{NP}_4$: C, 41.1; H, 2.35; N, 0.4. Found: C, 41.45; H, 2.4; N, 0.65. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 21.2 [m, P–Au(III)] and 38.0 [m, P–Au(I)].

[Au(C₆F₅)₃PPh₂C(AuPPh₃)₂PPh₂]₂AuClO₄ (5). To a suspension of complex **1** (0.246 g, 0.1 mmol) in dichloromethane (20 mL) was added $[\text{Au}(\text{acac})\text{PPh}_3]^{17}$ (0.223 g, 0.4 mmol). After being stirred for 48 h, the turbid solution was filtered through a 1 cm pad of Celite. Concentration of the solvent to ca. 4 mL and addition of hexane led to complex **5**. Yield: 80%. Mp: 99 °C dec. Anal. Calcd for $\text{C}_{156}\text{H}_{100}\text{Au}_7\text{ClF}_{30}\text{O}_4\text{P}_8$: C, 46.3; H, 2.45. Found: C, 46.5; H, 2.55. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 22.1 [m, 2P–Au(III)], 35.2 [m, 2P–Au(I)], and 39.0 [s, 4P (PPh₃)].

Crystal Structure Determination of Compound 2·2CH₂Cl₂. The crystal was mounted in inert oil on a glass fiber. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ Å}$) on a Siemens R3 diffractometer with an LT-2 low-temperature attachment. The scan type was ω . Cell constants were refined from setting angles of 50 reflections in the range $2\theta = 20\text{--}21^\circ$. Absorption corrections were applied on the basis of ψ -scans.

The structure was solved by the heavy-atom method and refined anisotropically (except for the C atoms and solvent) on F^2 using the program SHELXL-93.¹⁸ One butyl group of the cation is disordered over two sites, and the solvent is not well resolved. Hydrogen atoms were included using a riding model. Other data are collected in Table 3.

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Supplementary Material Available: Tables of crystal data, data collection, and solution and refinement parameters, hydrogen atomic coordinates and thermal parameters, bond distances and angles, and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

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