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Synthesis, Structural Characterization, and Luminescence Studies of Gold(I) and Gold(III) Complexes with a Triphosphine Ligand

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We have synthesized a series of trinuclear and tetranuclear gold(I) complexes [(μ-dpmp)(AuX)$_3$] (dpmp = bis(diphenylphosphinomethyl)phenylphosphine; X = Cl (**1**), C_6F_5 (**2**)), [Au$_3$(μ-dpmp)$_2$](CF_3SO_3)$_3$ (**3**), and [Au$_4$(μ-dpmp)$_2$Cl$_2$](CF_3SO_3)$_2$ (**4**). Complex **4** displays a rhomboidal geometry for the gold atoms with short gold−gold distances of 3.1025(11) and 3.1059(14) Å. We have also prepared the mononuclear and dinuclear gold(III) complexes [(μ-dpmp){Au(C_6F_5)$_3$}$_n$] (n = 1 (**5**), 2 (**6**)). The crystal structure of **5** has been determined by X-ray diffraction studies, which show that gold is coordinated to the central phosphorus although two isomers are observed in solution. Treatment of **6** with gold(I) derivatives affords trinuclear mixed-valence gold(I)−gold(III) [(μ-dpmp){Au(C_6F_5)$_3$}$_2$(AuX)] (X = Cl (**7**), C_6F_5 (**8**)). The luminescent properties of these complexes in the solid state have been studied. Likewise, it has been found that the gold(I) complexes are luminescent but not so the gold(III) or mixed-valence complexes.

Introduction

One of the intriguing phenomena of gold(I) complexes is a weak gold−gold interaction, whose energy is similar to that of hydrogen bonds. This interaction has been rationalized by using relativistic and correlation effects.[1] Most of these gold(I) complexes possessing such gold interactions are luminescent,[1a,2] although Jones et al. reported recently that this interaction is not a necessary condition for the luminescence (at least in the case of diphosphine thiolate gold(I) compounds studied by them).[3]

The use of polyphosphine ligands favors both the metal centers proximity and the luminescence.[4] For instance, the tridentate ligand bis(diphenylphosphinomethyl)phenylphosphine (dpmp) has been employed to construct trinuclear derivatives containing Rh(I), Pt(II), Pd(II), Ag(I), Cu(I), Au(I), and Hg(II); all of them have shown to be luminescent when this property has been studied.[4,5]

In this study we describe the synthesis of a series of mono-, di-, tri-, and tetranuclear gold complexes with the dpmp ligand, with the gold centers in the oxidation states I, III, and mixed I−III. We report that gold(I) derivatives luminesce, while gold(III) and mixed gold(I)−gold(III) complexes do not. The crystal structures of [Au$_4$(μ-dpmp)$_2$Cl$_2$](CF_3SO_3)$_2$ and [Au(C_6F_5)$_3$(dpmp)] have been determined by X-ray diffraction studies. The tetranuclear derivative displays a rhomboidal geometry for the gold atoms with short metal−metal distances.

Experimental Section

General. All the reactions were carried out under an argon atmosphere at room temperature. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000−200 cm^{-1}, by using Nujol mulls between polyethylene sheets. ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian UNITY 300, GEMINI 2000, or Bruker ARX·300 apparatus in $CDCl_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to $SiMe_4$ (external, ^{1}H), $CFCl_3$ (external, ^{19}F), and 85% H_3PO_4 (external, ^{31}P). C, H, N, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. Melting points were measured on a Büchi apparatus and left uncorrected. Mass spectra were recorded on a VG Autospec using LSIMS technique (with Cs gun) and 3-nitrobenzyl alcohol as matrix. UV−vis absorption spectra either in solid or in dichloromethane solution were recorded at 300 K on a HITACHI U-3400. Photoemission spectra were obtained by exciting the samples with light from a 1000 W tungsten lamp passed through a 0.5 m double monochromator and detected through a 0.5 m monochromator with a photomultiplier detector. The luminescence spectra were corrected for instrumental response using a standard tungsten−halogen lamp calibrated against a National Institute of Standards and Technology lamp.

Preparation of Compounds. [(μ-dpmp)(AuCl)$_3$] (1). To a dichloromethane solution (10 mL) of [AuCl(tht)][6] (tht = tetrahydrothiophene; 0.096 g, 0.3 mmol) bis(diphenylphosphinomethyl)phenylphosphine[7] (dpmp; 0.051 g, 0.1 mmol) was added. After stirring for 3 h a white solid appeared which was filtered off and washed with dichloromethane (5 mL) and diethyl ether (5 mL). Yield of **1**: 70%, mp > 300 °C. IR:

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327 (Au$-$Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.8$-$7.2 (m, 25H, Ph), 4.32 ("q", 2H, $N = 12.6$ Hz, P$-$CH$_2-$P), 4.14 ("q", 2H, $N = 13.0$ Hz, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR (DMSO-d_6): δ 7.8$-$7.2 (m, 25H, Ph), 4.33 (d, 2H, ^2J(HH) = 14.7 Hz, P$-$CH$_2-$P), 4.16 (d, 2H, P$-$CH$_2-$P). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 25.6 (2P, ^2J(PP) = 56.6 Hz), 22.7 (1P). Anal. Calcd for $C_{32}H_{29}Au_3Cl_3P_3$: C, 31.95; H, 2.45. Found: C, 31.55; H, 2.1. LSIMS (*m/z*, %, assignment): 1167 (100, [M $-$ Cl]$^+$).

[(μ-dpmp){Au(C$_6$F$_5$)}$_3$] (2). To a dichloromethane solution (10 mL) of [Au(C$_6$F$_5$)tht]^8 (0.136 g, 0.3 mmol) was added dpmp (0.051 g, 0.1 mmol). The solution was stirred for 2 h. It was then concentrated to ca. 3 mL. Addition of hexane afforded **2** as a white solid which was washed with hexane (2 × 5 mL). Yield of **2**: 80%, mp 110 °C (decomp). IR: 956, 791 (C$_6$F$_5$) cm^{-1}. ^{1}H NMR: δ 7.6$-$7.0 (m, 25H, Ph), 3.50 ("q", 2H, $N = 12.1$ Hz, P$-$CH$_2-$P), 3.00 ("q", 2H, $N = 10.2$ Hz, P$-$CH$_2-$P). ^{19}F NMR: δ $-$ 117.0 (m, 4F$_o$), $-$117.5 (m, 2F$_o$), $-$160.2 (t, 2F$_p$), $-$161.3 (t, 1F$_p$), $-$164.0 (m, 4F$_m$), $-$164.8 (m, 2F$_m$). ^{31}P{^{1}H} NMR: δ 32.1 (2P, ^2J(PP) = 71.0 Hz), 27.6 (1P). Anal. Calcd for $C_{50}H_{29}Au_3F_{15}P_3$: C, 37.55; H, 1.85. Found: C, 37.9; H, 1.7. LSIMS (*m/z*, %, assignment): 1598 (7, M$^+$), 1431 (100, [M $-$ C$_6$F$_5$]$^+$).

[Au$_3$(μ-dpmp)$_2$](CF$_3$SO$_3$)$_3$ (3). To a dichloromethane solution (30 mL) of [Au(tht)$_2$](CF$_3$SO$_3$)^9 (0.3 mmol, prepared in situ) was added dpmp (0.101 g, 0.2 mmol). After stirring for 2 h, the solution was concentrated to ca. 5 mL. Then, diethyl ether (20 mL) was added to obtain **3** as a white solid. Complex **3** was washed with diethyl ether (2 × 5 mL). Yield of **3**: 82%, mp 160 °C (decomp). IR: 1257, 1223, 637 (CF$_3$SO$_3$) cm^{-1}. ^{1}H NMR: δ 7.8$-$7.0 (m, 50H, Ph), 5.00 (m, 4H, P$-$CH$_2-$P), 4.22 (m, 4H, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR: δ 7.8$-$7.0 (m, 50H, Ph), 5.05 (d, 4H, ^2J(HH) = 14.4 Hz, P$-$CH$_2-$P), 4.28 (d, 4H, P$-$CH$_2-$P). ^{31}P{^{1}H} NMR: δ 36.4 (2P), 33.1 (1P), A$_2$A$_2'$BB$'$ spin system with $J_{AA'} = 45$, $J_{AB} = 45.5$, $J_{A'B'} = 65$, and $J_{BB'} = 93$ Hz. Anal. Calcd for $C_{67}H_{58}Au_3F_9O_9P_6S_3$: C, 39.25; H, 2.85; S, 4.7. Found: C, 39.0; H, 2.8; S, 4.8. LSIMS (*m/z*, %, assignment): 1901 (85, [M $-$ CF$_3$SO$_3$]$^+$), 1601 (100, [M $-$ 3CF$_3$SO$_3$ $-$ 2H]$^+$).

[Au$_4$(μ-dpmp)$_2$Cl$_2$](CF$_3$SO$_3$)$_2$ (4). This product can be synthesized by three different ways: (a) To a dichloromethane solution (10 mL) of complex **3** (0.062 g, 0.03 mmol) at 0 °C was added Cl$_2$ (0.15 mmol in CCl$_4$). The solution was stirred for about 2 h, and then it was filtered through Celite. The clear solution was concentrated to ca. 2 mL, and diethyl ether (20 mL) was added to obtain **4** as a white solid. (b) A chloroform solution (30 mL) of complex **3** (0.103 g, 0.05 mmol) was stirred overnight; then, it was filtered through Celite and concentrated to ca. 5 mL. Addition of diethyl ether (20 mL) afforded **4** as a white solid. (c) To a dichloromethane solution (10 mL) of complex **3** (0.062 g, 0.03 mmol) was added HCl (0.15 mmol in Et$_2$O). After stirring for 2 h, the mixture was filtered through Celite and concentrated to ca. 2 mL. Addition of diethyl ether (20 mL) afforded complex **4** as a white solid. Yield: 90% (referred to gold), mp 200 °C (decomp). IR: 325 (Au$-$Cl) cm^{-1}. ^{1}H NMR: δ 7.8$-$6.9 (m, 50H, Ph), 4.82 (d, 8H, ^2J(HP) = 13.3 Hz, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR: δ 7.8$-$6.9 (m, 50H, Ph), 4.81 (s, 8H, P$-$CH$_2-$P). ^{31}P{^{1}H} NMR: δ 44.7 (4P), 23.1 (2P), A$_2$A$_2'$XX$'$ spin system with apparent coupling constants: $J_{AX} = J_{A'X'} = 41$, $J_{AX'} = J_{A'X} = 33$ Hz. ^{1}H NMR ($-$60 °C): δ 4.71 (m, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR ($-$60 °C): δ 4.72 (^2J(HH) = 15.2 Hz, P$-$CH$_2-$P), 4.63 (P$-$CH$_2-$P). ^{31}P{^{1}H} NMR ($-$60 °C): δ 44.0 (4P), 22.1 (2P). Anal. Calcd for $C_{66}H_{58}Au_4Cl_2F_6O_6P_6S_2$: C, 36.55; H, 2.7; S, 2.95. Found: C, 36.55; H, 2.35; S, 2.6. LSIMS (*m/z*, %, assignment): 2019 (27, [M $-$ CF$_3$SO$_3$]$^+$), 935 (100, [Au$_2$Cl(dpmp)]$^+$).

[{Au(C$_6$F$_5$)$_3$}(dpmp)] (5+5$'$). To a dichloromethane solution (10 mL) of [Au(C$_6$F$_5$)$_3$(tht)]^{10} (0.079 g, 0.1 mmol) was added dpmp (0.051 g, 0.1 mmol). The solution was stirred for 2 h, and then it was concentrated to ca. 2 mL. Addition of pentane (20 mL) afforded **5+5$'$** as white solids. A second fraction was obtained by concentration and cooling to $-$18 °C. The mixture was washed with pentane (2 × 3 mL). Yield of **5+5$'$**: 67%, mp 130 °C (decomp). IR: 969, 793 (C$_6$F$_5$) cm^{-1}. ^{1}H NMR: δ 7.8$-$7.0 (m, 25H, Ph), 3.4$-$2.0 (m, 4H, P$-$CH$_2-$P). ^{19}F NMR: δ $-$119.3 (m, F$_o$), $-$121.3 (m, F$_o$), $-$122.4 (m, F$_o$), $-$157.7 (t, F$_p$), $-$157.8 (t, F$_p$), $-$158.4 (t, F$_p$), $-$158.5 (t, F$_p$), $-$161.8 (m, F$_m$), $-$162.3 (m, F$_m$), $-$162.6 (m, F$_m$). ^{31}P{^{1}H} NMR of **5**: δ 12.9 (t, ^2J(PP) = 81.3 Hz) and $-$28.4 (d). ^{31}P{^{1}H} NMR of **5$'$**: 14.7 (d, ^2J(PP) = 47.8 Hz), $-$24.5 (d, ^2J(PP) = 106.8 Hz) and $-$36.3 (dd). Anal. Calcd for $C_{50}H_{29}AuF_{15}P_3$: C, 49.85; H, 2.45. Found: C, 49.6; H, 2.15. LSIMS (*m/z*, %, assignment): 1205 (20, [M + H]$^+$), 703 (100, [Au(dpmp)]$^+$).

[(μ-dpmp){Au(C$_6$F$_5$)$_3$}$_2$] (6). (a) To a dichloromethane solution (30 mL) of [Au(C$_6$F$_5$)$_3$(tht)] (0.315 g, 0.4 mmol) was added dpmp (0.102 g, 0.2 mmol). The solution was stirred for 3 h, and then it was concentrated to ca. 5 mL. Addition of hexane (20 mL) afforded **6** as a white solid. A second fraction was obtained by concentration and cooling to $-$18 °C. Complex **6** was washed with hexane (2 × 5 mL). (b) To a dichloromethane solution (20 mL) of **5** (0.06 g, 0.05 mmol) was added [Au(C$_6$F$_5$)$_3$(tht)] (0.039 g, 0.05 mmol). The solution was stirred for 3 h, and then it was concentrated to ca. 5 mL. Addition of hexane (20 mL) afforded **6** as a white solid. A second fraction was obtained by concentration and cooling to $-$18 °C. Complex **6** was washed with hexane (2 × 5 mL). Yield of **6**: 75%, mp 225 °C (decomp). IR: 969, 793 (C$_6$F$_5$) cm^{-1}. ^{1}H NMR: δ 7.8$-$6.8 (m, 25H, Ph), 2.90 (dd, 2H, ^2J(HH) = 14.7 and ^2J(HP) = 9.1 Hz, P$-$CH$_2-$P), 2.25 ("t", 2H, N = 13.5 Hz, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR: δ 7.8$-$6.8 (m, 25H, Ph), 2.94 (d, 2H, ^2J(HH) = 14.8 Hz, P$-$CH$_2-$P), 2.29 (d, 2H, P$-$CH$_2-$P). ^{19}F NMR: δ $-$120.8 (m, 2F$_o$), $-$121.2 (m, 2F$_o$), $-$122.8 (m, 2F$_o$), $-$157.0 (t, 2F$_p$), $-$157.9 (t, 1F$_p$), $-$161.0 (m, 2F$_m$), $-$161.6 (m, 2F$_m$), $-$162.0 (m, 2F$_m$). ^{31}P{^{1}H} NMR: δ 14.0 (d, 2P, ^2J(PP) = 47.0 Hz), $-$41.5 (t, 1P). Anal. Calcd for $C_{68}H_{29}Au_2F_{30}P_3$: C, 42.9; H, 1.55. Found: C, 43.05; H, 1.6. LSIMS (*m/z*, %, assignment): 1902 (4, [M]$^+$), 703 (100, [Au(dpmp)]$^+$).

[(μ-dpmp){Au(C$_6$F$_5$)$_3$}$_2$(AuX)], X = Cl (7), C$_6$F$_5$ (8). To a dichloromethane solution (10 mL) of **6** (0.095 g, 0.05 mmol) was added [AuX(tht)] (0.05 mmol; X = Cl (0.016 g), X = C$_6$F$_5$ (0.023 g)). The solution was stirred for 2 h, and then it was concentrated to ca. 1 mL. Addition of pentane (15 mL) afforded the complexes as white solids. A second fraction was obtained by concentration and cooling to $-$18 °C. Complexes **7** and **8** were washed with pentane (2 × 3 mL). Yield of **7**: 70%, mp 145 °C (decomp). IR: 970, 793 (C$_6$F$_5$), 341 (Au$-$Cl) cm^{-1}. ^{1}H NMR: δ 7.8$-$6.8 (m, 25H, Ph), 3.08 (m, 2H, P$-$CH$_2-$P), 2.78 (m, 2H, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR: δ 7.8$-$6.8 (m, 25H, Ph), 3.05 (d, 2H, ^2J(HH) = 15.5 Hz, P$-$CH$_2-$P), 2.71 (d, 2H, P$-$CH$_2-$P). ^{19}F NMR: δ $-$121.4 (m, 4F$_o$), $-$122.7 (m, 2F$_o$), $-$155.8 (t, 2F$_p$), $-$157.2 (t, 1F$_p$), $-$160.5 (m, 4F$_m$), $-$161.6 (m, 2F$_m$). ^{31}P{^{1}H} NMR: δ 11.5 (d, 2P, ^2J(PP) = 19.5 Hz), 8.6 (t, 1P). Anal. Calcd for $C_{68}H_{29}Au_3F_{30}P_3$: C, 38.25; H, 1.35. Found: C, 38.05; H, 1.2. LSIMS (*m/z*, %, assignment): 703 (100, [Au(dpmp)]$^+$).

Yield of **8**: 60%, mp 140 °C (decomp). IR: 969, 794 (C$_6$F$_5$) cm^{-1}. ^{1}H NMR: δ 7.6$-$6.8 (m, 25H, Ph), 3.12 (m, 2H, P$-$CH$_2-$P), 2.71 (m, 2H, P$-$CH$_2-$P). ^{1}H{^{31}P} NMR: δ 7.6$-$6.8 (m, 25H, Ph), 3.16 (d, 2H, ^2J(HH) = 15.8 Hz, P$-$CH$_2-$P), 2.74 (d, 2H, P$-$CH$_2-$P). ^{19}F NMR: δ $-$117.4 (m, 2F$_o$-Au^I), $-$121.4 (m, 8F$_o$), $-$122.6 (m, 4F$_o$), $-$155.9 (t, 4F$_p$), $-$157.3 (t, 2F$_p$), $-$157.9 (t, 1F$_p$-Au^I), $-$160.7 (m, 8F$_m$), $-$161.7 (m, 4F$_m$), $-$163.0 (m, 2F$_m$-Au^I). ^{31}P{^{1}H} NMR: δ 21.0 (t, 1P, ^2J(PP) = 11.9 Hz), 11.2 (d, 2P). Anal. Calcd for $C_{74}H_{29}Au_3ClF_{35}P_3$: C, 39.2; H, 1.3. Found: C, 38.8; H, 1.35. LSIMS (*m/z*, %, assignment): 1431 (100, [M-5C$_6$F$_5$]$^+$).

Crystal Structure Determinations of 4 and 5. Crystal data and details of both the data collection and the structure refinement of **4** and **5** are given in Table 1. Crystals of **4**·1CH$_2$Cl$_2$ were grown from dichloromethane/isopropyl ether. A colorless plate ca. 0.30 × 0.20 × 0.09 mm was mounted in inert oil on a glass fiber. A total of 7613 intensities were registered using monochromated Mo Kα radiation (λ = 0.710 73 Å, $2\theta_{max} = 50°$) on a Siemens P4 four-circle diffractometer; 6795 unique reflections ($R_{int} = 0.0518$) were used for all calculations. Cell constants were refined from setting angles of 66 reflections in the range $2\theta = 10-25°$. Absorption corrections based on ψ scans were applied; transmission factors 0.518$-$0.948. The structure was solved by direct methods and refined anisotropically on F^2 using the program SHELXL-93.^{11} H atoms were included using a riding model. Disorder in the dichloromethane solvate was observed: partial occupancies were

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Scheme 1

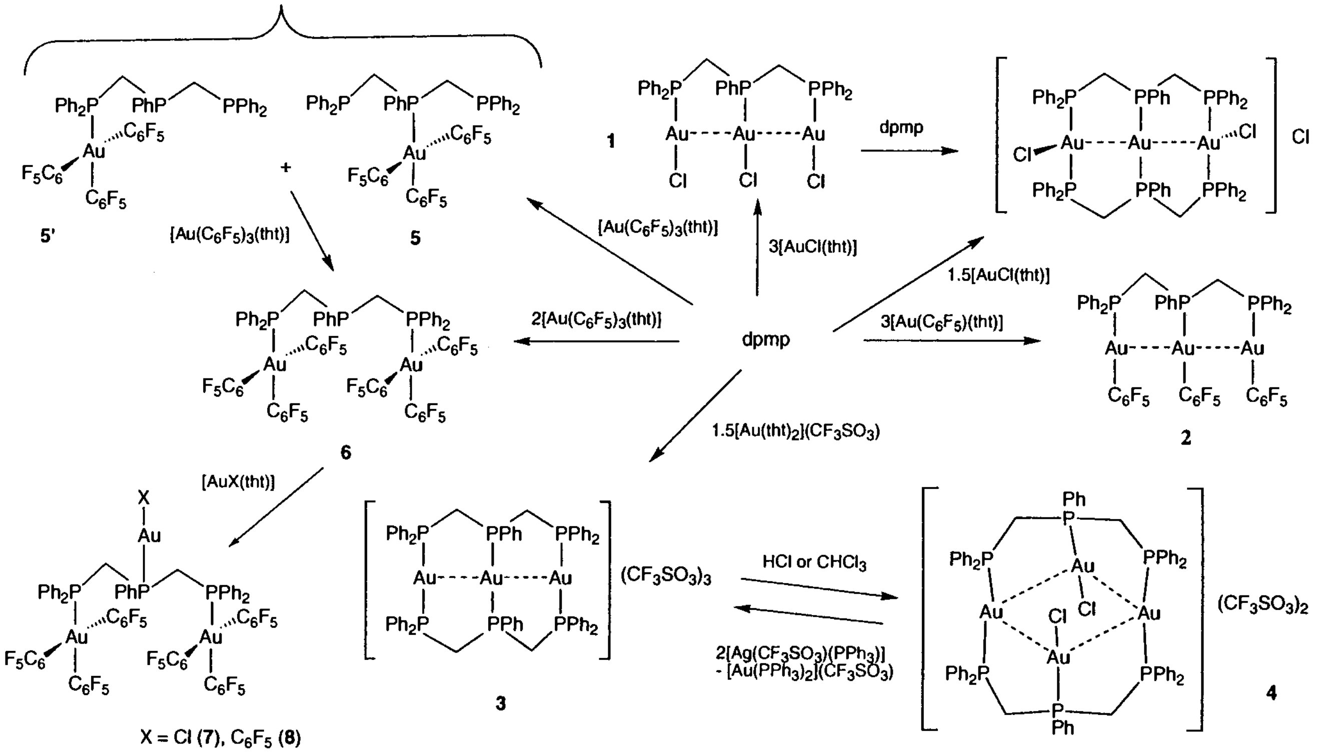

Table 1. Details of Data Collection and Structure Refinement for the Complexes **4** and **5**

	$4 \cdot 1CH_2Cl_2$	5
empirical formula	$C_{67}H_{60}Au_4Cl_4F_6O_6P_6S_2$	$C_{50}H_{29}AuF_{15}P_3$
fw	2254.76	1204.61
space group	$P\bar{1}$	$P2(1)/c$
V (Å^3)	1990.7(7)	4500(2)
Z	1	4
D_{calc} (g cm^{-3})	1.881	1.778
a (Å)	11.167(2)	12.930(2)
b (Å)	13.495(3)	16.378(3)
c (Å)	15.468(3)	21.262(9)
α (deg)	107.21(2)	–
β (deg)	102.02(2)	91.99(2)
γ (deg)	108.50(2)	–
T (°C)	−100	−100
λ(Mo Kα), Å	0.710 73	0.710 73
μ(Mo Kα), cm^{-1}	77.13	34.75
R^a (F, $F > 4\sigma(F)$)	0.0631	0.0438
wR^b (F^2, all reflcns)	0.1826	0.0941

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$.

used for the chlorine atoms during the final stage of refinement. No hydrogen atoms were located for this molecule. The composition and related parameters are based on a 1:1 ratio dichloromethane/complex, although the exact value cannot be determined. The final wR(F^2) was 0.1825 for all reflections, with a conventional R(F) of 0.0632 for 431 parameters. A total of 46 restraints were applied involving local phenyl ring symmetry (FLAT/SAME SHELXL93); $S = 0.955$; max $\Delta\rho = 2.56$ e Å^{-3} (located at the gold atoms).

Crystals of **5** were grown from dichloromethane/pentane. A colorless plate ca. 0.30 × 0.26 × 0.11 mm was mounted in inert oil on a glass fiber. A total of 10058 intensities were registered using monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å, $2\theta_{max} = 50°$) on a Stoe-Siemens four circle diffractometer; 7905 unique reflections ($R_{int} = 0.0482$) were used for all calculations. Cell constants were refined from setting angles of 64 reflections in the range $2\theta = 20-32°$. Absorption corrections based on ψ scans were applied; transmission factors 0.668−0.961. The structure was solved by direct methods and refined anisotropically on F^2 using the program SHELXL-93.[11] H atoms were included using a riding model. The final wR(F^2) was 0.0941 for all reflections, with a conventional R(F) of 0.0438 for 622 parameters without restraints; $S = 1.045$; max $\Delta\rho = 1.419$ eÅ^{-3}.

Results and Discussion

The reaction of bis(diphenylphosphinomethyl)phenylphosphine (dpmp) with [AuCl(tht)] (tht = tetrahydrothiophene) in molar ratio 1:3 in dichloromethane gives an insoluble, white solid **1**. This complex is insoluble in most common organic solvents, but it is soluble in dimethyl sulfoxide (DMSO), which allows us to characterize it by means of NMR and mass spectrometry. **1** reacts with another dpmp to give $[Au_3(\mu\text{-dpmp})_2Cl_2]Cl$ (see Scheme 1). The latter, which can be synthesized by reaction of dpmp and [AuCl(tht)] (molar ratio 2:3), has recently been described by Che et al.[5c] We also carried out the reaction of dpmp with $[Au(C_6F_5)(tht)]$ or $[Au(tht)_2](CF_3SO_3)$ in the appropriate molar ratio to obtain complexes **2** and **3** (see Scheme 1). These derivatives are air and moisture stable, white solids at room temperature. Their IR spectra show absorptions at 327 (**1**) cm^{-1} due to ν(Au−Cl),[12] 956 and 791 cm^{-1} from the pentafluorophenyl groups[13] (**2**), and 1257, 1223, and 637 cm^{-1} from triflate anions[14] (**3**). The ^{19}F NMR spectrum of **2** shows the pattern of two different pentafluorophenyl groups in a 2:1 proportion. In the $^{31}P\{^1H\}$ NMR spectra two types of phosphorus in 2:1 ratio are observed: **1** and **2** show an A_2B spin system with signals centered at 25.6 (2P) and 22.7 (1P) ppm ($J_{AB} = 56.6$ Hz) for **1** and 32.1 (2P) and 27.6 (1P) ppm ($J_{AB} = 71.0$ Hz) for **2**, while **3** shows a more complicated spin system

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($A_2A'_2BB'$) centered at 36.4 (2P) and 33.1 (1P). In the ^{1}H NMR spectra, two signals are always found for the methylene protons. A ^{1}H{^{31}P} NMR experiment carried out for complex **1** shows two doublets for these protons, which means that there are not two different methylene groups, but that the two protons in each methylene are diastereotopic, as it is found for the free triphosphine ligand. The same result was obtained when the ^{1}H{^{31}P} NMR experiment was carried out for complex **3**. Furthermore a COSY experiment carried out for this derivative shows that these two signals for the methylene protons are correlated, which means that an unique isomer is present for **3** although it can exist in two isomers (cis/trans, regarding the orientation of the central phenyl groups).[5e] The LSIMS mass spectrum of **2** shows the parent peak at *m/z* (%) = 1598 (7), while for **3** a peak is observed at 1901 (85), corresponding to $[M\text{-}CF_3SO_3]^+$; the base peaks appear at 1167 ($[M - Cl]^+$), 1431 ($[M - C_6F_5]^+$), and 1601 ($[M - 3CF_3SO_3 - 2H]^+$), respectively, for **1**−**3**.

We tried to oxidize these complexes to obtain mixed-valence gold derivatives; but, only complicated mixtures were obtained. And yet, only when chlorine was added to complex **3**, a unique product was obtained, the tetranuclear gold(I) complex **4**. This product can also be obtained by reaction of **3** with HCl in dichloromethane or by stirring **3** in chloroform overnight (see Scheme 1), but not by adding (PPN)Cl ($PPN^+ = N(PPh_3)_2{}^+$); therefore, it is HCl and not chlorine which is producing the reaction. The process was monitored by NMR spectroscopy at room temperature. Apart from **3** and **4**, some other products were observed but always in a low proportion and accompanied with some gold decomposition. Complex **4** reacts with triflate(phosphino)silver(I) salts to give complex **3** again along with bis(phosphine)gold(I) as byproduct.

Complex **4** is a white solid, whose main features are as follows: the presence of a medium intensity absorption at 325 cm^{-1} from ν(Au−Cl) in the IR spectrum; an $A_2A'_2XX'$ spin system in the ^{31}P{^{1}H} NMR spectrum centered at 44.7 (2P) and 23.1 (1P), which points out the presence of two triphosphines; one doublet for the methylene protons in the ^{1}H NMR spectrum, which becomes a singlet in a ^{1}H{^{31}P} NMR experiment. The ^{1}H NMR spectrum at −60 °C shows a multiplet centered at 4.71, which becomes an AB spin system in a ^{1}H{^{31}P} NMR experiment, as expected for the diastereotopic methylene protons, although in this case the chemical shifts are very similar. The ^{31}P{^{1}H} NMR spectrum at −60 °C stays almost unchanged; therefore, it is unclear whether a fluxional process, which might be taking place, can make diastereotopic protons equivalent at room temperature. The LSIMS mass spectrum shows a peak at *m/z* (%) = 2019 (27), corresponding to $[M - CF_3SO_3]^+$, while the base peak appears at 935 ($[Au_2Cl(dpmp)]^+$).

The geometry of this tetranuclear derivative was confirmed by an X-ray diffraction study. The molecular structure of the cation of **4** is shown in Figure 1; selected bonds and angles are shown in Table 2. The cation of **4** is centrosymmetric and displays a rhomboidal geometry for the gold atoms with short metal−metal distances (Au−Au−Au, 67.75(3) and 112.25(3)°; Au⋯Au, 3.1025(11) and 3.1059(14) Å). The diagonal Au⋯Au distances are 3.461(2) Å (Au2−Au2a) and 5.154(2) Å (Au1−Au1a). This rhomboidal geometry has been observed for other loose Au^{I}_4 clusters,[15] but it contrasts with that seen in related polynuclear gold(I) derivatives, such as $[Au_4(\mu\text{-dpmp})_2(SCN)_2][SCN]Cl$,[16] where gold atoms are in a nearly linear chain, or $[Au_4(\mu\text{-dpma})_2Cl_2]X_2$ (X = PF_6^-, NO_3^-; dpma = {(diphenylphosphino)methyl}phenylarsine),[17] where gold atoms are in a bent chain.

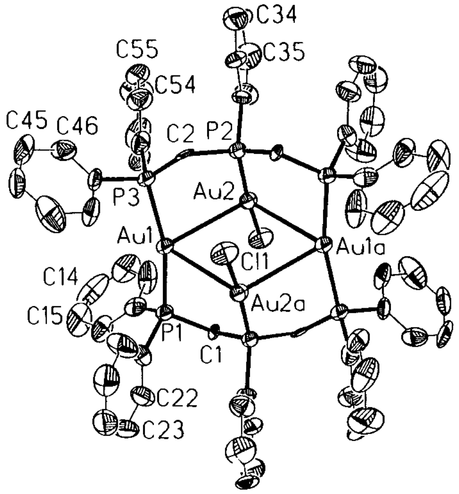

Figure 1. Molecular structure of the cation of complex **4** (solvent omitted). Ellipsoids are drawn at the 50% probability level, and all H atoms have been omitted.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complex **4**[a]

Au(1)−P(1)	2.323(4)	Au(1)−P(3)	2.326(4)
Au(1)−Au(2a)	3.1025(11)	Au(1)−Au(2)	3.1059(14)
Au(2)−P(2)	2.264(4)	Au(2)−Cl(1)	2.306(4)

P(1)−Au(1)−P(3)	164.7(2)	Au(2a)−Au(1)−Au(2)	67.75(3)
P(2)−Au(2)−Cl(1)	169.1(2)	Au(1a)−Au(2)−Au(1)	112.25(3)
C(21)−P(1)−C(11)	108.8(7)	C(21)−P(1)−C(1)	106.3(8)
C(11)−P(1)−C(1)	103.9(7)	C(21)−P(1)−Au(1)	113.1(5)
C(11)−P(1)−Au(1)	107.7(5)	C(1)−P(1)−Au(1)	116.6(5)
C(31)−P(2)−C(1a)	107.7(7)	C(31)−P(2)−C(2)	108.3(7)
C(1a)−P(2)−C(2)	102.4(7)	C(31)−P(2)−Au(2)	110.4(5)
C(1a)−P(2)−Au(2)	113.3(5)	C(2)−P(2)−Au(2)	114.2(5)
C(51)−P(3)−C(2)	107.8(8)	C(51)−P(3)−C(41)	109.1(8)
C(2)−P(3)−C(41)	102.4(8)	C(51)−P(3)−Au(1)	111.5(5)
C(2)−P(3)−Au(1)	114.4(5)	C(41)−P(3)−Au(1)	111.2(5)

[a] Symmetry transformations used to generate equivalent atoms: a, $-x + 3$, $-y + 1$, $-z + 1$.

The P−Au−P and P−Au−Cl units are bent (164.7(2) and 169.1(2)°, respectively). Thus, the direction of the bend facilitates the approach of the gold atoms. Au⋯Au distances (3.1025(11) and 3.1059(14) Å) are of the same order as the values found in other polynuclear gold(I) complexes containing dpmp or related phosphine ligands: longer than those found in $[Au_3(\mu\text{-dpmp})_2Cl_2]Cl$ (2.946(3), 2.963(3) Å),[5c] $[Au_3(\mu\text{-dpmp})_2][SCN]_3$ (3.0137(8), 3.0049(8) Å),[16] or $[Au_4(\mu\text{-dpma})_2Cl_2]X_2$ (X = PF_6^-, NO_3^-) (2.965(1)−3.110(2) Å)[17] (for most of the values found in the latter complex), but shorter than those observed in $[(\mu\text{-dpma})(AuCl)_3]$ (3.131(1), 3.138(1) Å)[17] or $[Au_4(\mu\text{-dpmp})_2(SCN)_2][SCN]Cl$ (3.057(1)−3.150(1) Å)[16] (for most of the values found in the latter complex). Au−Cl bond distances (2.306(4) Å) are as expected for P−Au−Cl units. Au−P bond lengths (2.264(4), 2.323(4), and 2.326(4) Å) are normal and compare well with those found in the related polynuclear complexes mentioned hereinabove.[5c,16,17] Au2−P2 and Au2a−

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P2a, 2.264(4) Å, are shorter than the others, probably as a consequence of the minor trans influence of Cl.

We have also synthesized gold(III) derivatives containing this triphosphine ligand by using a different approach (see Scheme 1). The reaction of dpmp with $[Au(C_6F_5)_3(tht)]$ in a 1:1 molar ratio affords a mononuclear complex, which is a mixture of two isomers **5** and **5′**, because of the coordination of gold to the central or the lateral phosphorus. This is to our knowledge the only dpmp mononuclear derivative with two free phosphorus, which can be used to further coordination. Furthermore, the addition of $[Au(C_6F_5)_3(tht)]$ in 1:1 molar ratio evolves cleanly to the formation of a unique derivative **6**, which can also be obtained from $[Au(C_6F_5)_3(tht)]$ and the triphosphine. Dinuclear derivatives of dpmp are less common than trinuclear, and only some palladium and platinum derivatives have been reported.[18] Complex **6** reacts with [AuCl(tht)] or $[Au(C_6F_5)(tht)]$ to give the mixed-valence gold(III)−gold(I)−gold(III) derivatives **7** and **8**.

Complexes **5**−**8** are air and moisture stable, white solids at room temperature. In the IR spectra absorptions at 341 (**7**) cm^{-1}, due to ν(Au−Cl), and at ca. 970 and 795 cm^{-1}, from the pentafluorophenyl groups (**5**−**8**), are observed. The $^{31}P\{^1H\}$ NMR spectrum of $[Au(C_6F_5)_3(dpmp)]$ shows an AX_2 spin system because of an isomer with gold attached to the central phosphorus and an AMX spin system for the isomer with gold coordinated to a lateral phosphorus. These isomers appear approximately as a 45:55 mixture (for **5**:**5′**). Complex **5′** should be a racemic mixture after the central phosphorus becomes chiral because of the coordination of the metallic fragment. For the other complexes the $^{31}P\{^1H\}$ NMR spectra always show an A_2X spin system: one kind of phosphorus, whose chemical shift stays almost unchanged (14.0, 11.5, and 11.2 ppm, respectively), and a second one, whose chemical shift changes strongly because of its different coordination (−41.5, 8.6, and 21.0 ppm, respectively). Moreover, the coupling constant phosphorus−phosphorus goes down: from 47.0 in **6** to 19.5 in **7** and 11.9 Hz in **8**. At any rate, the said values are smaller than those found in the pentafluorophenyl gold(I) complex **2** (71 Hz). As found in the previous gold(I) trinuclear complexes, there are two signals for the methylene protons in the ^1H NMR spectra, which become two doublets in a $^1H\{^{31}P\}$ NMR experiment (except for **5** which spectrum is more complicated). Once again, this finding means that the methylene protons are diastereotopic.

The ^{19}F NMR spectrum of **6** shows three different ortho and meta fluorine (in a 1:1:1 ratio) but only two para fluorine (in a 2:1 ratio). The latter points out that the two $Au(C_6F_5)_3$ units are equivalent, and the former, that the pentafluorophenyl rings in cis position cannot rotate. By heating a solution in toluene-d_8, it has been determined that the coalescence temperature is 85 °C; therefore, above this temperature there is no hindered rotation and only two kinds of pentafluorophenyl rings in a 2:1 ratio are observed. On the contrary, only two kinds of ortho fluorine are observed (2:1 ratio) in an acetone-d_6 solution at room temperature; this solvent dependence points out to an association/dissociation process rather than a simple rotation, as shown elegantly for a $Pd-C_6F_5$ complex by Espinet and coworkers.[19] Although the AuR_3 fragment has important steric requirements, the dpmp ligand should be able to accommodate them by coordination to the most external phosphorus in a trans geometry if necessary. Moreover, the ligand accepts an additional AuX unit and the pentafluorophenyl groups from AuR_3 can rotate (only two kind of ortho fluorine are observed) even at −60 °C, although **6** does not react with an excess of either $[Au(C_6F_5)_3(tht)]$ or $[Au(PPh_3)]^+$. Therefore, the explanation of the ^{19}F NMR spectra of **6**−**8** is unclear and should be related to their stereochemistry. Moreover, we deplore the fact that we have been unable to get crystals good enough to solve the X-ray structure of **6**. As stated above, the ^{19}F NMR spectra of **7** and **8** show only two kinds of pentafluorophenyl rings in a 2:1 ratio. Furthermore, another pentafluorophenyl is observed for **8** because of the $Au(C_6F_5)$ fragment. Finally for **5** two kinds of $Au(C_6F_5)_3$ units are observed as expected for the presence of two isomers.

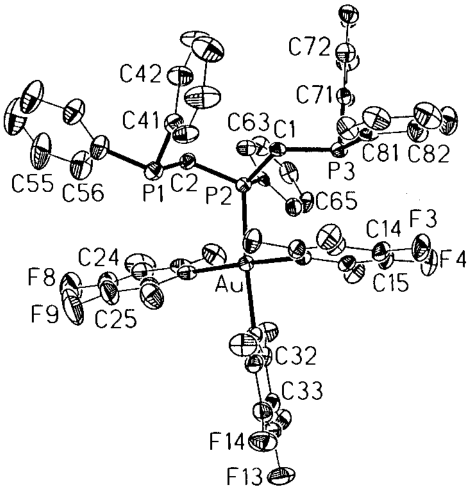

Figure 2. Molecular structure of complex **5**. Ellipsoids are drawn at the 50% probability level, and all H atoms have been omitted.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Complex **5**

Au−C(11)	2.078(6)	Au−C(31)	2.079(7)
Au−C(21)	2.082(7)	Au−P(2)	2.356(2)
C(11)−Au−C(31)	87.6(3)	C(11)−Au−C(21)	172.2(3)
C(31)−Au−C(21)	89.5(3)	C(11)−Au−P(2)	92.4(2)
C(31)−Au−P(2)	171.8(2)	C(21)−Au−P(2)	91.5(2)

The LSIMS mass spectra of **5**−**6** show the parent peaks at *m/z* (%) 1205 (20) and 1902 (4), while for **7** and **8** only highly fractionated peaks are obtained; the base peaks appear at 703 ($[Au(dpmp)]^+$) for **5**−**7** and at 1431 ($[M - 5C_6F_5]^+$) for **8**.

The crystal structure of complex **5** has been established by X-ray diffraction. Apparently at −18 °C only the isomer with gold attached to the central phosphorus atom crystallizes, although $^{31}P\{H\}$ NMR data show the presence of the two isomers in $CDCl_3$ solution even at −60 °C. The molecular structure is shown in Figure 2; selected bonds lengths and angles are shown in Table 3. The gold(III) center displays a distorted square planar coordination that tends toward a tetrahedral one: the dihedral angle between the planes formed by P2−Au−C21 and C31−Au−C11 is 10.9°. There are no interactions between gold center and the lateral phosphorus atoms of the triphosphine. Au−C bond distances (2.078(6)−2.082(7) Å) are similar to the longest values found in other tris(pentafluorophenyl)gold(III) complexes, such as $[Au(C_6F_5)_3(S_2C\text{-}PEt_3)]$ (2.037(3)−2.076(4) Å),[20] $[(\mu\text{-}S_2C\text{-}PEt_3)\{Au(C_6F_5)_3\}_2]$ (2.048(16)−2.090(13) Å),[20] or $NBu_4[\{Au(C_6F_5)_3PPh_2CHPPh_2\}_2Au]$ (2.057(8)−2.080-

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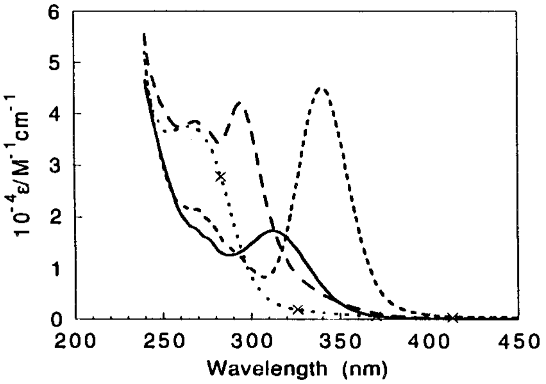

Figure 3. 300 K absorption spectra of complex **2** (—), **3** (- - -), **4** (— —), and **8** (··×··) in CH_2Cl_2 solution.

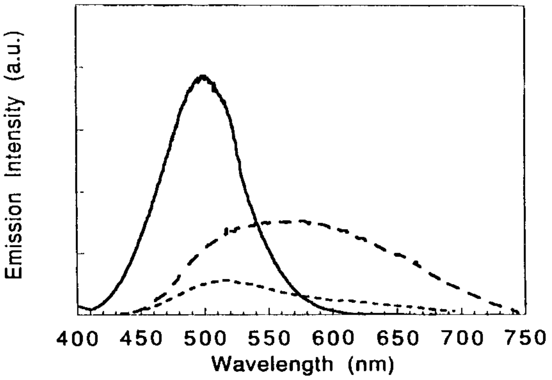

Figure 4. 300 K emission spectra of complex **2** (—, excitation 370 nm), **3** (— —, excitation 420 nm), and **4** (- - -, excitation 370 nm) in the solid state.

(8) Å).[21] The Au−P bond distance, 2.356(2) Å, is of the same order as Au(III)−P bond distances found in other gold(III) derivatives.[21−24]

The optical properties of the complexes were measured, except for **5** because it is a mixture of isomers. The optical absorption spectra in dichloromethane (complexes **2**, **3**, **4**, and **8**) are plotted in Figure 3; the absorption spectra of **6** and **7** are very similar to **8**. Similar absorption bands are observed for solid samples. The absorption spectra of gold(III) and gold(I)−gold(III) complexes show one absorption band about 250 nm; no absorption at wavelengths higher than 300 nm is detected in these compounds. The trinuclear gold(I) derivatives show absorption bands about 310 nm for compound **2** and 350 nm for compound **3**. The tetranuclear gold(I) compound is between the two cases. The red-shift in trinuclear gold(I) complexes has been attributed to weak gold−gold interactions.[16]

The solid state emissions at 300 K have been studied, and the results are shown in Figure 4. Optimal excitation was observed in the low-energy side of the absorption bands, due presumably to auto absorption of the emitting light. Tri- and tetranuclear gold(I) complexes are luminescent, except for the insoluble complex **1**. Emission is evidently related to gold(I)−gold(I) interaction, being most intense for trinuclear complexes. An emission about 600 nm (for complex **3**) is typical for a metal centered transition as found in the analogue derivative $[Au_3(\mu\text{-dpmp})_2(SCN)_3]$.[16] The origin of the emission at 500 nm for complexes **2** and **4** is not clear yet; different assignments for this emission have been proposed.[2b,c,3,5c,25] Dinuclear gold(III) complex **6**, which contains both triphosphine and pentafluorophenyl ligands as derivative **3** but two gold(III) centers instead of three gold(I) centers, is not luminescent. This finding supports the metal-centered character of the emission observed in our gold(I) complexes and the unlikelihood of this emission being ascribable to the ligand. Although a gold(I) center is included, derivatives **7** and **8** are not luminescent, which points out the absence of any interaction between gold(I) and gold(III) atoms.

Conclusions

We have prepared tri- and tetranuclear gold(I) derivatives with the triphosphine dpmp, the former having a rhomboidal geometry for the gold atoms and showing short gold−gold contacts. We have also synthesized a mononuclear gold(III) derivative with two free phosphorus, capable of furthering coordination and yielding dinuclear gold(III) and trinuclear gold(I)−gold(III) complexes. We have shown that gold(I) derivatives luminesce, while gold(III) and mixed gold(I)−gold(III) complexes do not.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (Project PB97-1010-C02-01) for financial support.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **4** and **5** are available on the Internet only. Access information is given on any current masthead page.

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