Organometallic Gold(I) and Gold(III) Complexes Containing 1,3,5-Triaza-7-phosphaadamantane (TPA): Examples of Water-Soluble Organometallic Gold Compounds

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The organometallic gold(I) complexes [Au(C≡CCRR′OH)(TPA)] (R = R′ = H, Me, Ph and R = Me, R′ = Et) and [Au(C_6F_5)(TPA)] as well as the gold(III) complexes *trans*-[Au(C_6F_5)$_2$(TPA)$_2$]OTf and [Au(C_6F_5)$_3$(TPA)] (TPA = 1,3,5-triaza-7-phosphaadamantane) were prepared and fully characterized by spectroscopic methods and, in the case of *rac*-[Au{C≡CC(Et)(Me)OH}(TPA)] and [Au(C_6F_5)$_3$(TPA)], by X-ray crystallography. The alkynyl complexes [Au(C≡CCRR′OH)(TPA)] (R = R′ = H, Me and R = Me, R′ = Et) represent rare examples of organometallic gold(I) complexes that are soluble and stable in water.

Introduction

Alkynyl complexes of gold(I) containing phosphine ligands have been known for many years and have been studied in great detail.[1,2] Recent research efforts in this field have focused on studying luminescence,[3] nonlinear optical properties,[4] and the supramolecular chemistry of gold(I) acetylide complexes.[5] The phosphine ligand in the majority of known alkynylgold(I) complexes is either an arylphosphine including PPh_3, P(4-$MeOC_6H_4$)$_3$, PPh_2Me, $PPhMe_2$, or, less frequently, PMe_3 or PCy_3 (Cy = cyclohexyl). To the best of our knowledge, none of the known alkynyl complexes of gold are soluble in water. The rapid development of "green chemistry" and the desire to be able carry out important industrial chemical processes in water has led to a surge in research in aqueous organometallic chemistry, in particular the development of water-soluble catalysts.[6] A spectacular example of commercial success in this field is the Rhurchemie/Rhône-Poulenc hydroformylation process carried out using the water-soluble organometallic rhodium complex [RhH(CO)(TPPTS)$_3$] (TPPTS = trisulfonated triphenylphosphine sodium salt) in an aqueous biphasic system on a scale of more than 600 000 tons per year.[7] Among the known water-soluble phosphines 1,3,5-triaza-7-phosphaadamantane (TPA) is unique due to its small steric demand (cone angle similar to PMe_3), its resistance to oxidation, and its solubility in a wide variety of solvents. The synthesis of TPA was first reported in 1974,[8] but the coordination chemistry of this ligand has been explored only recently.[9] Some water-soluble gold(I) complexes containing TPA have been reported by Fackler Jr. and co-workers,[10−13] but alkynyl complexes containing this phosphine have never been investigated. Similarly, no gold(III) compounds containing TPA have ever been reported. We have been studying the gold-catalyzed addition of water and methanol to terminal acetylenes using both organometallic gold(III) and gold(I) complexes.[14] We found, however, that most gold complexes we examined were either inactive or very poor catalysts for this reaction, which may be in part due to their insolubility and/or instability in the aqueous reaction medium. In an attempt to improve solubility and stability of organometallic gold(I) and gold(III) complexes in water, we were interested in synthesizing some gold(I) and gold(III) complexes that were both water-soluble and stable in water. The results of this investigation are presented herein.

Results and Discussion

Gold(I) Alkynyl Complexes. The strategy we employed to obtain water-soluble gold(I) alkynyl complexes was to utilize

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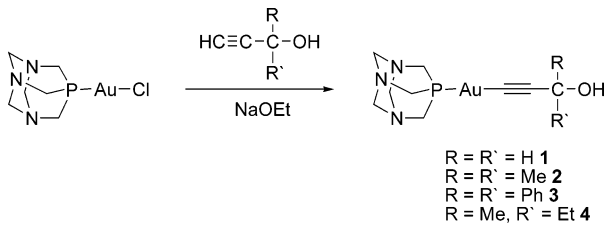
Scheme 1



a combination of organometallic ligands with solubilizing groups in combination with the highly water-soluble TPA ligand. The readily available propargyl alcohols, HC≡CRR′OH (R = R′ = H, Me, Ph and R = Me, R′ = Et), seemed an obvious ligand choice due to the presence of a hydroxy group. Some gold(I) complexes containing propargyl groups [Au(C≡CCR$_2$OH)(P)] (R = H, Me, P = PPh$_3$; R = H, P = PCy$_3$) have previously been described;[15,16] however because of the large phosphine ligands, these complexes are insoluble in water. The reaction of [AuCl(TPA)] with the propargyl alcohols HC≡CCRR′OH (R = R′ = H, Me, Ph; R = Me, R′ = Et) in the presence of base affords the alkynylgold(I) complexes [Au(C≡CCRR′OH)(TPA)] (R = R′ = H **1**, Me **2**, Ph **3**; R = Me, R′ = Et **4**) as colorless or pale yellow solids in good yields (Scheme 1).

Complexes **1**−**4** show singlet resonances at ca. −50 ppm in their ^{31}P{^{1}H} NMR spectra, consistent for linear gold(I) compounds containing TPA acting as a P-donor ligand. The proton NMR spectra show, in addition to the signals from the propargyl ligands, a singlet resonance and an AB quartet (ca. 13 Hz geminal H−H coupling) due to the NCH$_2$P and NCH$_2$N methylene groups, respectively. The presence of only a singlet for the NCH$_2$P methylene protons is unusual since two-bond P−H coupling would be expected. However, by use of 2D (HETCOR) and ^{1}H{^{31}P} NMR spectra we could unambiguously confirm the assignment of the TPA ligand protons. It is interesting to note that the solvent also affects the NMR signal of the NCH$_2$P methylene groups; in free TPA they resonate as a doublet with $^2J_{P-H}$ = 9 Hz in D$_2$O, whereas in CDCl$_3$ a singlet is observed. In the ^{13}C NMR spectra of complexes **2** and **4** the resonances of only the Au−C≡*C* carbon atoms, in addition to the TPA and alkyne signals, were observed at 111 and 110 ppm, respectively; very similar chemical shifts have been reported for other alkynylgold(I) complexes.[17] Due to the large quadrupole moment of gold, the Au−C carbon signals are very rarely observed in ^{13}C NMR spectra. The poor solubility of complexes **1** and **3** did not allow us to measure the ^{13}C NMR spectra of these compounds. The IR spectra of complexes **1**−**4** show a weak band due to the C≡C stretch at ca. 2100 cm^{-1}, characteristic for alkynyls σ-bonded to a gold(I) center, as well as a very broad band at ca. 3400 cm^{-1} due to the O−H stretch. The FAB+ mass spectra of complexes **1**−**4** do not show molecular ion peaks; in all cases the base peak corresponds to loss of the hydroxyl group. This spectral datum is consistent with the proposed structure (Scheme 1), consisting of linear alkynyl gold(I) complexes containing P-coordinated TPA ligands. This was confirmed by an X-ray diffraction study of *rac*-[Au{C≡CC(Et)(Me)OH}(TPA)], **4**. The basic structure of complex **4** consists of a TPA ligand and the chiral alkyne linearly coordinated to a gold atom. Three of such units self-assemble

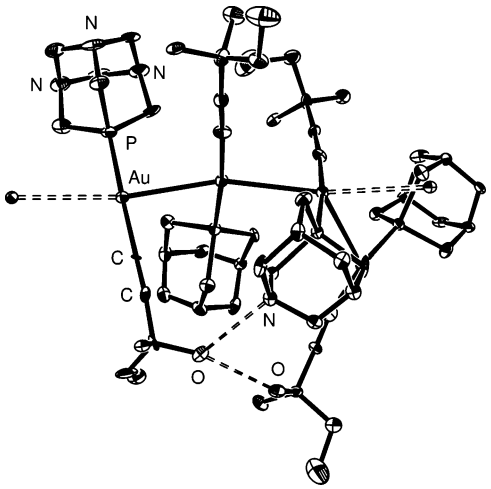


Figure 1. ORTEP[21] view of one tetranuclear unit of complex **4**. Ellipsoids show 30% probability; hydrogen atoms omitted for clarity.

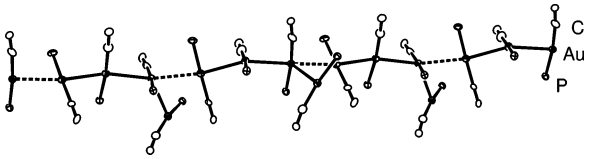


Figure 2. Polymeric structure of complex **4**. For clarity only the P atoms of the TPA ligands and the C≡C of the propargyl groups are shown.

in a head-to-tail arrangement, with a torsion angle of ca. 105°, through short intramolecular gold−gold contacts [3.1178(1) and 3.1164(9) Å] into a trinuclear chain. In addition, a further single molecule of **4** is attached, again via a short gold−gold contact of 3.1388(11) Å, to the last gold atom in the chain (Figure 1). These tetranuclear units are then connected via slightly longer gold−gold contacts of 3.3294(9) Å to form an infinite chain polymer with gold "side chains" as shown in Figure 2. In addition to the aurophilic interactions present in the polymer, the tetranuclear units are held together by hydrogen-bonding interactions between hydroxyl groups (O−O ca. 2.75 Å) as well as between hydroxy groups and one of the TPA nitrogen atoms (O−N ca. 2.87 Å) as shown in Figure 1. Curiously, the distribution of the two enantiomers in the polymer does not follow any particular pattern such as *R R*, *S S*, or *S R*, instead it seems to be completely random; however, in each tetranuclear unit the number of *R* and *S* enantiomers is exactly equal. The gold−gold distances present in the structure [3.1178(10), 3.1164(9), 3.1388(11), and 3.3294(9) Å] fall in the range typically observed for aurophilic bonds between two gold(I) centers.[18] Although similar chain polymers are observed in the gold(I) cyano complexes [Au(TPA)$_2$][Au(CN)$_2$] [*d*(Au···Au) = 3.45 Å][19] and [Au(CN)(PMe$_3$)] [*d*(Au···Au) = 3.32 Å],[20] the polymeric structure of complex **4** containing gold "side chains" finds no precedence in the literature.

The average Au−P distance in complex **4** [2.269(5) Å] is slightly longer than that in [AuCl(TPA)] [2.226(2) Å][10] and slightly shorter than that in [AuPh(TPA)] [2.289(5) Å][12] but similar to that found in [Au(C≡C^{t}Bu)(PPh$_3$)] [2.271(2) Å].[15]

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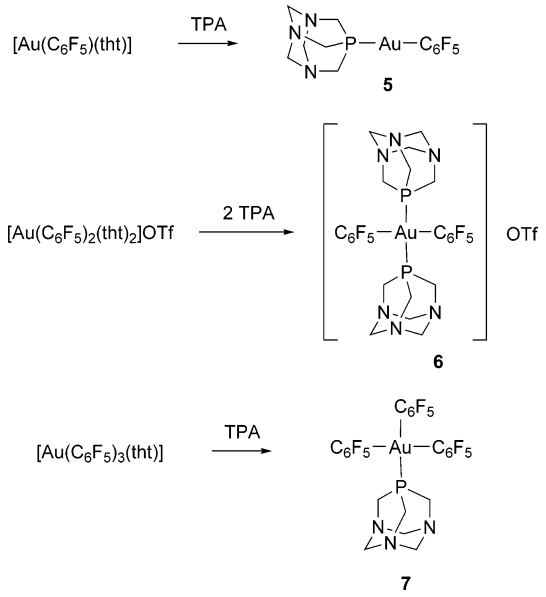
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Au(1)−P(1)	2.258(4)	Au(3)−P(3)	2.276(5)
Au(1)−C(7)	1.992(15)	Au(3)−C(31)	2.027(16)
Au(2)−P(2)	2.266(4)	Au(4)−P(4)	2.277(5)
Au(2)−C(19)	2.020(18)	Au(4)−C(43)	2.077(5)
Au(1)−Au(2)	3.1388(11)	Au(1)−Au(3)	3.1178(10)
Au(1)−Au(4)	3.3294(9)	Au(3)−Au(4)*	3.1164(9)
C(7)−Au(1)−P(1)	172.2(4)	C(19)−Au(2)−P(2)	166.1(4)
C(31)−Au(3)−P(3)	173.7(5)	C(43)−Au(4)−P(4)	178.5(3)

Scheme 2



The Au−C bond lengths in complex **4** show much greater variation (Table 1) than the Au−P distances; however the average Au−C bond distance in **4** [2.019(14) Å] is shorter than those in [AuPh(TPA)] [2.040(2) Å][12] and [Au(C≡CCH$_2$Br)(PCy$_3$)] [2.080(12) Å][15] but longer than that observed in [Au(C≡C^{t}Bu)(PPh$_3$)] [1.997(8) Å].[15]

The aim of producing water-soluble organometallic gold(I) complexes was indeed achieved: the TPA alkynyl gold(I) complexes **2** and **4** are soluble (ca. 8 mg/mL) and also stable in water. Surprisingly, complex **1**, with the least bulky R groups, is only very poorly soluble in water (ca. 0.7 mg/mL) and dmso and completely insoluble in other common organic solvents. Similarly, the phenyl derivative (**3**) is poorly soluble in dmso and, as was expected, insoluble in water.

Gold(I) and Gold(III) C$_6$F$_5$ Complexes. Since we have extensively studied gold(I) and gold(III) containing one, two, and three C$_6$F$_5$ groups in the past,[22] we wished to prepare some TPA analogues in the hope to obtain water-soluble C$_6$F$_5$ derivatives. The neutral gold(I) complex [Au(C$_6$F$_5$)(TPA)] (**5**) as well as the cationic and neutral gold(III) complexes *trans*-[Au(C$_6$F$_5$)$_2$(TPA)$_2$]OTf (**6**) and [Au(C$_6$F$_5$)$_3$(TPA)] (**7**) were prepared by displacement of the weakly coordinated tetrahydrothiophene (tht) ligand from [Au(C$_6$F$_5$)(tht)], *trans*-[Au(C$_6$F$_5$)$_2$(tht)$_2$]OTf, and [Au(C$_6$F$_5$)$_3$(tht)], respectively (Scheme 2).

The ^{31}P{^{1}H} and ^{1}H NMR spectra of complexes **5**−**7** display resonances due to the TPA ligand, with chemical shifts and coupling constants similar to those of complexes **1**−**4**. However, the ^{19}F{^{1}H} NMR spectra provide some further information in order to confirm the structures of these compounds. The C$_6$F$_5$ group gives rise to three resonances for the *ortho*-, *meta*-, and *para*-fluorine atoms. For complexes **5** and **6** just one set of C$_6$F$_5$ signals is observed in addition to a singlet resonance due to the triflate anion of complex **6**. In contrast, the ^{19}F{^{1}H} NMR spectrum of compound **7** shows two sets of C$_6$F$_5$ signals in a 1:2 ratio, corresponding to the C$_6$F$_5$ groups *trans* and *cis* to the TPA ligand. The FAB mass spectra of **5**−**7** show intense molecular ion peaks and, in the case of complex **7**, additional peaks corresponding to the loss of one, two, and three C$_6$F$_5$ groups. The *trans* stereochemistry of complex **6** was deduced from the IR spectrum. A single band at 801 cm^{-1} is characteristic of two mutually *trans* C$_6$F$_5$ groups;[23] in the starting material also one single band at 797 cm^{-1} is observed. The structure of complex **7** was confirmed by an X-ray diffraction study. A view of one of the two independent molecules in the unit cell is shown in Figure 3, and selected bond lengths and angles are listed in Table 2. The complex consists of one TPA molecule and three C$_5$F$_6$ groups coordinated to the gold atom in a slightly distorted square-planar arrangement with CAuC and CAuP angles ranging from 87.67(8)° to 94.14(6)° (molecule A) and 87.67(8)° to 92.36(6)° (molecule B). The Au−P distances [2.3285(10) and 2.3228(10) Å] are considerably shorter than those found in other gold(III) phosphine complexes such as [Au(C$_6$F$_5$)$_3${PPh$_2$CH$_2$CH(OMe$_2$)}] 2.3692(8) Å,[24] [Au(C$_6$F$_5$)$_3${PPh$_2$(2-HSC$_6$H$_4$)}] 2.3884(16) Å,[25] and [AuMe$_3$(PPh$_2$)] 2.350(6) Å.[26] This Au−P

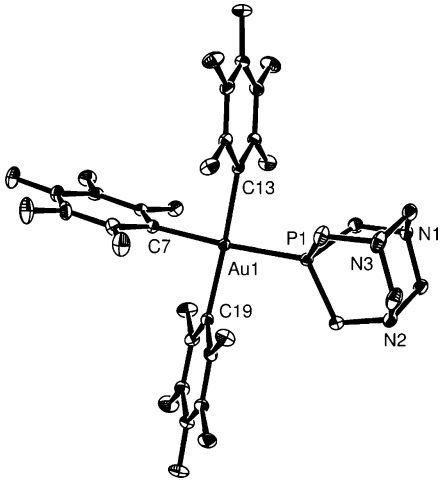


Figure 3. ORTEP[21] view of complex **7** showing one of the two molecules in the unit cell. Ellipsoids show 50% probability levels.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 7

Au(1)−P(1)	2.3285(10)	Au(1)−C(13)	2.079(2)
Au(1)−C(7)	2.066(2)	Au(1)−C(19)	2.068(2)
Au(2)−P(2)	2.3228(10)	Au(2)−C(37)	2.066(2)
Au(2)−C(31)	2.069(2)	Au(2)−C(43)	2.074(2)
C(7)−Au(1)−C(19)	90.02(8)	C(37)−Au(2)−C(31)	90.88(8)
C(7)−Au(1)−C(13)	87.67(8)	C(37)−Au(2)−C(43)	176.25(8)
C(19)−Au(1)−C(13)	177.31(8)	C(31)−Au(2)−P(2)	179.09(6)
C(7)−Au(1)−P(1)	174.51(6)	C(31)−Au(2)−C(43)	87.67(8)
C(19)−Au(1)−P(1)	94.14(6)	C(37)−Au(2)−P(2)	89.15(6)
C(13)−Au(1)−P(1)	88.07(6)	C(43)−Au(2)−P(2)	92.36(6)

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bond shortening is likely due to the low steric bulk of the TPA ligand, as evident by the similarity of the Au−P distances in complex **7** with those in $[AuI_3(PMe_3)]$ 2.334(2) Å; the analogous complex containing the more bulky $PPhMe_2$ ligand has slightly longer Au−P distances of 2.342(2) and 2.345(2) Å.[27] The Au−C bond lengths for the C_6F_5 groups *trans* and *cis* to the phosphine [molecule A: 2.066(2), 2.079(2), and 2.068(2) Å, molecule B: 2.069(2), 2.074(2), and 2.066(2) Å, respectively] are almost equal, with one of the *trans* Au−C distances being slightly longer. The same observations, and almost identical Au−C bond lengths, have been reported for other tris(pentaflurophenyl)gold(III) compounds.[24,25] To the best of our knowledge complex **7** represents the first structurally characterized gold(III) derivative of TPA.

Unfortunately, none of the C_6F_5 complexes described here are soluble in water. However, perhaps surprisingly, $[Au(C_6F_5)_3(TPA)]$ (**7**) is soluble in MeOH, whereas the cationic complex **6** containing two TPA ligands, which could be expected to be more water soluble, is soluble in acetone but poorly soluble in CH_2Cl_2 and $CHCl_3$.

The findings presented here illustrate that water solubility of a given complex is difficult to predict, and thus the tailored design of water-soluble gold compounds is currently still based on trial and error studies. However, as our results of the propargylgold(I) complexes show, the combination of a water-soluble ligand with a ligand possessing solubilizing groups (here −OH) can give water-soluble complexes. The presence of a water-soluble ligand alone seems not enough to make a complex water soluble, as evidenced by the water-insoluble complex $[Au(C_6F_5)(TPA)]$. Further work is currently in progress to attempt to design more water-soluble gold derivatives by ligand modification and to examine the catalytic properties of some of these compounds in aqueous medium.

In conclusion we have prepared and characterized a series of organometallic gold(I) and gold(III) complexes including the first gold(III) complexes containing TPA as well as examples of organometallic gold compounds that are soluble and stable in water.

Experimental Section

General Procedures. ^1H, ^{13}C, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer. Chemical shifts are quoted relative to external TMS (^1H), 85% H_3PO_4 (^{31}P), $CFCl_3$ (^{19}F); coupling constants are reported in Hz. FAB mass spectra were measured on a VG Autospec spectrometer in positive ion mode using NBA as matrix. IR spectra were recorded as KBr disks on a Perkin-Elmer SpectrumOne instrument. Elemental analyses were obtained in-house using a Perkin-Elmer 240B microanalyzer. TPA,[28] $[AuCl(TPA)]$,[10] $[Au(C_6F_5)(tht)]$,[29] and $[Au(C_6F_5)_3(tht)]$[29] were prepared by published procedures; all other reagents were obtained commercially and used as received. *trans*-$[Au(C_6F_5)_2(tht)_2]OTf$ was prepared from *trans*-$[^nBu_4N][AuBr_2(C_6F_5)_2]$ and 2 equiv of $[Ag(OTf)(tht)]$.

Synthesis of [Au(C≡CCRR′OH)(TPA)] Complexes. To a solution of NaOEt (0.033 g, 0.485 mmol) in EtOH (10 mL) was added $[AuCl(TPA)]$ (0.100 g, 0.257 mmol) and the appropriate alkyne (0.385 mmol). The mixture was allowed to stir at room temperature overnight. Depending on the solubility of the product, different workup procedures were used: For complexes **1**, **2**, and **4** the resulting solutions were taken to dryness and the solid residue was extracted with CH_2Cl_2. After filtration through Celite and concentration in a vacuum the complexes were isolated by addition of pentane. In the case of complex **3**, the precipitated product was isolated by filtration and washed well with water, EtOH, and pentane.

[Au(C≡CCH$_2$OH)(TPA)], 1: pale yellow solid (93% yield); $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ −48.78; ^1H NMR (DMSO-d_6) δ 3.97 (s, 2 H, CH_2O), 4.24 (s, 6 H, CH_2P), 4.41 (AB q, J = 12.6 Hz, 6 H, CH_2N), 4.74 (br s, 1 H, OH); FAB-MS m/z 392 $[M - OH]^+$; IR (KBr disk) 3400 ν(−OH), 2118 cm^{-1} ν(C≡C). Anal. Calcd for $C_9H_{15}AuN_3OP$ (409.2): C 26.42, H 3.70, N 10.27. Found: C 26.35, H 3.61, N 9.96.

[Au(C≡CC{Me}$_2$OH)(TPA)], 2: pale yellow solid (86% yield); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −50.72; ^1H NMR ($CDCl_3$) δ 1.50 (s, 6 H, Me), 3.24 (br s, 1 H, O*H*), 4.37 (s, 6 H, CH_2P), 4.54 (AB q, J = 13.1 Hz, 6 H, CH_2N); ^{13}C NMR ($CDCl_3$) δ 32.79 (Me), 52.42 (d, J = 20.2 Hz, N*C*H$_2$P), 65.10 (*C*OH), 73.22 (d, J = 7.4 Hz, N*C*H$_2$N), 111.24 (Au−C≡*C*), Au−*C*≡C not observed; FAB-MS m/z 420 $[M - OH]^+$; IR (KBr disk) 3407 ν(−OH), 2100 cm^{-1} ν(C≡C). Anal. Calcd for $C_{11}H_{19}AuN_3OP$ (437.2): C 30.22, H 4.38, N 9.61. Found: C 30.34, H 4.22, N 9.52.

[Au(C≡CC{Ph}$_2$OH)(TPA)], 3: colorless solid (96% yield); $^{31}P\{^1H\}$ NMR (DMSO-d_6) δ −48.43; ^1H NMR (DMSO-d_6) δ 4.25 (s, 6 H, CH_2P), 4.42 (AB q, J = 12.6 Hz, 6 H, CH_2N), 6.23 (br s, 1 H, O*H*), 7.14 (tt, J = 7.3/1.3 Hz, 2 H, Ph *p*-H), 7.24 (t, J = 7.8 Hz, 4 H, Ph *m*-H), 7.53 (dd, J = 7.0/1.3 Hz, 4 H, Ph *o*-H); FAB MS m/z 545 $[M - OH]^+$; IR (KBr disk) 3430 ν(−OH), 2112 cm^{-1} ν(C≡C). Anal. Calcd for $C_{21}H_{23}AuN_3OP$ (561.4): C 44.93, H 4.13, N 7.49. Found: C 44.94, H 4.01, N 7.12.

***rac*-[Au(C≡CCMe{Et}OH)(TPA)], 4:** pale yellow solid (86% yield); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −50.49; ^1H NMR ($CDCl_3$) δ 1.04 (t, J = 7.6 Hz, 3 H, CH_3), 1.44 (s, 3 H, Me), 1.65 (q, J = 7.3 Hz, 2 H, CH_2), 3.11 (br s, 1 H, O*H*), 4.34 (s, 6 H, CH_2P), 4.53 (AB q, J = 13.1 Hz, 6 H, CH_2N); ^{13}C NMR ($CDCl_3$) δ 9.40 (*C*H$_3$), 30.27 (Me), 37.26 (*C*H$_2$), 52.16 (d, J = 20.5 Hz, N*C*H$_2$P), 68.44 (*C*OH), 72.96 (d, J = 7.3 Hz, N*C*H$_2$N), 109.72 (Au−C≡*C*), Au−*C*≡C not observed; FAB-MS m/z 434 $[M - OH]^+$; IR (KBr disk) 3413 ν(−OH), 2105 cm^{-1} ν(C≡C). Anal. Calcd for $C_{12}H_{21}AuN_3OP$ (451.2): C 31.94, H 4.69, N 9.31. Found: C 32.06, H 4.24, N 9.11. Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.

[Au(C$_6$F$_5$)(TPA)], 5. A solution of $[Au(C_6F_5)(tht)]$ (110 mg, 0.243 mmol) in CH_2Cl_2 (10 mL) was treated with solid TPA (38 mg, 0.242 mmol) and stirred for 2 h. The solution was filtered through Celite and concentrated in a vacuum. Addition of pentane afforded the complex as a colorless solid in 66% yield: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −48.40; ^1H NMR ($CDCl_3$) δ 4.26 (s, 6 H, CH_2P), 4.50 (AB q, J = 13.1 Hz, 6 H, CH_2N); $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −161.93 (m, *m*-F), −157.66 (t, J = 20.7 Hz, *p*-F), −116.27 (m, *o*-F); FAB MS m/z 522 $[M]^+$, 354 $[M - C_6F_5]^+$. Anal. Calcd for $C_{12}H_{12}AuF_5N_3P$ (521.2): C 27.65, H 2.32, N 8.06. Found: C 27.70, H 2.17, N 8.20.

***trans*-[Au(C$_6$F$_5$)$_2$(TPA)$_2$]OTf, 6.** To a solution of TPA (25 mg, 0.159 mmol) in acetone (10 mL) was added solid *cis*-$[Au(C_6F_5)_2(tht)_2]OTf$ (61 mg, 0.071 mmol). After stirring for 2 h the solution was evaporated to dryness and the resulting solid washed with Et_2O and dried. The complex was obtained as a pale yellow solid in 69% yield: $^{31}P\{^1H\}$ NMR (acetone-d_6) δ −20.75; ^1H NMR (acetone-d_6) δ 4.55 (s, 6 H, CH_2P), 4.59 (AB q, J = 13.1 Hz, 6 H, CH_2N); $^{19}F\{^1H\}$ NMR (acetone-d_6) δ −156.27 (m, *m*-F), −151.88 (t, J = 20.7 Hz, *p*-F), −119.34 (m, *o*-F), −75.58 (s, OTf); FAB-MS m/z 845 $[M]^+$. Anal. Calcd for $C_{25}H_{24}AuF_{13}N_6OP$ (994.5): C 30.19, H 2.43, N 8.45. Found: C 30.34, H 2.34, N 8.29.

[Au(C$_6$F$_5$)$_3$(TPA)], 7. To a solution of $[Au(C_6F_5)_3(tht)]$ (100 mg, 0.127 mmol) in CH_2Cl_2 (5 mL) was added TPA (20 mg, 0.127 mmol). After stirring for ca. 2 h the solution was concentrated in

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Table 3. Details of Crystal Data and Structure Refinement for Complexes 4 and 7

	4	**7**
empirical formula	$C_{12.50}H_{22}AuClN_3O_{1.75}P$	$C_{24}H_{12}AuF_{15}N_3P$
fw	505.72	855.30
temp/K	100	150
wavelength/Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	P2(1)/c	P-1
a/Å	18.489(4)	10.256(2)
b/Å	21.169(4)	13.206(3)
c/Å	18.701(4)	20.794(4)
α/deg	90	79.12(3)
β/deg	112.47(3)	76.88(3)
γ/deg	90	71.28(3)
V/Å^3	6764(2)	2577.1(9)
Z	16	4
density (calcd)/(Mg/m^3)	1.986	2.204
abs coeff/mm^{-1}	8.956	5.902
F(000)	3888	1624
cryst habit	pale yellow needle	colorless block
cryst size/mm	0.26 × 0.038 × 0.033	0.25 × 0.21 × 0.18
θ range for data collecn/deg	3.70−25.03	3.73−32.02
index ranges	$-22 \le h \le 21$, $-25 \le k \le 25$, $-10 \le l \le 22$	$-12 \le h \le 15$, $-18 \le k \le 18$, $-30 \le l \le 29$
no. of reflns collected	23 026	24 589
no. of indep reflns	6899 (R(int) = 0.0360)	15 308 (R(int) = 0.0108)
no. of data/restraints/params	6899/22/740	15 308/0/793
R1 ($I > 2\sigma(I)$)[a]	0.0512	0.0180
wR2 (all data)[b]	0.1448	0.0403
S (all data)[c]	1.034	1.007
largest diff peak, hole/(e Å^{-3})	1.819, −0.754	1.514, −1.082

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$. [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of refined parameters.

a vacuum and pentane was added. The resulting colorless solid was isolated by filtration, washed with pentane, and dried. The product was obtained in 65% yield: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −55.83; ^1H NMR ($CDCl_3$) δ 4.18 (s, 6 H, CH_2P), 4.49 (AB q, J = 13.1 Hz, 6 H, CH_2N); $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −160.77 (m, *cis*-*m*-F), −158.87 (m, *trans*-*m*-F), −156.47 (t, J = 19.5 Hz, *cis*-*p*-F), −154.12 (t, J = 19.5 Hz, *trans*-*p*-F), −121.93 (m, *cis*-*o*-F), −120.88 (m, *trans*-*o*-F); FAB-MS *m*/*z* 856 $[M]^+$, 688 $[M - C_6F_5]^+$, 521 $[M - 2C_6F_5]^+$, 354 $[M - 3C_6F_5]^+$. Anal. Calcd for $C_{24}H_{12}AuF_{15}N_3P$ (855.3): C 33.70, H 1.41, N 4.91. Found: C 33.73, H 1.32, N 5.03. Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.

X-ray Crystallography. Crystals of complex **4** and **7** were mounted in oil on a glass fiber, and data were collected on an Oxford Diffraction Xcalibur 2 CCD diffractometer at 100 and 150 K, respectively. Data were reduced and absorption corrections applied using CrysalisRED[30] and SADABS.[31] The structures were solved using SIR-92[32] (**4**) and direct methods[33] (**7**). Both structures were refined to F_o^2 using full-matrix least squares.[33] All hydrogen atoms were placed on calculated positions and refined as riding on their respective carbon atoms. Complex **4** contained a disordered CH_2Cl_2 molecule in which one of the chlorine atoms was refined with a 60:40 site occupancy and fixed C−Cl distances of 1.75 Å. Furthermore, the crystal contained three waters of crystallization, the hydrogen atoms of which could not be located. One of the water molecules was disordered and was refined with a 55:45 site occupancy. Crystallographic and refinement details for complexes **4** and **7** are summarized in Table 3.

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Supporting Information Available: Crystallographic details for complexes **4** and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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