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Gold(I) and Silver(I)/Gold(I) Complexes Derived from $C_6Me_4(C{\equiv}CH)_2$-1,2

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$C_6Me_4(C{\equiv}CH)_2$-1,2 [$Ar(C{\equiv}CH)_2$] reacts with $PPN[Au(acac)_2]$ (acac = acetylacetonato, PPN = $(Ph_3P)_2N$) (2:1) or with $[AuCl(SMe_2)]$ and NEt_3 (1:2:2) to give $PPN[Au\{C{\equiv}CArC{\equiv}CH\}_2]$ (**1**) or $[Au_2\{\mu\text{-}Ar(C{\equiv}C)_2\}]_n$ (**2**), respectively. Dinuclear complexes of general formula $[Au_2L_2\{\mu\text{-}Ar(C{\equiv}C)_2\}]$ can be obtained by reacting **2** with the appropriate ligand L (1:2) [L = ^tBuNC (**3**), PMe_3 (**4**), PTo_3 (**5**, To = C_6H_4Me-4)] or L_2 (1:1) (L_2 = $Ph_2P(CH_2)_nPPh_2$, *n* = 4 (**6**), 6 (**7**)]. The analogous complexes $[(AuNHEt_2)_2\{\mu\text{-}Ar(C{\equiv}C)_2\}]$ (**8**) and $[\{AuC(NH^tBu)(NEt_2)\}_2\{\mu\text{-}Ar(C{\equiv}C)_2\}]$ (**9**) result from the reactions of $Ar(C{\equiv}CH)_2$ with $PPN[AuCl_2]$ and $NHEt_2$ (1:2:4) or **3** with an excess of $NHEt_2$, respectively. The reaction of **5** with $AgClO_4$ (2:1) gives the heteropentanuclear "AgAu$_4$" complex $[Ag\{(AuPTo_3)_2\{\mu\text{-}Ar(C{\equiv}C)_2\}\}_2]ClO_4$ (**10**). The X-ray crystal structures of **3**, **7**, **9**·1/3$CHCl_3$, and **10**·2$CHCl_3$ have been determined.

Introduction

Metal complexes with bridging $R(C{\equiv}C)_2^{2-}$ spacers (−R− being various aromatic rings) have been shown to display electrical conductivity and nonlinear optical or liquid crystalline properties.[1] Among the many arenediethynyl metal complexes described so far, there is no *ortho*-disubstituted derivative of gold and few such derivatives of other metals; thus, only three of them have been structurally characterized by X-ray diffraction methods, namely, $[C_6H_4(C{\equiv}CSnMe_3)_2$-1,2],[2] $[C_6H_4\{C{\equiv}CPdCl(PEt_3)_2\}_2$-1,2], and $[C_6H_4\{C{\equiv}CPd(PEt_3)_2\}_2$-1,2$]_4$.[3] The known neutral arenediethynyl gold complexes are of the types (i) $[Au_2\{\mu\text{-}R(C{\equiv}C)_2\}]_n$,[4,5] (ii) $[(AuL)_2\{\mu\text{-}R(C{\equiv}C)_2\}]$ (L = phosphine,[5,6] isocyanide[4,5]), (iii) $[(Au_2L_2)\{\mu\text{-}R(C{\equiv}C)_2\}]_n$ (L_2 = diphosphine,[1,5] diisocyanide),[4,5] (iv) $[AuCl\{\{(\mu\text{-}PP)Au\{\mu\text{-}R(C{\equiv}C)_2\}Au\}_n(\mu\text{-}PP)AuCl]$ (PP = diphosphine),[1] and (v) $[\{Au_2\{\mu\text{-}R(C{\equiv}C)_2\}\}_2(\mu\text{-}PP)_2\}]$,[6] derived from the dialkynes $R(C{\equiv}CH)_2$ [R = C_6H_4-1,4, ($C_6H_2Me_2$-2,5)-1,4 or (C_6H_3Me)-3,5]. Three of them were characterized by X-ray crystallography,[5,7] showing infinite chain or ribbon structures, and displayed interesting photophysical properties.[7] The latter have been attributed in part[8,9] to the short intermolecular Au···Au contacts that are present in most of the structurally characterized luminescent gold(I) complexes.[5,7,8,10] Puddephatt has recently reviewed the synthesis and characterization of polymers, rings, and oligomers containing gold(I) centers.[11]

On the basis of our previous experience on the synthesis of alkynylgold(I) complexes[12−16] by the "acac method",[17] we have described some new arenediethynylgold(I) complexes of the types i and ii,[18,19] R being C_6Me_4-1,4, C_6H_4-1,3, C_6HMe_3-2,4,6, and also $PPN[Au\{C{\equiv}CC_6H_4C{\equiv}CAuPPh_3\text{-}3\}_2]$, $(PPN)_2[(AuX)_2\{\mu\text{-}C_6HR_3\text{-}2,4,6\text{-}(C{\equiv}C)_2\}]$ (R = H, X = Cl; R = Me, X = Cl, SCN), $(PPN)_3[Au\{C{\equiv}CC_6H_4C{\equiv}CAuCl\text{-}3\}_2]$,[18] and $[\{AuC(NEt_2)$-

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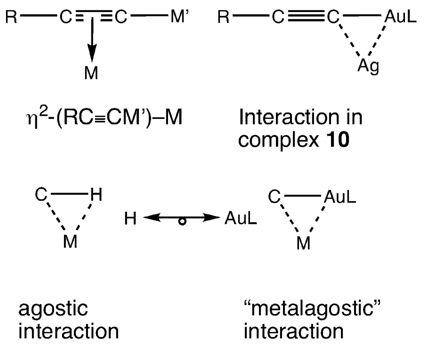
Chart 1



$(NH^{t}Bu)\}_2\{C{\equiv}CC_6H_4C{\equiv}C\text{-}3\}]$.[20] Using the same method, we have recently reported the synthesis and crystal structure of the heteronuclear metallamacrocyclic triangle $PPN[\{Au\{Pt(PMe_3)_2\}_2\}\{\mu\text{-}Ar(C{\equiv}C)_2\}_3]$[21] (Ar = C_6Me_4-3,4,5,6) by reacting *trans*-$[Pt(C{\equiv}CArC{\equiv}CH\text{-}2)_2(PMe_3)_2]$ with $PPN[Au(acac)_2]$. The growing interest in the search for novel metallamacrocycles is associated with their ability to mimic biological systems and their relationship with supramolecular chemistry, intramolecular self-assembly, molecular recognition, crystal engineering, nanotechnology, and catalysis. The concepts, principles, and strategies on which the development of this chemistry is based have recently been widely reviewed.[22–24] Despite the connection of metallamacrocyclic complexes with such varied and interesting fields, the triangular architecture is surprisingly scarce[24] compared to the number of molecular polygons described to date.[23–25] Therefore, *ortho*-arenediethynyl complexes could serve as building blocks to construct molecular triangles selectively, or at least preferentially, if the C≡C−M−C≡C group is linear, because the ligand has the appropriate disposition [C≡CM−(aryl centroid)−MC≡C angle = 60°].

In this paper, we report the first *ortho*-arenediethynyl gold(I) complexes including neutral and anionic species and a cationic pentanuclear "Au_4Ag" complex resulting from the use of two molecules of $[(AuPTo_3)_2\{\mu\text{-}Ar(C{\equiv}C)_2\}]$ acting as ligands toward Ag(I). Related alkynyl-metal complexes have been structurally characterized, showing η^2-(RC≡CM′)−M interactions (see Chart 1; M = Ag, M′ = Ti,[26,27] Ru,[28] Re,[29] Rh,[30,31] Ir,[30] Pt,[32,33] Cu,[34] Ag,[35] Au,[36] and Hg[37]). Two or three η^2-RC≡CM′ ligands per Ag(I) are generally involved in such interactions, and only three complexes with four such alkynyl ligands disposed around one Ag(I), none of them containing gold as does our complex, have been structurally characterized.[27,33] Taking into account the isolobal character of H and $AuPR_3$,[38] our pentanuclear "Au_4Ag" complex can be considered as containing four C−($AuPR_3$)···Ag "agostic" interactions,[39] which could be termed "metalagostic" contacts (see Chart 1). Although Au···Ag interactions are not as common as the Au···Au aurophilic interactions, they have been observed previously.[40,41]

Experimental Section

General Comments. IR spectroscopy, mass spectrometry ($FAB^{+/-}$), elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described elsewere.[42] The molar conductivity of the neutral complexes gave very low values (0−5 Ω^{-1} cm^2 mol^{-1}). The NMR spectra were measured on Bruker Avance 200, 300, or 400 MHz spectrometers. Chemical shifts are referred to TMS (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). Unless otherwise stated the reactions were carried out at room temperature without any precautions to avoid oxygen or moisture. The syntheses of $C_6Me_4(C{\equiv}CH)_2$-1,2,[43] $PPN[Au(acac)_2]$,[44] and $[AuCl(SMe_2)]$[45] were previously reported. All other chemicals were obtained from commercial sources and used as received. The solvents were distilled before use.

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Synthesis of PPN[Au{C≡CArC≡CH}$_2$]·0.5H$_2$O (1). To a solution of $C_6Me_4(C{\equiv}CH)_2$-1,2 [$Ar(C{\equiv}CH)_2$] (204 mg, 1.12 mmol) in CH_2Cl_2 (5 mL) was added a solution of PPN[Au(acac)$_2$] (261 mg, 0.28 mmol) in the same solvent (5 mL). The mixture was stirred for 5 h and then filtered through a short pad of anhydrous $MgSO_4$. The solution was concentrated under reduced pressure to dryness and the solid residue stirred with Et_2O (3 × 20 mL). The suspension was filtered to give a brown powder, which was dried under reduced pressure (ca. 1 mbar) to give **1**. Yield: 187 mg, 61%. Mp: 163 °C (dec). Anal. Calcd for $C_{64}H_{57}AuNO_{0.5}P_2$: C, 69.44; H, 5.19; N, 1.27. Found: C, 69.42; H, 4.89; N, 1.14. IR (cm^{-1}): ν(CH), 3305(w); ν(C≡C), 2093(w). Λ_M (Ω^{-1} cm^2 mol^{-1}): 76. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.37 (m, 30 H, PPN), 3.21 (s, 2 H, ≡CH), 2.44 (s, 6 H, Me), 2.36 (s, 6 H, Me), 2.14 (s, 12 H, Me) 1.8 (br, 1 H, H_2O). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.9 (m, *p*-PPN), 131.9 (m, *o*-PPN), 129.5 (m, *m*-PPN), 126.8 (d, *i*-PPN, $^1J_{CP}$ = 108 Hz), 96.6 (C≡C), 83.6 (≡CH), 82.5 (*C*≡CH), 19.1 (Me), 18.7 (Me), 16.9 (Me), 16.5 (Me). MS-FAB$^-$ (*m/z*, %): 559 (M$^-$, 50%).

Synthesis of [Au$_2${*μ*-Ar(C≡C)$_2$}]$_n$ (2). A suspension of [AuCl(SMe$_2$)] (1.480 g, 5 mmol) and $Ar(C{\equiv}CH)_2$ (458 mg, 2.5 mmol) in a mixture of CH_2Cl_2 (20 mL) and NEt_3 (0.750 mL) was stirred for 15 min. The suspension was filtered and the solid washed with CH_2Cl_2 (2 × 10 mL) and Et_2O (10 mL) and dried under reduced pressure (ca. 1 mbar) to give **4** as a pale brown solid, which proved to be insoluble in all common solvents. Yield: 1.31 g, 91%. Mp: 120 °C (dec). Anal. Calcd for $C_{14}H_{12}Au_2$: C, 29.29; H, 2.11. Found: C, 30.42; H, 2.29 (see Discussion). IR (cm^{-1}): ν(C≡C), 2018(w), 1970(br).

Synthesis of [(AuL)$_2${*μ*-Ar(C≡C)$_2$}] [L = ^{t}BuNC (3), PMe$_3$ (4), PTo$_3$ (5, To = C$_6$H$_4$Me-4)]. To a suspension of **2** (**3**: 435 mg, 0.76 mmol; **4**: 506 mg, 0.88 mmol; **5**: 417 mg, 0.73 mmol) in CH_2Cl_2 (20 mL) was added the appropriate ligand (**3**, ^{t}BuNC: 0.180 mL, 1.6 mmol; **4**, PMe$_3$: 1 M in toluene, 2.2 mL, 2.2 mmol; **5**, PTo$_3$: 464 mg, 1.5 mmol). The resulting solution (**3**, **5**) or suspension (**4**) was stirred at room temperature for 10 (**3**) or 30 min (**4**, **5**) (**4**, under a nitrogen atmosphere). The solution was filtered thorugh a short pad of Celite, the solvent was removed under vacuum to dryness, and the solid residue was stirred with 2 × 20 mL of *n*-pentane (**3**) or Et_2O (**5**) and filtered. Pale yellow microcrystals of **3** or a white amorphous powder of **5**·0.6Et$_2$O were obtained after recrystallizing the crude solids from CH_2Cl_2/*n*-pentane or CH_2Cl_2/Et_2O, respectively, and drying at reduced pressure for 1 h. The bright yellow suspension of **4** was filtered and the solid washed with Et_2O (2 × 15 mL) and dried at reduced pressure for 1 h. **4** is insoluble in all common solvents.

3: Yield: 430 mg, 76%. Mp: 142 °C (dec). Anal. Calcd for $C_{24}H_{30}Au_2N_2$: C, 38.93; H, 4.08; N, 3.78. Found: C, 38.57; H, 3.94; N, 3.65. IR (cm^{-1}): ν(C≡N), 2216(s); ν(C≡C), 2134(w). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.48 (s, 6 H, Me), 2.16 (s, 6 H, Me), 1.48 (s, 18 H, ^{t}Bu). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 147.7 (CN), 135.1, 132.8, 130.1, 126.1, 103.4 (C≡C), 57.8 (*C*Me$_3$), 29.5 (C*Me$_3$*), 18.6 (Me), 16.6 (Me). Crystals of **3** suitable for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a solution of the compound in $CDCl_3$.

4: Yield: 0.533 g, 83%. Mp: 174 °C (dec). Anal. Calcd for $C_{20}H_{30}Au_2P_2$: C, 33.07; H, 4.16. Found: C, 33.44; H, 4.27. IR (cm^{-1}): ν(C≡C), 2090 (w).

5·0.6Et$_2$O: Yield: 612 mg, 71%. Mp: 174 °C. Anal. Calcd for $C_{58.4}H_{60}Au_2O_{0.6}P_2$ (**7**·0.6Et$_2$O): C, 57.15; H, 4.93. Found: C, 57.54; H, 4.72. IR (cm^{-1}): No ν(C≡C) band is observed. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.49−7.39 (m, 12 H, PTo$_3$), 7.16−7.11 (m, 12 H, PTo$_3$), 3.46 (q, 2.4 H, CH$_2$, Et$_2$O), 2.57 (s, 6 H, Me), 2.32 (s, 18 H, Me, PTo$_3$), 2.19 (s, 6 H, Me), 1.21 (t, 3.6 H, Me, Et$_2$O). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 141.3 (m, *p*-PTo$_3$), 135.6, 134.3 (d, *o*-PTo$_3$, $^2J_{CP}$ = 14 Hz), 132.9, 129.5 (d, *m*-PTo$_3$, $^3J_{CP}$ = 6 Hz), 127.5 (d, *i*-PTo$_3$, $^1J_{CP}$ = 56 Hz), 125.4, 103.0 (d, CAu, $^2J_{CP}$ = 25 Hz), 65.8 (Et$_2$O), 21.4 (Me, PTo$_3$), 19.5 (Me), 16.8 (Me), 15.2 (Et$_2$O). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 40.79 (s, PTo$_3$).

Synthesis of [Au$_2${*μ*-Ar(C≡C)$_2$}{*μ*-Ph$_2$P(CH$_2$)$_n$PPh$_2$}] [*n* = 4 (6), 6 (7)]. To a suspension of **2** (**6**: 380 mg, 0.66 mmol; **7**: 133 mg, 0.23 mmol) in CH_2Cl_2 (20 mL) was added the appropriate diphosphine (**6**: dppb, 282 mg, 0.66 mmol; **7**: dpph, 105 mg, 0.23 mmol). The reaction mixture was stirred for 30 min (**7**) or 1 h (**6**) and filtered through a short column of Celite. The solution was concentrated to dryness (**6**) or to 1 mL (**7**), and Et_2O (20 mL) was added. The resulting suspension was filtered, and the white solid thus collected was air-dried.

6: Yield: 580 mg, 88%. Mp: 211 °C. Anal. Calcd for $C_{42}H_{40}Au_2P_2$: C, 50.41; H, 4.03. Found: C, 50.66; H, 3.97. IR (cm^{-1}): No ν(C≡C) band is observed. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.40 (m, 20 H, PPh$_2$), 2.55 (s, 6 H, Me), 2.39 (m, 4 H, CH$_2$), 2.18 (s, 6 H, Me), 1.93 (m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 134.5, 133.3 (d, *o*-Ph, $^2J_{CP}$ = 12 Hz), 132.8, 131.4 (*p*-Ph), 130.5 (d, *i*-Ph, $^1J_{CP}$ = 53 Hz), 129.0 (d, *m*-Ph, $^3J_{CP}$ = 10 Hz), 126.8, 103.8 (C≡C), 28.1 (d, AuPCH$_2$, $^1J_{CP}$ = 26 Hz), 25.9 (CH$_2$), 19.5 (Me), 16.6 (Me). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 36.01 (s). MS-FAB$^+$ (*m/z*, %): 1001 (M$^+$, 100%).

7: Yield: 168 mg, 71%. Mp: 233 °C (dec). Anal. Calcd for $C_{44}H_{44}Au_2P_2$: C, 51.37; H, 4.31. Found: C, 51.13; H, 4.35. IR (cm^{-1}): No ν(C≡C) band is observed. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71−7.43 (m, 20 H, Ph), 2.57 (s, 6 H, Me), 2.33 (m, 4 H, CH$_2$), 2.19 (s, 6 H, Me), 1.71 (m, 4 H, CH$_2$), 1.45 (m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.5, 135.8, 133.8 (d, *o*-Ph, $^2J_{CP}$ = 13 Hz), 133.4, 131.7 (d, *p*-Ph, $^4J_{CP}$ = 3 Hz), 131.5 (d, *i*-Ph, $^1J_{CP}$ = 52 Hz), 129.4 (d, *m*-Ph, $^3J_{CP}$ = 10 Hz), 126.3 (d, *C*≡CAu, $^3J_{CP}$ = 3 Hz), 103.0 (d, CAu, $^2J_{CP}$ = 27 Hz), 30.4 (d, CH$_2$, $^2J_{CP}$ = 17 Hz), 29.2 (d, CH$_2$, $^1J_{CP}$ = 34 Hz), 25.2 (d, CH$_2$, $^3J_{CP}$ = 6 Hz), 20.0 (Me), 17.2 (Me). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 37.51 (s). MS-FAB$^+$ (*m/z*, %): 1029 (M$^+$, 85%). Crystals of **7** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH_2Cl_2 and Et_2O.

Synthesis of [(AuNHEt$_2$)$_2${*μ*-Ar(C≡C)$_2$}] (8). To a mixture of $Ar(C{\equiv}CH)_2$ (85 mg, 0.46 mmol) and PPN[AuCl$_2$] (748 mg, 0.93 mmol) in degassed CH_2Cl_2 (15 mL) was added NHEt$_2$ (3 mL), and the solution was stirred under a nitrogen atmosphere for 2 h. The solvent was removed under reduced pressure, and the dry residue was stirred with a mixture of CH_2Cl_2 (5 mL) and NHEt$_2$ (10 mL). The suspension was filtered, and the white microcrystalline solid collected was dried under reduced pressure for 0.5 h. The limited stability of **8** in solution in the absence of NHEt$_2$ prevented measurement of its ^{13}C NMR spectrum. Yield: 274 mg, 83%. Mp: 113 °C (dec). Anal. Calcd for $C_{22}H_{34}Au_2N_2$: C, 36.68; H, 4.76; N, 3.89. Found: C, 36.70; H, 4.79; N, 3.95. IR (cm^{-1}): ν(NH), 3180(s); ν(C≡C), 2098(w). ^{1}H NMR (300 MHz,$CDCl_3$): δ 5.15 (m, 2 H, NH), 3.28 (m, 8 H, CH$_2$), 2.44 (s, 6 H, Me), 2.15 (s, 6 H, Me), 1.12 (m, 12 H, CH$_2$*Me*). Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **8** in a mixture of NHEt$_2$ and CH_2Cl_2. Although the crystallographic data showed the structure to be as expected, it could not be refined satisfactorily because of disordered ethyl groups.

Synthesis of [{AuC(NH^{t}Bu)NEt$_2$}$_2${*μ*-Ar(C≡C)$_2$}] (9). A solution of **3** (315 mg, 0.43 mmol) in a mixture of CH_2Cl_2 (10 mL) and NHEt$_2$ (2 mL) was stirred for 2 h and then filtered through Celite. The solution was concentrated under vacuum (to ca. 3 mL), and *n*-pentane (30 mL) was added. Upon stirring the resulting oily material with *n*-pentane (3 × 10 mL), a bright yellow powder formed, which was filtered and air-dried. Yield: 240 mg, 63%. Mp: 131 °C (dec). Anal. Calcd for $C_{32}H_{52}Au_2N_4$: C, 43.34; H, 5.91; N, 6.32. Found: C, 43.47; H, 5.89; N, 6.37. IR (cm^{-1}): ν(NH), 3338(s); ν(C≡C), 2097(s). ^{1}H NMR

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Table 1. Crystallographic Data for Complexes 3, 7, 9·1/3CHCl$_3$, and 10·2CHCl$_3$

	3	**7**	**9**·1/3CHCl$_3$	**10**·2CHCl$_3$
formula	$C_{24}H_{30}Au_2N_2$	$C_{44}H_{44}Au_2P_2$	$C_{32.33}H_{52.33}Au_2ClN_4$	$C_{114}H_{110}AgAu_4Cl_7O_4P_4$
M_r	740.43	1028.67	926.50	2811.79
cryst size (mm)	0.13 × 0.05 × 0.03	0.28 × 0.09 × 0.08	0.26 × 0.12 × 0.10	0.25 × 0.10 × 0.05
cryst syst	monoclinic	orthorhombic	rhombohedral	triclinic
space group	*C*2/*c*	*Pnna*	$R\bar{3}$	$P\bar{1}$
cell constants				
a, Å	14.6653(16)	19.1819(14)	36.7765(16)	15.0818(8)
b, Å	12.0080(14)	25.361(2)	36.7765(16)	17.2044(11)
c, Å	15.0930(16)	15.9512(11)	14.4639(11)	42.493(3)
α, deg	90	90	90	90.689(5)
β, deg	114.840(5)	90	90	98.936(5)
γ, deg	90	90	120	102.289(5)
V (Å^3), Z	2412.0(5), 4	7759.8(10), 8	16941.7(17), 18	10630.8(12), 4
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ(calc) (Mg m^{-3})	2.039	1.761	1.635	1.757
μ (mm^{-1})	12.162	7.666	7.879	5.970
F(000)	1384	3968	8088	5472
T (K)	133(2)	133(2)	133(2)	133(2)
$2\theta_{max}$ (deg)	60.06	50.06	60.08	50.06
no. of reflns measd	15549	78323	90439	134650
no. of indep reflns	3530	6871	11010	37232
transmissions	0.746 and 0.426	0.648 and 0.370	0.494 and 0.301	0.7545 and 0.3168
R_{int}	0.0476	0.0712	0.0413	0.1004
no. of data/rest/params	3530/24/132	6871/110/433	11010/81/377	37232/141/985
R_w(F^2, all reflns)	0.0520	0.1399	0.0693	0.0878
R(F, > 4σ(F))	0.0248	0.0609	0.0238	0.0491
max $\Delta\rho$ (e Å^{-3})	1.526/−0.893	3.108/−1.887	2.288/−1.674	1.761/−1.107

(400 MHz, CDCl$_3$): δ 5.81 (s, 2 H, NH), 4.06 (q, 4 H CH$_2$, $^3J_{HH}$ = 7 Hz,), 3.22 (q, 4 H, CH$_2$, $^3J_{HH}$ = 7 Hz), 2.52 (s, 6 H, Me), 2.15 (s, 6 H, Me), 1.64 (s, 18 H, ^{t}Bu), 1.27 (t, 6 H, Me, $^3J_{HH}$ = 7 Hz), 1.15 (t, 6 H, Me, $^3J_{HH}$ = 7 Hz). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 206.97 (AuCN$_2$), 135.6, 134.1, 132.2, 126.6, 105.4 ($C\equiv C$), 54.5 (*C*Me$_3$), 54.3 (CH$_2$), 54.2 (CH$_2$), 32.4 (C*Me$_3$*), 19.8 (Me), 17.2 (Me), 15.4 (CH$_2$*Me*), 15.3 (CH$_2$*Me*). Crystals of **9**·1/3CHCl$_3$ suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CHCl$_3$ and *n*-pentane.

Synthesis of [Ag{(AuPTo$_3$)$_2${μ-Ar(C≡C)$_2$}}$_2$]ClO$_4$ (10). To a solution of **5** (0.160 g, 0.14 mmol) in degassed CH$_2$Cl$_2$ (10 mL) was added a solution of AgClO$_4$ (0.014 g, 0.07 mmol) in Et$_2$O (5 mL), and the mixture was stirred under nitrogen atmosphere for 23 h, filtered through Celite, and concentrated to dryness under reduced pressure. The residue was stirred with Et$_2$O (20 mL) for 0.5 h, and the suspension was filtered. The microcrystalline yellow powder collected was washed with Et$_2$O (10 mL) and dried under vacuum. Yield: 155 mg, 86%. Mp: 207 °C (dec). Anal. Calcd for $C_{112}H_{108}AgAu_4ClO_4P_4$: C, 52.28; H, 4.23. Found: C, 52.03; H, 4.23. IR (cm^{-1}): ν(ClO), 1096(s). No ν($C\equiv C$) band is observed. Λ_M (Ω^{-1} cm^2 mol^{-1}): 129. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37−7.22 (m, 24 H, Ar, PTo$_3$), 6.96−6.95 (m, 24 H, Ar, PTo$_3$), 2.27 (s, 36 H, Me, PTo$_3$), 2.04 (s, 12 H, Me), 1.99 (s, 12 H, Me). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 141.2 (d, p-PTo$_3$, $^4J_{C\ P}$ = 3 Hz), 135.0, 134.1 (d, o-PTo$_3$, $^2J_{CP}$ = 14 Hz), 133.7, 130.3, 129.3 (d, m-PTo$_3$, $^3J_{CP}$ = 12 Hz), 126.7 (d, i-PTo$_3$, $^1J_{CP}$ = 59 Hz), 123.5, 109.9 (d, CAu, $^2J_{CP}$ = 25 Hz), 21.4 (Me, PTo$_3$), 19.1 (Me), 16.7 (Me). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ 37.52 (s, AuPTo$_3$). Crystals of **10**·2CHCl$_3$ suitable for an X-ray diffraction study were obtained by slow diffusion of Et$_2$O into a 1:1 acetone/CH$_2$Cl$_2$ solution.

X-ray Structure Determinations. Data were registered using Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer. Absorption corrections were based on multiple scans (program SADABS). Structures were refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). To improve stability of refinement, restraints to local ring symmetry and to light atom displacement factors were employed. Methyl hydrogens were identified in difference syntheses (for exceptions see below) and refined as rigid groups allowed to rotate but not tip; other hydrogens were included using a riding model. Crystal data are presented in Table 1. *Special features/exceptions*: Compound **7** displays U values that are rather high for low-temperature data (U_{eq} for C atoms up to 0.12 Å^2). Its methyl hydrogens were not found in difference syntheses and were therefore not included in the refinement (note that there is no reliable method of geometrically placing methyl hydrogens in the absence of a significant torsional energy barrier). The NH hydrogens of compound **9** were refined freely but with N−H distances restrained equal. The methyl hydrogen atoms at C12 and C13 were indistinct but were included in the refinement with higher U values. The chloroform molecule is ordered (with 3-fold symmetry) but has high U values. There is significant residual electron density near the 3-fold axis that might correspond to further (disordered) solvent, but no corresponding model could be refined, and these peaks were therefore neglected. For compound **10**, carbon atoms were refined isotropically and tolyl rings were refined as rigid groups with idealized geometry. All methyl hydrogen positions should be interpreted with caution. The four chloroform and two perchlorate residues were ordered, but some atoms displayed high U values.

Results and Discussion

Synthesis. The synthesis of PPN[Au{$C\equiv CArC\equiv CH$}$_2$] (Ar = C$_6$Me$_4$-3,4,5,6, **1**) from Ar($C\equiv CH$)$_2$ and PPN[Au(acac)$_2$] required a 2-fold excess of the alkyne over the stoichiometric 2:1 molar ratio (Scheme 1). In an attempt to prepare the triangular (PPN)$_3$[Au$C\equiv CArC\equiv C$]$_3$ we reacted Ar($C\equiv CH$)$_2$ with PPN[Au(acac)$_2$] (1:1), but, unfortunately, extensive decomposition to metallic gold took place.

Complex [Au$_2${μ-Ar(C≡C)$_2$}]$_n$ (**2**) was obtained by reacting Ar($C\equiv CH$)$_2$ with [AuCl(SMe$_2$)] and NEt$_3$ (1:2:2); Cl and SMe$_2$ ligands are displaced from the coordination sphere of gold by the Ar($C\equiv C$)$_2^{2-}$ ligand generated in situ by deprotonation of the dialkyne with the amine. The insolubility of complex **2** in all common organic solvents suggests it to be a polymer in which gold would complete its usual linear dicoordination with η^2-(RC≡CAu)−Au interactions, as found in related

Table 2. Selected Bond Lengths and Angles in $10\cdot 2CHCl_3$

Bond Lengths (Å)

Au(1)−C(1)	1.994(9)	Au(4)−Ag(1)	3.2009(9)	Au(6)−C(160)	1.995(10)
Au(1)−P(1)	2.275(3)	Ag(1)−C(1)	2.451(9)	Au(6)−P(6)	2.273(3)
Au(1)−Ag(1)	3.2240(9)	Ag(1)−C(10)	2.476(9)	Au(6)−Ag(2)	3.3328(9)
Au(2)−C(10)	1.997(10)	Ag(1)−C(15)	2.482(9)	Au(7)−C(165)	1.984(10)
Au(2)−P(2)	2.270(3)	Ag(1)−C(24)	2.482(9)	Au(7)−P(7)	2.278(3)
Au(2)−Ag(1)	3.1950(9)	Au(5)−C(151)	1.983(10)	Au(7)−Ag(2)	3.5134(9)
Au(3)−C(15)	1.967(10)	Au(5)−P(5)	2.269(3)	Ag(2)−C(160)	2.463(9)
Au(3)−P(3)	2.275(3)	Au(5)−Ag(2)	3.4457(9)	Ag(2)−C(165)	2.468(10)
Au(3)−Ag(1)	3.3397(9)	Au(8)−C(174)	1.999(10)	Ag(2)−C(174)	2.480(9)
Au(4)−C(24)	2.004(10)	Au(8)−P(8)	2.282(3)	Ag(2)−C(151)	2.498(10)
Au(4)−P(4)	2.277(3)	Au(8)−Ag(2)	3.1662(9)		

Bond Angles (deg)

C(1)−Au(1)−P(1)	173.3(3)	C(15)−Ag(1)−C(24)	112.0(3)	C(1)−C(2)−C(3)	178.8(11)
C(151)−Au(5)−P(5)	175.3(3)	C(174)−Ag(2)−C(151)	107.2(3)	C(151)−C(152)−C(153)	176.8(11)
C(10)−Au(2)−P(2)	175.8(3)	Au(2)−Ag(1)−Au(4)	89.06(2)	C(9)−C(10)−Au(2)	174.6(9)
C(174)−Au(8)−P(8)	179.7(3)	Au(8)−Ag(2)−Au(6)	73.63(2)	C(160)−C(159)−C(158)	176.0(11)
C(15)−Au(3)−P(3)	171.9(3)	Au(2)−Ag(1)−Au(1)	162.09(3)	C(9)−C(10)−Ag(1)	92.6(7)
C(160)−Au(6)−P(6)	171.6(3)	Au(8)−Ag(2)−Au(5)	74.80(2)	C(159)−C(160)−Au(6)	172.2(9)
C(24)−Au(4)−P(4)	172.0(3)	Au(2)−Ag(1)−Au(3)	72.15(2)	C(16)−C(15)−Au(3)	173.0(8)
C(165)−Au(7)−P(7)	173.5(3)	Au(6)−Ag(2)−Au(5)	148.29(3)	C(159)−C(160)−Ag(2)	91.6(7)
C(1)−Ag(1)−C(10)	110.4(3)	Au(4)−Ag(1)−Au(1)	108.29(2)	C(16)−C(15)−Ag(1)	89.4(6)
C(160)−Ag(2)−C(165)	103.0(3)	Au(8)−Ag(2)−Au(7)	159.08(3)	C(166)−C(165)−Au(7)	165.9(9)
C(1)−Ag(1)−C(15)	112.8(3)	Au(4)−Ag(1)−Au(3)	160.39(3)	C(15)−C(16)−C(17)	175.2(10)
C(160)−Ag(2)−C(174)	108.9(3)	Au(6)−Ag(2)−Au(7)	86.62(2)	C(174)−C(173)−C(172)	176.6(11)
C(1)−Ag(1)−C(24)	107.5(3)	Au(1)−Ag(1)−Au(3)	90.93(2)	C(24)−C(23)−C(22)	176.8(11)
C(160)−Ag(2)−C(151)	108.5(3)	Au(5)−Ag(2)−Au(7)	124.24(3)	C(173)−C(174)−Au(8)	178.0(9)
C(10)−Ag(1)−C(15)	105.0(3)	C(2)−C(1)−Au(1)	172.7(9)	C(23)−C(24)−Au(4)	172.3(9)
C(165)−Ag(2)−C(174)	116.6(3)	C(152)−C(151)−Au(5)	167.4(9)	C(173)−C(174)−Ag(2)	89.2(7)
C(10)−Ag(1)−C(24)	109.0(3)	C(2)−C(1)−Ag(1)	94.3(7)	C(23)−C(24)−Ag(1)	92.1(7)
C(165)−Ag(2)−C(151)	112.3(3)	C(152)−C(151)−Ag(2)	91.7(7)		

complexes;[46] the insolubility prevented us from measuring its NMR spectra and recrystallizing it to obtain good elemental analyses. However, its nature was proved by its reactivity toward different neutral ligands. Thus, **2** reacted with L (1:2) or L_2 (1:1) ligands to give complexes $[Au_2L_2\{\mu\text{-}Ar(C\equiv C)_2\}]$ [L = ^tBuNC (**3**), PMe_3 (**4**), PTo_3 (**5**, To = C_6H_4Me-4); L_2 = $Ph_2P(CH_2)_nPPh_2$, n = 4 (**6**), 6 (**7**)]. The analogous complex $[(AuNHEt_2)_2\{\mu\text{-}Ar(C\equiv C)_2\}]$ (**8**) was obtained by reacting PPN$[AuCl_2]$ with $Ar(C\equiv CH)_2$ and $NHEt_2$ in CH_2Cl_2 using a 2:1:4 molar ratio. One possible reaction pathway for this process would be the deprotonation of the alkyne by the base to give a monoalkynyl ligand, capable of replacing one of the chloro ligands in PPN$[AuCl_2]$ to give $[NH_2Et_2]Cl$ and PPN$[Au\{C\equiv CArC\equiv CH\}Cl]$, in which the chloro ligand would be substituted by $NHEt_2$ to give **8** and (PPN)Cl. This last step could be favored by the excess of base and the poor solubility of **8**, probably attributable to the formation of intermolecular hydrogen bonds. When complex **8** is dissolved in the absence of excess $NHEt_2$, it gradually decomposes to give **2** with liberation of $NHEt_2$, which prevented the measuring of its ^{13}C NMR spectrum. Although these results suggest the possibility of obtaining **8** by reacting **2** with $NHEt_2$, we have established that once it precipitates, **2** does not react with $NHEt_2$ even when it is used as the solvent.

The synthesis of carbenegold(I) complexes from the homologous isocyanide derivatives and primary or secondary amines is well documented,[15,47] and we have used this method to prepare $[\{AuC(NH^tBu)NEt_2\}_2\{\mu\text{-}Ar(C\equiv C)_2\}]$ (**9**) from (**3**) and $NHEt_2$. The alternative synthesis of **9** from the amine complex **8** and ^tBuNC failed since complex **2** precipitated instead. This result seems reasonable in view of the above-mentioned decomposition of **8** in the absence of excess $NHEt_2$ to give **2**, which only reacts with ^tBuNC to give **3** if the isocyanide is used in a large excess.

The reaction of **5** with $AgClO_4$ (2:1) gave the heteropentanuclear complex $[Ag\{(AuPTo_3)_2\{\mu\text{-}Ar(C\equiv C)_2\}\}_2]ClO_4$ (**10**) (Scheme 2) favored by both the limited coordinative ability of the perchlorate anion and the appropriate *ortho* disposition of the $C\equiv CAuPTo_3$ groups in **5**. Complex **10** behaves in acetone solution as a 1:1 electrolyte (Λ_M = 129 Ω^{-1} cm^2 mol^{-1}).[48] The related reaction between **3** and $AgClO_4$ gave a mixture of products in which $[Ag\{(AuCN^tBu)_2\{\mu\text{-}Ar(C\equiv C)_2\}\}_2]ClO_4$ was shown by NMR to be the major species, but unfortunately we could not obtain it pure even after repeated recrystallization. A complex mixture was also obtained when complex **6** was reacted with $AgClO_4$ (2:1).

X-ray Crystal Structures. The crystal structures of $[(AuCN^tBu)_2\{\mu\text{-}Ar(C\equiv C)_2\}]$ (**3**; Figures 1−3), $[Au_2\{\mu\text{-}Ar(C\equiv C)_2\}\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}]$ (**7**; Figure 4), $[\{AuC(NH^tBu)NEt_2\}_2\{\mu\text{-}Ar(C\equiv C)_2\}]\cdot 1/3CHCl_3$ (**9**·1/3$CHCl_3$; Figures 5 and 6), and $[Ag\{(AuPTo_3)_2\{\mu\text{-}Ar(C\equiv C)_2\}\}_2]ClO_4\cdot 2CHCl_3$ (**10**·2$CHCl_3$; Figure 7) have been determined. A comparative study of the structural data reveals many similarities regarding various structural parameters that vary only very slightly within these complexes. Thus, (i) the gold atoms are in essentially linear environments [angles at gold: 174.28(16)−178.96(14)°], (ii) the C≡C bond distances are in the narrow range of 1.184(11)−1.214(5) Å, (iii) the $Au-C_{alkynyl}$ bond distances [1.979(4)−2.031(15) Å] are similar for all complexes and seem to depend only slightly on the nature of the other ligands, (iv) the Au−P distances in the

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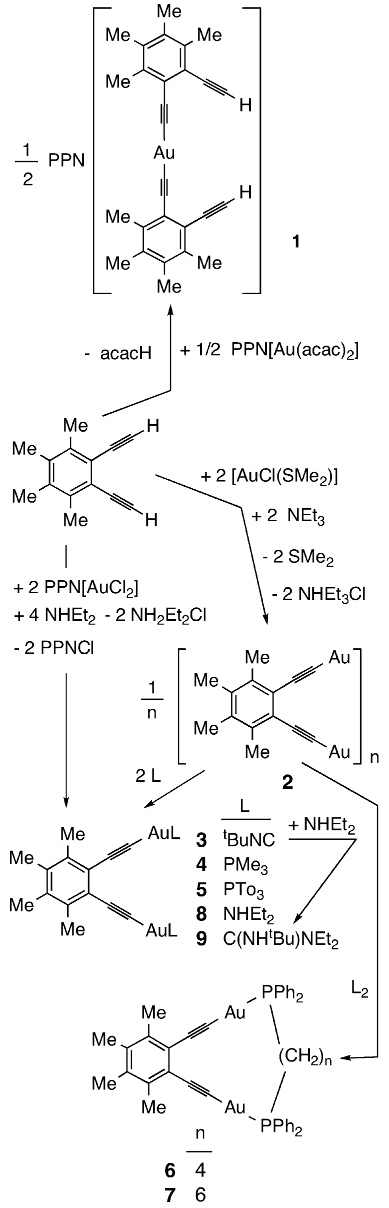
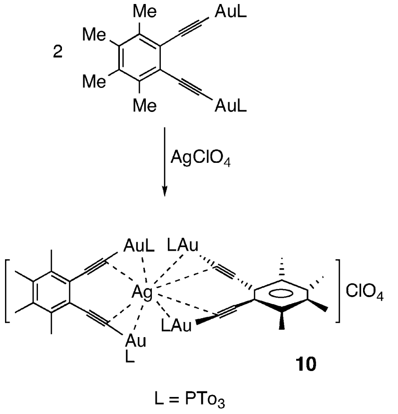
Scheme 1



Scheme 2



alkynyl(phosphine)gold(I) are in the range 2.270(3)–2.278(3) Å, and (v) the distances Au–$C_{\text{trans to alkynyl}}$ are in the range 1.970(4)–2.046(3) Å. All these values are consistent with those found for other (alkynyl)Au(I) complexes.[49]

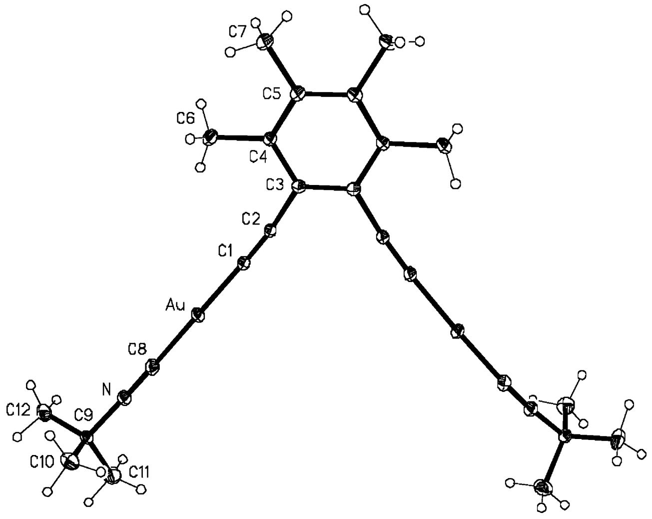


Figure 1. Thermal ellipsoid plot (30% probability) of **3**. Selected bond lengths (Å) and angles (deg): Au–C(8) 1.970(4), Au–C(1) 1.979(4), N–C(8) 1.148(5), N–C(9) 1.472(5), C(1)–C(2) 1.197(5), C(8)–Au–C(1) 174.28(16), C(8)–N–C(9) 172.9(4), C(2)–C(1)–Au 176.5(3), C(1)–C(2)–C(3) 174.1(4), N–C(8)–Au 173.5(4).

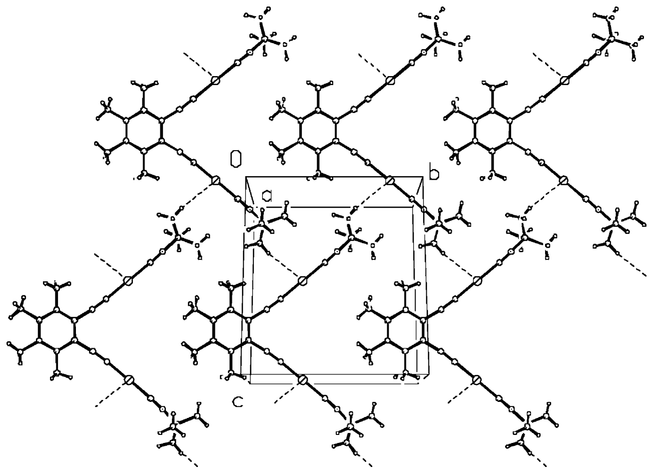


Figure 2. One of the layers in the crystal of **3**. The shortest intermolecular distances in the sheets correspond to C–H···Au contacts (H···Au = 2.95 Å, C–H···Au = 159°).

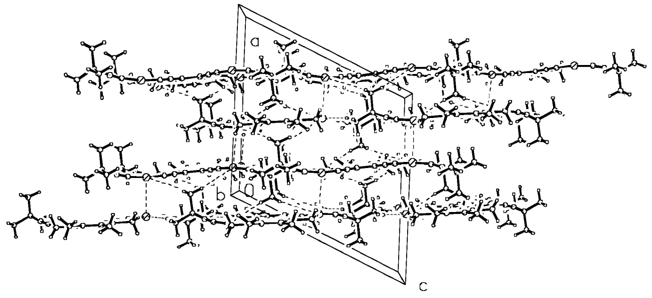


Figure 3. Packing diagram for complex **3** viewed parallel to the layers. The shortest distances between layers correspond to C–H···Au (H···Au = 2.94, 3.06 Å, C–H···Au = 161, 136°), and Au···Au [3.5692(4) Å] contacts.

The molecule of **3** (Figure 1) displays crystallographic 2-fold symmetry. The molecules pack in sheets (Figure 2), parallel to the planes (40−2), which, in turn, stack to give a three-dimensional supramolecular structure

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[49] CCDC *CSD version 5.25*, December 2004.

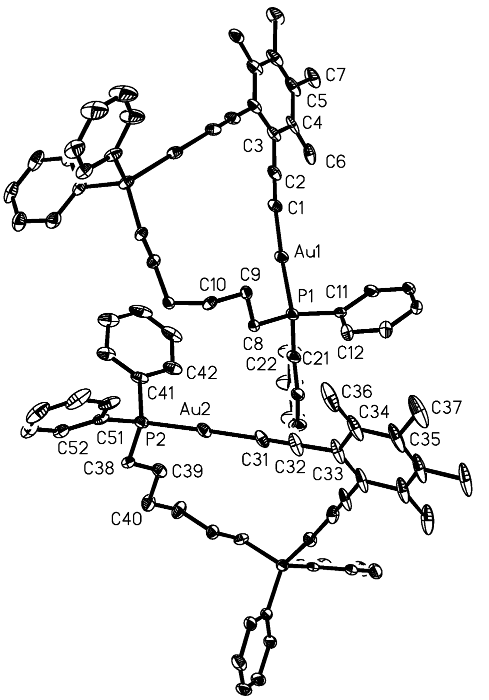

Figure 4. Thermal ellipsoid plot (20% probability) of **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 1.990(13), Au(1)−P(1) 2.275(4), Au(2)−C(31) 2.031(15), Au(2)−P(2) 2.278(3), C(1)−C(2) 1.211(18), C(31)−C(32) 1.169(19), C(1)−Au(1)−P(1) 175.1(4), C(31)−Au(2)−P(2) 176.9(4), C(2)−C(1)−Au(1) 170.8(13), C(1)−C(2)−C(3) 178.0(15), C(32)−C(31)−Au(2) 178.0(13), C(31)−C(32)−C(33) 178.7(16).

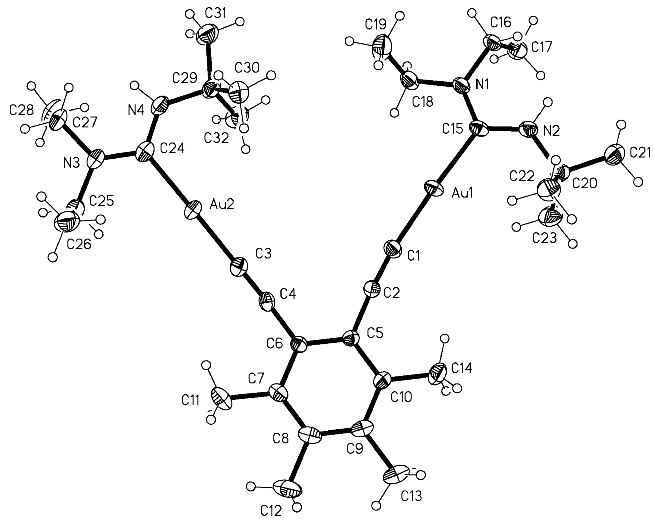

Figure 5. Thermal ellipsoid plot (50% probability) of **9**·1/3$CHCl_3$ (solvent omitted). Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 1.986(3), Au(1)−C(15) 2.046(3), Au(2)−C(3) 1.980(3), Au(2)−C(24) 2.046(3), N(1)−C(15) 1.338(4), N(2)−C(15) 1.345(4), N(3)−C(24) 1.342(4), N(4)−C(24) 1.334(5), C(1)−C(2) 1.214(4), C(3)−C(4) 1.214(5), C(1)−Au(1)−C(15) 177.05(13), C(3)−Au(2)−C(24) 178.96(14), C(2)−C(1)−Au(1) 173.5(3), C(4)−C(3)−Au(2) 176.0(3).

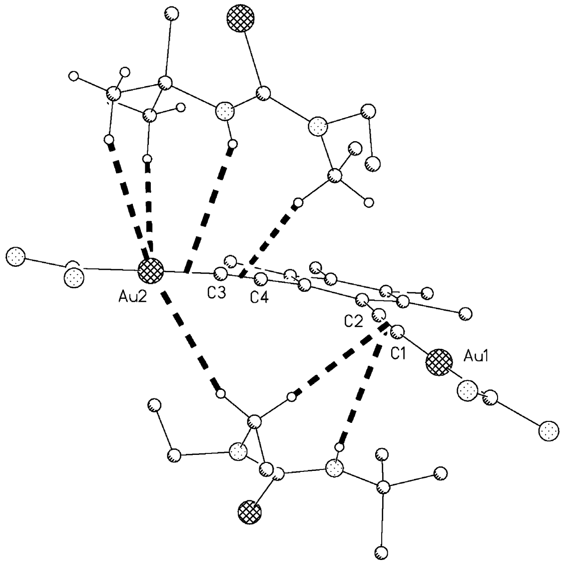

Figure 6. Short intermolecular contacts in the packing of complex **9**. Only the relevant molecular fragments are shown; the parent molecule is in the middle. For further explanation see text.

(Figure 3). This packing seems to be attributable to C-H···Au intermolecular interactions, which could be established since the methyl hydrogen sites were clearly identified in the X-ray analysis. Thus, the shortest intermolecular distances, normalized to C−H 1.08 Å for all structures in this paper, correspond to C−H···Au intralayer [C(12)−H(12B)···Au#5; H···Au = 2.95 Å, C···Au = 3.982(4) Å, C−H···Au = 159°, Figure 2] or interlayer interactions [C(10)−H(10A)···Au#3; H···Au = 2.94 Å, C···Au = 3.979(5) Å, C−H···Au = 161° and C(10)−H(10B)···Au#4; H···Au = 3.06 Å, C···Au = 3.912(4) Å, C−H···Au = 136°, Figures 2 and 3]. Weak Au···Au contacts [3.5692(4) Å] are also observed. These H···Au and Au···Au distances are slightly longer than the sum of the van der Waals radii of the corresponding elements (H···Au = 2.86 Å; Au···Au = 3.32 Å),[50] but the C−H···Au bond angles are in the range found in "classical" C−H···E (E = O,[51] N)[52] or O−H···O=C[51] and N−H···O[53] hydrogen bonds. The distinction between hydrogen bonds and van der Waals interactions is mainly based on the directionality of the former versus the isotropic character of the latter, while the lengthening of the H···E distance by less than 0.3 Å, as in **3**, has not been considered critical.[51] In the past few years an increasing number of nonclassical hydrogen bond interactions, including X−H···M,[54,55] have been reported, M being an electron-rich metal and X being, in most cases, N or O but also C. Some of the latter involve gold.[20,56,57] They are different from agostic interactions, which produce narrower angles.[39] Although the search

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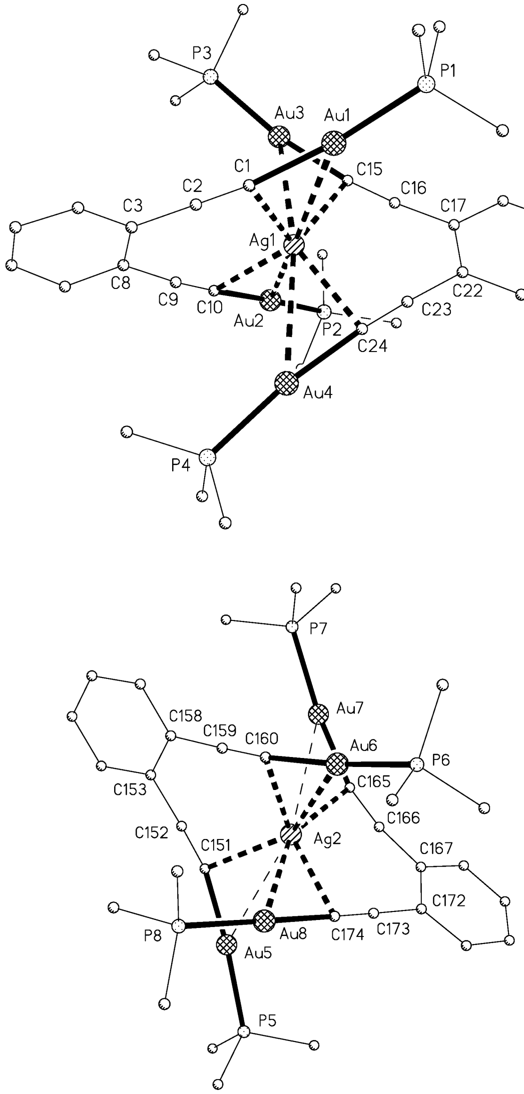

Figure 7. Ball-and-stick plot of both cations of **10**·2CHCl$_3$. For clarity, hydrogen atoms are omitted and the To groups are represented by the *ipso* carbon. Selected bond lengths (Å) and angles (deg) are listed in Table 2.

for C−H···M interactions is not well integrated into common program systems and, in many cases, such interactions fail to be reported,[58] we suggest that they should be routinely taken into account since by themselves, or acting cooperatively with Au···Au,[55,59] they could explain the packing architecture in many complexes, particularly when no other stronger intermolecular interactions are present. We point out however the criterion that the hydrogen positions must be reliable, which is often not the case for methyl groups lacking significant torsional barriers; in the absence of significant electron density maxima corresponding to the hydrogen atoms, the refinement program will choose apparently sensible hydrogen positions that are, however, quite inappropriate. It should be noticed that in **3** and in [AuX(CNBu^t)] (X = Cl,[60] Br[61]), the C−H bonds involved in C−H···Au interactions belong to ^{t}BuNC ligands, suggesting that the polarity of the C−H bond could be enhanced by the proximity of the electronegative nitrogen atom. In addition, it has been shown that aurophilicity and hydrogen bonding can work cooperatively in assembling gold complexes into dimers, oligomers, three-dimensional structures, or even, despite unfavorable electrostatic interactions, infinite chains of cations.[13,42,57,62]

The crystal structure of **7** involves two independent molecules, each with 2-fold symmetry (Figure 4); for the lower numbered molecule, the 2-fold axis is parallel to the *x* axis and for the higher numbered molecule to the *z* axis. The connectivities are identical, but the conformations of the (CH$_2$)$_6$ chains are different; the torsion angles along the atom sequence P1−C8−C9−C10−C10′−C9′ are 176°, −70°, and −68°, but the corresponding values in the other molecule are 179°, 179°, and 77°. Each gold atom is bonded to one of the C≡C fragments of the Ar(C≡C)$_2$ ligand and to one of the phosphorus atoms of the 1,6-bis(diphenylphosphino)hexane ligand, resulting in a 16-membered metallamacrocycle. The great bite and flexibility of the diphosphine ligand, along with the *ortho* disposition of both ethynyl fragments, allow the gold atoms to be in essentially linear environments. The absence of reliable positions for the methyl hydrogens precludes the analysis of any associated short contacts that might be present.

The crystal structure of **9**·1/3CHCl$_3$ (Figure 5) shows a dinuclear complex in which both gold atoms are linearly coordinated. The Au−C$_{carbene}$ bond distance [2.046(3) Å] is similar to those found in other gold(I) carbene complexes previously described.[20,63,64] The skeleton of the carbene ligands is almost planar, the mean deviation of the seven-atom fragments C(NC$_2$)NHC from their respective mean planes being only 0.02 and 0.03 Å, whereby the gold atoms lie marginally outside these planes by 0.035(2) and 0.0557(2) Å. The C−NHBu^t distances [1.334(5), 1.345(4) Å] and C−NEt$_2$ [1.342(4), 1.338(4) Å] are similar to each other and intermediate between those corresponding to single and double C(sp^2)−N(sp^2) bonds.[65] Both the planar geometry and the similar C−N distances suggest extensive electronic delocalization in the fragment CN$_2$, analogous to that previously found in other carbene complexes.[16] Although the partial double character of the C−NHBu^t bond allows two possible conformations for the carbene ligand (*E* or *Z*), the crystal structure of **9** shows that only the *Z*-isomer is present, as has previously been found in other gold complexes with the same carbene.[16] This could have steric reasons since, in this isomer, the most bulky substituent (^{t}Bu) is *cis* with respect to the metallic fragment, thus avoiding contact with the more congested NEt$_2$ group.

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It is noticeable in Figure 5 that the butyl groups approach the gold atoms quite closely; the intramolecular 1,6-contacts are H(23A)···Au1 2.50, H(22C)···Au1 2.66, H(30C)···Au2 2.65, and H(32A)···Au2 2.59 Å. The angles at hydrogen are necessarily quite narrow (126−134°). The intermolecular contacts of **9** are complicated (Figure 6). In the absence of classical acceptors, the NH donors would be expected to seek regions of higher electron density such as multiple bonds. The donor N(2)−H(02), normalized to N−H 1.01 Å, approaches the bond C(3)−Au(2) with H···Cent 2.91 Å, angle 133°, operator (i) $2/3-y$, $1/3+x-y$, $1/3+z$ (Cent = bond midpoint). Similarly N(4)−H(04) is associated with the bond C(1)−C(2) with H···Cent 2.93 Å, angle 136°, operator (ii) $2/3+x-y$, $1/3+x$, $1/3-z$. Short C−H···π contacts are observed for C(27)−H(27A) to C(1)−C(2) [H···Cent 2.59 Å, angle 174°, operator (ii)] and C(16)−H(16A) to C(3)−C(4) [H···Cent 2.62 Å, angle 148°, operator (i)]. Finally, Au(2) is involved in three short C−H···Au contacts: from H(21C) (2.75 Å, 155°, operator (i)), H(22A) (2.99 Å, 146°, operator (i)), and H(27B) (2.98 Å, 157°, operator (ii)). The net effect of all these contacts is seen in Figure 6; the central molecule is connected with two neighboring molecules.

This plethora of contacts deserves further comment. First, any contact taken for itself might be considered marginally significant. Second, it is not clear in some cases whether a single atom or a bond should be regarded as the acceptor for the contact. Third, it is conceivable that the steric accessibility of the linear regions of the molecule enable closer packing, rather than that attractive interactions are involved. Nevertheless, the overall effect is impressive. Finally, the atom Au(1) may be involved in intermolecular interactions to methyl hydrogens at C(13) and C(14), but we are not convinced of the complete reliability of these hydrogen positions and so present no numerical values.

The asymmetric unit in the crystal structure of **10**·2$CHCl_3$ contains two pentanuclear "$AgAu_4$" cations, two perchlorate anions, and four molecules of chloroform. The two cations are qualitatively similar, consisting of a silver ion encased by four AuC≡C fragments (Figure 7), but nonetheless display some important differences, the second cation being less regular. The silver atom contacts with the four gold atoms [Ag(1)···Au: 3.2240(9), 3.1950(9), 3.3397(9), 3.2009(9) Å; Ag(2)···Au: 3.4457(9), 3.1662(9), 3.3328(9), 3.5134(9) Å] at distances shorter, with two exceptions for Ag(2), than the sum of the van der Waals radii of the elements (3.38 Å).[66] There are no Au···Au contacts at distances shorter than 4 Å. The four silver to α-carbon atoms distances [Ag(1)···C_α: 2.451(9), 2.476(9), 2.482(9), 2.482(9) Å; Ag(2)···C_α: 2.463(9), 2.468(10), 2.480(9), 2.498(10) Å] are in the range found in other complexes where the C≡C−Ag angle is, as in **10**, in the range 80−100° (2.242−2.595 Å; mean value 2.412 Å).[67] The Ag···C_β distances are appreciably longer (Ag(1): 2.755−2.808 Å; Ag(2): 2.633−2.803 Å). This unsymmetrical disposition of the silver atom with respect to the C≡C fragments is probably forced by the existing numismophilic[41] Ag···Au contacts. In fact, in Ag(η^2-RC≡CR′) complexes the Ag−C distances are similar and in the range 2.2−2.5 Å (mean value 2.295 Å).[68]

The gold atoms are disposed around the Ag(1) atom in a distorted square planar environment [mean deviation from least-squares plane: 0.11 Å; deviations of C atoms from plane: C(1), C(10) 1.4, C(15), C(24) −1.4 Å; Au(1)−Ag(1)−Au(3) 90.93(2)°, Au(2)−Ag(1)−Au(4) 89.06(2)°, Au(2)−Ag(1)−Au(1) 162.09(3)°, Au(4)−Ag(1)−Au(1) 108.29(2)°, Au(2)−Ag(1)−Au(3) 72.15(2)°, Au(4)−Ag(1)−Au(3) 160.39(3)°], while around Ag(2) the geometry is more distorted but still planar [mean deviation from least-squares plane: 0.06 Å; deviations of C atoms from plane: C(151) 1.2, C(160) 1.3, C(165) −1.4, C(174) −1.6 Å; Au(8)−Ag(2)−Au(6) 73.63(2)°, Au(8)−Ag(2)−Au(5) 74.80(2)°, Au(6)−Ag(2)−Au(5) 148.29(3)°, Au(8)−Ag(2)−Au(7) 159.08(3)°, Au(6)−Ag(2)−Au(7) 86.62(2)°, Au(5)−Ag(2)−Au(7) 124.24(3)°]. The four α-carbon atoms are in a pseudo-tetrahedral disposition with respect to the Ag(1) [range 105.0(3)−112.8(3)°, mean value 109.5°] or Ag(2) centers [range 103.0(3)−116.6(3)°, mean value 109.4°]. The mean Au−C···Ag angle is 96°. Taking into account the above data and the isolobal character of H and $AuPR_3$,[38] complex **10** can be considered as containing four C−($AuPR_3$)···Ag "agostic" interactions, which could be termed "metalagostic" contacts to distinguish them from the normal C−H···M agostic interactions (see Chart 1).[39]

Complex **10** shows for the first time the coordination of one Ag(I) to four "C≡CAu" fragments, although three silver complexes have been reported in which, as in **10**, four "C≡CM" (M = Pt, Ti)[27,33] fragments are disposed around silver. In [$\{Au(C_2Ph)_2\}_2(AgPPh_3)_2$] each $AgPPh_3$ group is bonded to two AuC≡CPh moieties.[34]

NMR Spectra. The insolubility of **2** precluded the measurement of its NMR spectra, while the slow decomposition of **8** in solution (see above) allowed us to measure only the ^1H NMR spectrum. In the ^{13}C NMR spectrum of **1** four resonances are observed for all the inequivalent Me groups (see Experimental Section), while in the ^1H NMR spectrum only three resonances are observed, one of them being twice the intensity of the others. As expected, in the spectra of complexes **2**, **3**, and **5**−**10** the Me groups in the C_6Me_4 fragment give rise to two singlets ($\Delta\delta$ = 0.05−0.38 ppm). In the ^1H NMR spectra, the resonances at lower field can be assigned to the Me groups in *ortho* position with respect to the C≡CAu fragments since the spectra of some (alkynyl)gold(I) complexes containing $C_6H_4(C{\equiv}C)_2$-1,3, C_6HMe_3-2,4,6-$(C{\equiv}C)_2$-1,3[19] and $C_6H_3N(C{\equiv}C)_2$-3,5[69] ligands allowed us to conclude that the C≡CAu fragments produce the deshielding of the H or CH_3 in *ortho* position with respect to those in *meta* position. The spectra show also the expected resonances for the auxiliary ligands in the ranges previously found for other alkynylgold(I) complexes with isocyanide,[4,19] phosphino,[12,15,70] carbene,[15,63] or diethylamino ligands.[15]

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The NMR spectra (^1H, ^{13}C, ^{31}P) of complex **10** show the equivalence of the four $AuPTo_3$ and the two C_6Me_6 groups.

IR Spectra. In the IR spectra of complexes **1**−**10** the ν(C≡C) stretching modes give rise to one (**1**, **3**, **4**, **8**, **9**, in the range 2090−2134 cm^{-1}) or two (**2**: 2108, 1970 cm^{-1}) weak absorptions (strong for **9**) or are not observed (**5**−**7**, **10**). The spectrum of **1** shows a weak absorption at 3305 cm^{-1} assignable to ν(C−H) in the C≡CH fragments. In the spectrum of **3** the strong band at 2216 cm^{-1} corresponds to the ν(C≡N) in the isocyanide ligand, while in those of **8** and **9**, one strong band at 3180 and 3338 cm^{-1}, respectively, are assignable to ν(N−H).

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Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **3**, **7**, **9**·1/3$CHCl_3$, and **10**·2$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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