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Macrocyclic gold(I) complexes and [2]catenanes containing carbonyl functionalized diacetylide ligands

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Abstract

The carbonyl derivatized bis(alkyne) O=C(4-$C_6H_4OCH_2C{\equiv}CH)_2$ was converted into the imine derivatives RN=C(4-$C_6H_4OCH_2C{\equiv}CH)_2$ [R = OH, $NHC(O)NH_2$, NHC_6H_3-2,4-$(NO_2)_2$] and into the 4-bromomethyl-1,3-dioxolane derivative $BrCH_2C_2H_3O_2C$(4-$C_6H_4OCH_2C{\equiv}CH)_2$. The alkyne units in these compounds react with [AuCl(SMe_2)] in the presence of base to form the corresponding digold(I) diacetylide complexes, that exist as insoluble oligomers or polymers. They reacted with the diphosphines Ph_2PZPPh_2 [Z = CC, *trans*-HC=CH and $(CH_2)_n$, $n = 3–5$] to give macrocyclic gold(I) complexes of the type [Au_2(μ-LL)(μ-PP)], where LL is the diacetylide and PP the diphosphine ligand. The ability of these macrocyclic complexes to self-assemble to [2]catenanes has been studied. The ketone and imine derivatives do not form [2]catenanes because the orientation of the aryl groups is unfavorable, but the 1,3-dioxolane derivatives may catenate if the ring size is optimum.

Keywords: Gold; Acetylide; Macrocycle; [2]Catenane; Self-assembly

1. Introduction

The vast majority of known catenanes, which are of current interest as supramolecular compounds with potential applications in nanoscale devices, are based on organic or inorganic molecules [1–7]. The first organometallic [2]catenane was reported in 1993 [8]. Several elegant strategies for synthesis of [2]catenanes have been developed and, if the [2]catenane is to be thermodynamically favored with respect to the separate ring complexes, it is recognized that inter-ring secondary bonding forces, such as π–π interactions, dipole–dipole attractions or hydrogen bonding, should operate in such a way as to counteract the usual entropy effects that favor dissociation [6,7].

Linear gold(I) units are versatile building-blocks for constructing organometallic network polymers and rings because of favorable geometry, low steric effects and the potential to bind to other gold(I) units through aurophilic attractions [9,10]. These secondary gold–gold bonds typically have energies of 7–11 kcal mol^{-1} with gold–gold distances ranging from 2.75 to 3.40 Å [11], and they can be very useful in self-assembly of complex structures. For example, aurophilic attractions play a part in favoring [2]catenane formation from gold(I) macrocycles, and the effect has been exploited in the synthesis of several organometallic [2]catenanes containing gold(I) centers and diacetylide bridging ligands [12–15]. It has been shown that both the 'hinge group' in the diacetylide ligand (X, Scheme 1) and the 'spacer group' between the phosphorus atoms (Z, Scheme 1) are important in determining whether macrocyclic complexes or [2]catenanes are formed as major components in the equilibrium of Scheme 1. Short and sterically demanding spacer groups such as $(CH_2)_2$, HC=CH, C≡C and [Fe($C_5H_4)_2$] favor macrocycles, while longer

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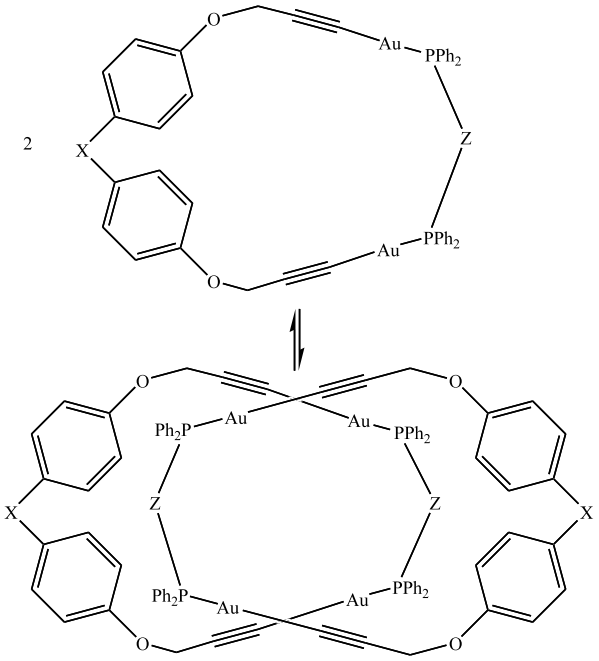


Scheme 1. X, hinge group; Z, spacer group.

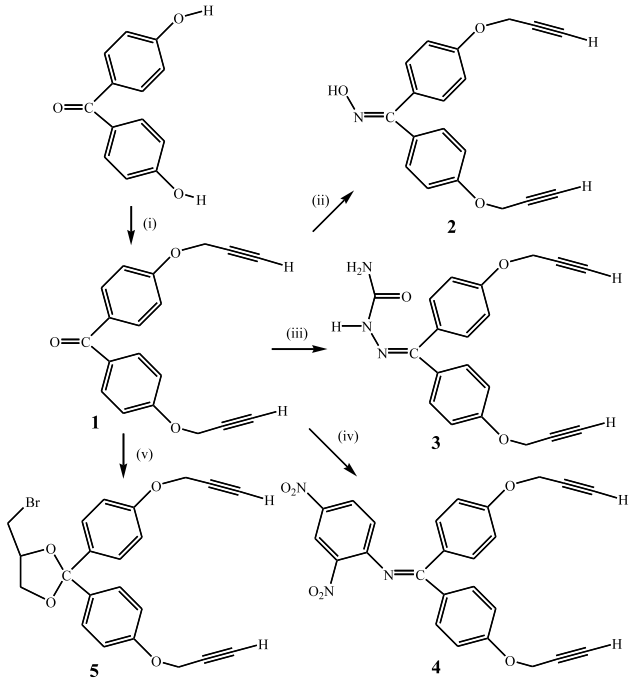
spacer groups such as $(CH_2)_4$ and $(CH_2)_5$ may favor the [2]catenanes, depending on the nature of the hinge group. The case where the spacer group is $(CH_2)_3$ often leads to an equilibrium containing both the macrocycle and [2]catenane, and sometimes more complex products [12–15]. The hinge group effect controls the twist of the aryl rings of the diacetylide units with respect to the XC_2 plane (Scheme 1). Twist angles of both aryl groups in the range 45–90° are good for [2]catenane formation, but one or more such angles that are close to zero are not because the macrocycle cavity is blocked by the in-plane aryl group [12–16]. The unfavorable twist arises when the group X can form π-bonds and so conjugate with one of the adjacent aryl groups. This π-bonding often leads to twist angles close to 0 and 90° for the two aryl groups, and the result is that no catenanes are formed with π-donor hinge groups X = O or S [12–16].

The aim of the present work was to prepare a series of digold(I) macrocycles derived from the diacetylene precursor $O{=}C(4\text{-}C_6H_4OCH_2CCH)_2$, in which the hinge group X is a carbonyl group. Since the carbonyl group is unsaturated it was considered unlikely that it would form [2]catenanes, but the carbonyl group can be transformed into a variety of other functional groups [17]. Some of these, including imine derivatives such as oximes, semicarbazones, and 2,4-dinitrophenylhydrazones, would retain the unsaturation of the hinge group but others, such as cyclic ketal derivatives formed by reaction with diols or epoxides [18], would not and so might favor self-assembly to [2]catenanes. Hence, the current hypotheses about [2]catenane formation [12–16] can be tested and perhaps a catenation switch or trigger might be developed by converting an unsaturated to a saturated hinge group X.

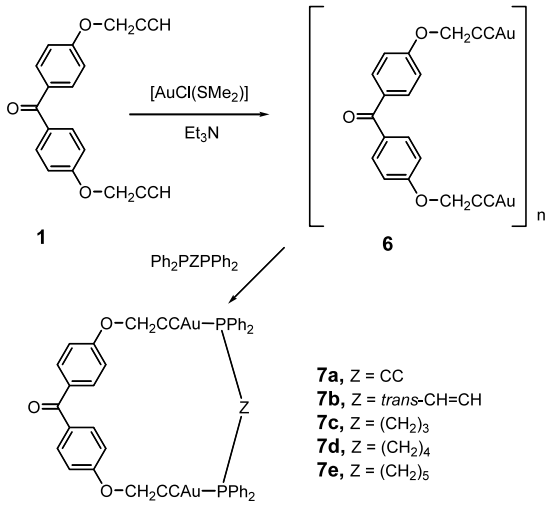
2. Results and discussion

The starting bis(alkyne) $O{=}C(4\text{-}C_6H_4OCH_2CCH)_2$, **1**, was prepared in almost quantitative yield by the reaction of $O{=}C(4\text{-}C_6H_4OH)_2$ with propargyl bromide and potassium carbonate [19]. Compound **1** could then be converted into the corresponding imine derivatives $RN{=}C(4\text{-}C_6H_4OCH_2CCH)_2$ [R = OH, **2**; $NHC(O)NH_2$, **3**; $NH\{C_6H_3\text{-}2,4\text{-}(NO_2)_2\}$, **4**]. Compounds **2** and **3** were formed by reaction of **1** with hydroxylamine hydrochloride or semicarbazide hydrochloride respectively in the presence of base, while **4** was prepared by reaction of **1** with 2,4-dinitrophenylhydrazine (DNP) under acidic conditions. The 4-bromomethyl-1,3-dioxolane (**5**) was prepared by the tin(IV)chloride catalysed reaction of (**1**) with epibromohydrin (Scheme 2) [20]. The bis(alkynes) were readily characterized by their using ^1H and ^{13}C NMR spectra, IR and mass spectra (Section 3). Attempts to prepare dioxolanes by reaction of **1** with diols (ethylene glycol, propylene glycol) were unsuccessful, since complete conversion was difficult to achieve and the products hydrolysed partly during chromatography.

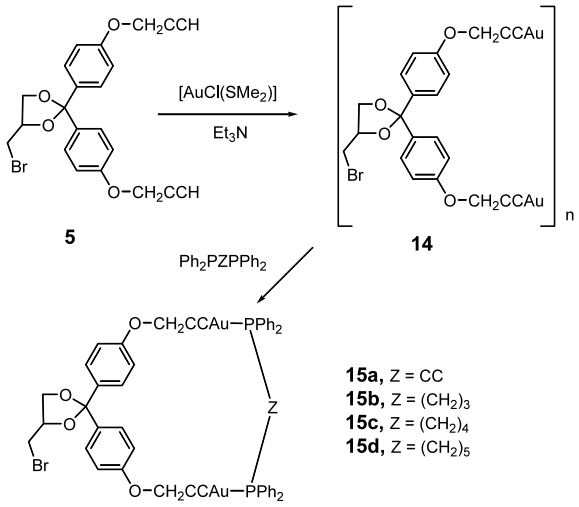
Reaction of the bis(alkyne) **1** with $[AuCl(SMe_2)]$ in the presence of Et_3N gave the corresponding yellow, insoluble oligomeric digold(I) diacetylide complex [{O=



Scheme 2. Reagents: (i) $BrCH_2CCH$, K_2CO_3; (ii) $HONH_2{\cdot}HCL$; (iii) $H_2NC(=O)NHNH_2{\cdot}HCL$; (iv) $H_2NNHC_6H_3(NO_2)_2$; (v) $BrCH_2CHCH_2O$.



Scheme 3.

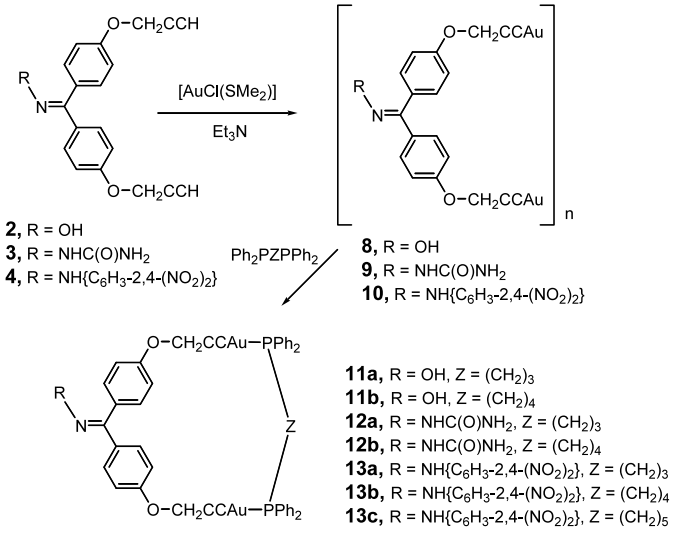


Scheme 5.

$C(4\text{-}C_6H_4OCH_2CCAu)_2\}_n$], **6**, that could be converted to the soluble diphosphine derivatives **7a**–**7e** according to Scheme 3. Similarly the imine derivatives **2**–**4** could be converted to the insoluble digold(I) oligomers [{RN=$C(4\text{-}C_6H_4OCH_2CCAu)_2\}_n$] [R = OH, **8**; R = $NHC(O)NH_2$, **9**; R = $NH\{C_6H_3\text{-}2,4\text{-}(NO_2)_2\}$, **10**, and then to the corresponding soluble diphosphine derivatives **11**–**13** (Scheme 4). Finally, the ketal derivative **5** was converted to the digold(I) derivative **14** and then to the diphosphine derivatives **15a**–**15d** according to Scheme 5. These reactions all occurred in high yields.

The IR spectrum of each of the oligomeric digold(I) complexes **6**, **8**–**10**, **14** shows a weak $\nu(C{\equiv}C)$ stretch at ca. 2000 cm^{-1}, considerably lower (ca. 100 cm^{-1}) than those of the precursor bis(alkyne) compounds **2**–**5**. This lowering of the C≡C stretch is characteristic for the alkynyl group acting as a π-donor to the gold(I) centers [21]. For example, bis(alkyne) **1** and its digold(I) derivative **6** gave $\nu(C{\equiv}C) = 2121$ and 2008 cm^{-1}, respectively. The organic functional groups gave IR bands in the expected regions. For example, the oligomeric complex **6** gave $\nu(C{=}O) = 1647$ cm^{-1} for the ketone group. None of these oligomeric complexes was sufficiently soluble to allow characterization by NMR.

The soluble ketone complexes **7a**–**7e** each give a singlet in the ^{31}P NMR spectra and a single resonance for the OCH_2 protons of the propargyl groups in the ^1H NMR spectra, assigned to the simple macrocyclic compounds. The macrocycles evidently have effective C_{2v} symmetry in solution, as expected [12–16]. The structure of complex **7e**, containing the diphosphine ligand $Ph_2P(CH_2)_5PPh_2$, was confirmed crystallographically (Fig. 1Table 1) and shown to contain a 26-membered macrocyclic ring.



Scheme 4.

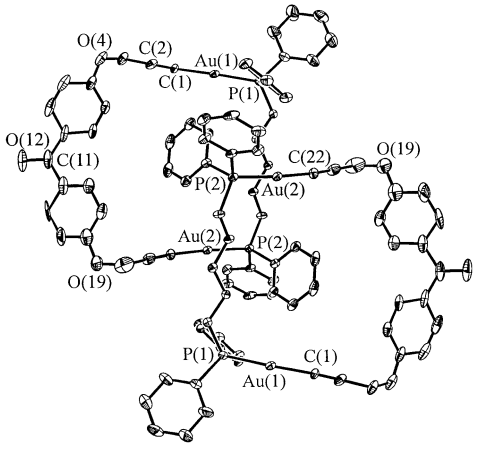


Fig. 1. A view of the structure of complex **7e**, showing two adjacent macrocyclic rings. The closest approach of two gold atoms is the intermolecular distance Au–Au = 6.99 Å; the transannular distance Au–Au = 8.61 Å.

Table 1
Selected bond distances (Å) and angles (°) in complex **7e**

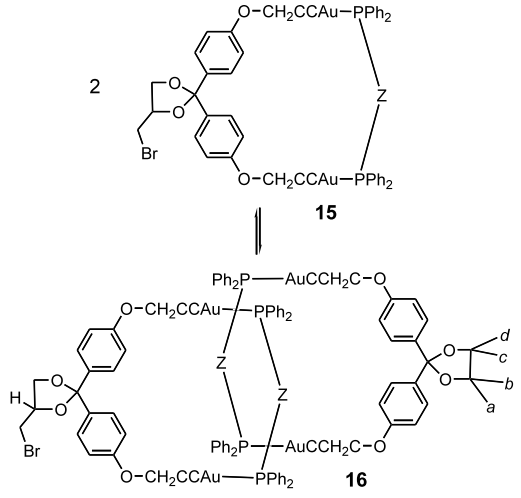
Au(1)–C(1)	2.028(9)	Au(2)–C(22)	2.010(10)
Au(1)–P(1)	2.280(2)	Au(2)–P(2)	2.269(3)
C(1)–C(2)	1.18(1)	C(21)–C(22)	1.19(1)
C(11)–O(12)	1.22(2)		
C(1)–Au(1)–P(1)	176.7(3)	C(22)–Au(2)–P(2)	174.5(3)
C(2)–C(1)–Au(1)	177(1)	C(21)–C(22)–Au(2)	175(1)
C(1)–C(2)–C(3)	179(1)	C(22)–C(21)–C(20)	173(2)
O(12)–C(11)–C(10)	122(2)	O(12)–C(11)–C(13)	119(2)
C(10)–C(11)–C(13)	120(1)		

Fig. 1 shows two neighboring rings of complex **7e** that clearly do not catenate. The intramolecular gold–gold distance is 8.61 Å and the closest intermolecular gold–gold distance is 6.99 Å, indicating the absence of aurophilic attractions. The neighboring rings pack so that the phenyl group of one ring partially penetrates the cavity of the other (Fig. 1). The twist angles of the two aryl rings with respect to the plane of the hinge atom C(11) are 40 and 24°, and so are in the range that does not favor catenane formation [12–16]. The ring size is certainly large enough to allow catenation, the minimum ring size being established as 24-membered [12–16], so the unfavorable orientation of the aryl groups arising from conjugation with the carbonyl group is presumed to disfavor the threading needed for catenation.

The imine complexes **11**–**13** (Scheme 4), as a consequence of the presence of the angular =NR groups, have lower symmetry (C_s) compared to the ketone derivatives **7** (C_{2v}). Hence they are expected to give two resonances in the ^{31}P NMR spectra and two OCH_2 resonances in the ^{1}H NMR spectra and, in favorable cases, this pattern was observed. For example, complex **13a** gave two singlet resonances in the ^{31}P NMR at $\delta =$ 38.28 and 38.45, and two singlet OCH_2 resonances in the ^{1}H NMR spectrum at $\delta = 4.88$ and 4.96. In many cases, only one ^{31}P resonance was observed. For example, complex **11a** gave a singlet resonance at $\delta = 37.22$ in the ^{31}P NMR, though the overall C_s symmetry is shown by the presence of two OCH_2 resonances in the ^{1}H NMR at $\delta = 4.79$ and 4.85. Low temperature ^{31}P NMR spectra of complex **11a** also gave only one ^{31}P resonance, so it is likely that the chemical shifts are accidentally degenerate rather than that the phosphine groups are fluxional at room temperature. The NMR data for the imine complexes do not indicate formation of [2]catenanes, and MALDI-TOF MS give parent ions for the macrocyclic complexes **11**–**13** but no evidence for the [2]catenanes. The [2]catenanes would be expected to be topologically chiral and so should give more complex NMR spectra than those observed. No crystals suitable for structure determination were obtained for these complexes, but it is likely that the aryl twist angles are similar to those for the ketone derivatives and in the range that does not favor catenation.

The cyclic ketal complexes **15** have the lowest symmetry of the macrocycles prepared. The presence of the chiral C*H(CH_2Br)(O)(CH_2) center causes the complexes to have C_1 symmetry, with all atoms inequivalent except for equivalent protons and carbon atoms of the individual aryl groups. A [2]catenane could then give four geometrical isomers since all four possible positions of the CH_2Br group on the second ring are inequivalent (Scheme 6). The complex with the ligand $Ph_2PCCPPh_2$ gave the macrocycle **15a** whose ^{1}H NMR spectrum reflected the expected low symmetry but whose ^{31}P NMR spectrum gave only a singlet, presumably as a result of accidental degeneracy of the chemical shifts. The structure of complex **15a** was determined and is shown in Fig. 2A, with selected bond distances and angles in Table 2. The complex exists in the form of a 23-membered macrocycle. There was disorder of the atoms of the cyclic ketal unit and the associated bromomethyl group, and these atoms are less well defined than the rest of the structure.

Individual rings are twisted to allow bridging by the short-bite and rigid diphosphine ligand $Ph_2PCCPPh_2$, as is most clearly seen in the side view of Fig. 2B. The individual macrocycles are ordered into chains through strong inter-ring aurophilic attractions with Au···Au = 3.0414(8) Å as shown in Fig. 2B and C. Within each chain, the molecules are related by a screw axis and so have the same chirality (isotactic), but neighboring chains have opposite chirality. It should be noted, however, that the ketal units are disordered and so the symmetry of these chains is almost certainly less than the crystallographic ideal. The twist angle for each of the aryl groups with respect to the hinge unit in **15a** is 74°, and this conformation is one that should favor catenation. The 23-membered ring with the rigid, short-bite



Scheme 6. Four isomers of **16** can have CH_2Br group in positions a–d.

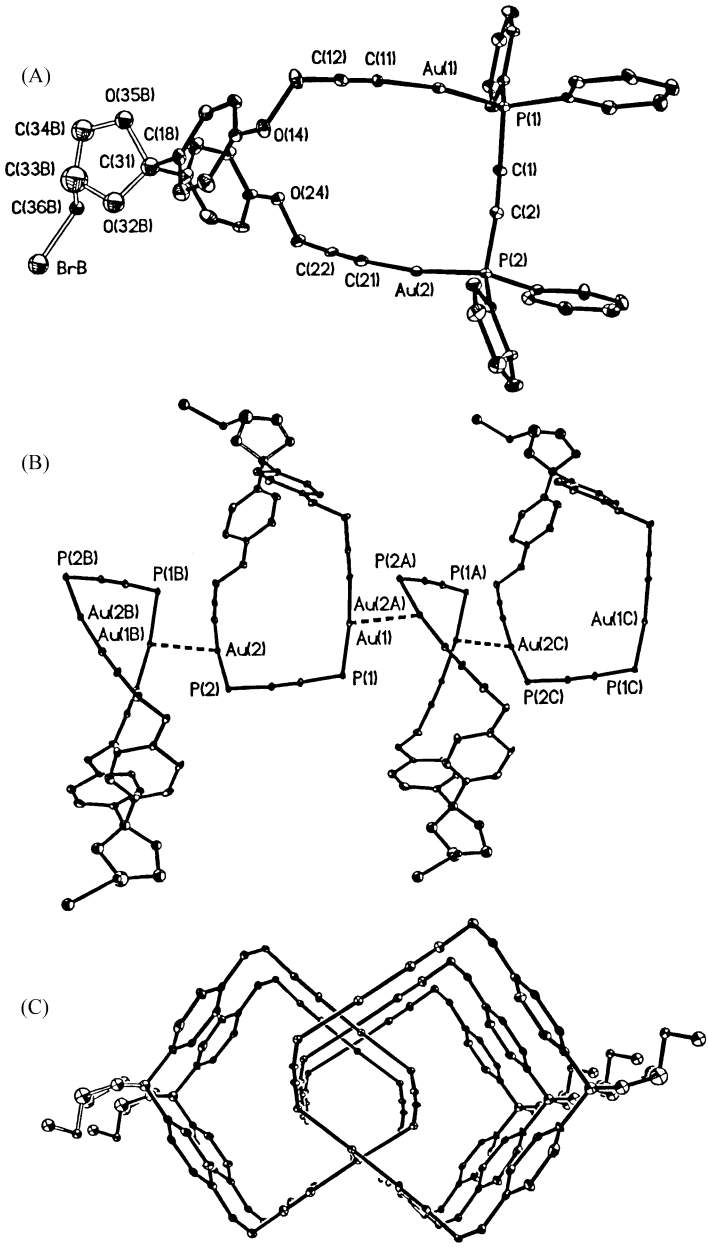


Fig. 2. The structure of complex **15a**. (A) The 23-membered macrocycle, with one component of the disordered cyclic ketal unit. (B) A side view of four adjacent macrocycles, showing the ring twist and the aurophilic bonds that link the macrocycles [Au(1)–Au(2) = 3.0414(8) Å]. (C) A top view along the chain direction. In (B) and (C) the phenyl groups are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) in complex **15a**

Au(1)–C(11)	2.01(2)	Au(2)–C(21)	2.01(3)
Au(1)–P(1)	2.273(5)	Au(2)–P(2)	2.269(5)
C(1)–C(2)	1.20(2)	C(11)–C(12)	1.17(2)
Au(1)–Au(2A)	3.0414(8)		
C(11)–Au(1)–P(1)	172.3(4)	C(21)–Au(2)–P(2)	171.8(5)
C(2)–C(1)–P(1)	177(2)	C(1)–C(2)–P(2)	174(2)
C(12)–C(11)–Au(1)	175(1)	C(22)–C(21)–Au(2)	176(2)
C(11)–C(12)–C(13)	176(2)	C(21)–C(22)–C(23)	178(2)

diphosphine does not form a large enough cavity however, so no catenation can occur.

The corresponding complex with the ligand $Ph_2P(CH_2)_3PPh_2$ was formed as a mixture of isomers, but crystallization gave the pure [2]catenane **16b**. This complex is sparingly soluble in CD_2Cl_2 but a freshly prepared solution gave the spectrum of the [2]catenane only. The ^{31}P NMR spectrum contained only a singlet at $\delta = 31.91$, while the same number of ring resonances as for the simple macrocycle **15a** was observed. More complex spectra were expected for **16b** since a mixture of several isomers is expected (Scheme 6). The presence

of the [2]catenane is signalled by the presence of much more shielded aromatic resonances compared to **15a**, arising because of the tight contact with phenylphosphorus groups of the interlocked ring [12–16]. Thus, **16b** has aromatic resonances *ortho* to oxygen at $\delta =$ 6.08, 6.10, whereas **15a** has these resonances at $\delta =$ 7.02, 7.05. Complex **16b** slowly equilibrated with a second isomer, identified as the simple macrocycle **15b**, over a period of days (Scheme 6). Complex **15b** had a ^{31}P NMR resonance at $\delta = 35.90$, and its aromatic resonances *ortho* to oxygen were at $\delta = 7.00$, 7.02. The structure of complex **16b** was determined and is shown in Fig. 3, with selected bond distances and angles in Table 3.

The structure is clearly a [2]catenane in which two 24-membered macrocycles are interlocked across the diphosphine ligand backbones. The catenane is stabilized by the presence of two close gold–gold contacts [Au(1)···Au(3) = 3.2672(4) Å and Au(2)···Au(4) = 3.2981(4) Å] as well as by several secondary phenyl-C_6H_4 and phenyl–phenyl interactions. There is considerable bowing of the CCAuP units, with angles CCAu and CAuP distorted from linearity and in the range 170–174°, in order to allow closer mutual approach of pairs of gold atoms.

The twist angles of the aryl groups with respect to the hinge atom plane in **16b** are 84, 86° for ring A and 77, 81° for ring B, in the range that favors [2]catenane formation [12–16]. These angles are not very different from the twist angles for **15a** of 74, 74°, but very different from those of the ketone derivative **7e** of 24, 40°. Hence, in these compounds, the aryl twist angles are primarily determined by the nature of the bonding to the hinge group and the angles do not change markedly on [2]catenane formation.

The interesting problem of isomerism in **16b**, which contains two chiral carbon atoms and is also topologically chiral [16], is not fully resolved by the structure determination. The structure was modelled by a 50:50 disorder of the bromomethyl group between two positions on each ring, but there was also evidence for further unresolved disorder. It is likely therefore that all possible isomers are present and that they co-crystallize

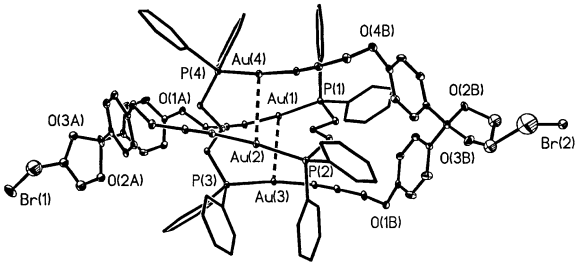


Fig. 3. The [2]catenane structure of complex **15b**, showing the interring aurophilic attractions [Au(1)–Au(3) = 3.2672(4); Au(2)–Au(4) = 3.2981(4) Å].

Table 3
Selected bond distances (Å) and angles (°) in complex **15b**

Au(1)–C(4A)	1.992(6)	Au(1)–P(1)	2.272(2)
Au(2)–C(13A)	1.998(7)	Au(2)–P(2)	2.275(2)
Au(3)–C(4B)	2.002(7)	Au(3)–P(3)	2.274(2)
Au(4)–C(13B)	1.998(7)	Au(4)–P(4)	2.277(2)
Au(1)–Au(3)	3.2672(4)	Au(2)–Au(4)	3.2981(4)
C(4A)–C(5A)	1.192(9)	C(12A)–C(13A)	1.198(10)
C(4B)–C(5B)	1.187(10)	C(12B)–C(13B)	1.183(9)
C(4A)–Au(1)–P(1)	170.9(2)	C(13A)–Au(2)–P(2)	171.9(2)
C(4B)–Au(3)–P(3)	171.9(2)	C(13B)–Au(4)–P(4)	173.5(2)
C(5A)–C(4A)–Au(1)	169.9(7)	C(12A)–C(13A)–Au(2)	172.7(7)
C(5B)–C(4B)–Au(3)	172.9(6)	C(12B)–C(13B)–Au(4)	173.2(7)
C(4A)–C(5A)–C(6A)	175.9(9)	C(13A)–C(12A)–C(11A)	176.1(7)
C(4B)–C(5B)–C(6B)	176.0(8)	C(13B)–C(12B)–C(11B)	176.8(8)
C(4A)–Au(1)–Au(3)	85.2(2)	C(13A)–Au(2)–Au(4)	84.3(2)
C(4B)–Au(3)–Au(1)	86.0(2)	C(13B)–Au(4)–Au(2)	81.1(2)
P(1)–Au(1)–Au(3)	102.73(5)	P(2)–Au(2)–Au(4)	102.97(5)
P(3)–Au(3)–Au(1)	101.96(5)	P(4)–Au(4)–Au(2)	104.99(5)

in a disordered manner. Only one component of the disorder of each ketal unit is shown in Fig. 3. It seems that the bromomethyl groups are far enough removed from the interlocking diphosphine groups that they can position themselves independently of one another, and that their position also has only local influence on the NMR parameters. The isomers will therefore have very similar energies and essentially identical NMR spectral properties.

Can the concept of a catenation switch be realized in this system? The principle is established since converting the ketone unit in **7c** to the ketal unit in **15b** should lead to partial [2]catenane formation, as shown by study of the separate systems. Unfortunately, the reaction conditions needed to effect the change in functional group (high temperature, acid catalyst) leads to decomposition of the gold acetylide units, so a direct demonstration was not possible. However, the ketal is susceptible to hydrolysis and a solution of **15b** in moist acetone/dichloromethane underwent slow hydrolysis with formation of **7c**. This then confirms that such transformations are possible, in this case involving decatenation. Success requires a labile metal center to allow easy threading/dethreading, and easy transformation between functional groups that favor or disfavor the catenation. It is likely that more successful catenation switches will be developed based on these principles.

3. Experimental

NMR spectra were recorded using Varian Mercury 400 and Inova 600 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane, while ^{31}P chemical shifts are reported relative to 85% H_3PO_4 as an external standard. IR

spectra were recorded using a Perkin Elmer 2000 FT-IR as KBr disks. MALDI-TOF mass spectra were recorded using a Micromass MALDI-LR instrument in positive ion mode. The samples were dissolved in CH_2Cl_2 and spotted onto a dried layer of matrix (1 ml α-cyano-4-hydroxycinnamic acid 10 mg/ml in CAN/EtOH 50:50). The samples were analysed in reflection mode and MS spectra were externally calibrated using a tryptic digest of alcohol dehydrogenase. All reactions involving gold complexes were carried out in reactions vessels shielded from light. The complex [AuCl(SMe$_2$)] was prepared by a literature procedure [22].

3.1. $O{=}C(4\text{-}C_6H_4OCH_2CCH)_2$, **1**

$BrCH_2C{\equiv}CH$ (2.2 g, 18.6 mmol) and K_2CO_3 (1.6 g, 13.7 mmol) was added to a solution of $OC(4\text{-}C_6H_4OH)_2$ (2.0 g, 9.3 mmol) in acetone (60 ml). The mixture was heated under reflux for about 24 h. The cooled solution was filtered to give a pale yellow filtrate. The solvent was removed under reduced pressure and the resultant off-white solid dried in vacuum. Yield: 2.6 g, 95%. ^{1}H NMR ($CDCl_3$) δ 2.58 (t, $J = 2.4$ Hz, 2H, ≡C*H*), 4.77 (d, $J = 2.4$ Hz, 4H, OCH_2), 7.03, 7.78 (d, $J = 8.6$ Hz, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 55.8 (O*C*H$_2$), 76.1 (≡*C*H), 77.8 (OCH$_2$*C*), 114.1, 131.1 131.9, 160.4 (*C*$_6$H$_4$), 193.9 (*C*=O); EI-MS *m*/*z* 291 [M]$^+$; IR (KBr disk, cm^{-1}) 3300, 3271 (s, ≡CH), 2121 (w, C≡C), 1646 (s, C=O).

3.2. $2,4\text{-}(NO_2)_2C_6H_3N{=}C(4\text{-}C_6H_4OCH_2CCH)_2$, **2**

2,4-Dinitrophenyl hydrazine (0.25 g, 1.26 mmol) was suspended in MeOH (5 ml) and concentrated sulfuric acid (0.5 ml) was added with cooling to give a yellow solution. To this was added suspension of **1** (0.35 g, 1.21 mmol) in MeOH (5 ml) and the mixture heated under reflux for 30 min. The resulting brick red precipitate was isolated by filtration and washed with water (200 ml). The dried solid was recrystallized from 1-BuOH to give 0.52 g (91%) brick red feathery needles. ^{1}H NMR (CD_2Cl_2) δ 3.15, 3.25 (t, $J = 2.4$ Hz, 1H, ≡C*H*), 4.78, 4.78 (d, $J = 2.4$ Hz, 2H, OCH_2), 7.10, 7.30, 7.45, 7.68 (d, $J = 8.6$ Hz, 4H, C_6H_4), 8.32 (d, $J = 9.4$ Hz, 1H, DNP), 8.44 (dd, $J = 9.8/2.7$ Hz, 1H, DNP), 8.95 (d, $J = 2.3$ Hz, 1H, DNP), 11.20 (s, 1H, N*H*); ^{13}C NMR (CD_2Cl_2) δ 56.41, 56.58 (O*C*H$_2$), 76.19, 76.42 (≡*C*H), 78.54, 78.65 (OCH$_2$*C*≡), 115.25, 116.68, 117.07, 123.94, 125.20, 129.94, 130.10, 130.41, 130.52, 130.89, 138.31, 145.10, 159.44, 159.84 (*C*$_6$H$_4$), 155.56 (*C*=N); EI-MS *m*/*z* 470 [M]$^+$; IR (KBr disk, cm^{-1}) 3310 (w, NH), 3290, 3271 (s, ≡CH), 2127 (w, C≡C); Anal. Found: C, 63.83; H, 3.86; N, 11.75. Calc. for $C_{25}H_{18}N_4O_6$: C, 63.83; H, 3.86; N, 11.91.

3.3. $HON{=}C(4\text{-}C_6H_4OCH_2CCH)_2$, **3**

A mixture of **1** (0.50 g, 1.72 mmol) and hydroxylamine hydrochloride (0.50 g, 7.30 mmol) in EtOH (10 ml) and pyridine (2.5 ml) was heated under reflux for 24 h. The solvents were removed under vacuum and water (30 ml) was added to the residue. The resulting oil was extracted into ether and the organic phase was washed with 5% HCl and water. Evaporation of the solvent gave a white solid (0.42 g, 80%). ^{1}H NMR (DMSO-d_6) δ 3.50, 3.53 (t, $J = 2.4$ Hz, 1H, ≡C*H*), 4.71, 4.75 (d, $J = 2.4$ Hz, 2H, OCH_2), 6.87, 6.94, 7.16, 7.21 (d, $J = 8.6$ Hz, 2H, C_6H_4), 11.00 (s, 1H, O*H*); ^{13}C NMR (DMSO-d_6) δ 55.27, 55.31 (O*C*H$_2$), 78.21 (≡*C*H), 78.92, 79.03 (OCH$_2$*C*≡), 114.00, 114.34, 125.96, 128.19, 129.97, 130.27, 156.69, 157.31 (*C*$_6$H$_4$), 153.89 (*C*=N); EI-MS *m*/*z* 305 [M]$^+$, 288 [M–OH]$^+$; IR (KBr disk, cm^{-1}) 3287 (s, ≡CH), 3070 (br, OH), 2125 (w, C≡C); Anal. Found: C, 74.77; H, 5.14; N, 4.88. Calc. for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.50.

3.4. $H_2NC(O)NHN{=}C(4\text{-}C_6H_4OCH_2CCH)_2$, **4**

This was prepared similarly from **1** (0.50 g, 1.72 mmol) and semicarbazide hydrochloride (0.50 g, 4.48 mmol). Yield: 0.40 g (67%). ^{1}H NMR (DMSO-d_6) δ 3.58, 3.65 (t, $J = 2.4$ Hz, 1H, C≡C*H*), 4.81, 4.89 (d, $J = 2.4$ Hz, 2H, OCH_2), 6.63 (br. s, 2H, NH_2), 6.94, 7.17, 7.22, 7.48 (d, $J = 8.6$ Hz, 4H, C$_6H_4$), 7.79 (br. s, 1H, N*H*); ^{13}C NMR (DMSO-d_6) δ 56.27, 56.35 (O*C*H$_2$), 79.16, 79.36 (≡*C*H), 79.81, 79.83 (OCH$_2$*C*≡), 115.19, 116.43, 125.32, 128.94, 130.48, 131.42, 158.34 (*C*$_6$H$_4$), 146.75 (C=N), 156.50 (*C*=O); HR-MS found *m*/*z* 347.12639, calculated for $C_{20}H_{17}N_3O_3$ *m*/*z* 347.12699; IR (KBr disk, cm^{-1}) 3476, 3454 (s, ≡CH), 3286, 3206 (br. s NH, NH$_2$), 2124 (w, C≡C), 1696 (s, C=O).

3.5. $OCH_2CH(CH_2Br)OC(4\text{-}C_6H_4OCH_2CCH)_2$, **5**

Stannic chloride (344 μl 1.0 M solution in CH_2Cl_2, 3.44 mmol) was added slowly to a solution of epibromohydrin (0.548 g, 4.00 mmol) and **1** (1.00 g, 3.44 mmol) in dichloromethane (20 ml). The reaction mixture was stirred at room temperature for 2.5 h, then neutralised by addition of potassium carbonate and concentrated in vacuum. Ether (30 ml) was added to the residue and the etheral extract was washed with water, dried and concentrated in vacuum to give a pale yellow oil (0.892 g, 61%). ^{1}H NMR (CD_2Cl_2) δ 2.57, 2.58 (m, 1H, ≡C*H*), 3.36, 3.52 (m, 1H, CH_2Br), 3.94, 4.01 (m, 1H, CHOCH_2), 4.43 (m, 1H, *H*C), 4.69, 4.70 (m, 2H, OCH_2C≡), 6.91, 6.94, 7.39, 7.41 (m, 2H, C$_6H_4$); ^{13}C NMR (CD_2Cl_2) δ 34.90 (*C*H$_2$Br), 55.84 (O*C*H$_2$C≡), 69.16 (CHO*C*H$_2$), 75.85 (H*C*), 76.27 (≡*C*H), 77.74 (*C*≡CH), 113.90, 114.22, 130.98, 132.01, 135.26, 135.58, 160.48 (*C*$_6$H$_4$); HR-MS found *m*/*z* 426.0467, calc. for

$C_{22}H_{19}BrO_4$ *m/z* 426.0467; IR (neat on NaCl plates, cm^{-1}) 3302 (s, ≡CH), 2123 (w, C≡C).

3.6. *[O=C(4-$C_6H_4OCH_2CCAu)_2]_n$*, **6**

To a solution of [(Me_2S)AuCl] (1.31 mmol) in THF (40 ml) and MeOH (20 ml) was added a solution of compound **1** (0.655 mmol) in THF (20 ml) and Et_3N (2.16 mmol, 0.3 ml). Instantly a yellow precipitate formed. The mixture was stirred for 2 h and then the precipitate isolated by filtration. The solid was washed with THF, MeOH, Et_2O and pentane and then dried in air. Yield: 80%. IR (KBr disk, cm^{-1}) 2008 (w, C≡C), 1647 (s, C=O); Anal. Found: C, 33.52; H, 1.72. Calc. for $C_{19}H_{12}Au_2O_3$: C, 33.45; H, 1.77.

Similarly were prepared: **[2,4-(NO_2)$_2C_6H_3$N=C(4-$_6H_4OCH_2CCAu)_2]_n$, 8**, IR (KBr disk, cm^{-1}) 3284 (m, NH), 2007 (w, C≡C), 1624 (s, C=N); Anal. Found: C, 34.38; H, 1.89; N, 6.33. Calc. for $C_{25}H_{16}Au_2N_4O_6$: C, 34.82; H, 1.87; N, 6.50. **[HON=C(4-$C_6H_4OCH_2C-CAu)_2]_n$, 9**, IR (KBr disk, cm^{-1}) 3382 (bs, OH), 2002 (w, C≡C). **[H_2NC(O)NHN=C(4-$C_6H_4OCH_2CCAu)_2]_n$, 10**, IR (KBr disk, cm^{-1}) 3479, 3348 (s, NH, NH_2), 2010 (w, C≡C), 1680 (s, C=O). **[OCH$_2$CH(CH$_2$Br)OC(4-$C_6H_4OCH_2CCAu)_2]_n$, 14**, IR (KBr disk, cm^{-1}) 2013 (w, C≡C); Anal. Found: C, 32.77; H, 2.03. Calc. for $C_{19}H_{12}Au_2O_3$: C, 32.26; H, 2.09.

3.7. *[O=C(4-$C_6H_4OCH_2CC)_2Au_2(Ph_2PCCPPh_2)$], 7a*

A mixture of digold(I) diacetylide oligomer [O=C(4-$_6H_4OCH_2CCAu)_2]_n$, **6** (0.108 mmol) and diphosphine $Ph_2PCCPPh_2$ (0.091 mmol) was stirred in CH_2Cl_2 (20 ml) for 3 h. After this time the resulting solution was filtered through Celite and concentrated in vacuum. Addition of pentane precipitated the product, which was isolated by filtration, washed with Et_2O and pentane, and dried under vacuum. Yield: 70%. Anal. Found: C, 49.95; H, 2.89. Calc. for $C_{45}H_{32}Au_2O_3P_2$: C, 50.20; H, 3.00. ^{1}H NMR (CD_2Cl_2) δ 4.88 (s, 4H, OCH_2), 7.21 (d, $J = 7.8$ Hz, 4H, C_6H_4), 7.46–7.60 (m, 12H, PPh_2), 7.68–7.75 (m, 8H, PPh_2), 7.77 (d, $J = 7.8$ Hz, 4H, C_6H_4); ^{31}P NMR (CD_2Cl_2) δ 18.25.

Similarly were prepared from the appropriate digold(I) diacetylide and diphosphine ligand: **7b**: Anal. Found: C, 50.02; H, 3.19. Calc. for $C_{45}H_{34}Au_2O_3P_2$: C, 50.11; H, 3.18. ^{1}H NMR (CD_2Cl_2) δ 4.87 (s, 4H, OCH_2), 6.97 (t, $J = 20.6$ Hz, 2H, HC=), 7.25 (d, $J = 8.7$ Hz, 4H, C_6H_4), 7.48–7.62 (m, 20H, PPh_2), 7.70 (d, $J = 8.7$ Hz, 4H, C_6H_4); ^{31}P NMR (CD_2Cl_2) δ 39.35. **7c**: Anal. Found: C, 49.99; H, 3.21. Calc. for $C_{46}H_{38}Au_2O_3P_2$: C, 50.47; H, 3.50. **7d**: Anal. Found: C, 50.44; H, 3.36. Calc. for $C_{47}H_{40}Au_2O_3P_2$: C, 50.91; H, 3.64. ^{1}H NMR (CD_2Cl_2) δ 1.78, 2.41 (br. s, 2H, CH_2), 4.89 (s, 4H, OCH_2), 7.20 (d, $J = 8.8$ Hz, 4H, C_6H_4), 7.43–7.68 (m, 20H, PPh_2), 7.79 (d, $J = 8.8$ Hz, 4H, C_6H_4); ^{31}P NMR (CD_2Cl_2) δ 38.69. **7e**: Anal. Found: C, 50.95; H, 3.73. Calc. for $C_{48}H_{42}Au_2O_3P_2$: C, 51.35; H, 3.77. ^{1}H NMR (CD_2Cl_2) δ 1.50 (br. s, 6H, CH_2), 2.29 (br. s, 4H, CH_2), 4.80 (s, 4H, OCH_2), 7.10 (d, $J = 8.6$ Hz, 4H, C_6H_4), 7.33–7.60 (m, 20H, PPh_2), 7.73 (d, $J = 8.6$ Hz, 4H, C_6H_4); ^{31}P NMR (CD_2Cl_2) δ 37.44. **11a**: Anal. Found: C, 50.01; H, 3.53; N, 1.02. Calc. for $C_{47}H_{41}Au_2NO_3P_2$: C, 49.77; H, 3.54; N, 1.26. ^{1}H NMR (CD_2Cl_2) δ 1.86 (br. s, 2H, CH_2), 2.77 (br. s, 4H, CH_2), 4.79, 4.85 (s, 2H, OCH_2), 6.84–7.77 (m, 28H, C_6H_4, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 34.54; MALDI-TOF MS (*m/z*) 1110 $[M+H]^+$. **11b**: Anal. Found: C, 44.76; H, 3.77; N, 1.03. Calc. for $C_{47}H_{41}Au_2NO_3P_2 \cdot 6H_2O$: C, 45.15; H, 4.44; N, 1.12. ^{1}H NMR (CD_2Cl_2) δ 1.74, 2.41 (br. s, 4H, CH_2), 4.80, 4.85 (s, 2H, OCH_2), 6.87–7.74 (m, 28H, C_6H_4, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 37.22; MALDI-TOF MS (*m/z*) 1124 $[M+H]^+$. **12a**: Anal. Found: C, 48.47; H, 3.68; N, 3.53. Calc. for $C_{47}H_{41}Au_2N_3O_3P_2 \cdot 1/4CH_2Cl_2$: C, 48.37; H, 3.58; N, 3.58. ^{1}H NMR ($CDCl_3$) δ 1.56 (br. s, 2H, CH_2), 2.64 (br. s 4H, CH_2), 4.82, 4.87 (s, 2H, OCH_2), 6.64 (d, $J =$ 9.4 Hz, 2H, C_6H_4), 7.42–7.76 (m, 29H, C_6H_4, PPh_2, NH_2, NH); ^{31}P NMR ($CDCl_3$) δ 35.45; MALDI-TOF MS (*m/z*) 1152 $[M+H]^+$. **12b**: Anal. Found: C, 49.03; H, 3.78; N, 3.55. Calc. for $C_{48}H_{43}Au_2N_3O_3P_2$: C, 49.43; H, 3.72; N, 3.61. ^{1}H NMR ($CDCl_3$) δ 1.58, 2.68 (br. s, 4H, CH_2), 4.75, 4.86 (s, 2H, OCH_2), 6.97 (d, $J = 9.4$ Hz, C_6H_4), 7.44–7.74 (m, 29H, C_6H_4, PPh_2, NH, NH_2); ^{31}P NMR ($CDCl_3$) δ 38.55; MALDI-TOF MS (*m/z*) 1166 $[M+H]^+$. **13a**: Anal. Found: C, 48.73; H, 3.30. Calc. for $C_{52}H_{42}Au_2N_4O_6P_2$: C, 48.97; H, 3.32. ^{1}H NMR ($CDCl_3$) δ 1.82, 2.76 (br. s, 4H, CH_2), 4.88, 4.96 (s, 2H, OCH_2), 7.18 (d, $J = 8.6$ Hz, 2H, C_6H_4), 7.41–7.68 (m, 24H, PPh_2, C_6H_4), 7.71 (d, $J = 8.6$ Hz, 2H, C_6H_4), 8.20 (d, $J = 9.6$ Hz, 1H, DNP), 8.34 (dd, $J = 9.6$, 2.7 Hz, 1H, DNP), 9.03 (d, $J = 2.7$ Hz, 1H, DNP), 11.19 (s, 1H, NH); ^{31}P NMR (CD_2Cl_2) δ 38.28, 38.45; MALDI-TOF MS (*m/z*) 1275 $[M+H]^+$. **13b**: Anal. Found: C, 45.25; H, 3.38; N, 3.48. Calc. for $C_{53}H_{44}Au_2N_4O_6P_2 \cdot 2CH_2Cl_2$: C, 45.32; H, 3.32; N, 3.85. ^{1}H NMR (CD_2Cl_2) δ 1.77, 2.39 (br. s, 4H, CH_2), 4.85, 4.96 (s, 2H, OCH_2), 7.16 (d, $J = 8.6$ Hz, 2H, C_6H_4), 7.41–7.68 (m, 24H, PPh_2, C_6H_4), 7.71 (d, $J = 8.6$ Hz, 2H, C_6H_4), 8.20 (d, $J = 9.6$ Hz, 1H, DNP), 8.34 (dd, $J = 9.6$, 2.7 Hz, 1H, DNP), 9.03 (d, $J =$ 2.7 Hz, 1H, DNP), 11.19 (s, 1H, NH); ^{31}P NMR (CD_2Cl_2) δ 38.28, 38.45; MALDI-TOF MS (*m/z*) 1289 $[M+H]^+$. **13c**: Anal. Found: C, 49.85; H, 3.57; N, 4.50. Calc. for $C_{54}H_{46}Au_2N_4O_6P_2$: C, 49.78; H, 3.56; N, 4.30. ^{1}H NMR (CD_2Cl_2) δ 1.57 (br. s, 6H, CH_2), 2.37 (br. s, 4H, CH_2), 4.84, 4.93 (s, 2H, OCH_2), 7.15–7.57 (m, 26H, PPh_2, C_6H_4), 7.64 (d, $J = 8.6$ Hz, 2H, C_6H_4), 8.19 (d, $J = 9.4$ Hz, 1H, DNP), 8.33 (dd, $J = 9.4$, 2.3 Hz, 1H, DNP), 9.02 (d, $J = 2.3$ Hz, 1H, DNP), 11.28 (s, 1H, NH); ^{31}P NMR (CD_2Cl_2) δ 37.20; MALDI-TOF MS (*m/z*) 1303 $[M+H]^+$. **15a**: Anal. Found: C, 47.52; H, 3.12. Calc. for $C_{48}H_{37}Au_2BrO_4P_2$: C, 47.50; H, 3.07. ^{1}H

NMR (CD_2Cl_2) δ 3.31, 3.50 (m, 1H, BrCH_2), 3.91, 4.07 (m, 1H, CHOCH_2), 4.39 (m, 1H, CH), 4.79, 4.80 (s, 2H, OCH_2), 7.02, 7.05 (d, $J = 8.6$ Hz, 4H, C_6H_4), 7.31–7.77 (m, 24H, C_6H_4, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 18.76. **15b/16b**: Anal. Found: C, 48.04; H, 3.68. Calc. for $C_{49}H_{43}Au_2BrO_4P_2$: C, 47.78; H, 3.52. **15b** (ring): ^{1}H NMR (CD_2Cl_2) δ 1.80 (m, 2H, CH_2), 2.46 (m, 4H, CH_2), 3.34, 3.52 (m, 1H, BrCH_2), 3.92, 4.11 (m, 1H, CHOCH_2), 4.48 (m, 1H, CH), 4.80, 4.81 (br. m, 4H, OCH_2), 7.00, 7.02 (m, 4H, C_6H_4), 7.3–7.8 (m, 24H, C_6H_4, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 35.90. **16b** (catenane): ^{1}H NMR (CD_2Cl_2) δ 1.53 (m, 2H, CH_2), 2.16 (m, 4H, CH_2), 3.02, 3.29 (m, 1H, BrCH_2), 3.72, 3.88 (m, 1H, CHOCH_2), 4.21 (m, 1H, CH), 4.65 (br. m, 4H, OCH_2), 6.08, 6.10 (d, $J = 8$ Hz, 2H, C_6H_4), 6.93, 6.95 (d, $J = 8$ Hz, 2H, C_6H_4), 7.30–7.42 (m, 20H, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 31.91. **15c**: Anal. Found: C, 47.77; H, 3.59. Calc. for $C_{50}H_{45}Au_2BrO_4P_2$: C, 48.21; H, 3.64. ^{1}H NMR (CD_2Cl_2) δ 1.71 (br. s, 4H, CH_2), 2.33 (br. s, 4H, CH_2), 3.33, 3.52 (m, 1H, BrCH_2), 3.93, 4.09 (m, 1H, CHOCH_2), 4.42 (m, 1H, CH), 4.79, 4.80 (s, 4H, OCH_2), 7.03, 7.05 (d, $J = 9$ Hz, 4H, C_6H_4), 7.41–7.63 (m, 24H, C_6H_4, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 38.89. **15d**: Anal. Found: C, 49.03; H, 3.88. Calc. for $C_{51}H_{47}Au_2BrO_4P_2$: C, 48.63; H, 3.76. ^{1}H NMR (CD_2Cl_2) δ 1.55 (br. s, 6H, CH_2), 2.34 (br. s, 4H, CH_2), 3.36, 3.54 (m, 1H, BrCH_2), 3.95, 4.10 (m, 1H, CHOCH_2), 4.43 (m, 1H, CH), 4.79, 4.80 (s, 4H, OCH_2), 7.03, 7.05 (d, $J = 8.6$ Hz, 4H, C_6H_4), 7.39–7.67 (m, 24H, C_6H_4, PPh_2); ^{31}P NMR (CD_2Cl_2) δ 37.55.

4. Structure determinations

Data for **6d**, **10a** and **10b** were collected at −73 °C by using a Nonius Kappa CCD diffractometer operating with Mo–K_α radiation using COLLECT software [23]. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out using DENZO and absorption correction was carried out using SCALEPACK [23]. Hydrogen atoms were included at geometrically determined positions riding on their respective carbon atoms. All calculations were performed using the SHELXTL 5.1 crystallographic software package [24]. The crystallographic details for the complexes are listed in Table 4.

7e. CH_3CN: A colorless plate was mounted on a glass fibre. All of the non-hydrogen atoms were refined with anisotropic thermal parameters.

15a. $1.3CH_2Cl_2$: A colorless needle was mounted on a glass fibre. The five-membered ring connected at C31 was disordered and was modelled as three parts with 50:30:20 occupancy, while two solvent molecules with 0.8 and 0.5 occupancy were refined anisotropically and isotropically, respectively. The bond lengths of the disordered ring were fixed with reasonable values and were refined isotropically. The bond distances of the dichloromethane molecules were also fixed. All other non-hydrogen atoms were refined anisotropically.

15b. $3.5CHCl_3$: A colorless square prism was mounted on a glass fibre. There was disorder in the five membered ring hinge groups with a bromomethyl

Table 4
Crystallographic data for compounds **7e**, **15a** and **15b**

	7e. MeCN	**15a**. $1.3CH_2Cl_2$	**15b**. $3.5CHCl_3$
Formula	$C_{50}H_{45}Au_2NO_3P_2$	$C_{49.5}H_{40}Au_2BrCl_3O_4P_2$	$C_{101.5}H_{89.5}Au_4Br_2Cl_{10.5}O_8P_4$
Formula weight	1163.74	1323.96	2881.02
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	13.0195(4)	19.1699(8)	17.9062(2)
b (Å)	14.0979(5)	14.0774(10)	18.3527(2)
c (Å)	14.2496(6)	20.2440(12)	19.2385(3)
α (°)	62.937(2)	90	100.076(1)
β (°)	70.657(2)	112.671(3)	110.919(1)
γ (°)	80.313(2)	90	108.954(1)
V (Å^3)	2197.15(14)	5041.0(5)	5273.81(12)
Z	2	4	2
ρ_{calc} (g cm^{-3})	1.759	1.744	1.814
μ (mm^{-1})	6.785	6.848	6.684
F(0 0 0)	1128	2538	2774
Absorption correction	Integration	Integration	Integration
θ limits (°)	2.68/27.57	2.58/25.16	2.61/30.06
Measured reflections	23 584	25 035	68 348
Unique reflections	10 010	7728	30 686
Parameters	475	506	1075
GOF on F^2	1.102	1.044	1.039
R_1, wR_2 [$I > 2\sigma(I)$]	0.0602, 0.1614	0.0747, 0.1870	0.0535, 0.1227

substituent. This disorder was modelled as a mixture of two half occupancy groups. The atoms of these rings were modelled isotropically, except for the bromine atoms of one set of bromethyl groups which were anisotropic. There were indications of a third disorder component of one ring, but no suitable model could be refined. The half occupancy chloroform molecule was modelled isotropically. All other non-hydrogen atoms were refined with anisotropic thermal parameters.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No's 193955, 193956, 193957. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] J.-P. Sauvage, C. Dietrich-Buchecker (Eds.), Molecular Catenanes, Rotaxanes and Knots, Wiley-VCH, Weinheim, 1999.
[2] M. Fujita, Acc. Chem. Res. 32 (1999) 53.
[3] A.R. Pease, J.O. Jeppesen, J.F. Stoddart, Y. Lio, C.P. Collier, J.R. Heath, Acc. Chem. Res. 34 (2001) 433.
[4] G.F. Swiegers, T.J. Malefetse, Chem. Rev. 100 (2000) 3483.
[5] V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart, Angew. Chem. 112 (2000) 3484.
[6] S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.
[7] G. Schill, Catenanes, Rotaxanes and Knots, Academic Press, New York, 1971.
[8] G.-J.M. Gruter, F.J.J. de Kanter, P.R. Markies, T. Nomoto, O.S. Akkerman, F. Bickelhaupt, J. Am. Chem. Soc. 115 (1993) 12179.
[9] R.J. Puddephatt, Coord. Chem. Rev. 216–217 (2001) 313.
[10] R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (1998) 1055.
[11] H. Schmidbaur, Chem. Soc. Rev. 24 (1995) 391.
[12] C.P. McArdle, M.C. Irwin, M.C. Jennings, R.J. Puddephatt, Angew. Chem. Int. Ed. Engl. 38 (1999) 3376.
[13] C.P. McArdle, J.J. Vittal, R.J. Puddephatt, Angew. Chem. Int. Ed. Engl. 39 (2000) 3819.
[14] C.P. McArdle, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, Chem. Eur. J. 7 (2001) 3572.
[15] C.P. McArdle, M.C. Irwin, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, Chem. Eur. J. 8 (2002) 723.
[16] C.P. McArdle, S. Van, M.C. Jennings, R.J. Puddephatt, J. Am. Chem. Soc. 124 (2002) 3959.
[17] R.L. Reeves, in: S. Patai (Ed.), The Chemistry of the Carbonyl Group, Interscience Publishers, New York, 1966, p. 567.
[18] P.J. Kocienski, Protecting Groups, Thieme, Stuttgart, 2000.
[19] I. Iwai, J. Ide, Chem. Pharm. Bull. 11 (1963) 1042.
[20] S. Sugai, H. Ikawa, Y. Hasegawa, Y. Seiichiro, T. Kutsuma, S. Akaboshi, Chem. Pharm. Bull. 32 (1984) 967.
[21] D.M.P. Mingos, J. Yau, S. Menzer, D.J. Williams, Angew. Chem. Int. Ed. 34 (1995) 1894.
[22] A. Tamaki, J.K. Kochi, J. Organomet. Chem. 64 (1974) 411.
[23] "COLLECT, DENZO, SCALEPACK," Data Collection Software, Nonius BV, 1999.
[24] G.M. Sheldrick, SHELXTL 5.1, Universität Göttingen, 1998.