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Syntheses and X-ray Structural Characterizations of Three-Coordinate Au(I) and Ag(I) Complexes with the Potentially Tetradentate Ligand Tris(2-(diphenylphosphino)ethyl)amine (NP_3): $[Au_2(NP_3)_2](BPh_4)_2$, $Au(NP_3)PF_6$, $Au(NP_3)NO_3$, $Ag(NP_3)NO_3$, and $Ag(NP_3)PF_6$. The Au(I) Compounds Are Luminescent

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Reaction of the tetradentate "tripodlike" ligand tris(2-(diphenylphosphino)ethyl)amine (NP_3) with LAuX [L = PPh_3, $P(CH_2CH_2CN)_3$, THT; X = Cl^-, NO_3^-, PF_6^-, BPh_4^-] and AgX (X = NO_3^-, PF_6^-) produces the three-coordinate complexes $[Au_2(NP_3)_2](BPh_4)_2$ (dimer) (**1**), $Au(NP_3)PF_6$ (monomer) (**2**), and $Au(NP_3)NO_3$ (monomer) (**3**), the four-coordinate $Ag(NP_3)NO_3$ (monomer) (**4**), and the three-coordinate complex $Ag(NP_3)PF_6$ (monomer) (**5**). Compound **1** crystallizes with four molecules of dichloroethane in the triclinic space group $P\bar{1}$ (No. 2) with cell constants $a = 14.648(7)$ Å, $b = 15.759(11)$ Å, $c = 16.316(18)$ Å, $\alpha = 84.74(8)°$, $\beta = 70.81(6)°$, $\gamma = 67.22(5)°$, and $Z = 1$. Refinement of 5229 reflections and 593 parameters yields $R = 0.0435$ and $R_w = 0.0430$. Complex **1** has an inversion center in the solid state. Compound **2** crystallizes in the monoclinic space group Cc (No. 9) with cell constants $a = 17.589(6)$ Å, $b = 12.909(4)$, $c = 18.414(5)$ Å, $\beta = 90.95(2)°$, and $Z = 4$. Refinement of 6118 reflections and 485 parameters gives $R = 0.0256$ and $R_w = 0.0268$. Compound **3** crystallizes in the monoclinic space group Cc (No. 9) with cell constants $a = 17.270(3)$ Å, $b = 12.710(2)$ Å, $c = 17.720(2)$ Å, $\beta = 91.31(2)°$, and $Z = 4$. The structure converges to a conventional R factors of 0.0218 and 0.0218 for 6118 observations with 485 parameters. Compound **4** crystallizes in monoclinic space group Cc (No. 9) with cell constants $a = 16.85(2)$ Å, $b = 12.950(5)$ Å, $c = 17.629(6)$ Å, $\beta = 92.67(5)°$, and $Z = 4$. Final $R = 0.0363$ and $R_w = 0.0383$ result from the refinement of 3493 total reflections with 386 parameters. Compound **5** crystallizes in the trigonal space group $R\bar{3}$ (No. 146) with cell constants $a = 17.741(3)$ Å, $b = 17.741(3)$ Å, $c = 11.489(3)$ Å, $\gamma = 120°$, and $Z = 3$. Refinement of 1558 reflections and 162 parameters gives $R = 0.0333$ and $R_w = 0.0350$. Compounds **2** and **3** exhibit a brilliant luminescence under UV irradiation.

Introduction

Although the tetradentate "tripodlike" ligand tris(2-(diphenylphosphino)ethyl)amine (NP_3) was synthesized[1] more than two decades ago, the chemistry of this ligand with transition metals has received very little attention. Only a few complexes of this ligand with transition metals, $[H(NP_3)NiCo]BPh_4$,[2] $Ni(NP_3)$,[3] $HCo(NP_3)$,[3] $[(NP_3)Pt(CH_2Cl)]BPh_4$,[4] $(NP_3)Pd$,[5] and $[(NP_3)RhI]BPh_4$,[6] have been characterized structurally. All the complexes are monomeric. No dimeric complex of this ligand has been reported. NP_3 acts in these complexes as a tridentate ligand when the three phosphorus atoms are involved in coordination or as a tetradentate ligand when the three phosphorus atoms and the nitrogen atom bond to the metal atom. The particular coordination observed depends upon the nature of the metal and its oxidation state.

A linear two-coordinate geometry is most often observed[7,8] with Au(I) and Ag(I), but three- and four-coordination also are well established. With multidentate phosphine ligands such as a tripodal ligand like NP_3, three- and four-coordination to a single metal center have not been reported. Balch and Fung[9] have shown that the phosphorus analogue of NP_3 causes the formation of a dimer in which one of the arms of the PP_3 ligands functions as a bridge and all four P atoms of each ligand are coordinated to the metal atoms (Chart I, **G**).

Chart I shows some of the coordination modes observed structurally for gold(I) phosphine complexes. There are several structural reports concerning linear gold(I) phosphine complexes (**A**,[10,11] **E**[12,13]). Increased coordination using monodentate phosphines has also been observed (**B**,[14,15] **C**[15,16]). However, the formation of dinuclear gold(I) complexes using bidentate phosphines is favored to give a gold–gold separation of about 3.0 Å (**E**,[12,13] **F**[17]) and the formation of mononuclear gold(I) complexes with bidentate phosphines has been observed (**D**[18,19]). There were some recent reports where dinuclear gold(I) complexes form with

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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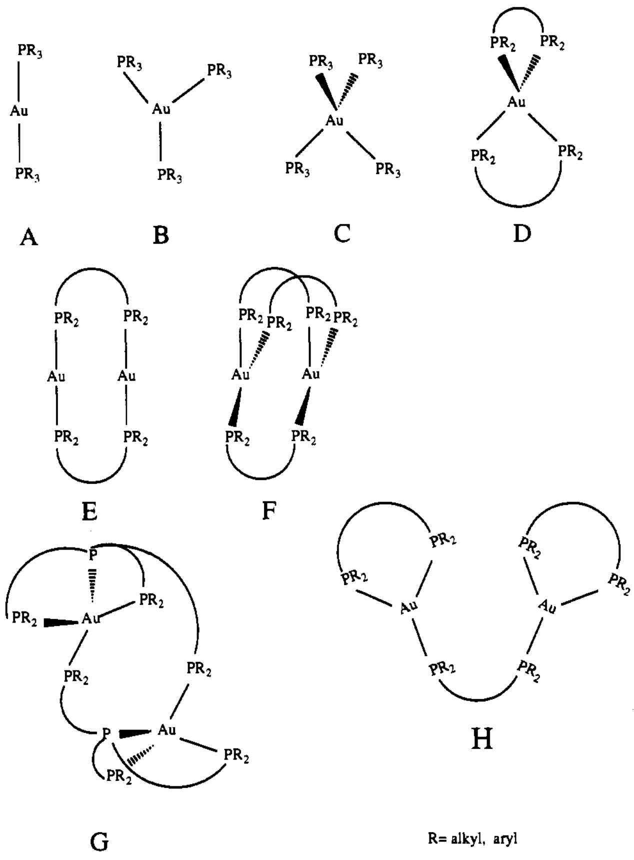
0020-1669/93/1332-5800$04.00/0

Chart I



multidentate or bulky bidentate ligands (G, H[20]) and no gold-gold interaction was reported.

Linear Ag(I) complexes containing bulky phosphines[21] such as (t-Bu)$_3$P or (mesityl)$_3$P and an unusual diphosphine[22] 2,11-bis((diphenylphosphino)methyl)benzo[c]phenanthrene are known. Three- and four-coordinate Ag(I) complexes with monodentate phosphines such as Ag(PPh$_3$)$_3$X[22-25] (X = BF$_4^-$, Cl$^-$, I$^-$, NO$_3^-$) and [Ag(PPh$_3$)$_4$][SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)][26] and bidentate phosphines[27] [Ag(cdppet)$_2$][SnPh$_3$(NO$_3$)$_2$] (cdppet = cis-1,2-bis(diphenylphosphino)ethylene), [Ag$_2$(dppm)$_2$(NO$_3$)$_2$],[28] and [Ag$_4$(dppm)$_4$(μ-NO$_3$)$_2$](PF$_6$)$_2$ are also known. All of these complexes have been characterized structurally. In [Ag$_4$(dppm)$_4$(NO$_3$)$_2$](PF$_6$)$_2$, two dimers of the cation [Ag$_2$(dppm)$_2$]$^{2+}$ are bridged by two oxygen atoms of each NO$_3^-$ anion. In this complex, each Ag(I) atom is coordinated by two phosphorus atoms of two dppm ligands and one oxygen atom of the NO$_3^-$ anion to give a three-coordinate Ag(I) center with a nearly trigonal planar geometry. Similarly, in [Ag$_2$(dppm)$_2$(NO$_3$)$_2$] each Ag(I) atom is coordinated by two phosphorus atoms of two dppm ligands and two oxygen atoms of each NO$_3^-$ anion, resulting in a four-coordinate distorted tetrahedral environment around each Ag(I) center.

No chemistry of the NP$_3$ ligand with either Au(I) or Ag(I) has been reported previously. Continuing our studies of the luminescent properties of three-coordinate group 11 complexes,[29] we have examined the coordination behavior of the NP$_3$ ligand toward Au(I) and Ag(I). We report here the syntheses and structural results for the three-coordinate Au(I) dimers [Au$_2$(NP$_3$)$_2$](X)$_2$ (X = PF$_6^-$, BPh$_4^-$, NO$_3^-$ (**1**)), the three-coordinate monomers Au(NP$_3$)X (X = PF$_6^-$ (**2**); X = NO$_3^-$ (**3**)), the four-coordinate monomer Ag(NP$_3$)NO$_3$ (**4**), and three-coordinate monomer Ag(NP$_3$)PF$_6$ (**5**).

Experimental Section

Preparation and Characterization of Compounds. Unless otherwise stated, all the reactions described were carried out under an atmosphere of dry nitrogen or argon; solvents were purified by standard methods. The complexes [AuP(CH$_2$CH$_2$CN)$_3$NO$_3$, (THT)AuCl (THT = tetrahydrothiophene), and Ph$_3$PAuX (X = NO$_3^-$, Cl$^-$, PF$_6^-$) were synthesized by literature procedures.[11,30,31] The compounds AgNO$_3$ and AgPF$_6$ were purchased from Johnson Matthey, Inc., and Aldrich Chemical Co., respectively. The ligand[1] NP$_3$ was prepared according to the literature. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded in CDCl$_3$ solutions on Varian XL-200 and XL-400 spectrometers. Emission and excitation spectra were recorded on a Perkin-Elmer fluorimeter, Model LS5.

Synthesis of [Au$_2$(NP$_3$)$_2$](BPh$_4$)$_2$ (1). (THT)AuCl (200 mg, ~0.62 mmol) was dissolved in CH$_2$Cl$_2$/CH$_3$CN (6 mL/4 mL). To this stirred solution was added NP$_3$ (408 mg, 0.62 mmol) in one portion at room temperature. The resultant clear, colorless solution was further stirred for 5 h. NaBPh$_4$ (213.3 mg, 0.62 mmol) was added, and a colorless solid (NaCl) immediately precipitated. The resultant mixture was stirred for 2 h. A clear, colorless solution was obtained after removing the colorless solid (NaCl) by filtration. Addition of diethyl ether to this solution yielded a white solid (0.655, 90%) which exhibits a brilliant greenish yellow luminescence in the solid state at room temperature; λ_{max} = 470 nm. The compound may be recrystallized from ClCH$_2$CH$_2$Cl or CH$_3$CN with pentane or Et$_2$O. ^{31}P{^{1}H} NMR in CDCl$_3$/CH$_3$CN: 25.88 (s), 27.57 (s) ppm (ratio 2:1).

Synthesis of Au(NP$_3$)PF$_6$ (2). To a stirred solution of [AuP(CH$_2$CH$_2$CN)$_3$]Cl (50 mg, 0.12 mmol) in CH$_3$CN (5 mL) was added TlPF$_6$ (41 mg, 0.12 mmol) in one portion to give a white solid (TlCl). After 1 h, a clear, colorless solution was obtained by filtration, which presumably contained [CH$_3$CNAuP(CH$_2$CH$_2$CN)$_3$]PF$_6$. NP$_3$ (78.4 mg, 0.12 mmol) was added to this solution, and the resultant mixture was stirred for 3 h at room temperature. A white solid, Au(NP$_3$)PF$_6$, was isolated (95.55 mg, 80%) from the colorless solution upon addition of diethyl ether. This solid exhibits a bright yellow luminescence; λ_{max} = 500 nm. Crystals of this complex were obtained from the ClCH$_2$CH$_2$Cl solution by slow diffusion of diethyl ether. ^{31}P{^{1}H} NMR: 26.12 (s), −146 (septet) ppm.

Synthesis of Au(NP$_3$)BPh$_4$ (2′). NP$_3$ (67.9 mg, 0.104 mmol) was added on one portion to a stirred solution of (THT)AuCl (50 mg, 0.16 mmol) in CH$_2$Cl$_2$/CH$_3$CN (2 mL/1 mL). The mixture was stirred for 5^1/$_2$ h at room temperature to give a clear, colorless solution. NaBPh$_4$ (53.3 mg, 0.104 mmol) was added in one portion to the solution, whereupon a precipitate formed (NaCl). The resultant mixture was further stirred for 1 h. A clear, colorless solution was obtained after filtration, which gave a white solid upon addition of pentane (yield 91.15 mg, 75% based on the NP$_3$). This solid luminesces bright yellow at room temperature under a hand-held UV lamp. ^{31}P{^{1}H} NMR: 26.12 (s) ppm.

Synthesis of Au(NP$_3$)NO$_3$ (3). ClAuP(CH$_2$CH$_2$CN)$_3$ (100 mg, 0.24 mmol) was dissolved in CH$_3$CN (3 mL). To this stirred solution was added AgNO$_3$ (40.77 mg, 0.24 mmol) in one portion. An immediate reaction with the appearance of a white solid (AgCl) was observed. After 1 h of reaction, the AgCl was removed by filtration. NP$_3$ (156 mg, 0.24 mmol) was added to the above filtrate to give a clear, colorless solution. The resultant mixture was stirred for 12 h at room temperature. Upon addition of diethyl ether, a bulky white solid, **3**, was precipitated in 80% yield. This was purified by recrystallization from a ClCH$_2$CH$_2$Cl/pentane system. The colorless crystals of **3** exhibit a blue luminescence under a hand-held UV lamp. The compound Au(NP$_3$)NO$_3$ was also prepared in good yield from Ph$_3$PAuNO$_3$ by using an analogous procedure. ^{31}P{^{1}H} NMR: 26.12 (s) ppm.

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Table I. Crystallographic Data for **1–3**

	1	**2**	**3**
formula	$C_{132}H_{124}B_2N_2P_6Au_2 \cdot C_8H_{16}Cl_8$	$C_{42}H_{42}NF_6P_4Au$	$C_{42}H_{42}N_2O_3P_3Au$
mol wt	2735.68	995.652	912.693
space group	$P\bar{1}$ (No. 2)	*Cc* (No. 9)	*Cc* (No. 9)
a, Å	14.648(7)	17.589(6)	17.270(3)
b, Å	15.759(11)	12.909(4)	12.710(2)
c, Å	16.316(18)	18.414(5)	17.720(2)
α, deg	84.74(8)	90.00	90.00
β, deg	70.81(6)	90.95(2)	91.31(1)
γ, deg	67.22(5)	90.00	90.00
V, Å^3	3276(4)	4180(2)	3889(1)
Z	1	4	4
d_{cal}, g/cm^3	1.38	1.55	1.44
μ(Mo Kα), cm^{-1}	25.16	37.2	39.75
temp, K	298	298	298
radiation (λ, Å)		graphite-monochromated Mo Kα (0.71073)	
transm factors: max, min	0.575, 0.432	0.874, 0.827	0.781, 0.682
R,[a] R_w[b]	0.0435, 0.0430	0.0256, 0.0268	0.0218, 0.0218

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum\sqrt{w}(|F_o| - |F_c|)]/\sum\sqrt{w}|F_o|$.

Table II. Crystallographic Data for **4** and **5**

	4	**5**
formula	$C_{42}H_{42}N_2O_3P_3Ag$	$C_{42}H_{42}NF_6P_4Ag$
mol wt	823.595	906.554
space group	*Cc* (No. 9)	$R\bar{3}$ (No. 146)
a, Å	16.85(2)	17.741(3)
b, Å	12.950(5)	17.741(3)
c, Å	17.629(6)	11.489(3)
α, deg	90.00	90.00
β, deg	92.67(5)	90.00
γ, deg	90.00	120.00
V, Å^3	3842(3)	3131(1)
Z	4	3
d_{cal}, g/cm^3	1.72	1.74
μ(Mo Kα), cm^{-1}	6.70	6.74
temp, K	298	298
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)	
transm factors: max, min	no cor	0.936, 0.808
R,[a] R_w[b]	0.0363, 0.0383	0.0333, 0.0350

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $[\sum\sqrt{w}(|F_o| - |F_c|)]/\sum\sqrt{w}|F_o|$.

Synthesis of Ag(NP$_3$)NO$_3$ (4). To a stirred solution of AgNO$_3$ (20 mg, 0.12 mmol) in CH$_3$CN/CH$_2$Cl$_2$ (2 mL/1 mL) was added NP$_3$ (76.9 mg, 0.12 mmol) in one portion to give a clear solution. The resultant mixture was stirred for 2 h at room temperature. Et$_2$O (3 mL) was added to give a white solid (92.01 mg, 95%), [Ag(NP$_3$)NO$_3$] (**4**). The compound was purified by recrystallization from a CH$_3$CN/Et$_2$O system. $^{31}P\{^1H\}$ NMR: −6.59 (dd) ppm ($^1J(^{107}Ag, ^{31}P)$ = 320.24 Hz, $^1J(^{109}Ag, ^{31}P)$ = 369.66 Hz).

Synthesis of Ag(NP$_3$)PF$_6$ (5). AgPF$_6$ (20 mg, 0.078 mmol) was dissolved in CH$_3$CN (3 mL). To this stirred solution was added NP$_3$ (51.66 mg, 0.078 mmol) in one portion. The resultant clear solution was stirred overnight at room temperature. Upon addition of Et$_2$O, a white solid was isolated. The white solid (64.49 mg, 90%), Ag(NP$_3$)PF$_6$, was isolated by filtration. The compound was then purified by recrystallization from CH$_3$CN/Et$_2$O and ClCH$_2$CH$_2$Cl/pentane systems. $^{31}P\{^1H\}$ NMR in CDCl$_3$ at −45 °C: −7.20 (dd) ($^1J(^{107}Ag, ^{31}P)$ = 319.3 Hz, $^1J(^{109}Ag, ^{31}P)$ = 368.38 Hz), −146 (septet) ppm.

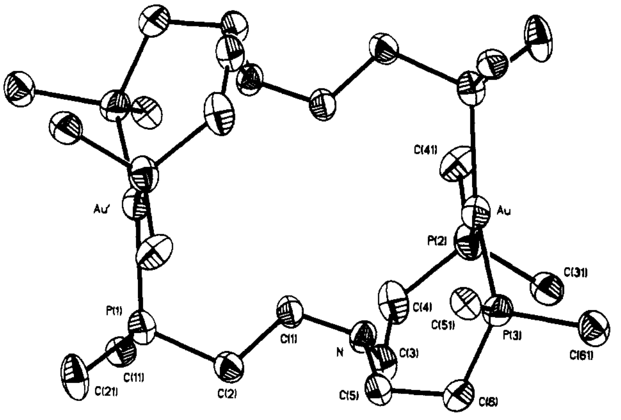

Figure 1. Structure of the dimer cation in [Au$_2$(NP$_3$)$_2$](BPh$_4$)$_2$ (**1**) (40% thermal ellipsoids viewed perpendicular to the Au–Au′ vector). Aromatic carbons have been omitted for clarity.

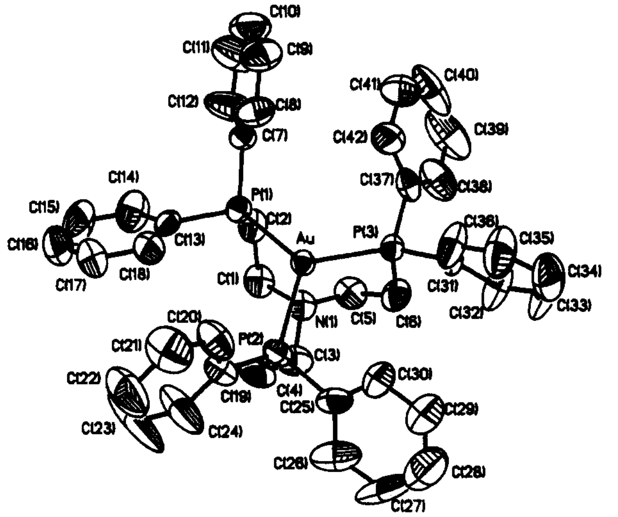

Figure 2. Structure of the cation in Au(NP$_3$)PF$_6$ (**2**). The thermal ellipsoids have been drawn at the 50% probability level.

X-ray Data Collection and Refinement of the Structures. The structure determination procedures (Nicolet R3m/E diffractometer, SHELXTL 5.1 software) are described in detail elsewhere.[32] Complexes **1**, **3**, **5** and **2**, and **4** were recrystallized from CH$_2$Cl$_2$, ClCH$_2$Cl/pentane, ClCH$_2$CH$_2$Cl/pentane, and CH$_3$CN/Et$_2$O mixed solvents, respectively. A single colorless crystal of [Au$_2$(NP$_3$)$_2$](BPh$_4$)$_2$·4ClCH$_2$CH$_2$Cl (**1**) of unknown dimensions, a rectangular colorless crystal of Au(NP$_3$)PF$_6$ (**2**) of dimensions 0.4 × 0.2 × 0.2 mm, a crystal of Au(NP$_3$)NO$_3$ (**3**) of dimensions 0.8 × 0.2 × 0.1 mm, a crystal of Ag(NP$_3$)NO$_3$ (**4**) of dimensions 0.15 × 0.2 × 0.35 mm, and one of Ag(NP$_3$)PF$_6$ (**5**) of dimensions 0.4 × 0.3 × 0.1 mm were mounted on glass fibers with epoxy resin, and data were collected. No decay was observed for the chosen standard reflections. Crystallographic data are contained in Table I for compounds **1–3** and in Table II for compounds **4** and **5**. The data have been corrected for decay and for Lorentz and polarization effects. An empirical absorption correction (DIFABS) was also applied. Heavy-atom positions were determined from a sharpened Patterson map and used as the initial phasing model for difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to the carbon atoms in idealized positions at a distance of 0.96 Å. Phenyl rings of structures **1** and **4** were refined as idealized hexagons (C–C = 1.395 Å).

Molecular modeling was performed using the CAChe Scientific, Inc. (a Tektronix Co.), modeling package.

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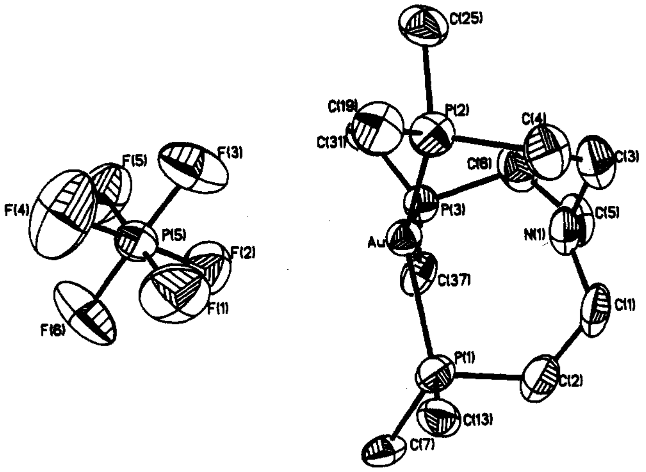

Figure 3. Structure of $Au(NP_3)PF_6$ (**2**) (50% probability), showing the nonplanar geometry about the gold and nitrogen atoms. Aromatic carbons have been removed for clarity.

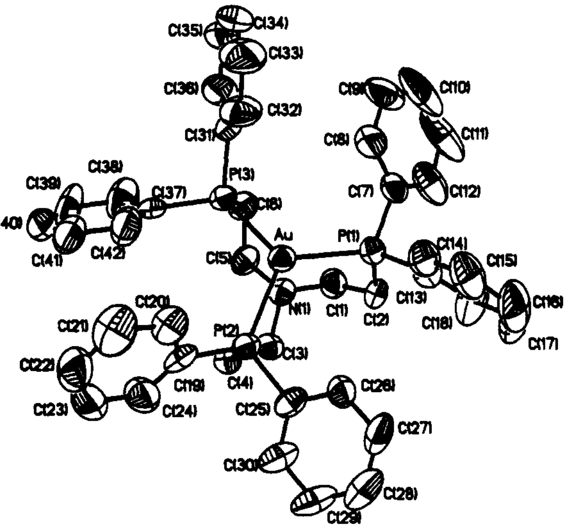

Figure 4. Structure of the cation in $Au(NP_3)NO_3$ (**3**). The thermal ellipsoids have been drawn at the 50% probability level.

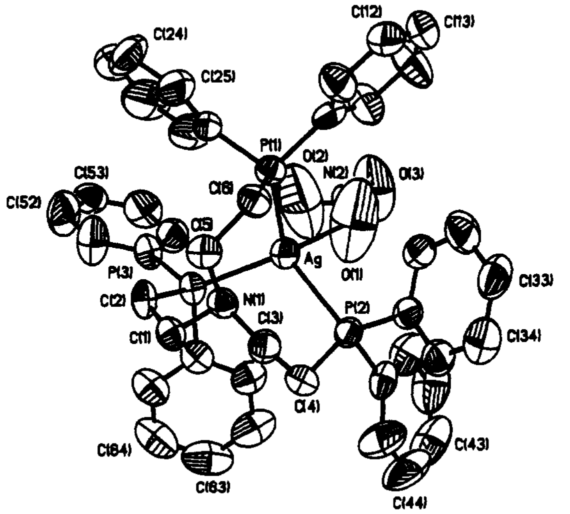

Figure 5. Structure of the complex $Ag(NP_3)NO_3$ (**4**). The thermal ellipsoids have been drawn at the 50% probability level. Aromatic carbons have been omitted for clarity.

Results

The chloride, nitrate, and hexafluorophosphate analogs of $[Au_2(NP_3)_2](BPh_4)_2$ have been prepared. The chloride salt is not very soluble in organic solvents. The nitrate and PF_6^- salts are

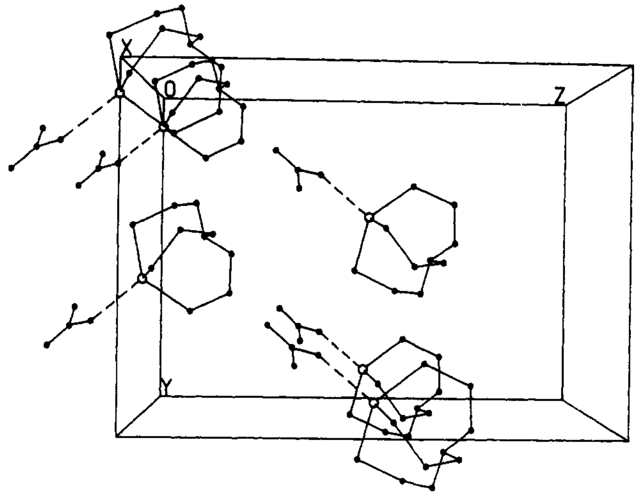

Figure 6. Packing diagram of the unit cell of $Ag(NP_3)NO_3$ (**4**) showing the packing of NO_3.

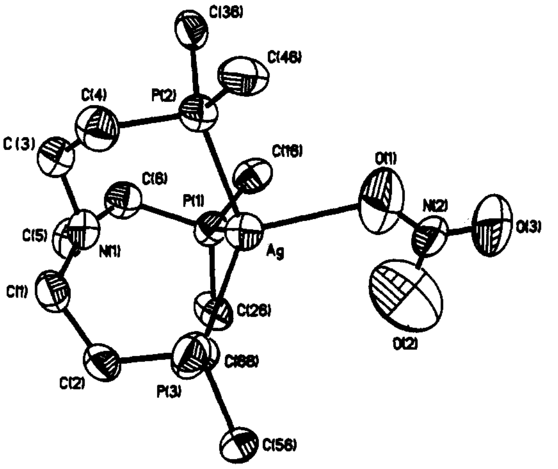

Figure 7. Structure of $Ag(NP_3)NO_3$ (**4**) (50% probability), showing the nonplanar geometry about the silver and nitrogen atoms. Aromatic carbons have been omitted for clarity.

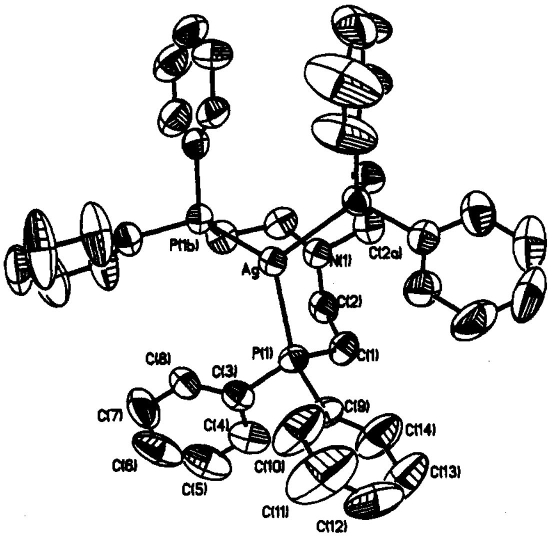

Figure 8. Structure of the cation in $Ag(NP_3)PF_6$ (**5**). The thermal ellipsoids have been drawn at the 50% probability level.

microcrystalline solids, somewhat more soluble in organic solvents. All of these compounds exhibit a brilliant greenish yellow luminescence under a hand-held UV lamp. Reactions between $(THT)AuCl$ and NP_3 in a 1:1 ratio gives the dimer $Au_2(NP_3)_2Cl_2$ in 95% yield. To form monomeric $Au(NP_3)X$ complexes ($X = PF_6^-$, BPh_4^-, NO_3^-, Cl^-) from $(THT)AuCl$, an excess of

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2 \times 10$)[a] for $[(N(CH_2CH_2PPh_2)_3)_2Au_2][BPh_4]_2$ (**1**)

atom	*x*	*y*	*z*	U_{iso}[b]	atom	*x*	*y*	*z*	U_{iso}[b]
Au	−695(1)	1048(1)	−1592(1)	46(1)	C(51)	313(7)	−1147(5)	−2713(5)	52(6)
P(1)	−742(2)	−1501(2)	1899(2)	45(1)	C(62)	−2257(6)	368(5)	−3258(5)	61(7)
P(2)	−2245(2)	2003(2)	−508(2)	50(1)	C(63)	−2602(6)	792(5)	−3949(5)	79(8)
P(3)	−845(2)	−121(2)	−2288(2)	47(1)	C(64)	−1998(6)	1177(5)	−4594(5)	105(10)
N	−1599(6)	−218(5)	−213(4)	41(4)	C(65)	−1049(6)	1139(5)	−4548(5)	135(12)
C(1)	−1033(8)	−583(6)	396(6)	43(5)	C(66)	−703(6)	716(5)	−3857(5)	101(9)
C(2)	−1262(8)	−1341(6)	998(6)	47(5)	C(61)	−1308(6)	330(5)	−3213(5)	52(6)
C(3)	−2684(8)	437(7)	197(6)	56(6)	B	−3158(9)	−2482(8)	−2205(7)	49(6)
C(4)	−2735(8)	1366(7)	439(6)	59(6)	C(72)	−1380(6)	−3127(5)	−1779(4)	60(6)
C(5)	−1557(8)	−947(7)	−748(6)	48(5)	C(73)	−837(6)	−3406(5)	−1179(4)	76(8)
C(6)	−1786(8)	−594(7)	−1592(6)	56(6)	C(74)	−1383(6)	−3364(5)	−294(4)	87(10)
C(12)	−2729(6)	−159(5)	2763(4)	57(6)	C(75)	−2472(6)	−3043(5)	−9(4)	81(8)
C(13)	−3526(6)	316(5)	3504(4)	78(7)	C(76)	−3015(6)	−2764(5)	−610(4)	63(6)
C(14)	−3456(6)	41(5)	4326(4)	76(7)	C(71)	−2468(6)	−2806(5)	−1495(4)	51(6)
C(15)	−2589(6)	−708(5)	4407(4)	93(8)	C(78)	−4869(6)	−2712(4)	−2212(5)	61(6)
C(16)	−1792(6)	−1183(5)	3666(4)	71(7)	C(79)	−5466(6)	−3243(4)	−2119(5)	71(7)
C(11)	−1862(6)	−908(5)	2844(4)	47(6)	C(80)	−5128(6)	−4139(4)	−1834(5)	81(8)
C(22)	−934(7)	−3222(7)	2047(6)	104(10)	C(81)	−4194(6)	−4504(4)	−1641(5)	72(7)
C(23)	−670(7)	−4136(7)	2288(6)	159(16)	C(82)	−3596(6)	−3973(4)	−1733(5)	57(6)
C(24)	147(7)	−4544(7)	2634(6)	161(15)	C(77)	−3934(6)	−3077(4)	−2018(5)	50(5)
C(25)	700(7)	−4036(7)	2740(6)	135(11)	C(84)	−4180(6)	−878(6)	−2796(4)	64(7)
C(26)	436(7)	−3121(7)	2500(6)	82(7)	C(85)	−4779(6)	65(6)	−2723(4)	85(9)
C(21)	−380(7)	−2714(7)	2154(6)	61(6)	C(86)	−5051(6)	563(6)	−1957(4)	87(8)
C(32)	−3273(6)	2326(5)	−1733(5)	80(8)	C(87)	−4724(6)	119(6)	−1265(4)	83(8)
C(33)	−4125(6)	2733(5)	−2039(5)	97(9)	C(88)	−4125(6)	−824(6)	−1339(4)	66(7)
C(34)	−5057(6)	3376(5)	−1513(5)	88(9)	C(83)	−3853(6)	−1323(6)	−2104(4)	49(5)
C(35)	−5138(6)	3613(5)	−682(5)	74(7)	C(90)	−1797(7)	−2186(5)	−3647(6)	71(7)
C(36)	−4286(6)	3207(5)	−377(5)	66(6)	C(91)	−1037(7)	−2451(5)	−4460(6)	96(9)
C(31)	−3354(6)	2563(5)	−902(5)	51(6)	C(92)	−792(7)	−3295(5)	−4855(6)	97(8)
C(42)	−2216(6)	3768(6)	−473(4)	60(6)	C(93)	−1307(7)	−3873(5)	−4437(6)	99(9)
C(43)	−2042(6)	4459(6)	−146(4)	73(7)	C(94)	−2068(7)	−3608(5)	−3624(6)	74(7)
C(44)	−1773(6)	4330(6)	614(4)	91(9)	C(89)	−2313(7)	−2765(5)	−3228(6)	57(6)
C(45)	−1678(6)	3510(6)	1047(4)	99(10)	C1(1)	5055(6)	2661(5)	4666(5)	237(5)
C(46)	−1852(6)	2819(6)	720(4)	81(8)	C(95)	3809(17)	2545(19)	5062(19)	228(20)
C(41)	−2121(6)	2948(6)	−40(4)	52(6)	C(96)	3114(17)	3024(23)	5877(15)	251(21)
C(52)	1267(7)	−1168(5)	−2695(5)	63(6)	Cl(2)	3727(8)	2514(7)	6665(7)	320(9)
C(53)	2180(7)	−1937(5)	−3036(5)	87(9)	Cl(3)	5519(9)	5214(6)	3600(6)	277(8)
C(54)	2138(7)	−2687(5)	−3394(5)	86(8)	C(97)	4166(14)	5910(21)	4096(28)	367(34)
C(55)	1184(7)	−2667(5)	−3411(5)	89(8)	C(98)	3690(12)	5281(23)	4036(31)	347(41)
C(56)	272(7)	−1897(5)	−3071(5)	77(8)	Cl(4)	2319(9)	5903(8)	4442(7)	358(10)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the U_{ij} tensor.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[(N(CH_2CH_2PPh_2)_3)_2)Au_2][BPh_4]_2$ (**1**)

Au–N	3.172(6)	N–C(5)	1.476(15)
Au–P(2)	2.399(2)	Au–P(3)	2.364(4)
Au–P(2)	2.364(3)	N–C(3)	1.482(10)
N–C(1)	1.440(14)		
P(2)–Au–P(3)	116.5(1)	P(2)–Au–P(1′)	114.4(1)
P(3)–Au–P(1′)	128.9(1)		

(THT)AuCl (1.5 equiv of Au per NP_3) was required, whereas 1 equiv of Ph_3PAuX or $P(CH_2CH_2CN)_3AuX$ ($X = PF_6^-$, NO_3^-, BPh_4^-) yielded the monomer under the same reaction conditions. Both sets of compounds, dimeric $[Au_2(NP_3)_2]X_2$ ($X = Cl^-$, BPh_4^-, PF_6^-) and monomeric $Au(NP_3)X$ ($X = PF_6^-$, BPh_4^-, NO_3^-), are stable in air and water. The nature of products obtained in these reactions is independent of the organic solvent used in the synthesis or recrystallization. Reactions between AgX ($X = NO_3^-$, PF_6^-) and NP_3 produced only mononuclear products. These compounds are stable in air at room temperature.

The structures of the Au(I) dimer cation, **1**, the monomer cations, **2** and **3**, and the monomers of Ag(I), **4** and **5**, are as shown in Figures 1, 2, 4, 5, and 8. Atomic coordinates for **1**–**5** are given in Tables III, V, VII, IX, and XI, and selected bond lengths and angles are given in Tables IV, VI, VIII, X, and XII, respectively. The distance between the two Au(I) centers in compound **1** is 6.376(7) Å, and the shortest Au(I)···N distance is 3.172(6) Å. In complex **1**, two of the phosphorus atoms of each ligand chelate to one gold atom while the third phosphorus atom bridges to the other Au(I) center with no evidence of Au···N bonding. Thus, each Au(I) center is three-coordinate. The bridging arms of NP_3 ligands produce a 16-membered ring around the two Au(I) centers (Figure 1). Each Au(I) center in the dimeric complex has roughly a trigonal planar geometry. The complete molecule of compound **1** has an inversion center.

Compounds **2** and **3** consist of one Au(I) center and one NP_3 ligand with PF_6^- or NO_3^- as a counterion. The Au(I) center in each compound coordinates to three phosphorus atoms with at most a weak interaction with the nitrogen atom of the NP_3 ligand. The Au(I)···N distance in each compound is 2.683(6) Å. The geometry around the Au(I) center is roughly trigonal planar with the nitrogen atom apical to the coordination triangle.

The Ag(I) compounds **4** and **5** contain the NP_3 ligand coordinated through three phosphorus atoms to the metal. The NO_3^- is weakly coordinated to Ag(I) through an oxygen atom in **4** while PF_6^- is not interacting in **5** with the metal. The Ag(I)···O(1) distance in compound **4** is 2.55(1) Å. The distances between the Ag(I) center and N atom of NP_3 ligand are 2.924(4) Å for **4** and 2.662(3) Å for **5**, too long for any recognized bonding interactions. Furthermore, the geometry around the Ag(I) center in **4** is distorted tetrahedrally toward AgP_3O coordination, but in compound **5**, the Ag(I) center is coordinated in a trigonal planar fashion.

The $^{31}P\{^1H\}$ NMR of $[Au(NP_3)_2]_2(BPh_4)_2$ shows two separate singlets at 27.57 and 25.88 ppm with a peak height ratio of 1:2, indicating that two different sets of phosphorus atoms are present in this molecule. The $^{31}P\{^1H\}$ NMR of both Au(I) monomers **2** and **3** show a singlet at 26.12 ppm while **2** also shows a septet

Table V. Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for $[Au(Ph_2PCH_2CH_2)_3N]PF_6$ (**2**)

atom	*x*	*y*	*z*	U_{iso}[b]
Au	0	5737(1)	0	37(1)
P(1)	−593(1)	4257(1)	473(1)	43(1)
P(2)	1319(1)	5647(2)	−188(1)	49(1)
P(3)	−731(1)	6742(2)	−829(1)	42(1)
N(1)	35(4)	4516(5)	−1177(4)	51(2)
C(1)	−219(5)	3494(6)	−914(5)	60(3)
C(2)	−849(5)	3555(7)	−369(5)	59(3)
C(3)	824(6)	4494(8)	−1418(6)	71(4)
C(4)	1372(8)	4513(10)	−777(8)	73(5)
C(5)	−489(6)	4988(8)	−1709(5)	65(3)
C(6)	−460(6)	6167(8)	−1699(5)	64(3)
C(7)	−1487(6)	4372(7)	955(7)	45(3)
C(8)	−1556(5)	5190(8)	1428(5)	67(4)
C(9)	−2230(8)	5336(11)	1803(6)	89(5)
C(10)	−2807(7)	4649(12)	1729(8)	98(6)
C(11)	−2739(7)	3839(12)	1270(11)	128(8)
C(12)	−2072(6)	3677(10)	911(10)	122(7)
C(13)	−38(5)	3323(6)	1023(4)	48(3)
C(14)	−208(8)	2316(8)	1087(7)	89(5)
C(15)	241(10)	1655(9)	1534(8)	107(6)
C(16)	863(8)	2017(10)	1909(7)	93(5)
C(17)	1031(7)	3039(10)	1858(7)	92(5)
C(18)	594(5)	3694(9)	1399(6)	71(4)
C(19)	1989(5)	5430(8)	552(5)	59(3)
C(20)	1866(6)	5965(8)	1201(6)	74(4)
C(21)	2332(9)	5841(10)	1797(9)	102(6)
C(22)	2936(8)	5135(15)	1751(9)	124(7)
C(23)	3065(11)	4659(20)	1133(12)	195(12)
C(24)	2594(9)	4788(15)	537(8)	130(7)
C(25)	1744(4)	6731(8)	−697(5)	59(3)
C(26)	2354(7)	6616(12)	−1166(7)	98(5)
C(27)	2620(8)	7539(18)	−1533(7)	118(8)
C(28)	2310(10)	8469(16)	−1394(9)	115(7)
C(29)	1732(8)	8580(11)	−940(8)	107(6)
C(30)	1434(6)	7688(8)	−610(7)	83(4)
C(31)	−594(5)	8140(6)	−931(4)	47(3)
C(32)	−573(8)	8628(10)	−1593(6)	95(5)
C(33)	−496(10)	9685(12)	−1616(9)	121(7)
C(34)	−395(8)	10263(9)	−1012(8)	94(5)
C(35)	−376(9)	9764(9)	−358(7)	104(6)
C(36)	−466(8)	8716(8)	−320(5)	79(4)
C(37)	−1769(5)	6657(6)	−809(5)	51(3)
C(38)	−2235(7)	6647(10)	−1393(7)	95(5)
C(39)	−3005(9)	6579(13)	−1356(12)	132(8)
C(40)	−3335(8)	6582(10)	−697(13)	129(9)
C(41)	−2889(6)	6589(11)	−82(9)	114(6)
C(42)	−2110(6)	6614(10)	−131(7)	87(5)
P(5)	−63(1)	7888(2)	1902(1)	50(1)
F(1)	104(5)	6695(5)	2048(4)	110(3)
F(2)	−702(4)	7581(5)	1321(4)	90(2)
F(3)	525(4)	7862(6)	1253(4)	108(3)
F(4)	551(5)	8167(7)	2483(5)	152(4)
F(5)	−240(5)	9061(5)	1740(5)	104(3)
F(6)	−666(5)	7897(7)	2512(4)	130(4)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the U_{ij} tensor.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for $Au(NP_3)PF_6$ (**2**)

Au–N	2.683(6)	N(1)–C(1)	1.476(11)
Au–P(1)	2.350(2)	N(1)–C(5)	1.465(12)
Au–P(3)	2.365(2)	N(1)–C(3)	1.463(14)
Au–P(2)	2.352(2)		
P(1)–Au–P(2)	117.3(1)	P(2)–Au–P(3)	116.4(1)
P(1)–Au–P(3)	117.2(1)		

Table VII. Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for $[Au(Ph_2PCH_2CH_2)_3N]NO_3$ (**3**)

atom	*x*	*y*	*z*	U_{iso}[b]
Au	0	5660(1)	0	47(1)
P(1)	1347(1)	5557(2)	−188(1)	49(1)
P(2)	−638(1)	4151(1)	453(1)	47(1)
P(3)	−732(1)	6705(2)	−863(1)	49(1)
N(1)	43(3)	4452(4)	−1241(3)	46(2)
C(1)	858(4)	4421(6)	−1468(4)	60(3)
C(2)	1431(4)	4396(6)	−793(4)	59(3)
C(3)	−237(4)	3405(6)	−1001(4)	51(3)
C(4)	−900(4)	3477(6)	−429(4)	54(3)
C(5)	−459(4)	4988(6)	−1812(4)	57(3)
C(6)	−415(4)	6183(6)	−1764(4)	64(3)
C(7)	1800(4)	6607(6)	−734(4)	59(3)
C(8)	1490(5)	7612(7)	−686(6)	93(4)
C(9)	1789(6)	8447(9)	−1081(7)	140(6)
C(10)	2407(7)	8302(11)	−1516(6)	171(7)
C(11)	2711(6)	7327(10)	−1597(5)	137(6)
C(12)	2420(5)	6467(8)	−1186(4)	92(4)
C(13)	2013(4)	5331(6)	608(4)	61(3)
C(14)	1873(5)	5879(6)	1259(4)	70(3)
C(15)	2345(5)	5732(7)	1897(5)	90(4)
C(16)	2965(5)	5049(11)	1877(6)	107(5)
C(17)	3107(7)	4524(10)	1249(8)	128(6)
C(18)	2637(5)	4656(9)	591(5)	102(4)
C(19)	−1571(4)	4275(5)	914(4)	56(3)
C(20)	−1672(5)	5150(7)	1364(4)	73(3)
C(21)	−2388(7)	5320(10)	1702(6)	107(5)
C(22)	−2982(6)	4606(11)	1588(7)	104(5)
C(23)	−2877(5)	3734(8)	1161(6)	102(5)
C(24)	−2163(5)	3586(7)	835(5)	82(4)
C(25)	−103(4)	3198(5)	1013(4)	54(3)
C(26)	589(4)	3502(7)	1390(4)	60(3)
C(27)	1012(4)	2835(7)	1854(4)	79(3)
C(28)	741(5)	1823(7)	1954(4)	89(4)
C(29)	76(6)	1486(7)	1597(5)	89(4)
C(30)	−348(5)	2166(6)	1127(4)	75(3)
C(31)	−561(4)	8130(6)	−871(4)	60(3)
C(32)	−398(5)	8605(6)	−194(5)	86(4)
C(33)	−298(6)	9664(7)	−155(8)	114(6)
C(34)	−338(5)	10266(7)	−787(7)	113(5)
C(35)	−502(5)	9823(8)	−1458(7)	113(5)
C(36)	−620(5)	8730(7)	−1503(5)	87(4)
C(37)	−1787(4)	6621(5)	−906(4)	54(3)
C(38)	−2224(5)	6647(8)	−1556(6)	103(4)
C(39)	−3039(5)	6591(8)	−1538(7)	136(6)
C(40)	−3402(5)	6527(7)	868(8)	147(7)
C(41)	−2972(6)	6497(9)	−231(8)	152(6)
C(42)	−2169(5)	6536(8)	−253(6)	104(4)
N(2)	4925(4)	2861(6)	1999(4)	85(3)
O(1)	4344(16)	2441(26)	1984(20)	174(16)
O(2)	5443(10)	2308(16)	2087(10)	181(10)
O(3)	5004(9)	3745(11)	1757(10)	149(8)
O(4)	5124(15)	2222(24)	1587(11)	256(16)
O(5)	5277(12)	3446(22)	2296(15)	265(16)
O(6)	4304(18)	2861(27)	2284(15)	162(14)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the U_{ij} tensor.

Table VIII. Selected Interatomic Distances (Å) and Angles (deg) for $Au(NP_3)NO_3$ (**3**)

Au- - -N	2.685(6)	Au- - -O(2)	4.304(5)
Au–P(1)	2.361(2)	Au–P(2)	2.362(2)
Au–P(3)	2.369(2)	N(1)–C(1)	1.474(9)
N(1)–C(5)	1.482(9)	N(1)–C(3)	1.481(9)
P(1)–Au–P(2)	118.1(1)	P(1)–Au–P(3)	117.0(1)
P(2)–Au–P(3)	115.4(1)		

at −146 ppm for PF_6^-. This indicates that the phosphorus atoms in these compounds are in identical environments in solution.

The $^{31}P\{^1H\}$ NMR for the Ag(I) nitrate complex **4** shows two sets of doublets centered at −6.59 ppm, indicating that all phosphorus atoms around the Ag(I) center are equivalent and are each coupled to ^{107}Ag and ^{109}Ag isotopes. The two sets of doublets have coupling constants 320.24 and 369.66 Hz, respectively. Similarly, the $^{31}P\{^1H\}$ NMR for hexafluorophosphate complex **5** shows two sets of doublets centered at −7.20 ppm. The equivalent phosphorus atoms are coupled to the $^{107}Ag(I)$ and $^{109}Ag(I)$ isotopes with coupling constants of 319.3 and 368.38 Hz, respectively. The $^{31}P\{^1H\}$ NMR chemical shift of **4** is 0.61 ppm downfield from that of **5**. This difference in chemical shift

Table IX. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)[a] for $N(CH_2CH_2PPh_2)_3AgONO_2$ (**4**)

atom	x	y	z	U_{iso}[b]
Ag	0	957(1)	0	50(1)
O(1)	216(3)	2217(15)	−1086(9)	261(10)
O(2)	−690(11)	1851(14)	−1566(11)	249(10)
O(3)	−82(8)	2968(9)	−2082(6)	168(5)
N(2)	−136(5)	2382(6)	−1598(5)	72(3)
P(1)	−632(1)	1943(2)	1014(1)	46(1)
C(11)	−452(4)	3787(5)	1885(3)	71(4)
C(12)	−319(4)	4847(5)	1957(3)	82(5)
C(13)	−192(4)	5442(5)	1314(3)	93(5)
C(14)	−198(4)	4977(5)	600(3)	114(6)
C(15)	−331(4)	3918(5)	528(3)	80(4)
C(16)	−458(4)	3323(5)	1171(3)	52(3)
C(21)	−2062(5)	1568(6)	262(4)	93(5)
C(22)	−2887(5)	1482(6)	179(4)	135(8)
C(23)	−3354(5)	1651(6)	800(4)	132(9)
C(24)	−2996(5)	1907(6)	1504(4)	122(7)
C(25)	−2171(5)	1993(6)	1588(4)	86(5)
C(26)	−1704(5)	1824(6)	966(4)	61(3)
P(2)	1450(1)	620(2)	334(1)	47(1)
C(31)	1615(3)	2503(4)	1089(4)	60(3)
C(32)	1963(3)	3195(4)	1612(4)	85(5)
C(33)	2688(3)	2956(4)	1985(4)	77(4)
C(34)	3065(3)	2023(4)	1835(4)	77(4)
C(35)	2717(3)	1331(4)	1312(4)	63(3)
C(36)	1993(3)	1571(4)	939(4)	49(3)
C(41)	2077(5)	937(5)	−1054(4)	90(5)
C(42)	2551(5)	730(5)	−1664(4)	126(7)
C(43)	3076(5)	−103(5)	−1629(4)	124(8)
C(44)	3126(5)	−730(5)	−985(4)	128(7)
C(45)	2652(5)	−523(5)	−375(4)	99(5)
C(46)	2127(5)	311(5)	−410(4)	61(4)
P(3)	−770(1)	−658(2)	−295(1)	49(1)
C(51)	−2394(4)	−1219(6)	−462(3)	97(5)
C(52)	−3131(4)	−1239(6)	−856(3)	101(6)
C(53)	−3223(4)	−774(6)	−1569(3)	81(5)
C(54)	−2578(4)	−288(6)	−1886(3)	92(5)
C(55)	−1841(4)	−268(6)	−1491(3)	72(4)
C(56)	−1749(4)	−733(6)	−779(3)	52(3)
C(61)	518(4)	−1353(5)	−1080(4)	63(3)
C(62)	983(4)	−2086(5)	−1433(4)	94(5)
C(63)	734(4)	−3112(5)	−1479(4)	102(6)
C(64)	20(4)	−3406(5)	−1173(4)	103(6)
C(65)	−446(4)	−2674(5)	−821(4)	74(4)
C(66)	−197(4)	−1647(5)	−775(4)	57(3)
N(1)	110(4)	−318(5)	1370(3)	45(2)
C(1)	−209(5)	−1323(6)	1172(5)	51(3)
C(2)	−945(5)	−1268(7)	623(5)	54(3)
C(3)	952(5)	−385(7)	1613(5)	54(3)
C(4)	1490(5)	−493(7)	949(5)	59(3)
C(5)	−360(5)	197(7)	1946(4)	51(3)
C(6)	−296(5)	1381(7)	1917(5)	51(3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic U defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table X. Selected Interatomic Distances (Å) and Angles (deg) for $N(CH_2CH_2PPh_2)_3AgONO_2$ (**4**)

Ag- - -N	2.924(4)	Ag- - -O(1)	2.55(1)
Ag–P(1)	2.477(3)	Ag–P(2)	2.524(3)
Ag–P(3)	2.502(3)	N(1)–C(1)	1.445(10)
N(1)–C(3)	1.466(11)	N(1)–C(5)	1.476(10)
Ag- - -P_3 plane	0.745		
P(1)–Ag–P(2)	111.4(1)	P(1)–Ag–P(3)	110.2(1)
P(2)–Ag–P(3)	113.0(1)		

may be caused by weak solution coordination of the NO_3^- anion in **4** as observed in the crystal structure.

The emission spectrum of **1** in the solid state shows a maximum intensity at 500 nm with excitation at 320 nm. When complex **2** is excited at 330 nm, the solid emission spectrum reveals a peak at 470 nm.

Table XI. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)[a] for $N(CH_2CH_2PPh_2)_3AgPF_6$ (**5**)

atom	x	y	z	U_{iso}[b]
Ag	0	0	5992	44(1)
P(1)	1374(2)	1335(1)	5525(2)	47(1)
N(1)	0	0	3654(10)	48(4)
C(1)	1184(6)	1543(6)	4018(7)	59(5)
C(2)	852(6)	710(6)	3260(8)	60(5)
C(3)	2356(6)	1240(6)	5461(8)	56(4)
C(4)	3084(7)	1809(8)	4789(11)	86(6)
C(5)	3815(8)	1703(11)	4784(14)	108(9)
C(6)	3830(7)	1081(11)	5403(13)	115(8)
C(7)	3115(9)	503(9)	6080(15)	108(8)
C(8)	2398(7)	617(8)	6106(12)	73(6)
C(9)	1744(7)	2366(7)	6277(10)	57(5)
C(10)	1897(12)	2430(8)	7404(11)	129(10)
C(11)	2177(15)	3188(12)	8018(13)	182(16)
C(12)	2298(9)	3902(9)	7499(15)	111(8)
C(13)	2086(14)	3865(9)	6368(18)	138(12)
C(14)	1828(10)	3110(8)	5749(14)	118(9)
P(2)	0	0	−593(3)	61(1)
F(1)	523(7)	805(5)	196(8)	158(6)
F(2)	−545(6)	−807(5)	−1408(7)	123(5)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic U defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table XII. Selected Interatomic Distances (Å) and Angles (deg) for $N(CH_2CH_2PPh_2)_3AgPF_6$ (**5**)

Ag- - -N	2.662(3)	Ag–P(1)	2.464(2)
N(1)–C(2)	1.474(8)	Ag- - -P_3 plane	0.534
P(1)–Ag–P(1b)	115.4(1)	P(1)–Ag–P(1a)	115.4(1)
C(2)–N(1)–C(2a)	111.0(5)	P(1a)–Ag–P(1b)	115.4(1)

MM2 calculations performed using the CAChe molecular modeling system indicate that the NP_3 ligand geometry causes the metal to be displaced from the P_3 plane in a direction away from the nitrogen center. The geometry of the minimized structure shows the distance from the P_3 plane decreases as one changes from Au(I), Ag(I) to Cu(I). This is opposite to what is observed in the structures of Au(I), Ag(I) and NP_3 nitrate complexes. These calculations also show that the conformation in which the electron pair of the nitrogen in the NP_3 ligand is directed toward the P_3 plane is energetically a more favorable conformation for the P_3 coordinated ligand.

Discussion

As Balch and Fung[9] recently demonstrated, Au(I) complexes of the ligand PP_3 (PP_3 = tris(2-diphenylphosphino)ethyl)-phosphine) are four-coordinated at the metal center and exist as dimers. With the nitrogen analog studied here, NP_3, three-coordinate dimers of type **1** form (Figure 1) but, in addition, three-coordinate monomer cations can be isolated. These encapsulated species such as **2** (Figure 2) have all ligand P atoms coordinated to the same metal center. The nitrogen atom on the ligand does not appear to participate in the coordination. It is located on an axis perpendicular to the AuP_3 plane at a distance of about 2.7 Å from the metal. The three P atoms are coordinated to Au(I) at approximately the same distance (2.36 Å), forming an approximate equilateral triangle in which the Au(I) atom is at the center. There is no tetrahedral distortion about Au(I) toward the ligand nitrogen as would be expected for a four-coordinate Au(I) complex. As seen in Figure 3, the Au(I) atom actually is positioned on the opposite side of the P_3 plane from the N atom. This observation, along with the fact that the lone pair of electrons in the valence shell of N is directed toward the Au(I) atom (as determined by the orientation of the pyramidal geometry about N and calculated by MM2 modeling), suggests that while some interaction between the N and the Au(I) atom may be present, it is not bonding.

In the case of the Ag(I) complexes, only one type of coordination has been observed for NP_3. All three phosphorus atoms of the NP_3 ligand are involved in coordination to the Ag(I) center. In the nitrate complex **4**, there is a weak Ag(I)···O(1) interaction at the distance of 2.55(1) Å (Figure 5). The Ag(I) atom is found to be out of the P_3 plane on the side of the nitrate group. In the analogous Au(I) nitrate complex **3**, no nitrate interaction is observed. The Ag(I) hexafluorophosphate complex (Figure 8) shows only the trigonal phosphorus coordination. In both the nitrate and hexafluorophosphate salts, the ligand N atom is noninteractive at 2.924 Å in **4** and 2.662 Å in **5** from the Ag(I) atom.

Complex **1** apparently exists as a dimer in solution at both room and low temperatures and in the solid state. The solid luminesces at room temperature with $\lambda_{max} = 470$ nm. No change is observed in the $^{31}P\{^1H\}$ NMR spectra between ambient temperatures and −45 °C.

Compounds **2** and **3** exhibit a brilliant luminescence in the solid state at room temperature. The luminescence of $Au(NP_3)X$ ($X = BPh_4^-$, PF_6^-, NO_3^-) depends on the nature of counterion present in the complex. The BPh_4^- and PF_6^- salts exhibit a yellow luminescence, whereas the NO_3^- salt, **3**, gives a blue luminescence. While a detailed understanding of the origin of this difference in luminescent properties of these three-coordinate Au(I) phosphine complexes with different counterions is not yet known, the effect presumably arises from changes in the coordination geometry about the Au(I). Experimental and theoretical studies of luminescent three-coordinate (triphenylphosphine)gold(I) xanthate complexes establish that the excited state is strongly influenced by the P–Au–P angle in these P_2S-coordinated Au(I) complexes.[33] A detailed study of the photophysics of these luminescent mononuclear complexes is in progress. Neither Ag(I) compound reported here has been shown to be luminescent at room temperature.

In the Au(I) dimer, **1**, two of the three Au–P distances [Au–P(3) = 2.364(4) Å and Au–P(1′) = 2.364(3) Å] are the same while the third [Au–P(2) = 2.399(2) Å] is longer by 0.035 Å. In the monomer, **2**, the Au–P(1) = 2.350(2) Å and Au–P(2) = 2.352(2) Å distances are the same, and the third, Au–P(3) = 2.365(2) Å, is longer by only 0.015 Å. These observed distances are close to those found[17] in $[Au_2(Me_2PCH_2PMe_2)_3](BF_4)_2$, a three-coordinate Au(I) dimer. In the nitrate salt, **3**, all three Au–P distances are the same [2.364(2) Å]. In both **2** and **3**, the Au(I) atom is out of the plane of the three coordinated phosphorus atoms by about 0.41 Å. The range of Au–P distances observed in these complexes, 2.399(2)–2.350(2) Å, is comparable with the Au–P distances in other complexes containing three-coordinate Au(I) monodentate[14,15] and bidentate[17] phosphine ligands. The Au–P distances in all three structures **1**–**3** are slightly longer (ca. 0.04 Å) than those in the linear Au(I) complexes[10–13] and shorter (ca. 0.05 Å) than those in the regular tetrahedral[16] complex $[Au(PPh_2Me)_4]PF_6$ and the distorted tetrahedral complexes[9,18] $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ and $[Au(diphos)_2]Cl\cdot 2H_2O$.

The P–Au–P angles in the Au(I) complexes **1**–**3** are 114.4(1)–128.9(1), 116.4(1)–117.3(1), and 115.4(1)–118.1(1)°, respectively, slightly distorted from the ideal 120° but comparable with other structures.[14,17] The nitrogen atom of the NP_3 ligand in complexes **2** and **3** is closer by 0.40 and 0.76 Å, respectively, to the Au(I) than the center of the plane of its neighboring carbon atoms. This distortion can be seen in Figure 3 for compound **2**. The positions of the Au(I) centers in **2** and **3** are 0.41 and 0.43 Å, respectively, from the P(1)P(2)P(3) plane in the direction away from the N atom.

In the silver complexes, similar observations are made. In **1**, the Ag(I)–P distances are all slightly different, 2.477(3), 2.524(3), and 2.502(3) Å, but in **5**, they are equal, 2.467(3) Å. These distances are longer than the Ag(I)–P distances in the linear complexes,[21,22,28] shorter than those observed[26] in $[Ag(PPh_3)_4]^+$, where Ag(I) coordinates to four Ph_3P ligands, but comparable with the Ag(I)–P distances in complexes[23,25] containing an Ag(I) center coordinated to three Ph_3P ligands. The geometry around the Ag(I) center is close to trigonal planar. The P–Ag(I)–P angles, 110.2(1)–118.0(1)°, are comparable with the range found for other AgP_3NO_3 complexes,[25] 110.2(1)–118.0(1)°, but smaller than in[23] $[(Ph_3P)_3AgX]$ ($X = BF_4^-$, I^-), 114.9(1)–119.3(1)°. Hence the best description of the coordination in **4** is that of a distorted tetrahedron with AgP_3O coordination while in **5**, where the P–Ag–P angles are all equal to 115.4(1)°, a pyramidally distorted trigonal planar description of the geometry is more appropriate.

The Ag(I) and all four atoms of the nitrate anion in **4** are essentially coplanar. The Ag(I)–O separation is 2.55(1) Å. This is shorter than the distances found in the analogous triphenylphosphine complex[25] [2.78(1) and 2.67(1) Å] and closer to the range observed for ionic $AgNO_3$ (2.5–2.8 Å).[34] Therefore we conclude that crystalline $Ag(NP_3)NO_3$ consists of $[Ag(NP_3)]^+$ cations with holes between them which are occupied with NO_3^- anions arranged in such a way that there is a weak interaction between Ag(I) centers and an oxygen of the nitrate. This is illustrated in the packing diagram, Figure 6.

The nonbonding NP_3 ligand Ag(I)···N distance [2.924(4) Å] in **4** is significantly longer than this distance [2.662(3) Å] in the PF_6^- salt, **5**. The Ag(I) center of **4**, compared to that of **5**, is further from the plane defined by P(1)P(2)P(3) in the direction away from the N atom of the NP_3 ligand (Tables X and XI) because of the weak Ag(I)···O interaction. These results unambiguously demonstrate that the Ag(I) center displays a preference for bonding to the oxygen atom of the nitrate anion over the ligand nitrogen atom. However, the Au(I) analogs, $Au(NP_3)PF_6$ (**2**) and $Au(NP_3)NO_3$ (**3**), show the same ligand Au(I)···N distance in both structures, mitigating against Au···O bonding.

It is apparent that the cationic group 11 phosphine complexes with Ag(I) have a greater tendency to bind to oxygen than do phosphine Au(I) complexes. Furthermore, there is little tendency for cationic $[AuL_2]^+$ or $[AuL_3]^+$ (L = phosphine) complexes to expand their coordination number through bonding to either N or O ligands,[10] even though four-coordination with P ligands is common.

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Supplementary Material Available: Tables of crystal data and data collection and refinement details (12 pages). Ordering information is given on any current masthead page.

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