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

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Z. Naturforsch. 59b, 1488-1496 (2004); received August 26, 2004

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

The new dialkynyldigold(I) complexes $[Ar(OCH_2C \equiv CAu)_2]_n \{Ar = 1,4-C_6H_4(CMe_2-4-C_6H_4)_2, 4,4'-C_6H_4C_6H_4 \text{ and } 1,5-C_{10}H_6\}$ 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 $[Au(C \equiv CR)L]$, often with L = tertiary phosphine ligand, but many diphosphine derivatives [(AuC \equiv CR)₂(μ -LL)] or diacetylide derivatives $[R'(C \equiv CAuL)_2]$, 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 $[R'(C \equiv CAu)_2(\mu - LL)]_n$ [7], or digold or tetragold macrocycles, $[R'(C \equiv CAu)_2(\mu - LL)]$ or $[R'(C \equiv CAu)_2(\mu - LL)]_2$ 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 $[R'(C \equiv CAu)_2(\mu - LL)]_2$, 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'(OCH₂C≡ CAu)₂, in combination with diphosphine ligands can exist either as large macrocycles, such as $\mathbf{A} - \mathbf{C}$, Chart 1, or as zigzag polymers [11, 12]. The macrocyclic complexes [X(C₆H₄-4-OCH₂C≡CAu)₂(μ -LL)], **C**, can exist in equilibrium with the interlocked [2]catenanes, **E**, or when X = cyclohexylidene and LL = Ph₂P(CH₂)₄PPh₂, as a doubly braided [2] catenane [{C₆H₁₀(C₆H₄-4-OCH₂C≡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-C₆H₄(CMe₂-4-C₆H₄- $OCH_2C\equiv CH)_2$, 1, 4,4'-C₆H₄C₆H₄($OCH_2C\equiv CH)_2$, 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(SMe₂)] in the presence of base gave the corresponding digold(I) diacetylide 1,4-C₆H₄(CMe₂-4-C₆H₄OCH₂C \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 $v(C \equiv C)$. 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



Chart 2.

as $(PhC \equiv CAu)_n$ and $(t-BuC \equiv CAu)_6$ [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.

Reactions of the digold(I) diacetylides, 4-6, with diphosphine ligands gave the corresponding complexes [{R'(OCH₂C \equiv CAu)₂(μ -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 [$\{1,4-C_6H_4(CMe_2-4-C_6H_4-OCH_2C \equiv CAu\}$

Table 1. Selected bond lengths (Å) and angles (°) for complex $7f^a$.

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

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



Fig. 1. Molecular structure of $[1,4-C_6H_4(CMe_2-4-C_6H_4 OCH_2C\equiv CAu)_2(\mu$ -trans-Ph₂PCH=CHPPh₂)], **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(μ -LL)_{*x*}], **7a**-**7e** for LL = Ph₂P(CH₂)_{*n*}PPh₂ with n = 2 - 6 respectively, and **7f** when LL = *trans*-Ph₂PCH=CHPPh₂. The reaction of **4** with Ph₂PCH₂PPh₂ gave a soluble product, but it could not be isolated in analytically pure form and its ³¹P 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 ³¹P 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 ³¹P NMR spectra contained only one singlet resonance, as expected for a single isomer.

The IR spectrum of the complex $[1,4-C_6H_4(CMe_2-4-C_6H_4-OCH_2C\equiv CAu)_2(\mu-Ph_2PCH=CHPPh_2)]$, 7f,

displays a weak band at 2134 cm⁻¹ corresponding to the $v(C \equiv C)$ stretch. In the ¹H NMR spectrum, there were single resonances for the CMe2, OCH2 and CH=CH protons and, in the ³¹P 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 $173.8(2)^{\circ}$ 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)- $Au(1)...Au(2)-C(10) = 90.7^{\circ}$ 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-C₆H₄(CMe₂-4-C₆H₄-OCH₂C≡CAu)₂(μ -Ph₂P(CH₂)_nPPh₂)], **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 $[\{4,4'-C_6H_4C_6H_4(OCH_2C\equiv CAu)_2(\mu-LL)\}_x]$, **8a**-**8f** for LL = Ph₂P(CH₂)_nPPh₂ with n = 1 - 6 respectively, and **8g** with LL = *trans*-Ph₂PCH=CHPPh₂. In all cases, the ³¹P 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 $[\{4,4'-C_6H_4C_6H_4(OCH_2 C \equiv CAu)_2(\mu-Ph_2PCH_2PPh_2)\}_2]$, **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 $Au(1)P(1)...P(2)Au(2) = 18^{\circ}$, as in other gold(I) complexes with bridging Ph₂PCH₂PPh₂ ligands [9,10]. The angles at gold are roughly linear with CAuP = 175.6(3) and $175.7(3)^{\circ}$, 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 -OCH2- 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'-C₆H₄C₆H₄(OCH₂C≡CAu)₂(μ -LL)}_x], is likely to be unique for **8a**, with LL = Ph₂PCH₂PPh₂, 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 $[1,5-C_{10}H_6(OCH_2C\equiv CAu)_2]_n$, 6, with diphosphine ligands gave the complexes [$\{1,5 C_{10}H_6(OCH_2C\equiv CAu)_2(\mu-LL)_x$], 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 ³¹P 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.

		Diphosphine	Emission
Complex	Medium	Spacer X	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
0	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 [$\{4,4'-C_6H_4C_6H_4(OCH_2C\equiv C-C_6H_4C_6H_4(OCH_2C\equiv C-C_6H_4C_6H_4C_6H_4C_6H_4(OCH_2C\equiv C-C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4C_6H_4$ $\operatorname{Au}_{2}(\mu-\operatorname{Ph}_{2}\operatorname{P}(\operatorname{CH}_{2})_{n}\operatorname{PPh}_{2})_{x}], \mathbf{8}, \text{ gave only single}$ 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(SMe₂)] [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 (¹H, ¹³C) or 85% H₃PO₄ (³¹P). 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-C₆H₄(CMe₂-4-C₆H₄OH)₂ (10.0 g, 28.9 mmol), 3bromopropyne (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 (CDCl₃): $\delta(^{1}H) = 7.15$ [d, 4H, ${}^{3}J(\text{HH}) = 9 \text{ Hz}, \text{ OArH}_{2,6}], 7.08 \text{ [s, 4H, CArC]}, 6.86 \text{ [d, 4H,}$ ${}^{3}J(\text{HH}) = 9 \text{ Hz}, \text{ OArH}_{3,5}], 4.64 \text{ [d, }{}^{4}J(\text{HH}) = 2 \text{ Hz}, \text{ OCH}_{2}],$ 3.00 [t, 2H, ⁴*J*(HH)=2 Hz, CCH], 1.62 [s, 12H, CCH₃]; $\delta(^{13}C) = 155.40, 147.72, 143.85 [ipso-C's], 127.78 [ArC_{3.5}],$ 126.20 [C-Ar-C], 114.14 [ArC2.6], 78.82 [CCH], 75.31 [CCH], 55.92 [OCH2], 41.92 [CCH3], 30.88 [CH3]; IR (Nujol): $v(C \equiv C) = 2127 \text{ cm}^{-1}$, $v(C \equiv CH) = 3271$, 3284 cm⁻¹; EI-MS: m/z = 422.224, calcd. m/z = 422.227.

[1,4-C₆H₄(CMe₂-4-C₆H₄OCH₂C \equiv CAu)₂J_n, **4**. To a solution of [AuCl(SMe₂)] (0.500 g, 1.70 mmol) in THF (20 ml)/MeOH (10 ml) was added a solution of [1,4-C₆H₄(CMe₂-4-C₆H₄OCH₂C \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'-C₆H₄C₆H₄(OCH₂C≡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.

 $[1,4-C_6H_4(CMe_2-4-C_6H_4OCH_2C\equiv C-Au)_2(\mu-Ph_2P-$ (CH₂)₂PPh₂)], **3a**. A solution of Ph₂P(CH₂)₂PPh₂ (0.098 g, 0.25 mmol) in CH₂Cl₂ (10 ml) was added to a suspension of complex 4 (0.200 g, 0.25 mmol) in CH₂Cl₂ (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 (CD₂Cl₂): δ (¹H)= 7.40 - 7.65 [m, 20H, Ph], 7.12 [d, 4H, ${}^{3}J(\text{HH}) = 8.5 \text{ Hz}, \text{ArH}_{2.6}], 7.10 \text{ [s, 4H, CArC]}, 6.96 \text{ [4H,}$ OArH_{3,5}], 4.76 [s, 4H, OCH₂], 2.63, 2.51 [m, 4H, CH₂P]; $\delta(^{31}P) = 39.59, 40.13$. IR(Nujol): $v(C \equiv C) = 2130 \text{ cm}^{-1}$. Analysis for C₅₆H₅₂O₂P₂Au₂: 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 Ph₂P(CH₂)₃PPh₂ (0.101 g, 0.25 mmol). Yield: 0.167 g, 55%. NMR (CD₂Cl₂): $\delta({}^{1}$ H)= 7.66 – 7.61, 7.44 – 7.40 [m, 20H, Ph], 7.10 [d, 4H, ${}^{3}J$ (HH) = 9 Hz, OArH_{2,6}], 7.09 [s, 4H, CArC], 6.90 [d, 4H, ${}^{3}J$ = 8.6 Hz, OArH_{3,5}], 4.75 [s, 4H, OCH₂], 2.78 [m, 4H, CH₂P], 1.82 [m, 2H, CH₂P], 1.60 [s, 12H, CCH₃]; $\delta({}^{31}$ P)=34.85 (s). IR(Nujol): $\nu(C=C) = 2125 \text{ cm}^{-1}$. Analysis for C₅₇H₅₄O₂P₂Au₂: calcd. C 55.80, H 4.44; found C 56.43, H 4.54.

 $[1, 4-C_{6}H_{4}(CMe_{2}-4-C_{6}H_{4}OCH_{2}C \equiv C-Au)_{2}(\mu-Ph_{2}P-$

 $(CH_2)_4PPh_2$)], **7c**, from **4** (0.200 g, 0.25 mmol) and Ph₂P(CH₂)₄PPh₂ (0.105 g, 0.246 mmol). Yield: 0.143 g, 47%. NMR (CD₂Cl₂): δ (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, OCH₂], 2.51 [m, 4H, CH₂P], 1.69 [m, 4H, CH₂], 1.62 [s, 12H, CCH₃]; δ (³¹P) = 35.98 (s). IR(Nujol): ν (C=C)=2134 cm⁻¹. Analysis for C₅₈H₅₆O₂P₂Au₂: 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 Ph₂P(CH₂)₅PPh₂ (0.112 g, 0.25 mmol). Yield: 0.155 g, 50%. NMR (CD₂Cl₂): δ (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, OCH₂], 2.44 [m, 4H, CH₂P], 1.59 [m, 6H, CH₂], 1.63 [s, 12H, CCH₃]; δ (³¹P) = 36.93 (s). IR(Nujol): v(C=C)=2133 cm⁻¹. Analysis for C₅₉H₅₈O₂P₂Au₂: calcd. C 56.47, H 4.66; found C 56.26, H 4.86.

 $(CH_2)_6 PPh_2)$], **7e**, from **4** (0.210 g, 0.26 mmol) and Ph₂P(CH₂)₆PPh₂ (0.117 g, 0.26 mmol). Yield: 0.168 g, 51%. NMR (CD₂Cl₂): δ (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, OCH₂], 2.32 [m, 4H, CH₂P], 1.39 [m, 8H, CH₂], 1.63 [s, 12H, CCH₃]; δ (³P) = 38.03 (s). IR(Nujol): ν (C=C) = 2134 cm⁻¹. Analysis for C₆₀H₆₀O₂P₂Au₂: calcd. C 56.79, H 4.77; found C 57.17, H 5.04.

[1,4-C₆H₄CMe₂-4-C₆H₄OCH₂C \equiv C-Au)₂(µ-trans-Ph₂-PCH=CHPPh₂)], **7f**, from **4** (0.400 g, 0.49 mmol) and trans-Ph₂PCH=CHPPh₂ (0.195 g, 0.49 mmol). Yield: 0.318 g, 54%. NMR (CD₂Cl₂): δ (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, OCH₂], 1.60 [s, 12H, CCH₃]; δ (³¹P) = 33.47 (s). IR(Nujol): ν (C \equiv C) = 2134 cm⁻¹. Analysis for C₅₆H₅₀O₂P₂Au₂: 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-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K_4)_2(\mu-Ph_2PCH_2-K$

*PPh*₂)}₂*J*, **8a**. A solution of Ph₂PCH₂PPh₂ (0.176 g, 0.46 mmol) in CH₂Cl₂ (10 ml) was added to a suspension of complex **5** (0.300 g, 0.46 mmol) in CH₂Cl₂ (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 (CD₂Cl₂): δ (¹H)= 7.27 − 7.61 [m, 24H, Ph, Ar], 6.90 [d, 4H, ³J = 8.8 Hz, ArH), 4.80 [s, 4H, OCH₂], 3.62 [t, 2H, ³J(PH) = 11.2 Hz, CH₂P]; δ (³¹P) = 32.99 (s). IR(Nujol): v(C≡C) = 2124 cm⁻¹. Analysis for C₄₃H₃₄O₂P₂Au₂: 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, ³*J*(HH) = 8 Hz, Ar], 4.81 [s, 4H, OCH_2], 2.62 [sbr, 4H, CH_2P]; $\delta(^{31}P) = 39.86$ (s). IR(Nujol): $v(C\equiv C)=2133$ cm⁻¹. Analysis for C₄₄H₃₆O₂P₂Au₂: calcd. C 50.21, H 3.45; found C 50.52, H 3.41.

[4,4'-C₆H₄C₆H₄(*OC*H₂C \equiv C-*Au*)₂(μ -*Ph*₂*P*(*C*H₂)₃*P*-*Ph*₂)], **8c**, from **5** (0.500 g, 0.76 mmol) and Ph₂P(CH₂)₃PPh₂ (0.315 g, 0.76 mmol). Yield: 0.457, 56%. NMR (CD₂Cl₂): δ (¹H)= 7.3 - 7.6 [m, 24H, Ph, Ar], 7.03 [d, 4H, ³*J*(HH) = 9 Hz, Ar], 4.73 [s, 4H, OCH₂], 2.76 [m, 4H, CH₂P], 1.83 [m, 2H, CH₂P]; δ (³¹P) = 34.62 (s). IR(Nujol): ν (C \equiv C)=2120 cm⁻¹. Analysis for C₄₅H₃₈O₂P₂Au₂: 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 ₂ Cl ₂	8a
Empirical formula	$C_{58}H_{54}Au_2Cl_4O_2P_2$	C86H68Au4O4P4
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)
Ζ	4	4
Density	1.714	1.576
(calculated) [g/cm ³]		
Absorption	5.779	6.801
coefficient [mm ⁻¹]		
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'-C₆H₄C₆H₄(*O*CH₂C≡*C*-*Au*)₂(μ -*Ph*₂*P*(*CH*₂)₄*P*-*Ph*₂)], **8d**, from **5** (0.500 g, 0.76 mmol) and Ph₂P(CH₂)₄PPh₂ (0.326 g, 0.76 mmol). Yield: 0.464, 56%. NMR (CD₂Cl₂): δ (¹H)= 7.3 – 7.6 [m, 24H, Ph], 7.05 [s, 4H, ³*J*(HH) = 9 Hz, Ar], 4.82 [s, 4H, OCH₂], 2.39 [m, 4H, CH₂P], 1.68 [m, 4H, CH₂]; δ (³¹P) = 36.82 (s). IR(Nujol): ν (C≡C) = 2133 cm⁻¹. Analysis for C₄₆H₄₀O₂P₂Au₂: calcd. C 51.12, H 3.73; found C 51.41, H 4.04.

[4,4'-C₆H₄C₆H₄(*O*CH₂C≡*C*-*Au*)₂(μ -*Ph*₂*P*(CH₂)₅*P*-*Ph*₂)], **8e**, from **5** (0.250 g, 0.38 mmol) and Ph₂P(CH₂)₅PPh₂ (0.174 g, 0.38 mmol). Yield: 0.262 g, 62%. NMR (CD₂Cl₂): δ (¹H)= 7.4 – 7.6 [m, 24H, Ph, Ar], 7.05 [s, 4H, ³*J*(HH) = 8 Hz, Ar), 4.81 [s, 4H, OCH₂], 2.35 [m, 4H, CH₂P], 1.53 [m, 6H, CH₂]; δ (³¹P) = 35.21 (s). IR(Nujol): ν (C≡C)=2132 cm⁻¹. Analysis for C₄₈H₄₂O₂P₂Au₂: calcd. C 51.57, H 3.87; found C 51.98, H 3.84.

[4,4'-C₆H₄C₆H₄(*OC*H₂C≡*C*-*Au*)₂(μ -*Ph*₂*P*(*C*H₂)₆*P*-*Ph*₂)], **8f**, from **5** (0.300 g, 0.46 mmol) and Ph₂P(*C*H₂)₆PPh₂ (0.208 g, 0.46 mmol). Yield: 0.370 g, 73%. NMR (CD₂Cl₂): $\delta^{(1}$ H)= 7.4 – 7.6 [m, 24H, Ph], 7.06 [d, 4H, ³*J*(HH) = 8 Hz, Ar], 4.82 [s, 4H, OCH₂], 2.35 [m, 4H, CH₂P], 1.50 [m, 4H, CH₂], 1.37 [m, 4H, CH₂]; $\delta^{(31}$ P) = 33.15 (s). IR(Nujol): ν (C≡C) = 2134 cm⁻¹. Analysis for C₅₀H₄₄O₂P₂Au₂: calcd. C 52.00, H 4.00; found C 51.89, H 3.76.

[4,4'-C₆H₄C₆H₄(*OC*H₂C \equiv C-Au)₂(μ -trans-Ph₂PCH= CHPPh₂)], **8g**, from **5** (0.500 g, 0.76 mmol) and trans-Ph₂ PCH=CHPPh₂ (0.303 g, 0.76 mmol). Yield: 0.459 g, 57%. NMR (CD₂Cl₂): δ (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, OCH₂]; δ (³¹P) = 34.80 (s). IR(Nujol): $v(C\equiv C)=2133 \text{ cm}^{-1}$. 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-C₁₀H₆(*OCH*₂C≡*C*-*Au*)₂(μ -*Ph*₂*P*(*CH*₂)₂*PPh*₂)], **9a.** A solution of Ph₂P(CH₂)₂PPh₂ (0.400 g, 0.64 mmol) in CH₂Cl₂ (10 ml) was added to a suspension of **6** (0.253 g, 0.64 mmol) in CH₂Cl₂ (10 ml). The product was isolated as above as a colorless solid. Yield: 0.379 g, 58%. NMR (CD₂Cl₂): δ (¹H)=7.82 [d, 2H, ³J(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, CH₂O], 2.62 [sbr, 4H, CH₂P]; δ (³¹P) = 39.95 (s). IR(Nujol): ν (C≡C) = 2133 cm⁻¹. Analysis for C₄₂H₃₄O₂P₂Au₂: 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): $\delta(^1\text{H}) = 7.80$ [d, 2H, $^3J(\text{HH}) = 8$ 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, CH₂O], 2.70 [sbr, 4H, CH₂P], 1.79 [sbr, 2H, CH₂P]; $\delta(^{31}\text{P}) = 35.10$ (s). IR(Nujol): $\nu(C\equiv C) = 2134$ cm⁻¹. Analysis for C₄₃H₃₆O₂P₂Au₂: calcd. C 49.63, H 3.49; found C 50.10, H 3.50.

[1,5-C₁₀H₆(*OCH*₂C≡*C*-*Au*)₂(μ -*Ph*₂*P*(*CH*₂)₄*PPh*₂)], **9c**, from **6** (0.400 g, 0.64 mmol) and Ph₂P(CH₂)₄PPh₂ (0.271 g, 0.64 mmol). Yield: 0.369 g, 55%. NMR (CD₂Cl₂): δ (¹H) = 7.81 [d, 2H, ³*J*(HH) = 8 Hz, ArH_{4,8}], 7.35 - 7.57 [m, 22H, Ph and ArH_{3,7}], 7.05 [d, 2H, ³*J*(HH) = 8 Hz, ArH_{2,6}], 4.98 [s, 4H, CH₂O], 2.38 [m, 4H, CH₂P], 1.63 [m, 4H, CH₂]; δ (³¹P) = 36.90 (s). IR(Nujol): ν (C≡C) = 2133 cm⁻¹. Analysis for C₄₄H₃₈O₂P₂Au₂: calcd. C 50.11, H 3.63; found C 50.16, H 3.52.

 $\begin{array}{l} [1,5\text{-}C_{10}H_6(OCH_2C\equiv C\text{-}Au)_2(\mu\text{-}Ph_2P(CH_2)_5PPh_2)], \, \textbf{9d}, \\ \text{from } \mathbf{6} \quad (0.200 \ \text{g}, \ 0.32 \ \text{mmol}) \quad \text{and} \quad Ph_2P(CH_2)_5PPh_2 \\ (0.144 \ \text{g}, 0.32 \ \text{mmol}). \ \text{Yield:} \ 0.148 \ \text{g}, 44\% \ \text{NMR} \ (CD_2Cl_2): \\ \delta(^1\text{H}) = 7.85 \ \text{[d}, 2\text{H}, \ ^3J(\text{HH}) = 8 \ \text{Hz}, \ \text{ArH}_{4,8}], \ 7.36 - 7.63 \\ \text{[m}, 22\text{H}, \ \text{Ph} \ \text{and} \ \text{ArH}_{3,7}], \ 7.06 \ \text{[d}, 2\text{H}, \ ^3J = 8 \ \text{Hz}, \ \text{ArH}_{2,6}], \\ 5.08 \ \text{[s}, \ 4\text{H}, \ \text{CH}_2\text{O}], \ 2.14 \ \text{[sbr}, \ 4\text{H}, \ \text{CH}_2\text{P}], \ 1.42 \ \text{[sbr}, \ 6\text{H}, \\ \text{CH}_2\text{P}]; \ \delta(^{31}\text{P}) = 37.80 \ (\text{s}). \ \text{IR}(\text{Nujol}): \ \nu(C\equiv\text{C}) = 2133 \ \text{cm}^{-1}. \\ \text{Analysis for} \ C_{45}\text{H}_{40}\text{O}_2\text{P}_2\text{Au}_2: \ \text{calcd.} \ \text{C} \ 50.58, \ \text{H} \ 3.77; \ \text{found} \\ \text{C} \ 50.10, \ \text{H} \ 3.52. \end{array}$

[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 Ph₂P(CH₂)₆PPh₂ (0.144 g, 0.32 mmol). Yield: 0.199 g, 58%. NMR (CD₂Cl₂): δ (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, CH₂O], 2.31 [sbr, 4H, CH₂P], 1.52 [sbr, 8H, CH₂]; δ (³¹P) = 37.54 (s). IR(Nujol): v(C \equiv C)=2133 cm⁻¹. Analysis for C₄₆H₄₂O₂P₂Au₂: 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- $Ph_2PCH=$ CHPPh₂ (0.189 g, 0.48 mmol). Yield: 0.318 g, 65%. NMR (CD₂Cl₂): $\delta(^{1}\text{H}) = 7.82$ [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, CH₂O]; $\delta(^{31}\text{P}) = 21.27$ (s). IR(Nujol): $\nu(\text{C=C}) = 2133$ cm⁻¹. Analysis for C₄₂H₃₂O₂P₂Au₂: 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**:

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Crystals of $[1,4-C_6H_4CMe_2-4-C_6H_4OCH_2C\equiv C-Au)_2(\mu$ trans-Ph2PCH=CHPPh2)] were grown by slow diffusion of ether into a solution of 7f in CH₂Cl₂. 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 CH₂Cl₂ were refined with anisotropic thermal motion, with fixed C-Cl bond lengths of 1.76(2) Å. **5a**: Crystals of $[Au_2(\mu CCCH_2OC_6H_4C_6H_4OCH_2CC)_2(\mu-Ph_2PCH_2PPh_2)_2$] were grown by slow diffusion of ether into a solution of 8a in CH₂Cl₂ 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 Å³ in size) at (0,0,0) and (1/2, 1/2, 1/4). For each void 93 electrons were removed $(CH_2Cl_2 = 42 e and ether = 42 e).$

Acknowledgements

We thank the NSERC (Canada) for financial support and for a scholarship to WH. RJP thanks the Government of Canada for a Canada Research Chair.

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