

New arenediethynylgold(I) complexes. Crystal structures of $[\text{Ph}_3\text{PAuC}\equiv\text{C}(\text{phenylendiyl-1,3})\text{C}\equiv\text{CAuPPh}_3]$ and $[\text{Ph}_3\text{PAuC}\equiv\text{C}(\text{mesitylendiyl-1,3})\text{C}\equiv\text{CAuPPh}_3]$

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Dedicated to Professor Rafael Usón in recognition of his leading role in organometallic chemistry

Abstract

By reacting the dialkynes $\text{HC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CH}$ [Ar = 1,3- C_6H_4 (mphen), 1,3-(C_6HMe_3 -2,4,6) (mes), 1,4-(C_6Me_4 -2,3,5,6) (dur)] with $[\text{AuClL}]$ [L = dimethylsulfide (dms), tetrahydrothiophene (tht)] in the presence of an excess of Et_3N the polymeric complexes $[\text{AuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAu}]_n$ [Ar = mphen (**1**), mes (**2**) dur (**3**)] were prepared. Upon reaction of these complexes with two equivalents of phosphine or isocyanide ligands (L), complexes $[\text{LAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuL}]$ [Ar = mes, L = ^tBuNC (**4**), XyNC (**5**); Ar = dur, L = PPh₃ (**6**), ^tBuNC (**7**)] were prepared in good yields. The complex $[\text{^tBuNCAuC}\equiv\text{C}(\text{mphen})\text{C}\equiv\text{CAuCN^tBu}]$ (**8**) was prepared by reaction of the corresponding diethynylarene with 2 equiv. of $[\text{AuCl}(\text{CN}^t\text{Bu})]$ in the presence of NEt_3 . By reacting the appropriate diethynylarene with 2 equiv. of $[\text{Au}(\text{acac})\text{PPh}_3]$, complexes $[\text{Ph}_3\text{PAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuPPh}_3]$ [Ar = mphen (**9**), mes (**10**)] were prepared. The carbene complex $[\text{^tBuNH}(\text{Et}_2\text{N})\text{CAuC}\equiv\text{C}(\text{mes})\text{C}\equiv\text{CAu}(\text{NH}^t\text{Bu})(\text{NEt}_2)]$ (**11**) was obtained by reacting the corresponding isocyanide complex **4** with diethylamine. The crystal structures of complexes **9** and **10** have been determined by X-ray diffraction studies. In both cases one of the gold atoms is in an essentially linear environment [CAuP: 176.95(14) (**9**), 177.19(8)° (**10**)] while the other CAuP bond angle is appreciably bent [170.07(11) (**9**), 171.22(8)° (**10**)].

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1. Introduction

Polymeric species in which metal centers are bridged by $-\text{C}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{C}-$ spacers (R being various groups including aromatic rings) are attracting great attention because some are known to display electrical conduct-

ing, nonlinear optical or liquid crystalline properties [1]. Diethynylarenegold(I) complexes of the types $[\text{AuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAu}]_n$ [2–4], $[\text{LAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuL}]$, (L = phosphine [3,5], isocyanide) [2,3], $[\text{AuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAu}(\text{LL})]_n$, (LL = diphosphines [1,3,4], diisocyanide [2,3]), $[\text{ClAuPR}_2\text{CH}_2\text{PR}_2\text{AuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuPR}_2\text{CH}_2\text{PR}_2\text{AuCl}]$ [1] and $[\{\text{AuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAu}\}_2\{\text{CH}_2(\text{PR}_2)_2\}_2]$ [5] have been prepared, Ar groups including C_6H_4 -1,4, ($\text{C}_6\text{H}_2\text{Me}_2$ -2,5)-1,4 and $\text{C}_6\text{H}_3\text{Me}$ -5-1,3. Most such complexes have been obtained from the reaction of $[\text{AuCl}(\text{SM}_2)]$ with the appropriate dialkyne (2:1) in the

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presence of base [1,2] or by the reactions of these polymers with the appropriate ligands [6] although in some cases special methods have been used [5]. In such complexes, apart from some peculiar large ring structures [5], interesting photophysical properties [6,7] have been found that are attributed in part [8–11] to the existence of the short intermolecular Au···Au contacts present in most of the structurally characterized luminescent gold(I) complexes [3,7,8,12]. Only three crystal structures of arenediethynylgold(I) complexes have been reported so far, namely those of $[LAuC\equiv C(Ar)C\equiv CAuL]$ ($Ar = 1,4-(C_6H_2Me_2-2,5)$, $L = PMe_3$ [7], $Ar = 3,5-C_6H_3Me$, $L = P(OMe)_3$, $PMePh_2$) [3]. All three display infinite chains of linear or angular digold molecules associated by short Au···Au contacts. Additionally, in the structure of the complex with $L = PMePh_2$, parallel ribbons form by interaction of two such chains. Puddephatt has recently reviewed this chemistry [13]. Some diethynylgold(I) complexes have been reported while this paper was being prepared [4,14].

We report here (i) the synthesis of diethynylidurene and diethynylmesitylene, (ii) new arenediethynylgold(I) complexes of the types $[AuC\equiv C(Ar)C\equiv CAu]_n$ and $[LAuC\equiv C(Ar)C\equiv CAuL]$ derived from these diethynylarenes and from the previously described diethynyl-1,3-benzene and (iii) the crystal structures of two diethynylarenegold(I) derivatives. None of these three diethynyl groups are represented in the alkynylgold complexes previously described.

2. Experimental

2.1. Instrumentation, materials and reagents

The IR spectra, elemental analyses and melting point determinations were carried out as described earlier [15]. Technical grade solvents were purified by standard procedures. Unless otherwise stated, the reactions were carried out at room temperature (r.t.) without special precautions against moisture. The syntheses of the dialkynes $HC\equiv C(Ar)C\equiv CH$ [$Ar = mes = 1,3-(C_6HMe_3-2,4,6)$; $dur = 1,4-(C_6Me_4-2,3,5,6)$] (see Chart 1), derived from mesitylene and durene are described below, while that for $Ar = mphen = 1,3-C_6H_4$ [16] was previously described. The 1H and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ with Varian Unity 300 or Bruker AC-200 spectrometers. Chemical shifts, given in ppm, are referred to TMS [1H , $^{13}C\{^1H\}$] or H_3PO_4 [$^{31}P\{^1H\}$]. Molar conductivities were measured in acetone solution (ca. $5 \times 10^{-4} \text{ mol l}^{-1}$) and are in the range 0–3 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

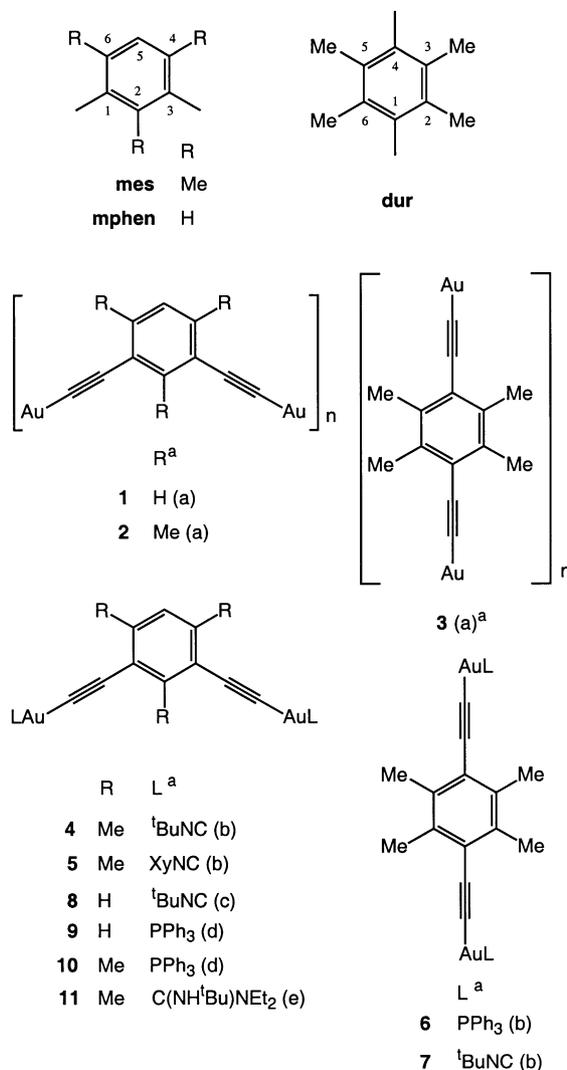


Chart 1.

2.2. X-ray structure determinations

Numerical data are presented in Table 1. Crystals were mounted on glass fibres and transferred to the cold gas stream of the diffractometer (Bruker Smart 1000 CCD). Data were recorded with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in ω - and ϕ -scan mode. Absorption corrections were applied on the basis of multiple scans (SADABS). Structures were solved by the heavy-atom method and refined anisotropically on F^2 (SHELXL-97 [57]). Hydrogen atoms were included using a riding model or with rigid methyl groups. To increase stability of refinement, a system of restraints to local ring geometry and light atom U values was employed in each case. *Special features of refinement*: In compound 9, the residual electron density near the gold atoms is high, probably because of an imperfect absorption

Table 1
Crystallographic data

	9	10
Formula	C ₄₆ H ₃₄ Au ₂ P ₂	C ₄₉ H ₄₀ Au ₂ P ₂
f_w	1042.60	1084.68
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.0219(10)	9.9763(6)
b (Å)	12.8300(12)	12.9029(8)
c (Å)	16.2393(16)	17.0115(11)
α (°)	80.922(3)	81.654(3)
β (°)	75.008(3)	74.554(3)
γ (°)	71.777(3)	71.257(3)
V (Å ³)	1909.1(3)	1994.5
Z	2	2
ρ_{calc} (g cm ⁻³)	1.814	1.806
μ (mm ⁻¹)	7.791	7.461
T (K)	143(2)	133(2)
R_w (F^2) ^a	0.0966	0.0527
R (F) ^b	0.0359	0.0221
$\Delta\rho$ (e Å ⁻³)	4.0	1.6

^a $wR_2(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\} / \sum\{w(F_o^2)^2\}]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

^b $R_1(F) = \sum||F_o| - |F_c|| / \sum|F_o|$ for reflections with $F > 2\sigma(F)$.

correction for an irregular plate. In compound **10**, the ring C41–46 is disordered over two positions, which were refined isotropically with idealized geometry.

2.3. Syntheses

2.3.1. Synthesis of *mes*I₂

Mesitylene (2.8 ml, 20 mmol) was added to a suspension containing I₂ (5.1 g, 20 mmol) and IPh(CF₃CO₂)₂ [17] (9.5 g, 22 mmol) in CCl₄ (30 ml). The reaction mixture was stirred for 1.25 h and filtered through Celite. The solution was concentrated under vacuum almost to dryness and cold ethanol (ca. –15 °C, 15 ml) was added. The resulting suspension was filtered, and the white solid was washed with cold EtOH and suction dried in the air. Yield 5.4 g, 73%. M.p. 62 °C. ¹H NMR (200 MHz): δ 2.40 (s, 6H, Me); 2.91 (s, 3H, Me), 6.97 (s, 1H).

2.3.2. Synthesis of Me₃SiC≡C(*mes*)C≡CSiMe₃

To a solution containing mesI₂ (2.83 g, 7.6 mmol), [PdCl₂(PPh₃)₂] (97 mg, 0.14 mmol) and CuI (56 mg, 0.3 mmol) in NHET₂ (50 ml) was added Me₃SiC≡CH (4 ml, 29 mmol) under a nitrogen atmosphere and the reaction mixture was stirred for 43 h. The reaction mixture was concentrated under vacuum to dryness and the residue was extracted with diethyl ether (4 × 50 ml). The combined extracts were dried over anhydrous Na₂SO₄ for 1 h and then filtered. The solution was concentrated to ca. 130 ml and chromatographed through a neutral Al₂O₃ column. The first yellow effluent was collected, concentrated to dryness and recrystallized from EtOH

(15 ml) to give colorless needles. Yield 1.48 g, 62%. IR (cm⁻¹): ν (C≡C), 2146. ¹H NMR (200 MHz): δ 0.26 (s, 18H, SiMe₃), 2.38 [s, 6H, Me (mes)], 2.55 [s, 3H, Me (mes)], 6.88 [s, 1H, H (mes)].

2.3.3. Synthesis of HC≡C(*mes*)C≡CH

A solution containing Me₃SiC≡C(*mes*)C≡CSiMe₃ (520 mg, 1.7 mmol) and KOH (100 mg, 1.8 mmol) in MeOH (50 ml) was stirred at 50 °C for 6 h. The solution was diluted with water (150 ml) and extracted with a mixture of *n*-pentane and diethyl ether (1.7:1, 3 × 80 ml). The combined extracts were dried over anhydrous MgSO₄ for 0.5 h and filtered. The solution was concentrated to dryness to give a bright yellow oil. Yield 230 mg, 81%. IR (cm⁻¹): ν (≡C–H), 3308; ν (C≡C), 2102. ¹H NMR (200 MHz): δ 2.34 [s, 6H, Me (mes)], 2.53 [s, 3H, Me (mes)], 3.40 (s, 2H, CH), 6.85 [s, 1H, H (mes)]. ¹³C{¹H} NMR (50.3 MHz): δ 19.6 (Me), 21.1 (Me), 80.9 (C≡CH), 84.9 (C≡CH), 119.7, 128.0, 141.1, 143.6 ppm.

2.3.4. Synthesis of Me₃SiC≡C(*dur*)C≡CSiMe₃

To a suspension containing durI₂ [17] (1.85 g, 4.80 mmol), [PdCl₂(PPh₃)₂] (101 mg, 0.14 mmol) and CuI (62 mg, 0.32 mmol) in NHET₂ (30 ml) was added Me₃SiC≡CH (1.5 ml, 10.56 mmol) under a nitrogen atmosphere and the reaction mixture was stirred for 21 h. The suspension was concentrated to dryness and the residue extracted with *n*-pentane (4 × 50 ml). The combined extracts were dried over anhydrous Na₂SO₄ for 1 h and filtered. The solution was concentrated to ca. 150 ml and chromatographed on neutral alumina using *n*-pentane as eluent. The first effluent was collected and concentrated (10 ml) to give colorless needles. Yield 665 mg, 51%. ¹H NMR (200 MHz): δ 0.32 (s, 18H, SiMe₃), 2.43 [s, 12H, Me (dur)].

2.3.5. Synthesis of HC≡C(*dur*)C≡CH

To a solution of KOH (56 mg, 0.39 mmol) in H₂O (12 ml) was added Me₃SiC≡C(*dur*)C≡CSiMe₃ (1.13 g, 3.47 mmol) and MeOH (60 ml). The reaction mixture was heated at 80 °C for 10 h and left at r.t. overnight. It was then treated with a saturated solution of NaCl in H₂O (50 ml) and extracted with *n*-pentane (3 × 100 ml). The extracts were dried over anhydrous Na₂SO₄ for 1 h and filtered. The solution was concentrated to dryness to give the crude title compound, which was purified by sublimation onto a cold finger. Yield 550 mg, 87%. M.p.: 102 °C. IR (cm⁻¹): ν (≡C–H), 3320, ν (C≡C), 2162. ¹H NMR (200 MHz): δ 2.43 [s, 12H, Me (dur)], 3.56 (s, 2H, CH) ppm.

2.3.6. Synthesis of [AuC≡C(*Ar*)C≡CAu] [*Ar* = *mphen* (**1**), *mes* (**2**), *dur* (**3**)]

The addition of triethylamine (**1**, 0.263 ml, 1.90 mmol; **2**, 0.4 ml, 2.87 mmol; **3**, 15 ml, 107 mmol) to a solution

containing the appropriate diethynylarene $\text{HC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CH}$ ($\text{Ar} = \text{mphen}$, 120 mg, 0.95 mmol; mes , 227 mg, 1.35 mmol; dur , 105 mg, 0.58 mmol) and two equivalents of $[\text{AuCl}(\text{SMe}_2)]$ (**1**) or $[\text{AuCl}(\text{tht})]$ (**2**, **3**, $\text{tht} = \text{tetrahydrothiophene}$) in degassed dichloromethane (15 ml) caused immediate precipitation of a yellow (**1**, **2**) or orange (**3**) solid. The suspension was stirred for 10 min, filtered, washed with dichloromethane (3×10 ml) and diethyl ether (5 ml) and air-dried to give complexes **1–3**. **1**: m.p. 150 °C (dec.). Analyses (see Section 3). IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$, 2108. **2**: m.p. 162 °C (dec.). Analyses (see Section 3). IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$, 2104. **3**: m.p. 154 °C (dec.). Analyses (see Section 3). IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$, 2015.

2.3.7. Synthesis of $[\text{LAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuL}]$ [$\text{Ar} = \text{mes}$, $\text{L} = {}^t\text{BuNC}$ (**4**), XyNC ($\text{Xy} = \text{C}_4\text{H}_3\text{Me}_2$, **2,6**) (**5**); $\text{Ar} = \text{dur}$, $\text{L} = \text{PPh}_3$ (**6**), ${}^t\text{BuNC}$ (**7**)]

To a suspension containing ca. 0.2 mmol of **2** (for **4**, **5**) or **3** (for **6**, **7**) in degassed dichloromethane (20 ml) 4 equiv. of the appropriate ligand were added. After 1 h of stirring the reaction mixture was filtered through Celite. The solution was concentrated (2 ml) and diethyl ether (20 ml) was added to precipitate a yellow (**4**, **5**) or pale yellow (**6**) or white (**7**) solid that was filtered under vacuum and air-dried. **4**: yield 75%. M.p. 170 °C (dec.). Anal. Calc. for $\text{C}_{23}\text{H}_{28}\text{Au}_2\text{N}_2$: C, 38.03; H, 3.89; N, 3.86. Found: C, 38.20; H, 3.70; N, 4.09%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2220. ${}^1\text{H}$ NMR (200 MHz): δ 1.55 (s, 18H, ${}^t\text{Bu}$), 2.44 (s, 6H, Me), 2.72 (s, 3H, Me), 6.83 [s, 1H, Ar (Mes)] ppm. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (50.3 MHz): δ 20.4 (Me), 21.4 (Me), 29.6(C–Me₃), 58.2(C–Me₃), 100.5(C–CAu), 121.6(C–Au), 127.0, 129.4, 138.6, 142.7, 147.0 (CN) ppm. **5**: yield 74%. M.p. 200 °C (dec.). Anal. Calc. for $\text{C}_{31}\text{H}_{28}\text{Au}_2\text{N}_2$: C, 45.27; H, 3.43; N, 3.41. Found: C, 45.60; H, 3.39; N, 3.37%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2204(s). ${}^1\text{H}$ NMR (200 MHz): δ 2.44 (s, 12H, Me), 2.48 (s, 6H, Me), 2.78 (s, 3H, Me), 6.87 [s, 1H, (mes)], 7.14–7.36 (m, 6H, Xy) ppm. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (50.3 MHz): δ 18.7 (Me), 21.6 (Me), 121.8, 128.4, 130.7, 136.2, 139.1 ppm. **6**: yield 75%. M.p. 115 °C (dec.). Anal. Calc. for $\text{C}_{50}\text{H}_{42}\text{Au}_2\text{P}_2$: C, 54.66; H, 3.85. Found: C, 54.24; H, 4.05. ${}^1\text{H}$ NMR (200 MHz): δ 2.53 (s, 12H, Me), 7.42–7.60 (m, 30H, PPh₃) ppm. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (50.3 MHz): δ 19.08 (Me), 129.06 (d, *m*-C, PPh₃, ${}^3J_{\text{CP}} = 11$ Hz), 130.02 (d, *i*-C, PPh₃, $J_{\text{CP}} = 55$ Hz), 131.4 (d, *p*-C, PPh₃, ${}^4J_{\text{CP}} = 3$ Hz), 134.4 (d, *o*-C, PPh₃, ${}^2J_{\text{CP}} = 12$ Hz), 135.4 (CMe), ppm. ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR (121 MHz) δ 42.94 (s, PPh₃) ppm. **7**: Yield 80%. M.p. 172 °C. Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{Au}_2\text{N}_2$: C, 38.93; H, 4.08; N, 3.78. Found: C, 39.54; H, 4.26; N, 3.79%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2222; $\nu(\text{C}\equiv\text{C})$, 2018. ${}^1\text{H}$ NMR (200 MHz): δ 1.55 (s, 18H, ${}^t\text{Bu}$), 2.45 (s, 12H, C₆Me₄) ppm. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (50.3 MHz): δ 18.79 (Me), 29.75 (C–Me₃), 58.39 (C–Me₃), 101.99 (C–CAu), 123.48 (C–Au), 130.83 (C–C≡C), 135.41 (C–Me), 147.81 (C–N) ppm.

2.3.8. $[{}^t\text{BuNC AuC}\equiv\text{C}(\text{mphen})\text{C}\equiv\text{CAuCN}{}^t\text{Bu}]$ (**8**)

NEt_3 (5 ml) was added to a solution containing $[\text{AuCl}(\text{CN}{}^t\text{Bu})]$ (300 mg, 0.95 mmol) and 1,3-diethynylbenzene (60.5 mg, 0.48 mmol) in dichloromethane (15 ml). The suspension was stirred for 24 h and concentrated under vacuum to dryness. The solid residue was dissolved in dichloromethane (2 ml) and diethyl ether (20 ml) was added to precipitate a solid that was filtered, washed with water (2×5 ml), dissolved in dichloromethane (20 ml) and filtered through MgSO_4 . The solution was concentrated under vacuum (1 ml) and diethyl ether (20 ml) was added to precipitate **8** as a pale yellow solid. Yield 57%. M.p. 209 °C (dec.). Anal. Calc. for $\text{C}_{20}\text{H}_{22}\text{Au}_2\text{N}_2$: C, 35.10; H, 3.24; N, 4.09. Found: C, 34.94; H, 3.03; N, 4.03%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2226; $\nu(\text{C}\equiv\text{C})$, 2109. ${}^1\text{H}$ NMR (200 MHz): δ 1.57 (s, 18H, ${}^t\text{Bu}$), 7.10 [t, 1H, H5 (mphen), ${}^3J_{\text{HH}} = 8$ Hz], 7.29 [dd, 2H, H4+H6 (mphen), ${}^3J_{\text{HH}} = 8$ Hz, ${}^4J_{\text{HH}} = 1.5$ Hz], 7.54 [t, 1H, H2 (mphen), ${}^4J_{\text{HH}} = 1.5$ Hz] ppm. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (75.4 MHz): δ 29.77 (s, Me), 58.52 (s, CMe₃), 102.93 (s, CCAu), 121.83 (s, CAu), 124.43 [s, C1 (mphen)], 127.55 [s, C5 (mphen)], 131.13 [s, C4+C6 (mphen)]; 136.21 [s, C2 (mphen)] ppm.

2.3.9. Synthesis of $[\text{Ph}_3\text{PAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuPPh}_3]$ [$\text{Ar} = \text{mphen}$ (**9**) mes (**10**)]

To a solution of the appropriate diethynylarene (**9**: 35.4 mg, 0.21 mmol; **10**: 153 mg, 0.91 mmol) in degassed dichloromethane (30 ml) was added $[\text{Au}(\text{acac})\text{PPh}_3]$ (**9**: 234.5 mg, 0.42 mmol; **10**: 1117 mg, 2 mmol) and the reaction mixture was stirred for 1.5 h (**9**) or 7 h (**10**) under a nitrogen atmosphere. The resulting solution was filtered through Celite, concentrated under vacuum (**9**: 2 ml; **10**: 5 ml) and diethyl ether (**9**: 40 ml; **10**: 70 ml) was added to precipitate a white (**9**: 172 mg, 0.17 mmol) or bright yellow (**10**: 593 mg, 0.456 mmol) solid, which was filtered and dried in a nitrogen atmosphere. **9**: yield 79%. M.p. 151 °C. Anal. Calc. for $\text{C}_{46}\text{H}_{34}\text{Au}_2\text{P}_2$: C, 52.97; H, 3.29. Found: C, 52.74; H, 3.13%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$, 2099. ${}^1\text{H}$ NMR (200 MHz): δ 7.13 [t, 1H, H5 (mphen), ${}^3J_{\text{HH}} = 8$ Hz], 7.37 [dd, 2H, H4+H6 (mphen), ${}^3J_{\text{HH}} = 8$ Hz, ${}^4J_{\text{HH}} = 2$ Hz], 7.41–7.59 (m, 30H, PPh₃), 7.65 [t, 1H, H2 (mphen), ${}^4J_{\text{HH}} = 2$ Hz] ppm. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (50.3 MHz): δ 104.10 (s, C≡CAu), 124.61 [s, C1+C3 (mphen)], 127.58 [s, C₅ (mphen)], 129.09 (d, *m*-C, PPh₃, ${}^3J_{\text{CP}} = 11.4$ Hz), 130.35 (d, *i*-C, PPh₃, $J_{\text{CP}} = 58$ Hz), 131.12 [s, C4+C6 (mphen)], 131.47 (d, *p*-C, PPh₃, ${}^4J_{\text{CP}} = 2.3$ Hz); 131.95 (s, CAu); 134.31 (d, *o*-C, PPh₃, ${}^2J_{\text{CP}} = 13.9$ Hz); 135.81 (s, C2) ppm. ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR (121 MHz): δ 42.51 (s, PPh₃) ppm. Crystals of **9** suitable for an X ray diffraction study were grown by the liquid diffusion method using dichloromethane and diethyl ether. **10**: yield 60%. M.p. 220 °C (dec.). Anal. Calc. for $\text{C}_{49}\text{H}_{40}\text{Au}_2\text{P}_2$: C, 54.26; H, 3.72. Found: C, 53.42; H, 3.74. ${}^1\text{H}$ NMR (200 MHz): δ 2.50 (s, 6H, Me), 2.84 (s, 3H, Me), 6.86 (s, 1H, mes), 7.43–7.61 (m, 30H, PPh₃)

ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz): δ 21.0 (Me), 21.8 (Me), 101.5 ($\text{C}\equiv\text{CAu}$), 122.0, 127.2, 129.1(d, m-C, PPh_3 , $^3J_{\text{CP}} = 11$ Hz), 130.0 (d, *i*-C, PPh_3 , $J_{\text{CP}} = 55$ Hz), 131.4 (d, *p*-C, PPh_3 , $^4J_{\text{CP}} = 1$ Hz), 134.3 (d, *o*-C, PPh_3 , $^2J_{\text{CP}} = 14$ Hz), 138.6, 142.8 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz): δ 43.0 (s, PPh_3) ppm. Crystals of **10** suitable for an X ray diffraction study were grown as for **9**.

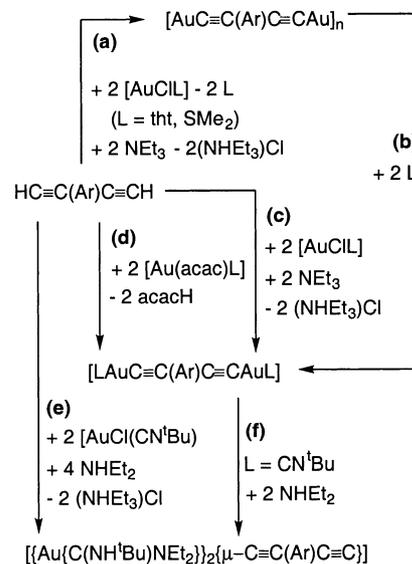
2.3.10. $[(^t\text{BuNH})(\text{Et}_2\text{N})\text{CAu}\text{C}\equiv\text{C}(\text{mes})\text{C}\equiv\text{CAu}\text{C}(\text{NH}^t\text{Bu})(\text{NEt}_2)]$ (**11**)

Diethylamine (2.5 ml, 24 mmol) was added to a solution of complex **4** (276 mg, 0.38 mmol) in degassed dichloromethane (10 ml), the resulting solution was stirred for 2.5 h, concentrated under vacuum to dryness and the residue stirred with *n*-pentane (20 ml) to give **11** as a white solid. Yield: 72%. M.p. 90 °C. *Anal.* Calc. for $\text{C}_{31}\text{H}_{50}\text{Au}_2\text{N}_4$: C, 42.67; H, 5.77; N, 6.42. Found: C, 42.23; H, 6.06; N, 6.62%. IR (cm^{-1}): $\nu(\text{NH})$, 3332; $\nu(\text{C}\equiv\text{C})$, 2102. ^1H NMR (200 MHz): δ 1.13 [t, 6H, Me (NEt_2)], 1.29 [t, 6H, Me (NEt_2)], 1.65 (s, 18H, ^tBu), 2.46 [s, 6H, Me (mes)], 2.78 [s, 3H, Me (mes)], 3.24 (q, 4H, CH_2), 4.05 (q, 4H, CH_2), 5.83 (s, 2H, NH), 6.79 (s, 1H, mes) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz): δ 12.3, 14.4, 21.4, 22.2, 32.1, 40.3, 54.4, 54.6, 103.7, 123.3, 127.2, 133.9, 138.0, 142.5, 206.8 ppm.

3. Results and discussion

3.1. Synthesis

The reactions in dichloromethane between various diethynylarenes $\text{HC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CH}$ and complexes $[\text{AuClL}]$ [$\text{L} = \text{dimethylsulfide}$ (dms), tetrahydrothiophene (tht)] in the presence of an excess of triethylamine (method a) produce the insoluble complexes $[\text{AuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAu}]_n$, [$\text{Ar} = 1,3\text{-C}_6\text{H}_4$ (mphen) (**1**), $1,3\text{-}(\text{C}_6\text{HMe}_3\text{-}2,4,6)$ (mes) (**2**), $1,4\text{-}(\text{C}_6\text{Me}_4\text{-}2,3,5,6)$ (dur) (**3**)] (see Chart 1 and Scheme 1). The by-product $(\text{NHEt}_3)\text{Cl}$ can be readily separated by exploiting its solubility in dichloromethane. To account for both the insolubility and the small sulfur and nitrogen content shown by the elemental analyses of these complexes [**1**: *Anal.* Calc. for $\text{C}_{10}\text{H}_4\text{Au}_2 \cdot 0.3\text{NEt}_3$: C, 25.84; H, 1.56; N, 0.76. Found: C, 27.42; H, 1.42; N, 0.60%. **2**: *Anal.* Calc. for $\text{C}_{13}\text{H}_{10}\text{Au}_2$: C, 27.88; H, 1.80. Found: C, 30.97; H, 2.78; N, 0.88; S, 0.71%. **3**: *Anal.* Calc. for $\text{C}_{14}\text{H}_{12}\text{Au}_2$: C, 29.29; H, 2.11. Found: C, 27.02; H, 2.28; N, 0.20; S, 0.96%] we assume that the bidentate dialkynyl ligand, resulting from the deprotonation of the corresponding dialkyne by the base NEt_3 , replaces both the chloro and the labile sulfur donor ligand to give an open chain polymeric species in which some gold atoms complete their coordination spheres by side-on coordination to one $\text{C}\equiv\text{C}$ bond while others coordinate triethylamine or the corresponding sulfur donor ligand. The absence of



Scheme 1.

sulfur in the elemental analysis of **1** allowed us to estimate the approximate $\text{NEt}_3/\mathbf{1}$ ratio to be about 0.3/1. The reactions of these polymers to give the well-characterized monomers **4–7** support their proposed nature. This method has been used previously for the synthesis of complexes homologous to **1–3** with $\text{Ar} = 4,4'\text{-C}_6\text{H}_4\text{C}_6\text{H}_4$, $4\text{-}(\text{C}_6\text{H}_2\text{Me}_2\text{-}2,5)$ [**2**].

For the synthesis of neutral dinuclear complexes of the type $[\text{LAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuL}]$ we have used up to four different synthetic methods (see b–e in Scheme 1). Upon reaction of the polymeric complexes **1** and **2** with two equivalents of phosphine or isocyanide ligands (L), complexes $[\text{LAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuL}]$ [$\text{Ar} = \text{mes}$, $\text{L} = ^t\text{BuNC}$ (**4**), XyNC (**5**); $\text{Ar} = \text{dur}$, $\text{L} = \text{PPh}_3$ (**6**), $^t\text{BuNC}$ (**7**)] form in good yields (method b) although this method had been found inconvenient for the synthesis of other alkynylgold(I) phosphine derivatives [**18**]. Complexes **4–7** result from the replacement of both the labile ligands (NEt_3 and dms or tht) and the $\pi(\text{C}\equiv\text{C}) \rightarrow \text{Au}$ interactions in **2** or **3** by the strong donor L ligands. We have prepared the homologous complex $[\text{BuNC}\text{AuC}\equiv\text{C}(\text{mphen})\text{C}\equiv\text{CAuCN}^t\text{Bu}]$ (**8**) through a different method involving the reaction of two equivalents of $[\text{AuCl}(\text{CN}^t\text{Bu})]$ with the corresponding diethynylarene in the presence of NEt_3 (method c). Complexes of the same type, namely $[\text{Ph}_3\text{PAuC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CAuPPh}_3]$ [$\text{Ar} = \text{mphen}$ (**9**), mes (**10**)], can be obtained by reacting the appropriate diethynylarene with two equivalents of $[\text{Au}(\text{acac})\text{PPh}_3]$ (method d). We have previously shown that acetylacetonatogold(I) complexes deprotonate organic substrates containing weakly acidic hydrogen atoms to give a variety of gold(I) complexes [**19–37**] including alkynyl derivatives [**38–40**]. The extension of this method to the preparation of complexes **9** and **10** provides further examples of the synthetic utility of the ‘acac method’ [**41**].

The carbene complex $[(^t\text{BuNH})(\text{Et}_2\text{N})\text{CAu} \equiv \text{C}(\text{mes})\text{C} \equiv \text{CAu}(\text{NH}^t\text{Bu})(\text{NEt}_2)]$ (**11**) was obtained by reacting the corresponding isocyanide complex (**4**) with diethylamine (method e). It is well documented that alcohols and primary and secondary amines add to isocyanidegold(I) complexes to give the corresponding carbene derivatives [40,42–46].

3.2. Structure of complexes

3.2.1. Crystal structures of **9** and **10**

Figs. 1 and 2 show the crystal structures of complexes **9** and **10**, respectively. The crystal data are collected in Table 1. Complexes **9** and **10** are isostructural. In both cases one of the gold atoms is in an essentially linear environment [CAuP: 176.95(14)° (**9**), 177.19(8)° (**10**)] while the other CAuP bond angle is appreciably bent [170.07(11)° (**9**), 171.22(8)° (**10**)]. The Au–C, AuP and C≡C bond distances are in the ranges 1.998(5)–2.046(4), 2.2703(7)–2.2821 and 1.204(4)–1.215(4) Å, respectively, and are similar to those found in other alkynylgold(I) complexes [1,10,40,46–54] No short Au···Au contacts were observed.

3.2.2. NMR spectroscopy

The insolubility of the polymeric complexes **1–3** in most common organic solvents prevented the measurement of their NMR spectra. We attribute to the limited solubility of **5** the fact that some of the expected resonances are absent in its ^{13}C NMR spectrum even after one night of data acquisition. The spectra of complexes containing the same dialkynyl fragment display the same pattern for the diethynylarene protons (see Section 2). Thus, complexes **8** and **9** display triplet resonances for the protons in two- and five-positions (see Chart 1) and a doublet of doublets for those in four- and six-positions. In the ^1H NMR spectra of complexes **4**, **5**, **10** and **11**, the three singlet resonances observed with intensities 1:3:6 correspond to the proton in the

five-position and the inequivalent methyl groups in the 2- and 4+6-positions, respectively. In complexes **6** and **7** one singlet is observed for all equivalent Me groups in the alkynyl ligand. The spectra show also the resonances due to the neutral ligands. Thus, the presence of PPh_3 in **6**, **9** and **10** is evidenced by a multiplet (7.4–7.6 ppm) in their ^1H NMR spectra and a singlet resonance in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at around 40 ppm, as found for other alkynylphosphinegold(I) complexes [39,46]. The isocyanide ligand present in **4**, **7** and **8** ($^t\text{BuNC}$) or **5** (XyNC) is responsible for a methyl resonance around 1.6 ppm (^tBu) or 2.44 (Xy). In addition, **5** shows a multiplet (7.14–7.36 ppm) for the aromatic isocyanide protons. The partial double bond character of the C–N bonds in carbene complexes gives rise to the possible existence of isomers *Z* and *E* [55]. The ^1H NMR spectrum of the carbene complex **11** show one single resonance for the NH and ^tBu protons but two sets from the ethyl protons. This could be attributed to the formation of only one of the isomers and to the rapid interchange of positions between the proton and the *tert*-butyl group, the latter suggesting a weak π contribution to the N–C(H) ^tBu bond. The same NMR pattern has been found in other carbene complexes by us [46] and others [55].

The assignment of the $^{13}\text{C}\{^1\text{H}\}$ resonances was made by comparison with those in the free dialkynes [56]. The carbon nuclei of the alkynyl moieties appear in the ranges 121–132 (C–Au) and 98–128 (C≡C–Au) ppm, downfield shifted with respect to those in the corresponding alkynes, as observed for other alkynylgold complexes [46]. The ^{13}C NMR spectrum of the carbene complex **11** displays, as the corresponding ^1H NMR spectrum, two sets of resonances for the ethyl carbon nuclei.

3.2.3. IR spectroscopy

With the exception of **4–7** and **10**, these complexes show a weak $\nu(\text{C} \equiv \text{C})$ band (see Section 2) slightly

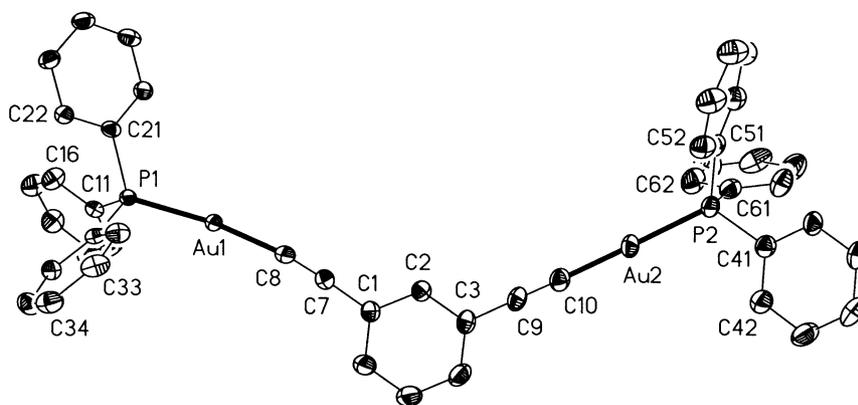


Fig. 1. Thermal ellipsoid plot (50% probability level) of **9**. Selected bond lengths (Å) and angles (°): Au(1)–C(8) 2.001(4), Au(1)–P(1) 2.2750(11), Au(2)–C(10) 1.998(5), Au(2)–P(2) 2.2725(12), C(7)–C(8) 1.210(6), C(9)–C(10) 1.209(7), C(8)–Au(1)–P(1) 170.07(11), C(10)–Au(2)–P(2) 176.95(14), C(8)–C(7)–C(1) 175.7(4), C(7)–C(8)–Au(1) 170.2(4), C(10)–C(9)–C(3) 176.7(5), C(9)–C(10)–Au(2) 176.1(4).

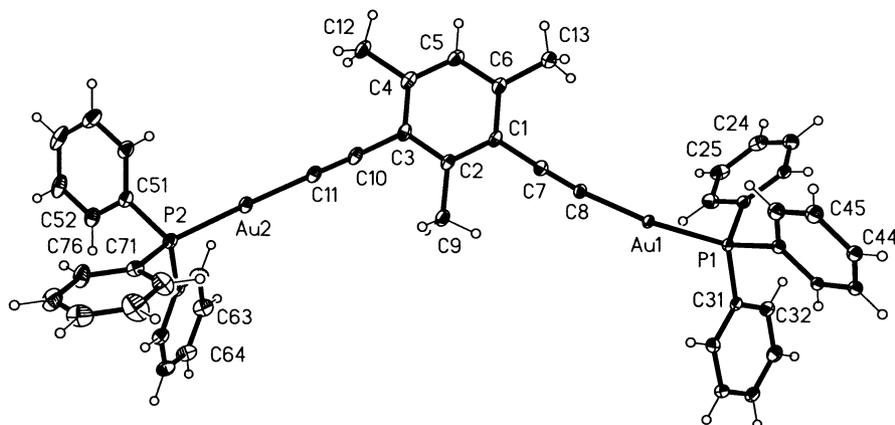


Fig. 2. Thermal ellipsoid plot (50% probability level) of **10**. Selected bond lengths (Å) and angles (°): Au(1)–C(8) 2.006(3), Au(1)–P(1) 2.2821(7), Au(2)–C(11) 2.003(3), Au(2)–P(2) 2.2703(7), C(7)–C(8) 1.215(4), C(10)–C(11) 1.204(4), C(8)–Au(1)–P(1) 171.22(8), C(11)–Au(2)–P(2) 177.19(8), C(8)–C(7)–C(1) 175.0(3), C(7)–C(8)–Au(1) 171.2(2), C(11)–C(10)–C(3) 178.6(3), C(10)–C(11)–Au(2) 177.5(3).

shifted to lower energy with respect to the corresponding band in the free alkynes $\text{HC}\equiv\text{C}(\text{Ar})\text{C}\equiv\text{CH}$ [Ar = mphen, 2120; mes, 2102; dur, 2100 cm^{-1}]. Bands due to the neutral ligands are also observed in the spectra of complexes with PPh_3 (at around 1100, 750, 700, 540 and 500 cm^{-1}), isocyanide [$\nu(\text{C}\equiv\text{N})$ in the range 2204–2226 cm^{-1}] or carbene [$\nu(\text{N}=\text{H})$ at around 3300 cm^{-1}].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 178874 and 178875 for compounds **9** and **10**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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