4438 *Inorg. Chem.* **1997,** *36,* 4438−4443

Gold(I) Complexes with N-Donor Ligands. 2.[1] Reactions of Ammonium Salts with $[Au(acac\text{-}\kappa C^2)(PR_3)]$ To Give $[Au(NH_3)L]^+$, $[(AuL)_2(\mu_2\text{-}NH_2)]^+$, $[(AuL)_4(\mu_4\text{-}N)]^+$, or $[(AuL)_3(\mu_3\text{-}O)]^+$. A New and Facile Synthesis of $[Au(NH_3)_2]^+$ Salts. Crystal Structure of $[\{AuP(C_6H_4OMe\text{-}4)_3\}_3(\mu_3\text{-}O)]CF_3SO_3$

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Received February 26, 1997[⊗]

The complexes $[Au(acac\text{-}\kappa C^2)(PR_3)]$ (acac = acetylacetonate, R = Ph, C_6H_4OMe-4) react with $(NH_4)ClO_4$ to give amminegold(I), $[Au(NH_3)(PR_3)]ClO_4$, amidogold(I), $[(AuPR_3)_2(\mu_2\text{-}NH_2)]ClO_4$, or nitridogold(I), $[(AuPR_3)_4(\mu_4\text{-}N)]ClO_4$, complexes, depending on the reaction conditions. Similarly, $[Au(acac\text{-}\kappa C^2)(PPh_3)]$ reacts with $(NH_3R')OTf$ (OTf = CF_3SO_3) (1:1) or with $[H_3N(CH_2)_2NH_2]OTf$ (1:1) to give (amine)gold(I) complexes $[Au(NH_2R')(PPh_3)]OTf$ (R′ = Me, $C_6H_4NO_2$-4) or $[(AuPPh_3)_2\{\mu_2\text{-}H_2N(CH_2)_2NH_2\}](OTf)_2$, respectively. The ammonium salts $(NH_2R'_2)OTf$ (R′ = Et, Ph) react with $[Au(acac\text{-}\kappa C^2)(PR_3)]$ (R = Ph, C_6H_4OMe-4) (1:2) to give, after hydrolysis, the oxonium salts $[(AuPR_3)_3(\mu_3\text{-}O)]OTf$ (R = Ph, C_6H_4OMe-4). When NH_3 is bubbled through a solution of [AuCl(tht)] (tht = tetrahydrothiophene), the complex $[Au(NH_3)_2]Cl$ precipitates. Addition of $[Au(NH_3)_2]Cl$ to a solution of $AgClO_4$ or TlOTf leads to the isolation of $[Au(NH_3)_2]ClO_4$ or $[Au(NH_3)_2]OTf$, respectively. The crystal structure of $[(AuPR_3)_3(\mu_3\text{-}O)]OTf{\cdot}Me_2CO$ (R = C_6H_4OMe-4) has been determined: triclinic, space group $P\bar{1}$, $a = 14.884(3)$ Å, $b = 15.828(3)$ Å, $c = 16.061(3)$ Å, $\alpha = 83.39(3)°$, $\beta = 86.28(3)°$, $\gamma = 65.54(3)°$, R1 (wR2) = 0.0370 (0.0788). The $[(AuPR_3)_3(\mu_3\text{-}O)]^+$ cation shows an essentially trigonal pyramidal array of three gold atoms and one oxygen atom with O−Au−P bond angles of *ca.* 175° and Au···Au contacts in the range 2.9585(7)−3.0505(14) Å. These cations are linked into centrosymmetric dimers through two short Au···Au [2.9585(7), 3.0919(9) Å] contacts. The gold atoms of the dimer form a six-membered ring with a chair conformation.

Introduction

Although the affinity of gold for nitrogen is low and most compounds with gold−nitrogen bonds are of limited stability,[2] examples of all possible aurated ammonium salts $[(AuL)_nNR_{4-n}]^+$ ($n = 1-4$)[3−10] and even hypercoordinated complexes $[(AuL)_5(\mu_5\text{-}N)]^{2+}$ [4,11] have been reported. However, the first three members of these series, *i.e.*, $[Au(NH_3)(PR_3)]^+$, $[(AuPR_3)_2(\mu_2\text{-}NH_2)]^+$, and $[(AuPR_3)_3(\mu_3\text{-}NH)]^+$, are still unknown. Schmidbaur has studied the reaction between $[(AuPR_3)_3(\mu_3\text{-}O)]^+$ (R = ^tBu) and a large excess of ammonia and obtained mixtures for which FAB mass spectra show, as parent peaks, those corresponding to $[(AuPR_3)_2(\mu_2\text{-}NH_2)]^+$ or $[(AuPR_3)_3(\mu_3\text{-}NH)]^+$ complexes depending on the Au:NH_3 molar ratio.[12] In this paper, we report the first isolation of complexes of the types $[Au(NH_3)(PR_3)]^+$ and $[(AuPR_3)_2(\mu_2\text{-}NH_2)]^+$, as well as $[(AuPR_3)_4(\mu_4\text{-}N)]^+$, from $(NH_4)ClO_4$ and $[Au(acac\text{-}\kappa C^2)(PR_3)]$. A fully aurated complex derived from $[H_3N{-}NH_3]^{2+}$ has been isolated.[13]

We have previously shown that (acetylacetonato)gold(I) complexes are useful reagents for preparing neutral, cationic, and anionic gold(I) complexes with alkyl,[14] alkynyl (including ethynyl),[14,15] hydrosulfido,[16] phosphido,[17] thiolato,[18] ylide,[14,15,19]

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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S0020-1669(97)00225-5 CCC: $14.00

and amine, $[Au(NR_3)L]^+$ (NR_3 = primary, secondary, or tertiary amines), ligands.[1] We also report here some attempts to use this method to prepare complexes of the type $[(AuL)_2(\mu_2\text{-}NR_2)]^+$, whose number is very limited.[4-7]

Recently, Mingos presented a preliminary report on the synthesis of $[Au(NH_3)_2]X$ (X = BF_4, SbF_6, Br).[20] The full paper corresponding to this work appeared while this paper was being reviewed.[21] We describe a different preparation of other salts of this interesting gold(I) complex in almost quantitative yield, and we recently used this complex to prepare (acetimine)-gold(I) complexes.[22]

Experimental Section

IR and NMR spectroscopy, elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described elsewere.[23] Chemical shifts are referred to TMS (^1H) or H_3PO_4 [$^{31}P\{^1H\}$]. Mass spectra (FAB^+) were measured with a Fisons VG-Autospec spectrometer using 3-nitrobenzyl alcohol as the matrix. Unless otherwise stated, all reactions were carried out at room temperature and without special precautions against moisture. The solvents were distilled over Na/benzophenone (THF, diethyl ether), P_2O_5 and then Na_2CO_3 (dichloromethane), $CaCl_2$ (*n*-hexane), and $KMnO_4$ (acetone). *n*-Pentane was used as received. **Warning!** perchlorate salts with organic cations may be explosive.

$[Au(acac\text{-}\kappa C^2)(PPh_3)]$ was prepared as previously described.[24] The same method was successfully applied to the synthesis of $[Au(acac\text{-}\kappa C^2)\{P(C_6H_4OMe\text{-}4)_3\}]$. Yield: 78%. Anal. Calcd for $C_{26}H_{28}AuO_5P$: C, 48.16; H, 4.35. Found: C, 47.84; H, 3.47. NMR, δ: ^1H ($CDCl_3$, 300 MHz) 2.37 (s, 6H, Me), 3.84 (s, 9H, OMe), 4.59 (d, 1H, CH, $^3J_{HP}$ 10 Hz), 6.95 (m, 6H, C_6H_4), 7.34 (m, 6H, C_6H_4); $^{31}P\{^1H\}$ (121 MHz) 35.04 (s). $[Ph_2NH_2]OTf$ and $[Et_2NH_2]OTf$ were prepared according to literature methods.[1] Similarly, dropwise addition of HO_3SCF_3 to a solution of ethylenediamine (1:1 molar ratio) in diethyl ether precipitated $[NH_3(CH_2)_2NH_2]OTf$ as a white solid. Yield: 99%. Mp: 82 °C. Anal. Calcd for $C_3H_9F_3N_2O_3S$: C, 17.14; H, 4.32; N, 13.33; S, 15.26. Found: C, 17.21; H, 4.34; N, 13.14; S, 16.26. ^1H NMR, δ (acetone-d_6, 200 MHz): 2.87−4.06 (complex set of multiplets). $(NH_4)ClO_4$ was purchased from Probus and recrystallized from acetone and diethyl ether.

$[Au(NH_3)(PPh_3)]ClO_4$ (1a). $[Au(acac\text{-}\kappa C^2)(PPh_3)]$ (337 mg, 0.60 mmol) was dissolved in 10 mL of tetrahydrofuran (THF), and the solution was added dropwise to a suspension of $(NH_4)ClO_4$ (78 mg, 0.66 mmol) in THF (10 mL). The resulting mixture was stirred for 1 h and then filtered through Celite, and the filtrate was concentrated to 2 mL. Addition of diethyl ether (20 mL), filtration, washing the solid with diethyl ether, recrystallization from THF and diethyl ether, and finally washing the solid with pentane gave **1a**. Yield: 262 mg, 76%. Mp: 95 °C. $\Lambda_M = 132\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($3 \times 10^{-4}\ mol\cdot L^{-1}$). IR: ν(NH) 3173, 3244, 3318 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 3.85 (s, br, 3H, NH_3), 7.44−7.57 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$; δ): 30.79 (s). Anal. Calcd for $C_{18}H_{18}AuClNO_4P$: C, 37.55; H, 3.15; N, 2.43. Found: C, 37.50; H, 3.11; N, 2.24.

$[Au(NH_3)\{P(C_6H_4OMe\text{-}4)_3\}]ClO_4$ (1b). This complex was similarly prepared from $[Au(acac\text{-}\kappa C^2)\{P(C_6H_4OMe\text{-}4)_3\}]$ (359 mg, 0.55 mmol) and $(NH_4)ClO_4$ (72 mg, 0.61 mmol). Yield: 276 mg, 75%. Mp: 166 °C. $\Lambda_M = 91\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($4 \times 10^{-4}\ mol\cdot L^{-1}$). IR: ν(NH) 3172, 3249, 3329 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 3.76 (s, br, 3H, NH_3), 3.84 (s, 9H, Me), 6.99 (dd, 6H, C_6H_4, $^3J_{HH}$ = 9 Hz, $^4J_{PH}$ = 1.8 Hz), 7.45 (dd, 6H, C_6H_4, $^3J_{PH}$ = 6.9 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 26.7 (s). Anal. Calcd for $C_{21}H_{24}AuClNO_7P$: C, 37.88; H, 3.63; N, 2.10. Found: C, 38.28; H, 3.61; N, 2.01.

$[(AuPPh_3)_2(\mu_2\text{-}NH_2)]ClO_4$ (2a). $[Au(acac\text{-}\kappa C^2)(PPh_3)]$ (174 mg, 0.31 mmol) and $[Au(NH_3)(PPh_3)]ClO_4$ (**1a**) (150 mg, 0.26 mmol) were mixed together in a twin-necked flask. The flask was evacuated and filled with N_2 several times, and degassed CH_2Cl_2 (5 mL) was then added. The resulting mixture was stirred for 10 min under N_2 and concentrated to 1 mL, and diethyl ether (20 mL) was added to give an off-white solid that was recrystallized from CH_2Cl_2 and diethyl ether. Yield: 211 mg, 78%. Mp: 111 °C. $\Lambda_M = 110\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($3 \times 10^{-4}\ mol\cdot L^{-1}$). IR: ν(NH) 3248, 3323 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 2.58 (s, br, 2H, NH_2), 7.38−7.55 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 30.72 (s). Mass spectrum: *m/z* (assignment, percent abundance) 459 ($AuPR_3^+$, 35), 721.5 [$Au(PR_3)_2^+$, 22], 934.2 (M^+, 100). Anal. Calcd for $C_{36}H_{32}Au_2ClNO_4P_2$: C, 41.82; H, 3.12; N, 1.36. Found: C, 41.73; H, 3.02; N, 1.34.

$[\{Au\{P(C_6H_4OMe\text{-}4)_3\}\}_2(\mu_2\text{-}NH_2)]ClO_4$ (2b). $[Au(acac\text{-}\kappa C^2)\{P(C_6H_4OMe\text{-}4)_3\}]$ (117 mgr, 0.18 mmol) was dissolved in degassed CH_2Cl_2 (5 mL), the solution was filtered, and the filtrate was added dropwise to a solution of $[Au(NH_3)\{P(C_6H_4OMe\text{-}4)_3\}]ClO_4$ (**1b**) (120 mg, 0.18 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was filtered through Celite, the filtrate was concentrated to 2 mL, and diethyl ether (20 mL) was added to precipitate a cream-colored solid, which was washed with diethyl ether (3 × 15 mL) to give **2b**. Yield: 167 mg, 76%. Mp: 99 °C. $\Lambda_M = 123\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($5 \times 10^{-4}\ mol\cdot L^{-1}$). IR: ν(NH) 3268, 3332 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 2.37 (br, 2H, NH_2), 3.82 (s, 18 H, Me), 6.83 (dd, 12H, C_6H_4, $^3J_{HH}$ = 8.7 Hz, $^4J_{PH}$ = 1.8 Hz), 7.313 (dd, 12H, C_6H_4, $^3J_{PH}$ = 12.7 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 26.6 (s). Mass spectrum: *m/z* (assignment, percent abundance) 2210 ([$(AuPR_3)_4(\mu_4\text{-}N)$], 8), 1114 ($M^+$, 86), 901 [$Au(PR_3)_2^+$, 33], 549 ($AuPR_3^+$, 100). Anal. Calcd for $C_{42}H_{44}Au_2ClNO_{10}P_2$: C, 41.55; H, 3.65; N, 1.15. Found: C, 41.46; H, 3.55; N, 1.08

$[(AuPPh_3)_4(\mu_4\text{-}N)]ClO_4$ (3a). Solid $(NH_4)ClO_4$ (7.36 mg, 0.063 mmol) was added to a solution of $[Au(acac\text{-}\kappa C^2)(PPh_3)]$ (140 mg, 0.25 mmol) in THF (15 mL). The initial solution was stirred, forming a suspension, which was then stirred for 1.5 h. Volatiles were removed *in vacuo*, and the oily residue was washed with diethyl ether (2 × 10 mL) and then stirred in diethyl ether (15 mL) for 3 h. **3a** appeared as a pale cream-colored solid, which was filtered off, washed with diethyl ether (5 mL), and dried under nitrogen. Yield: 86 mg, 70%. Mp: 203 °C dec. $\Lambda_M = 108\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($10^{-4}\ mol\cdot L^{-1}$). ^1H NMR (300 MHz, $CDCl_3$; δ): 7.09−7.47 (m, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, −60 °C, $CDCl_3$; δ): 28.302 (no well-defined triplet). Anal. Calcd for $C_{72}H_{60}Au_4ClNO_4P_4$: C, 44.34; H, 3.10; N, 0.72. Found: C, 44.20; H, 3.03; N, 0.55.

$[\{AuP(C_6H_4OMe\text{-}4)_3\}_4(\mu_4\text{-}N)]ClO_4$ (3b). Solid $(NH_4)ClO_4$ (6.8 mg, 0.057 mmol) was added to a solution of $[Au(acac\text{-}\kappa C^2)\{P(C_6H_4OMe\text{-}4)_3\}]$ (150 mg, 0.23 mmol) in THF (15 mL), and the resulting suspension was stirred for 2.5 h and then filtered. The pale yellow filtrate was concentrated (1 mL), and diethyl ether (20 mL) was added to precipitate an oily solid, which was washed with diethyl ether (2 × 10 mL) and recrystallized from dichloromethane and diethyl ether to give **3b** as a pale cream-colored solid, which was filtered off and dried under nitrogen atmosphere. Yield: 80 mg, 60%. Mp: 104 °C. $\Lambda_M = 126\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($2 \times 10^{-4}\ mol\cdot L^{-1}$). ^1H NMR (300 MHz, $CDCl_3$; δ): 3.80 (s, 3 H, OMe), 6.71 (dd, 2H, C_6H_4, $^3J_{HH}$ = 8.4

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Hz, $^4J_{PH}$ = 1.2 Hz), 7.31 (dd, 2H, C_6H_4, $^3J_{PH}$ = 12.6 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 20.21 (s). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 55.62 (s, OMe), 115.08 (d, C_6H_4, $^3J_{CP}$ = 13 Hz), 119.79 (d, C_6H_4, $^1J_{CP}$ = 67.5 Hz), 135.22 (d, C_6H_4, $^2J_{CP}$ = 15.1 Hz), 162.47 (s). Mass spectrum (FAB): *m/z* (assignment, percent abundance) 2211.1 (M^+, 100), 1662.4 [$HN(AuPR_3)_3^+$, 6.3], 1114.2 [$H_2N(AuPR_3)_2^+$, 31.1], 901 [$Au(PR_3)_2^+$, 39.6], 549.1 [$AuPR_3^+$, 65.2]. Anal. Calcd for $C_{84}H_{84}Au_4ClNO_{16}P_4$: C, 43.66; H, 3.66; N, 0.61. Found: C, 43.57; H, 3.56; N, 0.54.

[Au(NH$_2$Me)(PPh$_3$)]OTf (4). [Au(acac-κC^2)(PPh_3)] (250 mg, 0.45 mmol) was added to a suspension of (NH_3Me)OTf (81 mg, 0.45 mmol) in diethyl ether (15 mL). The resulting suspension was stirred for 3 h and filtered, and the cream-colored solid was washed with diethyl ether (3 × 20 mL) and recrystallized from CH_2Cl_2 and diethyl ether to give **4**. Yield: 218 mg, 76%. Mp: 146 °C dec. $\Lambda_M = 120\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($4.5 \times 10^{-4}\ mol\cdot L^{-1}$) IR: ν(NH) 3148, 3234 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 2.81 (t, 3H, Me, $^3J_{HH}$ = 5.8 Hz), 4.58 (br, 2H, NH_2), 7.47−7.59 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 30.52 (s). Anal. Calcd for $C_{20}H_{20}AuF_3NO_3PS$: C, 37.57; H, 3.18; N, 2.19; S, 5.02. Found: C, 37.80; H, 3.19; N, 2.19; S, 4.96.

[Au(NH$_2$C$_6$H$_4$NO$_2$-4)(PPh$_3$)]OTf (5). [Au(acac-κC^2)(PPh_3)] (196 mg, 0.35 mmol) was added to a suspension of ($NH_3C_6H_4NO_2$-4)OTf (101 mg, 0.35 mmol) in diethyl ether (15 mL). The resulting suspension was stirred for 5 h and filtered, and the cream-colored solid was washed with diethyl ether (3 × 20 mL) and recrystallized from dichloromethane and diethyl ether to give **5**. Yield: 184 mg, 70%. Mp: 153 °C. $\Lambda_M = 108\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($4 \times 10^{-4}\ mol\cdot L^{-1}$). IR: ν(NH) 3066, 3175 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 7.39−7.56, 7.99, 8.02 (m, 19 H, Ph + C_6H_4). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 29.92 (s). Anal. Calcd for $C_{25}H_{21}AuF_3N_2O_5PS$: C, 40.07; H, 2.83; N, 3.74; S, 4.28. Found: C, 40.35; H, 2.83; N, 3.79; S, 4.33.

[(AuPPh$_3$)$_2${μ_2-H$_2$N(CH$_2$)$_2$NH$_2$}](OTf)$_2$ (6). To a suspension of ($H_2NCH_2CH_2NH_3$)OTf (75 mg, 0.36 mmol) in diethyl ether (20 mL) was added [Au(acac-κC^2)(PPh_3)] (200 mg, 0.36 mmol). The resulting suspension was stirred for 15 h and filtered, and the resulting solid was washed with diethyl ether (3 × 15 mL) and recrystallized from CH_2Cl_2 and diethyl ether to give **6** as a cream-colored solid. Yield: 163 mg, 68%. Mp: 166 °C dec. $\Lambda_M = 169\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($6 \times 10^{-4}\ mol\cdot L^{-1}$). IR: ν(NH) 3193, 3110, $\delta(NH_2)$: 1589 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; δ): 3.48 (s, 4H, CH_2), 7.48−7.56 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 30.3 (s). Anal. Calcd for $C_{40}H_{38}Au_2F_6N_2O_6P_2S_2$: C, 37.63; H, 3.00; N, 2.19; S, 5.02. Found: C, 37.59; H, 3.11; N, 2.26; S, 5,23.

[(AuPPh$_3$)$_3$(μ_3-O)]OTf (7a). A solution of (Et_2NH_2)OTf (38 mg, 0.17 mmol) in acetone (10 mL) was added dropwise to a solution of [Au(acac-κC^2)(PPh_3)] (220 mg, 0.39 mmol) in acetone (10 mL). After the reaction mixture was stirred for 10 h, the formation of some metallic gold was observed. The suspension was filtered through anhydrous $MgSO_4$, and the clear solution obtained was concentrated (2 mL). Upon addition of diethyl ether (20 mL), complex **7a** precipitated as a white solid, which was filtered off, washed with diethyl ether (2 × 5 mL), and air-dried. Yield: 62 mg, 31%. Mp: 222 °C dec. $\Lambda_M = 103\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($1.13 \times 10^{-4}\ mol\cdot L^{-1}$). ^1H NMR (300 MHz, $CDCl_3$; δ): 7.3−7.6 (m, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 23.69 (s). Anal. Calcd for $C_{55}H_{45}Au_3F_3O_4P_3S$: C, 42.82; H, 2.94; S, 2.08. Found: C, 42.72; H, 2.85; S, 2.15.

[{AuP(C$_6$H$_4$OMe-4)$_3$}$_3$(μ_3-O)]OTf (7b). Similarly, from the reaction of (Ph_2NH_2)OTf (43 mg, 0.13 mmol) and [Au(acac-κC^2)-{$P(C_6H_4OMe-4)_3$}] (174 mg, 0.27 mmol) in acetone (15 mL) for 0.5 h, **7b** was obtained. Yield: 78 mg, 48%. Mp: 175 °C. $\Lambda_M = 93\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ($6.5 \times 10^{-4}\ mol\cdot L^{-1}$). ^1H NMR (300 MHz, $CDCl_3$; δ): 3.80 (s, 27H, OMe), 6.81 (dd, 18 H, C_6H_4, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 1.8 Hz), 7.37 (dd, 18H, C_6H_4, $^3J_{PH}$ = 12.6 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$; δ): 19.27 (s). Anal. Calcd for $C_{64}H_{63}Au_3F_3O_{13}P_3S$: C, 42.40; H, 3.50; S, 1.77. Found: C, 42.22; H, 3.44; S, 1.76.

Crystal Structure Determination of 7b. A colorless 0.5 × 0.3 × 0.1 mm tablet of **7b**·Me_2CO, obtained by liquid diffusion of Me_2CO/Et_2O, was mounted in inert oil on a glass fiber and transferred to a diffractometer (Siemens P4 with an LT2 low-temperature attachment). A set of 12 562 reflections ($2\theta_{max}$ 50°, 12 039 unique, R_{int} 0.019) was collected using Mo Kα radiation. Unit cell parameters were determined from a least-squares fit of 56 accurately centered reflections (10° < 2θ < 23°). An absorption correction based on ψ scans was applied, with transmission factors of 0.493−0.981. The structure was solved by direct methods and refined anisotropically on F^2.[25] Hydrogen atoms were included by using a riding model or as rigid methyl groups. The triflate anion is disordered over two sites. Tables 1 and 2 give crystallographic data and important bond lengths and angles, respectively.

Table 1. Crystal Data for **7b**·Me_2CO

empirical formula	$C_{67}H_{69}Au_3F_3O_{14}P_3S$
M_r	1871.09
space group	$P\bar{1}$
a (Å)	14.884(3)
b (Å)	15.828(3)
c (Å)	16.061(3)
α (deg)	83.39(3)
β (deg)	86.28(3)
γ (deg)	65.54(3)
V(Å^3)	3421(1)
Z	2
T (K)	173(2)
λ (Å)	Mo Kα (0.710 73)
ρ_{calc} (g cm^{-3})	1.817
F(000)	1816
μ, mm^{-1}	6.588
no. of independent reflections	12 058
no. of parameters	484
no. of restraints	425
R1[a]	0.0370
wR2[b]	0.0869
$S(F^2)$	1.04
max $\Delta\rho$ (e Å^{-3})	1.3

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **7b**·Me_2CO

Au(1)−Au(2)	3.0505(14)	Au(1)−Au(3)	2.9585(7)
Au(2)−Au(3)	3.0078(7)	Au(1)−Au(3)[a]	3.0919(9)
Au(1)−O(1)	2.063(4)	Au(2)−O(1)	2.026(5)
Au(3)−O(1)	2.066(4)	Au(1)−P(1)	2.222(2)
Au(2)−P(2)	2.210(2)	Au(3)−P(3)	2.219(2)
O(1)−Au(1)−P(1)	175.67(13)	O(1)−Au(1)−Au(3)	44.27(13)
P(1)−Au(1)−Au(3)	131.44(5)	O(1)−Au(1)−Au(2)	41.29(13)
P(1)−Au(1)−Au(2)	138.21(5)	Au(3)−Au(1)−Au(2)	60.05(2)
O(1)−Au(1)−Au(3)[a]	71.24(13)	P(1)−Au(1)−Au(3)[a]	110.75(6)
Au(3)−Au(1)−Au(3)[a]	89.20(3)	Au(2)−Au(1)−Au(3)[a]	109.23(4)
O(1)−Au(2)−P(2)	175.33(14)	O(1)−Au(2)−Au(3)	43.21(13)
P(2)−Au(2)−Au(3)	141.43(5)	O(1)−Au(2)−Au(1)	42.22(12)
P(2)−Au(2)−Au(1)	137.93(5)	Au(3)−Au(2)−Au(1)	58.46(2)
O(1)−Au(3)−P(3)	175.04(13)	O(1)−Au(3)−Au(1)	44.20(12)
P(3)−Au(3)−Au(1)	132.10(5)	O(1)−Au(3)−Au(2)	42.17(12)
P(3)−Au(3)−Au(2)	134.72(5)	Au(1)−Au(3)−Au(2)	61.49(3)
O(1)−Au(3)−Au(1)[a]	72.48(12)	P(3)−Au(3)−Au(1)[a]	111.95(5)
Au(1)−Au(3)−Au(1)[a]	90.80(3)	Au(2)−Au(3)−Au(1)[a]	110.36(3)
Au(2)−O(1)−Au(1)	96.5(2)	Au(2)−O(1)−Au(3)	94.6(2)
Au(1)−O(1)−Au(3)	91.5(2)		

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

[Au(NH$_3$)$_2$]Cl (8a). [AuCl(tht)] (200 mg, 0.62 mmol) was dissolved in 15 mL of acetone, and NH_3 was bubbled through the solution until no more white precipitate was formed. The suspension was stirred for 5 min and filtered, and the white solid was washed with diethyl ether (2 × 10 mL) and air-dried. Yield: 159 mg, 96%. Mp: 188 °C. IR: ν(NH) 3074, 3167, 3224 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6; δ): 4.626 (s, br, NH_3). Anal. Calcd for H_6AuClN_2: C, 0.00; H, 2.27; N, 10.51. Found: C, 0.19; H, 2.16; N, 10.29.

[Au(NH$_3$)$_2$]ClO$_4$ (8b). [$Au(NH_3)_2$]Cl (**8a**) (104 mg, 0.4 mmol) was added to a solution of $AgClO_4$ (89 mg, 0.43 mmol) in acetone (10 mL), and the resulting suspension was stirred for 20 min. AgCl was

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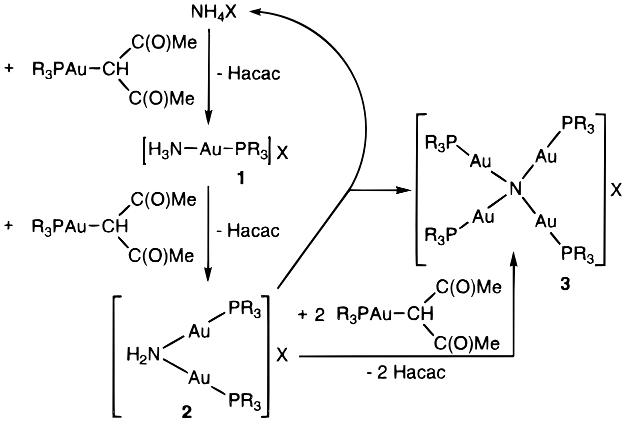
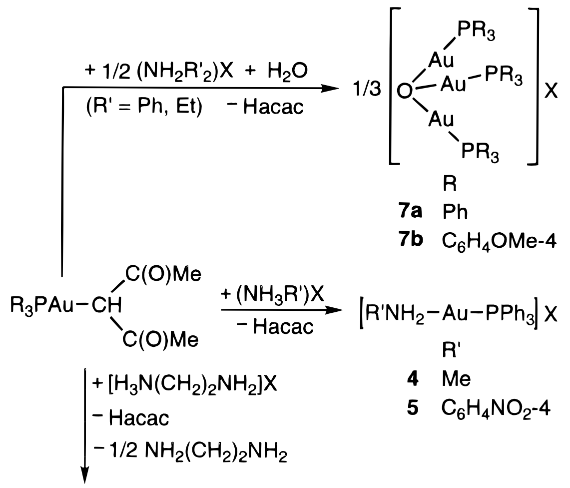
(25) Sheldrick, G. M. SHELXL 93. University of Göttingen, 1993.

Scheme 1. Synthesis of Complexes **1**−**3**



a, R = Ph; **b**, R = C_6H_4OMe-4; X = ClO_4

Scheme 2. Synthesis of Complexes **4**−**7**



X = OTf

removed by filtration, the solution was concentrated (2 mL), and diethyl ether (20 mL) was added to precipitate **8b** as a white solid. Yield: 119 mg, 92%. Mp: 184 °C dec. $\Lambda_M = 139\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (6×10^{-4} $mol\cdot L^{-1}$). IR: ν(NH), 3258, 3323 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6; δ): 4.49 (t, br, NH_3 $^1J_{HN}$ = 37 Hz). Anal. Calcd for $H_6AuClN_2O_4$: C, 0.00; H, 1.83; N, 8.48. Found: C, 0.07; H, 1.66; N, 8.66.

[Au(NH$_3$)$_2$]OTf (8c). To a suspension of $[Au(NH_3)_2]Cl$ (**8a**) (196 mg, 0.74 mmol) in acetone (10 mL) was added TlOTf (260 mg, 0.74 mmol). The suspension was stirred for 10 min, and TlCl was removed by filtration. The solution was concentrated (2 mL), and diethyl ether (20 mL) was added to precipitate **8c** as a white solid. Yield: 201 mg, 72%. Mp: 134 °C dec. $\Lambda_M = 132\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$ (8×10^{-4} $mol\cdot L^{-1}$). IR: ν(NH) 3207, 3306 cm^{-1}. ^1H NMR (300 MHz, acetone-d_6; δ): 4.53 (t, br, NH_3, $^1J_{HN}$ = 39 Hz). Anal. Calcd for $CH_6AuF_3N_2O_3S$: C, 3.16; H, 1.59; N, 7.37; S, 8.44. Found: C, 3.25; H, 1.54; N, 7.05; S, 8.33.

Results and Discussion

Dropwise addition of a tetrahydrofuran solution of [Au(acac-κC^2)(PR_3)] (acac = acetylacetonate; R = Ph, C_6H_4OMe-4) to a suspension of $(NH_4)ClO_4$ in the same solvent (molar ratio 1:1.1) gives $[Au(NH_3)(PR_3)]ClO_4$ [R = Ph (**1a**), C_6H_4OMe-4 (**1b**)] (see Scheme 1). If the order of addition of reagents is reversed (when R = C_6H_4OMe-4), a mixture containing **1b**, $[(AuPR_3)_2(\mu_2\text{-}NH_2)]ClO_4$ (**2b**), $[(AuPR_3)_4(\mu_4\text{-}N)]ClO_4$ (**3b**), and $[Au(PR_3)_2]ClO_4$ (by ^{31}P NMR) is obtained.

Whereas the complex $[(AuPR_3)_2(\mu_2\text{-}NH_2)]ClO_4$ [R = C_6H_4OMe-4 (**2b**)] can be obtained by dropwise addition of a dichloromethane solution of [Au(acac-κC^2)(PR_3)] to a solution of $[Au(NH_3)(PR_3)]ClO_4$ (**1b**) in the same solvent, its analogue with R = Ph (**2a**) must be prepared under a nitrogen atmosphere using dry solvents. These reactions have been followed in $CDCl_3$ by ^{31}P NMR spectroscopy at room temperature, proving that complexes **2a**,**b** are immediately formed. However, **2b** decomposes in solution to give the nitrido complex **3b** as the only phosphorus-containing compound, which explains the fact that NMR data and FAB mass spectra of analytically pure samples of **2b** always show the presence of small amounts of **3b.** On the other hand, **2a** is stable for at least 3 h, provided the solvent is dry. Otherwise, formation of the oxonium salt $[\{AuPPh_3\}_3(\mu_3\text{-}O)]ClO_4$ is immediately observed. An attempt to prepare **2a** by reacting [Au(acac-κC^2)(PPh_3)] and $(NH_4)ClO_4$, 2:1 in THF, led to a mixture containing **1a** and $[(AuPPh_3)_4(\mu_4\text{-}N)]ClO_4$ (**3a**) along with the oxonium salt $[(AuPPh_3)_3(\mu_3\text{-}O)]ClO_4$.

Various attempts to prepare the imido complexes $[(AuPR_3)_3(\mu_3\text{-}NH)]ClO_4$ proved unsuccessful. We studied the reactions of **2b** and [Au(acac-κC^2)(PR_3)] (R = C_6H_4OMe-4), 1:1, at 0 °C in CH_2Cl_2 for 10 min or at −60 °C in THF for 5 min. Upon addition of diethyl ether, the ^{31}P NMR spectra of the isolated solids show them both to contain mixtures of the reagents along with the nitrido complex **3b**. Additionally, in the reaction at −60 °C, a small amount of $[(AuPR_3)_3(\mu_3\text{-}O)]^+$ is present. The reaction of **2a** with [Au(acac-κC^2)(PPh_3)], 1:1, at room temperature under nitrogen atmosphere using degassed CH_2Cl_2, gives after 10 min of stirring a mixture of the starting complexes and the oxonium salt $[(AuPPh_3)_3(\mu_3\text{-}O)]ClO_4$. On the other hand, the reaction of $(NH_4)ClO_4$ with [Au(acac-κC^2)(PPh_3)] (1:3, in THF, 1 h) gives upon concentration and addition of diethyl ether a solid whose $^{31}P\{^1H\}$ NMR shows the presence of **1a**, **3a**, and $[(AuPPh_3)_3(\mu_3\text{-}O)]ClO_4$. The species $[(AuPR_3)_3(NH)]^+$ is observed in the FAB mass spectrum of **3b**.

The syntheses of the nitrido complexes $[(AuPR_3)_4(\mu_4\text{-}N)]ClO_4$ [R = Ph (**3a**), C_6H_4OMe-4 (**3b**)] are easily achieved by reacting $(NH_4)ClO_4$ with [Au(acac-κC^2)(PR_3)] in a 1:4 or 1:5 molar ratio (see Scheme 1). Our method is simpler and gives a higher yield than those previously reported for the two tetraaurated compounds $[(AuL)_4(\mu_4\text{-}N)]BF_4$ (L = PPh_3, PMe_3), prepared by reacting $[(AuL)_3(\mu_3\text{-}O)]BF_4$ with NH_3, $(Me_3Si)_2NH$, or $[(Me_3PAu)_3(\mu_3\text{-}NSiMe_3)]^+$.[6,8] While in the ^{31}P NMR of **3a** a poorly defined triplet is observed due to $^{31}P-^{14}N$ coupling, in the spectrum of **3b** a singlet is observed.

Similarly, the reactions of [Au(acac-κC^2)(PPh_3)] with the ammonium salts (NH_3R')OTf (1:1) (R′ = Me, $C_6H_4NO_2$-4; OTf = CF_3SO_3) (1:1) give the complexes $[Au(NH_2R')(PR_3)]OTf$ [R′ = Me (**4**), $C_6H_4NO_2$-4 (**5**)] (Scheme 2). The reaction of [Au(acac-κC^2)(PPh_3)] with $[H_3N(CH_2)_2NH_2]OTf$, which was intended to produce $[(AuPPh_3)\{NH_2(CH_2)_2NH_2\}]OTf$, gave instead the dinuclear complex $[(AuPPh_3)_2\{\mu_2\text{-}H_2N(CH_2)_2NH_2\}](OTf)_2$ (**6**) and $NH_2(CH_2)_2NH_2$. **6** can also be obtained, though in lower yield, by reacting [Au(acac-κC^2)(PPh_3)] with $[H_3N(CH_2)_2NH_3](OTf)_2$, 2:1. While there are a few reported $[Au(NH_2R')(PR_3)]^+$ complexes [R = Me, R′ = ^{t}Bu, $PhCH_2$;[6] R = Ph, R′ = $C_6H_4NO_2$-2, C_6H_4OMe-4[1]], complex **6** is the first dinuclear species of this type. A family of polyaurated diamines $[(AuPPh_3)_3N\text{-}X\text{-}N(AuPPh_3)]^{2+}$ [X = $(CH_2)_2$ and 1,4-, 1,3-, and 1,2-C_6H_4],[26] dendritic amines,[9] and mixed dinuclear complexes $[RAu\{H_2N(CH_2)_xNH_2\}AuL]^{n+}$ [n = 0, R = C_6F_5, L = Cl, C_6F_5,

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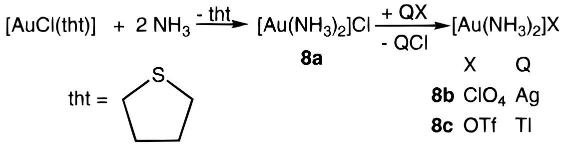
(26) Grohmann, A.; Schmidbaur, H. *Inorg. Chem.* **1992**, *31*, 3378.

Scheme 3. Synthesis of Complexes **8a**−**c**



$x = 2, 3$; $n = 1$, R = C_6F_5, X = PPh_3, $x = 2$][27] have also been reported.

We recently reported the synthesis of other monoaurated ammonium salts $[Au(L)(PPh_3)]^+$ (L = primary, secondary, or tertiary amine).[1] For primary and secondary amines, this study showed that the result depends on the nature of the solvent. The desired monoaurated ammonium salts could only be prepared in diethyl ether, in which they are insoluble. The failure to prepare such complexes in acetone was attributed to the fact that the corresponding acetone-soluble complexes $[Au(NH_nR_{3-n})(PPh_3)]^+$ ($n = 1, 2$) would react further with [Au(acac-κC^2)PPh$_3$)] to give di- and triaurated ammonium salts. I.e.: $[(AuL)(NH_nR_{3-n})]^+ + [Au(acac\text{-}\kappa C^2)L] \rightarrow [(AuL)_2(\mu_2\text{-}NH_{n-1}R_{3-n})]^+$; $[(AuL)_2(\mu_2\text{-}NH_{n-1}R_{3-n})]^+ + [Au(acac\text{-}\kappa C^2)L] \rightarrow [(AuL)_3(\mu_3\text{-}NH_{n-2}R_{3-n})]^+$. To prove this hypothesis, and because complexes of the type $[(AuL)_2(\mu_2\text{-}NR_2)]X$ are very rare,[4−7] we reacted $[Au(acac\text{-}\kappa C^2)(PR_3)]$ (R = Ph, C_6H_4OMe-4) with $(R'_2NH_2)OTf$ (R′ = Ph, Et) (2:1) in acetone. However, the complexes $[\{AuPR_3\}_3(\mu_3\text{-}O)]OTf$ [R = Ph (**7a**), C_6H_4OMe-4 (**7b**)] were obtained, certainly as a result of the hydrolysis of the desired $[(AuPR_3)_2(\mu_2\text{-}NR'_2)]^+$ complexes (Scheme 2). Similar behavior was previously observed for $[Au(PPh_3)(qncd)]BF_4$, which in the presence of traces of water gives quinuclidinium and oxonium salts.[10] $[(AuPR_3)_3(\mu_3\text{-}O)]X$ salts are known for a variety of phosphines and anions, although not with $P(C_6H_4OMe\text{-}4)_3$ or with OTf.[7,28−33] They are usually prepared from coordinatively unsaturated R_3PAu^+ cations in alkaline or acid media with better yields than obtained by our method. Recently, $[(LAu)_4(\mu_4\text{-}O)]^{2+}$ (L = PR_3, R = Ph, *o*-tolyl) complexes have been reported.[34]

Recently, Mingos presented a preliminary report of the synthesis of several $[Au(NH_3)_2]X$ salts by bubbling ammonia through a solution of $[Au(NCPh)_2]X$ (X = BF_4, SbF_6; yield approximately 90%) or by introducing NH_3 into a solution of $[AuBr_2]^-$ (yield not specified but lower than those of the other salts).[20] Since one of us prepared [AuCl(tht)] (tht = tetrahydrothiophene) and showed for the first time its synthetic utility,[35] most gold chemists have used it as starting material.[36] Therefore, it seems interesting to show that it can also be used to prepare $[Au(NH_3)_2]^+$, rather than the less familiar $[Au(NCPh)_2]^+$ complex.[21,33,37] In fact, bubbling NH_3 through a solution of [AuCl(tht)] (tht = tetrahydrothiophene) in acetone precipitates the complex $[Au(NH_3)_2]Cl$ (**8a**) quantitatively (Scheme 3). Other salts could be prepared by reacting **8a** with the corresponding silver or thallium salt. Thus, by reaction of **8a** with $AgClO_4$ or TlOTf, and after removal of AgCl or TlCl, $[Au(NH_3)_2]X$ [X = ClO_4 (**8b**) or OTf (**8c**)] can be isolated in high (72−92%) yield. These two salts behave in solution as 1:1 electrolytes. The insolubility of **8a** precludes conductivity measurements. We have formulated it according to the structure of its bromide analogue.[20]

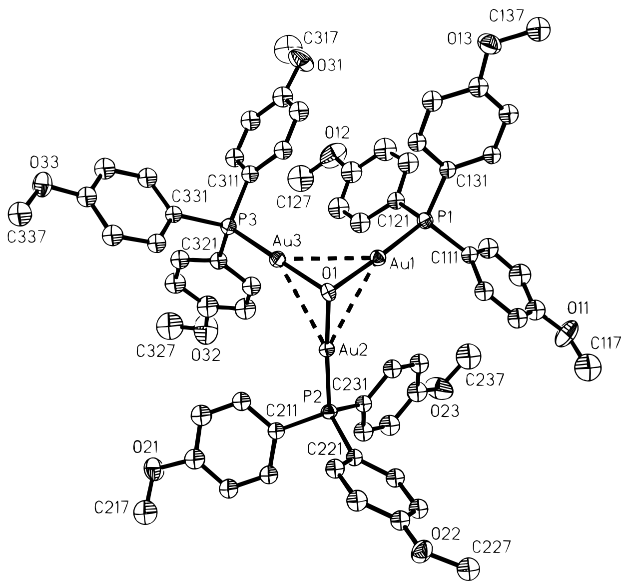


Figure 1. ORTEP diagram showing the labeling scheme of the asymmetric unit of **7b**·Me_2CO. H atoms are omitted for clarity.

Crystal Structure of 7b. The crystal structure of **7b**·Me_2CO has been determined (see Figure 1). Like all previous crystal structures of trigold oxonium compounds,[29−32] it shows a nearly trigonal pyramidal array of three gold atoms and one oxygen atom with O−Au−P bond angles of *ca.* 175°. The Au−O [2.026(5)−2.066(4) Å], Au−P [2.210(2)−2.222(2) Å], and Au···Au distances [2.9585(7)−3.0505(14) Å] and the Au−O−Au bond angles [91.5(2)−96.5(2)°] are in the ranges found in one crystalline form of its homologue with PPh_3.[30] The $[(AuPR_3)_3(\mu_3\text{-}O)]^+$ cations are combined via interionic Au_4

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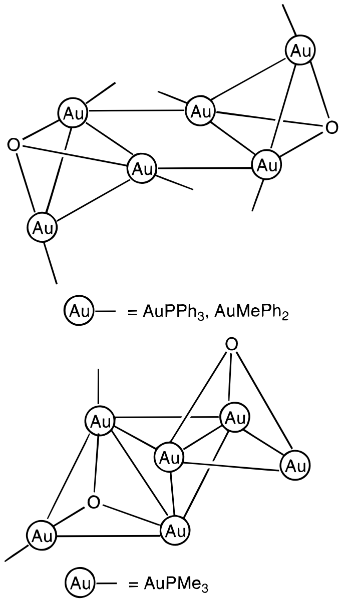
Chart 1



aggregations into centrosymmetric dimers. The gold atoms of the dimer form a six-membered ring with a chair conformation. This type of intermolecular bonding is also found in the structures of complexes with PPh_2Me and PPh_3 (see Chart 1).[29,30] Other trigold oxonium compounds with bulkier phosphines (R = *o*-tolyl,[30] ^{i}Pr[32]) have been isolated as monomeric cations without intermolecular Au···Au bonding, whereas in the analogue with the smallest tertiary phosphine, PMe_3, the Au_4 core is tetrahedral (see Chart 1).[31]

Intermolecular bond distances Au(1)−Au(3#) in **7b** [3.0919(9) Å] are significantly longer than the intramolecular Au···Au. This represents a difference from all other such complexes, in which inter- and intramolecular contacts are similar.[29−31] However, the intermolecular Au···Au bond distances in **7b** are some of the shortest reported [cf. 3.162(6)[29] and 3.1332(9)[30] for L = PPh_3, 3.220(1)−3.312 Å for L = PMe_3,[31] but 3.0616(12) Å for L = PPh_2Me[30]].

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (Project PB92-0982-C) and the Fonds der Chemischen Industrie for financial support. R.G. and M.C.R.d.A. thank the Ministerio de Educación y Ciencia (Spain) for a Grant and for a Contract, respectively.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure of **7b**·Me_2CO is available on the Internet only. Access information is given on any current masthead page.

IC970225J