Macrocyclic Gold(I) Complexes with Bridging Diacetylide and Diphosphine Ligands

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Dedicated to Professor Hubert Schmidbaur, the undisputed champion of gold chemistry, on the occasion of his 70th birthday

The new dialkynyldigold(I) complexes $[Ar(OCH_2C{\equiv}CAu)_2]_n$ {Ar = 1,4-C_6H_4(CMe_2-4-C_6H_4)$_2$, 4,4'-$C_6H_4C_6H_4$ and 1,5-$C_{10}H_6$} react with diphosphines LL = $Ph_2P(CH_2)_nPPh_2$ (n = 1 to 6) and *trans*-$Ph_2PCH{=}CHPPh_2$ to give luminescent macrocyclic digold(I) or tetragold(I) complexes with bridging diphosphine and diacetylide ligands. The digold(I) complex [1,4-C_6H_4(CMe_2-4-$C_6H_4OCH_2C{\equiv}CAu)_2$($\mu$-LL)], with LL = *trans*-$Ph_2PCH{=}CHPPh_2$, forms a 28-membered ring, and the rings associate through aurophilic bonding in the solid state. In contrast, the tetragold(I) complex [4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CAu)_2$($\mu$-LL)], with LL = $Ph_2PCH_2PPh_2$, forms a more rigid 42-membered ring.

Key words: Gold, Macrocycle, Diacetylide, Diphosphine, Luminescence

Introduction

The construction of macrocyclic complexes with a sufficiently large cavity to accommodate guest molecules or to form interlocked structures such as catenanes and rotaxanes is of great interest in supramolecular chemistry [1]. Alkynylgold(I) complexes are useful in this field because they are easy to prepare, they have high thermal stability, and they exhibit useful emission or non-linear optical properties [2 – 7]. The simplest compounds have the formula [Au(C≡CR)L], often with L = tertiary phosphine ligand, but many diphosphine derivatives [(AuC≡CR)$_2$(μ-LL)] or diacetylide derivatives [R'(C≡CAuL)$_2$], with R' = a bridging spacer group, are also known [2 – 7]. Phosphinoacetylide ligands can bridge between gold centers to give binuclear or polynuclear complexes [6, 7].

Gold(I) complexes with diacetylide and diphosphine ligands can yield polymers [R'(C≡CAu)$_2$(μ-LL)]$_n$ [7], or digold or tetragold macrocycles, [R'(C≡CAu)$_2$(μ-LL)] or [R'(C≡CAu)$_2$(μ-LL)]$_2$ respectively [7 – 12]. The degree of aggregation is determined by the rigidity *versus* flexibility of the diacetylide ligand and by the bite distance and preferred conformation of the neutral bridging ligand LL [7, 8]. In addition, the presence of aurophilic (Au…Au) bonding [9, 10] may influence the structure by orienting the diphosphine digold units, as for example in formation of the tetragold(I) complex [R'(C≡CAu)$_2$(μ-LL)]$_2$, with R' = 1,4-C_6H_4 and LL = $Ph_2PCH_2PPh_2$ [7, 8].

Gold complexes of diacetylide ligands containing flexible angular propargyloxy units, R'($OCH_2C{\equiv}CAu)_2$, in combination with diphosphine ligands can exist either as large macrocycles, such as **A** – **C**, Chart 1, or as zigzag polymers [11, 12]. The macrocyclic complexes [X(C_6H_4-4-$OCH_2C{\equiv}CAu)_2$(μ-LL)], **C**, can exist in equilibrium with the interlocked [2]catenanes, **E**, or when X = cyclohexylidene and LL = $Ph_2P(CH_2)_4PPh_2$, as a doubly braided [2] catenane [{C_6H_{10}(C_6H_4-4-$OCH_2C{\equiv}CAu)_2$(μ-LL)}$_2$]$_2$ [12]. The natural lability at the linear gold(I) center allows easy equilibration between these isomers [9, 12]. The tetragold derivatives, such as **E** (Chart 1), are so far known only for more rigid diacetylide ligands [7, 8].

Since the factors that determine the nature of the self-assembly processes in reactions of digold(I) diacetylides with diphosphines are still not fully understood, it was of interest to investigate further examples of gold(I) complexes with diacetylide and diphosphine bridging ligands, in order to determine the degree of aggregation. This article reports complexes based on

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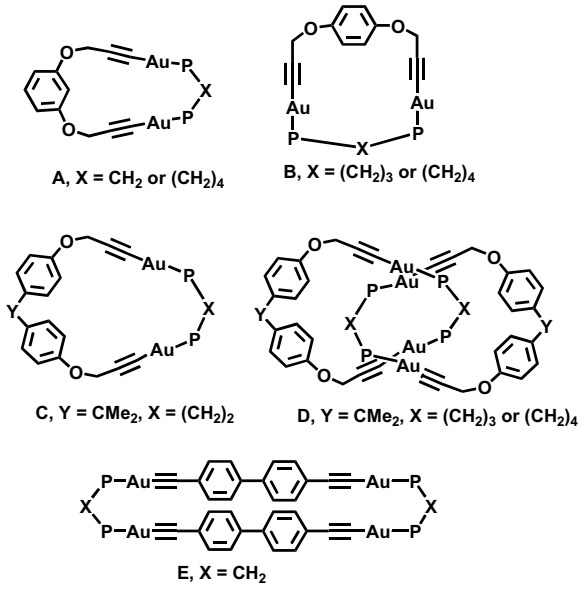

Chart 1. P = PPh_2.

three new diacetylide ligands, with varying flexibility and bite distance, in combination with the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ $(n = 1-6)$ and *trans*-$Ph_2PCH{=}CHPPh_2$, and the structures of a digold and a tetragold macrocycle.

Results and Discussion

Synthesis and structures of gold(I) acetylide macrocycles

The diacetylene ligands 1,4-C_6H_4(CMe_2-4-C_6H_4-$OCH_2C{\equiv}CH)_2$, **1**, 4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CH)_2$, **2**, and 1,5-$C_{10}H_6(OCH_2C{\equiv}CH)_2$, **3**, (Chart 2) were prepared by standard methods [13]. They have decreasing sizes of the spacer groups, while ligand **1** is much more flexible than **2** and **3**. In each case, reaction with two equivalents of [AuCl(SMe_2)] in the presence of base gave the corresponding digold(I) diacetylide 1,4-C_6H_4(CMe_2-4-$C_6H_4OCH_2C{\equiv}CAu)_2$, **4**, 4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CAu)_2$, **5**, and 1,5-$C_{10}H_6$ $(OCH_2C{\equiv}CAu)_2$, **6**, which were isolated as yellow, insoluble solids. The infrared spectra of compounds **4**, **5** and **6** contained bands at 1999, 2009, and 2000 cm^{-1}, respectively, assigned to ν(C≡C). These vibrations are shifted to lower frequency by approximately 100 cm^{-1} from the free ligands, and suggests the presence of linearly coordinated gold(I) centers with both η^1 and η^2 coordination of the alkynyl groups to gold(I), as in simple alkynylgold(I) compounds such as $(PhC{\equiv}CAu)_n$ and $(t\text{-}BuC{\equiv}CAu)_6$ [14]. The structures **4**–**6** in Chart 2 show only the σ-bonds to the alkynyl groups since the nature of the oligomerization through π-bonding is uncertain.

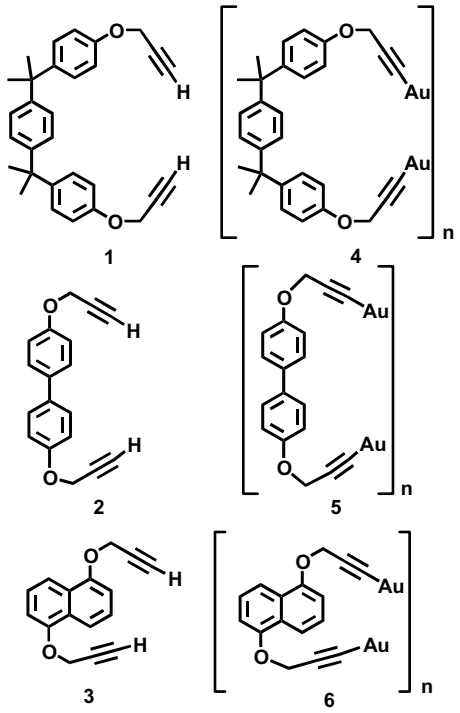

Chart 2.

Reactions of the digold(I) diacetylides, **4**–**6**, with diphosphine ligands gave the corresponding complexes $[\{R'(OCH_2C{\equiv}CAu)_2(\mu\text{-LL})\}_x]$, **7**–**9** respectively, which were isolated as air-stable, white solids. The complexes were soluble in dichloromethane, in contrast to the known insoluble polymeric complexes, suggesting that they have macrocyclic structures, but the size of the macrocycle ($x = 1$ or 2) and possibility of catenation is to be determined. Molecular modeling indicated moderate ring strain for the simple macrocycles $(x = 1)$ for the complexes with LL = $Ph_2P(CH_2)_nPPh_2$ only when $n = 1$, and very little ring strain in any case when $x = 2$; entropy effects favor the smaller ring with $x = 1$ [12]. The complexes failed to give parent ions in the mass spectra, so they were characterized by their IR and NMR spectra and, when crystals could be grown, by X-ray structure determination.

Reaction of [1,4-C_6H_4(CMe_2-4-C_6H_4-$OCH_2C{\equiv}$ $CAu)_2$], **4**, with diphosphine ligands, LL, gave the complexes [{1,4-C_6H_4(CMe_2-4-C_6H_4-$OCH_2C{\equiv}$C

Table 1. Selected bond lengths (Å) and angles (°) for complex **7f**[a].

Au(1)-C(2)	2.00(1)	Au(2)-C(10)	2.02(1)
Au(1)-P(1)	2.275(2)	Au(2)-P(2)	2.270(2)
Au(1)-Au(2)	2.9644(5)	P(2)-C(71)	1.76(2)
C(2)-Au(1)-P(1)	172.0(2)	C(10)-Au(2)-P(2)	173.8(2)
C(2)-Au(1)-Au(2)	92.7(2)	C(10)-Au(2)-Au(1)	88.0(2)
P(1)-Au(1)-Au(2)	95.00(5)	P(2)-Au(2)-Au(1)	97.92(5)

[a] Symmetry transformations used to generate equivalent atoms: $-x+1, -y+1, -z+1$.

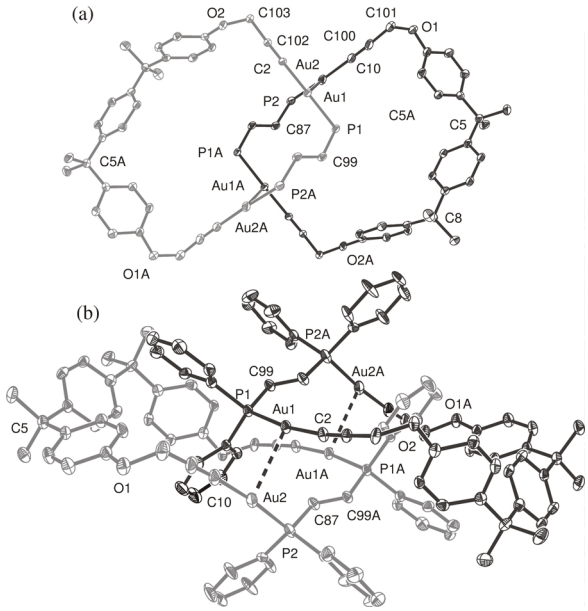

Fig. 1. Molecular structure of [1,4-C_6H_4(CMe_2-4-C_6H_4 $OCH_2C{\equiv}CAu)_2$(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)], **7f**: (a) Top view of a pair of macrocycles, with phenyl groups omitted for clarity. (b) Side view, showing interpenetration of each macrocycle by a phenyl group of its neighbor.

$Au)_2(\mu\text{-LL})\}_x]$, **7a**–**7e** for LL = $Ph_2P(CH_2)_nPPh_2$ with $n = 2-6$ respectively, and **7f** when LL = *trans*-$Ph_2PCH{=}CHPPh_2$. The reaction of **4** with $Ph_2PCH_2PPh_2$ gave a soluble product, but it could not be isolated in analytically pure form and its ^{31}P NMR spectrum contained many resonances, indicating that it exists in solution as a complex mixture. Complex **7a** ($n = 2$) was isolated in analytically pure form but the ^{31}P NMR spectrum contained two singlet resonances with approximately equal intensities, indicating that it exists in solution as a mixture of two isomers. In all other cases, the ^{31}P NMR spectra contained only one singlet resonance, as expected for a single isomer.

The IR spectrum of the complex [1,4-C_6H_4(CMe_2-4-C_6H_4-$OCH_2C{\equiv}CAu)_2$(μ-$Ph_2PCH{=}CHPPh_2$)], **7f**, displays a weak band at 2134 cm^{-1} corresponding to the ν(C≡C) stretch. In the ^{1}H NMR spectrum, there were single resonances for the CMe_2, OCH_2 and CH=CH protons and, in the ^{31}P NMR spectrum, a singlet resonance at 33.5, indicating a symmetrical structure. The molecular structure of, **7f**, is shown in Fig. 1, with relevant bond parameters listed in Table 1. The complex forms a digold(I) macrocycle with a 28 atom circumference. The transannular Au…Au distance is 6.46 Å and the longest transannular distances are C(5)…P(1A) = 12.56 Å and O(1)…C(103A) = 12.68 Å. Clearly, the macrocycle cavity is large enough to allow catenation, but pairs of macrocycles associate instead one above the other (such that there is a center of symmetry located between them) as shown in Fig. 1. The conformation of the diphosphine ligand is neither *syn* nor *anti*, with dihedral angle Au(1)-P(1)…P(2A)-Au(2A) = 80°. The angles P-Au-C = 172.0(2) and 173.8(2)° are distorted from linearity, with each gold atom displaced towards the neighboring molecule so as to form an inter-ring aurophilic bond [Au(1)…Au(2) = 2.964(1) Å]. The large cavity of each macrocycle is occupied by pairwise interpenetration of a phenyl group of the neighboring molecule, as shown in Fig. 1. In this conformation of the macrocycle pairs, there are two aurophilic bonds and multiple attractive aryl…aryl interactions between pairs of phenylphosphorus groups and between phenyl groups and aryloxy groups. The dihedral angle C(2)-Au(1)…Au(2)-C(10) = 90.7° is ideal for forming a strong aurophilic bond [9].

These pairs of macrocycles of complex **7f** presumably dissociate in solution to give the individual macrocycles. The structures of the other macrocycles in the solid state have not been determined because suitable single crystals could not be grown, but it is likely that they also exist as the simple macrocycles in solution. For the complexes [1,4-C_6H_4(CMe_2-4-C_6H_4-$OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_nPPh_2$)], **7a**–**7e**, the ring size ranges from 28 (**7a**, $n = 2$) to 32 (**7e**, $n = 6$) atoms. The structure of the second isomer of **7a**, when $n = 2$, is unknown.

The reaction of [4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CAu)_2]_n$ with diphosphines gave the complexes [$\{$4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CAu)_2(\mu\text{-LL})\}_x$], **8a**–**8f** for LL = $Ph_2P(CH_2)_nPPh_2$ with $n = 1-6$ respectively, and **8g** with LL = *trans*-$Ph_2PCH{=}CHPPh_2$. In all cases, the ^{31}P NMR spectra contained only a single resonance, indicating that each compound exists in solution as a single isomer. The molecular structure

Table 2. Selected bond lengths (Å) and angles (°) for complex **8a** [a].

Au(1)-C(1)	2.00(1)	Au(1)-P(1)	2.266(2)
Au(1)-Au(2)	3.2129(5)	Au(2)-C(20)	2.03(1)
Au(2)-P(2)	2.272(2)	C(1)-C(2)	1.17(1)
C(1)-Au(1)-P(1)	175.7(3)	C(20)-Au(2)-P(2)	175.6(3)
P(1)-Au(1)-Au(2)	84.20(6)	C(1)-Au(1)-Au(2)	100.0(3)
P(2)-Au(2)-Au(1)	89.99(6)	C(20)-Au(2)-Au(1)	94.1(3)
C(20)-C(19)-C(18)	179(1)	C(19)-C(20)-Au(2)	173(1)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y-1, -z+1$.

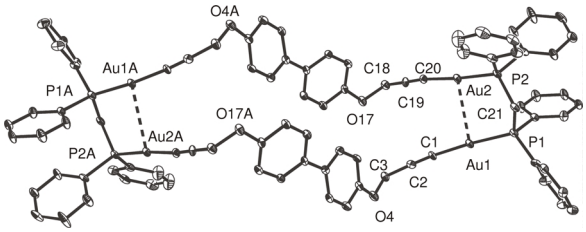

Fig. 2. Molecular structure of [{4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PCH_2PPh_2)\}_2$], **8a**.

of **8a**, LL = $Ph_2PCH_2PPh_2$, was determined and is shown in Fig. 2, with selected bond lengths and angles listed in Table 2. The complex exists as the tetragold(I) macrocycle $(x = 2)$, and is present as a remarkable 42-membered ring, which adopts an extended chair conformation with a center of symmetry at the midpoint of the macrocycle. The bridging diphosphine ligand has the *syn* conformation, with dihedral angle Au(1)P(1)...P(2)Au(2) = 18°, as in other gold(I) complexes with bridging $Ph_2PCH_2PPh_2$ ligands [9, 10]. The angles at gold are roughly linear with CAuP = 175.6(3) and 175.7(3)°, and there is a transannular aurophilic bond with Au(1)...Au(2) = 3.213(1) Å. The gold acetylide units are directed slightly apart, with increasing transannular distances C(1)...C(20) = 3.77 Å, C(2)...C(19) = 4.11 Å, C(3)...C(18) = 4.69 Å, and O(4)...O(17) = 4.99 Å, and this appears to occur in order to optimize the offset side-by-side, transannular aryl...aryl interactions between the biphenyl groups [shortest CC distances are C(7)...C(14) = 3.50 and C(9)...C(12) = 3.65 Å]. The closest analogy to the structure of **8a** is the found in the rigid rod diacetylide derivative **E** (Chart 1) [7, 15], but the additional -OCH_2- spacer units in **8a** give much greater flexibility in forming the chair conformation rather than the planar conformation in **E**.

The double ring $(x = 2)$ for the complexes **8**, [{4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CAu)_2(\mu\text{-LL})\}_x$], is likely to be unique for **8a**, with LL = $Ph_2PCH_2PPh_2$, since the

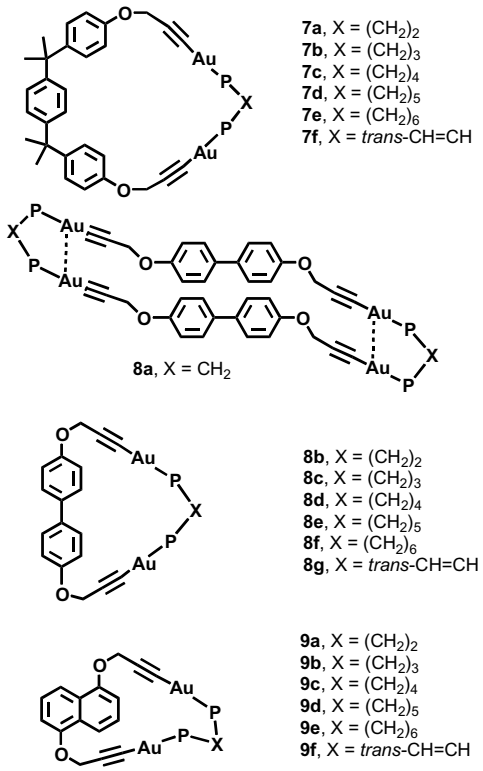

Chart 3. P = PPh_2.

transannular aurophilic bonding will be absent, or at least much weaker, for the complexes **8b**–**8g** with other diphosphine ligands. None of these complexes yielded single crystals suitable for X-ray structure determination, but we tentatively propose that they have the simpler macrocyclic structures with $x = 1$.

The reaction of $[1,5\text{-}C_{10}H_6(OCH_2C{\equiv}CAu)_2]_n$, **6**, with diphosphine ligands gave the complexes [{1,5-$C_{10}H_6(OCH_2C{\equiv}CAu)_2(\mu\text{-LL})\}_x$], **9a**–**9e** for LL = $Ph_2P(CH_2)_nPPh_2$ with $n = 2-6$ respectively, and **9f** with LL = *trans*-$Ph_2PCH{=}CHPPh_2$. In all these cases, the ^{31}P NMR spectra contained only a single resonance, indicating that each compound exists in solution as a single isomer. The similar reaction of complex **6** with LL = $Ph_2PCH_2PPh_2$ gave a mixture of complexes that could not be purified. This behavior is similar to that observed in formation of complexes **7** from the precursor **4** and, by analogy, it is likely that all of the isolated complexes have the macrocyclic structures with $x = 1$. The ring sizes (taking the shortest route through the naphthyl groups) then vary from 18 in **9a** to 22 in **9e**. A summary of the proposed structures is shown in Chart 3.

Table 3. Luminescence data for phosphine gold(I) acetylide macrocycles[a].

Complex	Medium	Diphosphine Spacer X	Emission max, nm
7a	solid	$(CH_2)_2$	425, 664
	CH_2Cl_2		415
7b	solid	$(CH_2)_3$	454, 603
	CH_2Cl_2		415
7c	solid	$(CH_2)_4$	452, 563
	CH_2Cl_2		426
7d	solid	$(CH_2)_5$	458, 574
	CH_2Cl_2		416
7e	solid	$(CH_2)_6$	448, 554
	CH_2Cl_2		413
7f	solid	CH=CH	467, 555
	CH_2Cl_2		447
8a	solid	CH_2	501
	CH_2Cl_2		446
8b	solid	$(CH_2)_2$	503
	CH_2Cl_2		427
8c	solid	$(CH_2)_3$	514
	CH_2Cl_2		431
8d	solid	$(CH_2)_4$	503
	CH_2Cl_2		456
8e	solid	$(CH_2)_5$	470
	CH_2Cl_2		467
8f	solid	$(CH_2)_6$	496
	CH_2Cl_2		480
8g	solid	CH=CH	487
	CH_2Cl_2		461

[a] Excitation was at 350 nm in each case.

Luminescence of the gold(I) complexes

The photophysical properties of the gold acetylide macrocycles are summarized in Table 3. Upon excitation at 350 nm, the gold(I) complexes [1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2P(CH_2)_n$-$PPh_2)$], **7a**–**7e**, in solution in dichloromethane, displayed single emission bands with maxima between 413 (**7e**) to 426 (**7c**) nm but, in the solid state, two emission bands were observed in each case. A higher energy emission band in the range 425 (**7a**) to 458 (**7d**) nm is assigned to an excited state having mostly intraligand π-π^* (acetylide) character, while a lower energy band in the range 554 (**7e**) to 664 (**7a**) nm is assigned to a metal centered emissive state, based on literature precedents [2, 9]. Both bands are red shifted compared to the solution state, as a result of either enhanced Au…Au bonding or π-stacking in the solid state. The complexes [{4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-$Au)_2(\mu$-$Ph_2P(CH_2)_nPPh_2)\}_x$], **8**, gave only single emission peaks either in solution in dichloromethane or in the solid state. The emission maxima ranged between 427 (**8b**) and 480 (**8f**) nm in solution, and between 470 (**8e**) and 514 (**8c**) nm in the solid state. Red-shifts, on going from solution to solid state, of 47 to 83 nm were observed when $n = 1-4$, but smaller shifts of 19 and 7 nm were observed when $n = 5$ and 6 respectively.

Experimental Section

The complex [$AuCl(SMe_2)$] [16] and ligands **2** and **3** [13] were prepared by literature methods. NMR spectra were recorded by using a Varian Mercury 400 MHz spectrometer. Chemical shifts are reported relative to TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). IR spectra were recorded as Nujol mulls by using a Perkin-Elmer 2000 FTIR. Emission spectra were recorded at room temperature using a Fluorolog-3 spectrofluorometer. For recording the emission and excitation spectra, solutions were placed in quartz cuvettes, while solids were ground finely with FTIR grade 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.

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}CH)_2$], **1**. A mixture of 1,4-$C_6H_4(CMe_2$-4-$C_6H_4OH)_2$ (10.0 g, 28.9 mmol), 3-bromopropyne (6.43 ml, 80% solution, 57.8 mmol) and potassium carbonate (11.97 g, 86.6 mmol) in acetone (100 ml) was heated under reflux for 24 h. The reaction mixture was filtered to remove KBr, the solvent was removed under vacuum, and the yellow oily residue extracted with ether. The ether solution was washed with aqueous sodium bicarbonate, then dried with magnesium sulphate, filtered, and the solvent removed under vacuum. The product was recrystallized from MeOH (50 ml) to give a colorless solid which was collected by filtration and washed with ether. Yield: 5.8 g, 48%. NMR ($CDCl_3$): δ(^{1}H) = 7.15 [d, 4H, ^3J(HH) = 9 Hz, $OArH_{2,6}$], 7.08 [s, 4H, CArC], 6.86 [d, 4H, ^3J(HH) = 9 Hz, $OArH_{3,5}$], 4.64 [d, ^4J(HH) = 2 Hz, OCH_2], 3.00 [t, 2H, ^4J(HH)=2 Hz, CCH], 1.62 [s, 12H, CCH_3]; δ(^{13}C) = 155.40, 147.72, 143.85 [*ipso*-C's], 127.78 [$ArC_{3,5}$], 126.20 [C-Ar-C], 114.14 [$ArC_{2,6}$], 78.82 [CCH], 75.31 [CCH], 55.92 [OCH_2], 41.92 [CCH_3], 30.88 [CH_3]; IR (Nujol): ν(C≡C) = 2127 cm^{-1}, ν(C≡CH) = 3271, 3284 cm^{-1}; EI-MS: $m/z = 422.224$, calcd. $m/z = 422.227$.

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}CAu)_2]_n$, **4**. To a solution of [$AuCl(SMe_2)$] (0.500 g, 1.70 mmol) in THF (20 ml)/MeOH (10 ml) was added a solution of [1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}CH)_2$] (0.36 g, 0.85 mmol) and sodium acetate (0.31 g, 2.55 mmol) in THF (10 ml)/MeOH (10 ml). The reaction mixture was stirred for 3 h, forming a yellow precipitate which was collected by filtration, washed with THF, MeOH, ether, and pentane and dried. Yield: 0.643 g, 93%. IR(Nujol): 1999 (w) cm^{-1}.

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-$Au)_2]_n$, **5**. This was prepared similarly from [$AuCl(SMe_2)$] (0.50 g, 1.70 mmol) and

4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}CH)_2$ (0.22 g, 0.85 mmol). Yield: 0.512 g, 92%. IR(Nujol): 2009 (w) cm^{-1}.

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2]_n$, **6**. This was prepared similarly from [$AuCl(SMe_2)$] (1.00 g, 3.40 mmol) and 1,5-$C_{10}H_6(OCH_2C{\equiv}CH)_2$ (0.40 g, 1.70 mmol). Yield: 0.953 g, 89%. IR(Nujol): 2000 (w) cm^{-1}.

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}C$-Au$)_2(\mu$-Ph_2P-$(CH_2)_2PPh_2)]$, **3a**. A solution of $Ph_2P(CH_2)_2PPh_2$ (0.098 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was added to a suspension of complex **4** (0.200 g, 0.25 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 3 h, then decolorizing charcoal (100 mg) was added and the mixture stirred for 15 min. The mixture was filtered and pentane (100 ml) was added to the filtrate to precipitate the product as a colorless solid, which was collected by filtration, washed with ether and pentane, and dried under vacuum. Yield: 0.16 g, 54%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.40 – 7.65 [m, 20H, Ph], 7.12 [d, 4H, ^3J(HH) = 8.5 Hz, $ArH_{2,6}$], 7.10 [s, 4H, CArC], 6.96 [4H, $OArH_{3,5}$], 4.76 [s, 4H, OCH_2], 2.63, 2.51 [m, 4H, CH_2P]; $\delta(^{31}P)$ = 39.59, 40.13. IR(Nujol): ν(C≡C)=2130 cm^{-1}. Analysis for $C_{56}H_{52}O_2P_2Au_2$: calcd. C 55.45, H 4.32; found C 56.11, H 4.80.

Similarly prepared were:

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}C$-Au$)_2(\mu$-Ph_2P-$(CH_2)_3PPh_2)]$, **7b**, from **4** (0.200 g, 0.25 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.101 g, 0.25 mmol). Yield: 0.167 g, 55%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.66 – 7.61, 7.44 – 7.40 [m, 20H, Ph], 7.10 [d, 4H, ^3J(HH) = 9 Hz, $OArH_{2,6}$], 7.09 [s, 4H, CArC], 6.90 [d, 4H, ^3J = 8.6 Hz, $OArH_{3,5}$], 4.75 [s, 4H, OCH_2], 2.78 [m, 4H, CH_2P], 1.82 [m, 2H, CH_2P], 1.60 [s, 12H, CCH_3]; $\delta(^{31}P)$=34.85 (s). IR(Nujol): ν(C≡C) = 2125 cm^{-1}. Analysis for $C_{57}H_{54}O_2P_2Au_2$: calcd. C 55.80, H 4.44; found C 56.43, H 4.54.

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}C$-Au$)_2(\mu$-Ph_2P-$(CH_2)_4PPh_2)]$, **7c**, from **4** (0.200 g, 0.25 mmol) and $Ph_2P(CH_2)_4PPh_2$ (0.105 g, 0.246 mmol). Yield: 0.143 g, 47%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.44 – 7.65, [m, 20H, Ph], 7.43 [d, 4H, ^3J = 7.2 Hz, $OArH_{2,6}$], 7.40 [s, 4H, CArC], 6.88 [d, 4H, ^3J = 8.8 Hz, $OArH_{3,5}$], 4.73 [s, 4H, OCH_2], 2.51 [m, 4H, CH_2P], 1.69 [m, 4H, CH_2], 1.62 [s, 12H, CCH_3]; $\delta(^{31}P)$ = 35.98 (s). IR(Nujol): ν(C≡C)=2134 cm^{-1}. Analysis for $C_{58}H_{56}O_2P_2Au_2$: calcd. C 56.14, H 4.55; found C 55.89, H 4.59.

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}C$-Au$)_2(\mu$-Ph_2P-$(CH_2)_5PPh_2)]$, **7d**, from **4** (0.200 g, 0.25 mmol) and $Ph_2P(CH_2)_5PPh_2$ (0.112 g, 0.25 mmol). Yield: 0.155 g, 50%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.65 – 7.39 [m, 20H, Ph], 7.12 [d, 4H, ^3J = 8 Hz, $OArH_{2,6}$], 7.14 [s, 4H, CArC], 6.88 [d, 4H, ^3J = 8 Hz, $OArH_{3,5}$], 4.72 [s, 4H, OCH_2], 2.44 [m, 4H, CH_2P], 1.59 [m, 6H, CH_2], 1.63 [s, 12H, CCH_3]; $\delta(^{31}P)$ = 36.93 (s). IR(Nujol): ν(C≡C)=2133 cm^{-1}. Analysis for $C_{59}H_{58}O_2P_2Au_2$: calcd. C 56.47, H 4.66; found C 56.26, H 4.86.

[1,4-$C_6H_4(CMe_2$-4-$C_6H_4OCH_2C{\equiv}C$-Au$)_2(\mu$-Ph_2P-$(CH_2)_6 PPh_2)]$, **7e**, from **4** (0.210 g, 0.26 mmol) and $Ph_2P(CH_2)_6PPh_2$ (0.117 g, 0.26 mmol). Yield: 0.168 g, 51%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.57 – 7.36 [m, 20H, Ph], 7.13 [d, 4H, ^3J = 8.8 Hz, $OArH_{2,6}$], 7.15 [s, 4H, CArC], 6.88 [d, 4H, ^3J = 8.7 Hz, $OArH_{3,5}$], 4.73 [s, 4H, OCH_2], 2.32 [m, 4H, CH_2P], 1.39 [m, 8H, CH_2], 1.63 [s, 12H, CCH_3]; $\delta(^{31}P)$ = 38.03 (s). IR(Nujol): ν(C≡C) = 2134 cm^{-1}. Analysis for $C_{60}H_{60}O_2P_2Au_2$: calcd. C 56.79, H 4.77; found C 57.17, H 5.04.

[1,4-$C_6H_4CMe_2$-4-$C_6H_4OCH_2C{\equiv}C$-Au$)_2(\mu$-trans-Ph_2-$PCH{=}CHPPh_2)]$, **7f**, from **4** (0.400 g, 0.49 mmol) and *trans*-$Ph_2PCH{=}CHPPh_2$ (0.195 g, 0.49 mmol). Yield: 0.318 g, 54%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.49 – 7.36 [m, 20H, Ph], 7.10 [d, 4H, ^3J = 9 Hz, $OArH_{2,6}$], 7.04 [s, 4H, CArC], 7.03 [t, 2H, ^2J(PH)= 19 Hz, CH=], 6.81 [d, 4H, ^3J = 9 Hz, $OArH_{3,5}$], 4.71 [s, 4H, OCH_2], 1.60 [s, 12H, CCH_3]; $\delta(^{31}P)$ = 33.47 (s). IR(Nujol): ν(C≡C) = 2134 cm^{-1}. Analysis for $C_{56}H_{50}O_2P_2Au_2$: calcd. C 55.55, H 4.16; found C 55.76, H 4.25.

[{4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au$)_2(\mu$-$Ph_2PCH_2$-$PPh_2)\}_2]$, **8a**. A solution of $Ph_2PCH_2PPh_2$ (0.176 g, 0.46 mmol) in CH_2Cl_2 (10 ml) was added to a suspension of complex **5** (0.300 g, 0.46 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 3 h, then decolorizing charcoal (100 mg) was added and the mixture stirred for a further 15 min. The solution was filtered and pentane (100 ml) was added to precipitate the product as a colorless solid, which was collected by filtration, washed with ether and pentane, and dried under vacuum. Yield: 0.164 g, 34%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.27 – – 7.61 [m, 24H, Ph, Ar], 6.90 [d, 4H, ^3J = 8.8 Hz, ArH), 4.80 [s, 4H, OCH_2], 3.62 [t, 2H, ^3J(PH) = 11.2 Hz, CH_2P]; $\delta(^{31}P)$ = 32.99 (s). IR(Nujol): ν(C≡C) = 2124 cm^{-1}. Analysis for $C_{43}H_{34}O_2P_2Au_2$: calcd. C 49.73, H 3.30; found C 49.27, H 2.95.

Similarly were prepared:

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au$)_2(\mu$-$Ph_2P(CH_2)_2P$-$Ph_2)]$, **8b**, from **5** (0.200 g, 0.31 mmol) and $Ph_2P(CH_2)_2PPh_2$ (0.122 g, 0.31 mmol). Yield: 0.204 g, 63%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.37 – 7.59 [m, 24H, Ph, Ar], 7.05 [d, 4H, ^3J(HH) = 8 Hz, Ar], 4.81 [s, 4H, OCH_2], 2.62 [sbr, 4H, CH_2P]; $\delta(^{31}P)$ = 39.86 (s). IR(Nujol): ν(C≡C)=2133 cm^{-1}. Analysis for $C_{44}H_{36}O_2P_2Au_2$: calcd. C 50.21, H 3.45; found C 50.52, H 3.41.

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au$)_2(\mu$-$Ph_2P(CH_2)_3P$-$Ph_2)]$, **8c**, from **5** (0.500 g, 0.76 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.315 g, 0.76 mmol). Yield: 0.457, 56%. NMR (CD_2Cl_2): $\delta(^1H)$= 7.3 – 7.6 [m, 24H, Ph, Ar], 7.03 [d, 4H, ^3J(HH) = 9 Hz, Ar], 4.73 [s, 4H, OCH_2], 2.76 [m, 4H, CH_2P], 1.83 [m, 2H, CH_2P]; $\delta(^{31}P)$ = 34.62 (s). IR(Nujol): ν(C≡C)=2120 cm^{-1}. Analysis for $C_{45}H_{38}O_2P_2Au_2$: calcd. C 50.67, H 3.59; found C 50.98; H 3.85.

Table 4. Crystal data and experimental details for **7f** and **8a**.

Complex	7f.2CH_2Cl_2	**8a**
Empirical formula	$C_{58}H_{54}Au_2Cl_4O_2P_2$	$C_{86}H_{68}Au_4O_4P_4$
Formula weight	1380.69	2077.15
Temperature [K]	200(2)	150(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions	$a = 16.4885(4)$	$a = 29.0161(14)$
[Å, °]	$b = 14.7849(5)$	$b = 13.2611(4)$
	$c = 23.1772(6)$	$c = 23.9963(11)$
	$\beta = 108.757(2)$	$\beta = 108.2611(4)$
Volume [Å^3]	5350.1(3)	8752.1(6)
Z	4	4
Density (calculated) [g/cm^3]	1.714	1.576
Absorption coefficient [mm^{-1}]	5.779	6.801
F(000)	2696	3968
Crystal size [mm^3]	$0.10 \times 0.10 \times 0.05$	$0.25 \times 0.15 \times 0.13$
Absorption correction	integration	integration
Data / restraints / params	12294 / 34 / 667	9634 / 0 / 394
Final R indices	$R1 = 0.0524$,	$R1 = 0.0558$,
$[I > 2\sigma(I)]$	$wR2 = 0.1108$	$wR2 = 0.1484$

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_4P$-$Ph_2)]$, **8d**, from **5** (0.500 g, 0.76 mmol) and $Ph_2P(CH_2)_4PPh_2$ (0.326 g, 0.76 mmol). Yield: 0.464, 56%. NMR (CD_2Cl_2): $\delta(^1H) = 7.3 - 7.6$ [m, 24H, Ph], 7.05 [s, 4H, ^3J(HH) = 9 Hz, Ar], 4.82 [s, 4H, OCH_2], 2.39 [m, 4H, CH_2P], 1.68 [m, 4H, CH_2]; $\delta(^{31}P)$ = 36.82 (s). IR(Nujol): ν(C≡C) = 2133 cm^{-1}. Analysis for $C_{46}H_{40}O_2P_2Au_2$: calcd. C 51.12, H 3.73; found C 51.41, H 4.04.

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_5P$-$Ph_2)]$, **8e**, from **5** (0.250 g, 0.38 mmol) and $Ph_2P(CH_2)_5PPh_2$ (0.174 g, 0.38 mmol). Yield: 0.262 g, 62%. NMR (CD_2Cl_2): $\delta(^1H) = 7.4 - 7.6$ [m, 24H, Ph, Ar], 7.05 [s, 4H, ^3J(HH) = 8 Hz, Ar), 4.81 [s, 4H, OCH_2], 2.35 [m, 4H, CH_2P], 1.53 [m, 6H, CH_2]; $\delta(^{31}P)$ = 35.21 (s). IR(Nujol): ν(C≡C)=2132 cm^{-1}. Analysis for $C_{48}H_{42}O_2P_2Au_2$: calcd. C 51.57, H 3.87; found C 51.98, H 3.84.

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_6P$-$Ph_2)]$, **8f**, from **5** (0.300 g, 0.46 mmol) and $Ph_2P(CH_2)_6PPh_2$ (0.208 g, 0.46 mmol). Yield: 0.370 g, 73%. NMR (CD_2Cl_2): $\delta(^1H) = 7.4 - 7.6$ [m, 24H, Ph], 7.06 [d, 4H, ^3J(HH) = 8 Hz, Ar], 4.82 [s, 4H, OCH_2], 2.35 [m, 4H, CH_2P], 1.50 [m, 4H, CH_2], 1.37 [m, 4H, CH_2]; $\delta(^{31}P)$ = 33.15 (s). IR(Nujol): ν(C≡C) = 2134 cm^{-1}. Analysis for $C_{50}H_{44}O_2P_2Au_2$: calcd. C 52.00, H 4.00; found C 51.89, H 3.76.

[4,4'-$C_6H_4C_6H_4(OCH_2C{\equiv}C$-Au)$_2$($\mu$-trans-$Ph_2PCH$=$CHPPh_2)]$, **8g**, from **5** (0.500 g, 0.76 mmol) and *trans*-Ph_2PCH=$CHPPh_2$ (0.303 g, 0.76 mmol). Yield: 0.459 g, 57%. NMR (CD_2Cl_2): $\delta(^1H) = 7.35 - 7.55$ [m, 24H, Ph, Ar], 7.10 [t, 2H, ^3J(PH) = 19.0 Hz, CH=], 7.02 [d, 4H, ^3J = 8.6 Hz, Ar], 4.72 [s, 4H, OCH_2]; $\delta(^{31}P)$ = 34.80 (s). IR(Nujol): ν(C≡C)=2133 cm^{-1}. Analysis for $C_{44}H_{34}O_2P_2Au_2$: calcd. C 50.30, H 3.26; found C 49.99, H 3.03.

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_2PPh_2)]$, **9a**. A solution of $Ph_2P(CH_2)_2PPh_2$ (0.400 g, 0.64 mmol) in CH_2Cl_2 (10 ml) was added to a suspension of **6** (0.253 g, 0.64 mmol) in CH_2Cl_2 (10 ml). The product was isolated as above as a colorless solid. Yield: 0.379 g, 58%. NMR (CD_2Cl_2): $\delta(^1H)$=7.82 [d, 2H, ^{3}J(HH) = 8 Hz, $ArH_{4,8}$], 7.38 – 7.60 [m, 22H, Ph and $ArH_{3,7}$], 7.06 [d, 2H, ^3J = 8 Hz, $ArH_{2,6}$], 4.99 [s, 4H, CH_2O], 2.62 [sbr, 4H, CH_2P]; $\delta(^{31}P)$ = 39.95 (s). IR(Nujol): ν(C≡C) = 2133 cm^{-1}. Analysis for $C_{42}H_{34}O_2P_2Au_2$: calcd. C 49.14, H 3.34; found C 49.21, H 3.39.

Similarly were prepared:

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_3PPh_2)]$, **9b**, from **6** (0.200 g, 0.32 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.131 g, 0.32 mmol). Yield: 0.135 g, 41%. NMR (CD_2Cl_2): $\delta(^1H)$ = 7.80 [d, 2H, ^3J(HH) = 8 Hz, $ArH_{4,8}$], 7.20 – 7.60 [m, 22H, Ph and $ArH_{3,7}$], 7.08 [d, 2H, ^3J = 8 Hz, $ArH_{2,6}$], 5.00 [s, 4H, CH_2O], 2.70 [sbr, 4H, CH_2P], 1.79 [sbr, 2H, CH_2P]; $\delta(^{31}P)$ = 35.10 (s). IR(Nujol): ν(C≡C) = 2134 cm^{-1}. Analysis for $C_{43}H_{36}O_2P_2Au_2$: calcd. C 49.63, H 3.49; found C 50.10, H 3.50.

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_4PPh_2)]$, **9c**, from **6** (0.400 g, 0.64 mmol) and $Ph_2P(CH_2)_4PPh_2$ (0.271 g, 0.64 mmol). Yield: 0.369 g, 55%. NMR (CD_2Cl_2): $\delta(^1H)$ = 7.81 [d, 2H, ^3J(HH) = 8 Hz, $ArH_{4,8}$], 7.35 – 7.57 [m, 22H, Ph and $ArH_{3,7}$], 7.05 [d, 2H, ^3J(HH) = 8 Hz, $ArH_{2,6}$], 4.98 [s, 4H, CH_2O], 2.38 [m, 4H, CH_2P], 1.63 [m, 4H, CH_2]; $\delta(^{31}P)$ = 36.90 (s). IR(Nujol): ν(C≡C) = 2133 cm^{-1}. Analysis for $C_{44}H_{38}O_2P_2Au_2$: calcd. C 50.11, H 3.63; found C 50.16, H 3.52.

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_5PPh_2)]$, **9d**, from **6** (0.200 g, 0.32 mmol) and $Ph_2P(CH_2)_5PPh_2$ (0.144 g, 0.32 mmol). Yield: 0.148 g, 44% NMR (CD_2Cl_2): $\delta(^1H)$ = 7.85 [d, 2H, ^3J(HH) = 8 Hz, $ArH_{4,8}$], 7.36 – 7.63 [m, 22H, Ph and $ArH_{3,7}$], 7.06 [d, 2H, ^3J = 8 Hz, $ArH_{2,6}$], 5.08 [s, 4H, CH_2O], 2.14 [sbr, 4H, CH_2P], 1.42 [sbr, 6H, CH_2P]; $\delta(^{31}P)$ = 37.80 (s). IR(Nujol): ν(C≡C) = 2133 cm^{-1}. Analysis for $C_{45}H_{40}O_2P_2Au_2$: calcd. C 50.58, H 3.77; found C 50.10, H 3.52.

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2$($\mu$-$Ph_2P(CH_2)_6PPh_2)]$, **9e**, from **6** (0.200 g, 0.32 mmol) and $Ph_2P(CH_2)_6PPh_2$ (0.144 g, 0.32 mmol). Yield: 0.199 g, 58%. NMR (CD_2Cl_2): $\delta(^1H)$ = 7.83 [d, 2H, ^3J = 8 Hz, $ArH_{4,8}$], 7.40 – 7.65 [m, 22H, Ph and $ArH_{3,7}$], 7.05 [d, 2H, ^3J = 8 Hz, $ArH_{2,6}$], 5.02 [s, 4H, CH_2O], 2.31 [sbr, 4H, CH_2P], 1.52 [sbr, 8H, CH_2]; $\delta(^{31}P)$ = 37.54 (s). IR(Nujol): ν(C≡C)=2133 cm^{-1}. Analysis for $C_{46}H_{42}O_2P_2Au_2$: calcd. C 50.70, H 3.91; found C 51.03, H 3.86.

[1,5-$C_{10}H_6(OCH_2C{\equiv}C$-Au)$_2$($\mu$-trans-$Ph_2PCH$=$CHP$-$Ph_2)]$, **9f**, from **6** (0.300 g, 0.48 mmol) and *trans*-Ph_2PCH=

$CHPPh_2$ (0.189 g, 0.48 mmol). Yield: 0.318 g, 65%. NMR (CD_2Cl_2): $\delta(^1H)$ = 7.82 [m, 2H, $ArH_{4,8}$], 7.58 – 7.38 [m, 24H, Ph, $ArH_{3,7}$, CH=], 7.04 [m, 2H, $ArH_{2,6}$], 4.98 [s, 4H, CH_2O]; $\delta(^{31}P)$ = 21.27 (s). IR(Nujol): ν(C≡C)=2133 cm^{-1}. Analysis for $C_{42}H_{32}O_2P_2Au_2$: calcd. C 49.24, H 3.15; found C 49.87, H 3.17.

X-ray structure determinations

Crystals were mounted on glass fibers. Data were collected using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B.V., 1998). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The absorption correction was carried out by integration using SCALEPACK (Nonius B.V., 1998). The crystal data and refinement parameters for **3f** and **5a** are listed in Table 4. The SHELXTL-NT V5.1 (Sheldrick, G. M.) suite of programs was used to solve the structures by direct methods. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. *Complex* **7f**: Crystals of [1,4-$C_6H_4CMe_2$-4-$C_6H_4OCH_2C$≡C-Au)$_2$(μ-*trans*-Ph_2PCH=$CHPPh_2$)] were grown by slow diffusion of ether into a solution of **7f** in CH_2Cl_2. The centre of the dimer was located on a crystallographic centre of symmetry. The phenyl ring, C71-C76, was disordered and was modeled with 70/30 occupancy. Two molecules of CH_2Cl_2 were refined with anisotropic thermal motion, with fixed C–Cl bond lengths of 1.76(2) Å. **5a**: Crystals of [Au_2(μ-$CCCH_2OC_6H_4C_6H_4OCH_2CC$)$_2$($\mu$-$Ph_2PCH_2PPh_2$)$_2$] were grown by slow diffusion of ether into a solution of **8a** in CH_2Cl_2 at −4 °C. The molecule was located on a symmetry element. There was disordered solvent present which could not be modeled successfully. The program SQUEEZE found two voids (each 1045 $Å^3$ in size) at (0,0,0) and (1/2, 1/2, 1/4). For each void 93 electrons were removed (CH_2Cl_2 = 42 e and ether = 42 e).

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