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Synthesis of Luminescent Gold(I) and Gold(III) Complexes with a Triphosphine Ligand

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We have synthesized and characterized a series of trinuclear gold(I) complexes [$(AuX)_3$(μ-triphos)] (triphos = bis(2-diphenylphosphinoethyl)phenylphosphine; X = Cl **1**, Br **2**, I **3**, C_6F_5 **4**) and di- and trinuclear gold(III) complexes [$\{Au(C_6F_5)_3\}_n$(μ-triphos)] (n = 2 (**5**), 3 (**6**)). The crystal structure of **6** [$\{Au(C_6F_5)_3\}_3$(μ-triphos)] has been determined by X-ray diffraction studies, which show the triphosphine in a conformation resulting in very long gold−gold distances, probably associated with the steric requirements of the tris(pentafluorophenyl)gold(III) units. Complex **6** crystallizes in the triclinic space group $P(-1)$ with a = 12.7746(16) Å, b = 18.560(2) Å, c = 21.750(3) Å, α = 98.215(3)°, β = 101.666(3)°, γ = 96.640(3)°, and Z = 2. Chloride substitutions in complex **1** afford trinuclear gold(I) complexes [$(AuX)_3$(μ-triphos)] (X = Fmes (1,3,5-tris(trifluoromethyl)phenyl) **7**, p-SC_6H_4-Me **8**, SCN **9**) and [$Au_3Cl_{3-n}(S_2CNR_2)_n$(μ-triphos)] (R = Me, n = 3 (**10**), 2 (**12**), 1 (**14**); R = CH_2Ph, n = 3 (**11**), 2 (**13**), 1 (**15**)). The luminescence properties of these complexes in the solid state have been studied; at low temperature most of them are luminescent, including the gold(III) derivative **6**, with the intensity and the emission maxima being clearly influenced by the nature and the number of the ligands bonded to the gold centers.

Introduction

A large number of polydentate phosphine complexes of transition metals have been synthesized and characterized that have potential catalytic and biomedical activity. Additionally, they promote short metal−metal distances, which can lead to interesting electrochemical and optical properties.[1−10]

Photoluminescence studies have shown that a variety of mono- and polynuclear phosphine−gold(I) or phosphine−thiolate−gold(I) derivatives display luminescence in the visible region. The emissions have been generally assigned as a phosphorescence arising from metal-centered transitions or sulfur to gold charge transfer modified by the presence of gold−gold contacts.[11−14]

In contrast to the extensive studies of the photochemical and photophysical properties of gold(I) complexes, few investigations of this type have been conducted on related gold(III) complexes; luminescent gold(III) complexes are rare and only some cyclometalated, diimine or dithiolate derivatives have been reported.[15−19]

In this paper we report the synthesis and optical properties of a series of triphosphine di- or trinuclear gold(I) or gold(III) derivatives containing different kind of ligands such as halide, fluorophenyl, thiolate, thiocyanate, and dithiocarbamate.

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}, using Nujol mulls between polyethylene sheets. ^1H, $^1H\{^{31}P\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX·300 or GEMINI 2000 apparatus in $CDCl_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to $SiMe_4$ (external, ^1H), $CFCl_3$ (external, ^{19}F), and 85% H_3PO_4 (external, ^{31}P). C, H, N, and S analyses

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were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec using the LSIMS technique (with Cs gun) and 3-nitrobenzyl alcohol as matrix. UV−vis absorption spectra in dichloromethane solution were recorded at 298 K on a Unicam UV/Vis 2. The luminescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorometer.

Preparation of Compounds. [(AuX)$_3$(μ-triphos)] X = Cl 1, Br 2, I 3, C_6F_5 4. To a 10 mL dichloromethane solution of [AuX(tht)][20,21] (tht = tetrahydrothiophene; 0.3 mmol; X = Cl, 0.096 g; C_6F_5 0.136 g) or [AuX(AsPh$_3$)][22] (0.3 mmol; X = Br, 0.175 g; I 0.189 g) was added bis(2-diphenylphosphinoethyl)phenylphosphine (triphos; 0.053 g, 0.1 mmol). After 2 h of stirring, the solution was concentrated to ca. 3 mL. Addition of diethyl ether (**1**−**2**) or petroleum ether (**3**−**4**) afforded complexes **1**−**4** as white solids, which were washed with more diethyl ether or petroleum ether (2 × 5 mL). Yield of **1**: 95%. Λ: 2.1 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.7−7.4 (m, 25H, Ph), 2.75 (m, 2H, P−CH$_2$), 2.31 (m, 6H, P−CH$_2$). ^{31}P{^{1}H} NMR: δ 34.0, 31.8, AB$_2$ spin system with $^3J_{AB}$ = 54.7 Hz. Anal. Calcd for $C_{34}H_{33}Au_3Cl_3P_3$: C, 33.15; H, 2.7. Found: C, 32.8; H, 2.65. LSIMS (*m*/*z*, %, assignment): 1195 (100, [M − Cl]$^+$), 963 (40, [Au$_2$Cl(triphos)]$^+$). Yield of **2**: 80%. Λ: 3.4 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.7−7.4 (m, 25H, Ph), 2.81 (m, 2H, P−CH$_2$), 2.37 (m, 6H, P−CH$_2$). ^{31}P{^{1}H} NMR: δ 35.2, 33.3, AB$_2$ spin system with $^3J_{AB}$ = 52.0 Hz. Anal. Calcd for $C_{34}H_{33}Au_3Br_3P_3$: C, 29.9; H, 2.4. Found: C, 30.35; H, 2.9. LSIMS (*m*/*z*, %, assignment): 1285 (100, [M − Br]$^+$), 1007 (49, [Au$_2$Br(triphos)]$^+$). Yield of **3**: 77%. Λ: 3.5 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.8−7.4 (m, 25H, Ph), 2.88 (m, 2H, P−CH$_2$), 2.41 (m, 6H, P−CH$_2$); ^{31}P{^{1}H} NMR: δ 36.5, 35.7, AB$_2$ spin system with $^3J_{AB}$ = 50.5 Hz. Anal. Calcd for $C_{34}H_{33}Au_3I_3P_3$: C, 27.1; H, 2.2. Found: C, 27.4; H, 2.5. LSIMS (*m*/*z*, %, assignment): 1378 (100, [M − I]$^+$), 1055 (30, [Au$_2$I(triphos)]$^+$). Yield of **4**: 75%. Λ: 3.8 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.8−7.4 (m, 25H, Ph), 2.8−2.4 (m, 8H, P−CH$_2$). ^{19}F NMR: δ -117.34 (m, 4F$_o$), −117.60 (m, 2F$_o$), −159.28 (t, 2F$_p$), −159.35 (t, 1F$_p$), −163.2 to −163.5 (m, 6F$_m$). ^{31}P{^{1}H} NMR: δ 39.6. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −90 °C): δ 35.9 (br, 2P), 34.9 (br, 1P). Anal. Calcd for $C_{52}H_{33}Au_3F_{15}P_3$: C, 38.4; H, 2.05. Found: C, 38.6; H, 2.25. LSIMS (*m*/*z*, %, assignment): 1459 (65, [M − C$_6$F$_5$]$^+$), 1095 (100, [Au$_2$(C$_6$F$_5$)(triphos)]$^+$).

[{Au(C$_6$F$_5$)$_3$}$_2$(μ-triphos)] 5. To a dichloromethane solution (10 mL) of [Au(C$_6$F$_5$)$_3$(tht)][23] (0.157 g, 0.2 mmol) was added triphos (0.053 g, 0.1 mmol). The solution was stirred for 2 h. Then, it was concentrated to ca. 2 mL. Addition of cold hexane (10 mL) afforded **5** as a white solid. A second fraction was obtained by concentration and cooling to −18 °C. Complex **5** was washed with hexane (2 × 5 mL). Yield of **5**: 68%. Λ: 13.2 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.6−6.9 (m, 25H, Ph), 2.5−2.0 (m, 8H, P−CH$_2$). ^{19}F NMR: δ −120.9 (m, 4F$_o$), −121.5 (m, 16F$_o$), −122.0 (m, 4F$_o$), −122.7 (m, 8F$_o$), −123.0 (m, 4F$_o$), −155.6 (t, 4F$_p$), −156.3 (t, 4F$_p$), −156.7 (t, 1F$_p$), −157.3 (t, 4F$_p$), −157.6 (t, 1F$_p$), −157.7 (t, 1F$_p$), −158.1 (t, 2F$_p$), −158.4 (t, 1F$_p$), −160.2 to −160.6 (m, 16F$_m$), −161.2 (m, 8F$_m$), −161.8 to −162.2 (m, 12F$_m$). ^{31}P{^{1}H} NMR: δ 16.3 (m, 6P), −11.4 (d, $^3J_{PP}$ = 35.2 Hz, 1P), −11.7 (d, $^3J_{PP}$ = 29.2 Hz, 1P), −15.4 (t, $^3J_{PP}$ = 34.2 Hz, 1P). Anal. Calcd for $C_{70}H_{33}Au_2F_{30}P_3$: C, 43.55; H, 1.7. Found: C, 43.5; H, 2.0. LSIMS (*m*/*z*, %, assignment): 1763 (10, [M − C$_6$F$_5$]$^+$), 731 (100, [Au(triphos)]$^+$).

[{Au(C$_6$F$_5$)$_3$}$_3$(μ-triphos)] 6. To a dichloromethane solution (10 mL) of [Au(C$_6$F$_5$)$_3$(tht)] (0.236 g, 0.3 mmol) was added triphos (0.053 g, 0.1 mmol). The solution was stirred for 2 h and then concentrated to ca. 2 mL. Addition of cold hexane (10 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**: 65%. Λ: 19.3 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.9−6.8 (m, 25H, Ph), 2.02 (m, 8H, P−CH$_2$). ^{19}F NMR: δ −121.5 (m, 4F$_o$), −122.0 (m, 8F$_o$), −123.1 (m, 4F$_o$), −123.8 (m, 2F$_o$), −153.1 (t, 2F$_p$), −156.0 (t, 4F$_p$), −156.5 (t, 1F$_p$), −157.3 (t, 2F$_p$), −159.2 (m, 4F$_m$), −160.2 to −160.5 (m, 8F$_m$), −161.3 to −161.6 (m, 6F$_m$). ^{31}P{^{1}H} NMR: δ 16.7 (m, 2P), 14.5 (m, 1P). Anal. Calcd for $C_{88}H_{33}Au_3F_{45}P_3$: C, 40.2; H, 1.25. Found: C, 40.15; H, 1.45. LSIMS (*m*/*z*, %, assignment): 1763 (25, [M − Au − 4C$_6$F$_5$]$^+$), 731 (100, [Au(triphos)]$^+$).

[{Au(Fmes)}$_3$(μ-triphos)] 7. To a freshly prepared diethyl ether solution of [Li(Fmes)][24] (Fmes = 1,3,5-tris(trifluoromethyl)phenyl; 0.6 mmol) was added complex **1** (0.123 g, 0.1 mmol). After 20 h of stirring, two drops of water were added to hydrolyze the excess lithium reagent. The mixture was dried and filtered through a sodium sulfate sinter. The clear solution was evaporated to dryness. The white residue was washed with pentane (2 × 5 mL). Yield of **7**: 55%. Λ: 7.6 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 8.2−7.4 (m, 31H, Ph and Fmes), 2.85 (m, 2H, P−CH$_2$), 2.55 (m, 2H, P−CH$_2$), 2.34 (m, 4H, P−CH$_2$); ^{19}F NMR: δ -60.19 (s, 6F$_o$), −60.55 (s, 12F$_o$), −63.54 (s, 3F$_p$), −63.56 (s, 6F$_p$). ^{31}P{^{1}H} NMR: δ 43.1, 41.4, A$_2$B spin system with $^3J_{AB}$ = 56.2 Hz. Anal. Calcd for $C_{61}H_{39}Au_3F_{27}P_3$: C, 37.2; H, 2.0. Found: C, 37.45; H, 2.35. LSIMS (*m*/*z*, %, assignment): 1688 (5, [M − (Fmes)]$^+$), 1210 (75, [Au$_2$(Fmes)(triphos)]$^+$).

[{Au(p-SC$_6$H$_4$Me)}$_3$(μ-triphos)] 8. To a 10 mL dichloromethane solution of complex **1** (0.123 g, 0.1 mmol) was added a freshly prepared methanol solution (10 mL) of [Na(SC$_6$H$_4$Me)] (prepared from NaOMe and p-HSC$_6$H$_4$Me; 0.3 mmol). After 2 h of stirring, the mixture was evaporated to dryness. Dichloromethane was added to the residue, which was then filtered and concentrated. The white product **8** was precipitated by addition of pentane and washed with pentane (2 × 5 mL). Yield of **8**: 60%. Λ: 27.6 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.8−7.4 (m, 37H, Ph), 2.77 (m, 2H, P−CH$_2$), 2.47 (m, 6H, P−CH$_2$), 2.26 (s, 9H, Me). ^{31}P{^{1}H} NMR: δ 37.3 (m, 1P), 35.3 (m, 2P). ^{31}P{^{1}H} NMR (−60 °C): δ 37.3 (m, 1P), 35.3 (m, 2P). Anal. Calcd for $C_{55}H_{54}Au_3P_3S_3$: C, 44.2; H, 3.6; S, 6.45. Found: C, 44.4; H, 3.35; S, 6.1. LSIMS (*m*/*z*, %, assignment): 1371 (100, [M − SC$_6$H$_4$Me]$^+$), 1051 (74, [Au$_2$(SC$_6$H$_4$Me)(triphos)]$^+$).

[{Au(SCN)}$_3$(μ-triphos)] 9. To a dichloromethane solution (10 mL) of of complex **1** (0.123 g, 0.1 mmol) was added an aqueous (5 mL) solution of KSCN (0.029 g, 0.3 mmol). The solid dissolved rapidly, and the resulting clear solution was stirred for about 2 h. Then the organic layer was extracted, dried with anhydrous Na$_2$SO$_4$,and filtered. Concentration to ca. 2 mL and addition of diethyl ether (10 mL) afforded complex **9** as a white solid, which was washed with diethyl ether (2 × 5 mL). Yield of **9**: 60%. Λ: 30.5 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.8−7.5 (m, 25H, Ph), 2.80 (m, 2H, P−CH$_2$), 2.50 (m, 6H, P−CH$_2$). ^{31}P{^{1}H} NMR: δ 33.9 (s). ^{31}P{^{1}H} NMR (−60 °C): δ 34.0 (s). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 33.8 (s). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −90 °C): δ 30.7 (s). Anal. Calcd for $C_{55}H_{54}Au_3P_3S_3$: C, 34.2; H, 2.55; N, 3.25; S, 7.4. Found: C, 33.8; H, 2.65, N, 3.2; S, 7.05. LSIMS (*m*/*z*, %, assignment): 1241 (100, [M − SCN]$^+$), 986 (58, [Au$_2$(SCN)(triphos)]$^+$).

[Au$_3$Cl$_{3-n}$(S$_2$CNMe$_2$)$_n$(μ-triphos)]; n = 3 (10), 2 (12), 1 (14). To a dichloromethane solution (20 mL) of **1** (0.123 g, 0.1 mmol) was added NaS$_2$CNMe$_2$ (0.3 mmol, 43 mg; 0.2 mmol, 29 mg; 0.1 mmol, 14 mg). The solid dissolved rapidly, and the resulting yellow solution was stirred for about 2 h and then filtered through Celite and concentrated to ca. 2 mL. Addition of diethyl ether (20 mL) afforded complexes **10**, **12**, or **14** as yellow solids, which were washed with diethyl ether (2 × 5 mL). Yield of **10**: 75%. Λ: 15.3 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 7.8−7.3 (m, 25H, Ph), 3.49 (s, 18H, Me), 2.80 (m, 2H, P−CH$_2$), 2.40 (m, 6H, P−CH$_2$). ^{31}P{^{1}H} NMR: δ 36.6 (m, 1P), 34.8 (m, 2P). ^{31}P{^{1}H} NMR (−60 °C): δ 37.0, 34.7 (s), AB$_2$ spin system with $^3J_{AB}$ = 56.6 Hz. Anal. Calcd for $C_{43}H_{51}Au_3N_3P_3S_6$: C, 34.75; H, 3.45; N, 2.85; S, 12.95. Found: C, 34.4; H, 3.65, N, 2.7; S, 12.65. LSIMS (*m*/*z*, %, assignment): 1366 (31, [M − S$_2$CNMe$_2$]$^+$), 1049 (34, [Au$_2$(S$_2$CNMe$_2$)(triphos)]$^+$), 731 (100, [Au(triphos)]$^+$). Yield of **12**: 70%. Λ: 88.9 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 8.1−7.3 (m, 25H, Ph), 3.52 (s, 12H, Me), 3.20−2.50 (m, 8H, P−CH$_2$). ^{31}P{^{1}H} NMR: δ 32.5 (br). ^{31}P{^{1}H} NMR (−60 °C): δ 31.0 (s, 2P), 30.2 (s, 1P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −90 °C): δ 31.0 (s, 2P), 28.7 (s, 1P). Anal. Calcd for $C_{40}H_{45}Au_3ClN_2P_3S_4$: C, 34.25; H, 3.25; N, 2.0; S, 9.15. Found: C, 33.9; H, 3.15, N, 2.0; S, 8.95. LSIMS (*m*/*z*, %, assignment): 1366

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Table 1. Crystallograhic Data for Complex **6**

chem formula	$C_{88}H_{41}Au_3Cl_3F_{45}P_3$	
fw	2743.37	
temp	−130(2) °C	
cryst syst	triclinic	
space group	$P(-1)$	
unit cell dimens	$a = 12.7746(16)$ Å	$\alpha = 98.215(3)°$
	$b = 18.560(2)$ Å	$\beta = 101.666(3)°$
	$c = 21.750(3)$ Å	$\gamma = 96.640(3)°$
volume	4942.5(10) Å^3	
Z	2	
density (obsd)	not measured	
density (calcd)	1.843 Mg/m^3	
abs coeff	4.699 mm^{-1}	
final R indices [$I > 2\sigma(I)$]	R1^a = 0.0532, wR2^b= 0.1336	
R indices (all data)	R1 = 0.0898, wR2 = 0.1539	
largest diff. peak and hole	3.202 and −3.080 e Å^{-3}	

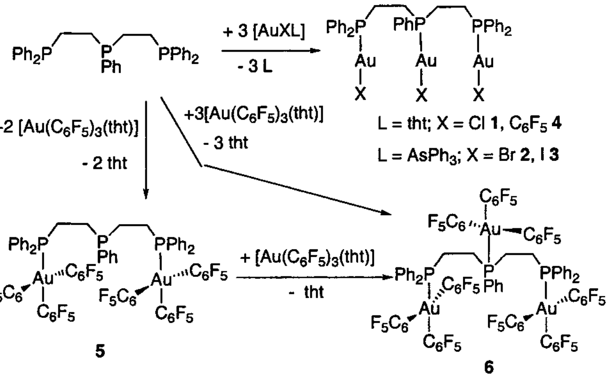
^{a} R1(F)= $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2($F^2$) = $[\Sigma\{w(F_o^2 - F_c^2)2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

(52, [M − Cl]$^+$), 1281 (7, [M − S_2CNMe_2]$^+$), 1048 (33, [$Au_2(S_2CNMe_2)$(triphos)]$^+$), 731 (100, [Au(triphos)]$^+$). Yield of **14**: 72%. Λ: 61.5 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 8.3−7.5 (m, 25H, Ph), 3.65 (s, 6H, Me), 3.42 (br, 2H, P−CH_2), 3.10 (br, 2H, P−CH_2), 2.60 (br, 4H, P−CH_2). $^{31}P\{^1H\}$ NMR: δ 29.8 (br); $^{31}P\{^1H\}$ NMR (−60 °C): δ 28.5 (s), 27.8 (s), 26.0 (s). Anal. Calcd for $C_{37}H_{39}Au_3Cl_2NP_3S_2$: C, 33.75; H, 3.0; N, 1.05; S, 4.9. Found: C, 33.55; H, 3.1, N, 1.1; S, 4.9. LSIMS (*m*/*z*, %, assignment): 1281 (100, [M − Cl]$^+$), 1196 (7, [M − S_2CNMe_2]$^+$), 1049 (16, [$Au_2(S_2CNMe_2)$(triphos)]$^+$), 731 (15, [Au(triphos)]$^+$).

[$Au_3Cl_{3-n}(S_2CN(CH_2Ph)_2)_n$(μ-triphos)]; *n* = 3 (11), 2 (13), 1 (15). To a dichloromethane solution (20 mL) of **1** (0.123 g, 0.1 mmol) was added a 3 mL aqueous solution of $NaS_2CN(CH_2Ph)_2$ (0.3 mmol, 89 mg; 0.2 mmol, 59 mg; 0.1 mmol, 29 mg). The solid dissolved rapidly, and the resulting yellow solution was stirred for about 2 h. Then the organic layer was extracted, dried with anhydrous Na_2SO_4, and filtered. Concentration to ca. 2 mL and addition of diethyl ether (15 mL) afforded complexes **11**, **13**, or **15** as yellow solids, which were washed with diethyl ether (2 × 5 mL). Yield of **11**: 68%. Λ: 19.8 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 8.0−7.2 (m, 55H, Ph), 5.14 (s, 12H, N−CH_2), 2.90 (m, 2H, P−CH_2), 2.40 (m, 6H, P−CH_2). $^{31}P\{^1H\}$ NMR: δ 36.4, 34.8, AB_2 spin system with $^3J_{AB}$ = 56.1 Hz. $^{31}P\{^1H\}$ NMR (−60 °C): δ 36.3, 34.6, AB_2 spin system with $^3J_{AB}$ = 56.3 Hz. Anal. Calcd for $C_{79}H_{75}Au_3N_3P_3S_6$: C, 48.85; H, 3.9; N, 2.15; S, 9.9. Found: C, 48.75; H, 3.9, N, 2.0; S, 9.7. LSIMS (*m*/*z*, %, assignment): 1669 (41, [M − $S_2CN(CH_2Ph)_2$]$^+$), 1200 (26, [$Au_2(S_2CN(CH_2Ph)_2)$(triphos)]$^+$), 731 (100, [Au(triphos)]$^+$). Yield of **13**: 72%. Λ: 21.8 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 8.2−7.2 (m, 45H, Ph), 5.10 (s, 8H, N−CH_2), 3.40−2.50 (m, 8H, P−CH_2); $^{31}P\{^1H\}$ NMR: δ 31.9 (s, 2P), 30.0 (s, 1P). $^{31}P\{^1H\}$ NMR (−60 °C): δ 31.2 (s, 2P), 29.5 (s, 1P). Anal. Calcd for $C_{64}H_{61}Au_3ClN_2P_3S_4$: C, 45.05; H, 3.6; N, 1.65; S, 7.5. Found: C, 44.75; H, 3.5, N, 1.55; S, 7.1. LSIMS (*m*/*z*, %, assignment): 1669 (19, [M − Cl]$^+$), 1200 (20, [$Au_2(S_2CN(CH_2Ph)_2)$(triphos)]$^+$), 731 (100, [Au(triphos)]$^+$). Yield of **15**: 75%. Λ: 18.4 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR: δ 8.3−7.5 (m, 35H, Ph), 5.20 (s, 4H, N−CH_2), 3.35 (br, 2H, P−CH_2), 2.95 (br, 2H, P−CH_2), 2.60 (br, 4H, P−CH_2). $^{31}P\{^1H\}$ NMR: δ 30.1 (br). $^{31}P\{^1H\}$ NMR (−60 °C): δ 30.4 (s), 27.2 (s), 25.0 (s). Anal. Calcd for $C_{49}H_{47}Au_3Cl_2NP_3S_2$: C, 40.05; H, 3.2; N, 0.95; S, 4.35. Found: C, 40.2; H, 3.55, N, 1.1; S, 4.6. LSIMS (*m*/*z*, %, assignment): 1432 (93, [M − Cl]$^+$), 1196 (60, [M − $S_2CN(CH_2Ph)_2$]$^+$), 731 (100, [Au(triphos)]$^+$).

Crystal Structure Determination of 6. Some crystallographic data of [$\{Au(C_6F_5)_3\}_3$(μ-triphos)] are given in Table 1. Colorless crystals of **6** were grown from dichloromethane and chloroform/petroleum ether. A tablet ca. 0.4 mm × 0.2 mm × 0.1 mm was mounted in an inert oil on a glass fiber. A total of 58818 reflections were collected on a Bruker SMART 1000 CCD diffractometer at −130 °C, using monochromated Mo Kα radiation (λ = 0.710 73 Å); 28562 independent reflections [R(int) = 0.0550] were used for all calculations; θ range for data collection from 1.35 to 30.03°; index ranges $-17 \le h \le 17$, $-26 \le k \le 26$, $-30 \le l \le 30$; completeness to θ = 30.00° was 98.8%. An absorption correction was based on multiple scans (program SADABS); transmission factors are in the range 0.573−0.962. The structure was refined anisotropically on F^2 (program SHELXL-97[25]) using a system of restraints (to light atom U values and local ring symmetry). H atoms were included using a riding model. Two ill-defined regions of residual electron density were tentatively interpreted as partially occupied solvent. Goodness-of-fit on F^2 is 1.031.

Scheme 1



Results and Discussion

Synthesis and Characterization. The reaction of bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) with the appropriate gold(I) complex [AuXL] (X = Cl, Br, I, C_6F_5; L = tetrahydrothiophene (tht), $AsPh_3$) containing an easily displaceable ligand in molar ratio 1:3 in dichloromethane leads to the trinuclear gold(I) complexes **1**−**4** (see Scheme 1). These derivatives are air-and moisture-stable white solids at room temperature. Their IR spectra show absorptions at 326 (**1**) cm^{-1} due to ν(Au−Cl)[26] or at 954 and 792 cm^{-1} from the pentafluorophenyl groups[27] (**4**). Their acetone solutions are nonconducting. The ^{1}H NMR spectra show the triphosphine protons, the CH_2CH_2 bridges being observed as two signals for **1**−**3** (integral 2:6) and a complicated multiplet for **4**. The ^{19}F NMR spectrum of **4** shows the pattern of two different pentafluorophenyl groups in a 2:1 ratio. The $^{31}P\{^1H\}$ NMR spectra of complexes **1**−**3** show an AB_2 spin system in which δ_{PPh} is always the lowest field resonance varying from 34.0 to 36.5 ppm while δ_{PPh_2} lies in the range 31.8−35.7 ppm; both signals are low-field shifted on going from Cl to Br to I, as found in [$(AuX)_2$(μ-dppm)] (dppm = bis(diphenylphosphine)methane) but in the opposite order to that in [$(AuX)_2$(μ-tppm)] (tppm = tris(diphenylphosphine)methane).[28] The $^{31}P\{^1H\}$ NMR spectrum of **4** shows only a singlet at 39.6 ppm, which only at 183 K changes to two broad and close resonances at 35.9 and 34.9 ppm in a 2:1 ratio; this can be interpreted as two isochronous phosphorus centers with a slightly different chemical shift on varying the temperature. The LSIMS mass spectra show the peak corresponding to [M − X]$^+$ at *m*/*z* (% abundance, X) = 1195 (100, Cl), 1285 (100, Br), 1378 (100, I) and 1459 (65, C_6F_5), respectively, for **1**−**4**.

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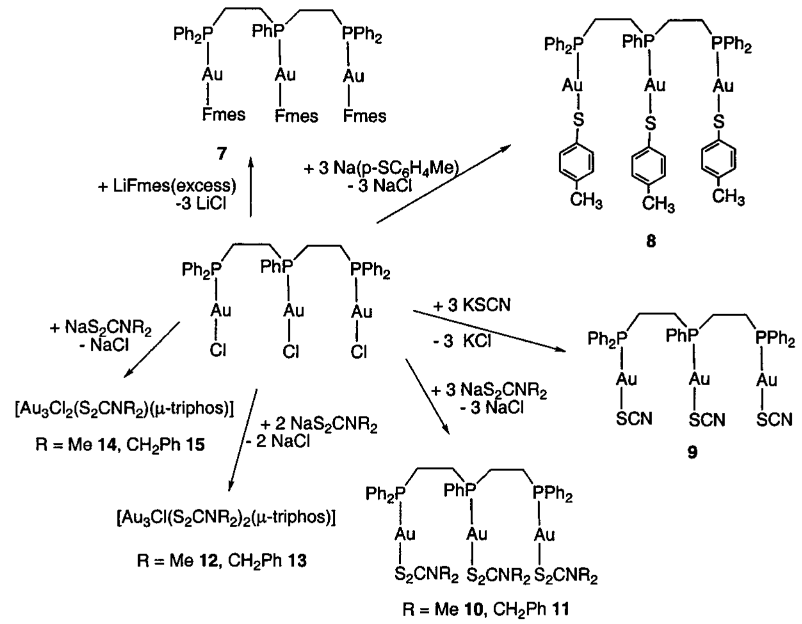
Scheme 2



We have also synthesized gold(III) derivatives containing this triphosphine ligand by reaction of triphos with $[Au(C_6F_5)_3(tht)]$ in a 1:2 or 1:3 molar ratio, which affords the dinuclear **5** or trinuclear complex **6**. Complex **5** reacts with $[Au(C_6F_5)_3(tht)]$ to give complex **6**. Complexes **5**−**6** are air- and moisture-stable, white solids at room temperature. Their acetone solutions are nonconducting. In the IR spectra, absorptions at ca. 970 and 795 cm^{-1} from the pentafluorophenyl groups are observed. The ^{19}F NMR spectrum of **6** shows two different tris(pentafluorophenyl)gold(III) units, while the spectrum of **5** is much more complex. The $^{31}P\{^1H\}$ NMR spectrum of **6** shows two resonances centered at 16.7 and 14.5 ppm in a 2:1 ratio, which are observed as multiplets because of P−P and P−F couplings. The $^{31}P\{^1H\}$ NMR spectrum of **5** is more complex and shows four resonances, one multiplet due to gold-coordinated phosphine at 16.3 ppm, two doublets from uncoordinated phosphine centered at −11.4 and −11.7 ppm, and a triplet at −15.4 ppm. Therefore, complex **5** must be a mixture of three isomers, which can be postulated as one containing uncoordinated PPh_2 and the other uncoordinated PPh (the chemical shifts are close to those found for PPh_2 and PPh in the free phosphine); the isomer with uncoordinated PPh_2 could be in two different conformations to give two doublets. The LSIMS mass spectra of **5**−**6** show a peak at m/z (%) = 1763 (10, $[M - C_6F_5]^+$, **5**; 25 $[M - Au\text{-}4C_6F_5]^+$, **6**) and the base peaks at 731 due to $[Au(triphos)]^+$.

The starting material that allows us to introduce other ligands is the trinuclear chloro-gold(I) derivative **1**, by means of chloro substitution reactions (see Scheme 2). Treatment of **1** $[(AuCl)_3(\mu\text{-triphos})]$ with a freshly prepared ether solution of Li(Fmes) (Fmes = 1,3,5-tris(trifluoromethyl)phenyl) leads to the organometallic complex **7** as a white solid. The same procedure but using a freshly prepared methanol solution of sodium *p*-methylphenylthiolate or an aqueous solution of potassium thiocyanate affords complexes **8** and **9**. The reaction of **1** with sodium dithiocarbamate in a 1:1, 1:2, or 1:3 molar ratio affords complexes **10**−**15** as yellow solids.

These derivatives are air- and moisture-stable solids at room temperature. The IR spectrum of **8** shows absorptions at 2117 and 2079 cm^{-1} from thiocyanate. Acetone solutions are nonconducting, although show some conductivity for **12** and **14** (with chloride and methyl dithiocarbamate) which means that for the latter there is some chloride dissociation in the solution.

Table 2. $^{31}P\{^1H\}$ NMR Data for Complexes **7**−**15** in $CDCl_3$ Solution[a]

complex	δ (18 °C) P^1, P^2, P^3	δ (−55 °C) P^1, P^2, P^3
7	43.1, 41.4, 43.1	
8	35.3, 37.3, 35.3	35.3, 37.3, 35.3
9	33.9[b]	34.0,[b] 30.7[b,c]
10	34.8, 36.6, 34.8	34.7, 37.0, 34.7
11	34.8, 36.4, 34.8	34.6, 36.3, 34.6
12	32.5[b]	31.0, 30.2, 31.0 31.0, 28.7, 31.0[c]
13	31.9, 30.0, 31.9	31.2, 29.5, 31.2
14	29.8[b]	28.5,[b] 27.8,[b] 26.0[b]
15	30.1[b]	30.4,[b] 27.2,[b] 25.0[b]

[a] P^1, P^2, and P^3 assigned as follows: P^1 and P^3 are the lateral phosphorus whereas P^2 is the central one. Coupling constants and spin system are given in the Experimental Section. [b] Broad signal that is not possible to assign to P^1, P^2, P^3. [c] Measured in CD_2Cl_2 at −90 °C.

The $^{31}P\{^1H\}$ NMR spectrum of **7** show an A_2B spin system with $\Delta\delta_{AB} = 1.7$ ppm (see Table 2 for chemical shifts) while in the ^{19}F NMR spectrum two kinds of *o*-CF_3 (in the ratio 6:12) and *p*-CF_3 (in the ratio 3:6) are observed, as expected for two different Fmes ligands, one *trans* to PPh and two *trans* to PPh_2. The $^{31}P\{^1H\}$ NMR spectrum of **8** is an ill-defined AB_2 spin system even at low temperature. In contrast, complex **9** displays only the resonance already described for **4**, which shows a shoulder at −55 °C but at − 90 °C becomes a singlet. This can again be interpreted as two isochronous phosphorus. Complex **10** shows an ill-defined AB_2 spin system in the $^{31}P\{^1H\}$ NMR spectrum which becomes well-defined at low temperature while for the analogous complex **11** an AB_2 spin system is found at both temperatures. In the $^{31}P\{^1H\}$ NMR spectrum of **12**, only one resonance is observed, which at −55 °C or at −90 °C splits into two singlet resonances, while for the similar complex **13** there are two singlet resonances at room and low temperature; several structures are possible and fluxional processes occur at least in the case of the methyl dithiocarbamate, which can involve the two dithiocarbamate ligands and the chloride. Finally, the $^{31}P\{^1H\}$ NMR spectra of **14**−**15** consist of a broad

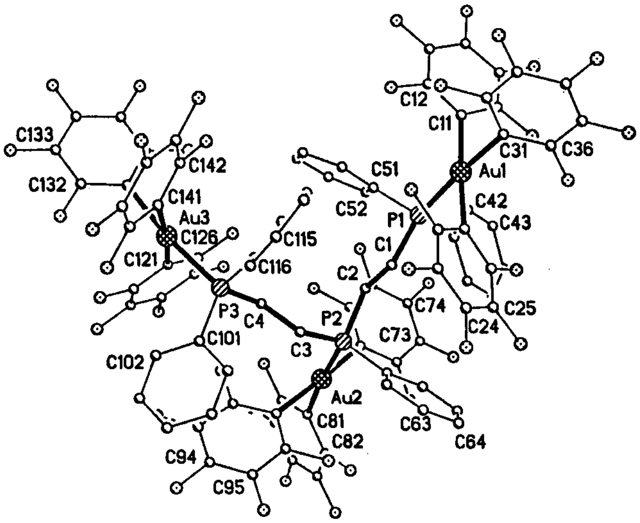


Figure 1. Molecular structure of complex **6**. All H atoms have been omitted.

resonance, split at low temperature into three singlet resonances with a very different chemical shift from those found in complexes **10**−**11**; this might indicate a bridging dithiocarbamate ligand as has been previously reported in $[Au_2(\mu\text{-}S_2CNR_2)(\mu\text{-dppe})](ClO_4)$ (R = Me, Et, CH_2Ph; dppe = 1,2-bis(diphenylphosphino)ethane)[13,29] or in $[Au_3Cl_2(S_2CNR_2)(\mu\text{-dpmp})]$ (R = Me, CH_2Ph; dpmp = bis(diphenylphosphinomethyl)phenylphosphine).[30] The ^1H NMR spectra at room temperature involve two multiplets for ethylidene bridges in complexes **8**−**11** (2:6 ratio in the range 2.9−2.4 ppm) while three resonances are observed in complexes **7** and **12**−**15** from 3.4 to 2.3 ppm; additionally, the resonances due to Fmes (around 8.2 ppm in complex **7**), *p*-Me in complex **8**, and the dithiocarbamate substituents (Me or CH_2-) are found in the appropriate ratio to the triphosphine proton resonances.

The LSIMS mass spectra show the peak corresponding to $[M - X]^+$ at *m*/*z* (complex, % abundance, X): 1688 (**7**, 5, Fmes), 1371 (**8**, 100, SC_6H_4Me), 1241 (**9**, 100, SCN), 1366 (**10**, 31, S_2CNMe_2; **12**, 52, Cl), 1669 (**11**, 41, $S_2CN(CH_2Ph)_2$; **13**, 19, Cl), 1281 (**14**, 100, Cl), 1432 (**15**, 93, Cl).

Crystal Structure of Complex 6. The geometry of the trinuclear gold(III) complex $[\{Au(C_6F_5)_3\}_3(\mu\text{-triphos})]$ has been determined by X-ray diffraction. The molecular structure is shown in Figure 1, with selected bonds and angles in Table 3. The triphosphine adopts a conformation that allows three bulky $Au(C_6F_5)_3$ units to be coordinated at the same time. The gold centers form a triangle with very long gold−gold distances: 7.095 Å for Au2−Au3, 8.348 Å for Au1−Au2, and 8.970 Å for Au1−Au3, which precludes any form of metal−metal bonding.

The gold(III) centers display slightly distorted square planar coordination (mean deviations from best planes: Au1 0.02, Au2 0.07, Au3 0.09 Å) with CAuC and CAuP angles ranging from 87.0(3) to 94.73(18)°; the interplanar angles between the coordination planes are 44° for Au1/Au2 and 86° for Au2/Au3. Au−C bond distances *trans* to the phosphine lie in the range 2.047(7)−2.057(7) Å, whereas those *trans* to pentafluorophenyl are 2.063(7)−2.079(7) Å. They are similar to those found in other tris(pentafluorophenyl)gold(III) complexes, such as $[Au(C_6F_5)_3(S_2C{-}PEt_3)]$ (2.037(3) Å *trans* to S; 2.067(4) and 2.076(4) Å *trans* to C),[31] $[(\mu\text{-}S_2C{-}PEt_3)\{Au(C_6F_5)_3\}_2]$ (2.048(16) and 2.058(20) *trans* to S, 2.062(14)−2.090(13) Å *trans* to C),[31] $NBu_4[\{Au(C_6F_5)_3PPh_2CHPPh_2\}_2Au]$ (2.063(8) and 2.080(8) *trans* to P, 2.057(8)−2.069(9) Å *trans* to C)[32] or $[N(PPh_3)_2][\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$ (2.073(6) Å *trans* to P, 2.052(5) and 2.058(6) *trans* to C).[33] Au(III)−P bond distances range from 2.3434(17) to 2.3564(17) Å, slightly shorter than those in $NBu_4[\{Au(C_6F_5)_3PPh_2CHPPh_2\}_2Au]$ (2.367(2) Å) or in $[N(PPh_3)_2][\{Au(C_6F_5)_3(\mu\text{-}PPh_2)\}_2Au]$ (2.365(2) Å) but longer that those in $[Au(C_6F_5)_3\{PPh_2C({=}CH_2)PPh_2\}Au(C_6F_5)]$ (2.382(2) Å)[34] and similar to those found in $AuMe_3PPh_3$ (2.350(6) and 2.347(6) Å).[35]

Table 3. Selected Bond Lengths [Å] and Angles [deg]

Au(1)−C(31)	2.054(7)	P(1)−C(41)	1.799(6)
Au(1)−C(21)	2.063(7)	P(1)−C(51)	1.807(7)
Au(1)−C(11)	2.079(7)	P(1)−C(1)	1.828(6)
Au(1)−P(1)	2.3564(17)	P(2)−C(61)	1.794(7)
Au(2)−C(81)	2.057(7)	P(2)−C(2)	1.810(6)
Au(2)−C(91)	2.073(7)	P(2)−C(3)	1.820(6)
Au(2)−C(71)	2.079(7)	P(3)−C(101)	1.797(7)
Au(2)−P(2)	2.3454(16)	P(3)−C(111)	1.815(7)
Au(3)−C(131)	2.047(7)	P(3)−C(4)	1.832(6)
Au(3)−C(141)	2.075(7)	C(1)−C(2)	1.529(9)
Au(3)−C(121)	2.078(7)	C(3)−C(4)	1.523(9)
Au(3)−P(3)	2.3434(17)		

C(31)−Au(1)−C(21)	87.7(3)	C(51)−P(1)−Au(1)	117.2(2)
C(31)−Au(1)−C(11)	88.8(2)	C(1)−P(1)−Au(1)	113.9(2)
C(21)−Au(1)−C(11)	176.4(2)	C(61)−P(2)−C(2)	106.3(3)
C(31)−Au(1)−P(1)	176.83(17)	C(61)−P(2)−C(3)	105.6(3)
C(21)−Au(1)−P(1)	90.56(18)	C(2)−P(2)−C(3)	106.0(3)
C(11)−Au(1)−P(1)	92.90(18)	C(61)−P(2)−Au(2)	108.8(2)
C(81)−Au(2)−C(91)	88.6(3)	C(2)−P(2)−Au(2)	113.8(2)
C(81)−Au(2)−C(71)	87.0(3)	C(3)−P(2)−Au(2)	115.6(2)
C(91)−Au(2)−C(71)	174.3(3)	C(101)−P(3)−C(111)	109.4(3)
C(81)−Au(2)−P(2)	174.32(17)	C(101)−P(3)−C(4)	106.3(3)
C(91)−Au(2)−P(2)	91.0(2)	C(111)−P(3)−C(4)	103.9(3)
C(71)−Au(2)−P(2)	93.69(18)	C(101)−P(3)−Au(3)	116.7(2)
C(131)−Au(3)−C(141)	87.8(3)	C(111)−P(3)−Au(3)	107.6(2)
C(131)−Au(3)−C(121)	88.2(3)	C(4)−P(3)−Au(3)	112.2(2)
C(141)−Au(3)−C(121)	173.5(2)	C(2)−C(1)−P(1)	112.0(4)
C(131)−Au(3)−P(3)	172.69(17)	C(1)−C(2)−P(2)	116.5(4)
C(141)−Au(3)−P(3)	89.81(18)	C(4)−C(3)−P(2)	114.2(4)
C(121)−Au(3)−P(3)	94.73(18)	C(3)−C(4)−P(3)	112.1(4)
C(41)−P(1)−C(51)	108.8(3)		
C(41)−P(1)−C(1)	105.3(3)		
C(51)−P(1)−C(1)	100.8(3)		
C(41)−P(1)−Au(1)	110.0(2)		

Photophysical Characterization. The optical absorption spectra in dichloromethane was measured for all the complexes, and the most intense absorption was always around 230 nm from the phenyl phosphine rings.[30,36] The spectra of complexes **1**, **3**, **13**, and **15** are plotted in Figure 2. Halo or organometallic gold(I) derivatives **1**−**4** and **7** show an absorption around 270 nm that is only a shoulder in the spectra of **3** and **7**; there is absorption up to 300 nm except for the iodo derivative, which shows an absorption at 300 nm. In the spectra of the pentafluo-

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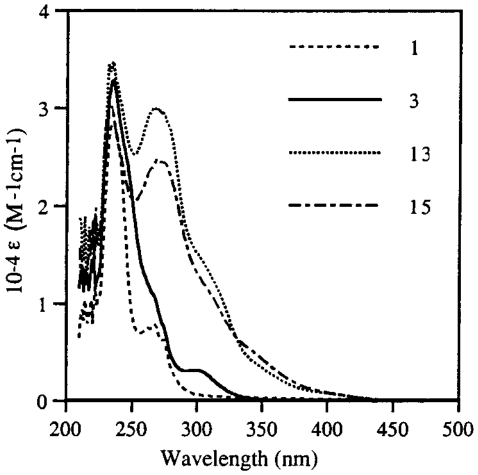

Figure 2. Absorption spectra in dichloromethane solution of complexes **1**, **3**, **13**, and **15**.

rophenyl gold(III) derivatives **5**−**6**, an intense aborption at about 256 nm is observed in addition to the phenyl absorption at 232 nm; again there is absorption up to 300 nm. Thiolate and thiocianate derivatives **8**−**9** show a shoulder about 260 nm; absorption continues up to about 400 nm for **8** or 350 nm for **9**. In dithiocarbamate gold(I) derivative spectra, the main features are the following: (a) again an intense phenyl absorption at 230 nm; (b) an absorption at 260 nm for methyl dithiocarbamate derivatives **10**, **12**, **14** or at 270 nm for benzyl dithiocarbamate derivatives **11**, **13**, **15**, which becomes less intense when the proportion of dithiocarbamate diminishes and has previously been assigned to these ligands;[13] (c) shoulders around 300−330 nm, more clearly seen for complex **10** at 296 nm and for complex **14** at 325 nm; in any case there is absorption up to around 400 nm. The absorptions in the range 300−350 nm can be assigned to sulfur to gold or to metal-centered transitions as reported for other phosphine−thiolate gold(I) derivatives[13,30,37] and for trinuclear tris(phosphine) gold(I) derivatives.[28,38,39]

The solid-state emission and excitation spectra for the triphosphine and complexes **1**−**15** have been determined at 298 and 77 K, and the results are summarized in Table 4. It is very important to note that sodium dithiocarbamate or thiocianate salts do not emit in the visible range, but the triphosphine does. There is an emission centered at 425 nm, while the excitation has a broad profile in the range 240−290 nm which must be related to $\pi-\pi^*$ phenyl ring transitions; at low temperature the excitation and emission spectra have the same profile and maxima. If the excitation frequency is higher than 310 nm, there is almost no emission. In Figure 3 are plotted the solid-state excitation and emission spectra of the triphosphine and complexes **2** and **3** at room temperature. The solid-state excitation and emission spectra of the triphosphine and complexes **2**, **6**, and **15** at low temperature are plotted in Figure 4.

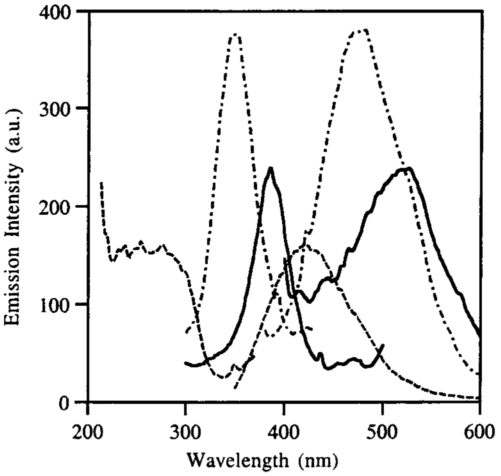

Figure 3. Solid-state excitation and emission spectra of the triphosphine (- - -) and complexes **2** (•-•-) and **3** (—) at room temperature.

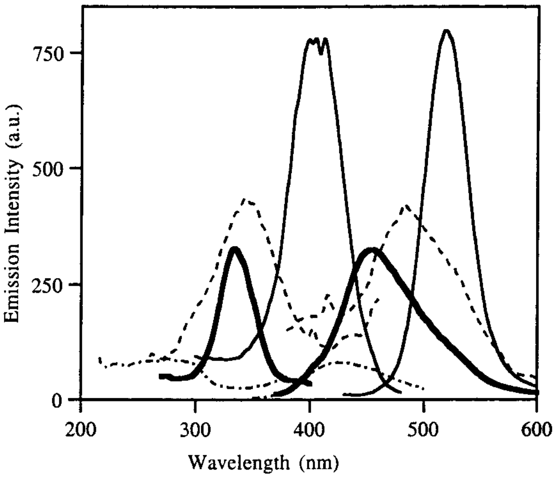

Figure 4. 77 K solid-state excitation and emission spectra of the triphosphine (•-•-) and complexes **2** (thick —), **6** (- - -), and **15** (—).

Table 4. Emision and Excitation Maxima (in nm) Measured for the Triphosphine and Complexes **1**−**15** in the Solid State at 298 and 77 K

complex	excitation 298 K	emission 298 K	excitation 77 K	emission 77 K
triphos	240−290	425	240−290	425
1			330	440
2	350	475	335	455
3	385	525	340	460
4			325	450
5				
6	340	450, 455	345	485
7			255	430
8			385	495
9	370	475	350	420 (sh), 460
10			455, 460	555
11			450	600
12			440 (sh), 455	550
13			415, 425	530
14	405 (sh), 430, 450 (sh)	520	405 (sh), 415	520
15			395, 410 (sh)	515

The bromo and iodo derivatives **2** and **3** emit at room temperature with an important red-shift from the free triphosphine (50 nm for **2** and 100 nm for **3**), the excitation maxima being centered at 350 and 385 nm, respectively, again strongly red-shifted from the triphosphine. Curiously, the chloro, pentafluorophenyl, and tris(trifluoromethyl)phenyl derivatives **1**, **4**, and **7** do not emit, even on using an excitation frequency below 300 nm. The luminescence properties are thus dramatically influenced by the halide anions, which indicates an important contribution of the halides in the energy levels involved in the electronic transitions, as described for other trinuclear gold(I)

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derivatives[28,40] At low temperature, complexes **1**−**4** and **7** emit with the maxima in the range 430−460 nm. In the series chloro, bromo, and iodo there is a slight red-shift in the excitation (330, 335, and 340 nm, respectively) and in the emission (440, 455, and 460 nm) and thus luminescence is slightly influenced by the halide anions, implying a totally different electronic transition nature. It is noteworthy that the Fmes derivative **7** is the most intense with respect to both excitation and emission spectra, whose profile and maxima are close to that of the triphosphine but much more intense. These data at low temperature provide evidence for a ligand-centered transition modified by the anionic ligands and the gold(I) centers, as has been already proposed for the series $[\{AuXPPhMe_2\}_n]$ (X = Cl, Br, I; $n = 2, 3$),[41] $[AuX(ER_3)]$ (X = Cl, Br; E = P, As),[42] or $[Au_{10}\{\mu\text{-}PPh_2N(^nPr)PPh_2\}_4(\mu_3\text{-}S)_4](PF_6)_2$,[43] instead of metal-centered transitions usually proposed in most luminescent triphosphine or diphosphine gold(I) complexes.[28,39,44]

Gold(III) complexes **5**−**6** have also been studied. The dinuclear derivative **5** emits neither at room temperature nor at low temperature, whereas the trinuclear derivative **6** emits at both temperatures. In comparison to the ligand spectra, not only are the excitation maxima red-shifted (by a minimum of 50 nm) but also the emission maxima (by 25 nm at room temperature and 60 nm at low temperature). In this case we cannot assign the emission clearly to the triphosphine, because the tris(pentafluorophenyl)gold(III) units play a decisive role. The number of such units has a dramatic influence in the luminescence properties which in the absence of any gold(III)−gold(III) contact seems to be associated to different molecular geometries and different isomers (as discussed above).

Thiolate derivative **8** does not emit at room temperature, whereas thiocyanate derivative **9** emits intensely with a maximum at 475 nm (excitation maximum at 370 nm). At low temperature complex **9** also emits intensely, with the maxima slightly blue-shifted. Complex **8** becomes luminescent at low temperature, the excitation and emission maxima being red-shifted compared to the previous values described in this paper. Here the assignment of the emissions is even more complicated, because sulfur to gold, or more generally ligand to metal transitions, in some cases shifted by gold−gold interactions, could be involved as proposed for mononuclear or dinuclear phosphine−thiolate gold(I) complexes.[11−13]

Dithiocarbamate derivatives **10**−**15** do not emit at room temperature except in the case of complex **14** containing only a methyl dithiocarbamate; the excitation and emission maxima (430 and 520 nm, respectively) are totally different from those found for the triphosphine but similar to those of some diphosphine or triphosphine dithiocarbamate derivatives. At low temperature all the complexes emit, the emission maxima being in the range 515−600 nm and the excitation maxima from 395 to 460 nm; in both types of spectra the maximum diminishes with the number of dithiocarbamate ligands, as we described for the analogous derivatives with the triphosphine dpmp (which has CH_2 bridges intead of CH_2CH_2 in triphos).[30] This fact can be explained because raising the number of dithiocarbamate ligands that can interact with the gold(I) centers to give tricoordinated gold(I) leads to a splitting of orbitals and consequently to a red shift of the emission maxima. Complex **14** (with one methyl dithiocarbamate) is strongly luminescent while complexes **10** and **11** (with three dithiocarbamates) and **13** (with two benzyl dithiocarbamates) are weakly luminescent.

In conclusion, we have prepared luminescent derivatives whose emission maxima range from 450 to 520 at room temperature and from 430 to 600 nm at low temperature. Some of them are strongly luminescent (**7**, **9**, and **14** at low temperature and **9** at room temperature) although most of them do not emit at room temperature and only **5** does not emit at low temperature. We can tentatively assign the nature of the emission as related to mainly a ligand (triphosphine) centered excited state for complex **7** to mainly a ligand to metal centered excited state for dithiocarbamate derivatives **10**−**15**, with most of the cases being very difficult to assign because several kinds of electronic transitions are plausible, and probably they are superimposed.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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