

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

José Vicente,[†] María-Teresa Chicote,^{*,†} and Miguel M. Alvarez-Falcón

Grupo de Química Organometálica, Departamento de Química Inorgánica,
Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Peter G. Jones^{*,‡}

Institut für Anorganische und Analytische Chemie der Technischen Universität,
Postfach 3329, 38023 Braunschweig, Germany

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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 $[Au_2\{\mu-Ar(C\equiv C)_2\}]_n$ (**2**), respectively. Dinuclear complexes of general formula $[Au_2L_2\{\mu-Ar(C\equiv C)_2\}]$ can be obtained by reacting **2** with the appropriate ligand L (1:2) [L = t -BuNC (**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 $[(AuNHet_2)_2\{\mu-Ar(C\equiv C)_2\}]$ (**8**) and $[AuC(NH^tBu)(NEt_2)_2\{\mu-Ar(C\equiv C)_2\}]$ (**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 $[Ag\{(AuPTO_3)_2\{\mu-Ar(C\equiv C)_2\}_2\}ClO_4]$ (**10**). The X-ray crystal structures of **3**, **7**, **9**·1/3CHCl₃, and **10**·2CHCl₃ 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 arene-diethynyl 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, $[C_6H_4(C\equiv CSnMe_3)_2]_n$ -1,2,² $[C_6H_4\{C\equiv CPdCl(PET_3)_2\}_2]_n$ -1,2,³ and $[C_6H_4\{C\equiv CPd(PET_3)_2\}_2]_n$ -1,2.³ The known neutral arene-diethynyl gold complexes are of the types (i) $[Au_2\{\mu-R(C\equiv C)_2\}]_n$,^{4,5} (ii) $[(AuL)_2\{\mu-R(C\equiv C)_2\}]$ (L = phosphine,^{5,6} isocyanide^{4,5}), (iii) $[(Au_2L_2)\{\mu-R(C\equiv C)_2\}]_n$ (L_2 = diphosphine,^{1,5} diisocyanide),^{4,5} (iv) $[AuCl\{\{\mu-PP\}Au\{\mu-R(C\equiv C)_2\}Au\}_n(\mu-PP)-AuCl]$ (PP = diphosphine),¹ and (v) $[(Au_2\{\mu-R(C\equiv C)_2\})_2(\mu-PP)_2]$,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 $Au\cdots Au$ 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 arene-diethynylgold(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 $PPN[Au\{C\equiv CC_6H_4C\equiv CAuPPh_3-3\}_2]$, $(PPN)_2[AuX_2\{\mu-C_6HR_3-2,4,6-(C\equiv C)_2\}]$ ($R = H$, $X = Cl$; $R = Me$, $X = Cl$, SCN), $(PPN)_3[Au\{C\equiv CC_6H_4C\equiv CAuCl-3\}_2]$,¹⁸ and $[(AuC(NEt_2)-$

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[†] E-mail: mch@um.es; jvs1@um.es. Web: <http://www.um.es/gqo>.

[‡] E-mail: p.jones@tu-bs.de.

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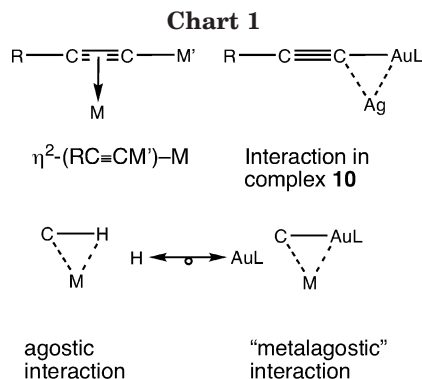
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(NH^tBu)₂{C≡CC₆H₄C≡C-3}.²⁰ Using the same method, we have recently reported the synthesis and crystal structure of the heteronuclear metallamacrocyclic triangle PPN[Au{Pt(PMe₃)₂}{μ-Ar(C≡C)₂}]₃ (Ar = C₆-Me₄-3,4,5,6) by reacting *trans*-[Pt(C≡CArC≡CH-2)₂(PMe₃)₂] 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 scarce²⁴ 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 “Au₄Ag” complex resulting from the use of two molecules of [(AuPTO₃)₂{μ-Ar(C≡C)₂}] acting as ligands toward Ag(I). Related alkynyl-metal complexes have been structurally characterized, showing η²-(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 Hg³⁷). Two or three η²-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 AuPR₃,³⁸ our pentanuclear “Au₄Ag” complex can be considered as containing four C–(AuPR₃)···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 auriphilic 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 elsewhere.⁴² The molar conductivity of the neutral complexes gave very low values (0–5 Ω^{–1} cm² mol^{–1}). The NMR spectra were measured on Bruker Avance 200, 300, or 400 MHz spectrometers. Chemical shifts are referred to TMS (¹H, ¹³C) or H₃PO₄ (³¹P). Unless otherwise stated the reactions were carried out at room temperature without any precautions to avoid oxygen or moisture. The syntheses of C₆Me₄(C≡CH)₂-1,2,⁴³ PPN[Au(acac)₂],⁴⁴ and [AuCl(SMe₂)]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]₂·0.5H₂O (1). To a solution of C₆Me₄(C≡CH)_{2-1,2} [Ar(C≡CH)₂] (204 mg, 1.12 mmol) in CH₂Cl₂ (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 MgSO₄. The solution was concentrated under reduced pressure to dryness and the solid residue stirred with Et₂O (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 C₆₄H₅₇AuNO_{0.5}P₂: 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 cm² mol⁻¹): 76. ¹H NMR (400 MHz, CDCl₃): 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, H₂O). ¹³C{¹H} NMR (100 MHz, CDCl₃): 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 [Au₂{μ-Ar(C≡C)₂}]_n (2). A suspension of [AuCl(SMe₂)] (1.480 g, 5 mmol) and Ar(C≡CH)₂ (458 mg, 2.5 mmol) in a mixture of CH₂Cl₂ (20 mL) and NEt₃ (0.750 mL) was stirred for 15 min. The suspension was filtered and the solid washed with CH₂Cl₂ (2 × 10 mL) and Et₂O (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 C₁₄H₁₂Au₂: 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 = ^tBuNC (3), PMe₃ (4), PTO₃ (5, To = C₆H₄Me-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 CH₂Cl₂ (20 mL) was added the appropriate ligand (3, ^tBuNC: 0.180 mL, 1.6 mmol; 4, PMe₃: 1 M in toluene, 2.2 mL, 2.2 mmol; 5, PTO₃: 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 through 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 Et₂O (5) and filtered. Pale yellow microcrystals of **3** or a white amorphous powder of **5**·0.6Et₂O were obtained after recrystallizing the crude solids from CH₂Cl₂/*n*-pentane or CH₂Cl₂/Et₂O, respectively, and drying at reduced pressure for 1 h. The bright yellow suspension of **4** was filtered and the solid washed with Et₂O (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 C₂₄H₃₀Au₂N₂: 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). ¹H NMR (200 MHz, CDCl₃): δ 2.48 (s, 6 H, Me), 2.16 (s, 6 H, Me), 1.48 (s, 18 H, ^tBu). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 147.7 (CN), 135.1, 132.8, 130.1, 126.1, 103.4 (C≡C), 57.8 (CMe₃), 29.5 (CMe₃), 18.6 (Me), 16.6 (Me). Crystals of **3** suitable for an X-ray diffraction study were obtained by slow diffusion of Et₂O into a solution of the compound in CDCl₃.

4: Yield: 0.533 g, 83%. Mp: 174 °C (dec). Anal. Calcd for C₂₀H₃₀Au₂P₂: C, 33.07; H, 4.16. Found: C, 33.44; H, 4.27. IR (cm⁻¹): ν(C≡C), 2090 (w).

5·0.6Et₂O: Yield: 612 mg, 71%. Mp: 174 °C. Anal. Calcd for C_{58.4}H₆₀Au₂O_{0.6}P₂ (7·0.6Et₂O): C, 57.15; H, 4.93. Found: C, 57.54; H, 4.72. IR (cm⁻¹): No ν(C≡C) band is observed. ¹H NMR (200 MHz, CDCl₃): δ 7.49–7.39 (m, 12 H, PTO₃), 7.16–7.11 (m, 12 H, PTO₃), 3.46 (q, 2.4 H, CH₂, Et₂O), 2.57 (s, 6 H, Me), 2.32 (s, 18 H, Me, PTO₃), 2.19 (s, 6 H, Me), 1.21 (t, 3.6 H, Me, Et₂O). ¹³C{¹H} NMR (50.3 MHz, CDCl₃): δ 141.3 (m,

p-PTO₃), 135.6, 134.3 (d, *o*-PTO₃, ²J_{CP} = 14 Hz), 132.9, 129.5 (d, *m*-PTO₃, ³J_{CP} = 6 Hz), 127.5 (d, *i*-PTO₃, ¹J_{CP} = 56 Hz), 125.4, 103.0 (d, CAu, ²J_{CP} = 25 Hz), 65.8 (Et₂O), 21.4 (Me, PTO₃), 19.5 (Me), 16.8 (Me), 15.2 (Et₂O). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ 40.79 (s, PTO₃).

Synthesis of [Au₂{μ-Ar(C≡C)₂}]_n{μ-Ph₂P(CH₂)_nPPh₂}] [n** = 4 (6), 6 (7)].** To a suspension of **2** (6: 380 mg, 0.66 mmol; 7: 133 mg, 0.23 mmol) in CH₂Cl₂ (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 Et₂O (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 C₄₂H₄₀-Au₂P₂: C, 50.41; H, 4.03. Found: C, 50.66; H, 3.97. IR (cm⁻¹): No ν(C≡C) band is observed. ¹H NMR (400 MHz, CDCl₃): δ 7.69–7.40 (m, 20 H, PPh₂), 2.55 (s, 6 H, Me), 2.39 (m, 4 H, CH₂), 2.18 (s, 6 H, Me), 1.93 (m, 4 H, CH₂). ¹³C{¹H} NMR (50 MHz, CDCl₃): 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, AuPCH₂, ¹J_{CP} = 26 Hz), 25.9 (CH₂), 19.5 (Me), 16.6 (Me). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 36.01 (s). MS-FAB⁺ (*m/z*, %): 1001 (M⁺, 100%).

7: Yield: 168 mg, 71%. Mp: 233 °C (dec). Anal. Calcd for C₄₄H₄₄Au₂P₂: C, 51.37; H, 4.31. Found: C, 51.13; H, 4.35. IR (cm⁻¹): No ν(C≡C) band is observed. ¹H NMR (400 MHz, CDCl₃): δ 7.71–7.43 (m, 20 H, Ph), 2.57 (s, 6 H, Me), 2.33 (m, 4 H, CH₂), 2.19 (s, 6 H, Me), 1.71 (m, 4 H, CH₂), 1.45 (m, 4 H, CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): 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, CH₂, ²J_{CP} = 17 Hz), 29.2 (d, CH₂, ¹J_{CP} = 34 Hz), 25.2 (d, CH₂, ³J_{CP} = 6 Hz), 20.0 (Me), 17.2 (Me). ³¹P{¹H} NMR (162 MHz, CDCl₃): 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 CH₂Cl₂ and Et₂O.

Synthesis of [(AuNHET₂)₂{μ-Ar(C≡C)₂}] (8). To a mixture of Ar(C≡CH)₂ (85 mg, 0.46 mmol) and PPN[AuCl₂] (748 mg, 0.93 mmol) in degassed CH₂Cl₂ (15 mL) was added NHET₂ (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 CH₂Cl₂ (5 mL) and NHET₂ (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 NHET₂ prevented measurement of its ¹³C NMR spectrum. Yield: 274 mg, 83%. Mp: 113 °C (dec). Anal. Calcd for C₂₂H₃₄Au₂N₂: 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). ¹H NMR (300 MHz, CDCl₃): δ 5.15 (m, 2 H, NH), 3.28 (m, 8 H, CH₂), 2.44 (s, 6 H, Me), 2.15 (s, 6 H, Me), 1.12 (m, 12 H, CH₂Me). 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 NHET₂ and CH₂Cl₂. 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^tBu)NEt₂}]₂{μ-Ar(C≡C)₂}] (9). A solution of **3** (315 mg, 0.43 mmol) in a mixture of CH₂Cl₂ (10 mL) and NHET₂ (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 C₃₂H₅₂-Au₂N₄: 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). ¹H NMR

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Table 1. Crystallographic Data for Complexes **3**, **7**, **9**·1/3CHCl₃, and **10**·2CHCl₃

	3	7	9 ·1/3CHCl ₃	10 ·2CHCl ₃
formula	C ₂₄ H ₃₀ Au ₂ N ₂	C ₄₄ H ₄₄ Au ₂ P ₂	C _{32.33} H _{52.33} Au ₂ ClN ₄	C ₁₁₄ H ₁₁₀ AgAu ₄ Cl ₇ O ₄ P ₄
<i>M_r</i>	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	<i>C2/c</i>	<i>Pnna</i>	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$
cell constants				
<i>a</i> , Å	14.6653(16)	19.1819(14)	36.7765(16)	15.0818(8)
<i>b</i> , Å	12.0080(14)	25.361(2)	36.7765(16)	17.2044(11)
<i>c</i> , 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)
<i>V</i> (Å ³), <i>Z</i>	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
<i>F</i> (000)	1384	3968	8088	5472
<i>T</i> (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
<i>R</i> _{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
<i>R_w</i> (<i>F</i> ² , all reflns)	0.0520	0.1399	0.0693	0.0878
<i>R</i> (<i>F</i> , > 4 σ (<i>F</i>))	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, CDCl₃): δ 5.81 (s, 2 H, NH), 4.06 (q, 4 H CH₂, ³*J*_{HH} = 7 Hz), 3.22 (q, 4 H, CH₂, ³*J*_{HH} = 7 Hz), 2.52 (s, 6 H, Me), 2.15 (s, 6 H, Me), 1.64 (s, 18 H, ^tBu), 1.27 (t, 6 H, Me, ³*J*_{HH} = 7 Hz), 1.15 (t, 6 H, Me, ³*J*_{HH} = 7 Hz). ¹³C{¹H} NMR (50 MHz, CDCl₃): δ 206.97 (AuCN₂), 135.6, 134.1, 132.2, 126.6, 105.4 (C=C), 54.5 (CMe₃), 54.3 (CH₂), 54.2 (CH₂), 32.4 (CMe₃), 19.8 (Me), 17.2 (Me), 15.4 (CH₂Me), 15.3 (CH₂Me). Crystals of **9**·1/3CHCl₃ suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CHCl₃ and *n*-pentane.

Synthesis of [Ag{(AuPTO₃)₂(μ -Ar(C $\equiv$ C)₂)₂}ClO₄ (10**).** To a solution of **5** (0.160 g, 0.14 mmol) in degassed CH₂Cl₂ (10 mL) was added a solution of AgClO₄ (0.014 g, 0.07 mmol) in Et₂O (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 Et₂O (20 mL) for 0.5 h, and the suspension was filtered. The microcrystalline yellow powder collected was washed with Et₂O (10 mL) and dried under vacuum. Yield: 155 mg, 86%. Mp: 207 °C (dec). Anal. Calcd for C₁₁₂H₁₀₈AgAu₄ClO₄P₄: 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 cm² mol⁻¹): 129. ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.22 (m, 24 H, Ar, PTO₃), 6.96–6.95 (m, 24 H, Ar, PTO₃), 2.27 (s, 36 H, Me, PTO₃), 2.04 (s, 12 H, Me), 1.99 (s, 12 H, Me). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.2 (d, p-PTO₃, ⁴*J*_{C-P} = 3 Hz), 135.0, 134.1 (d, o-PTO₃, ²*J*_{CP} = 14 Hz), 133.7, 130.3, 129.3 (d, m-PTO₃, ³*J*_{CP} = 12 Hz), 126.7 (d, i-PTO₃, ¹*J*_{CP} = 59 Hz), 123.5, 109.9 (d, CAu, ²*J*_{CP} = 25 Hz), 21.4 (Me, PTO₃), 19.1 (Me), 16.7 (Me). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 37.52 (s, AuPTO₃). Crystals of **10**·2CHCl₃ suitable for an X-ray diffraction study were obtained by slow diffusion of Et₂O into a 1:1 acetone/CH₂Cl₂ solution.

X-ray Structure Determinations. Data were registered using Mo K α 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:* Com-

pound **7** displays *U* values that are rather high for low-temperature data (*U*_{eq} for C atoms up to 0.12 Å²). 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 = C₆Me₄-3,4,5,6, **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[AuC $\equiv$ 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 [Au₂{ μ -Ar(C $\equiv$ C)₂}]_{*n*} (**2**) was obtained by reacting Ar(C $\equiv$ CH)₂ with [AuCl(SMe₂)] and NEt₃ (1:2:2); Cl and SMe₂ ligands are displaced from the coordination sphere of gold by the Ar(C $\equiv$ C)₂²⁻ 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 $\equiv$ CAu)–Au interactions, as found in related

Table 2. Selected Bond Lengths and Angles in 10·2CHCl₃

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 L₂ (1:1) ligands to give complexes [Au₂L₂{μ-Ar(C≡C)₂}] [L = ^tBuNC (**3**), PMe₃ (**4**), PtO₃ (**5**, To = C₆H₄Me-4); L₂ = Ph₂P(CH₂)_nPPh₂, n = 4 (**6**), 6 (**7**)]. The analogous complex [(AuNHET₂)₂{μ-Ar(C≡C)₂}] (**8**) was obtained by reacting PPN[AuCl₂] with Ar(C≡CH)₂ and NHET₂ in CH₂Cl₂ 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[AuCl₂] to give [NH₂Et₂]Cl and PPN[Au{C≡CArC≡CH}Cl], in which the chloro ligand would be substituted by NHET₂ 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 NHET₂, it gradually decomposes to give **2** with liberation of NHET₂, which prevented the measuring of its ¹³C NMR spectrum. Although these results suggest the possibility of obtaining **8** by reacting **2** with NHET₂, we have established that once it precipitates, **2** does not react with NHET₂ 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 [(AuCN^tBu)NEt₂]₂{μ-Ar(C≡C)₂} (**9**) from (**3**) and NHET₂. 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 NHET₂ to give **2**, which only reacts with ^tBuNC to give **3** if the isocyanide is used in a large excess.

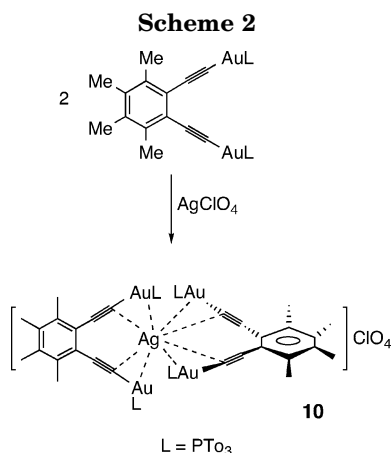
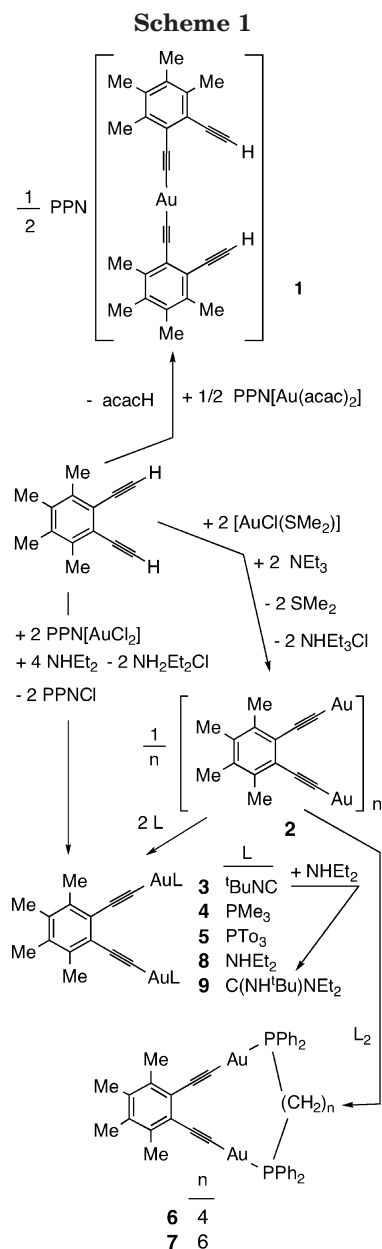
The reaction of **5** with AgClO₄ (2:1) gave the heteropentannuclear complex [Ag{(AuPTO₃)₂{μ-Ar(C≡C)₂}₂}-ClO₄] (**10**) (Scheme 2) favored by both the limited coordinative ability of the perchlorate anion and the appropriate *ortho* disposition of the C≡CAuPTO₃ groups in **5**. Complex **10** behaves in acetone solution as a 1:1 electrolyte (Λ_M = 129 Ω⁻¹ cm² mol⁻¹).⁴⁸ The related reaction between **3** and AgClO₄ gave a mixture of products in which [Ag{(AuCN^tBu)₂{μ-Ar(C≡C)₂}₂}]ClO₄ 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 AgClO₄ (2:1).

X-ray Crystal Structures. The crystal structures of [(AuCN^tBu)₂{μ-Ar(C≡C)₂}] (**3**; Figures 1–3), [Au₂{μ-Ar(C≡C)₂}]{μ-Ph₂P(CH₂)₆PPh₂} (**7**; Figure 4), [(AuCNH^tBu)NEt₂]₂{μ-Ar(C≡C)₂}·1/3CHCl₃ (**9**·1/3CHCl₃; Figures 5 and 6), and [Ag{(AuPTO₃)₂{μ-Ar(C≡C)₂}₂}]ClO₄·2CHCl₃ (**10**·2CHCl₃; 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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alkynyl(phosphine)gold(I) are in the range 2.270(3)–2.278(3) Å, and (v) the distances Au–C_{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

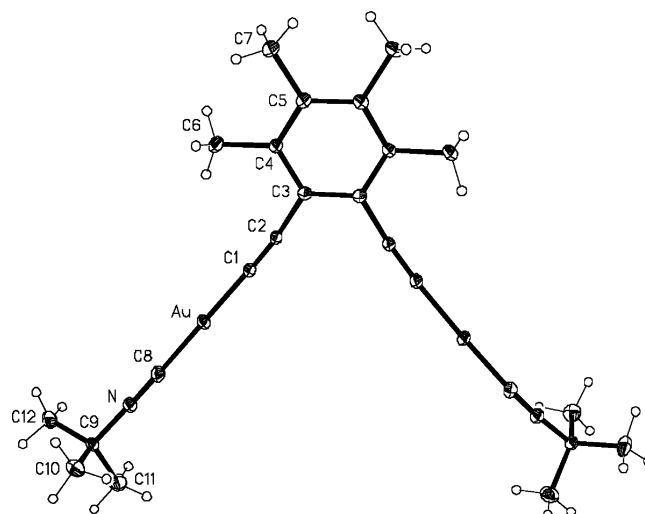


Figure 1. Thermal ellipsoid plot (30% probability) of **3**. Selected bond lengths (Å) and angles (deg): Au–C(8) 1.970(4), Au–C(1) 1.979(4), N–C(8) 1.148(5), N–C(9) 1.472(5), C(1)–C(2) 1.197(5), C(8)–Au–C(1) 174.28(16), C(8)–N–C(9) 172.9(4), C(2)–C(1)–Au 176.5(3), C(1)–C(2)–C(3) 174.1(4), N–C(8)–Au 173.5(4).

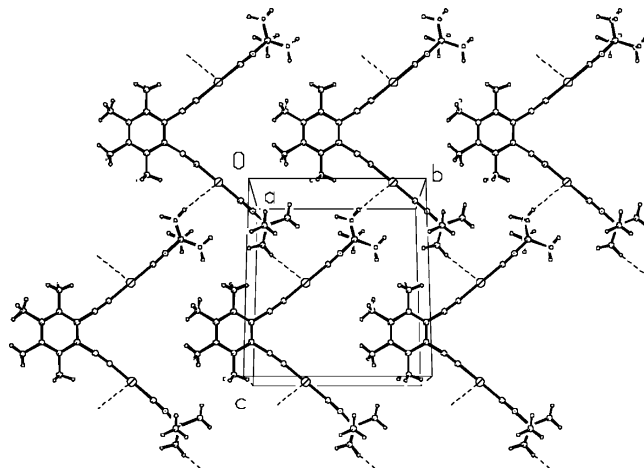


Figure 2. One of the layers in the crystal of **3**. The shortest intermolecular distances in the sheets correspond to C–H···Au contacts (H···Au = 2.95 Å, C–H···Au = 159°).

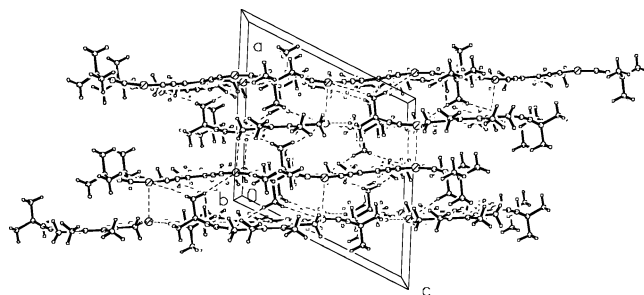


Figure 3. Packing diagram for complex **3** viewed parallel to the layers. The shortest distances between layers correspond to C–H···Au (H···Au = 2.94, 3.06 Å, C–H···Au = 161, 136°), and Au···Au [3.5692(4) Å] contacts.

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

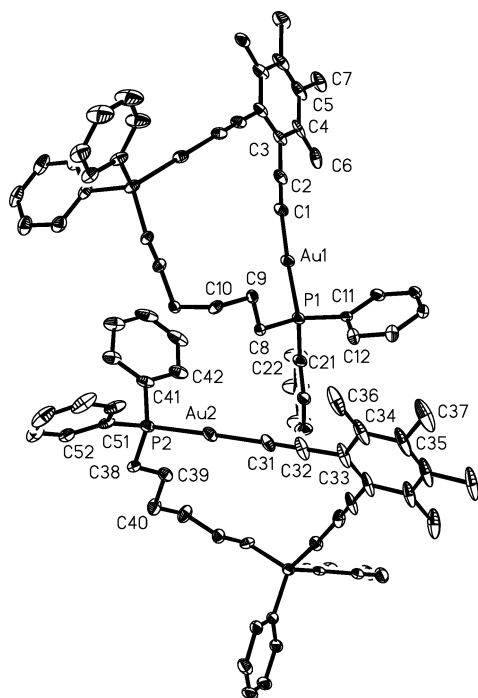


Figure 4. Thermal ellipsoid plot (20% probability) of **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)–C(1) 1.990(13), Au(1)–P(1) 2.275(4), Au(2)–C(31) 2.031(15), Au(2)–P(2) 2.278(3), C(1)–C(2) 1.211(18), C(31)–C(32) 1.169(19), C(1)–Au(1)–P(1) 175.1(4),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

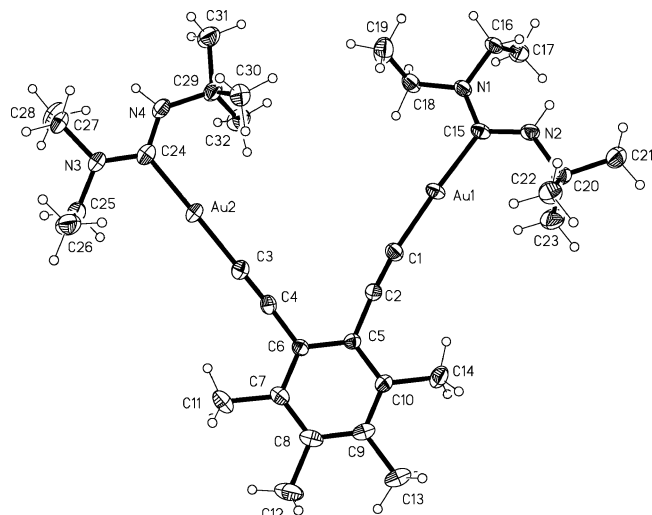


Figure 5. Thermal ellipsoid plot (50% probability) of **9**·1/3CHCl₃ (solvent omitted). Selected bond lengths (Å) and angles (deg): Au(1)–C(1) 1.986(3), Au(1)–C(15) 2.046(3), Au(2)–C(3) 1.980(3), Au(2)–C(24) 2.046(3), N(1)–C(15) 1.338(4), N(2)–C(15) 1.345(4), N(3)–C(24) 1.342(4), N(4)–C(24) 1.334(5), 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 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

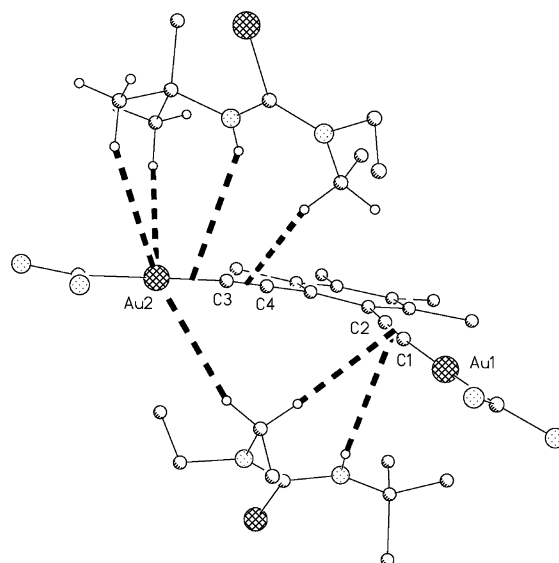


Figure 6. Short intermolecular contacts in the packing of complex **9**. Only the relevant molecular fragments are shown; the parent molecule is in the middle. For further explanation see text.

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=C⁵¹ and N–H···O⁵³ 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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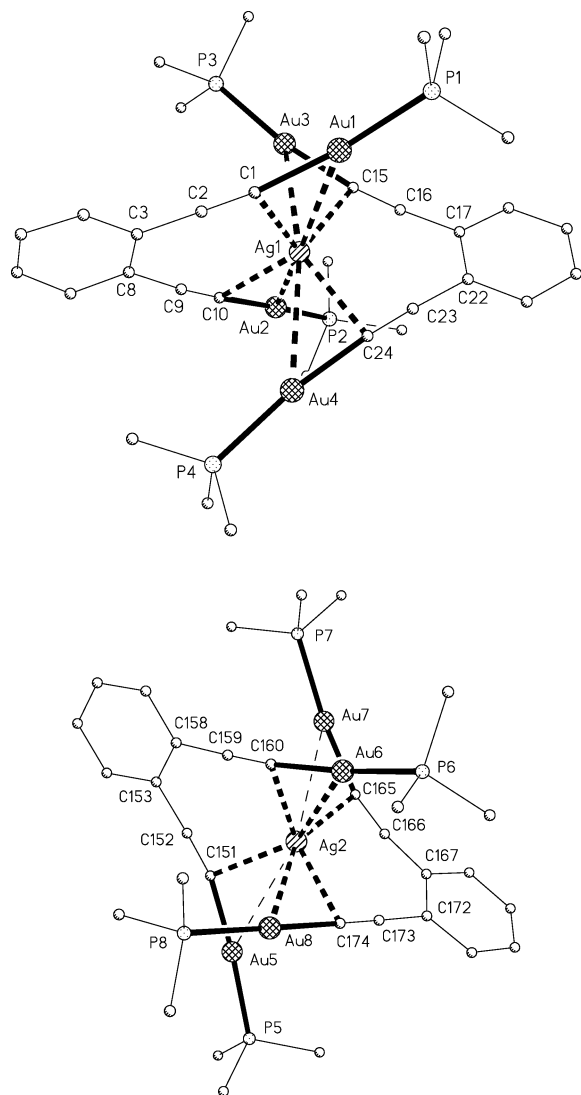


Figure 7. Ball-and-stick plot of both cations of **10**·2CHCl₃. For clarity, hydrogen atoms are omitted and the To groups are represented by the *ipso* carbon. Selected bond lengths (Å) and angles (deg) are listed in Table 2.

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 Br⁶¹), the C–H bonds

involved in C–H···Au interactions belong to ^tBuNC 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 (CH₂)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**·1/3CHCl₃ (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(NC₂)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–NEt₂ [1.342(4), 1.338(4) Å] are similar to each other and intermediate between those corresponding to single and double C(sp²)–N(sp²) bonds.⁶⁵ Both the planar geometry and the similar C–N distances suggest extensive electronic delocalization in the fragment CN₂, 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 (^tBu) is *cis* with respect to the metallic fragment, thus avoiding contact with the more congested NEt₂ 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**·2CHCl₃ contains two pentanuclear “AgAu₄” 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 numismophilic⁴¹ Ag⋯Au contacts. In fact, in Ag(η²-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 AuPR₃,³⁸ complex **10** can be considered as containing four C–(AuPR₃)⋯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(C₂Ph)₂}₂(AgPPh₃)₂] each AgPPh₃ 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 ¹³C 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 C₆Me₄ fragment give rise to two singlets (Δδ = 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 C₆H₄(C≡C)₂-1,3, C₆HMe₃-2,4,6-(C≡C)₂-1,3¹⁹ and C₆H₃N(C≡C)₂-3,5⁶⁹ ligands allowed us to conclude that the C≡CAu fragments produce the deshielding of the H or CH₃ 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 $\nu(\text{C}\equiv\text{C})$ stretching modes give rise to one (**1**, **3**, **4**, **8**, **9**, in the range $2090\text{--}2134\text{ cm}^{-1}$) 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 $\nu(\text{C–H})$ in the $\text{C}\equiv\text{CH}$ fragments. In the spectrum of **3** the strong band at 2216 cm^{-1} corresponds to the $\nu(\text{C}\equiv\text{N})$ in the isocyanide ligand, while in those of **8** and **9**, one strong band at 3180 and 3338 cm^{-1} , respectively, are assignable to $\nu(\text{N–H})$.

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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**· $1/3\text{CHCl}_3$, and **10**· 2CHCl_3 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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