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# Interpenetrating digold(I) diacetylide macrocycles

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The cyclic dialkynyldigold(I) complexes [1,2-$C_2H_4$(O-3-$C_6H_4OCH_2CCAu$)$_2$(μ-LL)] were prepared by reaction under basic conditions of the dialkyne 1,2-$C_2H_4$(O-3-$C_6H_4OCH_2CCH$)$_2$ with [AuCl($SMe_2$)] and the corresponding diphosphine ligands LL = $Ph_2P(CH_2)_nPPh_2$ ($n$ = 1–6), *trans*-$Ph_2PCH{=}CHPPh_2$ and $Ph_2PC{\equiv}CPPh_2$. The new organometallic macrocycles have ring sizes ranging from 23 to 28 atoms, and the complexes with LL = $Ph_2P(CH_2)_4PPh_2$ and *trans*-$Ph_2PCH{=}CHPPh_2$ have been structurally characterized. In both cases, the digold(I) macrocycles assemble into dimers in the solid state through Au ··· Au aurophilic bonding, with a phenyl group of each macrocycle occupying the cavity of the other. However, this extensive interpenetration occurs without the catenation observed in some similar complexes. The complexes give room temperature emissions above 400 nm in solution and the solid state, and a red shift of approximately 50 nm between emission maxima in the solution and the solid state spectra is suggested to be an indication of the strong interpenetration in the solid state.

## Introduction

The construction of macrocyclic complexes that incorporate large cavities is a rapidly developing area of research, since these compounds have potential for useful host–guest interactions and can form mechanically bonded supermolecules, such as rotaxanes and catenanes.[1] In particular, macrocycles containing metal–acetylide linkages have shown promise in the construction of electronic or optical devices,[2] or as luminescent chemical sensors.[3] Since polynuclear alkynylgold(I) complexes exhibit luminescent behavior,[4] they have been used as pendant groups to an attached macrocycle or within the macrocycle in sensors for the selective recognition of guest molecules.[5] The chromophore units respond with changing emission intensity and/or wavelength upon coordination of guest analytes. In addition, the linear two-coordinate geometry of gold(I) is ideal for forming molecules containing cavities,[6] and the common presence of secondary Au ··· Au (aurophilic) bonds, having strengths of 5–11 kcal mol$^{-1}$ and distances from 2.75–3.60 Å, can promote supramolecular association of several kinds.

Some known digold(I) macrocyclic complexes containing diacetylide and diphosphine bridging ligands are illustrated in Chart 1.[7] Using the digold(I) diacetylides derived from *o*-, *m*-, and *p*-bis(propargyloxy)benzene and the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n$ = 1–6), macrocyclic complexes **A** containing 15–22 membered rings were prepared,[7a] but the relatively small cavity size did not allow strong intermolecular association. With rigidly linear or angular diacetylides, tetragold(I) complexes **B** (Ar = 1,4-$C_6H_4$ or 4,4′-$C_6H_4C_6H_4$), containing larger 26- or 34-membered rings, or **C**, containing larger 24-membered rings were obtained, but the stretched rings were long and too narrow to allow intertwining.[7b,c] However, the ring complexes such as **D**, with a hinge group X = O, S, $CH_2$, $CMe_2$, or $C_6H_{10}$ (cyclohexylidene) and diphosphine ligands, $Ph_2P(CH_2)_nPPh_2$, chosen to give 23–27 membered rings by varying $n$, gave more complex behavior. If X = O or S, the compounds gave simple rings in all cases studied but, when X = $CH_2$ or $CMe_2$ and $n$ = 3–6, the compounds self-assembled to give [2]catenanes such as **E** ($n$ = 4) and, when X = $C_6H_{10}$ and $n$ = 4, even a doubly braided [2]catenane was obtained.[7d,e] This raised the question of what would happen if a multiple atom bridge X was used, thus giving both larger ring size and, if X is a flexible chain, greater ring distortions. Since it is known that secondary C–H ··· O interactions can aid in the assembly of supramolecular entities having the ability to selectively bind guest molecules,[8] it was decided to explore the effect of incorporating ether spacer units X in rings of type **D**. This paper reports the first example of such a series, incorporating an ethylene glycol spacer unit, X = $OCH_2CH_2O$. Macrocyclic complexes containing bridging diacetylide and diphosphine ligands with ring sizes of 23–28 atoms have been prepared, and two of these are shown to pack as face to face centrosymmetric pairs, with marked interpenetration and which are joined through Au ··· Au bonding. Previously, linear chains of rings linked side by side

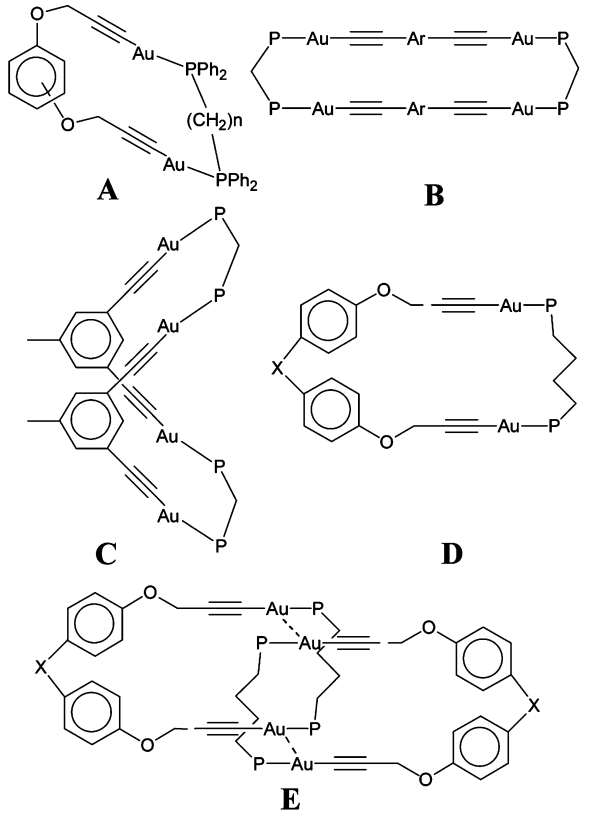


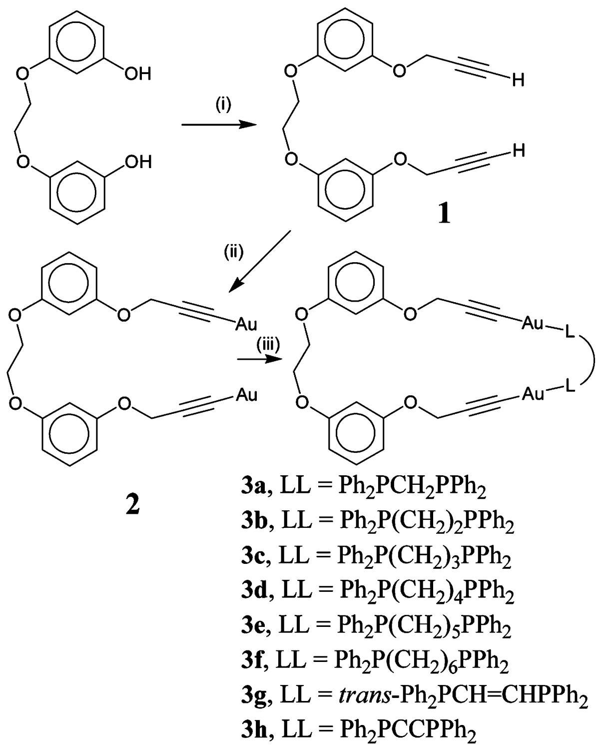
**Chart 1** Macrocyclic dialkynyl(diphosphine)gold(I) complexes.

through Au ··· Au bonding, and cationic gold rings linked through bridging dicyanoaurate(I) anions, were reported.[7] It is also important to note that gold(I) is often a labile metal center and that the facile exchange of gold-phosphine groups often allows the synthesis of interconnected complexes.[9]

## Results and discussion

### Synthesis and spectra of the complexes

The ligand 1,2-$C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CH)_2$, **1**, was prepared from 3,3-(ethylenedioxy)diphenol and 3-bromopropyne in the presence of base, according to Scheme 1. The complex was isolated as a pale yellow solid and characterized using NMR, IR, and MS. In the $^1H$ NMR spectrum, the alkyne proton appeared as a triplet at $\delta$ = 2.39, due to coupling to the $OCH_2CC$ protons at 4.67 ppm, with $^4J(HH)$ = 2 Hz. In the IR, an intense band at 2116 $cm^{-1}$ was assigned to $\nu(C{\equiv}C)$ while two peaks at 3289 and 3267 $cm^{-1}$ were assigned to $\nu(C{\equiv}C\text{–}H)$.



**Scheme 1** Synthesis of the macrocyclic complexes. Reagents: (i) $BrCH_2CCH$, $K_2CO_3$; (ii) $[AuCl(SMe_2)]$, NaOAc; (iii) LL.

The dialkyne, **1**, was readily converted to the oligomeric alkynylgold(I) complex, $[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2]_n$, **2**, by reaction with $[AuCl(SMe_2)]$ in the presence of base, as shown in Scheme 1. Complex **2** was isolated as an insoluble, deep yellow solid. In the IR spectrum, the C≡C stretching frequency (2000 $cm^{-1}$) was reduced by 116 $cm^{-1}$ compared to **1**, presumably because the gold atoms form a coordination polymer through both σ and π-bonding to the alkynyl groups.[10] The insoluble polymeric alkynylgold(I) complex was converted to the soluble macrocyclic complexes $[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4\text{-}OCH_2C{\equiv}CAu)_2(\mu\text{-LL})]$, **3**, by reaction with the corresponding diphosphine ligand, LL, as illustrated in Scheme 1. The complexes **3** were isolated as white powders, that were soluble in dichloromethane or nitrobenzene, and characterized by their IR and NMR spectra. For example, in the IR spectrum, complex **3b** gave a single weak band due to $\nu(C{\equiv}C)$ at 2130 $cm^{-1}$. In the $^{31}P$ NMR spectrum, a single resonance was observed at $\delta$ = 40.04, while in the $^1H$ NMR spectrum the $OCH_2CC$ and $OCH_2CH_2O$ resonances appeared as singlets at $\delta$ = 4.79 and 4.32, respectively.

**Table 1** Selected bond parameters (Å,°) for complex **3g**

| | | | |
|---|---|---|---|
| Au(1)–C(71) | 2.020(6) | Au(2)–C(8) | 2.026(6) |
| Au(1)–P(1) | 2.273(1) | Au(2)–P(2) | 2.274(1) |
| C(7)–C(8) | 1.170(8) | C(71)–C(70) | 1.166(9) |
| Au(1)–Au(2) | 3.0161(3) | | |
| C(71)–Au(1)–P(1) | 175.9(2) | C(8)–Au(2)–P(2) | 174.0(2) |
| C(71)–Au(1)–Au(2) | 85.7(2) | C(8)–Au(2)–Au(1) | 91.8(2) |
| P(1)–Au(1)–Au(2) | 96.93(4) | P(2)–Au(2)–Au(1) | 93.87(4) |
| C(70)–C(71)–Au(1) | 175.6(6) | C(7)–C(8)–Au(2) | 169.8(6) |
| C(10)–P(1)–Au(1) | 115.7(2) | C(9)–P(2)–Au(2) | 111.4(2) |

### The structures of complexes 3d and 3g

The structures of complexes **3d** and **3g** (Scheme 1) were determined crystallographically. The structure of **3g**, LL = *trans*-$Ph_2CH{=}CHPPh_2$, is shown in Fig. 1 and selected distances and angles are in Table 1. Fig. 1a shows that the complex exists as a 24-membered ring containing a diacetylide and a diphosphine ligand bridging between two gold(I) centers, and that these rings are closely associated into pairs through inter-ring Au ··· Au bonding. There is a center of symmetry located in the center of the resulting tetragold(I) aggregate, but the two rings are not catenated and so would be expected to exist separately in solution. The two rings in **3g** cross each other with corresponding dihedral angles C–Au ··· Au–C = 57° and P–Au ··· Au–P = 52°. The distances Au–C = 2.020(6) Å and Au–P = 2.273(1) Å are typical for alkynyl(phosphine)-gold(I) complexes.[4–7] The independent angles P–Au–C = 175.9(2) and 174.0(2)° are somewhat distorted from linearity,

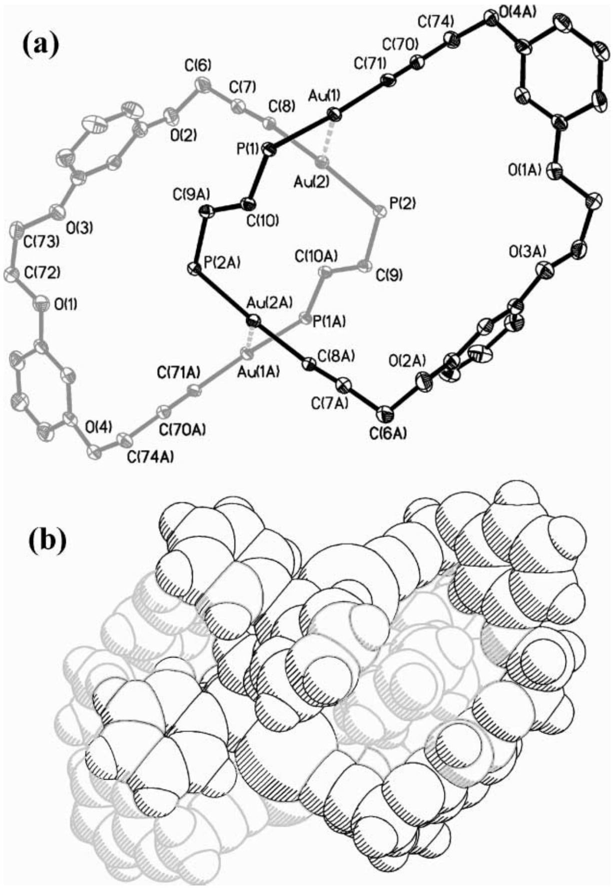


**Fig. 1** The structure of complex **3g**, $[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}trans\text{-}Ph_2PCH{=}CHPPh_2)]$, showing the association of two rings through Au ··· Au bonding: (a) the macrocyclic ring structure and Au ··· Au bonds (phenyl groups and hydrogen atoms are omitted for clarity); and (b) a space-filling model with all atoms included, illustrating the penetration of a phenyl group through each cavity. Symmetry operations for equivalent atoms: $-x + 2, -y + 1, -z + 1$.

**Table 2** Selected bond parameters (Å,°) for complex **3d**

| | | | |
|---|---|---|---|
| Au(1)–C(1) | 2.05(2) | Au(2)–C(20) | 2.06(3) |
| Au(1)–P(1) | 2.260(5) | Au(2)–P(2) | 2.281(6) |
| C(1)–C(2) | 1.16(3) | C(19)–C(20) | 1.01(3) |
| Au(1)–Au(2) | 3.074(1) | | |
| C(1)–Au(1)–P(1) | 172.9(5) | C(20)–Au(2)–P(2) | 175.9(5) |
| C(1)–Au(1)–Au(2) | 84.3(5) | C(20)–Au(2)–Au(1) | 87.5(5) |
| P(1)–Au(1)–Au(2) | 102.7(1) | P(2)–Au(2)–Au(1) | 96.5(1) |
| C(2)–C(1)–Au(1) | 174(2) | C(19)–C(20)–Au(2) | 164(2) |
| C(61)–P(1)–Au(1) | 111.1(6) | C(65)–P(2)–Au(2) | 115.0(7) |

and the distortion is in the sense that allows a closer Au ··· Au contact. The intermolecular Au ··· Au distance of 3.0161(3) Å indicates a strong aurophilic attraction, optimised by the crossed alignment of the associated C–Au–P groups,[11] while the intramolecular, transannular Au ··· Au distance of 6.303 Å is much too long for bonding.

Each ring in **3g** contains a large cavity, with longest transannular dimensions of 11.12 Å between the opposite $OCH_2C≡C$ atoms, and 9.41 Å between the $OCH_2CH_2$ and $Ph_2PCH=$ atoms. The angle between the planes of the two aryl groups of each $C_6H_4OCH_2CH_2OC_6H_4$ unit is 92°, with one ring lying roughly in the plane and the other roughly perpendicular to the macrocycle. The two rings are twisted but they are stacked roughly parallel. A remarkable feature of the structure is that a phenyl-phosphine group of one ring extends fully through the cavity of the other ring, as depicted in Fig. 1b. There are several secondary inter-ring aryl ··· aryl contacts which, together with the Au ··· Au bonding, provides strong binding of the two rings (Fig. 1b). Clearly the net inter-ring attractions are stronger in this observed structural form compared to the catenated structure analogous to **E** (Chart 1).

The structure of **3d**, LL = $Ph_2P(CH_2)_4PPh_2$, is shown in Fig. 2 with selected bond distances and angles in Table 2. The data were of poor quality, with disordered dichloromethane solvent molecules in the lattice, but the important structural features of the complex are clearly determined. The structure is similar to that of **3g** (Fig. 1). There is a 26-membered ring containing a diacetylide a diphosphine and two gold(I) centers, and two such rings are tightly associated but not catenated. The two rings are related by a center of symmetry, and the intermolecular distance Au ··· Au = 3.074(1) Å (Fig. 1a), with associated torsion angles C–Au ··· Au–C = 50.2° and P–Au ··· Au–P = 49.7°, similar to the values in **3g** and well-suited for formation of a strong aurophilic attraction. The transannular Au ··· Au distance is 7.890 Å, considerably longer than in **3g** as a result of the longer spacer group of the diphosphine, and this gives rise to a larger, more circular, cavity in **3d** compared to **3g**. The conformation of the flexible diacetylide ligand is different in the two complexes (Figs. 1a and 2a) to accommodate the different transannular gold–gold distances. Other comparative transannular dimensions for **3d** are 11.51 Å between the opposite $OCH_2C≡C$ atoms (11.12 Å in **3g**), and 8.09 Å between the $OCH_2CH_2$ and $Ph_2PC$ atoms (9.41 Å in **3g**). The diphosphine ligands in both **3d** and **3g** both tend to adopt the *anti* conformation,[12,13] but this is not compatible with ring formation. Still, neither adopts the *syn* conformation, but intermediate forms are preferred with dihedral angles Au(1)–P(1)–P(2a)–Au(2a) = 58° and 71° in **3d** and **3g**, respectively.

The similarity of the structures of **3d** and **3g** extends to the nature of the self-recognition, with a phenylphosphorus group of one ring completely enclosed in the cavity of the other, as shown in Fig. 2b. The larger cavity of **3d** allows deeper penetration than in **3g** (compare Figs. 2b and 1b). The ligand bis(diphenylphosphino)butane has previously been shown to be ideal for formation of [2]catenanes of type **E** (Chart 1, 25-membered ring when $n = 4$),[7d] and we had anticipated that **3d** might form a similar structure. However, this was not the case and it is clear that the combination of strong aurophilic attractions, combined with several weaker aryl–aryl attractions, favors the side-by-side association found for **3d**.

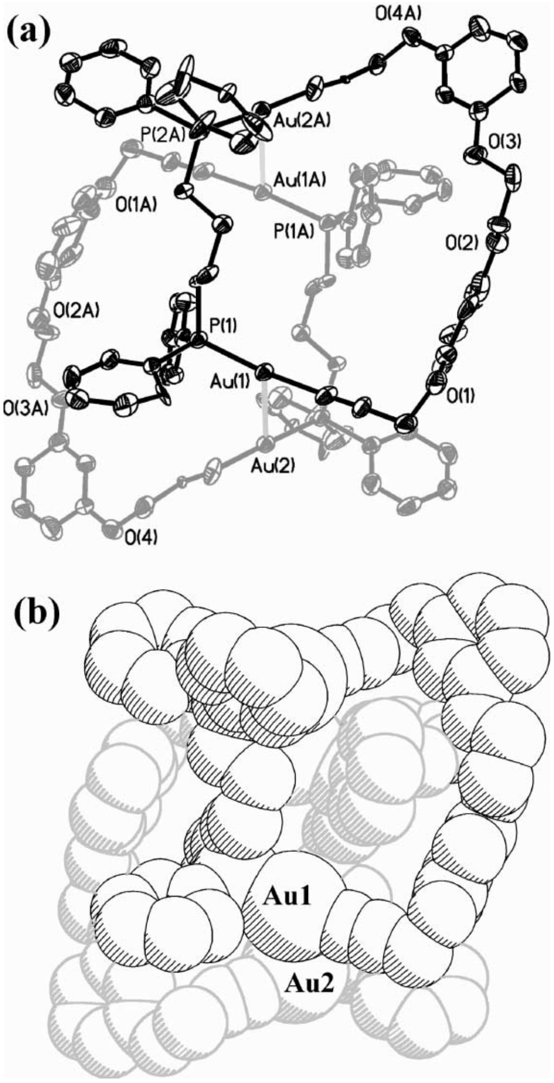


**Fig. 2** The molecular structure of complex **3d**, $[1,2-C_2H_4(O-3-C_6H_4OCH_2C≡CAu)_2(\mu-Ph_2P(CH_2)_4PPh_2)]_2$, with hydrogen atoms omitted for clarity: (a) the ring structure and intermolecular aurophilic bonding, and (b) a space-filling model showing the phenyl group of one molecule penetrating the cavity of the other. Symmetry operations for equivalent atoms: $-x + 1, -y, -z + 1$.

## Luminescence spectra

Luminescence spectra were recorded at room temperature for the gold(I) complexes **3**, in both the solid state and in dichloromethane solution, and the results are summarized in Table 3.

Based on assignments for other alkynyl(phosphine)gold(I) complexes, the emission is likely to occur from a triplet excited state formed primarily by σ(AuC)/Au(5d)–π*/Au(6p) excitation, and a significant red shift is expected when secondary Au ··· Au bonding is present and perturbs the energy levels.[12] A single broad emission band was observed in each case for complexes **3**, with no resolved fine structure. The emission maxima for **3a** and **3b** are similar in the solution and solid state spectra (no more than 6 nm difference, Table 3), suggesting similar structures in the two phases. For the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$, with $n = 1$ (**3a**) or 2 (**3b**), the bite distance is small enough to allow transannular Au ··· Au bonding and this leads to formation of a narrow cavity in the macrocycle. It is likely that the close association of pairs of rings in the solid state, proved crystallographically for **3d** and **3g**, is not present in the solid state structures of **3a** and **3b**. For the other complexes,

**Table 3** Luminescence data for the complexes

| Complex | Medium | Emission max/nm |
|---|---|---|
| **3a** | Solid | 470 |
| | $CH_2Cl_2$ | 464 |
| **3b** | Solid | 450 |
| | $CH_2Cl_2$ | 455 |
| **3c** | Solid | 468 |
| | $CH_2Cl_2$ | 410 |
| **3d** | Solid | 486 |
| | $CH_2Cl_2$ | 433 |
| **3e** | Solid | 467 |
| | $CH_2Cl_2$ | 426 |
| **3f** | Solid | 469 |
| | $CH_2Cl_2$ | 412 |
| **3g** | Solid | 467 |
| | $CH_2Cl_2$ | 430 |
| **3h** | Solid | 468 |
| | $CH_2Cl_2$ | 418 |

$\lambda$(excitation) was 350 nm in each case.

**3c**–**3h**, the diphosphines do not allow close enough approach of the gold atoms for formation of transannular Au ··· Au bonding, and so the emission in solution occurs at higher energy (410–430 nm range) compared to **3a** (464 nm) or **3b** (455 nm), and similar to values obtained for other alkynyl(phosphine)-gold(I) complexes which do not have Au ··· Au bonding.[4,5,7] In the solid state, there was a strong red shift in the emission maximum for each of complexes **3c**–**3h**, with band maxima in the range 450–486 nm (shift of 41–58 nm), strongly suggesting that intermolecular association occurs in each case. The data for the structurally characterized complexes **3d** (486 nm in solid, 433 nm in $CH_2Cl_2$ solution) and **3g** (467 nm in solid, 430 nm in $CH_2Cl_2$ solution) are typical, and so it is proposed that all complexes **3c**–**3h** self-associate in the solid state in the same way.

## Experimental

NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer, with $^1H$ NMR chemical shifts reported relative to TMS and $^{31}P$ chemical shifts reported relative to an 85% $H_3PO_4$ external standard. IR spectra were recorded as Nujol mulls using a Perkin-Elmer 2000 FTIR. Emission spectra were recorded at room temperature using a Fluorolog-3 spectrofluorimeter. For recording the emission and excitation spectra, solutions were placed in quartz cuvettes, while solid samples were ground finely, in some cases with added KBr. A 1 nm slit width was used for the solid samples and a 3 nm slit width for the solutions. **CAUTION!** Gold acetylides are potentially shock sensitive and should be handled in small quantities using protective equipment.

### Synthesis

**$1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CH)_2$, 1.** A solution of $1,2\text{-}C_2H_4\text{-}(O\text{-}3\text{-}C_6H_4OH)_2$ (2.50 g, 10.15 mmol), $BrCH_2CCH$ (2.42 g, 20.30 mmol) and $K_2CO_3$ (4.21 g, 30.45 mmol) in acetone (100 mL) was heated under reflux for five days. The reaction mixture was filtered to remove KBr, and the solvent was removed under vacuum to give the product as a yellow oil. This was extracted with ether, and the solution was washed with aqueous $NaHCO_3$, dried with $MgSO_4$, filtered, and the solvent removed under vacuum. Trituration ofthe product with pentane afforded a yellow solid (Yield 70%). NMR in $CDCl_3$: $\delta(^1H)$ 6.20–7.23 [m, 8H; Ar], 4.67 [d, $^4J$(HH) = 2 Hz, 4H, $CH_2CC$], 4.30 [s, 4H, $OCH_2CH_2O$], 2.39 [t, $^4J$(HH) = 2 Hz, 2H, CCH); $\delta(^{13}C)$ 102.10, 107.41, 107.69, 129.90, 158,.67, 159.69 [aryl]; 78.44 [*C*CH]; 75.53 [C*C*H]; 55.77 [*C*$H_2$CC]; 66.41 [$OCH_2$-$CH_2O$]. IR (Nujol): $\nu(C{\equiv}C)$ 2116, $\nu(C{\equiv}CH)$ 3289 and 3267 $cm^{-1}$; EI–MS: *m*/*z*: 322.120, calc. for $C_{20}H_{18}O_4$: 322.120.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2]_n$, 2.** A solution of **1** (0.109 g, 0.340 mmol) and sodium acetate (0.140 g, 1.698 mmol) in THF (10 mL)–MeOH (10 mL) was added to a suspension of $[AuCl(SMe_2)]$ (0.200 g, 0.679 mmol) in 1 : 1 THF–MeOH (20 mL), and the resultant mixture was stirred for 1 h at 0 °C. The mixture was filtered, and the yellow solid was washed with THF, MeOH and pentane (Yield 56%). The solid was insoluble in common organic solvents, and was light sensitive, so could not be purified and was characterized by its reactions described below. IR (Nujol): $\nu(C{\equiv}C)$ 2000 $cm^{-1}$. Anal. Calc. for $C_{20}H_{16}O_4Au_2{\cdot}2NaCl$: C, 28.9; H, 1.9. Found: C, 29.0; H, 1.9%.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dppm})]$, 3a.** A solution of dppm (0.062 g, 0.16 mmol) in $CH_2Cl_2$ (10 mL) was added to a suspension of **2** (0.116 g, 0.14 mmol) in $CH_2Cl_2$ (10 mL). The mixture was stirred for 3 h, treated with decolorizing charcoal (100 mg), stirred for 15 min, filtered, and the product was precipitated from the solution by addition of pentane. A colorless solid was collected by filtration, washed with ether, and dried (Yield 61%). NMR ($CD_2Cl_2$): $\delta(^1H)$ 7.3–7.6 [m, 22H; Ph and *o*-HAr], 7.29 [br, 2H, H–$C_5$Ar], 6.82 [s, 2H, H–$C_2$Ar], 6.55 [br, 2H, H–$C_{4\text{ or }6}$Ar], 4.69 [s, 4H; $CH_2CC$], 4.33 [s, 4H; $OCH_2$-$CH_2O$], 3.62 [s, 2H, dppm]; $\delta(^{31}P)$ 31.91 [s]. IR [Nujol): $\nu(C{\equiv}C)$ 2132 $cm^{-1}$. Anal. Calc. for $C_{45}H_{38}O_4P_2Au_2{\cdot}0.5CH_2Cl_2$: C, 47.9; H, 3.4. Found: C, 47.9; H, 3.2%. Similarly prepared were:

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dppe})]$, 3b.** Yield 35%. NMR ($CD_2Cl_2$): $\delta(^1H)$ 7.4–7.7 [m, 22H; Ph and *o*-HAr]; 7.21 [t, $^3J$(HH) = 8 Hz, 2H, H–$C_5$Ar], 6.86 [s, 2H, H–$C_2$Ar], 6.58 [d, $^3J$(HH) = 8 Hz, 2H, H–$C_{4\text{ or }6}$Ar], 4.79 [s, 4H, $CH_2CC$], 4.32 [s, 4H, $OCH_2CH_2O$], 2.62 [s, 4H, dppe]; $\delta(^{31}P)$ 40.04 [s]. IR (Nujol): $\nu(C{\equiv}C)$ 2130 $cm^{-1}$. Anal. Calc. for $C_{46}H_{40}O_4P_2Au_2$: C, 49.6; H, 3.6. Found: C, 50.0; H, 3.1%.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dppp})]$, 3c.** Yield 43%. NMR($CD_2Cl_2$): $\delta(^1H)$ 7.2–7.7 [m, 22H; Ph and *o*-HAr], 7.17 [t, $^3J$(HH) = 8 Hz, 2H, H–$C_5$Ar], 6.60 [m, 6H, Ar], 4.79 [s, 4H, $CH_2CC$], 4.29 [s, 4H, $OCH_2CH_2O$], 2.79 [m, 4H, dppp], 1.87 [m, 2H, dppp]; $\delta(^{31}P)$ 33.73 [s]. IR (Nujol): $\nu(C{\equiv}C)$ 2132 $cm^{-1}$. Anal. Calc. for $C_{47}H_{42}O_4P_2Au_2{\cdot}CH_2Cl_2$: C, 47.6; H, 3.7. Found: C, 48.0; H, 3.8%.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dppb})]$, 3d.** Yield 33%. NMR (DMSO): $\delta(^1H)$ 7.4–7.7 [m, 22H; Ph and *o*-HAr], 7.16 [t, $^3J$(HH) = 8 Hz, 2H, H–$C_5$Ar], 6.73 [s, 2H, H–$C_2$Ar], 6.55 [d, $^3J$(HH) = 8 Hz, 2H, H–$C_{4\text{ or }6}$Ar], 4.72 [s, 4H, $CH_2CC$], 4.25 [s, 4H, $OCH_2CH_2O$], 2.64 [m, 4H, dppb], 1.52 [m, 4H, dppb]; $\delta(^{31}P)$ 37.20 [s]. IR (Nujol): $\nu(C{\equiv}C)$ 2131 $cm^{-1}$. Anal. Calc. for $C_{48}H_{44}O_4P_2Au_2$: C, 50.5; H, 3.9. Found: C, 50.9; H, 4.0%.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dpppe})]$, 3e.** Yield 31%. NMR ($CD_2Cl_2$): $\delta(^1H)$ 7.4–7.6 [m, 22H; Ph and *o*-HAr], 7.17 [t, $^3J$(HH) = 8 Hz, 2H, H–$C_5$Ar], 6.74 [s, 2H, H–$C_2$Ar], 6.55 [d, $^3J$(HH) = 8 Hz, 2H, H–$C_{4\text{ or }6}$Ar], 4.75 [s, 4H, $CH_2CC$], 4.33 [s, 4H, $OCH_2CH_2O$], 2.60 [m, 4H, dpppe], 2.41 [m, 4H, dpppe], 1.64 [m, 2H, dpppe]; $\delta(^{31}P)$ 37.76 [s]. IR (Nujol): $\nu(C{\equiv}C)$ 2132 $cm^{-1}$. Anal. Calc. for $C_{49}H_{46}O_4P_2Au_2{\cdot}CH_2Cl_2$: C, 48.4; H, 3.9. Found: C, 48.6; H, 4.0%.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dpph})]$, 3f.** Yield 53%. NMR ($CD_2Cl_2$): $\delta(^1H)$ 7.3–7.7 [m, 22H; Ph and *o*-HAr], 7.20 [t, $^3J$(HH) = 8 Hz, 2H, H–$C_5$Ar], 6.70 [s, 2H, H–$C_2$Ar], 6.57 [d, $^3J$(HH) = 8 Hz, 2H, H–$C_{4\text{ or }6}$Ar], 4.75 [s br, 4H, $CH_2CC$], 4.30 [s, 4H; $OCH_2CH_2O$], 2.46 [s br, 4H, dpph], 1.62 [s br, 4H, dpph], 1.45 [s, 4H, dpph]; $\delta(^{31}P)$ 32.53 [s]. IR (Nujol): $\nu(C{\equiv}C)$ 2132 $cm^{-1}$. Anal. Calc. for $C_{50}H_{48}O_4P_2Au_2{\cdot}0.5CH_2Cl_2$: C, 50.1; H, 4.1. Found: C, 49.5; H, 4.3%.

**$[1,2\text{-}C_2H_4(O\text{-}3\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-dppee})]$, 3g.** Yield 62%. NMR ($CD_2Cl_2$): $\delta(^1H)$ 7.45–7.60 [m, 22H; Ph and *o*-HAr],

**Table 4** Crystal data and structure refinement

| | **3d** | **3g** |
|---|---|---|
| Formula | $C_{49.5}H_{49}Au_2ClO_{4.5}P_2$ | $C_{46}H_{38}Au_2O_4P_2$ |
| FW | 1207.21 | 1110.64 |
| $T$/K | 223(2) | 200(2) |
| $\lambda$/Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 10.6544(6) | 14.7711(5) |
| $b$/Å | 27.827(1) | 15.2895(5) |
| $c$/Å | 16.5665(9) | 18.3486(8) |
| $\beta$/° | 98.377(1) | 107.100(2) |
| Volume/Å$^3$, $Z$ | 4859.3(5), 4 | 3960.7(3), 4 |
| $D$(calc)/Mg m$^{-3}$ | 1.65 | 1.86 |
| Absorption coefficient/ mm$^{-1}$ | 6.194 | 7.524 |
| $F$(000) | 2348 | 2136 |
| Reflections/ independent reflections | 25358/8550 | 35062/9050 |
| Absorption correction | Integration | SADABS |
| $R1/wR2$ [$I > 2\sigma(I)$] | 0.1061/0.2817 | 0.0416/0.0993 |

7.15 [t, $^3J$(HH) = 8.0 Hz, 2H, H–C$_5$Ar], 6.98 [t, $J$(HP) = 18.1 Hz, 2H, dppee], 6.74 [s, 2H, H–C$_2$Ar], 6.53 [d, $^3J$(HH) = 7.5 Hz, 2H, H–C$_{4\text{ or }6}$Ar], 4.78 [s, 4H; CH$_2$CC], 4.31 [s, 4H; OCH$_2$CH$_2$O]; $\delta(^{31}$P) = 39.05 [s]. IR (Nujol): $\nu$(C≡C) 2132 cm$^{-1}$. Anal. Calc. for $C_{46}H_{38}O_4P_2Au_2$: C, 49.7; H, 3.4. Found: C, 49.5; H, 3.3%.

**[1,2-C$_2$H$_4$(O-3-C$_6$H$_4$OCH$_2$C≡CAu)$_2$(μ-dppa)], 3h.** Yield 35%. NMR (CD$_2$Cl$_2$): $\delta(^1$H) 7.4–7.7 [m, 22H; Ph and $o$-HAr], 7.18 [t, $^3J$(HH) = 8 Hz, 2H, H–C$_5$Ar], 6.79 [s, 2H, H–C$_2$Ar], 6.55 [d, $^3J$(HH) = 8 Hz, 2H, H–C$_{4\text{ or }6}$Ar], 4.81 [s, 4H, CH$_2$CC], 4.33 [s, 4H, OCH$_2$CH$_2$O]; $\delta(^{31}$P) 17.50 [s]. IR (Nujol): $\nu$(C≡C–Au) 2129, $\nu$(C≡CP) 2065 cm$^{-1}$. Anal. Calc. for $C_{46}H_{36}O_4P_2Au_2$: C, 49.8; H, 3.3. Found: C, 49.6; H, 3.1%.

### X-Ray data collection and structure determination

Crystals of **3g** were grown by slow diffusion of ether into a solution in dichloromethane at 4 °C. A tiny, colourless plate was mounted on a glass fibre. Data were collected at 200 K using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998) and no other absorption corrections were applied. The crystal data and refinement parameters are listed in Table 4.

The SHELXTL 5.1 program package was used to solve the structure by Patterson methods and refinement was by full-matrix least squares on $F^2$.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The largest residual electron density peak (2.383 e Å$^{-3}$) was associated with one of the gold atoms. The data for **3d**·0.5CH$_2$Cl$_2$·0.5H$_2$O were collected at −50 °C using a Siemens SMART 1K CCD diffractometer. The structure was solved using direct methods, completed by subsequent Fourier syntheses, and refined by full-matrix least-squares on $F^2$ using SHELXTL 5.10.[14] All atoms were refined anisotropically, except hydrogen atoms, which were treated as idealized contributions. Empirical absorption corrections were applied using SADABS.[15] No special constraints or restraints were applied in solving structure **3d**. The molecule was positioned on the inversion center in the monoclinic space group $P2_1/c$, and showed possible disorder, although this could not be refined successfully. There are large residuals, and the structure determination was only partly successful, but the connectivity is established.

CCDC reference numbers 181890 (**3g**) and 181891 (**3d**).

See http://www.rsc.org/suppdata/dt/b2/b201832b/ for crystallographic data in CIF or other electronic format.

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## References

1 (*a*) S. Leininger and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*b*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; (*c*) M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249.

2 *Comprehensive Supramolecular Chemistry*, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and K. S. Suslick, eds., Pergamon Press, Oxford, 1996.

3 M. H. Keefe, K. D. Benkstein and J. T. Hupp, *Coord. Chem. Rev.*, 2000, **205**, 201.

4 (*a*) V. W. W. Yam, K. K. W. Lo and M. C. Wong, *J. Organomet. Chem.*, 1999, **578**, 3; (*b*) M. J. Irwin, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1997, **16**, 3541; (*c*) C. M. Che, H. K. Yip, W. C. Lo and S. M. Peng, *Polyhedron*, 1994, **13**, 887; (*d*) C. M. Che, H. Y. Chao, V. M. Miskowski, Y. Li and K. K. Cheung, *J. Am. Chem. Soc.*, 2001, **123**, 4985.

5 (*a*) V. W. W. Yam, C. K. Li and C. L. Chan, *Angew. Chem., Int. Ed.*, 1998, **37**, 2856; (*b*) B. C. Tzeng, W. C. Lo, C. M. Che and S. M. Peng, *Chem. Commun.*, 1996, 181; (*c*) B. C. Tzeng, K. K. Cheung and C. M. Che, *Chem. Commun.*, 1996, 1681; (*d*) A. Burini, R. Bravi, J. P. Fackler Jr., R. Galassi, T. A. Grant, M. A. Omary, B. R. Pietroni and R. J. Staples, *Inorg. Chem.*, 2000, **39**, 3158; (*e*) W. H. Chan, T. C. W. Mak and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1998, 2275; (*f*) J. C. Vickery, M. M. Olmstead, E. Y. Fung and A. L. Balch, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1179; (*g*) E. Y. Fung, M. M. Olmstead, J. C. Vickery and A. L. Balch, *Coord. Chem. Rev.*, 1998, **171**, 151; (*h*) R. H. Uang, C. K. Chan, S. M. Peng and C. M. Che, *J. Chem. Soc., Chem. Commun.*, 1994, 2561.

6 (*a*) A. Grohmann and H. Schmidbaur, in *Comprehensive Organometallics II*, E. W. Abel, F. G. A. Stone and G. Wilkinson, eds., Elsevier, Oxford, 1995, vol. 3, pp. 1–56; (*b*) R. J. Puddephatt, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, eds., Pergamon Press, Oxford, 1987, vol. 5, pp. 861–923; (*c*) H. Schmidbaur, ed., *Gold: Progress in Chemistry, Biochemistry and Technology*, Wiley: Chichester, 1999.

7 (*a*) W. J. Hunks, M. A. MacDonald, M. C. Jennings and R. J. Puddephatt, *Organometallics*, 2000, **19**, 5063; (*b*) M. J. Irwin, L. M. Rendina, J. J. Vittal and R. J. Puddephatt, *Chem. Commun.*, 1996, 1281; (*c*) M. A. MacDonald and G. P. A. Yap, *Organometallics*, 2000, **19**, 2194; (*d*) C. P. McArdle, M. J. Irwin, M. C. Jennings and R. J. Puddephatt, *Angew. Chem., Int. Ed.*, 1999, **38**, 3376; (*e*) C. P. McArdle, J. J. Vittal and R. J. Puddephatt, *Angew. Chem., Int. Ed.*, 2000, **39**, 3819; (*f*) R. J. Puddephatt, *Chem. Commun.*, 1998, 1055; (*g*) C. P. McArdle, M. C. Jennings, J. J. Vittal and R. J. Puddephatt, *Chem. Eur. J.*, 2001, **7**, 3573; (*h*) R. J. Puddephatt, *Coord. Chem. Rev.*, 2001, **216–217**, 313.

8 (*a*) J. G. Hansen, N. Feeder, D. G. Hamilton, M. J. Gunter, J. Becher and J. K. M. Sanders, *Org. Lett.*, 2000, **2**, 449; (*b*) G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441; (*c*) M. J. Calhorda, *Chem. Commun.*, 2000, 801.

9 R. J. Cross and M. F. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 411.

10 D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1894.

11 (*a*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (*b*) S. S. Pathaneni and G. R. Desiraju, *J. Chem. Soc., Dalton Trans.*, 1993, 319; (*c*) P. Pyykkö, J. Li and N. Runeberg, *Chem. Phys. Lett.*, 1994, **218**, 133; (*d*) J. Li and P. Pyykkö, *Chem. Phys. Lett.*, 1992, **197**, 586.

12 (*a*) M. J. Irwin, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1997, **16**, 3541; (*b*) W. E. van Zyl, J. M. Lopez-de-Luzuriaga and J. P. Fackler Jr., *J. Mol. Struct.*, 2000, **516**, 99.

13 M. C. Brandys, M. C. Jennings and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 2000, 4601.

14 G. M. Sheldrick, SHELXTL 5.10 for Windows: Structure Determination Software Programs, Bruker Analytical X-Ray Systems, Inc., Madison, WI, 1997.

15 G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1998.