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# Gold(I) Complexes Derived from $C_6Me_3(C{\equiv}CH)_3$-1,3,5, $C_6Me_4(C{\equiv}CH)_2$-1,4, and $MeC_6H_4C{\equiv}CH$-4[§]

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$C_6Me_3(C{\equiv}CH)_3$-1,3,5 ($Ar(C{\equiv}CH)_3$) reacts with $[AuCl(SMe_2)]$ and $NEt_3$ (1:3:3) to give $[Au_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]_n$ (**1**). Complexes of the general formula $[\{AuL\}_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]$ can be obtained from **1** and excess isocyanide (L = $^tBuNC$ (**2**), XyNC (**3**)), by treating **2** with an excess of $NHEt_2$ (L = $C(NH^tBu)NEt_2$ (**4**)), or by reacting $[Ar(C{\equiv}CH)_3]$ with $[Au(acac)PPh_3]$ (1:3, L = $PPh_3$ (**5**)) or with $PPN[AuCl_2]$ (1:3, PPN = $Ph_3P{=}N{=}PPh_3$) and an excess of $NHEt_2$ (L = $NHEt_2$ (**6**)). The reaction of $C_6Me_4(C{\equiv}CH)_2$-1,4 ($Ar'(C{\equiv}CH)_2$) with $PPN[AuCl_2]$ (1:2) and an excess of $NHEt_2$ gives $[\{AuNHEt_2\}_2\{\mu\text{-}(C{\equiv}C)_2Ar'\}]$ (**7**), which reacts with 1,6-bis(diphenylphosphino)hexane (dpph) to give $[Au_2\{\mu\text{-}(C{\equiv}C)_2Ar'\}(\mu\text{-dpph})]_n$ (**8**). The reactions of the alkynes $[Ar(C{\equiv}CH)_3]$, $[Ar'(C{\equiv}CH)_2]$, and $ToC{\equiv}CH$ (To = 4-$MeC_6H_4$) with the appropriate amounts of $PPN[Au(acac)_2]$ (acac = acetylacetonato) allow the syntheses of the anionic complexes $PPN[Au\{C{\equiv}CAr(C{\equiv}CH)_2\}_2]$ (**9**), $PPN[Au\{C{\equiv}CAr'C{\equiv}CH\}_2]$ (**10**), $PPN[Au\{C{\equiv}CTo\}_2]$ (**11**), $(PPN)_{3n}[Au\{C{\equiv}CAr(C{\equiv}C)_2\}_2Au_2]_n$ (**12**), and $(PPN)_n[Au\{\mu\text{-}(C{\equiv}C)_2Ar'\}]_n$ (**13**). The X-ray crystal structures of **5**, **9**, and **11** have been determined.

## Introduction

The number of ethynyl(arene)gold complexes decreases notably as the number of $AuC{\equiv}C$ fragments in the complex increases. In fact, many (arenemonoethynyl)gold complexes have been described, most being of the type $[Au(C{\equiv}CR)L]_n$ (R = aryl group, L = monodentate ($n$ = 1) or bidentate ($n$ = 2) neutral ligand),[1−8] although a few of the general formulas $[Au(C{\equiv}CR)]_n$,[9−13] $Q[Au(C{\equiv}CR)Cl]$,[8] $Q[Au(C{\equiv}CR)_2]$,[7,11,14−16] and $Q[Au\{C{\equiv}C(Py)C{\equiv}CH\}_2]$ (py = pyridine-3,5-diyl)[12] are also known.

(Arenediethynyl)gold derivatives are less common, but some neutral or anionic complexes, including polymers, have been prepared from the dialkynes $Ar(C{\equiv}CH)_2$ (Ar = $C_6H_4$-1,3,[10] $C_6H_4$-1,4,[3] ($C_6H_3$Me-5)-1,3, ($C_6H_2Me_2$-2,5)-1,4,[4] ($C_6HMe_3$-2,4,6)-1,3,[17] $C_6Me_4$-2,3,5,6,[10] py-3,5,[12] $C_6H_2$-3,6-(15-crown-5)-4,5,[5] $C_4Me_4$-3,4,5,6[13]). Apart from showing interesting ribbon or infinite chain structures,[4,18] many of them are luminescent, a property attributable in part[2,6,14,19] to their short intermolecular Au···Au contacts, which are also present in most structurally characterized luminescent gold(I) complexes.[4,6,18,20] Their conjugated structures might lead to materials applications.[21]

(Arenetriethynyl)gold complexes are very scarce. As far as we are aware, only the explosive polymeric

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[§] Dedicated to Dr. José Antonio Abad, with best wishes, on the occasion of his retirement.

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(1) Bruce, M. I.; Dufly, D. N. *Aust. J. Chem.* **1986**, *39*, 1697. Chao, H.-Y.; Lu, W.; Li, Y.; Chan, M. C. W.; Che, C. M.; Cheung, K. K.; Zhu, N. *J. Am. Chem. Soc.* **2002**, *124*, 14696. Whittall, I. R.; Humphrey, M. G.; Hockless, D. C. R. *Aust. J. Chem.* **1997**, *50*, 991. Hurst, S. K.; Lucas, N. T.; Humphrey, M. G.; Asselberghs, I.; Vanboxel, R.; Persoons, A. *Aust. J. Chem.* **2001**, *54*, 447. Irwin, M. J.; Jia, G. C.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51. Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr., Sect. C* **1967**, *23*, 156.

(2) Li, D.; Hong, X.; Che, C. M.; Lo, W. C.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929.

(3) Jia, G. C.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565.

(4) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541.

(5) Lu, X.-X.; Li, C.-K.; Cheng, E. C.-C.; Zhu, N.; Yam, V. W. W. *Inorg. Chem.* **2004**, *43*, 2225.

(6) Xiao, H.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3699.

(7) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G.; Humphrey, M. G.; Cifuentes, M. P.; Samoc, M.; Luther-Davies, B. *Organometallics* **2000**, *19*, 2968.

(8) Vicente, J.; Singhal, A. R.; Jones, P. G. *Organometallics* **2002**, *21*, 5887.

(9) Coates, G. E.; Parkin, C. *J. Chem. Soc.* **1962**, 3220. Alejos, P.; Coco, S.; Espinet, P. *New J. Chem.* **1995**, *19*, 799.

(10) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Abrisqueta, M. D.; Hernández, F. J.; Jones, P. G. *Inorg. Chim. Acta* **2003**, *347*, 67.

(11) Vicente, J.; Chicote, M. T.; Álvarez-Falcón, M. M.; Fox, M. A.; Bautista, D. *Organometallics* **2003**, *22*, 4792.

(12) Vicente, J.; Chicote, M. T.; Álvarez-Falcón, M. M.; Bautista, D. *Organometallics* **2004**, *23*, 5707.

(13) Vicente, J.; Chicote, M. T.; Álvarez-Falcón, M. M.; Jones, P. G. *Organometallics* **2005**, *24*, 4666.

(14) Che, C. M.; Yip, H. K.; Lo, W. C.; Peng, S. M. *Polyhedron* **1994**, *13*, 887.

(15) Abu-Salah, O. M.; Al-Ohaly, A. R.; Al-Qahtani, H. A. *Inorg. Chim. Acta* **1986**, L29. Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **2000**, *19*, 2629.

(16) Ferrer, M.; Rodriguez, L.; Rossell, O.; Pina, F.; Lima, J. C.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **2003**, *82*, 678.

(17) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Alvarez-Falcón, M. M. *J. Organomet. Chem.* **2002**, *663*, 40.

(18) MacDonald, M. A.; Puddephatt, R. J.; Yap, G. P. A. *Organometallics* **2000**, *19*, 2194.

(19) Tzeng, B.-C.; Lo, W.-C.; Che, C.-M.; Peng, S.-M. *Chem. Commun.* **1996**, 181.

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complex $[Au_3\mu\text{-}\{C_6H_3(C{\equiv}C)_3\text{-}1,3,5\}]_n$[22] and a few derivatives of the type $[(AuL)_3\mu\text{-}\{C_6H_3(C{\equiv}C)_3\text{-}1,3,5\}]$, obtained by reacting the former with mono- or bidentate phosphine, phosphite, or isocyanide ligands, have been reported, including three of their crystal structures.[22,23] Molecules with 3-fold rotation symmetry, which can exhibit nonzero $\beta$ values despite being nonpolar, are promising candidates for second-order nonlinear optical materials design.[23] In addition, there is currently much interest[22] in extending the chemistry of gold beyond the most common one-directional linear complexes by using trifunctional core molecules, and 1,3,5-triethynylbenzene appears particularly well suited for this purpose.[24]

In this paper we report the synthesis of some new gold(I) arenemonoethynyl, -diethynyl, and -triethynyl complexes derived from the alkynes $MeC_6H_4C{\equiv}CH\text{-}4$, $C_6Me_4(C{\equiv}CH)_2\text{-}1,4$, and $C_6Me_3(C{\equiv}CH)_3\text{-}1,3,5$, some of which are unprecedented with respect to their composition or structural features. The crystal structures of $PPN[Au\{C{\equiv}CC_6Me_3(C{\equiv}CH)_2\text{-}3,5\}_2]$, $PPN[Au(C{\equiv}CC_6H_4\text{-}Me\text{-}4)_2]$, and $[\{AuPPh_3\}_3\{\mu\text{-}(C{\equiv}C)_3\text{-}1,3,5\text{-}C_6Me_3\}]$ have been determined.

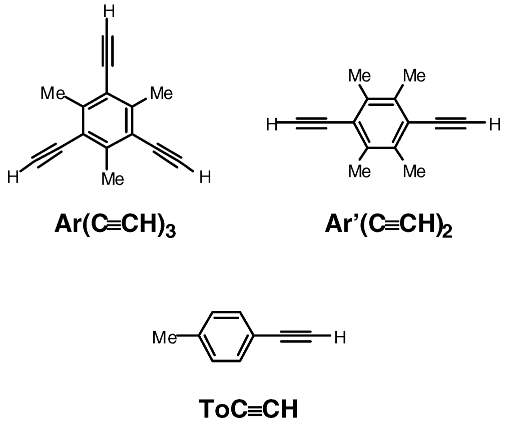
## Experimental Section

IR spectroscopy, mass spectrometry (FAB$^{+/-}$), elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described elsewhere.[25] The molar conductivity of the neutral complexes gave very low values (0−5 $\Omega^{-1}$ 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 $[AuCl(SMe_2)]$,[26] $[Au(acac)PPh_3]$ (acacH = acetylacetone), $PPN[AuCl_2]$, and $PPN[Au(acac)_2]$[27] were previously reported. All other chemicals were obtained from commercial sources and used as received. The solvents were distilled before use.

**Synthesis of $[Au_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]_n$ (1).** A suspension of $[AuCl(SMe_2)]$ (1.54 g, 5.2 mmol) and $Ar(C{\equiv}CH)_3$ (Ar = $C_6Me_3$-2,4,6 (see Chart 1); 335 mg, 1.7 mmol) in a mixture of $CH_2Cl_2$ (20 mL) and $NEt_3$ (0.850 mL, 6 mmol) was stirred for 10 min. The suspension was filtered, and the solid was washed with $CH_2Cl_2$ (2 × 20 mL) and $Et_2O$ (20 mL) and dried under reduced pressure (ca. 1 mbar) for 0.5 h to give $\mathbf{1}\cdot NEt_3\cdot 0.25SMe_2$ as a bright yellow powder. Its insolubility in all common solvents prevented the recording of its NMR spectra. Yield: 1.35 g, 1.5 mmol, 89%. Mp: 198 °C dec. Anal. Calcd for $C_{21.5}H_{25.5}Au_3NS_{0.25}$: C, 28.79; H, 2.87; N, 1.56; S, 0.89. Found: C, 28.64; H, 2.74; N, 1.31; S, 0.95. IR (cm$^{-1}$): $\nu$(C≡C), 2104 (w).

**Synthesis of $[(AuL)_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]$ (L = $^t$BuNC (2), XyNC (3)).** To a suspension of **1** (**2**, 101 mg, 0.13 mmol; **3**, 94 mg, 0.12 mmol) in $CH_2Cl_2$ (10 mL) was added the appropriate ligand (**2**, $^t$BuNC, 73 $\mu$L, 0.65 mmol; **3**, XyNC, 79 mg, 0.60 mmol), and the mixture was stirred for 40 min. The resulting solution was filtered through Celite, concentrated under vacuum (to ca. 3 mL), and slowly added dropwise to *n*-hexane (**2**, 50 mL) or $Et_2O$ (**3**, 25 mL). The suspension was stirred for 15 min and filtered, and the solid collected was air-dried to give **2** as a white powder or recrystallized from $CHCl_3$ and $Et_2O$ to give **3** as a pale yellow solid.

**Chart 1**


Ar(C≡CH)$_3$

Ar'(C≡CH)$_2$

ToC≡CH

**2**: yield 83 mg, 0.08 mmol, 62%; mp 136 °C. Anal. Calcd for $C_{30}H_{36}Au_3N_3$: C, 35.00; H, 3.52; N, 4.08. Found: C, 35.35; H, 3.73; N, 4.15. IR (cm$^{-1}$): $\nu$(C≡N), 2224 (s). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.72 (s, 9 H, Me), 1.55 (s, 27 H, $^t$Bu). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$): $\delta$ 142.1, 129.6, 122.2, 101.5 (C≡C), 58.8 (*C*Me$_3$), 30.2 (C*Me*$_3$), 21.4 (Me).

**3**: yield 107 mg, 0.09 mmol, 76%; mp 146 °C. Anal. Calcd for $C_{42}H_{36}Au_3N_3$: C, 42.98; H, 3.09; N, 3.58. Found: C, 42.66; H, 3.08; N, 3.52. IR (cm$^{-1}$): $\nu$(C≡N), 2192 (s). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 7.33−7.28 (m, 3 H, Xy), 7.17−7.13 (m, 6 H, Xy), 2.79 (s, 9 H, Me, Ar), 2.44 (s, 18 H, Me, Xy). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$): $\delta$ 129.1, 124.4, 120.1, 118.2, 112.8, 96.9 (C≡C), 32.4 (Me), 30.5 (Me).

**Synthesis of $[\{AuC(NH^tBu)NEt_2\}_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]$ (4).** Complex **2** (73 mg, 0.071 mmol) was stirred in a mixture of $CH_2Cl_2$ (10 mL) and $NHEt_2$ (1 mL, 9.62 mmol) for 2 h. The suspension was filtered through Celite, and the resulting solution was concentrated under reduced pressure (to ca. 1 mL). By addition of $Et_2O$ (40 mL) a solid was obtained, which was filtered off, recrystallized from $CH_2Cl_2$ and $Et_2O$, and air-dried to give **4** as a white powder. **4**: yield 52 mg, 0.041 mmol, 59%; mp 120 °C. Anal. Calcd for $C_{42}H_{69}Au_3N_6$: C, 40.39; H, 5.57; N, 6.73. Found: C, 40.70; H, 5.60; N, 6.48. IR (cm$^{-1}$): $\nu$(NH), 3386 (w); $\nu$(C≡C), 2101 (w). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 5.82 (s, 3 H, NH), 4.07 (q, 6 H, $CH_2$, $^3J_{HH}$ = 7.5 Hz), 3.22 (q, 6 H, $CH_2$, $^3J_{HH}$ = 7.5 Hz), 2.68 (s, 9 H, Me, Ar), 1.65 (s, 27 H, $^t$Bu), 1.28 (t, 9 H, Me, $^3J_{HH}$ = 7.5 Hz), 1.16 (t, 9 H, Me, $^3J_{HH}$ = 7.5 Hz). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$): $\delta$ 206.0 ($AuCN_2$), 143.1, 140.6, 123.0, 102.9 (C≡C), 54.2 ($CH_2$), 54.0 (*C*Me$_3$), 43.2 ($CH_2$), 32.0 (C*Me*$_3$), 20.6 (Me), 14.9 (Me), 11.8 (Me).

**Synthesis of $[(AuPPh_3)_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]$ (5).** To a solution of $[Au(acac)PPh_3]$ (998 mg, 1.79 mmol) in $CH_2Cl_2$ (15 mL) was added $[Ar(C{\equiv}CH)_3]$ (69 mg, 0.36 mmol), the mixture was stirred for 9 h and filtered through Celite, and the resulting solution was concentrated to dryness. The residue was stirred with $Et_2O$ (45 mL), and the suspension was filtered off. Recrystallization of the solid from $CH_2Cl_2$ and $Et_2O$ gave **5** as a bright yellow powder. **5**: yield 487 mg, 0.3 mmol, 87%; mp 155 °C. Anal. Calcd for $C_{69}H_{54}Au_3P_3$: C, 52.89; H, 3.47. Found: C, 52.50; H, 3.55. IR (cm$^{-1}$): no $\nu$(C≡C) is observed. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.60−7.41 (m, 45 H, $PPh_3$), 2.84 (s, 9 H, Me). $^{13}$C{$^1$H} NMR (50 MHz, $CDCl_3$): $\delta$ 141.5, 134.4 (d, o-$PPh_3$, $^2J_{CP}$ = 14 Hz), 131.3 (m, p-$PPh_3$), 130.1 (d, i-$PPh_3$, $^1J_{CP}$ = 55 Hz), 129.0 (d, m-$PPh_3$, $^3J_{CP}$ = 11 Hz), 121.9, 21.4 (Me). $^{31}$P{$^1$H} NMR (121.4 MHz, $CDCl_3$): $\delta$ 42.99 (s, $PPh_3$). Crystals of **5** suitable for an X-ray diffraction study were

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(20) Che, C. M.; Chao, H. Y.; Miskowski, V. M.; Li, Y. Q.; Cheung, K. K. *J. Am. Chem. Soc.* **2001**, *123*, 4985.

(21) Hirsch, A.; Hanack, M. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Kluwer Academic: New York, 1990.

(22) Irwin, M. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Yufit, D. S. *J. Chem. Soc., Chem. Commun.* **1997**, 219.

(23) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Maes, J.; Persoons, A.; Schmid, S.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *544*, 277.

(24) Gardner, G. B.; Kiang, Y. H.; Lee, S.; Asgaonkar, A.; Venkataram, D. *J. Am. Chem. Soc.* **1996**, *118*, 6946.

(25) Vicente, J.; Chicote, M. T.; Guerrero, R.; Saura-Llamas, I. M.; Jones, P. G.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **2001**, *7*, 638.

(26) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 411.

(27) Vicente, J.; Chicote, M. T. *Inorg. Synth.* **1998**, *32*, 172.

obtained by liquid diffusion of $Et_2O$ into a solution of the complex in $CH_2Cl_2$.

**Synthesis of [(AuNHEt$_2$)$_3${*μ*-(C≡C)$_3$Ar}] (6).** To a mixture of [Ar(C≡CH)$_3$] (40 mg, 0.21 mmol) and PPN[AuCl$_2$] (499 mg, 0.62 mmol) in degassed $CH_2Cl_2$ (11 mL) was added $NHEt_2$ (1.5 mL). After it was stirred for 4.5 h, the suspension was filtered off and the white solid collected was washed with $CH_2Cl_2$ (2 × 4 mL) and dried under reduced pressure (ca. 1 mbar). Yield: 200 mg, 0.2 mmol, 95%. Mp: 88 °C dec. Anal. Calcd for $C_{27}H_{42}Au_3N_3$: C, 32.44; H, 4.24; N, 4.20. Found: C, 32.32; H, 4.18; N, 4.18. IR ($cm^{-1}$): $\nu$(NH), 3156 (s); $\nu$(C≡C), 2108 (w). $^1H$ NMR (200 MHz, $d_6$-DMSO): $\delta$ 5.48 (m, 3 H, NH), 2.95 (m, 12 H, $CH_2$), 2.46 (s, 9 H, Me), 1.30 (t, 18 H, Me, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $d_6$-DMSO): $\delta$ 138.57, 123.54, 117.08, 98.00 (C≡C), 48.09 ($CH_2$), 21.03 (Me), 14.97 (Me).

**Synthesis of [(AuNHEt$_2$)$_2${*μ*-(C≡C)$_2$Ar′}] (7).** To a solution of PPN[AuCl$_2$] (1.04 g, 1.29 mmol) in a mixture of $CH_2Cl_2$ (10 mL) and $NHEt_2$ (7 mL) was added a solution of Ar′(C≡CH)$_2$ (Ar′ = $C_6Me_4$-2,3,5,6, 118 mg, 0.64 mmol) in $CH_2Cl_2$ (5 mL), and the mixture was stirred under a nitrogen atmosphere for 1.5 h. The resulting suspension was concentrated under vacuum (to ca. 10 mL) and filtered. The solid was dried under reduced pressure (ca. 1 mbar) for 0.5 h to give **7** as a white powder. **7**: yield 433 mg, 0.6 mmol, 94%; mp 99 °C dec. Anal. Calcd for $C_{22}H_{34}Au_2N_2$: C, 36.68; H, 4.76; N, 3.89. Found: C, 36.93; H, 4.86; N, 3.88. IR ($cm^{-1}$): $\nu$(NH), 3190 (s); $\nu$(C≡C), 2102 (w). $^1H$ NMR (400 MHz, $d_6$-DMSO): $\delta$ 5.21 (m, 2 H, NH), 2.63 (m, 8 H, N$CH_2$Me), 1.83 (s, 12 H, Me), 1.03 (t, 12 H, $NCH_2$*Me*, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $d_6$-DMSO): $\delta$ 134.9, 124.8, 118.5, 99.3 (C≡C), 48.5 (N$CH_2$Me), 19.4 (Me), 15.4 ($NCH_2$*Me*).

**Synthesis of [Au$_2${*μ*-Ar′(C≡C)$_2$}(*μ*-dpph)]$_n$ (8).** To a solution of 1,6-bis(diphenylphosphino)hexane (0.090 g, 0.20 mmol) in degassed $CH_2Cl_2$ (10 mL) was added complex **7** (0.143 g, 0.20 mmol), and the mixture was stirred for 1 h. The resulting suspension was then filtered and the solid washed with $CH_2Cl_2$ (2 × 5 mL) and dried under reduced pressure (ca. 1 mbar) to give **8** as a white powder. The insolubility of **8** in all common solvents prevented measurement of its NMR spectra. **8**: yield 197 mg, 0.19 mmol, 96%; mp 272 °C dec. Anal. Calcd for $C_{44}H_{44}Au_2P_2$: C, 51.37; H, 4.31. Found: C, 51.20; H, 4.35. IR ($cm^{-1}$): no $\nu$(C≡C) is observed. MS-FAB$^+$ (*m*/*z*, %): 1030 [M$^+$, 3].

**Synthesis of PPN[Au{C≡CAr(C≡CH)$_2$}$_2$] (9).** A solution of PPN[Au(acac)$_2$] (280 mg, 0.30 mmol) in acetone (15 mL) was slowly added dropwise to a solution of Ar(C≡CH)$_3$ (230 mg, 1.20 mmol) in the same solvent (5 mL). The mixture was stirred for 6 h, filtered through Celite, and concentrated under vacuum to dryness. The residue was stirred with $Et_2O$ (4 × 20 mL), the suspension was filtered, and the solid was air-dried to give **9** as a pale purple powder. **9**: yield: 283 mg, 0.25 mmol, 85%; mp 196 °C. Anal. Calcd for $C_{66}H_{52}AuNP_2$: C, 70.90; H, 4.69; N, 1.25. Found: C, 70.61; H, 4.68; N, 1.23. $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 75. IR ($cm^{-1}$): $\nu$(CH), 3320 (s), 3280 (s); $\nu$(C≡C), 2096 (s). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.67−7.37 (m, 30 H, PPN), 3.37 (s, 4 H, CH), 2.62 (s, 12 H, Me), 2.53 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 143.4, 139.4, 133.9 (m, p-PPN), 131.9 (m, m-PPN), 129.6 (m, o-PPN), 126.8 (dd, i-PPN, $^1J_{CP}$ = 108 Hz, $^3J_{CP}$ = 2 Hz), 118.9, 98.8 (C≡C), 83.6 (*C*CH), 82.0 (CH), 20.6 (Me), 19.8 (Me). MS-FAB$^-$ (*m*/*z*, %): 579 [M$^-$, 100]. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **9** in $CH_2Cl_2$.

**Synthesis of PPN[Au(C≡CAr′C≡CH)$_2$] (10).** To a solution of [Ar′(C≡CH)$_2$] (0.226 g, 1.24 mmol) in degassed $CH_2Cl_2$ (5 mL) was added a solution of PPN[Au(acac)$_2$] (0.290 g, 0.31 mmol) in the same solvent (20 mL), and the mixture was stirred under a nitrogen atmosphere for 2 h, filtered through Celite, and concentrated under vacuum (to ca. 10 mL). By addition of $Et_2O$ (30 mL) a white solid precipitated, which was filtered, washed with $Et_2O$ (5 mL), and air-dried to give **10**·2$H_2O$. **10**: yield 278 mg, 0.25 mmol, 82%; mp 229 °C dec. Anal. Calcd for $C_{64}H_{60}AuNO_2P_2$: C, 67.78; H, 5.33; N, 1.24. Found: C, 67.68; H, 5.28; N, 1.16. $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 97. IR ($cm^{-1}$): $\nu$(CH), 3286 (s); $\nu$(C≡C), 2086 (s). $^1H$ NMR (300 MHz, $d_6$-DMSO): $\delta$ 7.69−7.52 (m, 30 H, PPN), 4.44 (s, 2 H, CH), 3.42 (s, 4 H, $H_2O$), 2.33 (s, 12 H, Me), 2.29 (s, 12 H, Me). $^{13}C\{^1H\}$-HMBC NMR (100 MHz, $d_6$-DMSO): $\delta$ 148.0, 135.7, 135.3, 134.5 (m, p-PPN), 134.4, 132.8 (m, o-PPN), 130.4 (m, m-PPN), 128.8, 127.6 (dd, i-PPN, $^1J_{CP}$ = 106 Hz, $^3J_{CP}$ = 2 Hz), 119.2, 101.6 (C≡C), 90.2 (*C*≡CH), 88.3 (≡CH), 19.3 (Me), 19.0 (Me). MS-FAB$^-$ (*m*/*z*, %): 559 [M$^-$, 100].

**Synthesis of PPN[Au(C≡CTo)$_2$] (11).** A mixture of PPN[Au(acac)$_2$] (0.755 g, 0.81 mmol) and ToC≡CH (0.307 mL, 2.42 mmol) in degassed acetone (15 mL) was stirred for 8.25 h. On addition of $Et_2O$ (30 mL) a solid precipitated, which was filtered, washed with $Et_2O$ (2 × 5 mL), and air-dried to give **11**·$H_2O$ as a microcrystalline white solid. **11**: yield 756 mg, 0.78 mmol, 97%; mp 196 °C dec. Anal. Calcd for $C_{54}H_{46}AuNOP_2$: C, 65.92; H, 4.71; N, 1.42. Found: C, 66.20; H, 4.63; N, 1.71. $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 93. IR ($cm^{-1}$): $\nu$(C≡C), 2104 (s). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.70−7.39 (m, 30 H, PPN), 7.29−7.25 (m, 4 H, Ar), 6.92−6.88 (m, 4 H, Ar), 2.24 (s, 6 H, Me), 1.59 (s, 2 H, $H_2O$). $^{13}C\{^1H\}$-HMBC NMR (50 MHz, $CDCl_3$): $\delta$ 134.6 (Ar), 134.3 (m, p-PPN), 133.7 (CAu), 133.4 (Ar), 132.5 (m, m-PPN), 130.1 (m, o-PPN), 128.5 (Ar), 127.3 (dd, $^1J_{CP}$ = 107 Hz, $^3J_{CP}$ = 1.8 Hz, i-PPN), 125.2 (Ar), 102.9 (*C*≡CAu), 21.7 (Me). MS-FAB$^-$ (*m*/*z*, %): 427 [M$^-$, 100]. Crystals of **11** suitable for an X-ray diffraction study were obtained by slow diffusion of $Et_2O$ into a solution of the compound in $CH_2Cl_2$.

**Synthesis of (PPN)$_{3n}$[Au{*μ*-C≡CAr(C≡C)$_2$}$_2$Au$_2$]$_n$ (12).** A mixture of PPN[Au(acac)$_2$] (0.246 g, 0.26 mmol) and Ar(C≡CH)$_3$ (0.034 g, 0.18 mmol) in degassed $CH_2Cl_2$ (15 mL) was stirred under a nitrogen atmosphere for 4 h. The resulting suspension was filtered and the solid dried under reduced pressure (ca. 1 mbar) for 0.5 h to give **12**·3$CH_2Cl_2$ as a purple powder. The insolubility of **12** in all common solvents prevented measurement of its NMR spectra. **12**: yield 190 mg, 0.067 mmol, 74%; mp 207 °C dec. Anal. Calcd for $C_{141}H_{114}Au_3Cl_6N_3P_6$: C, 59.63; H, 4.05; N, 1.48. Found: C, 59.39; H, 4.05; N, 1.40. IR ($cm^{-1}$): $\nu$(C≡C), 2088 (w).

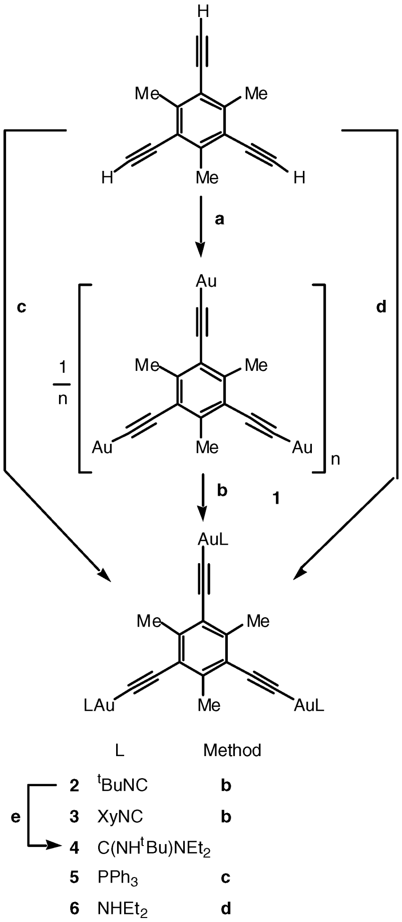
**Synthesis of (PPN)$_n$[Au{*μ*-Ar′(C≡C)$_2$}]$_n$ (13).** To a solution of PPN[Au(acac)$_2$] (0.210 g, 0.23 mmol) in degassed $CH_2Cl_2$ (10 mL) was added a solution of [Ar′(C≡CH)$_2$] (0.037 g, 0.20 mmol) in the same solvent (5 mL), and the mixture was stirred under a nitrogen atmosphere for 12 h. The resulting suspension was filtered, and the solid was washed with $CH_2Cl_2$ (20 mL) and dried under vacuum (ca. 1 mbar) for 1 h to give **13**·0.9$CH_2Cl_2$ as a pale yellow powder. Its insolubility in all common solvents prevented measurement of its NMR spectra. **13**: yield 179 mg, 0.18 mmol, 90%; mp 153 °C dec. Anal. Calcd for $C_{50.9}H_{43.8}AuCl_{1.8}NP_2$: C, 61.61; H, 4.45; N, 1.41. Found: C, 61.95; H, 4.47; N, 1.46. IR ($cm^{-1}$): $\nu$(C≡C), 2082 (w).

**X-ray Structure Determinations.** Data were registered using Mo K$\alpha$ 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, Göttingen, Germany). Methyl hydrogens were identified in difference syntheses and refined as rigid groups allowed to rotate but not tip; other hydrogens were included using a riding model. To improve the stability of the refinement, restraints to light-atom displacement parameters and local phenyl ring symmetry were employed (*DELU, SIMU, FLAT, SAME*). Crystal data are presented in Table 1. *Special features/exceptions*: compound **5** has high residual electron density that might be attributed to absorption errors; for compound **9**, acetylenic hydrogens were refined freely but with C−H distance restraints (*SADI*).

**Table 1. Crystallographic Data for Complexes $5\cdot CH_2Cl_2$, 9, and 11**

| | $5\cdot CH_2Cl_2$ | 9 | 11 |
|---|---|---|---|
| formula | $C_{70}H_{56}Au_3Cl_2P_3$ | $C_{66}H_{56}AuNP_2$ | $C_{54}H_{44}AuNP_2$ |
| $M_r$ | 1651.86 | 1122.02 | 965.81 |
| cryst size (mm) | 0.28 × 0.10 × 0.05 | 0.18 × 0.16 × 0.05 | 0.30 × 0.08 × 0.08 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $C2/c$ | $C2/c$ |
| cell constants | | | |
| $a$ (Å) | 24.554(2) | 27.829(2) | 17.5277(12) |
| $b$ (Å) | 16.6859(12) | 12.7529(11) | 17.6004(12) |
| $c$ (Å) | 15.0022(12) | 19.8249(14) | 15.3303(11) |
| α (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 100.265(3) | 133.930(4) | 115.354(4) |
| $\gamma$ (deg) | 90 | 90 | 90 |
| $V$ (Å$^3$), $Z$ | 6048.1(8) | 5067.2(7) | 4273.8(5) |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 | 0.710 73 |
| $\rho$(calcd) (Mg m$^{-3}$) | 1.814 | 1.471 | 1.501 |
| $\mu$, mm$^{-1}$ | 7.468 | 3.010 | 3.555 |
| $F$(000) | 3168 | 2272 | 1936 |
| $T$ (K) | 133(2) | 133(2) | 133(2) |
| $2\theta_{max}$ (deg) | 56.56 | 60.06 | 60.06 |
| no. of rflns measd | 85 546 | 39 441 | 40 559 |
| no. of indep rflns | 14 980 | 7397 | 6259 |
| transmissns | 0.802 and 0.455 | 0.894 and 0.650 | 0.802 and 0.466 |
| $R_{int}$ | 0.0667 | 0.0392 | 0.0369 |
| no. of data/restraints/ params | 14980/216/706 | 7397/97/328 | 6259/0/264 |
| $R_w$($F^2$, all rflns) | 0.0806 | 0.0645 | 0.0446 |
| $R$($F$, > 4$\sigma$($F$)) | 0.0343 | 0.0264 | 0.0194 |
| max $\Delta\rho$ (e Å$^{-3}$) | 5.205 and −2.647 | 1.451 and −0.423 | 0.988 and −0.489 |

**Scheme 1**[a]



[a] Legend: (**a**) +3[AuCl(SMe$_2$)], +3NEt$_3$, −3SMe$_2$, −3(NHEt$_3$)Cl; (**b**) +3L; (**c**) +3[Au(acac)PPh$_3$], −3Hacac; (**d**): +3 PPN[AuCl$_2$], +6NHEt$_2$, −3PPNCl, −3[NH$_2$Et$_2$]Cl; (**e**) +3HNEt$_2$.

## Results and Discussion

**Synthesis**. The complex [Au$_3${$\mu$-(C≡C)$_3$Ar}]$_n$ (**1**) (Ar = $C_6Me_3$-2,4,6; see Chart 1) was obtained by reacting Ar(C≡CH)$_3$ with [AuCl(SMe$_2$)] and NEt$_3$ (1:3:3.5) (Scheme 1); the Cl and SMe$_2$ ligands are both displaced from the coordination sphere of gold by the Ar(C≡C)$_3$$^{3-}$ ligand generated in situ by deprotonation of the trialkyne with the amine. The insolubility of complex **1** in all common solvents suggests that it is a polymer in which gold would complete its usual linear dicoordination by side-on coordination to a C≡C bond, as assumed for related complexes.[10] This is why we could not measure its NMR spectra. The sulfur and nitrogen contents shown in its elemental analyses, which we could not remove even after drying under reduced pressure for several hours, indicate the presence of SMe$_2$ and NEt$_3$ ligands that would coordinate to the terminal gold atoms in the polymer. The analytical data agree with the formulation **1**·NEt$_3$·0.25SMe$_2$.

The addition of an excess of isocyanide to suspensions of **1** in CH$_2$Cl$_2$ produced clear solutions from which [(AuL)$_3${$\mu$-(C≡C)$_3$Ar}] (L = $^t$BuNC (**2**), XyNC (**3**)) were isolated in good yield, resulting from the splitting of the weak $\sigma$(C≡C)→Au interactions and the substitution of the residual labile ligands SMe$_2$ and NEt$_3$ in **1**. More labile ligands such as tetrahydrothiophene (tht) or NHEt$_2$ did not react at all with **1**, which was recovered quantitatively even if a large excess of the ligands was used. We attempted these reactions with the aim of preparing complexes that could serve as starting materials more suitable than the insoluble polymer **1**. However, complexes of the general formula [(AuL)$_3${$\mu$-(C≡C)$_3$Ar}] can be prepared through a variety of alternative syntheses. Thus, the carbene complex [{AuC(NH$^t$Bu)NEt$_2$}$_3${$\mu$-(C≡C)$_3$Ar}] (**4**) was obtained by reacting the isocyanide derivative **2** with a large excess of NHEt$_2$, following a synthetic method that is well documented in the chemistry of gold (Scheme 1).[28] The complex [(AuPPh$_3$)$_3${$\mu$-(C≡C)$_3$Ar}] (**5**) was obtained by reacting [Au(acac)PPh$_3$] with Ar(C≡CH)$_3$ (3:1), providing one more example of the utility of the "acac method"[29] for the synthesis of gold(I) complexes from the appropriate [Au(acac)L] complex and a variety of mildly acidic species.[29] An excess of [Au(acac)PPh$_3$] was used over the stoichiometric 1:3 molar ratio, in order to avoid the formation of mixtures containing species resulting from the partial replacement of the acetylenic protons by AuPPh$_3$ fragments. The synthesis of **5** could offer an alternative route to [{Au(tht)}$_3${$\mu$-(C≡C)$_3$Ar}] by its reaction with [AuCl(tht)] (1:3), associated with the formation of the highly stable [AuCl(PPh$_3$)]. Although the latter indeed formed and was isolated quantitatively from the mother liquor, the expected tht complex decomposed to give **1**, probably as a consequence not only of the lability of the tht ligand but also of the insolubility of **1**. The complex [(AuNHEt$_2$)$_3${$\mu$-(C≡C)$_3$Ar}] (**6**), with a labile NHEt$_2$ ligand, was obtained by reacting PPN[AuCl$_2$] with Ar(C≡CH)$_3$ (3:1) and an excess of NHEt$_2$ in CH$_2$Cl$_2$ (Scheme 1). Complexes **4** and **6** are the only (arenetriethynyl)gold(I) complexes with

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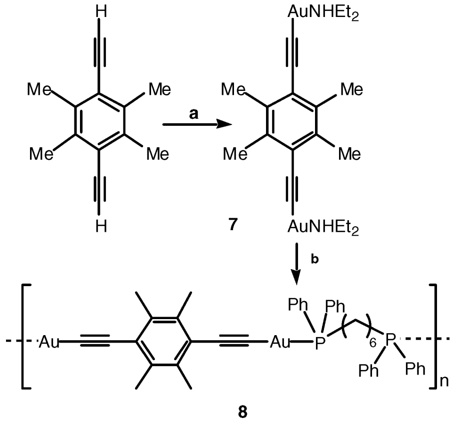
(28) Minghetti, G.; Bonati, F.; Banditelli, G. *Inorg. Chem.* **1976**, *15*, 1718. Bandini, A. L.; Banditelli, G.; Minghetti, G.; Peli, B.; Traldi, B. *Organometallics* **1989**, *8*, 590.

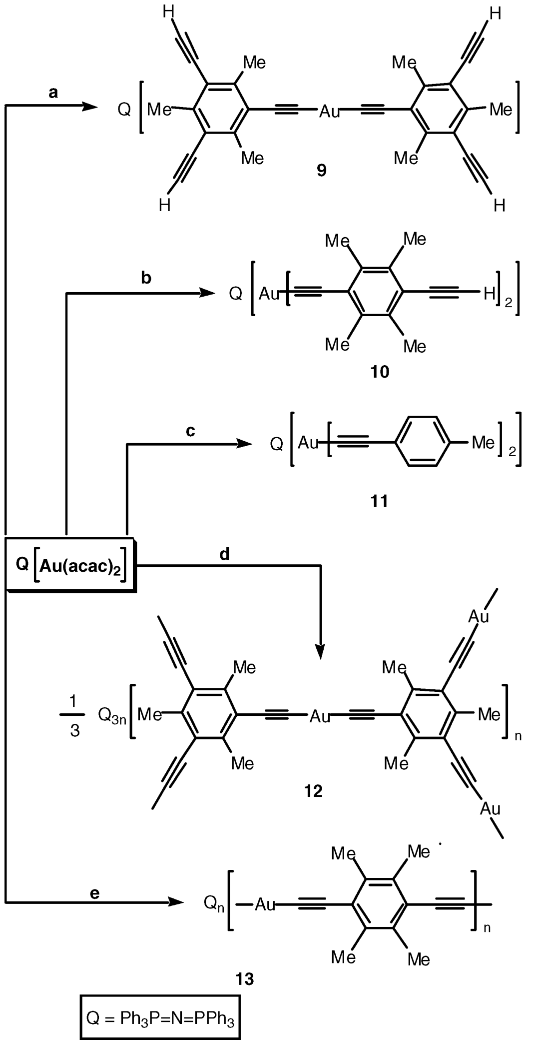
(29) Vicente, J.; Chicote, M. T. *Coord. Chem. Rev.* **1999**, *193−195*, 1143.

**Scheme 2**[a]



[a] Legend: (**a**) +2PPN[AuCl$_2$], +4NHEt$_2$, −2PPNCl, −2[NH$_2$Et$_2$]Cl; (**b**) +dpph, −2NHEt$_2$.

**Scheme 3**[a]



[a] Legend: (**a**) +2Ar(C≡CH)$_3$, −2Hacac; (**b**) +2Ar′(C≡CH)$_2$, −2Hacac; (**c**) +2ToC≡CH, −2Hacac; (**d**) +$^2/_3$Ar(C≡CH)$_2$, −2Hacac; (**e**) +Ar′(C≡CH)$_2$, −2Hacac.

ligands other than phosphine or isocyanide. Similarly, the complex [{AuNHEt$_2$}$_2${$\mu$-(C≡C)$_2$Ar′}] (**7**) was obtained from PPN[AuCl$_2$], Ar′(C≡CH)$_2$ (2:1; Ar′ = C$_6$Me$_4$-2,3,5,6, see Chart 1), and an excess of NHEt$_2$ (Scheme 2). The replacement of each of the C≡CH protons in the appropriate alkyne by an AuNHEt$_2$ fragment could occur through a multistep process involving the deprotonation of the alkyne by the base to give a monoalkynyl ligand; this would replace of one of the chloro ligands in PPN[AuCl$_2$] to give [NH$_2$Et$_2$]Cl and the corresponding PPN[Au(alkynyl)Cl] complex, in which the Cl ligand would be replaced by the excess amine to give (PPN)Cl and the corresponding [Au(alkynyl)NHEt$_2$] derivative. The final result could be favored by the slight (**7**) or almost zero (**6**) solubility of these complexes in CH$_2$Cl$_2$, which might be attributed to the formation of intermolecular hydrogen bonds. In contrast to **6**, which dissolves only in dmso, **7** dissolves slightly in CH$_2$Cl$_2$ or CHCl$_3$, but the solutions decompose within a few minutes to give the more insoluble polymer [Au$_2${(C≡C)$_2$Ar′}]$_n$, which we had prepared previously.[10] This process can be avoided by adding HNEt$_2$ to the solution, but once the polymer forms, it does not react with NHEt$_2$ to give **7** as previously mentioned. The addition of solid complex **7** into a solution of dpph in CH$_2$Cl$_2$ produced the replacement of the amino ligands in **7** by the diphosphine to give [Au$_2${$\mu$-(C≡C)$_2$Ar′}($\mu$-dpph)]$_n$ (**8**; Scheme 2). The order of addition of the reagents cannot be reversed, because otherwise, the insoluble complex **1** forms as a result of the instability of **7** in solution (see above).

The reactions of PPN[Au(acac)$_2$] with the various alkynes gave the anionic alkynylgold(I) complexes **9**−**13,** the nature of which depends on the alkyne and on the stoichiometric ratio of the reagents (Scheme 3). Thus, the synthesis of the bis(alkynyl)gold(I) complexes PPN[Au{C≡CAr(C≡CH)$_2$}$_2$] (**9**), PPN[Au(C≡CAr′C≡CH)$_2$] (**10**), and PPN[Au(C≡CTo)$_2$] (**11**) was achieved when a ≥4:1 (**9**, **10**) or ≥3:1 (**11**) alkyne to Au molar ratio was used instead of the stoichiometric 2:1 required. The excess of alkyne was necessary in the syntheses of **9** and **10** to avoid the formation of insoluble polymeric species (see below) and helped to improve the yield in the case of **11**. As far as we are aware, complexes **9** and **10** are, along with PPN[Au{C≡C(1,12-dicarba-*closo*-dodecaborane-10)C≡CH}$_2$][11] and [Au(C≡CC≡CH)(PPh$_3$)],[30] the only gold complexes bearing a partially aurated polyalkyne. This is interesting, since these species bear C≡CH fragments and thus could behave as terminal alkynes in which the replacement of each of the acidic acetylenic hydrogen atoms by another metal center, for example following the “acac method” or dehydrohalogenation reactions such as that of Hagihara,[31] coud give rise to homo- or heteronuclear $\sigma$-alkynyl complexes with extended electron delocalization. We have recently reported a family of such mixed Pt(II)/Au(I) complexes that we obtained by the opposite approach: i.e., by reacting various [PtL$_2${C≡CAr(C≡CH)$_n$}$_2$] complexes with (acetylacetonato)gold(I) derivatives.[32]

When PPN[Au(acac)$_2$] was reacted with the alkynes Ar(C≡CH)$_3$ and Ar′(C≡CH)$_2$ in an Au to alkyne molar ratio of ≥3:2 or ≥1:1, respectively, the polymeric complexes (PPN)$_{3n}$[Au{C≡CAr(C≡C)$_2$}$_2$Au$_2$]$_n$ (**12**) and (PPN)$_n$[Au{$\mu$-(C≡C)$_2$Ar′}]$_n$ (**13**) formed, as a consequence

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(30) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Smith, M. E.; White, A. H. *Dalton Trans.* **2002**, 995.

(31) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319.

(32) Vicente, J.; Chicote, M. T.; Álvarez-Falcón, M. M.; Jones, P. G. *Organometallics* **2005**, *24*, 2764.

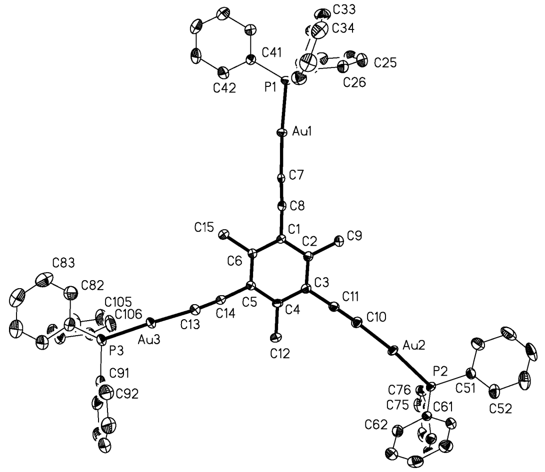

**Figure 1.** Thermal ellipsoid plot (50% probability) of $\mathbf{5}\cdot CH_2Cl_2$. H atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)−C(7) = 1.985(4), Au(2)−C(10) = 1.987(5), Au(3)−C(13) = 1.993(5), Au(1)−P(1) = 2.2692(12), Au(2)−P(2) = 2.2673(12), Au(3)−P(3) = 2.2747(14), C(7)−C(8) = 1.210(6), C(10)−C(11) = 1.206(6), C(13)−C(14) = 1.196(7); C(7)−Au(1)−P(1) = 176.14(13), C(10)−Au(2)−P(2) = 174.07(14), C(13)−Au(3)−P(3) = 175.4(2).

of the total replacement of the C≡CH protons by gold and its marked preference for a linear dicoordination. These complexes are, along with $(PPN)_n[Au(C{\equiv}CC_6H\text{-}5\text{-}R_3\text{-}2,4,6\text{-}C{\equiv}C)]_n$ (R = H, Me),[17] the first homoleptic ($\sigma$-alkynyl)gold(I) polymers.

An attempt to prepare the pentanuclear complex $PPN[Au\{C{\equiv}CAr(C{\equiv}CAuPTo_3)_2\}_2]$ by reacting **9** with $[Au(acac)PTo_3]$ (1:4) failed, and a mixture formed instead, from which **12** and $[\{AuPTo_3\}_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]$ were isolated in 84 and 82% yields, respectively. Both components were identified by IR: **12** by its elemental analyses and $[(AuPTo_3)_3\{\mu\text{-}(C{\equiv}C)_3Ar\}]$ by its NMR spectra ($^1$H, $\delta$ 7.49−7.20 (m, 36 H, $PTo_3$), 2.39 (s, 27 H, Me, $PTo_3$), 2.83 (s, 9 H, Me); $^{31}P\{^1H\}$, $\delta$ 40.92 (s, $PTo_3$)].

**X-ray Crystal Structures.** The crystal structures of $\mathbf{5}\cdot CH_2Cl_2$ (Figure 1), **9** (Figure 2), and **11** (Figure 3) were determined. In all these complexes the gold atoms are in essentially linear dicoordinate environments (angles at gold in the range 173.56(15)−179.12(9)°). The C≡C(Au) and $Au-C_{alkynyl}$ bond distances (in the ranges 1.196(7)−1.213(3) and 1.978(3)−1.987(5) Å, respectively) and also the Au−P distances in **5** (2.2673(12)−2.2747(14) Å) lie within the ranges found in other alkynylgold(I) complexes.[33]

The crystal structure of 1,3,5-triethynylbenzene is known, as well as those of three of its gold(I) derivatives, analogous to **5**, bearing $PPh_3$,[34] $^tBuNC$, and $P(OMe)_3$[22] ligands. Whereas the former displays short Au⋯Au contacts (3.311 Å), these are rather long in the $^tBuNC$ derivative (3.724 Å) and absent in that with $P(OMe)_3$. This is also the case in $\mathbf{5}\cdot CH_2Cl_2$, in which the shortest Au⋯Au contacts are 6.73 Å.

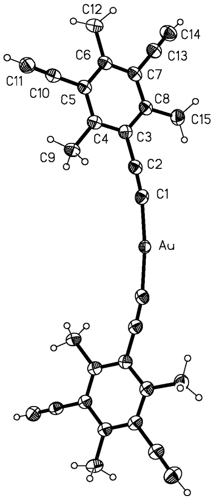

**Figure 2.** Thermal ellipsoid plot (50% probability) of the anion of **9** with the labeling scheme of the asymmetric unit. Some methyl H atoms are obscured. Selected bond lengths (Å) and angles (deg): Au−C(1) = 1.978(3), C(1)−C(2) = 1.208(4), C(10)−C(11) = 1.187(4), C(13)−C(14) = 1.165(4); C(1)−Au−C(1)#1 = 173.56(15), C(2)−C(1)−Au = 170.0(2), C(1)−C(2)−C(3) = 175.1(3).

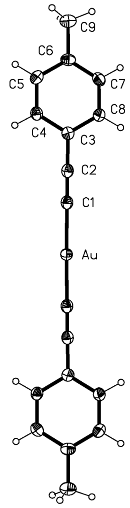

**Figure 3.** Thermal ellipsoid plot (50% probability) of the anion of **11** with the labeling scheme of the asymmetric unit. Selected bond lengths (Å) and angles (deg): Au−C(1) = 1.9860(19), C(1)−C(2) = 1.213(3); C(1)−Au−C(1)#2 = 179.12(9), C(2)−C(1)−Au = 178.87(16), C(1)−C(2)−C(3) = 178.68(19), P#1−N−P = 158.04(14).

The crystal structure of **9** consists of PPN cations and $[Au\{C{\equiv}CAr(C{\equiv}CH)_2\}_2]$ anions (Figure 2), each lying on a 2-fold symmetry axis. The C(3)C(2)C(1)AuC(1#)C(2#)C(3#) fragment is slightly bent (C(1)−Au−C(1#) = 173.56(15)° and C(6)⋯Au⋯C(6#) = 155.7°), and the two aromatic rings that support the alkynyl groups subtend an interplanar angle of 59.6°. Although the crystal structures of some anionic bis(alkynyl)gold(I) derivatives have been previously reported,[7,16,33,35,36] those of **9**, $PPN[Au\{C{\equiv}C(1,12\text{-dicarba-}closo\text{-dodecaborane(12)})C{\equiv}CH\}_2]$,[11] and $[Au(C{\equiv}CC{\equiv}CH)(PPh_3)]$[30] are the only ones to show partially aurated polyalkynes. The C≡CAu bond distances in the latter (1.188(10), 1.166(9), and 1.226(9) Å, respectively) are longer than C≡CH (1.097(11),

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[33] CCDC CSD version 5.25, December 2004.

[34] Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Maes, J.; Persoons, A.; Schmid, S.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *544*, 277.

[35] Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

[36] Smith, D. E.; Welch, A. J.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4616. Yam, V. W. W.; Cheung, K. L.; Yip, S. K.; Cheung, K. K. *J. Organomet. Chem.* **2003**, *681*, 196.

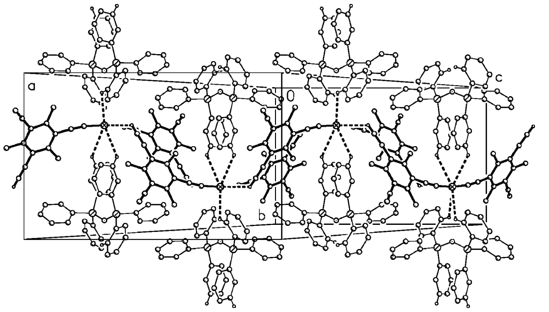

**Figure 4.** Packing diagram of **9** viewed perpendicular to the *yz* plane. C−H···Au interactions are shown by dashed lines. The anion chain is seen in the center of the figure and is drawn with thicker bonds. See text for further explanation.

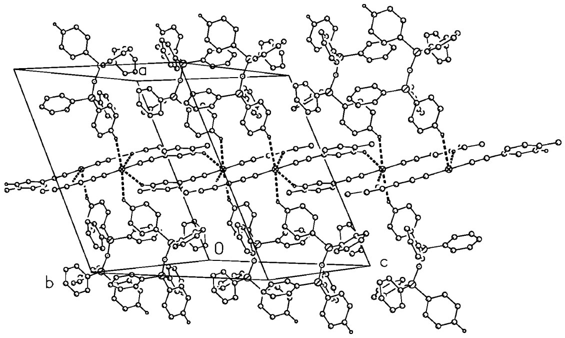

**Figure 5.** Packing diagram showing the C−H···Au hydrogen bonds (dashed lines) in **11**.

1.110(11), and 1.188(9) Å, respectively), which is also the case in **9** (1.208(4) vs 1.187(4) and 1.165(4) Å).

The anions of **9** form corrugated ribbons (Figure 4) parallel to the *z* axis. Each gold is involved in a short contact to three independent H atoms (and thus six in all); to H(11) of the neighboring anion at 3.07 Å, to H(25) at 3.10 Å, and to H(46) at 3.07 Å (for calculations, C−H bond lengths were normalized to 1.08 Å). The last two contacts represent the coordination of the anion chain by the cations. Although the contacts are far from linear (angles 120−135°) and one could argue that assemblies of linearly coordinated atoms are the most easily approached on steric grounds, we feel nevertheless that there is a case for considering the interactions as C−H···Au hydrogen bonds.[37−39] The lengthening of the H···Au distance by less than 0.3 Å with respect to the sum of the van der Waals radii (H···Au = 2.86 Å)[40] has not been considered critical.[37]

The crystal structure of **11** shows [Au(C≡CTo)$_2$] anions (Figure 3) and PPN cations; again, both of these lie on a 2-fold symmetry axis and the aromatic rings are slightly rotated with respect to each other (interplanar angle 18.6°). In contrast to the anions of compound **9**, there is no significant deviation from linearity, with C(6)···Au···C(6#) = 179°.

The packing of compound **11** (Figure 5) is similar to that of **9.** The anions form a double chain parallel to the *z* axis. Each gold atom forms two $C_{meta}$−H···Au hydrogen bonds with two neighboring anions (H(7)···Au = 2.85 Å, C(7)−H(7)−Au = 147°) and two $C_{para}$−H···Au hydrogen bonds with two cations (H(34)···Au = 2.76 Å, C(34)−H(34)−Au = 136°). The H···Au distances (much shorter than in compound **9** and also shorter than the sum of the van der Waals radii (2.86 Å))[40] and the C−H···Au angles are indicative of the presence of C−H···Au hydrogen bonds in complex **11**.[37−39] The anion−cation contacts, from cations above and below the anion chain, complete layers parallel to the *xz* plane. A further contact (not shown in Figure 5) is established between a methyl H and the ring centroid of a tolyl group (H···Centroid = 2.76 Å, C−H···Centroid = 145°).

X−H···M hydrogen bonds (M being metal and X being, in most cases, O, N, or C) have received little attention until quite recently.[39,41] These interactions are favored for electron-rich metals, such as late transition metals in low oxidation states, because the metal center acts as a Lewis base with respect to the hydrogen atom. These bonds are different from the X−H···M agostic interactions, in which the metal center acts as a Lewis acid with respect to the X−H bond density. The main structural differences between both types of interactions are the X−H−M angle, which is narrower for agostic (<100−130°) than for hydrogen bonds (>130°),[37−39] and the X−M bond distance, which is shorter for agostic than for hydrogen bond interactions.

Although many structures of gold(I) complexes show contacts interpretable as C-H···Au hydrogen bonds,[33] only a few have been discussed explicitly.[8,13,42] This could be attributed to the presence of other, classical hydrogen bonds or $Au^I$···$Au^I$ aurophilic interactions or to the fact that the search for C−H···M interactions is not well integrated into common program systems; correspondingly, it may be assumed that many such interactions fail to be reported.[43] Our results, which are the first reporting C−H···Au hydrogen bonds shorter than the sum of the van der Waals radii in a structure without other classical hydrogen bonds or $Au^I$···$Au^I$ aurophilic interactions, should spur ourselves and others to look for such interactions in all future crystal structures of gold complexes or, in general, for any X−H···metal contacts. However, we sound a note of caution. Hydrogen atom positions are imprecisely determined in the presence of heavy atoms. It is of course possible, and normal practice, to calculate the H atom positions, but some cases remain that cannot be calculated reliably (notably, methyl groups, especially those lacking significant rotational barriers).

**NMR Spectra.** The NMR spectra of the polymeric compounds **1**, **8**, **12**, and **13** could not be measured because of their insolubility. The spectrum of **9** shows the Me protons as two resonances at 2.62 and 2.53 ppm

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[37] Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891.

[38] Mascal, M. *Chem. Commun.* **1998**, 303. Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

[39] Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1997**, *16*, 1846.

[40] Bondi, A. *J. Phys. Chem.* **2001**, *68*, 441.

[41] Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 106. Crabtree, R. H.; Eisenstein, O.; Sini, G.; Peris, E. *J. Organomet. Chem.* **1998**, *567*, 7. Calhorda, M. J. *Chem. Commun.* **2000**, 801. Berenguer, J. R.; Fornies, J.; Gomez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2001**, *20*, 4847. Hascall, T.; Baik, M. H.; Bridgewater, B. M.; Shin, J. H.; Churchill, D. G.; Friesner, R. A.; Parkin, G. *Chem. Commun.* **2002**, 2644. Brammer, L. *Dalton Trans.* **2003**, 3145.

[42] Wong, W. Y.; Choi, K. H.; Lu, G. L.; Shi, J. X.; Lai, P. Y.; Chan, S. M.; Lin, Z. Y. *Organometallics* **2001**, *20*, 5446. Bardaji, M.; Jones, P. G.; Laguna, A. *Dalton Trans.* **2002**, 3624. Barranco, E. N.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G.; Ahrens, B. *Inorg. Chem.* **2000**, *39*, 680.

[43] Jones, P. G.; Ahrens, B. *Chem. Commun.* **1998**, 2307.

with relative intensities 2:1, which, along with the data collected from (arenealkynyl)gold complexes derived from $C_6H_4(C{\equiv}C)_2$-1,3, $C_6H(C{\equiv}C)_2$-1,3-$Me_3$-2,4,6,[10,17] and $C_6H_3N(C{\equiv}C)_2$-3,5,[12] allows us to conclude that the C≡CAu fragments cause the protons and methyl groups in ortho positions to be deshielded with respect to those in meta positions. In the carbene complex **4**, the partial multiple bond character of the C−N bond in the CNH$^t$Bu moiety can give rise to two possible isomers, *E* and *Z*, depending on the mutual disposition of the $^t$Bu and gold fragments. As only one resonance is observed in the $^1$H and $^{13}$C NMR spectra for each type of nucleus in the NH$^t$Bu fragment, only one of the isomers can exist in solution unless the C−NH$^t$Bu bond is weak enough to allow free rotation. In all the alkynylgold complexes with the same carbene ligand structurally characterized by us,[7,44] the crystal structure corresponds to the less crowded *Z* isomer, and we assume this to be also the case for **4**.

In the $^{13}C\{^1H\}$ NMR spectra the resonances from the $Au{-}C^{\alpha}{\equiv}C^{\beta}$ fragments are difficult to assign on the basis of the literature. Although most authors assign the resonance at lower field to the α-C,[20,35,45] opposite assignments can also be found,[46] along with others who do not describe these resonances[47,48] or attribute them to the C≡CAu fragment without distinction.[47,49] An HMBC experiment carried out for **11** allowed us to unequivocally assign the resonances at 133.7 and 102.9 ppm to the α- and β-C nuclei, respectively.

**IR Spectra**. Only the IR spectrum of **9** shows two medium-intensity bands at 3320 and 3280 cm$^{-1}$ assignable to ν(CC−H) stretching modes.[50] In the 2108−2082 cm$^{-1}$ region the IR spectra of complexes **9**−**11** show one band of medium intensity assignable to ν(C≡C)[50] (see the Experimental Section). A weak absorption is observed in the same region for complexes **1, 4, 6**, **7**, **12**, and **13**, while this band is absent in the spectra of **2**, **3**, **5**, and **8**. For the same alkyne, the ν(C≡C) wavenumber decreases in the series neutral > anionic mononuclear > anionic polymeric (**7** > **10** > **13** and **4**, **6** > **9** > **12**), probably because of the contribution of resonance forms of the type Au=C=C= favored by the negative charge at the gold atom and by the extended dπ−pπ electronic conjugation in the polymers.

**Mass Spectra**. The FAB$^-$-MS spectra of the anionic complexes **9**−**11** show the M$^-$ peak with 10% relative intensity. In the FAB$^+$-MS spectrum of **8** the peak of higher *m/z* value, at 1030 (3%), corresponds to the monomer. However, taking into account the insolubility of many complexes of the type $[Au_2(C{\equiv}CRC{\equiv}C)(LL)]_n$, (LL = diisocyanide or diphosphine ligand)[51] while the tetranuclear analogue $[Au_2(C{\equiv}CC{\equiv}C)(dppm)]_2$[30] is soluble, we tentatively assign to **8** a polymeric structure.

**Molar Conductivity in Solution.** The molar conductivities of the anionic derivatives **9**−**11**, soluble in acetone, gave values in the range of 75−99 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, slightly below those reported by Geary[52] for 1:1 electrolytes, which we attribute to the much larger size of the ions in these complexes with respect to those used in the reference study.

## Conclusions

We report the synthesis of a family of (arenemonoethynyl)-, (arenediethynyl)-, and some of the few existing (arenetriethynyl)gold(I) complexes. In addition, **4** and **6** are the only (arenetriethynyl)gold(I) complexes with ligands other than phosphine or isocyanide. Complexes **9** and **10** are some of the few gold complexes bearing a partially aurated polyalkyne, and **12** and **13** are, along with $(PPN)_n[Au(C{\equiv}CC_6H\text{-}5\text{-}R_3\text{-}2,4,6\text{-}C{\equiv}C)]_n$ (R = H, Me), the first homoleptic (σ-alkynyl)gold(I) polymers. The crystal structures of **9** and **11** show interesting features. Thus, in **9** we propose C−H···Au hydrogen bonds involving a hydrogen of the neighboring anion and two hydrogens of the cation, and in **11** we report the first C−H···Au hydrogen bonds shorter than the sum of the van der Waals radii in a structure without other classical hydrogen bonds or $Au^I\cdots Au^I$ aurophilic interactions.

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**Supporting Information Available:** CIF files giving crystal data for **5**, **9**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Alvarez-Falcón, M. M.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2003**, *22*, 4327.

(45) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 497. McArdle, C. P.; Van, S.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 3959. McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Vittal, J. J.; Puddephatt, R. J. *Chem. Eur. J.* **2002**, *8*, 723. Eisler, D.; Hong, W.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2002**, *21*, 3955.

(46) Naulty, R. H.; Cifuentes, M. P.; Humphrey, M. G.; Houbrechts, S.; Boutton, C.; Persoons, A.; Heath, G. A.; Hockless, D. C. R.; Luther-Davies, B.; Samoc, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4167. Hong, X.; Cheung, K. K.; Guo, C.-X.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1867.

(47) Lang, H.; Kocher, S.; Back, S.; Rheinwald, G.; van Koten, G. *Organometallics* **2001**, *20*, 1968.

(48) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163. Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A.; Hockless, D. C. R. *Organometallics* **1996**, *15*, 5738. Bruce, M. I.; Liddell, M. J. *J. Organomet. Chem.* **1992**, *427*, 263.

(49) Alder, M. J.; Flower, K. R.; Pritchard, R. G. *J. Organomet. Chem.* **2001**, *629*, 153. Back, S.; Gossage, R. A.; Lang, H.; van Koten, G. *Eur. J. Inorg. Chem.* **2000**, 1457.

(50) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic* Compounds, 4th ed.; Wiley-VCH: New York, 1981; p 110.

(51) Puddephatt, R. J. *Chem. Commun.* **1998**, 1055.

(52) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.