



Alkynyl derivatives of gold complexes containing C₆H₃-5-Me-2-EPh₂ (E = P, As) ligands

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ABSTRACT

[Au₂Cl₂{μ-2,2′-Ph₂As(5,5′-Me₂C₆H₃C₆H₃)AsPh₂}] reacts with phenylacetylene or ethynylferrocene to give the corresponding digold(I) bis(alkynyl) derivatives [Au₂(C≡CR)₂{μ-2,2′-Ph₂As(5,5′-Me₂C₆H₃C₆H₃)AsPh₂}] [R = Ph (4), Fc (5)]. In contrast, products resulting from the reaction with 1,3- or 1,4-diethynylbenzene (deb) depend markedly on the dichlorodigold(I) complex to ligand ratio. When an excess of alkyne is used, the expected bis(alkynyl) complexes [Au₂X₂{μ-2,2′-Ph₂As(5,5′-Me₂C₆H₃C₆H₃)AsPh₂}] [X = 1,3-deb (6), 1,4-deb (7)] are obtained, but when using a 1:1 molar ratio poorly soluble, presumably polymeric, species are formed. Attempts to prepare a digold(II) bis(alkynyl) derivative by treatment of [Au₂Cl₂(μ-C₆H₃-5-Me-2-PPh₂)₂] with ethynylferrocene in the presence of NaOMe gives a mixture of species, the recrystallization of which yielded a crystal of [{2-(FcC≡C)-4-MeC₆H₃PPh₂}Au(C≡CFC)] (1). The reaction of [Au₂Cl₂(μ-C₆H₃-5-Me-2-AsPh₂)₂] with phenylacetylene, 1,3- or 1,4-deb gives a mixture of unidentified products.

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1. Introduction

Transition metal alkynyl complexes have been extensively studied over the past few decades owing to their potential applications as non-linear optical materials, molecular wires, molecular electronics and luminescent materials [1]. Gold has been no exception and since the first report of the explosive gold carbide complex [AuCCH] [2], gold alkynyl chemistry has been the subject of several reviews [3]. Gold(I) alkynyl complexes have been extensively studied and often exhibit interesting luminescence behavior [4]. They have also been investigated for use as molecular wires [5] and for their non-linear optical properties [6]. In sharp contrast to gold(I), gold(III) alkynyl complexes are relatively uncommon and, to the best of our knowledge, there are no reports of gold(II) alkynyl complexes. Gold(III) complexes of the type [Au(C≡CF₃)Me₂(L)] (L = PMe₂Ph, PPh₃) [7–9] and [Au(C≡CR)Me₂(PPh₃)] (R = H, Me) have been prepared by Schmidbauer et al. [10] and the Yam group reported the first examples of the luminescent behavior of gold(III) alkynyl complexes of the type [Au(C[^]N[^]C)(C≡CR)] [HC[^]N[^]CH = 2,6-diphenylpyridine, R = Ph, C₆H₄-Cl-*p*, C₆H₄-OCH₃-*p*, C₆H₄-NH₂-*p*;

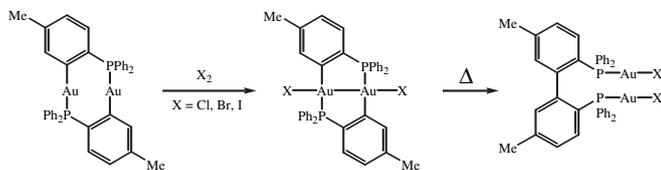
HC[^]N[^]CH = 2,6-bis(4-*t*-butylphenyl)pyridine, R = Ph] [11]. A series of gold(I)-gold(III) complexes of the type [Au^I(μ-{CH₂})₂PPh₂)₂Au^{III}(C≡CR)₂] [R=Ph, ^tBu, SiMe₃] has also been reported, and represents the first fully characterized examples of gold complexes containing two alkynyl ligands bound to a gold(III) center [12].

The chemistry of dinuclear gold complexes of the type [Au₂(μ-2-C₆R₄PPh₂)₂] (R = H [13,14], F [17]) and [Au₂(μ-C₆H₃-*n*-R-2-PPh₂)₂] (R = Me [15,16], F [17]; *n* = 5, 6) has been explored for over two decades. The complex [Au₂(μ-C₆H₃-5-Me-2-PPh₂)₂] undergoes oxidative addition at the dimetal unit with one equivalent of halogen to give, initially, the homodinuclear digold(II) complexes [Au₂X₂(μ-C₆H₃-5-Me-2-PPh₂)₂] (X = Cl, Br, I). The dihalodigold(II) complexes are thermodynamically unstable, and on heating to ca. 50 °C, rearrange to the C–C coupled digold(I) complexes [Au₂X₂{μ-2,2′-Ph₂P(5,5′-Me₂C₆H₃C₆H₃)PPh₂}] (X = Cl, Br, I), as shown in Scheme 1 [15].

The analogous arsenic-containing complexes [Au₂(μ-C₆H₃-*n*-Me-2-AsPh₂)₂] (*n* = 5, 6) have also been investigated in detail [18]. The 5-methyl substituted complex [Au₂(μ-C₆H₃-5-Me-2-AsPh₂)₂] behaves similarly to its phosphorus analogue, undergoing oxidative addition of halogens to give the symmetric dihalodigold(II) complexes [Au₂X₂(μ-C₆H₃-5-Me-2-AsPh₂)₂] (X = Cl, Br, I), which, on heating, rearrange to the C–C coupled products [Au₂X₂{μ-2,2′-

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Scheme 1. Reactivity of the digold(I) complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPh}_2)_2]$.

$\text{Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2$] ($\text{X} = \text{Cl, Br, I}$) [18]. As a logical extension to this work, we were interested in the reactions of these dichlorodigold complexes with various alkynes. Herein, we report the syntheses, structures and characterization of a series of new alkyngold complexes. We also examine the reaction of the dichlorodigold(II) complex $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPh}_2)_2]$ with ethynylferrocene in the hope that it might lead to the formation of the digold(II) alkyne complex $[\text{Au}_2(\text{C}\equiv\text{Cfc})_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPh}_2)_2]$.

2. Results and discussion

2.1. Reactions of dinuclear gold(II) complexes

To prevent the facile rearrangement of the dichlorodigold(II) complex, a dichloromethane solution of $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPh}_2)_2]$ was cooled to -20°C and treated with an excess of ethynylferrocene in the presence of NaOMe (Scheme 2). ^{31}P NMR spectroscopy showed that no reaction had taken place; it was not until the solution was allowed to warm to room temperature that the reaction proceeded. The ^{31}P NMR spectrum of the isolated orange solid showed four singlet resonances at δ 28.4, 30.5, 32.7 and 35.4, the first resonance being assigned to the known C–C coupled digold(I) complex $[\text{Au}_2\text{Cl}_2(\mu\text{-2,2'-Ph}_2\text{P}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{PPh}_2)]$. The mixture could not be separated and the identities of the other components have not been established. When the reaction was performed at room temperature, a mixture of only two products was obtained, the ^{31}P NMR spectrum of which showed two singlet resonances at δ 39.4 and 35.7. Attempts to separate this mixture by chromatography were unsuccessful. However, orange crystals were obtained by diffusion of hexane into a dichloromethane solution of the mixture, which were shown by X-ray

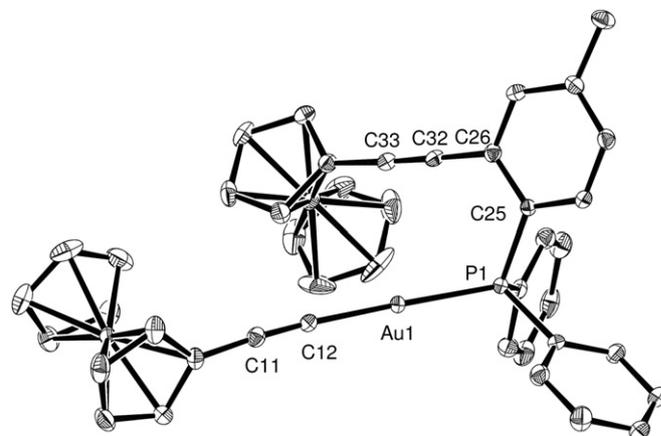
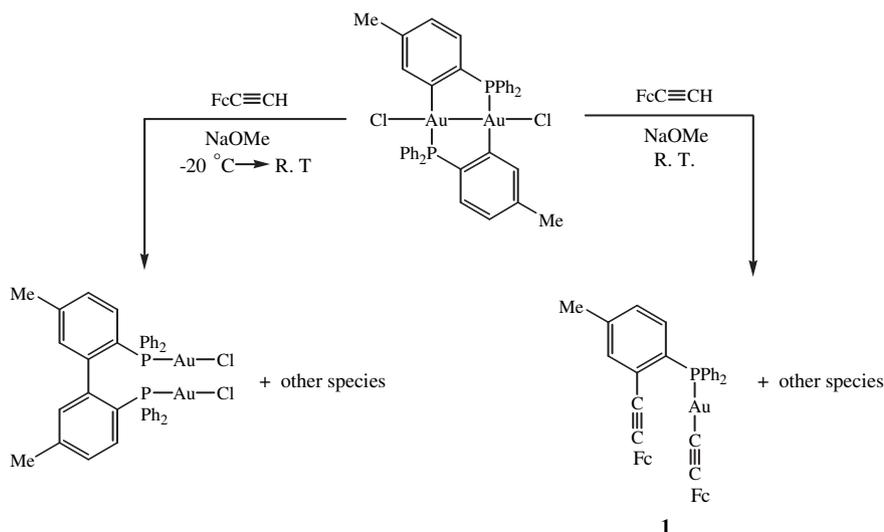


Fig. 1. Molecular structure of $[\{2\text{-}(\text{FcC}\equiv\text{C})\text{-4-MeC}_6\text{H}_3\text{PPh}_2\}\text{Au}(\text{C}\equiv\text{Cfc})]$ **1**. Ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: $\text{Au}(1)\text{-P}(1)$ 2.2692(7) Å, $\text{Au}(1)\text{-C}(12)$ 2.000(3) Å, $\text{C}(11)\text{-C}(12)$ 1.197(4) Å, $\text{C}(32)\text{-C}(33)$ 1.195(4) Å, $\text{P}(1)\text{-Au}(1)\text{-C}(12)$ 177.19(8) $^\circ$.

crystallography to be $[\{2\text{-}(\text{FcC}\equiv\text{C})\text{-4-MeC}_6\text{H}_3\text{PPh}_2\}\text{Au}(\text{C}\equiv\text{Cfc})]$ (**1**). The mechanism by which complex **1** is formed is not clear, however it appears reductive elimination at the metal centers and coupling of the aryl and alkyne groups takes place, possibly via an undetected gold(II) alkyne intermediate. In addition, a peak at m/z 892 was observed in the FAB-mass spectrum of the mixture, corresponding to the $[\text{M} + \text{H}]^+$ ion of **1**.

The molecular structure of **1** (Fig. 1) shows the expected, approximately linear, coordination about the gold(I) center, the P-Au-C angle being $177.19(8)^\circ$. The lengths of the two $\text{C}\equiv\text{C}$ bonds bound to the aryl group and gold atom [1.197(4) Å and 1.195(4) Å, respectively] are identical, within experimental error. The Au-P and Au-C distances [2.2692(7) Å and 2.000(3) Å, respectively] in **1** are similar to those in $[(\text{Ph}_3\text{P})\text{Au}(\text{C}\equiv\text{CC}_6\text{F}_5)]$ [2.274(3) Å and 1.993(14) Å, respectively] [19] and $[\{(\text{FcC}\equiv\text{C})\text{Ph}_2\text{P}\}\text{Au}(\text{C}\equiv\text{Cfc})]$ [2.2779(11) Å and 2.000(5) Å, respectively] [20]. The Au-P distance of 2.2692(7) Å is slightly longer than that in the structurally similar iodo analogue $[\text{Au}\{\text{Ph}_2\text{P}(\text{C}_6\text{H}_3\text{-2-1-3-Me})\}]$ [2.251(4) Å] [15], consistent with the greater *trans*-influence of σ -carbon donor ligands compared to iodide.



Scheme 2. Reaction of $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPh}_2)_2]$ with ethynylferrocene.

Attempts to prepare other alkynylgold complexes by treatment of $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPH}_2)_2]$ with phenylacetylene, 1,3- and 1,4-diethynylbenzene (deb) using a variety of bases (NaOMe, KOH and NaOAc) resulted in inseparable mixtures of unidentified products, as shown by ^{31}P NMR spectroscopy.

The reaction of $[\text{Au}_2\text{Cl}_2(\mu\text{-2-C}_6\text{H}_3\text{-5-Me-AsPh}_2)_2]$ with an excess of ethynylferrocene in the presence of NaOMe or NaOAc at room temperature gave an orange solid, which showed two methyl resonances at δ 2.27 and 2.36 in its ^1H NMR spectrum. Attempts to separate these complexes were unsuccessful. The FAB-mass spectrum of this mixture showed two peaks at m/z 1243 and 936, which may be due to the $[\text{M}-\text{C}\equiv\text{Cfc}+\text{H}]^+$ and $[\text{M}+\text{H}]^+$ ions of $[\text{Au}_2(\text{C}\equiv\text{Cfc})_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-AsPh}_2)_2]$ or more likely the rearranged gold(I) compound $[\text{Au}_2(\text{C}\equiv\text{Cfc})_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ (**2**), and $[\{2\text{-(FcC}\equiv\text{C)}\text{-4-MeC}_6\text{H}_3\text{AsPh}_2\}\text{Au}(\text{C}\equiv\text{Cfc})]$ (**3**), respectively. The assignment of the peak at m/z 936 to compound **3** is supported by the structural characterization of compound **1** above. Reaction of $[\text{Au}_2\text{Cl}_2(\mu\text{-2-C}_6\text{H}_3\text{-5-Me-AsPh}_2)_2]$ with other acetylene derivatives (phenylacetylene, 1,3- and 1,4-diethynylbenzene) using a variety of bases (NaOMe, KOH and NaOAc) led only to a mixture of unidentified species with complex ^1H NMR spectra.

2.2. Reactions of dinuclear gold(I) complexes

The biphenyldiyl gold(I) complex $[\text{Au}_2\text{Cl}_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ reacted cleanly with phenylacetylene or ethynylferrocene in the presence of NaOMe as base to afford the expected alkynyl derivatives $[\text{Au}_2(\text{C}\equiv\text{CR})_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [$\text{R} = \text{Ph}$ (**4**), Fc (**5**)] in yields of ca. 70%. The ^1H NMR spectra of complexes **4** and **5** each showed a single aromatic-methyl resonance at ca. δ 1.8 and the FAB-mass spectra each showed a peak corresponding to the $[\text{M}-\text{C}\equiv\text{CR}+\text{H}]^+$ fragment. The structures of **4** and **5** were confirmed by X-ray crystallography and are shown in Figs. 2 and 3, respectively; selected bond lengths and angles are summarized in Table 1.

The molecular structures of **4** and **5** are similar to those of the known dihalodigold(I) complexes $[\text{Au}_2\text{X}_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [$\text{X} = \text{Cl}, \text{Br}, \text{I}$] and their phosphorus

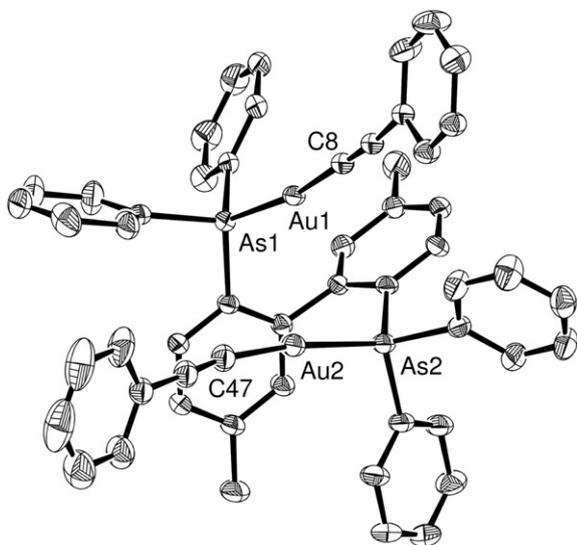


Fig. 2. Molecular structure of $[\text{Au}_2(\text{C}\equiv\text{CPh})_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ **4**. Ellipsoids show 20% probability levels and hydrogen atoms have been omitted for clarity.

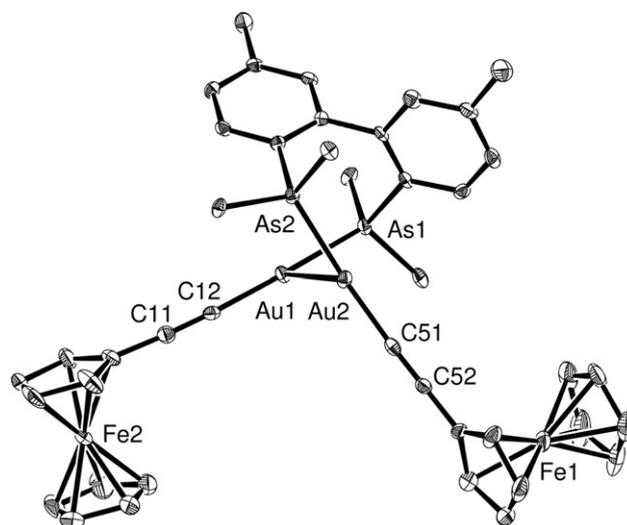


Fig. 3. Molecular structure of $[\text{Au}_2(\text{C}\equiv\text{Cfc})_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ **5**. Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the ipso carbon atoms of the AsPh_2 groups are shown.

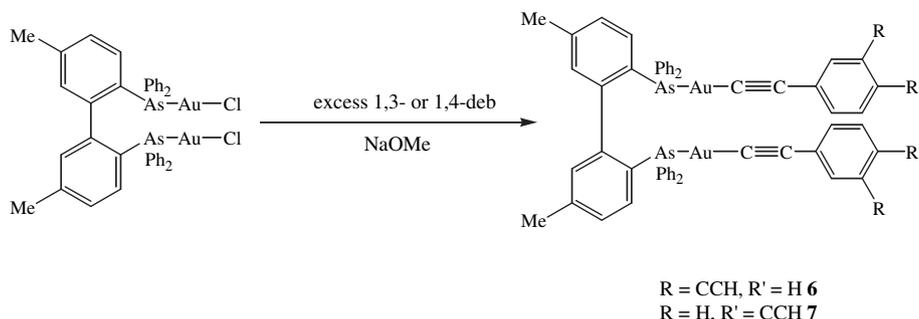
analogues [15], and consist of a biphenyldiyl backbone with two $\text{Ph}_2\text{AsAuC}\equiv\text{CR}$ ($\text{R} = \text{Ph}, \text{Fc}$) substituents in the 2 and 2' positions. The biphenyldiyl groups in **4** and **5** are twisted about the central C–C bond (the dihedral angle α being close to 90°) with the AsPh_2 -substituents in *anti*- and *syn*-type configurations, respectively. The $\text{Au}\cdots\text{Au}$ separations of 3.2413(3) Å and 3.0200(4) Å in **4** and **5**, respectively, are significantly greater than those in $[\text{Au}_2\text{X}_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [$\text{X} = \text{Cl}$ 2.9963(3) Å, Br 2.9913(3) Å, I 2.9932(3) Å] [18], possibly due to crystal packing effects. In **4** and **5**, the As–Au distances of ca. 2.38 Å *trans* to the σ -carbon ligands are longer than those found in their halide analogues (2.34–2.36 Å), consistent with the higher *trans*-influence of carbon ligands compared to the halides.

Treatment of $[\text{Au}_2\text{Cl}_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ with five equivalents of 1,3- or 1,4-diethynylbenzene (deb) gave the corresponding alkynyl derivatives $[\text{Au}_2\text{R}'_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [$\text{R}' = 1,3\text{-deb}$ (**6**); $1,4\text{-deb}$ (**7**)] (Scheme 3). The ^1H NMR spectra of **6** and **7** showed a single methyl resonance at δ 1.81 and 1.77, respectively, and the FAB-mass spectra each displayed a peak due to the $[\text{M}-(\text{deb})+\text{H}]^+$ fragment. The structure of **6** has been established by single-crystal X-ray diffraction (Fig. 4) and selected bond distances and angles are listed in Table 2.

Table 1

Selected bond distances (Å) and angles ($^\circ$) in $[\text{Au}_2(\text{C}\equiv\text{CR})_2\{\mu\text{-2,2'}\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [$\text{R} = \text{Ph}$ (**4**), Fc (**5**)].

	4		5
Au(1)–Au(2)	3.2413(3)	Au(1)–Au(2)	3.0200(4)
Au(1)–As(1)	2.3791(4)	Au(1)–As(1)	2.3846(6)
Au(2)–As(2)	2.3839(5)	Au(2)–As(2)	2.3863(7)
Au(1)–C(8)	1.9936(17)	Au(1)–C(12)	1.968(5)
Au(2)–C(47)	1.978(5)	Au(2)–C(51)	1.981(6)
As(1)–Au(1)–C(8)	171.16(7)	As(1)–Au(1)–C(12)	172.38(15)
As(1)–Au(1)–Au(2)	82.365(10)	As(1)–Au(1)–Au(2)	83.271(14)
C(8)–Au(1)–Au(2)	104.02(8)	C(12)–Au(1)–Au(2)	104.33(15)
As(2)–Au(2)–C(47)	172.28(14)	As(2)–Au(2)–C(51)	169.04(16)
As(2)–Au(2)–Au(1)	84.558(11)	As(2)–Au(2)–Au(1)	81.121(16)
C(47)–Au(2)–Au(1)	102.59(14)	C(51)–Au(2)–Au(1)	109.81(16)
α	87.88(13)	α	83.31(16)



Scheme 3. Reaction of $[\text{Au}_2\text{Cl}_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ with an excess of 1,3- and 1,4-diethynylbenzene.

The molecular structure of **6** is similar to that of **4** and **5**, with the biphenyl group in an *anti*-configuration with a dihedral angle α of ca. 85° . The Au \cdots Au separation [3.5210(4) Å] is greater than those found in **4** and **5**, presumably to accommodate the bulkier ligands. The Au–As distances [2.3697(5) and 2.3718(4) Å] are only slightly shorter than those observed in **4** and **5**.

In contrast to the reactions above, treatment of the biphenyldiyl digold(I) complex $[\text{Au}_2\text{Cl}_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ with only one equivalent of 1,3- or 1,4-deb in the presence of NaOMe in MeOH for 24 h gave yellow precipitates in high yields (Scheme 4). These solids were insoluble in common organic solvents, suggestive of polymeric species (**8** and **9**) although cyclic structures of varying ring sizes cannot be ruled out.

The polymeric material **9**, obtained from the reaction of $[\text{Au}_2\text{Cl}_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ with 1,4-deb, was analysed by Mössbauer spectroscopy and the spectrum and parameters are shown in Fig. 5. The spectrum showed a well-resolved quadrupole doublet, clearly indicating the gold atoms are in identical environments. From the correlation plot (Fig. 6 and Table 3), the oxidation state of the gold atom in this product was determined to be +1. The plot suggests that the gold atom is coordinated by arsenic and carbon donor groups; both the I.S. and Q.S. values are rather large, although the I.S. value is slightly smaller than those of other gold(I) atoms coordinated to arsenic and aromatic carbon atoms. A similar trend has been observed in P–Au–C systems; the I.S. values of $[(\text{Ph}_3\text{P})\text{AuC}\equiv\text{CPh}]$ and $[(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}(1\text{-hydroxy-cyclohexyl})]$ [21] containing the P–Au–C \equiv C fragment, are smaller than those of $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}2\text{-PPH}_2\text{-}6\text{-Me})_2]$

[22], $[\text{Au}_2(\mu\text{-C}_6\text{H}_4\text{-}2\text{-PEt}_2)_2]$ and $[\text{Au}_2(\mu\text{-C}_6\text{H}_4\text{-}2\text{-PPH}_2)_2]$ containing P–Au–C_{aryl} bonds [23].

3. Conclusion

The biphenyldiyl digold(I) complex $[\text{Au}_2\text{Cl}_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ reacts cleanly with phenylacetylene, ethynylferrocene or with an excess of 1,3- or 1,4-diethynylbenzene (deb) to give the expected alkyne derivatives $[\text{Au}_2(\text{C}\equiv\text{CR})_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [R = Ph (**4**), Fc (**5**)] and $[\text{Au}_2\text{R}'_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ [R' = 1,3-deb (**6**), 1,4-deb (**7**)], respectively. The structures of **4–6** have been confirmed by X-ray crystallography. In contrast, treating the digold(I) complex $[\text{Au}_2\text{Cl}_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ with a stoichiometric amount of 1,3- or 1,4-deb gives insoluble polymeric species. Mössbauer spectroscopy of the latter product indicates all the gold atoms are in identical environments and in the +1 oxidation state. The reaction of the dichlorodigold(II) complex $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-}5\text{-Me-}2\text{-PPH}_2)_2]$ with an excess of ethynylferrocene gives a mixture of products, one of which is $[\{2\text{-}(\text{Fc}\equiv\text{C})\text{-}4\text{-MeC}_6\text{H}_3\text{PPH}_2\}\text{Au}(\text{C}\equiv\text{CFc})]$ (**1**), as shown by X-ray crystallography.

4. Experimental

4.1. Physical measurements

^1H NMR spectra were recorded on a JEOL JNM-ECP 400 or Varian Gemini 300 NMR spectrometer as CDCl_3 solutions, referenced to residual solvent peaks. FAB-mass spectra were measured on a JEOL JMS-600H spectrometer in positive ion mode. Elemental analyses were carried out in-house on a Perkin–Elmer 2400 analyzer or at the Microanalytical Laboratory of the Research School of Chemistry, Australian National University.

Crystals suitable for single-crystal X-ray diffraction were obtained by layering a dichloromethane solution of the complex with hexane. All diffraction data were collected on a Bruker SMART CCD area detector diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Geometric and intensity data

Table 2

Selected bond distances (Å) and angles ($^\circ$) in $[\text{Au}_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{-}3\text{-C}\equiv\text{CH})_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ **6**.

Au(1) \cdots Au(2)	3.5210(4)	As(1)–Au(1)–C(10)	174.26(14)
Au(1)–As(1)	2.3697(5)	C(23)–As(1)–Au(1)	117.23(13)
Au(1)–C(10)	1.984(5)	As(2)–Au(2)–C(49)	173.78(16)
Au(2)–As(2)	2.3718(4)	C(35)–As(2)–Au(2)	118.27(11)
Au(2)–C(49)	1.990(5)	α	85.25(13)

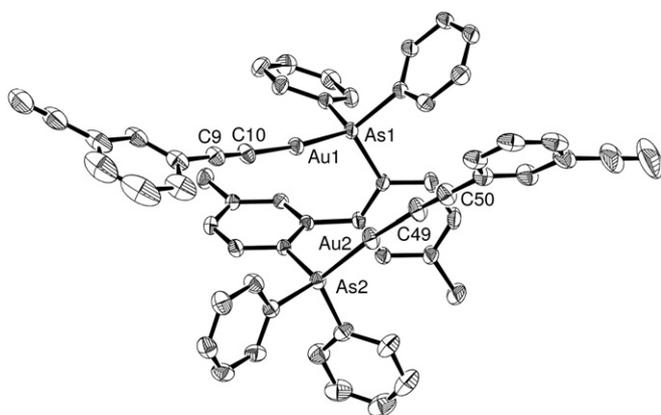
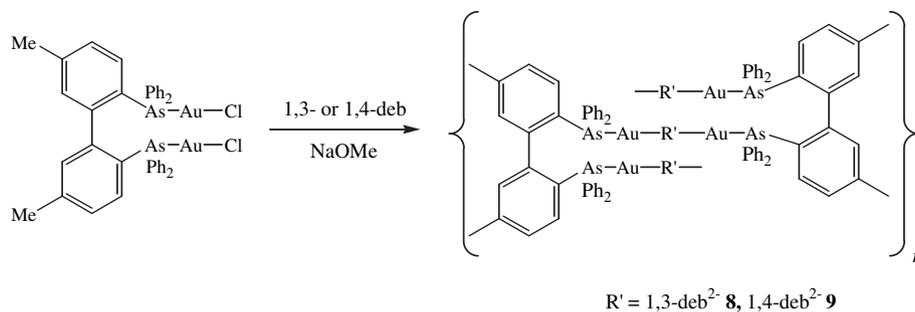


Fig. 4. Molecular structure of $[\text{Au}_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{-}3\text{-C}\equiv\text{CH})_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ **6**. Ellipsoids show 20% probability levels and hydrogen atoms have been omitted for clarity.



Scheme 4. Reaction of $[\text{Au}_2\text{Cl}_2\{\mu\text{-}2,2'\text{-Ph}_2\text{As}(5,5'\text{-Me}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3)\text{AsPh}_2\}]$ with one equivalent of 1,3- or 1,4-diethynylbenzene.

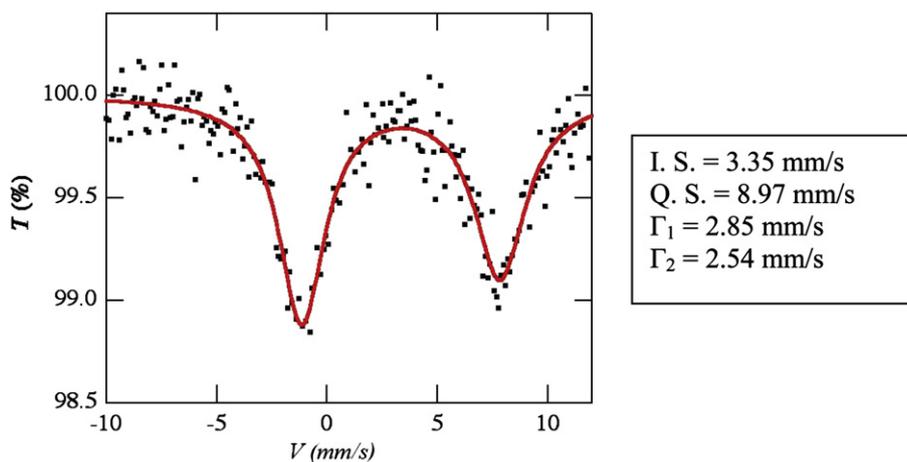


Fig. 5. ^{197}Au Mössbauer spectrum and parameters of compound **9** at 12 K.

were collected using SMART software [26]. The data were processed using SAINT [27], and corrections for absorption were applied using SADABS [28]. The data sets of **1**, **4** and **5** were further treated with a Xabs2 absorption correction as implemented in WinGX [29]. All structures were solved by direct methods using the SHELX-TL package [30]. Crystallographic data are summarized in Table 4. The structure of **5** contains heavily disordered dichloromethane solvent of crystallization. After an initial refinement, which revealed three sites in the asymmetric unit accessible to solvent molecules, the data set was treated with SQUEEZE as implemented in WinGX PLATON [31]. This procedure yielded 474 electrons per unit cell, corresponding to 118.5 electrons per asymmetric unit (expected: 126 electrons corresponding to three dichloromethane molecules). The crystallographic data have been deposited at the Cambridge Crystallographic Data Center [CCDC 755 637 (**4**), 755 638 (**6**), 755 639 (**1**) and 755 640 (**5**)].

The gold-197 Mössbauer spectrum of **9** was acquired at Toho University, Japan, on a Wissel Mössbauer spectrometer system using previously reported experimental conditions [25]. The I.S. values are given relative to the $^{197}\text{Pt}/\text{Pt}$ source at 12 K.

4.2. Syntheses

Most syntheses were performed under a dry argon atmosphere with use of standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable.

4.2.1. $[\{2\text{-}(\text{FcC}\equiv\text{C})\text{-}4\text{-MeC}_6\text{H}_3\text{PPh}_2\}\text{Au}(\text{C}\equiv\text{CFc})]$ (**1**)

A stirred solution of $[\text{Au}_2\text{Cl}_2\{\mu\text{-}C_6\text{H}_3\text{-}5\text{-Me-}2\text{-PPh}_2\}_2]$ (51 mg, 0.05 mmol) and ethynylferrocene (21 mg, 0.1 mmol) in

dichloromethane (10 mL) was treated with a 1.2-fold amount of NaOMe in methanol. The mixture was shielded from light and stirred overnight. The solution was evaporated to dryness and the residue was washed with hexane and dried *in vacuo* to afford an orange solid (26 mg). Attempts to separate the mixture were unsuccessful, but an X-ray quality crystal of **1** was obtained by

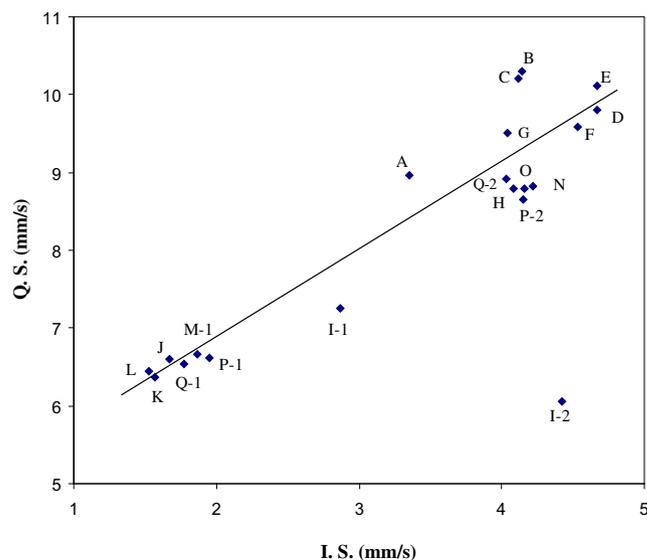


Fig. 6. Correlation plot for the gold(I) complexes listed in Table 3.

Table 3
¹⁹⁷Au Mössbauer parameters for gold complexes.

Entry	Compound	Au oxidation state	I.S. (mm/s)	Q.S. (mm/s)
A	9	I	3.35	8.97
B	[(Ph ₃ P)AuC≡CPh] ^a	I	4.12	10.21
C	[(Ph ₃ P)AuC≡C(1-hydroxycyclohexyl)] ^a	I	4.14	10.30
D	[Au ₂ (μ-C ₆ H ₃ -6-Me-2-PPPh ₂) ₂] ^b	I	4.67	9.81
E	[Au ₂ (μ-2-C ₆ H ₄ PEt ₂) ₂] ^c	I	4.67	10.12
F	[Au ₂ (μ-2-C ₆ H ₄ PPPh ₂) ₂] ^c	I	4.53	9.58
G	[Au ₂ (μ-2-C ₆ F ₄ PPPh ₂) ₂] ^d	I	4.04	9.51
H	[Au ₂ (μ-2-C ₆ H ₄ AsPh ₂) ₂] ^c	I	4.08	8.80
I	[Au(μ-2-C ₆ H ₃ -6-Me-2-PPPh ₂)(κ ² -C ₆ H ₃ -6-Me-2-PPPh ₂)Au] ^b	I (site 1)	2.87	7.26
		III (site 2)	4.42	6.06
J	[Au ₂ Cl ₂ {μ-2,2'-Ph ₂ As(5,5'-Me ₂ C ₆ H ₃ C ₆ H ₃)AsPh ₂ }] ^e	I	1.67	6.60
K	[Au ₂ Br ₂ {μ-2,2'-Ph ₂ As(5,5'-Me ₂ C ₆ H ₃ C ₆ H ₃)AsPh ₂ }] ^e	I	1.57	6.37
L	[Au ₂ I ₂ {μ-2,2'-Ph ₂ As(5,5'-Me ₂ C ₆ H ₃ C ₆ H ₃)AsPh ₂ }] ^e	I	1.53	6.44
M	[ClAu(μ-2-C ₆ H ₃ -6-Me-2-AsPh ₂)(κ ² -C ₆ H ₃ -6-Me-2-AsPh ₂)AuCl] ^b	I (site 1)	1.87	6.66
		III (site 2)	4.02	4.38
N	[Au ₂ (μ-C ₆ H ₃ -5-Me-2-AsPh ₂) ₂] ^e	I	4.22	8.82
O	[Au ₂ (μ-C ₆ H ₃ -6-Me-2-AsPh ₂) ₂] ^e	I	4.16	8.79
P	[ClAu{μ-2-C ₆ H ₃ -6-Me-2-AsPh ₂ }(κ ² -C ₆ H ₃ -6-Me-2-AsPh ₂)Au] ^b	I (site 1)	1.95	6.61
		I (site 2)	4.15	8.66
Q	[BrAu{μ-2-C ₆ H ₃ -6-Me-2-AsPh ₂ }(κ ² -C ₆ H ₃ -6-Me-2-AsPh ₂)Au] ^b	I (site 1)	1.77	6.54
		I (site 2)	4.03	8.92

^a Ref. [21].^b Ref. [22].^c Ref. [23].^d Ref. [24].^e Ref. [25].

layering a dichloromethane solution with hexane. ³¹P NMR: δ 39.4 and 35.7.

4.2.2. [Au₂(C≡CR)₂{μ-2,2'-Ph₂As(5,5'-Me₂C₆H₃C₆H₃)AsPh₂}] (R = Ph (**4**), Fc (**5**))

In a similar reaction to that described above, a stirred solution of [Au₂Cl₂{μ-2,2'-Ph₂As(5,5'-Me₂C₆H₃C₆H₃)AsPh₂}] (55 mg, 0.05 mmol)

and alkyne (0.09 mmol) in dichloromethane (10 mL) was treated with a 1.2-fold amount of NaOMe in methanol. The mixture was shielded from light and stirred overnight. The solution was evaporated to dryness, the residue was washed with hexane and dried *in vacuo* to afford the desired product as an orange solid.

4 (R = Ph): Yield: 43 mg, 70%. ¹H NMR: δ 1.82 (s, 6H, Me), 6.12 (s, 2H, arom), 7.16–8.02 (m, 34H, arom). FAB-MS (*m/z*): 1135 [M – C≡CPh + H]⁺, 837 [M – Au(CPh)₂ + H]⁺.

5 (R = Fc): Yield: 46 mg, 74%. ¹H NMR: δ 1.81 (s, 6H, Me), 4.15–4.51 (m, 18H, Cp), 6.08 (s, 2H, arom), 7.14–8.00 (m 24H, arom). FAB-MS (*m/z*): 1244 [M – C≡CPh + H]⁺. Anal. Calcd. For C₆₂H₅₀Au₂Fe₂: C 51.34, H 3.47. Found: C 50.66, H 3.40.

4.2.3. [Au₂R'₂{μ-2,2'-Ph₂As(5,5'-Me₂C₆H₃C₆H₃)AsPh₂}] [R' = 1,3-deb (**6**), 1,4-deb (**7**)]

In an analogous reaction to that described above, treatment of a dichloromethane solution of [Au₂Cl₂{μ-2,2'-Ph₂As(5,5'-Me₂C₆H₃C₆H₃)AsPh₂}] (55 mg, 0.05 mmol) and 1,3- or 1,4-diethynylbenzene (24 mg, 0.19 mmol) with a 1.2-fold amount of NaOMe in methanol gave the title products as orange solids.

6 (R' = 1,3-deb): Yield: 36 mg, 56%. ¹H NMR: δ 1.80 (s, 6H, Me), 3.14 (s, 2H, CCH), 6.1–8.0 (m, 34H, arom). FAB-MS (*m/z*): 1159 [M – deb + H]⁺. Anal. Calcd. For C₅₈H₄₂As₂Au₂: C 54.31, H 3.30. Found: C 54.28, H 3.33.

7 (R' = 1,4-deb): Yield: 29 mg, 45%. ¹H NMR: δ 1.80 (s, 6H, Me), 3.10 (s, 2H, CCH), 6.1–7.9 (m, 34H, arom). FAB-MS (*m/z*): 1159 [M – deb + H]⁺.

4.2.4. Polymeric species **8** and **9**

A stirred solution of [Au₂Cl₂{μ-2,2'-Ph₂As(5,5'-Me₂C₆H₃C₆H₃)AsPh₂}] (375 mg, 0.34 mmol) and 1,3- or 1,4-deb (44 mg, 0.35 mmol) in CH₂Cl₂ (40 mL) was treated with a 1.2-fold amount of NaOMe in methanol and the mixture stirred overnight. The yellow precipitate was isolated by filtration, washed with dichloromethane and hexane and dried *in vacuo*.

8: 308 mg, FAB-MS (*m/z*): 1476, 1369, 1159, 837.

9: 250 mg, FAB-MS (*m/z*): 1476, 1369, 1159, 837. Anal. Calcd. For C₄₈H₃₆As₂Au₂: C 49.85, H 3.14. Found: C 48.98, H 2.86.

Table 4
Crystal data and details of data collection and structure refinement for complexes **1** and **4–6**.

Compound	1	4	5	6
Formula	C ₄₃ H ₃₄ AuFe ₂ P	C ₅₄ H ₄₂ As ₂ Au ₂	C ₆₅ H ₅₆ As ₂ Au ₂ Cl ₆ Fe ₂	C ₅₈ H ₄₂ As ₂ Au ₂
fw	890.34	1234.65	1705.27	1282.69
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	C2/c	P2 ₁ /n	P2 ₁ /n
a (Å)	17.0195(14)	29.5545(18)	14.4181(11)	18.4294(11)
b (Å)	10.4469(9)	15.0123(9)	18.0381(13)	13.4576(8)
c (Å)	19.9245(16)	23.5493(14)	25.776(2)	19.8536(13)
α (°)	90	90	90	90
β (°)	106.596(2)	117.1380(10)	105.465(2)	92.7640(10)
γ (°)	90	90	90	90
V (Å ³)	3395.0(5)	9298.1(10)	6461.1(8)	4918.3(5)
Z	4	8	4	4
D _{calc} (mg m ⁻³)	1.742	1.764	1.753	1.732
μ (mm ⁻¹)	5.232	7.751	6.270	7.330
T (K)	173(2)	298(2)	100(2)	293(2)
Cryst dimens (mm)	0.23 × 0.22 × 0.20	0.40 × 0.28 × 0.22	0.31 × 0.30 × 0.17	0.54 × 0.27 × 0.26
Theta range (°)	1.86–28.33	1.56–28.34	1.64–28.40	1.47–28.35
Reflections collected	8427	11 528	16 103	36 326
Unique (R _{int})	24 520(0.0277)	34 146(0.0267)	47 369(0.0806)	36 326(0.0274)
Data/restraints/parameters	8427/0/425	11 528/4/488	16 103/0/613	12 212/0/562
Final R indices [I > 2σ(I)]	R1 = 0.0238, wR2 = 0.0548	R1 = 0.0298, wR2 = 0.0667	R1 = 0.0417, wR2 = 0.0774	R1 = 0.0342, wR2 = 0.0786
R indices (all data)	R1 = 0.0328, wR2 = 0.0571	R1 = 0.0583, wR2 = 0.0729	R1 = 0.0862, wR2 = 0.0863	R1 = 0.0612, wR2 = 0.0848
Largest diff. peak and hole (e Å ⁻³)	1.347, -0.735	1.075, -0.841	1.895, -1.539	1.419, -0.683

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