

Syntheses and molecular structures of some phosphine–gold(I) derivatives of 1,3-diynes

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Received 3 June 2005; received in revised form 23 August 2005; accepted 23 August 2005

Available online 15 December 2005

Abstract

The syntheses of several diynglgold(I) phosphine complexes, including $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol})_3\}$ (**1**), $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PR}_3)$ ($\text{R} = \text{Ph}$ **2-Ph**, tol **2-tol**), $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{PPh}_3)$ (**3**), $\{(\text{tol})_3\text{P}\}\text{Au}(\text{C}\equiv\text{C})_n\text{Au}\{\text{P}(\text{tol})_3\}$ [$n = 2$ (**4**), 3 (**6**), 4 (**7**)], $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}\{\text{P}(\text{tol})_3\}\}$ (**5**), $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{CAu}\{\text{P}(\text{tol})_3\}\}_2]$ (**8**), $[\text{Au}_2(\mu\text{-I})(\mu\text{-dppm})_2][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2]$ (**9**), $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{CAu}(\text{PR}_3)\}_2$ ($\text{R} = \text{Ph}$ **10-Ph**, tol **10-tol**) and $\{(\text{triphos})\text{Cu}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}\{\text{P}(\text{tol})_3\}\}$ (**11**) are described. Of these, the X-ray molecular structures of **1**, **2-tol**, **3**, **4** and **9** have been determined.

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Keywords: Diynyl–gold(I) complexes; Phosphine–gold(I) complexes; X-ray diffraction; Crystal structures

1. Introduction

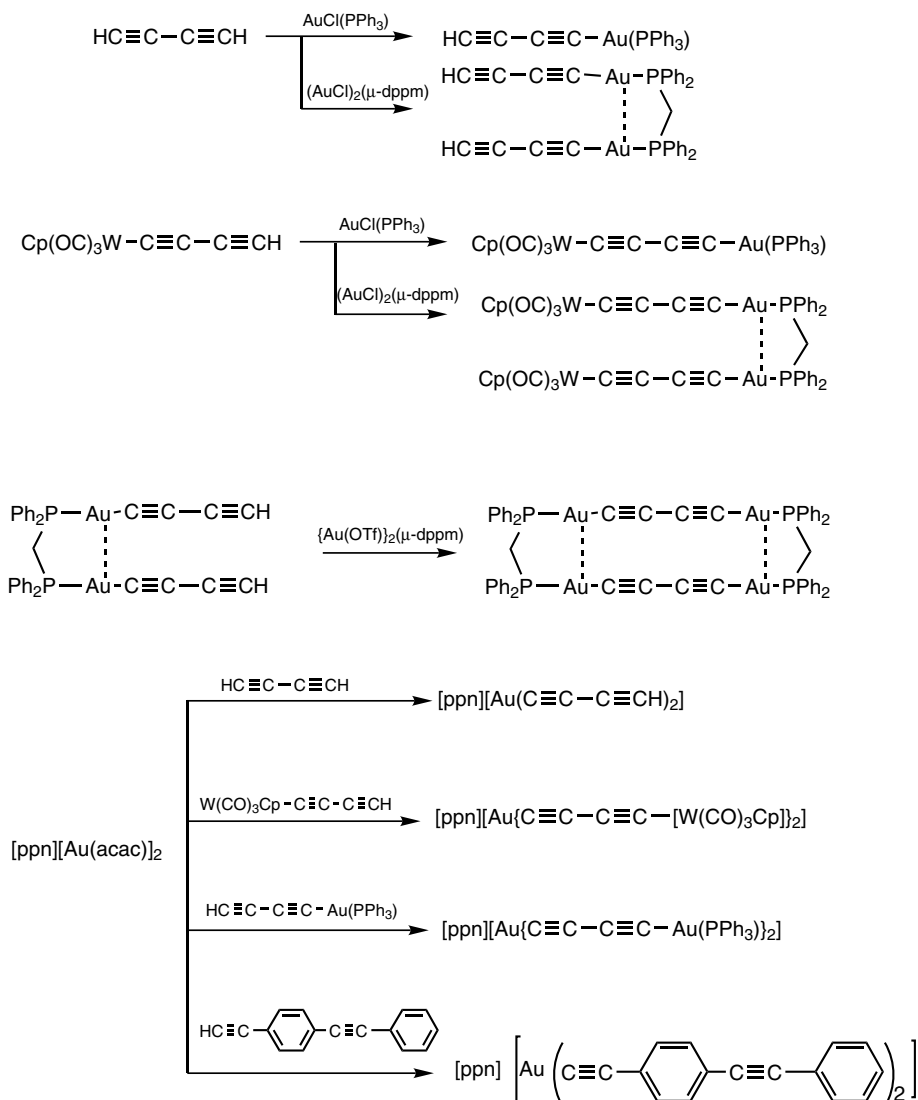
Contemporary interest in gold(I) chemistry derives in part from its tendency to adopt linear two-coordination [1] and the formation of weak gold–gold intramolecular interactions (aurophilicity) [2]. In conjunction with alkynyl or poly-ynyl groups, this can result in the formation of rigid-rod materials [3], which may have unusual non-linear optical [4] or photo-emission properties [5]. The conscious employment of the aurophilic character has resulted in design and construction of unusual geometries [6]. Our own interest has previously encompassed some of these features (Scheme 1) [7], while more recently, we have used elimination of phosphine–gold(I) halides as a component of reactions designed to give long carbon chains end-capped by redox-active metal centres, which are modifications of the well-known Sonogashira reaction [8]. In the course of this work, we have made and characterised sev-

eral derivatives of 1,3-diynes, which extend the earlier studies and are summarised in Scheme 2.

2. Results and discussion

Following established procedures, the reaction between $\text{AuCl}\{\text{P}(\text{tol})_3\}$ and buta-1,3-diyne was carried out in a thf/diethylamine solvent mixture in the presence of CuI to give pale yellow $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol})_3\}$ (**1**) in 63% yield. The IR spectrum of this compound contains $\nu(\equiv\text{CH})$ and $\nu(\text{C}\equiv\text{C})$ absorptions at 3300 and 2157 cm^{-1} , respectively, while its ^1H NMR spectrum contains singlet resonances at δ 1.66 and 2.38, assigned to the $\equiv\text{CH}$ and Me protons, respectively, and a multiplet between δ 7.20 and 7.43 for the C_6H_4 protons. In the ^{13}C NMR spectrum, resonances at δ 22.17 and between 125.7 and 142.0 arise from the tolyl groups; only three of the four diyngl carbons were found, at δ 60.14 (C_δ), 69.55 (C_γ) and 85.49 (C_β). The ^{31}P NMR spectrum contains a singlet at δ 40.3 from the $\text{P}(\text{tol})_3$ ligand.

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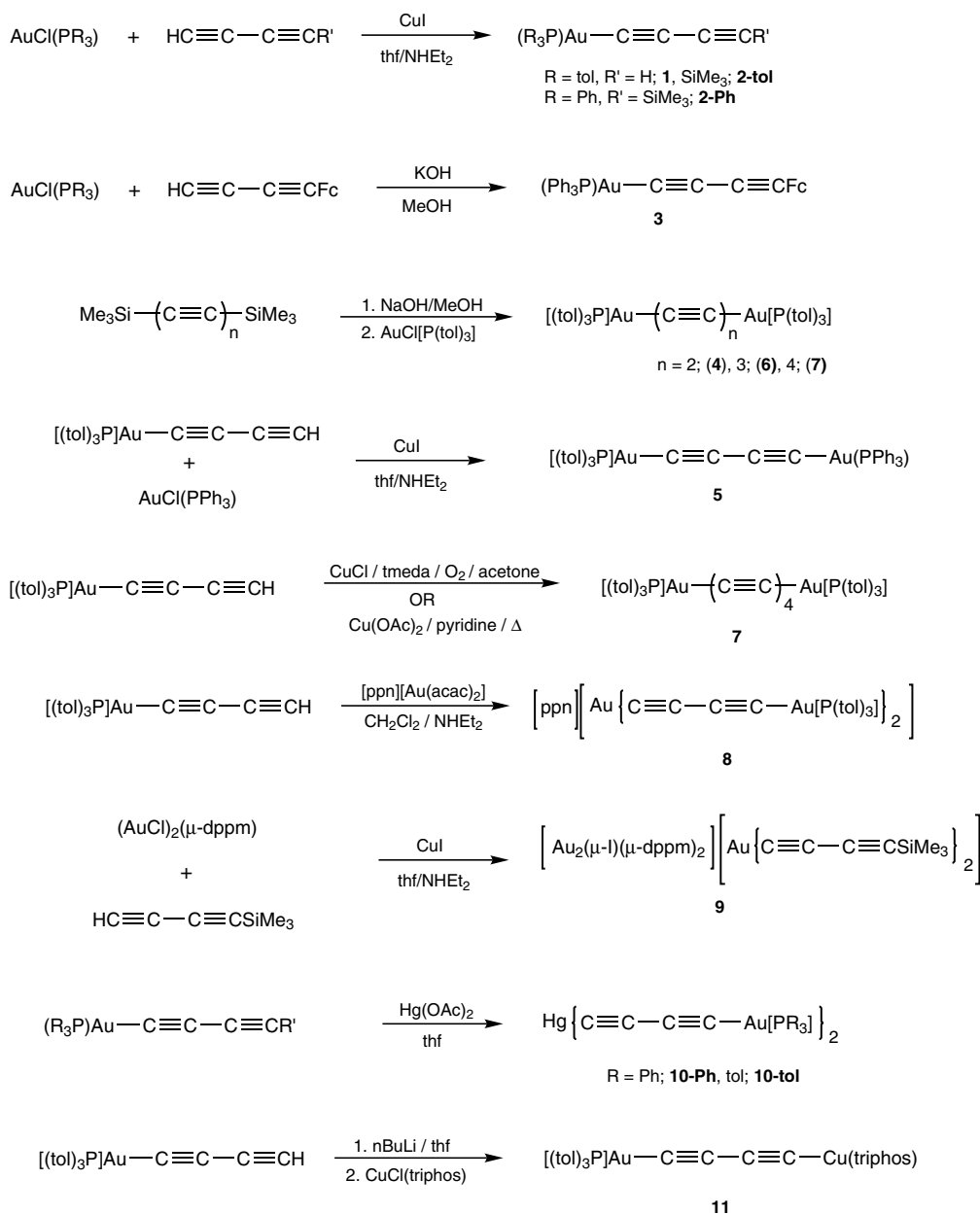
Scheme 1.

The related complexes $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PR}_3)$ ($\text{R} = \text{Ph}$ **2-Ph**, tol **2-tol**) were obtained in 77% and 67% yields from similar reactions of $\text{AuCl}(\text{PR}_3)$ employing $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$. Their spectroscopic properties include three $\nu(\text{C}\equiv\text{C})$ absorptions between 2184 and 2036 cm^{-1} (probably arising from Fermi coupling) and resonances at δ 0.14/0.13 (Ph/tol, SiMe_3), 2.37 (tol Me) and multiplets at δ 7.19–7.51 (aromatic). The ^{13}C NMR spectrum contains the expected resonances at δ $-0.12/-0.14$ (Ph/tol, SiMe_3), 21.41 (tol Me) and between δ 128.8 and 142.0 (aromatic). Again, only three of the diynyl carbons were found, at δ 78.71/78.89 (C_δ), 86.67/87.02 (C_γ) and 89.52/89.62 (C_β).

Treatment of a mixture of $\text{AuCl}(\text{PPh}_3)$ and $\text{HC}\equiv\text{CC}\equiv\text{CFc}$ in MeOH with KOH afforded orange $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{PPh}_3)$ (**3**) in 85% yield. This compound has weak $\nu(\text{C}\equiv\text{C})$ bands at 2191 and 2053 cm^{-1} , while the ^1H NMR spectrum contains multiplets for C_5H_4 (δ 3.83, 4.34) and Ph protons (δ 6.88–6.98, 7.10–7.16) accompanied by the Fe–Cp singlet at δ 4.01. In the ^{13}C NMR spectrum,

signals at δ 69.19 and 72.85 assigned at the C_5H_4 carbons, a multiplet between δ 128.2 and 134.9 to the Ph carbons, were accompanied by resonances at δ 66.61 (C_δ), 70.36 (C_{ipso} of Fc), 70.65 (Fe–Cp), 74.82 (C_γ) and 88.27 (C_β). The ^{31}P resonance for the PPh_3 ligand is at δ 41.4. In this case, M^+ in the ES-MS occurs at m/z 692.

The molecular structures of **1**, **2-tol** and **3** were determined by single-crystal X-ray diffractometry and plots of single molecules are shown in Fig. 1. Selected bond parameters are collected in Table 1. Generally, there are no unusual intermolecular interactions. The phosphine–gold(I) moiety is σ -bonded to the diynyl ligand [$\text{Au}-\text{C}(1)$ 2.272(3), 2.2779(9), 2.276(2) Å, respectively], while the short–long–short C–C separations along the chain are consistent with the diynyl formulation, with there being no evidence for π -electron delocalisation. In **1**, the H atom attached to C(4) was located in difference maps; in **2-tol**, C(4)–Si(4) is 1.808(5) Å, while in **3**, the C(4)–C(41) distance is 1.417(9) Å, a normal value for a $\text{C}(\text{sp})-\text{C}(\text{sp}^2)$ separation. The six-atom P–Au–C(1–4) chains are essentially linear,



Scheme 2.

with maximum deviations being 9° [at C(1) in **1**], 5.1° [at Au in **2-tol**] and 3.5° [at C(3) in **3**]. Total bending amounts to 20.5° (**1**), 19.55° (**2-tol**) and 11.4° (**9**).

Of note are the larger displacement ellipsoids for C(3) and C(4) in **1**, suggesting relatively larger vibrational amplitudes for these atoms, consistent with present ideas concerning the low bending force constant in chains of C(sp) atoms [9]. Molecules of **2-tol** co-crystallise with $\text{AuI}\{\text{P}(\text{tol})_3\}$ in the proportion 80/20. The individual components were independently isolable and refinable and data are quoted to the relevant statistics.

The symmetrical digold complex $\{(\text{tol})_3\text{P}\}\text{AuCC}\equiv\text{CC}\equiv\text{CAu}\{\text{P}(\text{tol})_3\}$ (**4**) was prepared by two routes. Treatment of a mixture of $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ and $\text{AuCl}\{\text{P}(\text{tol})_3\}$ in MeOH with NaOH gave the pale yellow

compound in 85% yield, while coupling of $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol})_3\}$ (**1**) with another equivalent of $\text{AuCl}\{\text{P}(\text{tol})_3\}$ in thf/NHEt₂ in the presence of CuI gave a 78% yield. The ¹H NMR spectrum contains signals at δ 2.29 (Me) and between δ 7.12 and 7.32 (C₆H₄), while the ¹³C NMR resonances at δ 21.39 (Me) and between δ 126.6 and 141.7 similarly arise from the P(tol)₃ ligand, which also gives a ³¹P resonance at δ 40.6. The two diynyl carbons are found at δ 88.11 (C_β) and 119.89 (C_α); the latter shows a doublet *J*(CP) coupling of 140 Hz. Related complexes containing PPh₃ [8] or PCy₃ [10] are known.

The molecular structure of **4** is shown in Fig. 2, with selected bond parameters in Table 1. The molecule is not centrosymmetric, but the dimensions of both halves are essentially identical. The Au–P distances are 2.275,

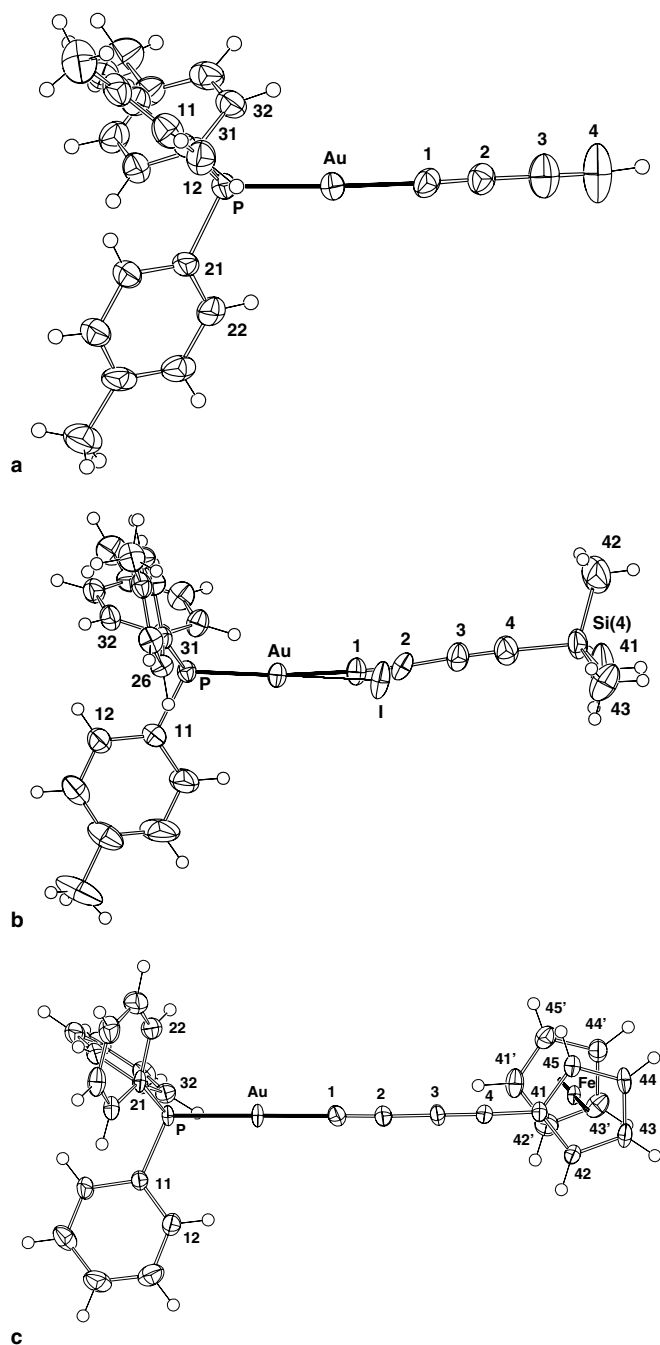


Fig. 1. Plots of single molecules of: (a) $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol})_3\}$ (**1**), (b) $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)\{\text{P}(\text{tol})_3\}$ (**2-tol**), also showing co-crystallised $\text{Au}\{\text{P}(\text{tol})_3\}$, and (c) $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{PPh}_3)$ (**3**).

2.273(1) Å and the Au–C separations are both 1.996(5) Å. Along the chain, the short–long–short separations support the diyndiyl formulation with no delocalisation of π -electron density. The P–Au–C₄–Au–P chain is essentially linear, with a maximum deviation at C(4) (10.8°) and total bending of 22.2°, all in the same sense; the separation P(1)··P(2) is 12.235(2) Å, some 0.20 Å shorter than the sum of interatomic distances (12.43 Å). In the cell (Fig. 2(b)), it can be seen that packing of individual molecules is influenced by Ph··Ph interactions.

The mixed ligand complex $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**5**) was obtained in 51% yield from $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ and $\text{AuCl}\{\text{P}(\text{tol})_3\}$ in thf/NHET_2 in the presence of CuI . In addition to the resonances from the PR_3 ligands, the ^{13}C NMR spectrum contained resonances assigned to the diyndiyl chain at δ 85.78 (C_β), 88.23 (C_γ), 125.80 (C_α, broad) and 126.96 (C_δ, broad); the ^{31}P NMR spectrum has two singlets at δ 40.2 [P(tol)₃] and 42.6 (PPh₃). Assignments are based on comparisons with the homo-disubstituted compounds.

Use of NaOH as base was also applicable to complexes containing longer carbon chains, reactions between $\text{AuCl}\{\text{P}(\text{tol})_3\}$ and $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ ($n = 3, 4$) giving the corresponding $\{(\text{tol})_3\text{P}\}\text{Au}(\text{C}\equiv\text{C})_n\text{Au}\{\text{P}(\text{tol})_3\}$ [$n = 3$ (**6**), 4 (**7**)] in 76 and 20% yields, respectively. Compound **7** was also obtained by oxidative coupling of **1** using either $\text{Cu}(\text{OAc})_2$ in pyridine (57%) or dioxygen in the presence of CuCl/tmeda (33%). These two compounds contained ^1H , ^{13}C and ^{31}P resonances for the P(tol)₃ ligands in the expected positions. In the IR spectrum, medium intensity $\nu(\text{C}\equiv\text{C})$ bands are found at 2139 and 2115 (**6**) and at 2167 and 2134 cm^{-1} (**7**), while we assign singlets at δ 81.63 (C_γ), 88.13 (C_β) and 127.94 (C_α, broad) (**6**) and at δ 60.91 (C_δ), 67.23 (C_γ), 86.94 (C_β, broad) and 131.29 (C_α, broad) (**7**) to the various carbons of the poly-ynyl chains. Che and co-workers have described analogues with PCy_3 for $n = 2\text{--}4$ [10] and have studied their $^3(\pi\pi^*)$ emissivities. In turn, theoretical studies have characterised the geometries of the singlet and triplet states [11].

The use of $[\text{ppn}][\text{Au}(\text{acac})_2]$ for the preparation of anionic gold(I) derivatives of alkynes has been described on several occasions [12]. During the present work, we have found that the direct reaction between $[\text{ppn}][\text{Au}(\text{acac})_2]$ and **1** in a dichloromethane/diethylamine solvent mixture afforded $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{CAu}\{\text{P}(\text{tol})_3\}_2\}]$ (**8**) in 39% yield as a creamy white solid. In the NMR spectra, signals for the P(tol)₃ ligand were found at δ_{H} 2.29 and δ_{C} 21.36 (Me), between δ_{H} 7.15 and 7.62 and δ_{C} 125.5 and 141.8 (C₆H₄) and at δ_{P} 39.62; the ppn resonance is at δ_{P} 22.21. The weak IR $\nu(\text{C}\equiv\text{C})$ band is at 2145 cm^{-1} . Overall, this compound is very similar to the PPh₃ analogue [7].

A similar anionic complex, $[\text{Au}_2(\mu\text{-I})(\mu\text{-dppm})_2][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2]$ (**9**), was obtained from the reaction between $(\text{AuCl})_2(\mu\text{-dppm})$ and $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ in a thf/NHET_2 mixture in the presence of CuI . This light yellow compound shows $\nu(\text{C}\equiv\text{C})$ at 2176 and 2122 cm^{-1} , while the ^1H NMR spectrum contains a singlet at δ 0.16 for the SiMe₃ protons, as well as multiplets at δ 4.57 and between δ 7.24 and 7.76 from the dppm protons. The ^{31}P resonance is at δ 27.7. Both components of the salt were found in the positive or negative ion mode ES-MS, the $[\text{Au}_2\text{I}(\text{dppm})_2]^+$ cation at m/z 1289 and the $[\text{Au}(\text{C}_4\text{-SiMe}_3)_2]^-$ anion at m/z 439, respectively.

The cation in **9** (Fig. 3(a)) has been structurally characterised on two previous occasions, with iodide [13, no atom coordinates available] and $[\text{Au}(\text{CN})_2]^-$ counter-ions [14], these being obtained serendipitously from reactions of

Table 1
Selected bond distances (Å) and angles (°)

Complex	1	2 ^a	3	4	9 ^b
<i>Bond distances (Å)</i>					
Au–P	2.272(3)	2.2779(9)	2.276(2)	2.275(1), 2.273(1)	
Au–C(1)	1.99(1)	1.993(6)	2.010(7)	1.996(5)	2.009, 1.984(8)
C(1)–C(2)	1.19(2)	1.163(9)	1.18(1)	1.196(6)	1.15, 1.21(1)
C(2)–C(3)	1.38(2)	1.418(8)	1.39(1)	1.390(6)	1.42, 1.39(1)
C(3)–C(4)	1.19(3)	1.229(7)	1.20(1)	1.215(6)	1.21, 1.21(1)
C(4)–X		1.808(5) [Si(4)]	1.417(9) [C(41)]	1.996(5) [Au(2)]	1.83, 1.84(1) [Si]
<i>Bond angles (°)</i>					
P–Au–C(1)	172.5(3)	174.9(2)	178.6(2)	178.7(2), 176.2(2)	
Au–C(1)–C(2)	171(1)	176.3(6)	177.3(6)	176.3(6)	174.0(7), 175(1)
C(1)–C(2)–C(3)	177(1)	176.6(6)	177.6(9)	178.6(6)	174, 175(1)
C(2)–C(3)–C(4)	179(1)	177.1(6)	176.5(7)	178.8(5)	177, 180(1)
C(3)–C(4)–X		177.7(4) [Si(4)]	178.6(8)	169.2(6) [Au(2)]	170(1), 170.5(9) [Si]

^a For **2**, AuI{P(tol)₃} component (19%): Au–I 2.598(3) Å, P–Au–I 177.85(6)°.

^b For **5**, [Au₂(μ-I)(μ-dppm)₂]⁺ cation: Au(1)–Au(2) 2.9576(4), Au(1,2)–I 3.1014, 3.1071(6), Au–P 2.310–2.320(3) Å; Au(1)–I–Au(2) 56.90(1), P–Au–P 164.70, 166.34(7), P–C(0)–P 115.9(4), 115.0(4)°. For anion, C(11)–Au(3)–C(21) 178.1(3)°.

{Au[μ-(PPh₂)₂CH]}₂ (containing deprotonated dppm ligands) with MeI, or from [Au₂(μ-dppm)₂][BH₃(CN)₂] with NaI; the latter was converted to the dicyanoaurate(I)

salt on attempted recrystallisation. In all three examples, the two gold atoms are bridged by the iodine, with a strongly acute Au–I–Au angle [56.90(1)° in **9**, 54.2(1)° in

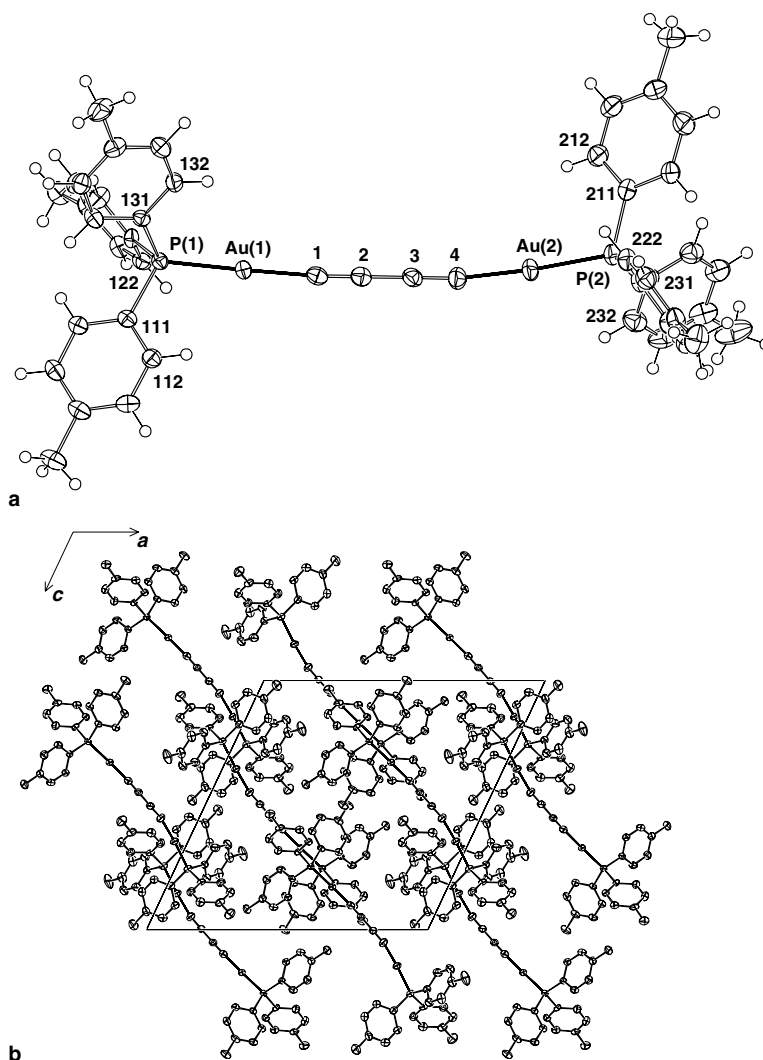


Fig. 2. Plots of: (a) a single molecule and (b) the packing in the unit cell, of {(tol)₃P}AuC≡CC≡CAu{P(tol)₃} (**4**).

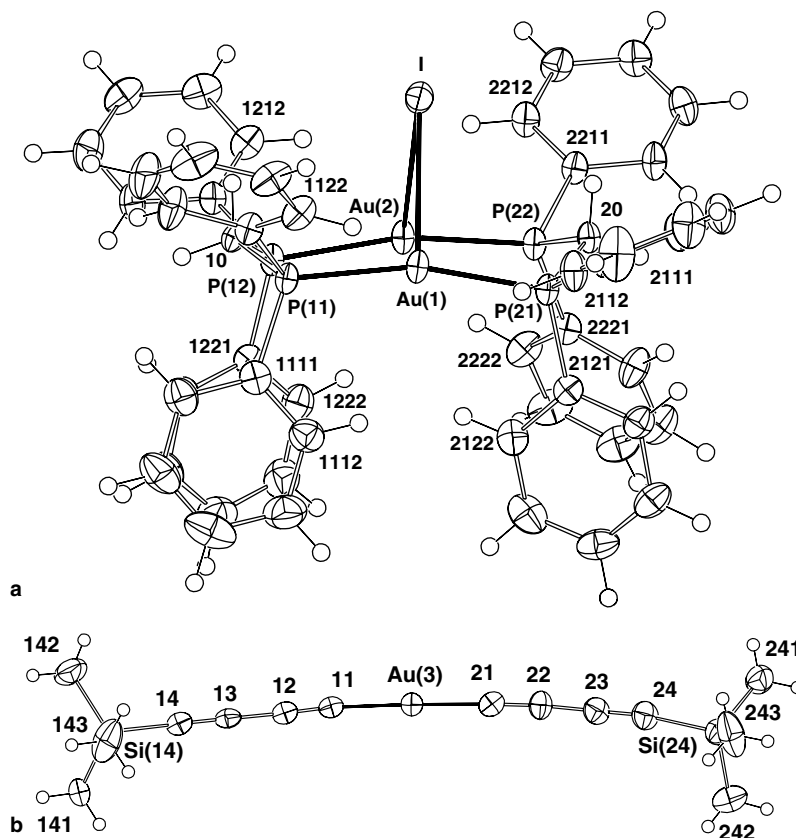


Fig. 3. Plots of: (a) the cation and (b) the anion in $[\text{Au}_2(\mu\text{-I})(\mu\text{-dppm})_2][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2]$ (**9**).

the $[\text{Au}(\text{CN})_2]^-$ salt]. For **9**, the two Au–I distances are 3.1014, 3.1071(6) Å, their near equality being similar to those in the iodide (3.127, 3.196(2) Å) but contrasting with those in the $[\text{Au}(\text{CN})_2]^-$ salt (3.161, 3.342(3) Å). The Au···Au separations are 2.9576(4) (**9**), 2.948(2) (iodide) and 2.967(1) Å (dicyanoaurate), while the closest approaches to the I atom are from the phenyls of adjacent cations $[\text{I}\cdots\text{C}(2213)]$ ($x, 1-y, 1-z$) 3.890(8) Å].

In the anion (Fig. 3(b)), the two Au–C(sp) distances are 2.009, 1.984(8) Å, with alternating short–long–short C–C separations along the chain $[\text{C}(n1)\text{--}\text{C}(n2)$ 1.15, 1.21(1), $\text{C}(n2)\text{--}\text{C}(n3)$ 1.42, 1.39(1), $\text{C}(n3)\text{--}\text{C}(n4)$ 1.21, 1.21(1) Å ($n = 1, 2$)]. The anion contains an 11-atom Si–C₄–Au–C₄–Si chain which is essentially linear, with angles at Au 178.1(3)° and ranging from 170 to 180° at C. Bending is all in the same sense, the total summing to 36.9° and resulting in the two Si atoms being 15.053(4) Å apart, some 0.20 Å shorter than the sum of interatomic distances (15.25 Å).

Bridging of two diyne-gold chains through mercury was achieved by direct reaction of $\text{Hg}(\text{OAc})_2$ with **1** in thf, when white $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol})_3]\}_2$ (**10-tol**) was isolated in 54% yield. The PPh_3 -analogue, $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3)\}_2$ (**10-Ph**) was obtained from a similar reaction of $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$. Weak $\nu(\text{C}\equiv\text{C})$ bands are found at 2166 and 2052 (**tol**) or 2100 and 2014 (**Ph**) cm^{-1} , while for **10-tol**, $\text{P}(\text{tol})_3$ resonances occur at δ_{H} 2.35 and δ_{C}

21.43 (Me), δ_{H} 7.18–7.39 and δ_{C} 126.8–141.7 (C_6H_4) and δ_{P} 40.6. Resonances at δ_{C} 72.52, 88.15 [$J(\text{CP})$ 29 Hz] and 102.52 are tentatively assigned to C_γ , C_α and C_δ , respectively, on the basis of the observed C–P coupling for C_α and the anticipated shift of C_δ upon coordination to the mercury centre. Only aromatic resonances were found for **10-Ph**.

The first complex containing two different Group 11 metal centres linked by a diyndiyl ligand was obtained by treating **1** with LiBu, followed by addition of $\text{CuCl}(\text{triphos})$ [$\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$], when creamy white $\{(\text{triphos})\text{Cu}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**11**) was isolated in 62% yield. The IR spectrum contains two $\nu(\text{C}\equiv\text{C})$ bands at 2158 and 2127 cm^{-1} , while only phosphorus ligand resonances are found in the ^1H [δ 1.44 (C–Me), 2.28 (P–CH₂), 2.36 (tol–Me), 6.82–7.46 (aromatic)], ^{13}C [21.43 (tol–Me), 36.47 and 37.53 (C–Me), 39.93 (P–CH₂) and 125.3–142.3 (aromatic)] and ^{31}P [–25.1 (triphos), 45.2 {P(tol)₃}] NMR spectra.

3. Conclusions

This paper has described the syntheses of several examples of phosphine–gold(I) complexes containing various diyne fragments, the molecular structures of four of these being determined by single-crystal X-ray diffraction studies. Some of these compounds have found use as

intermediates, particularly in the synthesis of longer carbon chains by elimination of phosphine–gold(I) halides, as described elsewhere [8].

4. Experimental

4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm²) coated with silica gel (Merck, 0.5 mm thick).

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (¹H at 300.13 MHz, ¹³C at 75.47 MHz, ³¹P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 mL injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used [15]. Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.3. Reagents

AuCl(PR₃) (R = Ph [16], tol [17]), [ppn][Au(acac)₂] [18], (AuCl)₂(μ-dppm) [19], Au(C≡CC≡CH)(PPh₃) [7], CuCl-(triphos) [20], HC≡CC≡CR (R = H [21], Fc [22]) and Me₃Si(C≡C)_nSiMe₃ (n = 2 [23], 3 [24], 4 [25]) were obtained as previously described.

4.3.1. Au(C≡CC≡CH){P(tol)₃} (1)

To a solution of AuCl{P(tol)₃} (2.0 g, 3.73 mmol) in thf/NHEt₂ (60 mL, 1/3) was added CuI (71 mg, 0.37 mmol) followed by HC≡CC≡CH (6.9 mL of a 2.7 M solution in thf, 18.6 mmol) and the mixture was stirred at r.t. for 30 min. The solvent was removed and the residue extracted with CH₂Cl₂ and loaded onto a SiO₂ column. The product was eluted with CH₂Cl₂, addition of hexane and reduction of solvent volume resulting in precipitation of pale yellow Au(C≡CC≡CH){P(tol)₃} (1) (1.3 g, 63%). Anal. Found: C, 54.51; H, 4.01. C₂₅H₂₂AuP requires: C, 54.56; H, 4.03; M, 550. IR (CH₂Cl₂): ν(≡CH) 3300; ν(C≡C) 2157 cm⁻¹. ¹H NMR: δ 1.66 (s, 1H, C≡CH), 2.38 (s, 9H, Me), 7.20–

7.43 (m, 12H, tol). ¹³C NMR: δ 22.17 (s, Me), 60.14 (s, C_δ), 69.55 (s, C_γ), 85.49 (br, C_β), 125.75–141.97 (m, tol). ³¹P NMR: δ 40.30.

4.3.2. Au(C≡CC≡CSiMe₃)(PPh₃) (2-Ph)

To a suspension of AuCl(PPh₃) (500 mg, 1.01 mmol) in thf/NHEt₂ (30 mL, 1/2) containing CuI (20 mg, 0.105 mmol) was added HC≡CC≡CSiMe₃ (185 mg, 1.52 mmol) and the mixture was stirred at r.t. for 1 h. The solvent was removed and the residue extracted with CH₂Cl₂ and loaded onto a SiO₂ column. The product was eluted with hexane. Reduction of solvent volume resulted in precipitation of pale yellow Au(C≡CC≡CSiMe₃)(PPh₃) (2-Ph) (450 mg, 77%). Anal. Found: C, 49.78; H, 3.38. C₂₅H₂₄AuPSi.0.5CH₂Cl₂ requires: C, 49.16; H, 4.05; M, 580. IR (nujol): ν(C≡C) 2184m, 2129m, 2038m cm⁻¹. ¹H NMR: δ 0.14 (s, 9H, SiMe₃), 7.51–7.42 (m, 15H, Ph). ¹³C NMR δ -0.12 (s, SiMe₃), 78.71 (s, C_δ), 86.67 (s, C_γ), 89.52 (br, C_β), 134.31–129.08 (m, Ph). ³¹P NMR: δ 42.41.

4.3.3. Au(C≡CC≡CSiMe₃){P(tol)₃} (2-tol)

To a solution of AuCl{P(tol)₃} (250 mg, 0.47 mmol) in thf/NHEt₂ (15 mL, 1/3) was added CuI (ca 5 mg) followed by HC≡CC≡CSiMe₃ (114 mg, 0.94 mmol). The yellow solution was stirred for 1 h in the dark and the solvent removed. Extraction with CH₂Cl₂ and passage through a SiO₂ column eluting with hexane yielded a pale yellow band which gave pale yellow solid Au(C≡CC≡CSiMe₃){P(tol)₃} (2-tol) (195 mg, 67%). Anal. Found: C, 53.98; H, 4.83%. Calc. for C₂₈H₃₀AuPSi: C, 54.02; H, 4.86; M, 623. IR (CH₂Cl₂): ν(C≡C) 2183m, 2131m, 2036m cm⁻¹. ¹H NMR: δ 0.13 (s, 9H, SiMe₃), 2.37 (s, 9H, Me), 7.19–7.42 (m, 12H, tol). ¹³C NMR: δ -0.14 (s, SiMe₃), 21.41 (s, Me), 78.89 (s, C_δ), 87.02 (s, C_γ), 89.62 (br, C_β), 125.82–142.00 (m, tol). ³¹P NMR: δ 40.25.

4.3.4. Au(C≡CC≡CFc)(PPh₃) (3)

KOH (100 mg, 1.8 mmol) was added to a suspension of AuCl(PPh₃) (105 mg, 0.212 mmol) and HC≡CC≡CFc (55 mg, 0.235 mmol) in dry MeOH (15 mL) and the mixture was stirred for 1 h. After cooling on ice, the precipitate was collected on a sinter and washed with cold MeOH to give Au(C≡CC≡CFc)(PPh₃) (3) (120 mg, 85%) as an orange powder. Anal. Found: C, 55.53; H, 3.40%. Calc. for C₃₂H₂₄AuFeP: C, 55.52; H, 3.49; M, 000. IR (nujol): ν(C≡C) 2191w, 2053w cm⁻¹. ¹H NMR (C₆D₆): δ 3.83, 4.34 (2 × m, 2 × 2H, C₅H₄), 4.01 (s, 5H, Fe–Cp), 6.88–6.98, 7.10–7.16 (2 × m, 8 + 7H, Ph). ¹³C NMR (C₆D₆): δ 66.61 (Cx), 69.19, 72.85 (2 × s, C₅H₄), 70.65 (Fe–Cp), 74.82, 88.27, 128.19–134.92 (m, Ph). ³¹P (C₆D₆): δ 41.36. ES-MS (MeOH, m/z): 692, M⁺.

4.3.5. {[P(tol)₃]}AuC≡CC≡C{Au[P(tol)₃]} (4)

(a) From Me₃SiC≡CC≡CSiMe₃. Me₃SiC≡CC≡CSiMe₃ (50 mg, 0.26 mmol) and NaOH (206 mg, 5.20 mmol) were dissolved in MeOH (25 mL) and stirred for 30 min.

$\text{AuCl}\{\text{P}(\text{tol})_3\}$ (276 mg, 0.52 mmol) was added and the mixture was stirred a further 1.5 h. The pale yellow precipitate which formed was collected and washed with MeOH, Et_2O and pentane and air-dried to give $\{[(\text{tol})_3\text{P}]\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**4**) (230 mg, 85%). Anal. Found: C, 52.43; H, 3.96%. Calc. for $\text{C}_{46}\text{H}_{42}\text{Au}_2\text{P}_2$: C, 52.58; H, 4.03; *M*, 1051. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2157 cm^{-1} . ^1H NMR: δ 2.29 (s, 9H, Me), 7.12–7.32 (m, 12H, tol). ^{13}C NMR: δ 21.39 (s, Me), 88.11 (br, C_β), 119.89 (d, $^2J_{\text{CP}} = 140\text{ Hz}$, C_α), 126.67–141.69 (m, tol). ^{31}P NMR: δ 40.57 (s).

(b) From **1** and $\text{AuCl}\{\text{P}(\text{tol})_3\}$. A Schlenk flask was charged with **1** (100 mg, 0.18 mmol), $\text{AuCl}\{\text{P}(\text{tol})_3\}$ (97 mg, 0.18 mmol), CuI (ca. 5 mg) and thf/NHEt₂ (20 mL, 1/2). The suspension cleared to give a yellow solution that was stirred for 1 h at r.t. The solution was filtered, solvent removed and a CH_2Cl_2 extract of the residue was passed through a SiO_2 column (CH_2Cl_2 –hexane, 1/1) to give pale yellow **4** (148 mg, 78%).

4.3.6. $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**5**)

To a solution of $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ (250 mg, 0.49 mmol) and $\text{AuCl}\{\text{P}(\text{tol})_3\}$ (264 mg, 0.49 mmol) in thf/NHEt₂ (30 mL, 1/3) was added CuI (ca. 5 mg) and the resulting yellow solution was stirred for 1 h. The yellow-brown precipitate was collected and washed with H₂O, EtOH, MeOH and Et₂O and air-dried to give $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**5**) (250 mg, 51%). Anal. Found: C, 51.09; H, 3.45%. Calc. for $\text{C}_{43}\text{H}_{36}\text{Au}_2\text{P}_2$: C, 51.20; H, 3.60; *M*, 1009. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2153 cm^{-1} . ^1H NMR: δ 2.35 (s, 9H, Me), 7.17–7.54 (m, 27H, tol). ^{13}C NMR: δ 21.44 (s, Me), 85.78 (br, C_β), 88.23 (br, C_γ), 125.80 (br, C_α), 126.96 (br, C_δ), 129.00–142.38 (m, tol). ^{31}P NMR: δ 40.24 [s, P(tol₃)], 42.60 (s, PPh₃).

4.3.7. $\{[(\text{tol})_3\text{P}]\text{Au}\}\{\text{C}\equiv\text{C}\}_3\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**6**)

A solution of $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_3\text{SiMe}_3$ (50 mg, 0.23 mmol) and NaOH (184 mg, 4.60 mmol) in MeOH (25 mL) was stirred for 30 min. $\text{AuCl}\{\text{P}(\text{tol})_3\}$ (246 mg, 0.46 mmol) was added and the mixture was stirred a further 1.5 h. The pale yellow precipitate was collected and washed with MeOH, Et₂O and pentane and air-dried to give $\{[(\text{tol})_3\text{P}]\text{Au}\}\{\text{C}\equiv\text{C}\}_3\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**6**) (188 mg, 76%). Anal. Found: C, 53.66; H, 3.87%. Calc. for $\text{C}_{48}\text{H}_{42}\text{Au}_2\text{P}_2$: C, 53.64; H, 3.94; *M*, 1075. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2139 sh , 2115 m cm^{-1} . ^1H NMR: δ 2.38 (s, 9H, Me), 7.20–7.40 (m, 12H, tol). ^{13}C NMR: δ 21.42 (s, Me), 81.63 (s, C_γ), 88.13 (br, C_β), 127.94 (br, C_α), 129.77–142.06 (m, tol). ^{31}P NMR: δ 40.26 (s).

4.3.8. $\{[(\text{tol})_3\text{P}]\text{Au}\}\{\text{C}\equiv\text{C}\}_4\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**7**)

(a) From $\text{AuCl}\{\text{P}(\text{tol})_3\}$ and $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_4\text{SiMe}_3$. A solution of $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_4\text{SiMe}_3$ (75 mg, 0.31 mmol) and NaOH (248 mg, 6.20 mmol) in MeOH (25 mL) was stirred for 30 min. $\text{AuCl}\{\text{P}(\text{tol})_3\}$ (302 mg, 0.56 mmol) was added and the mixture stirred for a further 1.5 h. A pale yellow

precipitate had formed and was collected and washed with MeOH, Et₂O and pentane and air-dried to give $\{[(\text{tol})_3\text{P}]\text{Au}\}\{\text{C}\equiv\text{C}\}_4\{\text{Au}[\text{P}(\text{tol})_3]\}$ (**7**) (60 mg, 20%). Anal. Found: C, 54.59; H, 3.77%. Calc. for $\text{C}_{50}\text{H}_{42}\text{Au}_2\text{P}_2$: C, 54.66; H, 3.85; *M*, 1099. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2167 w , 2134 m cm^{-1} . ^1H NMR: δ 2.36 (s, 9H, Me), 7.20–7.38 (m, 12H, tol). ^{13}C NMR: δ 21.42 (s, Me), 60.91 (s, C_δ), 67.23 (s, C_γ), 86.94 (br, C_β), 131.29 (br, C_α), 126.15–142.02 (m, tol). ^{31}P NMR: δ 40.26 (s).

(b) From $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol})_3\} + \text{CuCl}/\text{tmeda}$. The Hay catalyst was prepared from CuCl (100 mg, 1.01 mmol) in acetone (5 mL) and tmeda (0.15 mL, 0.3 mmol) which was added dropwise. The resulting blue solution was stirred a further 30 min. Dioxygen was bubbled through a solution of **1** (300 mg, 0.55 mmol) in acetone (25 mL). The Hay catalyst was added in 1 mL portions over 1 h after which the reaction was adjudged complete (t.l.c). The solvent was removed and the residue chromatographed on a SiO_2 column (hexane– CH_2Cl_2 , 1/1). Removal of the solvent from the bright yellow fraction yielded **7** (100 mg, 33%).

(c) From $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol})_3\}$ and $\text{Cu}(\text{OAc})_2/\text{pyridine}$. To a solution of **1** (100 mg, 0.18 mmol) in pyridine (3 mL) was added $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (55 mg, 0.27 mmol) and the mixture was stirred at 80 °C for 2 h. The solvent was removed and the dark brown residue passed down a SiO_2 column eluting with CH_2Cl_2 . A bright yellow fraction was collected and hexane (10 mL) added. Removal of the solvent gave yellow **7** (56 mg, 57%).

4.3.9. $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol})_3]\}_2]$ (**8**)

A solution of **1** (110 mg, 0.2 mmol) and $[\text{ppn}][\text{Au}(\text{acac})_2]$ (92 mg, 0.1 mmol) in $\text{CH}_2\text{Cl}_2/\text{NHEt}_2$ (10 mL, 10/1) was stirred at r.t for 2 h. The solvent was then removed and the residue extracted with CH_2Cl_2 and filtered into cold hexane. The cream-white precipitate was collected and washed with Et₂O ($2 \times 10\text{ mL}$) and *n*-pentane (20 mL) and air-dried to give $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol})_3]\}_2]$ (**8**) (72 mg, 39%). Anal. Found: C, 56.49; H, 4.06%. Calc. for $\text{C}_{86}\text{H}_{72}\text{Au}_3\text{NP}_4$: C, 56.31; H, 3.96; *M*, 1296. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2145 w cm^{-1} . ^1H NMR: δ 2.29 (s, 18H, Me), 7.15–7.62 (m, 54H, Ph, tol). ^{13}C NMR: δ 21.36 (s, Me), 125.54–141.81 (m, Ph, tol). ^{31}P NMR: δ 22.21 (s, ppn), 39.62 [s, P(tol₃)].

4.3.10. $[\text{Au}_2(\mu\text{-I})(\mu\text{-dppm})_2][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2]$ (**9**)

$\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (88 mg, 0.72 mmol) and CuI (20 mg, 0.07 mmol) were added to a suspension of $(\text{AuCl})_2(\mu\text{-dppm})$ (200 mg, 0.24 mmol) in thf/NHEt₂ (45 mL, 8/1). The resulting clear solution was stirred at r.t. for 2 h, a small amount of precipitate was filtered off, and the filtrate was evaporated. A benzene extract of the residue was added dropwise to stirred hexane to give a light yellow precipitate, which was filtered off and reprecipitated twice. Crystallisation ($\text{CH}_2\text{Cl}_2/\text{hexane}$) gave pure $[\text{Au}_2(\mu\text{-I})(\mu\text{-dppm})_2][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)_2]$ (**9**) (50 mg, 42%) as

pale lime-yellow crystals. Anal. Found: C, 44.27; H, 3.70%. Calc. for $C_{64}H_{62}Au_3IP_4Si_2$: C, 44.45; H, 3.61; M (cation), 1289; M (anion), 439. IR (CH_2Cl_2): $\nu(C\equiv C)$ 2176w, 2122m cm^{-1} . 1H NMR ($CDCl_3$): δ 0.16 (s, 18H, $SiMe_3$), 4.57 (m, 4H, CH_2), 7.24–7.76 (m, 40H, Ph). ^{31}P NMR ($CDCl_3$): δ 27.7 (s, dppm). ES-MS (positive ion, $C_2H_4Cl_2$, m/z): 1289, $[Au_2I(dppm)_2]^+$; (negative ion, $C_2H_4Cl_2$, m/z): 439, $[Au(C_4SiMe_3)_2]^-$.

4.3.11. $Hg\{C\equiv CC\equiv CAu(PPh_3)\}_2$ (**10-Ph**)

A solution of $Au(C\equiv CC\equiv CH)(PPh_3)$ (200 mg, 0.39 mmol) and $Hg(OAc)_2$ (62 mg, 0.19 mmol) in thf (15 mL) was refluxed for 1 h. After allowing to cool to r.t., a grey/white precipitate had formed which was collected and washed with H_2O , EtOH, MeOH and Et_2O and air-dried to give $Hg\{C\equiv CC\equiv CAu(PPh_3)\}_2$ (**10-Ph**) (114 mg, 49%). Anal. Found: C, 43.61; H, 2.27%. Calc. for $C_{44}H_{30}Au_2Hg_2P_2$: C, 43.49; H, 2.49; M , 967. IR (nujol): $\nu(C\equiv C)$ 2100w, 2014w cm^{-1} . 1H NMR: δ 7.34–7.52 (m, Ph). ^{13}C NMR δ 128.99–134.46 (m, Ph). ^{31}P NMR: δ 42.68 (s).

4.3.12. $Hg\{C\equiv CC\equiv CAu[P(tol)_3]\}_2$ (**10-tol**)

A solution of **1** (200 mg, 0.36 mmol) and $Hg(OAc)_2$ (57 mg, 0.18 mmol) in thf (15 mL) was warmed to 45 °C and stirred for 2 h. Filtration and addition of hexane (150 mL) to the filtrate produced a milky-white precipitate which was collected and washed with Et_2O (2×10 mL) and n -pentane (20 mL) and air-dried to give $Hg\{C\equiv CC\equiv CAu[P(tol)_3]\}_2$ (**10-tol**) (126 mg, 54%). Anal. Found: C, 46.35; H, 3.35%. Calc. for $C_{50}H_{42}Au_2HgP_2$: C, 46.22; H, 3.26; M , 1299. IR (nujol): $\nu(C\equiv C)$ 2166w, 2052w cm^{-1} .

1H NMR: δ 2.35 (s, 18H, Me), 7.18–7.39 (m, 24H, tol). ^{13}C NMR: δ 21.43 (s, Me), 72.52, 88.15 (d, $^3J_{PC} = 29$ Hz), 102.52, 126.80–141.70 (m, tol). ^{31}P NMR: δ 40.62 [s, $P(tol)_3$].

4.3.13. $\{[(tol)_3P]Au\}C\equiv CC\equiv C\{Cu(triphos)\}$ (**11**)

To a solution of **1** (100 mg, 0.18 mmol) in thf (30 mL) at -100 °C was added $nBuLi$ (73 μ L, 0.18 mmol of a 2.5 M solution in hexane). Stirring was continued for 15 min. $CuCl(triphos)$ (123 mg, 0.17 mmol) was added and the yellow solution turned into a cream-coloured suspension which on allowing to warm to r.t. slowly cleared to give a yellow solution. After stirring for 3.5 h at r.t. the solvent was removed. The residue was extracted with CH_2Cl_2 (min) and then filtered into cold hexane. A cream-white precipitate was collected and washed with Et_2O (2×5 mL) and n -pentane (2×5 mL) and air-dried to give $\{[(tol)_3P]Au\}C\equiv CC\equiv C\{Cu(triphos)\}$ (**11**) (130 mg, 62%). Anal. Found: C, 63.62; H, 5.07%. Calc. for $C_{66}H_{60}AuP_4Cu$: C, 64.05; H, 4.89; M , 1238. IR (nujol): $\nu(C\equiv C)$ 2158m, 2127w cm^{-1} . 1H NMR: δ 1.44 (s, 3H, CH_3), 2.28 (s, 6H, CH_2), 2.36 (s, 9H, Me), 6.82–7.46 (m, 42H, Ph, tol). ^{13}C NMR: δ 21.43 (s, Me), 36.47 (m, $C-CH_3$), 37.53 (s, $C-CH_3$), 39.93 (m, $P-CH_2$), 125.27–142.31 (m, Ph, tol). ^{31}P NMR: δ -25.08 (triphos), 45.20 [s, $P(tol)_3$].

4.4. Structure determinations

Full spheres of diffraction data were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after

Table 2
Crystal data and refinement detail

Complex	1	2^a	3	4	9
Formula	$C_{25}H_{22}AuP$	$C_{26.67}H_{28.28}AuI_{0.19}PSi_{0.81}$	$C_{32}H_{24}AuFeP$	$C_{46}H_{42}Au_2P_2$	$C_{64}H_{62}Au_3IP_4Si_2$
MW	550.4	623.6	692.3	1050.7	1729.1
Crystal system	Hexagonal	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P6_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	18.454(1)	12.454(2)	9.715(2)	19.691(2)	14.320(1)
b (Å)		11.623(2)	10.442(3)	11.507(1)	15.198(1)
c (Å)	12.4035(7)	18.781(3)	12.742(3)	19.286(2)	17.330(1)
α (°)			99.732(3)		77.276(2)
β (°)		103.404(4)	102.120(3)	115.219(3)	67.048(2)
γ (°)			91.681(3)		64.328(2)
V (Å ³)	3658	2645	1243	3953	3124
ρ_{calc}	1.49 ₉	1.56 ₆	1.85 ₀	1.76 ₅	1.83 ₈
Z	6	4	2	4	2
$2\theta_{max}$ (°)	75	75	55	60	65
μ (Mo $K\alpha$) (mm^{-1})	6.1	5.9	6.6	7.5	7.7
$T_{min/max}$	0.70	0.60	0.65	0.69	0.66
Crystal dimensions (mm^3)	$0.35 \times 0.08 \times 0.07$	$0.48 \times 0.07 \times 0.05$	$0.18 \times 0.14 \times 0.12$	$0.07 \times 0.05 \times 0.03$	$0.60 \times 0.07 \times 0.05$
N_{tot}	76293	54606	10698	55061	64271
N (R_{int})	6486 (0.068)	13925 (0.063)	5589 (0.038)	11506 (0.065)	22906 (0.069)
N_o	3353	7978	4819	7933	14069
R	0.043	0.037	0.046	0.032	0.050
R_w (n_w)	0.047(8)	0.033(2)	0.058(9)	0.031(2)	0.053(6)

^a The material modelled as diynyl co-crystallised with iodide, both components resolvable and refinable with occupancies 0.813(2) and complement.

“empirical”/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full-matrix least-squares refinements. All data were measured using monochromatic Mo K α radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})_H being refined. Conventional residuals R, R_w on $|F|$ are quoted [weights: $(\sigma^2(F) + 0.000n_w F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL-3.7 program system [26]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 2.

5. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 272500–272504. 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>).

Acknowledgements

We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for providing the mass spectra and the ARC for support of this work.

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