Articles

A Structural Probe for Organogold(I) Rings and [2]Catenanes

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The digold(I) diacetylides [4-RC_6H_9(4-$C_6H_4OCH_2C{\equiv}CAu)_2$], which contain a cyclohexylidene hinge group 4-RC_6H_9 with R = H or *t*-Bu, react with diphosphine ligands Ph_2PZPPh_2 to give the corresponding macrocycles or [2]catenanes [{4-RC_6H_9(4-$C_6H_4OCH_2C{\equiv}CAu)_2$($\mu$-$Ph_2PZPPh_2$)}$_y$] [Z = C≡C, $(CH_2)_2$, $(CH_2)_3$, or $(CH_2)_4$; y = 1, 2, or 4]. When R = *t*-Bu, the bulky *tert*-butyl group locks the cyclohexane ring conformation and so provides a good NMR spectroscopic probe of the structure. The organogold(I) [2]-catenane complexes are chiral when R = *t*-Bu, and the complex with Z = $(CH_2)_4$ gives an equilibrium in solution between ring, double-ring, and [2]catenane. When R = H and Z = $(CH_2)_3$, the variable-temperature NMR spectra give new insight into the fluxionality in the [2]catenane complex, and when R = H and Z = $(CH_2)_4$, it is shown that the complex exists in solution as the ring structure, although it crystallizes as a doubly braided [2]catenane.

Introduction

In the vibrant field of chemistry of inorganic and organometallic catenanes,[1−3] gold(I) compounds have a special position arising from the easy and reversible formation of catenanes by self-assembly.[1,4−9] Of the organometallic [2]catenanes, the largest known group is found in the family of organogold(I) rings and [2]catenanes of general formula [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2$($\mu$-$Ph_2PZPPh_2$)}$_y$] ($y$ = 1 for ring complex; y = 2 for singly braided [2]catenane; y = 4 for doubly braided [2]-catenane; typically X = CR_2, Z = $(CH_2)_n$ with n = 3−5), illustrated in Scheme 1.[1,4−9] The structures of many of these compounds in the solid state have been determined crystallographically, and some of the factors influencing formation of the [2]catenane over the macrocycle have been identified.[9] In particular, it has been shown that the [2]catenanes are most favored for the compounds with diacetylides having the hinge groups X = CRR′ (R, R′ = H, alkyl) and with diphosphines Ph_2PZPPh_2 with the spacer group Z = $(CH_2)_3$ and $(CH_2)_4$. The presence of secondary bonding interactions between the interlocked macrocycles, especially the presence of aurophilic attractions with distances Au···Au = 2.5−3.3 Å, can overcome unfavorable entropy associated with formation of the [2]-catenanes in solution.[4−9]

One of the most interesting complexes is the doubly braided [2]catenane (Scheme 1) identified crystallographically for the case with X = cyclohexylidene, C_6H_{10}, and Z = $(CH_2)_4$.[5] The compound was formed by self-assembly of four digold(I) diacetylide units with four diphosphine ligands to give two interlocked 50-membered rings. The structure (Scheme 1) showed that two of the four gold atoms in each ring were involved in aurophilic interactions, and so nonequivalent resonances would be expected in the NMR spectra for the phosphorus atoms and for the alkynyl units bound to the two types of gold atoms. The ^{1}H and ^{31}P NMR spectra at low temperature showed the expected features, but at room temperature, single sets of resonances were observed. It was suggested that the structure of the doubly braided catenane was maintained in solution but that easy fluxionality, involving a rocking motion of the intertwined rings with respect to each other, could lead to exchange between the nonequivalent gold atoms and their ligands. The activation energy for the two-site exchange was determined to be $\Delta G^{\ddagger}$ = 41(±1) kJ mol^{-1}.[5] The double-ring complex (Scheme 1) has not been crystallized, except as a component of the doubly braided [2]catenane,[5] but

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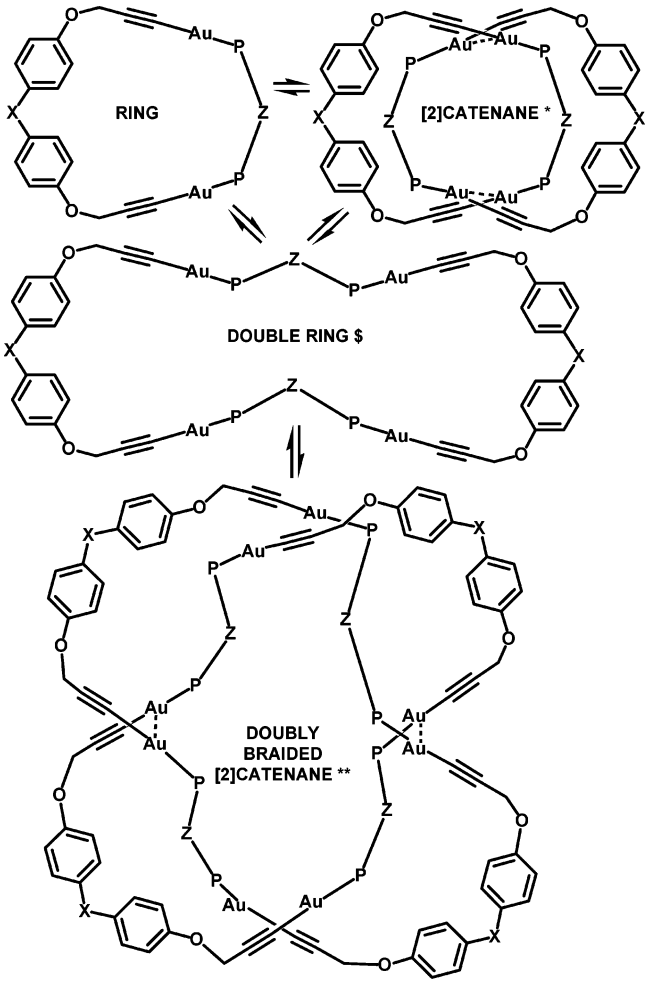
Scheme 1[a]

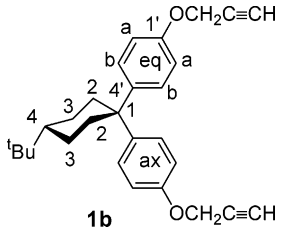


[a] P = PPh_2, X = O, S, Co, CH_2, CHR, CR_2, cyclohexylidene; Z = $(CH_2)_n$, with $n = 2-6$.

it has been identified in solution by NMR studies.[7] In addition, examples of the double-ring complexes are known with more rigid diacetylide ligands as well as in the cationic complex $[Au_4\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}_2\{\mu\text{-}1,2\text{-}C_6H_4(NHCO\text{-}4\text{-}C_5H_4N)_2\}]^{4+}$.[10,11]

Recently, it was shown that a solution prepared from a mixture of catenanes $[\{X(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)\}_2]$ and $[\{X'(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)\}_2]$ (for example, with X = CH_2 and X′ = CMe_2) formed an equilibrium mixture of the parent catenanes, the mixed ligand catenane $[\{X(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)\}\{X'(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)\}]$, and the ring complexes $[X(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)]$ and $[X'(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)]$, provided that Z = $(CH_2)_3$.[9] However, no such equilibrium was present when Z = $(CH_2)_4$, and it was deduced that the complexes existed in solution almost entirely as the simple ring complexes, even though they may crystallize as the pure [2]catenanes.[9] This finding prompted a new investigation of the doubly braided catenane complex with X = C_6H_{10} and Z = $(CH_2)_4$ to see if it too might dissociate to a ring or double-ring complex in solution. As part of this study, the related gold(I) complexes bearing the 4-*tert*-butylcyclohexylidene hinge group (X = 4-*t*-BuC_6H_9) have been prepared. The *tert*-butyl substituent controls the conformation of the cyclohexyl group

Chart 1



1b

and provides a particularly useful probe for structure determination of the gold(I) complexes in solution by NMR.[12,13]

Results and Discussion

Condensation of 4-*tert*-butylcyclohexanone with 2 equiv of phenol gave a new route to the bis(phenol) 4-*t*-$BuC_6H_9(4\text{-}C_6H_4OH)_2$.[12] Reaction of 4-$RC_6H_9(4\text{-}C_6H_4OH)_2$ [R = H or *t*-Bu] with propargyl bromide in the presence of base then gave the corresponding dipropargyl derivatives 4-$RC_6H_9(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$, **1a**, R = H;[5] **1b**, R = *t*-Bu. The ^1H and ^{13}C NMR spectra of the new derivative **1b** showed two sets of resonances corresponding to the axial and equatorial 4-$C_6H_4OCH_2C{\equiv}CH$ substituents of the cyclohexane ring (Chart 1).[12] It is well known that the bulky *tert*-butyl group causes the population of the cyclohexyl conformer with an equatorial *tert*-butyl group to be much greater than the one with an axial *tert*-butyl group and that this leads to distinctive axial and equatorial resonances.[13] The resonances corresponding to the axial (ax) and equatorial (eq) groups in **1b** were assigned on the basis of the 2D correlated $^1H-^1H$ (gCOSY) and $^1H-^{13}C$ (gHSQC) NMR spectra and from known trends in the ^1H NMR chemical shifts and coupling constants in other *tert*-butylcyclohexyl derivatives.[13] In the related cyclohexylidene derivative $C_6H_{10}(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$, **1a**, the axial and equatorial 4-$C_6H_4OCH_2C{\equiv}CH$ substituents of the cyclohexane ring are equivalent in the NMR spectra at room temperature as a result of the easy inversion of the cyclohexane chair conformation.[5]

The polymeric digold(I) diacetylide complexes $[\{4\text{-}RC_6H_9(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2\}_n]$, **2a**, R = H;[5] **2b**, R = *t*-Bu, were prepared by reaction of the corresponding diacetylene **1a** or **1b** with 2 equiv of chloro(dimethyl sulfide)gold(I) in the presence of base. The new complex **2b** was insoluble in common organic solvents and was characterized by elemental analysis and IR spectroscopy. The IR spectrum of **2b** gave a C≡C stretching frequency of 2006 cm^{-1}, considerably lower than the corresponding value for **1b** [ν(CC)= 2122 cm^{-1}], as expected for complexes of this type.[1,5]

Reaction of the digold(I) diacetylide oligomers **2a** and **2b** with diphosphine ligands Ph_2PZPPh_2 gave the gold(I) complexes $[\{4\text{-}RC_6H_9(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PZPPh_2)\}_y]$, **3a**, R = H, Z = C≡C; **3b**, R = *t*-Bu, Z = C≡C; **4a**, R = H, Z = $(CH_2)_2$; **4b**, R = *t*-Bu, Z = $(CH_2)_2$; **5a**, R = H, Z = $(CH_2)_3$; **5b**, R = *t*-Bu, Z = $(CH_2)_3$; the known complex **6a**, R = H, Z = $(CH_2)_4$;[5] **6b**, R = *t*-Bu, Z = $(CH_2)_4$. When discussing structures of the complexes, the double-ring, [2]catenane, and doubly braided [2]catenane isomers (Scheme 1) will be designated by $, *, or **, respectively. Thus isomer **3b** is the simple ring complex (*y* = 1) with R = *t*-Bu, Z = C≡C, **5a*** is the [2]catenane (*y* = 2)

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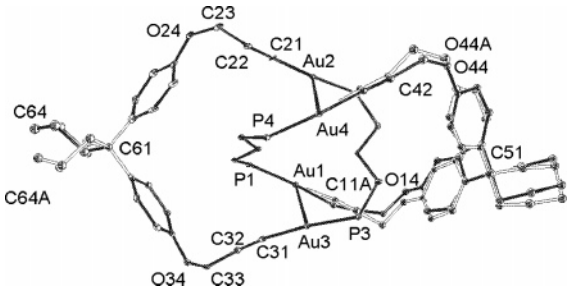


Figure 1. View of the structure of the [2]catenane complex **5a***. Phenyl groups are omitted for clarity. Selected bond distances (Å): Au(1)−C(11) 1.99(2); Au(1)−P(1) 2.267(4); Au(2)−C(21) 1.95(1); Au(2)−P(2) 2.296(5); Au(3)−C(31) 2.01(1); Au(3)−P(3) 2.274(4); Au(4)−C(41) 1.99(2); Au(4)−P(4) 2.282(5).

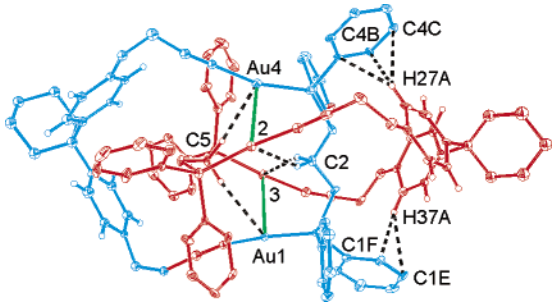


Figure 2. View of the structure of a single disorder component of complex **5a***, including the phenyl groups. Some of the short contacts involving hydrogen atoms are indicated by dashed lines.

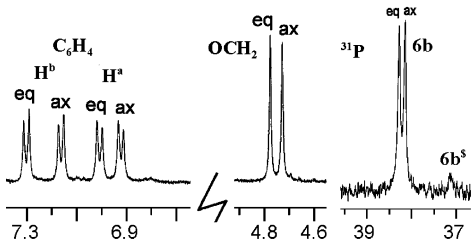


Figure 3. ^{1}H [400 MHz, in the C_6H_4 and OCH_2 regions only] and ^{31}P NMR spectra (162 MHz, 20 °C, CD_2Cl_2) of the macrocyclic complex **6b**, showing resonances assigned to axial (ax) and equatorial (eq) substituents. A trace of the double-ring isomer is indicated by **6b$** in the ^{31}P NMR spectrum.

with R = H, Z = $(CH_2)_3$, and **6a**** is the doubly braided [2]-catenane (y = 4) with R = H, Z = $(CH_2)_4$. The complexes were characterized in the solid state by elemental analysis and IR spectroscopy, and the structure of **5a*** was determined crystallographically. The structure of complex **6a**** was reported earlier.[5] The structures in solution were determined by NMR spectroscopy. Complex **4b** was essentially insoluble in all common organic solvents, and so characterization in solution was not possible. Given that related complexes with other hinge groups X and with Z = $(CH_2)_2$, including complex **4a**, are soluble and exist as the simple ring complexes (y = 1),[4−9] we tentatively suggest that complex **4b** is polymeric in nature (y = 4).

Molecular Structure of the [2]Catenane Complex 5a*. A view of the disordered [2]catenane structure of **5a*** is shown in Figure 1. The diphosphine−digold(I) units are not disordered, but there is disorder in the diacetylide units. There are two short Au···Au contacts with Au(1)···Au(3) = 3.293(1) Å and Au(2)···Au(4) = 3.272(1) Å, and so the two component rings are twisted away from orthogonality to allow these short contacts. The catenation is similar to that observed in related complexes with other hinge groups.[4−9]

The ring diacetylide unit defined by the hinge group atom C(61) in Figure 1 is ordered except for the cyclohexylidene group, which exists in both possible chair conformations. Clearly, inversion of the cyclohexylidene chair conformation will cause effective exchange of the axial and equatorial 4-C_6H_4-$OCH_2C{\equiv}CAuPCH_2$ substituents. The second ring diacetylide unit, defined by the hinge group atom C(51), is disordered in a different way, involving twisting of the entire diacetylide unit but without inversion of the cyclohexylidene chair conformation (Figure 1). In the disorder components, the axial and equatorial 4-$C_6H_4OCH_2C{\equiv}CAuPCH_2$ substituents of this diacetylide unit are therefore not exchanged.

Figure 2 shows the structure of the catenane with phenylphosphorus groups and some of the hydrogen atoms included. This figure is useful in understanding the ^{1}H NMR spectra to be discussed below. The central CH_2 group of the diphosphine ligand makes short contacts with the gold atoms [Au(1)···H(5A) 2.97; Au(2)···H(2A) 2.94; Au(3)···H(2B) 2.92; Au(4)···H(5B) 2.82 Å], but it is not clear if the interactions represent secondary bonding or if they represent van der Waals contacts arising through steric congestion. There are several aryl···aryl edge−face or vertex−face interactions that will cause significant effects on ^{1}H NMR chemical shifts. Note, for example, the interaction of C(37)−H with the adjacent phenyl group [H(37A)···C(1A) 3.1; H(37A)···C(1D) 3.1; H(37A)···C(1E) 2.9; H(37A)···C(1F) 2.8 Å], which will cause a ring shielding effect on this H^a resonance (Chart 1) in the [2]catenane compared to the simple macrocyclic complex.

Structures of the Complexes in Solution. 1. Complexes with the *tert*-Butylcyclohexylidene Hinge Group. In considering the structures of the gold(I) compounds as determined by NMR spectroscopy, it is important to consider the conformation of the cyclohexane ring and the axial chirality of the [2]-catenanes. Consider first the complexes **3b**−**6b** with the *tert*-butylcyclohexylidene hinge group. The *tert*-butyl group prefers to occupy the equatorial position, and this leads to two sets of resonances in the NMR spectra for the axial and equatorial 4-$C_6H_4OCH_2C{\equiv}CAuPCH_2$ substituent groups, which are *syn* and *anti* to the *tert*-butyl group. The spacer group in complex **3b** (Z = C≡C) is too short to allow catenation, and based on previous work with several different hinge groups, the macrocyclic structure can be predicted with confidence.[8] The spectra can therefore be used as a benchmark for a macrocyclic structure. The ^{31}P NMR spectrum of **3b** contained two closely spaced resonances for the axial and equatorial phosphorus atoms at $\delta(^{31}P)$ = 18.91 and 18.95. Similarly, there were two resonances for the OCH_2 protons at $\delta(^1H)$ = 4.73 and 4.79 and two resonances each for the hydrogen atoms of the C_6H_4 group, H^a [δ = 6.91, 7.01] and H^b [δ = 7.13, 7.30].

Figure 3 shows the ^{1}H NMR spectrum, in the regions of the C_6H_4 and OCH_2 resonances, and the ^{31}P NMR spectrum of complex **6b** in CD_2Cl_2 solution at room temperature. The spectra are very similar to those for **3b**, Z = C≡C, described above, and indicate that **6b** exists primarily as the simple macrocyclic digold(I) complex in this solution.

In dilute solution, the macrocyclic complex **6b** was the dominant isomer present in solvent CD_2Cl_2 (Figure 3), $C_6D_5NO_2$, or $CDCl_3$. However, in more concentrated solution in $CDCl_3$, the ^{1}H and ^{31}P NMR spectra were more complex and indicated the presence of two other isomers. Figure 4 shows the concentration dependence of the ^{31}P NMR spectrum at room temperature. The ring complex **6b** gives only one broad

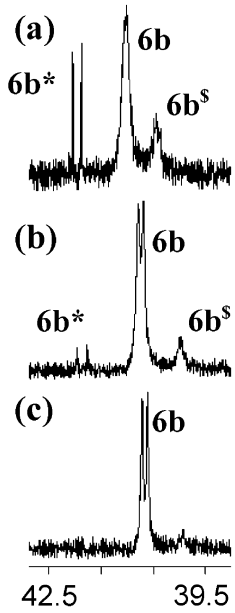


Figure 4. Concentration dependence of the ^{31}P NMR spectrum (162 MHz) of a mixture of isomers **6b**, **6b***, and **6b$**: (a) $c = 1.5 \times 10^{-2}$ M; (b) $c = 3.3 \times 10^{-3}$ M; (c) $c = 8.3 \times 10^{-4}$ M. Concentration c is the total concentration assuming that the complex was present only as **6b**.

resonance in the more concentrated solution (Figure 4a), as a result of exchange with the double-ring complex **6b$**.[7] There are also two sharp singlet resonances, which are attributed to the axial and equatorial phosphorus atoms of a [2]catenane species, which could be **6b*** or **6b****. At lower concentrations, the relative amounts of the higher molecular weight isomers, the [2]catenane **6b*** or **6b**** and the double-ring complex **6b$**, decrease with respect to the simple ring complex **6b** and the expected two singlets for **6b** are resolved, as the rate of exchange with **6b$** decreases (Figures 4b and 4c). The relative molecular weights of individual components can be estimated from their relative concentrations as a function of the total concentration (a greater concentration dependence is expected for the "tetramer" doubly braided [2]catenane, with $K(\text{eq}) = [\mathbf{6b^{**}}]/[\mathbf{6b}]$,[4] than for either "dimer" catenane or double ring). The integration of the ^{31}P NMR spectra in $CDCl_3$ solution at 293 K was complicated by variation in peak widths as a function of concentration (Figure 4), but they are accurate enough to show that the catenane is **6b***, formed by 2+2 self-assembly, rather than **6b****, formed by 4+4 self-assembly. Integration as a function of concentration at 293 K gave $K(\text{eq}) = [\mathbf{6b^{\$}}]/[\mathbf{6b}]^2 = 21(2)$ L mol^{-1} for equilibration of **6b** to give **6b$**, $K(\text{eq}) = [\mathbf{6b^{*}}]/[\mathbf{6b}]^2 = 8(3)$ L mol^{-1} for equilibration of **6b** to give **6b***, and $K(\text{eq}) = [\mathbf{6b^{*}}]/[\mathbf{6b^{\$}}] = 0.4(2)$ for equilibration of **6b$** to give **6b***.

Figure 5 shows the variable-temperature ^{1}H NMR spectra of **6b** in the region of the C_6H_4 resonances. At 60 °C (Figure 5a), the resonances of the complexes **6b** and **6b$** are coalesced [$\delta(H^a) = 6.92, 6.99$; $\delta(H^b) = 7.05, 7.23$ (overlapped with the peak due to $CHCl_3$)], but the resonances of the [2]catenane **6b*** [$\delta(H^a) = 6.28, 6.44$; $\delta(H^b) = 6.67, 6.70$] are separate and characteristically shielded compared to the macrocycle **6b**. At −25 °C (Figure 5c), the resonances of the complexes **6b** [$\delta(H^a) = 6.98, 7.02$; $\delta(H^b) = 7.14, 7.24$] and **6b$** [$\delta(H^a) = 6.80, 6.90$; $\delta(H^b) = 7.03, 7.22$] are separate, as a result of slower exchange, but the resonances for the two complexes have similar chemical shifts. A similar effect was observed in the region of the OCH_2 protons. At 60 °C, the resonances for **6b** and **6b$** are

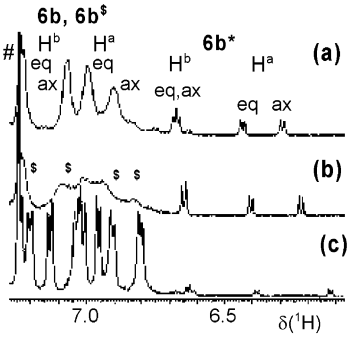


Figure 5. Variable-temperature ^{1}H NMR spectra (600 MHz, $CDCl_3$ solution) in the region of the C_6H_4 protons H^a and H^b (Chart 1): (a) 60 °C; (b) 25 °C; (c) −25 °C. The peak marked # is due to $CHCl_3$.

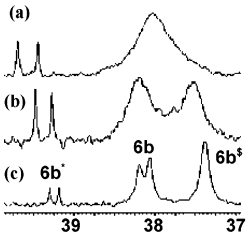


Figure 6. Variable-temperature ^{31}P NMR spectra [243 MHz, $CDCl_3$ solution] of the macrocyclic complex **6b**, in equilibrium with the [2]catenane **6b*** and double-ring **6b$** isomers: (a) 60 °C; (b) 25 °C; (c) 0 °C.

coalesced [$\delta(H) = 4.75, 4.80$], but at −25 °C separate resonances are observed [**6b**: $\delta(H) = 4.78, 4.85$; **6b$**: $\delta(H) = 4.67, 4.80$].

Figure 6 shows the variable-temperature ^{31}P NMR spectra. Coalescence of the resonances of **6b** and **6b$** is observed at 60 °C (Figure 6a), but the chemical exchange is slowed at low temperatures, and the expected two resonances for the axial and equatorial phosphorus atoms of **6b** are resolved and observed at −25 °C (Figure 6c). However, only a single broad resonance is observed for **6b$** even at low temperature (Figure 6c). By integration of the resonances for **6b** and **6b$** over the temperature range from 0 to −50 °C, when separate resonances were well resolved, the thermodynamic parameters for equilibration of **6b** to give **6b$** were found to be $\Delta H = -11(1)$ kJ mol^{-1} and $\Delta S = -14(2)$ J K^{-1} mol^{-1}. It was not possible to obtain thermodynamic parameters for formation of **6b*** because reliable integration of the broad peaks at low temperatures was not possible.

To study the relative sizes of the molecules, the ^{31}P DOSY spectrum [243 MHz, relaxation delay 2.5 s, 0 °C, $CDCl_3$ solution] of an equilibrium mixture of **6b**, **6b***, and **6b$** was recorded (Figure 7).[14] The spectrum shows that the diffusion rates follow the sequence **6b*** > **6b** > **6b$**, whereas, on the basis of the relative molecular weights only, the sequence **6b** > **6b*** = **6b$** would be expected. We suggest that lower solvation of the roughly spherical molecule **6b*** compared to the more open molecules **6b** and **6b$** might account for the difference. A similar difference in relative diffusion rates for the macrocycles [$\{PdCl_2(Ph_2P(CH_2)_{12}PPh_2)\}_n$], $n = 1$ and 2, has been reported as for **6b** and **6b$**, but the technique does not appear to have been used previously in studies of catenation.[14a]

(14) (a) Paulusse, J. M. J.; Sijbesma, R. P. *Chem. Commun.* **2003**, 1494. (b) Paulusse, J. M. J.; Huijbers, J. P. J.; Sijbesma, R. P. *Macromolecules* **2005**, 38, 6290. (c) Johnson, C. S. *Prog. Nucl. Magn. Res. Spectrosc.* **1999**, *34*, 203.

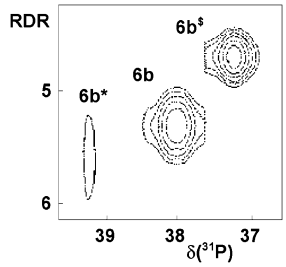


Figure 7. ^{31}P DOSY spectrum [243 MHz, relaxation delay 2.5 s, 0 °C, $CDCl_3$ solution] of an equilibrium mixture of **6b**, **6b***, and **6b**$^{\$}$. RDR = relative diffusion rate.

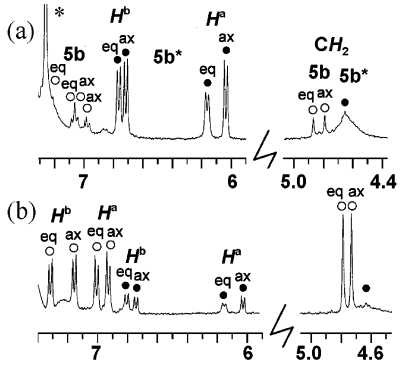


Figure 8. ^{1}H NMR spectra [400 MHz, 25 °C] of an equilibrium mixture of the macrocyclic complex **5b** (○) and the [2]catenane **5b*** (●) showing resonances assigned to axial (ax) and equatorial (eq) C_6H_4 and OCH_2 substituents: (a) spectrum in concentrated solution in $CDCl_3$, when the [2]catenane **5b*** is dominant (peak labeled * is due to $CHCl_3$); (b) spectrum in more dilute solution in CD_2Cl_2, when **5b** is dominant.

Chart 2

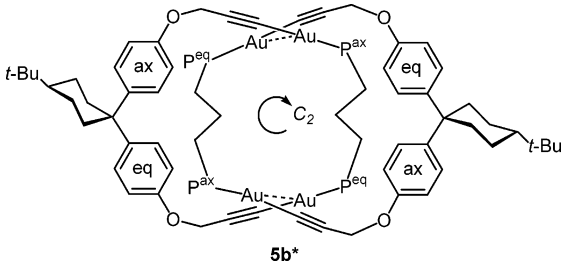


Figure 8 shows the ^{1}H and ^{31}P NMR spectra of an equilibrium mixture of the ring complex **5b** and the [2]catenane complex **5b*** in $CDCl_3$ and in CD_2Cl_2. In both solvents, the axial and equatorial resonances for C_6H_4 and OCH_2 are easily observed in the ^{1}H NMR spectra. The characteristic marked shift of the C_6H_4 resonances of the [2]catenane **5b*** with respect to the macrocycle **5b** is clearly seen in Figure 8 and arises from the aryl···aryl interactions (Figure 2).[4−9] It should be noted that the [2]catenane **5b*** exhibits axial chirality as a result of the presence of the *tert*-butylcyclohexylidene hinge groups.[9] The [2]catenane is expected to have effective C_2 symmetry (Chart 2), whereas the macrocycle has C_s symmetry. This change in symmetry on catenation does not change the expected number of C_6H_4 or ^{31}P resonances, but it does lead to a very broad ill-resolved resonance for the OCH_2 protons in the ^{1}H NMR spectra (Figure 8).

In the ^{31}P NMR spectrum (Figure 9), the axial and equatorial resonances for the [2]catenane **5b*** are resolved and appear as an "AB" multiplet, but those for the macrocyclic complex **5b** are not resolved.

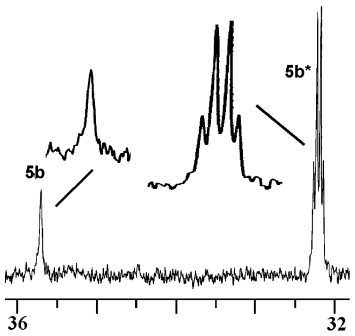
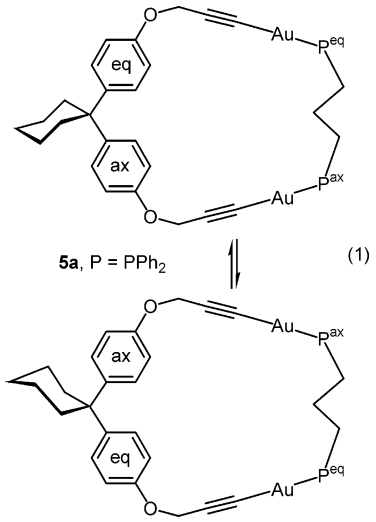


Figure 9. ^{31}P NMR spectrum [162 MHz, $CDCl_3$ solution] of a mixture of isomers **5b** and **5b***.

2. Complexes with the Cyclohexylidene Hinge Group. The NMR spectra of the complexes with the cyclohexylidene hinge group are simpler at room temperature but either similar or more complex compared to the *tert*-butylcyclohexylidene derivatives at low temperature. Figure 10 shows the ^{31}P NMR spectra of an equilibrium mixture of **5a**, **5a***, and an uncharacterized oligomeric isomer **5a**$^{\#}$. At room temperature, the resonance of the macrocyclic complex **5a** is broad as a result of exchange with **5a**$^{\#}$, but it is seen as a sharp singlet at −40 °C as this exchange process is slowed. At lower temperatures, the resonance again becomes broad and finally splits to give two resonances (Figure 10). These resonances correspond to the axial and equatorial phosphorus atoms, and they become effectively equivalent at higher temperatures as a result of inversion of the cyclohexylidene group (eq 1). On the basis of the coalescence



temperature of −70 °C, the activation energy for inversion of the cyclohexylidene ring is estimated to be 42.6(1.0) kJ mol^{-1}, which is very similar to the known activation energy for inversion of cyclohexane of $\Delta G^{\ddagger}$ = 43.1−43.9 kJ mol^{-1} (measured for cyclohexane-d_{11} in CS_2) with a coalescence temperature of T_c = −61 °C.[15] As expected, the equilibrium between the macrocycle **5a** and oligomeric isomer **5a**$^{\#}$ favors **5a**$^{\#}$ at lower temperatures (Figure 10), and it is clear, by comparing Figures 7 and 8, that the oligomeric form is relatively favored in the complexes with the cyclohexylidene compared to the *tert*-butylcyclohexylidene hinge group. The ^{31}P NMR resonance for the [2]catenane **5a*** is also expected to split at

(15) (a) Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760. (b) Bovey, F. A.; Hood, F. P.; Anderson, E. W.; Kornegay, R. L. *J. Chem. Phys.* **1964**, *41*, 2042.

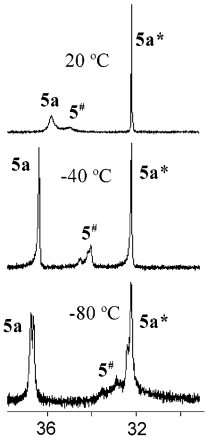


Figure 10. Variable-temperature ^{31}P NMR spectra [162 MHz, CD_2Cl_2 solution] of a mixture of isomers **5a**, **5a***, and **5a**$^{\#}$.

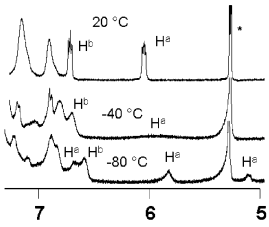
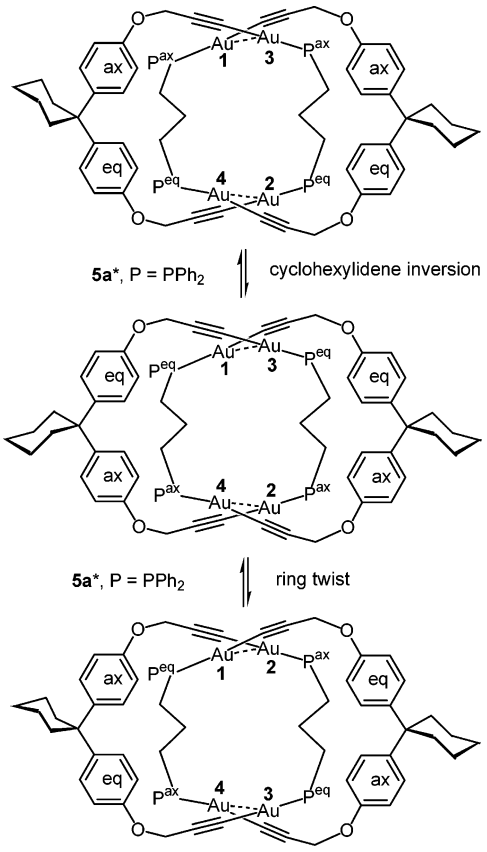


Figure 11. Variable-temperature ^{1}H NMR spectra [400 MHz] of a mixture of macrocyclic complex **5a** and [2]catenane complex **5a*** in CD_2Cl_2 solution. The peak marked ***** is due to $CHDCl_2$.

low temperature, but, although the peak clearly becomes broader at low temperature, the splitting is not fully resolved (Figure 10).

The variable-temperature ^{1}H NMR spectra of the mixture of isomers **5a**, **5a***, and **5a**$^{\#}$ in the region of the C_6H_4 groups are illustrated in Figure 11. The resonances due to the C_6H_4 groups of **5a** and **5a**$^{\#}$ are overlapped and so not easily interpreted, but the spectra of **5a*** are mostly resolved and are interesting. At room temperature, there are only two resonances [$\delta(H^a) = 6.11$; $\delta(H^b) = 6.77$], as expected, because inversion of the cyclohexylidene ring is rapid at this temperature. However, at lower temperatures, the H^a resonance becomes extremely broad and finally splits into three broad resonances at $\delta = 6.7$, 5.8, and 5.1 in a roughly 2:4:2 intensity ratio (Figure 11). The low-temperature NMR spectrum of **5a*** (Figure 11) is more complex than the room-temperature NMR spectrum of **5b** (Figure 8), which contains only two closely spaced H^a resonances [$\delta(H^a) = 6.02$, 6.15], corresponding to the axial and equatorial aryl groups. The low-temperature NMR spectrum of **5a*** can be interpreted in terms of the mechanism of fluxionality shown in Scheme 2, which is consistent with the solid-state structure (Figures 1, 2). Thus, inversion of one of the cyclohexylidene rings leads to formation of a new [2]catenane conformer with Au···Au bonding between P^{ax}−Au···Au−P^{ax} and P^{eq}−Au···Au−P^{eq} units rather than between pairs of P^{eq}−Au···Au−P^{ax} units (Scheme 2). The C_2-symmetric structure can be attained either by a second cyclohexylidene inversion or by rotation of the component macrocycles with respect to one another, in a process that requires making and breaking of pairs of Au···Au secondary bonds (Scheme 2). The activation energy for the fluxional process at the coalescence temperature of 233 K is $\Delta G^{\ddagger} = 43(1)$ kJ mol^{-1}. Because this is very similar to the known activation energy for cyclohexane inversion, it is suggested that the cyclohexylidene ring inversion is the key step. In support, we note that neither of the analogous [2]catenanes with the hinge

Scheme 2



group *t*-BuC_6H_9 or Me_2C shows the same type of effect in the low-temperature NMR spectra.

Conclusions

The NMR criteria established above indicate that the doubly braided [2]catenane **6a****, with X = C_6H_{10} and Z = $(CH_2)_4$, dissociates in solution to form the simple macrocyclic complex **6a**. This explains why no mixed ligand catenane is formed on mixing the complexes with X = C_6H_{10}, Z = $(CH_2)_4$ and with X = CMe_2, Z = $(CH_2)_4$, since both exist in solution as the simple macrocycle.[9] The activation energy for the fluxional process of **6a** in CD_2Cl_2 solution at the coalescence temperature $T_c = -68$ °C of $\Delta G^{\ddagger} = 41(\pm 1)$ kJ mol^{-1} is fully consistent with the cyclohexylidene inversion step, causing coalescence of axial and equatorial substituents of the macrocycle. It is remarkable that the very selective crystallization of the doubly braided [2]catenane complex **6a**** occurs from a solution in which this species cannot be detected by NMR.[5] The tetramerization of **6a** may occur at the growing crystal surface, although the possibility that there is a sufficient concentration of **6a**** in solution to allow crystallization cannot be discarded. Dissolution of **6a**** leads to very easy dissociation back to **6a**, a process that is largely entropy-driven. The easy, reversible oligomerization relies on the lability of the Au−P linkages, which allows facile, reversible ring opening and closing, ring expansion and contraction, and threading and unthreading reactions.

Finally, we note that the 4-*tert*-butylcyclohexylidene hinge group was introduced so that structure determination of complexes in solution would be simplified compared to the case with the simpler cyclohexylidene hinge group, when deceptively simple spectra can be obtained. It was successful in this respect, but it also affects the position of the equilibrium of self-

assembly. This unexpected phenomenon is most prominent for complexes **6**, for which **6a** (R = H) is always dominant in solution, whereas **6b** (R = *t*-Bu) is in equilibrium with both the double-ring **6b$** and [2]catenane **6b*** isomers.

Experimental Section

NMR spectra were recorded using a Varian Inova 600 or 400 or a Varian Mercury 400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to TMS, and ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4 as an external standard. The NMR labeling for the diacetylide groups is shown in Chart 1. IR spectra were recorded as KBr disks or as Nujol mulls between NaCl plates using a Perkin-Elmer 2000 FT-IR spectrometer. High-resolution mass spectra were measured by using a Finnigan MAT 8400 spectrometer. [AuCl(SMe_2)], C_6H_{10}(4-$C_6H_4OCH_2CCH)_2$, **1a**, and [{C_6H_{10}(4-$C_6H_4OCH_2CCAu)_2$}$_n$], **2a**, were prepared according to the literature.[12,16] Reactions involving gold compounds were protected from light by use of darkened reaction flasks. ***Caution:*** Some gold acetylides are potentially explosive; they should be prepared in small quantities and not subjected to shock.

1,1-Bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane. To a solution of phenol (8.46 g, 0.090 mol) and 4-*tert*-butylcyclohexanone (6.90 g, 0.045 mol) in glacial acetic acid (13 mL) was added concentrated sulfuric acid (6 mL). The reaction mixture was stirred for 4 days and then poured into water (200 mL) and neutralized by addition of sodium bicarbonate. The aqueous phase was extracted with diethyl ether (3 × 75 mL), then the combined organic phases were washed with a saturated aqueous solution of sodium bicarbonate. The organic phase was dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure to give the crude product as a dark orange oil. Recrystallization from hot chloroform gave the pure product as a white crystalline solid, mp 180−181 °C (lit.[12] mp 181−182 °C). Yield: 2.89 g (20%). This compound has been prepared previously by a different method, and the ^{1}H and ^{13}C NMR spectra (acetone-d_6) have been reported.[12]

1,1-Bis(4-prop-2-ynyloxyphenylene)-4-*tert*-butylcyclohexane, 1b. A mixture of 1,1-bis(4-hydroxyphenyl)-4-*tert*-butylcyclohexane (1.62 g, 5 mmol), potassium carbonate (2.08 g, 15 mmol), and propargyl bromide (2.7 mL of an 80% solution by weight in toluene, 24 mmol) in acetone (50 mL) was refluxed for 34 h. Once cooled, the mixture was filtered to remove insoluble inorganic salts, then the solvent of the filtrate was removed under reduced pressure. Water (50 mL) was added, and the aqueous phase was extracted with dichloromethane (3 × 35 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure to give a dark yellow viscous liquid, which was dried under vacuum for 8 h. Yield: 1.21 g (60%). IR (Nujol): ν(C≡C) 2122 cm^{-1}. NMR in $CDCl_3$: δ(^{1}H) 0.77 [s, 9H, CMe_3]; 1.10−1.23 [m, 3H,Cy H^3-ax + H^4-ax]; 1.69 [m, 2H, Cy H^3-eq]; 1.86 [m, 2H, Cy H^2-ax]; 2.49 [t, 1H, ^4J(HH) = 2 Hz, C≡CH-ax]; 2.52 [t, 1H, ^4J(HH) = 2 Hz, C≡CH-eq]; 2.65 [m, 2H, H^2-eq]; 4.61 [d, 2H, ^4J(HH) = 2 Hz, OCH_2-ax]; 4.67 [d, 2H, ^4J(HH) = 2 Hz, OCH_2-eq]; 6.81 [d, 2H, ^3J(HH) = 9 Hz, C_6H_4-H^a-ax]; 6.92 [d, 2H, ^3J(HH) = 9 Hz, C_6H_4-H^a-eq]; 7.08 [d, 2H, ^3J(HH) = 9 Hz, C_6H_4-H^b-ax]; 7.27 [d, 2H, ^3J(HH) = 9 Hz, C_6H_4-H^b-eq]; δ(^{13}C) = 23.76 [C^3]; 27.47 [CMe_3]; 32.33 [CMe$_3$]; 37.65 [C^2]; 44.72 [C^1]; 48.26 [C^4]; 55.70 [OCH_2-ax]; 55.79 [OCH_2-eq]; 75.29 [C≡CH-ax]; 75.32 [C≡CH-eq]; 78.80 [C≡CH]; 114.17 [C_6H_4-ax]; 114.52 [C_6H_4-eq]; 127.16 [C_6H_4-ax]; 128.97 [C_6H_4-eq]; 138.47 [$C4'$-ax]; 145.17 [$C4'$-eq]; 155.13 [$C1'$-ax]; 155.22 [$C1'$-eq]. EI-MS (*m*/*z*): calcd for $C_{28}H_{32}O_2$, 400.2402; found, 400.2390.

[{4-*t*-BuC_6H_9(4-$C_6H_4OCH_2C$≡C$Au)_2$}$_n$], 2b. A solution of **1b** (0.602 g, 1.5 mmol) and sodium acetate (0.616 g, 7.5 mmol) in THF (20 mL)/MeOH (20 mL) was added to a solution of [AuCl(SMe_2)] (0.885 g, 3.0 mmol) in THF (100 mL)/MeOH (50 mL). The mixture was stirred for 4 h. Then the yellow precipitate was isolated by filtration, washed with THF, MeOH, and pentane, and dried under vacuum. Yield: 1.04 g (88%). IR (KBr disk): ν(C≡C) 2006 cm^{-1}. Anal. Calcd for $C_{28}H_{30}Au_2O_2$: C, 42.44; H, 3.82. Found: C, 42.14; H, 3.55.

[Au_2{(C≡CCH_2O-4-$C_6H_4)_2$-1,1-C_6H_{10}}(Ph_2PC≡CPPh_2)], 3a. A mixture of [{C_6H_{10}(4-$C_6H_4OCH_2C$≡C$Au)_2$}$_n$], **2a** (0.130 g, 0.18 mmol), and Ph_2PC≡CPPh_2 (0.057 g, 0.15 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 4 h. Decolorizing charcoal (0.2 g) was added, the mixture was filtered, and the solvent was evaporated under vacuum to give the product, which was recrystallized from CH_2Cl_2/pentane. Yield: 68%. Anal. Calcd for $C_{50}H_{42}Au_2O_2P_2$: C, 53.11; H, 3.74. Found: C, 53.02; H, 3.68. IR: ν(C≡C) 2138 cm^{-1}. NMR in CD_2Cl_2: δ(^{1}H) 1.48 [m, 4H, Cy-C$^3H_2$]; 1.53 [m, 2H, Cy-C$^4H_2$); 2.22 [m, 4H, Cy-C$^2H_2$]; 4.77 [s, 4H, OCH_2]; 6.97 [d, 4H, ^3J(HH) = 9 Hz, C_6H_4−CH^a]; 7.23 [d, 4H, ^3J(HH) = 9 Hz, C_6H_4−CH^b]; 7.4−7.8 [m, 20H, PPh]; δ(^{31}P) 18.94 [s].

[Au_2{(C≡CCH_2O-4-$C_6H_4)_2$-1,1-C_6H_9-4-*t*-Bu}(Ph_2PC≡C-PPh_2)], 3b. A mixture of **2b** (0.148 g, 0.187 mmol) and Ph_2PC≡CPPh_2 (0.058 g, 0.147 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 4 h. The mixture was filtered over Celite, then the volume of the filtrate was reduced to 3 mL at reduced pressure. Pentane (90 mL) was added to give an off-white solid, which was isolated by filtration, washed with pentane, and dried under vacuum. Yield: 0.152 g (86%). IR (KBr disk): ν(C≡C) 2121 cm^{-1}. Anal. Calcd for $C_{54}H_{50}Au_2O_2P_2$: C, 54.65; H, 4.25. Found: C, 54.19; H, 4.40. NMR in CD_2Cl_2: δ(^{1}H) 0.75 [s, 9H, CMe_3]; 1.13−1.19 [m, 3H, Cy-H^3-ax + Cy-H^4-ax]; 1.67 [m, 2H, Cy-H^3-eq]; 1.80 [m, 2H, Cy-H^2-ax]; 2.71 [d, 2H, ^2J(HH) = 12 Hz, Cy-H^2-eq]; 4.73 [s, 2H, OCH_2-ax]; 4.79 [s, 2H, OCH_2-eq]; 6.91 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4−H^a-ax,]; 7.01 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4−H^a-eq,]; 7.13 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4−H^b-ax]; 7.30 [d, 2H, ^3J(HH) = 8 Hz, C_6H_4−H^b-eq]; 7.50 [m, 8H, PPh]; 7.56 [m, 4H, PPh]; 7.68−7.74 [m, 8H, PPh]; δ(^{31}P) 18.91 [s, *P*-ax]; 18.95 [s, *P*-eq].

[Au_2{(C≡CCH_2O-4-$C_6H_4)_2$-1,1-C_6H_{10}}{$Ph_2P(CH_2)_2PPh_2$}], 4a. This was prepared in a manner similar to that for **3a** from **2a** and $Ph_2P(CH_2)_2PPh_2$. Cream solid. Yield: 74%. IR (KBr disk): ν(C≡C) 2135 cm^{-1}. Anal. Calcd for $C_{50}H_{46}Au_2O_2P_2$: C, 52.92; H, 4.09. Found: C, 52.55; H, 4.07. NMR in CD_2Cl_2: δ(^{1}H) 1.31 [m, 2H, Cy-C$^4H_2$]; 1.48 [m, 4H, Cy-C$^3H_2$); 2.25 [m, 8H, Cy-C$^2H_2$ + PCH_2]; 4.75 [s, 4H, OCH_2]; 6.98 [d, 4H, ^3J(HH) = 9 Hz, C_6H_4−H^a]; 7.27 [d, 4H, ^3J(HH) = 9 Hz, C_6H_4−H^b]; 7.4−7.6 [m, 20H, PPh]; δ-(^{31}P) 40.29 [s].

[Au_2{(C≡CCH_2O-4-$C_6H_4)_2$-1,1-C_6H_9-4-*t*-Bu}{$Ph_2P(CH_2)_2$-PPh_2}], 4b. A mixture of **2b** (0.198 g, 0.250 mmol) and 1,2-bis-(diphenylphosphino)ethane (0.082 g, 0.206 mmol) in CH_2Cl_2 (10 mL) was stirred for 3 h. The product was insoluble and was isolated as an off-white solid. The isolated solid was insoluble in CH_2Cl_2, $CHCl_3$, and DMSO. Yield: 0.149 g (60%). IR (KBr disk): ν(C≡C) 2133 cm^{-1}. Anal. Calcd for $C_{54}H_{54}Au_2O_2P_2$: C, 54.46; H, 4.57. Found: C, 54.06; H, 4.41. The complex was insufficiently soluble to give NMR data.

[Au_2{(C≡CCH_2O-4-$C_6H_4)_2$-1,1-C_6H_{10}}{$Ph_2P(CH_2)_3PPh_2$}], 5a, and [2]Catenane 5a*. These were prepared in a manner similar to that for **3a** from **2a** (0.076 g, 0.096 mmol) and $Ph_2P(CH_2)_3$-PPh_2. Cream solid. Yield: 0.175 g (89%). IR (KBr disk): ν(C≡C) 2130 cm^{-1}. Anal. Calcd for $C_{51}H_{48}Au_2O_2P_2$: C, 53.32; H, 4.21. Found: C, 53.69; H, 4.08. **5a**: NMR in CD_2Cl_2: δ(^{1}H) 1.30 [m, 2H, Cy-C$^4H_2$]; 1.50 [m, 4H, Cy-C$^3H_2$); 1.85 [m, 2H, PCH_2CH_2]; 2.23 [m, 4H, Cy-C$^2H_2$]; 2.47 [m, 4H, PCH_2]; 4.74 [s, 4H, OCH_2]; 6.97 [d, 4H, ^3J(HH) = 9 Hz, C_6H_4−H^a]; 7.23 [d, 4H, ^3J(HH) = 9 Hz, C_6H_4−H^b]; 7.2−7.6 [m, 20H, PPh]; δ(^{13}C) 21.1 [t, *J*(PC) = 7 Hz, CH$_2$CH$_2$P]; 22.9 [s, Cy-C^4]; 23.4 [s, Cy-C^3]; 29.7 [dd, *J*(PC) = 16, 35 Hz, CH$_2$P]; 37.5 [s, Cy-C^2]; 45.1 [s, Cy-C^1]; 56.5 [s, CH$_2$O]; 97.8 [d, *J*(PC) = 28 Hz, CCAu]; 131.6 [d, *J*(PC) = 152

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Hz, *C*CAu]; δ(^{31}P) 35.92 [s]. **5a***: NMR in CD_2Cl_2: δ(^{1}H) 1.28 [m, 4H, Cy-C$^4H_2$]; 1.47 [m, 8H, Cy-C$^3H_2$]; 1.97 [m, 8H, Cy-C$^2H_2$]; 2.20 [m, 4H, PCH$_2$CH_2]; 2.75 [m, 8H, PCH_2]; 4.62 [br s, 8H, OCH_2]; 6.11 [d, 8H, ^3J(HH) = 9 Hz, C$_6H_4$−H^a]; 6.77 [d, 8H, ^3J(HH) = 9 Hz, C$_6H_4$−H^b]; 7.2−7.5 [m, 40H, P*Ph*]; δ(^{13}C) 19.9 [m, *C*H$_2$CH$_2$P]; 26.5 [s, Cy-C^4]; 26.8 [s, Cy-C^3]; 27.8 [dd, *J*(PC) = 15, 30 Hz, *C*H$_2$P]; 37.2 [s, Cy-C^2]; 43.8 [s, Cy-C^1]; 56.6 [s, *C*H$_2$O]; 100.2 [d, *J*(PC) = 30 Hz, *C*CAu]; 131.5 [d, *J*(PC) = 152 Hz, *C*CAu]; δ (^{31}P) 32.17 [s].

[Au$_2$\{(C≡CCH$_2$O-4-C$_6$H$_4$)$_2$-1,1-C$_6$H$_9$-4-*t*-Bu\}\{Ph$_2$P(CH$_2$)$_3$-PPh$_2$\}], 5b, and [2]Catenane 5b*. These were prepared in a manner similar to that for **3b**, from **2b** (0.076 g, 0.096 mmol) and Ph$_2$P(CH$_2$)$_3$PPh$_2$ (0.033 g, 0.080 mmol). The product was isolated as a pale pink solid. Yield: 0.079 g (82%). IR (KBr disk): ν(C≡C) 2129 cm^{-1}. Anal. Calcd for $C_{55}H_{56}Au_2O_2P_2$: C, 54.83; H, 4.68. Found: C, 54.52; H, 4.65. **5b**: NMR in CD_2Cl_2: δ(^{1}H) 0.76 [s, 9H, C*Me*$_3$]; 1.15 [m, 3H, Cy-*H*^{3}-ax + Cy-*H*^{4}-ax]; 1.69 [m, 2H, Cy-*H*^{3}-eq]; 1.80 [m, 2H, PCH$_2$CH_2]; 1.82 [m, 2H, Cy-*H*^{2}-ax]; 2.47 [m, 4H, PCH_2]; 2.75 [d, 2H, ^2J(HH) = 14 Hz, Cy-*H*^{2}-eq]; 4.72 [s, 2H, OCH_2-ax]; 4.78 [s, 2H, OCH_2-eq]; 6.92 [d, 2H, ^3J(HH) = 9 Hz, C$_6H_4$−H^a-ax]; 7.00 [d, 2H, 3*J*(HH) = 9 Hz, C$_6H_4$−H^a-eq]; 7.14 [d, 2H, ^3J(HH) = 9 Hz, C$_6H_4$−H^b-ax]; 7.30 [d, 2H, ^3J(HH) = 9 Hz, C$_6H_4$−H^b-eq]; 7.40−7.58 [m, 20H, P*Ph*]; δ(^{31}P) 36.29 [s]. **5b***: NMR in CD_2Cl_2: δ(^{1}H) 0.65 [s, 18H, C*Me*$_3$]; 1.15 [m, 6H, Cy-*H*^{3}-ax + Cy-*H*^{4}-ax]; 1.50 [m, 4H, PCH$_2$CH_2]; 1.69 [m, 4H, Cy-*H*^{3}-eq]; 1.82 [m, 4H, Cy-*H*^{2}-ax]; 2.56 [m, 8H, PCH_2]; 2.75 [d, 2H, ^2J(HH) = 14 Hz, Cy-*H*^{2}-eq]; 4.58−4.66 [br, 8H, OCH_2]; 6.02 [d, 4H, ^3J(HH) = 9 Hz, C$_6H_4$−H^a-ax]; 6.15 [d, 4H, ^3J(HH) = 9 Hz, C$_6H_4$−H^a-eq]; 6.73 [d, 4H, ^3J(HH) = 9 Hz, C$_6H_4$−H^b-ax]; 6.80 [d, 4H, ^3J(HH) = 9 Hz, C$_6H_4$−H^b-eq]; 7.40−7.70 [m, 40H, P*Ph*]; δ-(^{31}P) 32.50, 32.57 [AB quartet, ^4J(PP) = 6 Hz].

[Au$_2$\{(C≡CCH$_2$O-4-C$_6$H$_4$)$_2$-1,1-C$_6$H$_9$-4-*t*-Bu\}\{Ph$_2$P(CH$_2$)$_4$-PPh$_2$\}], 6b. This was prepared similarly from **2b** (0.082 g, 0.10 mmol) and Ph$_2$P(CH$_2$)$_4$PPh$_2$ (0.036 g, 0.084 mmol). The product was isolated as an off-white solid. Yield: 0.083 g (80%). IR (KBr disk): ν(C≡C) 2133 cm^{-1}. Anal. Calcd for $C_{56}H_{58}Au_2O_2P_2$: C, 55.18; H, 4.80. Found: C, 55.51; H, 4.69. NMR for **6b** in CD_2Cl_2: δ(^{1}H) 0.76 [s, 9H, C*Me*$_3$]; 1.09−1.21 [m, 3H, Cy-*H*^{3}-ax + Cy-*H*^{4}-ax]; 1.63−1.76 [m, 6H, PCH$_2$CH_2 + Cy-*H*^{3}-eq]; 1.77−1.82 [m, 2H, Cy-*H*^{2}-ax); 2.32 (br, 4H, PCH_2); 2.71 (d, 2H, ^2J(HH) = 13 Hz, Cy-*H*^{2}-eq]; 4.73 [s, 2H, OCH_2-ax]; 4.78 [s, 2H, OCH_2-eq]; 6.92 [d, 2H, ^3J(HH) = 8 Hz, C$_6$H$_4$-*H*^{a}-ax]; 7.01 [d, 2H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{a}-eq]; 7.16 [d, 2H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{b}-ax]; 7.30 [d, 2H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{b}-eq]; 7.41−7.50 [m, 12H, P*Ph*]; 7.56−7.61 [m, 8H, P*Ph*]; δ(^{31}P) 38.15 [s, *P*-ax]; 38.29 [s, *P*-eq]. Partial NMR for **6b*** in $CDCl_3$ at 0 °C: δ(^{1}H) 0.69 [s, 18H, C*Me*$_3$]; 4.60 [s, 4H, OCH_2-ax]; 4.75 [s, 4H, OCH_2-eq]; 6.21 [d, 4H, ^3J(HH) = 8 Hz, C$_6$H$_4$-*H*^{a}-ax]; 6.43 [d, 4H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{a}-eq]; 6.66 [d, 4H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{b}-ax]; 6.69 [d, 4H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{b}-eq]; δ(^{31}P) 39.65 [s, *P*-ax]; 39.77 [s, *P*-eq]. Partial NMR for **6b**$^{\$}$ in $CDCl_3$ at −40 °C: δ(^{1}H) 0.72 [s, 18H, C*Me*$_3$]; 4.67 [s, 4H, OCH_2-ax]; 4.80 [s, 4H, OCH_2-eq]; 6.82 [d, 4H, ^3J(HH) = 8 Hz, C$_6$H$_4$-*H*^{a}-ax]; 6.92 [d, 4H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{a}-eq]; 7.07 [d, 4H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{b}-ax]; 7.20 [d, 4H, ^3J(HH) = 8 Hz, C$_6H_4$-*H*^{b}-eq]; δ(^{31}P) 37.75 [br s, *P*-ax + *P*-eq].

Table 1. Crystal Data and Structure Refinement for 5a*·3CH$_2$Cl$_2$

formula, fw	$C_{105}H_{102}Au_4Cl_6O_4P_4$, 2552.31
T	150(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/n$
cell dimens	a = 12.2933(11) Å
	b = 48.841(4) Å
	c = 16.6524(16) Å
	β = 96.913(2)°
V	9925.6(16) Å^3
Z	4
d(calc)	1.708 Mg m^{-3}
abs coeff	6.170 mm^{-1}
no. of indep reflns	14 596 [R(int) = 0.0669]
abs corr	integration
no. of data/restr/params	14 596/103/908
Goof on F^2	0.920
R [$I > 2\sigma(I)$]	R_1 = 0.0657, wR_2 = 0.1469

Structure Determination. Crystals of **5a***·3CH$_2$Cl$_2$ were grown by slow diffusion of ether into a solution containing a mixture of isomers **5a**, **5a***, and **5a**$^{\#}$ in CH_2Cl_2. A thin, colorless plate was mounted on a glass fiber. 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 data were scaled using SCALEPACK (Nonius B.V., 1998), and no other absorption correction was applied. The crystal data and refinement parameters are listed in Table 1.

The SHELXTL-NT V5.1 (Sheldrick, G. M.) suite of programs was used to solve the structure by direct methods, followed by successive difference Fouriers. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. There was considerable disorder present in the structure. One entire (C$_6$H$_{10}$)(C$_6$H$_4$CH$_2$C≡C)$_2$ unit was disordered over two positions and modeled as a 50:50 isotropic mixture with geometric restraints applied. The second bridging cyclohexyl moiety was disordered over two positions and modeled as a 60:40 isotropic mixture with geometric restraints. The solvent molecules were poorly ordered and were modeled isotropically with appropriate occupancies and geometric restraints.

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Supporting Information Available: Complete X-ray data for **5a***·3CH$_2$Cl$_2$ are available in CIF format free of charge via the Internet at http://pubs.acs.org.

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