Selectivity in the Self-Assembly of Organometallic Gold(I) Rings and [2]Catenanes

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The selectivity of formation of organometallic rings or [2]catenanes [{X(4-$C_6H_4OCH_2$-C≡CAu)$_2$(μ-Ph_2PZPPh_2)$_n$}], n =1 or 2, respectively, has been studied as a function of the hinge group X and the diphosphine ligand [X = O, S, SO_2, CH_2, CMe_2, CPh_2, $C(CF_3)_2$, C_6H_{10}; Z = $(CH_2)_m$ with m = 2−5]. When Z = $(CH_2)_3$, mixing of pairs of compounds with different C_{2v}-symmetrical hinge groups (X, X′ = SO_2, CH_2, CMe_2, CPh_2, $C(CF_3)_2$, C_6H_{10}) led to formation of an equilibrium mixture containing the unsymmetrical [2]catenanes [{X(4-$C_6H_4OCH_2$-C≡CAu)$_2$(μ-Ph_2PZPPh_2)}{X′(4-$C_6H_4OCH_2C$≡CAu)$_2$(μ-Ph_2PZPPh_2)], as identified by NMR spectroscopy. The complexes with Z = $(CH_2)_4$ exist in solution predominantly as the macrocycles and so do not form analogous mixed diacetylide complexes. When the hinge group contained a prochiral carbon center (X = CHMe, CMePh, 1,1-indanylidene), only achiral macrocycles [X(4-$C_6H_4OCH_2C$≡CAu)$_2$(μ-Ph_2PZPPh_2)] were formed in solution when Z = $(CH_2)_4$, but mixtures containing both achiral macrocycles and chiral [2]catenane were formed when Z = $(CH_2)_3$. In several cases, the solid-state structures of the isolated complexes were not representative of the structures in solution, with macrocycles being dominant in solution and [2]catenanes formed preferentially during crystallization.

Introduction

The formation by self-assembly of inorganic catenanes, rather than simple macrocyclic complexes, often proceeds under thermodynamic control, whereby the presence of kinetically labile coordinate bonds allows "error-correcting". Under these conditions, high yields of catenanes can be obtained provided that secondary bonding interactions between the two mechanically interlocked rings are great enough to overcome the associated unfavorable entropy effects.[1] Secondary bonding effects used to promote catenation include hydrogen-bonding, $\pi-\pi$ interactions, and metallophilic interactions.[1−3] The structures of catenanes can be determined in the solid state by X-ray crystallography and in solution by NMR and ESI-MS or MALDI-MS techniques. The NMR method typically relies on the observation of significant differences in chemical shifts in the ^{1}H NMR spectra between the catenane and the simple ring, and the method can be used to monitor the equilibria and kinetics involved in catenane formation and dissociation.[4−6] Mass spectrometry, even with soft ionization methods, is less reliable since the mechanical link in most catenanes involving organometallic or coordination complex functionality is easily broken.

There has been great interest in acetylide complexes of gold, which have interesting chemical and photophysical properties, and so many gold(I) and gold(III) acetylides, with simple and complex architectures, have been characterized.[7,8] Diacetylide ligands in combination with diphosphine ligands are known to give macrocycles or polymers, depending on the geometry and flexibility of the component ligands, and the macrocycles may undergo further self-assembly to yield [2]catenanes and even a doubly braided [2]catenane (Scheme 1).[3,9−13]

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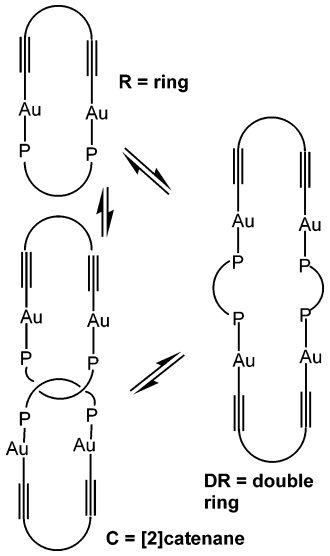
Scheme 1. Equilibrium between Ring, Double Ring, and [2]Catenane



For the compounds [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2$-PZP$Ph_2$)}$_n$], the nature of the hinge group X in the diacetylide ligand and the length of the spacer group Z in the diphosphine ligand are important factors in determining if the macrocycle (**R**, $n = 1$) or [2]catenane (**C**, $n = 2$) will be dominant, while the double ring (**DR**, $n = 2$, Scheme 1) may be present as a minor product in solution. In this diacetylide−diphosphine−digold(I) system, the formation of [2]catenanes has been limited to the cases with a hinge group X which forms a single-atom bridge, and with medium-sized spacer groups Z = $(CH_2)_3$ or $(CH_2)_4$.[3,9−12] For shorter spacer groups Z = C≡C, *trans*-HC═CH, or $(CH_2)_2$, the simple macrocyclic complexes ($n = 1$), which are formed by [1+1] self-assembly of the digold(I) diacetylide with the diphosphine ligand, are always isolated. In these cases in which the hinge group X forms a single-atom bridge, it seems that the 23-membered rings are too small to allow interpenetration to give [2]catenanes.[3] Longer spacer groups Z = $(CH_2)_5$, which give 26-membered rings when X is a single-atom bridge, and longer hinge groups also favor the formation of simple macrocycles (Table 1).[10,11,13] For example a 28-membered ring is formed when X = 1,4-$C_6H_4(CMe_2)_2$ and Z = *trans*-CH═CH.[13] Compounds that form 26- to 28-membered macrocycles do not catenate; instead, they tend to form loose side-by-side dimers in the solid state, in which a phenyl group of each macrocycle penetrates the cavity of the other.[10,11,13]

These experimental studies show that crystalline [2]-catenanes can be formed when X is a single-atom bridge and Z = $(CH_2)_3$ or $(CH_2)_4$. They arise by interpenetration of the 24- or 25-membered macrocycles and can be considered to be formed by [2+2] self-assembly of the digold(I) diacetylide and diphosphine components. Even in this optimum situation, the [2]catenanes are not always formed, as summarized in Table 1. The orientation of the aryl groups of the diacetylide ligand with respect to the C−X−C plane (termed the aryl twist angle, Θ, which is determined largely by the nature of the hinge group X) is a subtle factor that can determine if a [2]catenane can be prepared. The formation of a [2]-catenane is favored when Θ = 45−90° but not when Θ = ca. 0°, since the in-plane aryl group then blocks the cavity and disfavors the interpenetration needed for [2]-catenane formation. The case with Θ = ca. 0° is found with hinge groups X that can π-bond to the aryl groups (X = O, S, C═O, C═NR), and [2]catenanes are less favored in these cases than when X = CH_2, CHR, CR_2 (R = alkyl or aryl), SO_2, or a ketal, $C(OR)_2$ (Table 1).[3,9−12] The doubly braided [2]catenane crystallizes selectively in the case where Z = $(CH_2)_4$ and X = cyclohexylidene, C_6H_{10}.[3] When [2]catenanes are formed, the binding between the macrocycles is considered to involve some combination of aurophilic attractions and aryl−aryl attractions.[3]

Table 1. X-ray Structures of Alkynylgold(I) Rings and [2]Catenanes [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2$)}$_n$] (key: R = ring, C = [2]catenane, DC = doubly braided [2]catenane), as a Function of the Hinge Group X and Spacer Group Z[a]

X/Z = $(CH_2)_n$	$n = 2$[b]	$n = 3$	$n = 4$	$n = 5$
CH_2		**C**	C (3)	
CHMe		**C**		
CMe_2	R (3)[c]	C (3)	C (3)	
$C(CF_3)_2$			**C**	
CH(4-C_6H_4Br)		C (12)	C (12)	
CPh_2			**R**	
Cy		C (3)	DC (3)	
CO				R (10)
O			R (3)	**R**
S	**R**[d]		R (3)	
SO_2	R (11)[e]	C (11)		R (11)
ketal[f]	R (10)[d]	C (10)		
OCH_2CH_2O	R (13)[g]		R (13)	
1,4-$C_6H_4(CMe_2)_2$	R (13)[g]			

[a] Bold entries indicate structures from this work. References for known structures are given in parentheses. [b] Data are given for Z = $(CH_2)_2$ and also, when specified, for Z = CC, *trans*-CH═CH, and Fe(C_5H_4)$_2$. [c] Z = CC and $(CH_2)_2$. [d] Z = CC. [e] Z = CC and Fe(C_5H_4)$_2$. [f] ketal = C{$OCH_2CH(CH_2Br)O$}. [g] Z = *trans*-CH═CH.

The solid-state structures are not necessarily maintained in solution, because the lability of the gold−phosphorus bond allows equilibration between the macrocyclic (**R**, **DR**, Scheme 1), [2]catenane, and other isomeric forms. In solution, the gold(I) compounds with Z = $(CH_2)_3$ typically exist as a mixture of topological isomers including the simple ring (formed by [1+1] self-assembly), the [2]catenane and double ring (each formed by [2+2] self-assembly), and a hexamer of unknown structure (formed by [6+6] self-assembly), and the equilibrium has been studied in detail in the case with Z = $(CH_2)_3$ and X = CMe_2 by ^{1}H and ^{31}P NMR spectroscopy.[3d] Slow crystallization of the equilibrating mixture gave the pure gold(I) [2]catenane as determined by single-crystal X-ray structure determination. The gold(I) compounds with Z = $(CH_2)_4$ show only one species in solution, as observed by ^{1}H and ^{31}P NMR spectroscopy, and it has been assumed that this is the isomer observed in the solid state, as summarized in Table 1.[3,10−12] This paper describes new evidence,

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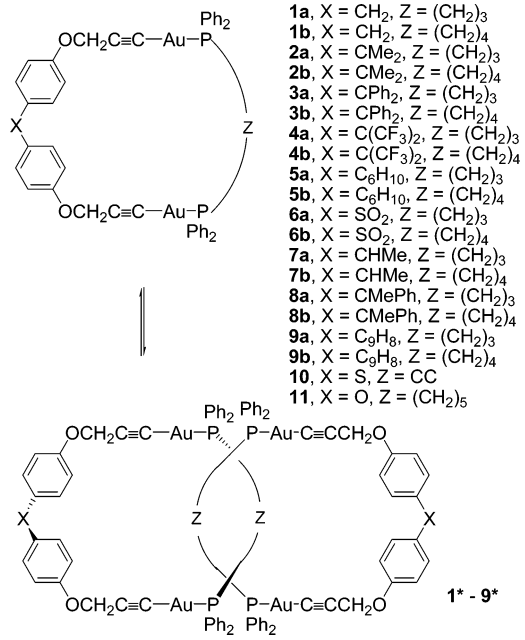
Scheme 2[a]



[a] C_6H_{10} = cyclohexylidene; C_9H_8 = 1,1-indanylidene.

obtained from ligand-exchange studies and from the synthesis of new compounds with prochiral centers at the hinge group, that indicates that the complexes with Z = $(CH_2)_4$ exist in solution predominantly as the simple ring, even though they may crystallize as the pure [2]-catenanes, and that the complexes with Z = $(CH_2)_3$ can form unsymmetrical [2]catenanes of the form [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2$)}{X′(4-$C_6H_4$-$OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2$)], when diacetylides with different hinge groups X and X′ are present.

Results

Synthesis of Gold(I) Compounds. The gold(I) complexes **1a**−**11** (Scheme 2) were prepared by general methods established previously.[3,9−12] The bis(phenols) X(4-$C_6H_4OH)_2$ were converted first to the propargyl ethers X(4-$C_6H_4OCH_2C{\equiv}CH)_2$ and then to the oligomeric digold(I) diacetylides [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2$}$_n$], which were insoluble in organic solvents, but which gave the soluble complexes [X(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2$-$PZPPh_2$)] on reaction with suitable diphosphine ligands. In the case of X = $C(CF_3)_2$, the oligomeric digold(I) diacetylide derivative could not be isolated, so the diphosphine complexes were prepared by reaction of the complexes [$Au_2Cl_2(\mu$-Ph_2PZPPh_2)] [Z = $(CH_2)_3$, $(CH_2)_4$] with silver trifluoroacetate (2 equiv) to give the corresponding trifluoroacetate complexes [$(AuO_2CCF_3)_2(\mu$-Ph_2PZPPh_2)],[14] which were then treated with triethylamine and the bis(alkyne) to give the corresponding complexes [$(CF_3)_2$C(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2$)]. The complexes with hinge group CHMe were also prepared by this method. Most complexes studied in this work have spacer groups Z = $(CH_2)_3$ or $(CH_2)_4$, since these are most likely to form [2]catenanes, but the structures of some complexes with smaller and larger spacer groups were determined for comparison purposes. The numbering system for the macrocycles is shown in full in Scheme 2, and the corresponding [2]-catenanes are denoted with an asterisk. Thus, for example, **1b** and **1b**** refer to the macrocycle and [2]-catenane respectively having X = CH_2 and Z = $(CH_2)_4$.

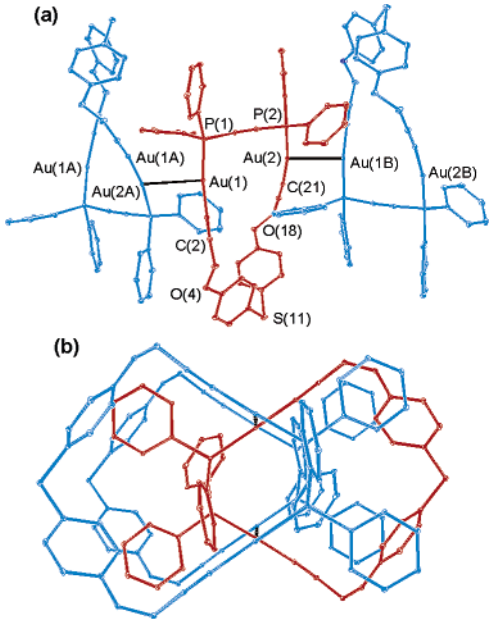


Figure 1. Structure of complex **10** (X = S, Z = CC), showing association of the macrocycles through aurophilic bonding: (a) view along the chain direction and (b) view down the chain direction.

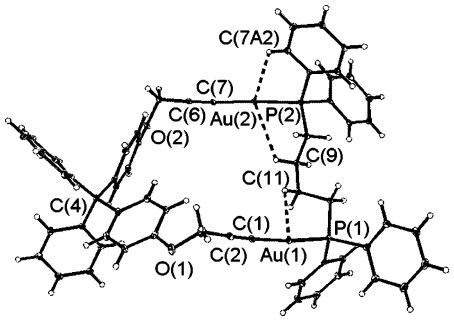


Figure 2. View of the structure of complex **3b** (X = CPh_2, Z = $(CH_2)_4$). Selected bond distances (Å) and angles (deg): Au(1)−P(1) 2.276(2); Au(2)−P(2) 2.279(2); Au(1)−C(1) 2.020-(7); Au(2)−C(7) 2.009(7); C(1)−C(2) 1.161(9); C(7)−C(6) 1.177(9); P(1)−Au(1)−C(1) 174.8(2); P(2)−Au(2)−C(7) 174.3-(2); Au(1)−C(1)−C(2) 176.8(8); Au(2)−C(7)−C(6) 175.4(7); C(1)−C(2)−C(3) 178(1); C(7)−C(6)−C(5) 177.1(8).

Characterization of the Complexes in the Solid State. The structures of several macrocycles (**3b**, **10**, and **11**) and [2]catenanes (**1a****, **4b****, and **7a****) were determined in order to probe the secondary bonding forces in the solid state, to provide a benchmark for studying the structures in solution, and, by comparison to earlier structure determinations (Table 1), to understand how substituent effects control the selectivity in forming macrocycles or [2]catenanes in the solid state.

Structures of the Macrocyclic Complexes. The structures of macrocycles **10**, **3b**, and **11** are shown in Figures 1−3 and illustrate how the structures vary as the ring size increases from 23 to 25 and 26, respectively. The structure of **10** (X = S, Z = C≡C, Figure 1) shows the presence of macrocycles organized into poly-

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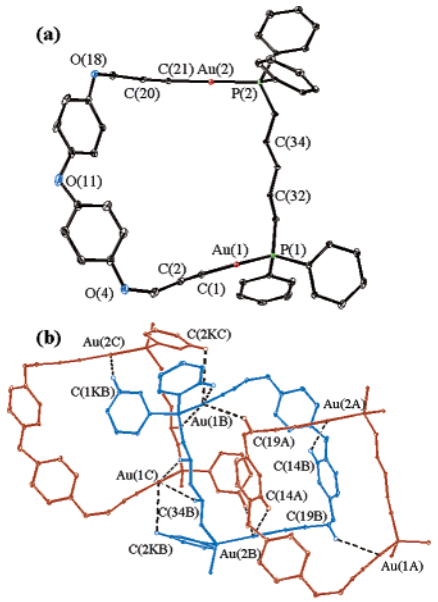

Figure 3. Views of the structure of complex **11** [X = O, Z = $(CH_2)_5$]: (a) individual macrocycle showing the large cavity; (b) interactions between neighboring molecules, showing the cavity partially occupied by a phenyl group from below and an aryl group from above, and showing some of the intra- and inter-macrocycle C−H···Au interactions (only the phenyl groups that are involved in forming close CH···Au contacts are shown, for clarity).

meric chains through aurophilic bonding[15] and is similar to that determined earlier with X = SO_2 and Z = C≡C [X = S: Au···Au = 3.0599(4) Å, CSC = 100.6(3)°, Θ = 50°, 76°; X = SO_2: Au···Au = 3.1819(3) Å, CSC = 104.7(3)°, Θ = 80°, 80°].[11] The largest differences are the angle CSC at the hinge atom and the aryl twist angles Θ, both of which are affected by the lone pairs of electrons on sulfur in complex **10**. The short spacer group Z = C≡C, with the associated transannular distance Au···Au = 6.19 Å in complex **10**, does not allow catenation to occur.

The molecular structure of the 25-membered macrocyclic complex **3b** is shown in Figure 2. The ring is large enough for catenation, with the transannular distance Au(1)···Au(2) = 7.73 Å, but the closest contact with a neighboring molecule occurs in a "side-by-side" contact. The main intermolecular forces appear to arise from aryl···aryl secondary bonds; the closest intermolecular distance Au(1)···Au(1A) = 5.33 Å and shows that there is no aurophilic bonding. The absence of catenation in **3b** can be attributed, at least in part, to the orientation of the four aryl groups around the carbon "hinge atom". Tetraarylmethanes typically have approximate S_4 symmetry,[16] in which the ideal aryl twist angles Θ will be 90° and 0°, and the 0° angle is unfavorable for catenation.[3] The structure of **3b** deviates slightly from ideal pseudo-S_4 symmetry, with aryl twist angles Θ = 66° and 17° for the phenylene groups, but the orientation with one small value of the aryl twist angle is unfavorable for catenation and so the simple ring structure of Figure 2 is observed. The aryl twist angles in analogous

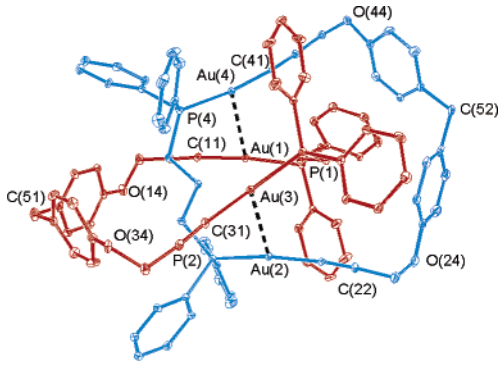

Figure 4. View of the structure of [2]catenane complex **1a*** (X = CH_2, Z = $(CH_2)_3$). Selected bond distances (Å) and angles (deg): Au(1)−Au(4) 3.3212(5); Au(2)−Au(3) 3.2937(6); Au(1)−P(1) 2.272(2); Au(2)−P(2) 2.271(2); Au(3)−P(3) 2.276(2); Au(4)−P(4) 2.277(2); Au(1)−C(11) 2.005(9); Au(2)−C(21) 1.990(8); Au(3)−C(31) 1.980(9); Au(4)−C(41) 2.000(8); P(1)−Au(1)−C(11) 171.4(3); P(2)−Au(2)−C(21) 169.8(3); P(3)−Au(3)−C(31) 173.1(3); P(4)−Au(4)−C(41) 173.1(3); Au(1)−C(11)−C(12) 173.6(9); Au(2)−C(21)−C(22) 172.2(9); Au(3)−C(31)−C(32) 173.3(8); Au(4)−C(41)−C(42) 174.2(9); C(11)−C(12)−C(13) 174(1); C(21)−C(22)−C(23) 174(1); C(31)−C(32)−C(33) 174(1); C(41)−C(42)−C(43) 177(1).

complexes with Z = $(CH_2)_4$ that form simple ring structures (Table 1) are Θ = 83° and 2° for X = O and Θ = 83° and 1° for X = S.[3] There are also some short intramolecular CH···Au contacts, indicated by dashed lines in Figure 2 [Au(1)···H(11B) = 2.88 Å, Au(2)···H(9A) = 2.97 Å, Au(2)···H(7AA) = 2.89 Å], that are close to the sum of the van der Waals radii [Au···H = 2.86 Å]. It is not obvious if these represent bonding interactions since the sterically open AuCC units will naturally be involved in close contacts. There are also some intermolecular CH···Au contacts, which are not shown. For example Au(1) has three short CH···Au contacts in the range 2.94−3.03 Å.

The molecular structure of the 26-membered macrocyclic complex **11** is shown in Figure 3. The ring is larger than in **3b**, and the transannular distance Au(1)···Au(2) = 8.57 Å is correspondingly larger, but the rings again pack side-by-side. A significant difference from **3b** is that there are several close Au···H contacts, which probably contribute to the intermolecular forces.[17] Some of these are shown in Figure 3b. For example, Au(1B) and Au(2A) each have four Au···H distances close to the sum of the van der Waals radii of 2.86 Å [Au(1B)···H(19A) 2.77; Au(1B)···H(32E) 3.00; Au(1B)···H(1FB) 3.03; Au(1B)···H(34E) 3.14 Å; Au(2A)···H(2BA) 2.91; Au(2A)···H(2IA) 2.92; Au(2A)···H(1KA) 2.92; Au(2A)···H(2HA) 3.08 Å]. There are also aryl···aryl secondary bonds, but the closest intermolecular distance Au(1)···Au(1A) = 5.77 Å, indicating the absence of aurophilic bonding. The aryl twist angles in complex **11** are Θ = 47° and 28°.

Structures of the [2]Catenanes. The structure of the [2]catenane complex **1a*** [X = CH_2, Z = $(CH_2)_3$] is shown in Figure 4. The complex is comprised of two

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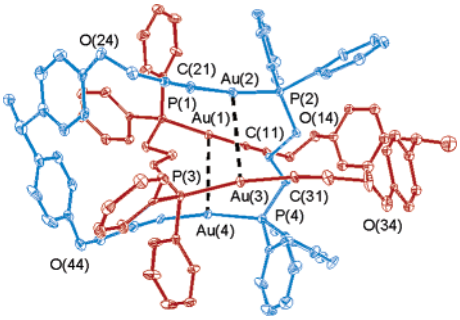


Figure 5. View of the structure of the chiral [2]catenane **7a*** (X = CHMe, Z = $(CH_2)_3$). Selected bond distances (Å) and angles (deg): Au(1)−Au(4) 3.3314(4); Au(2)−Au(3) 3.3622(4); Au(1)−P(1) 2.2756(18); Au(2)−P(2) 2.2787(18); Au(3)−P(3) 2.2742(18); Au(4)−P(4) 2.2666(18); Au(1)−C(11) 1.994(8); Au(2)−C(21) 1.989(7); Au(3)−C(31) 1.988(7); Au(4)−C(41) 2.004(7); P(1)−Au(1)−C(11) 174.1(2); P(2)−Au(2)−C(21) 173.3(2); P(3)−Au(3)−C(31) 171.2(2); P(4)−Au(4)−C(41) 168.9(2); Au(1)−C(11)−C(12) 174.1(6); Au(2)−C(21)−C(22) 175.5(7); Au(3)−C(31)−C(32) 172.3(7); Au(4)−C(41)−C(42) 170.5(7); C(11)−C(12)−C(13) 177.5(8); C(21)−C(22)−C(23) 177.7(8); C(31)−C(32)−C(33) 174.8(9); C(41)−C(42)−C(43) 173.2(9).

interlocked 24-membered rings, with inter-macrocycle aurophilic bonding indicated by the distances Au(1)−Au(4) = 3.3212(5) Å and Au(2)−Au(3) = 3.2937(6) Å. The gold atoms in each macrocycle are separated by distances Au(1)···Au(3) = 6.45 Å and Au(2)···Au(4) = 6.62 Å. The aryl twist angles Θ = 78° and 71° in one macrocycle and Θ = 89° and 69° in the other are in the range that favors catenation.[3]

The structure of the [2]catenane complex **7a*** [X = CHMe, Z = $(CH_2)_3$] is shown in Figure 5 and is similar to that of **1a***. The [2]catenane complex is chiral because there are two prochiral CHMe groups in each unit, but there is crystallographic disorder of the *R* and *S* enantiomers (disorder of the Me and H units of each CHMe group); only one component of the disorder is shown in Figure 5. The aurophilic bonding in **7a*** is indicated by the distances Au(1)−Au(4) = 3.3314(4) Å and Au(2)−Au(3) = 3.3622(4) Å. The transannular gold···gold separations are Au(1)···Au(3) = 6.44 Å and Au(2)···Au(4) = 6.64 Å.

The [2]catenane complex **4b*** [X = $C(CF_3)_2$, Z = $(CH_2)_4$] contains two interlocked 25-membered rings, as shown in Figure 6. The CF_3 substituents at the hinge group are of intermediate size, but the aryl twist angles are still in the range that favors catenation, with Θ = 50,46° and 46,43° for the component rings. The shortest gold···gold contact in **4b*** is Au(2)···Au(4) = 3.697(1) Å, which could represent a weak aurophilic secondary bond. The other shortest nonbonded contacts are Au(1)···Au(4) = 5.18 Å and Au(3)···Au(2) = 5.35 Å, which are clearly too long to represent Au···Au bonds. The transannular distances are Au(1)···Au(2) = 7.23 Å and Au(3)···Au(4) = 7.07 Å, and these values are only slightly different from the corresponding transannular distance in **3b** [7.73 Å], which forms a simple ring complex. These observations are consistent with the hypothesis that the aryl twist angle Θ has significant influence in determining the preferred structure. There are several short intra- and inter-macrocycle CH···Au contacts in the structure of complex **4b***, as shown in Figure 6b. These appear to complement the aryl···aryl

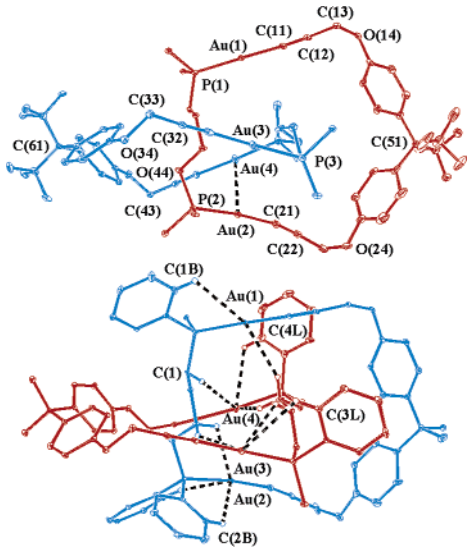


Figure 6. Views of the structure of [2]catenane **4b*** (X = $C(CF_3)_2$, Z = $(CH_2)_4$): above, showing the shortest Au··· Au contact; below, showing the intra- and inter-macrocycle C−H···Au interactions (fluorine atoms and several phenyl groups are omitted, for clarity). Selected bond distances (Å) and angles (deg): Au(1)−P(1) 2.283(3); Au(2)−P(2) 2.281(3); Au(3)−P(3) 2.276(4); Au(4)−P(4) 2.272(3); Au(1)−C(11) 2.01(1); Au(2)−C(21) 1.99(2); Au(3)−C(31) 2.00(2); Au(4)−C(41) 1.99(1); P(1)−Au(1)−C(11) 176.2(4); P(2)−Au(2)−C(21) 172.2(5); P(3)−Au(3)−C(31) 178.8(3); P(4)−Au(4)−C(41) 172.5(4); Au(1)−C(11)−C(12) 174(1); Au(2)−C(21)−C(22) 170(1); Au(3)−C(31)−C(32) 176(1); Au(4)−C(41)−C(42) 168(1).

attractions in providing a driving force for catenation in the absence of strong aurophilic bonding. Short CH···Au contacts have been noted in several gold(I) complexes, but this appears to be the first case noted in which it could stabilize one isomer with respect to another.[17]

Structures of the Complexes in Solution. The structures of the complexes in solution have been studied by ^1H and ^{31}P NMR spectroscopy.

Table 2 summarizes the observed ^{31}P NMR chemical shifts (CD_2Cl_2, 25 °C) for the complexes studied. The alkynylgold(I) compounds containing the diphosphine ligand Ph_2PZPPh_2 with Z = $(CH_2)_3$ typically equilibrate in solution to give a mixture containing the macrocycle **1a**−**9a**, the [2]catenanes **1a***−**9a***, and less intense peaks attributed to a double ring (**DR**, Scheme 1) and a hexamer of unknown structure. Each gives a characteristic resonance in the ^{31}P NMR spectrum at room temperature, and exchange between the [2]catenane and the other forms takes days to reach equilibrium.[3] The ^{31}P NMR resonances appear in a narrow chemical shift region for complexes with a variety of hinge groups: δ = 31.5−32.2 for the [2]catenane, δ = 35.7−36.0 for the macrocycle, and δ = 34−35 (broad) for the dimer and hexamer.[3,10−12] The ^{31}P NMR resonances for the macrocycles are observed as singlets in all cases, but the resonances of the [2]catenanes occur as singlets for compounds containing a C_{2v}-symmetric hinge group (**1a***−**6a***) and as two closely spaced doublets for the compounds containing a prochiral carbon at the hinge group (**7a***−**9a***). A characteristic feature of the ^1H NMR spectra is a large upfield shift for the protons of the diacetylide aryl groups in the [2]catenane compared

Table 2. ^{31}P NMR Data for the Gold(I) [2]Catenanes and Macrocyclic Rings in Solution and the Structures in Solid and Solution Phases[a]

complex	X	Z	δ (catenane)	δ (ring)	solid (ref)[b]
1a*, **1a**	CH_2	$(CH_2)_3$	32.00	35.98	1a*
1b*, **1b**	CH_2	$(CH_2)_4$		38.93	**1b*** (3)
2a*, **2a**	CMe_2	$(CH_2)_3$	31.96	35.89	**2a*** (3)
2b*, **2b**	CMe_2	$(CH_2)_4$		39.00	2b* (3)
3a*, **3a**	CPh_2	$(CH_2)_3$	32.07	35.78	
3b	CPh_2	$(CH_2)_4$		38.91	3b
4a*, **4a**	$C(CF_3)_2$	$(CH_2)_3$	31.57	35.69	
4b*, **4b**	$C(CF_3)_2$	$(CH_2)_4$		38.81	4b*
5a*, **5a**	C_6H_{10}	$(CH_2)_3$	32.17	35.92	5a*
5b**, **5b**	C_6H_{10}	$(CH_2)_4$		39.05	**5b**** (3)[c]
6a*, **6a**	SO_2	$(CH_2)_3$	31.58	35.91	**6a*** (11)
6b	SO_2	$(CH_2)_4$		38.79	
7a*, **7a**	CHMe	$(CH_2)_3$	31.97 (d), 32.10 (d)[d]	35.98	7a*
7b	CHMe	$(CH_2)_4$		38.98	
8a*, **8a**	CMePh	$(CH_2)_3$	32.07 (d), 32.36 (d)[d]	35.84	
8b	CMePh	$(CH_2)_4$		38.90	
9a*, **9a**	C_9H_8	$(CH_2)_3$	31.92 (d), 32.01 (d)[d]	35.86	
9b	C_9H_8	$(CH_2)_4$		38.93	
12	CMe_2, CH_2	$(CH_2)_3$	31.88, 32.15		
13	CMe_2, CPh_2	$(CH_2)_3$	32.00, 32.04		
14	CMe_2, $C(CF_3)_2$	$(CH_2)_3$	31.78, 31.95		
15	CMe_2, C_6H_{10}	$(CH_2)_3$	32.04, 32.14		
16	CMe_2, SO_2	$(CH_2)_3$	31.71, 31.83		
17	SO_2, C_6H_{10}	$(CH_2)_3$	31.86, 31.88		

[a] Spectra obtained in CD_2Cl_2 solution. Resonances occur as singlets unless otherwise stated. [b] Structure from X-ray determination, reference given if previously published. [c] Doubly braided [2]catenane. [d] "AB" multiplet, $^4J_{PP} = 6$ Hz.

to the macrocycle. For example, the C_6H_4 protons for **4a** appeared at $\delta = 7.11$ and 7.36, whereas those for **4a*** appeared at $\delta = 6.24$ and 6.89.

Using the NMR criteria established above, it is possible to identify isomers in solution. All of the complexes with Z = $(CH_2)_3$ crystallized as the [2]-catenanes **1a***−**9a*** and, when freshly dissolved, gave characteristic [2]catenane NMR spectra. Over time, equilibration with the simple macrocycle occurred. With smaller hinge groups [X = CH_2, CMe_2, C_6H_{10}, SO_2, CHMe], both macrocycle and [2]catenane were observed at equilibrium, but with larger hinge groups [X = CPh_2, $C(CF_3)_2$, CMePh], the equilibrium favored the macrocycle and the concentration of [2]catenane was too low to be detected. The structure of **8a*** (X = CMePh) in the solid state was confirmed to be the [2]catenane by a partial structure determination.

The alkynylgold(I) compounds with the diphosphine Ph_2PZPPh_2 with Z = $(CH_2)_4$ each gave only one singlet resonance in the ^{31}P NMR spectrum in the region δ = 38.8−39.0 and only a single set of resonances for the dialkynyl ligands. The simplest explanation is that the solutions contain a single isomer, which has effective mirror symmetry in all cases, and the implication then is that the compounds are present as the macrocycles in solution. It has previously been assumed that the solution and solid-state structures are the same, but this assumption now appears to be invalid.[3,12] Thus, if the complexes were present in solution as [2]catenanes, the complexes, such as **7b*** with X = CHMe, should give two resonances in the ^{31}P NMR spectrum. An earlier study of the complex with X = CH(4-C_6H_4Br) showed that, at very low temperatures, a trace of an "AB" resonance appeared in the ^{31}P NMR spectrum along with the dominant singlet resonance.[12] This observation is now interpreted in terms of a dominant presence of the macrocycle in solution, along with traces of the [2]-catenane at very low temperature. The NMR spectra of several of the complexes in Scheme 2 with Z = $(CH_2)_4$, including **7b**, were studied at temperatures down to −90°, but no significant changes were observed. The equilibrium between the macrocycle and the [2]catenane in solution is evidently much faster and more strongly favors the macrocycle when Z = $(CH_2)_4$ than when Z = $(CH_2)_3$, and freshly prepared solutions of the [2]catenanes show only resonances for the simple macrocycle. Further evidence for this new interpretation of the solution data is given below.

Identification of Unsymmetrical [2]Catenanes in Solution. The presence of labile gold−phosphorus bonds in the complexes allows threading and unthreading processes that interconvert the macrocycles and [2]-catenanes in solution. The use of two different diphosphine ligands Ph_2PZPPh_2 (defined by the spacer groups as Z and Z′) or two different dialkynyl ligands X(4-C_6H_4-$OCH_2CC)_2$ (defined by the hinge groups as X and X′) may then be expected to give mixtures of the symmetrical and unsymmetrical [2]catenanes in solution. A previous report described studies using a single hinge group X = CMe_2 and all combinations of pairs of diphosphine ligands Ph_2PZPPh_2 with Z = $(CH_2)_2$−$(CH_2)_5$, but no mixed [2]catenanes [{Me_2C(4-$C_6H_4OCH_2$-$CCAu)_2$(μ-Ph_2PZPPh_2)}{Me_2C(4-$C_6H_4OCH_2CCAu)_2$(μ-$Ph_2PZ'PPh_2$)}] were detected.[3] At the time, this result was surprising, but it can now be rationalized since the [2]catenane is probably present in solution in significant concentration only when Z = $(CH_2)_3$. A study of gold(I) complexes with mixed dialkynyl groups and with a single diphosphine ligand having Z = $(CH_2)_3$ or $(CH_2)_4$ has now been made.

Consider first the complexes having diphosphine ligands Ph_2PZPPh_2, with Z = $(CH_2)_3$, which have the greatest tendency to catenate. Figure 7 shows the ^{31}P NMR spectrum of a solution prepared by mixing equimolar amounts of complexes **2a*** (X = CMe_2) and **5a*** (X = C_6H_{10}) in CD_2Cl_2 solution and allowing time for equilibration to occur. By comparison with the spectra of the single-component complexes listed in Table 2, the broad

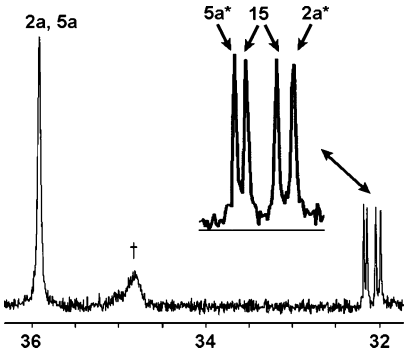
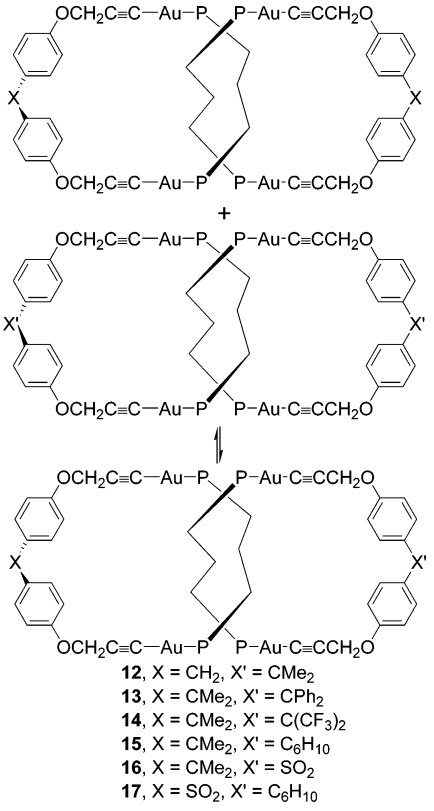


Figure 7. ^{31}P NMR spectrum (162 MHz, CD_2Cl_2, 25 °C) of an equilibrium mixture of macrocycles and [2]catenanes **2a/2a*** (X = X′ = CMe_2) and **5a/5a*** (X = X′ = C_6H_{10}) to give the mixed ligand [2]catenane **15** (X = CMe_2, X′ = C_6H_{10}). The broad peaks marked † are assigned to the double ring and hexamer isomers.

Scheme 3. Formation of Mixed Ligand [2]Catenanes



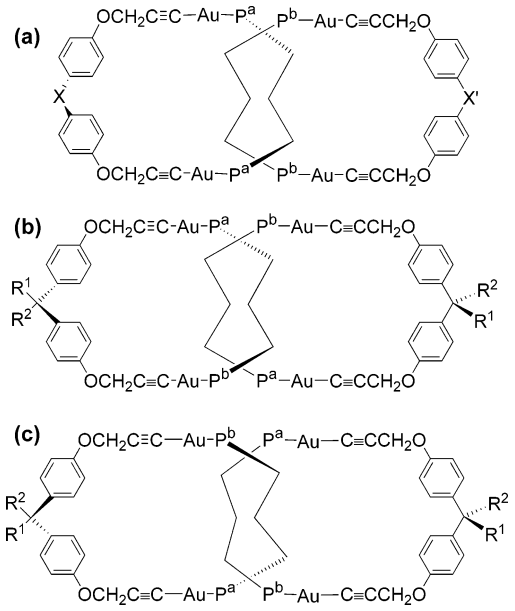
singlet resonance at δ = 35.9 (Figure 7) is assigned to the macrocycles **2a** and **5a**, which are formed by reversible dissociation from the parent [2]catenanes and which have accidentally degenerate chemical shifts. Sharp singlet resonances at δ = 31.96 and 32.17 are assigned to the parent [2]catenanes **2a*** and **5a***, and a broad unresolved resonance at δ = ca. 35.5 is assigned to double-ring and hexamer species. Most importantly, two new singlet resonances are observed at δ = 32.04 and 32.14, and these are assigned to the unsymmetrical [2]catenane **15**, [{$Me_2C(C_6H_4OCH_2CCAu)_2(\mu$-$Ph_2$-PZPPh$_2$)}{$C_6H_{10}(C_6H_4OCH_2CCAu)_2(\mu$-$Ph_2$PZPPh$_2$)}], Z = $(CH_2)_3$ (Scheme 3). If the equilibrium constants for dissociation of **2a*** and **5a*** are equal and if the redistribution between [2]catenanes is determined by statistical factors only, the ratio of the concentrations of catenanes is expected to be **2a***:**5a***:**15** = 1:1:2, and the intensities of the ^{31}P NMR peaks are consistent with the approximate statistical ratio in this case (Figure 7).

The unsymmetrical catenanes were observed in all cases when solutions were prepared containing complex **2a*** and another symmetrical [2]catenane **1a*** (X = CH_2), **3a*** (X = CPh_2), **4a*** (X = $C(CF_3)_2$), **5a*** (X = C_6H_{10}), or **6a*** (X = SO_2) having Z = $(CH_2)_3$ (Scheme 3). However, the ratio of concentrations of [2]catenanes defined by the combination of hinge groups XX:X′X′:XX′ = 1:1:2 was not always observed. It was noted earlier that the [2]catenane complexes **3a*** (X = CPh_2) and **4a*** (X = $C(CF_3)_2$) dissociate slowly in solution and exist predominantly as the simple rings **3a** and **4a**, respectively, at equilibrium. The NMR spectrum of a solution prepared from equimolar amounts of **2a*** (X = CMe_2) and **3a*** (X = CPh_2) initially showed the presence of the parent [2]catenanes and the corresponding ring complexes **2a** and **3a**. After 4 h, the concentration of **3a*** had decreased almost to zero, but **2a*** remained and the unsymmetrical [2]catenane **13** was detected. The mixed ligand [2]catenane **13** was still observed in solution after 2 weeks. From the peak intensities in the ^{31}P NMR spectra, the thermodynamic stability of the [2]catenanes toward dissociation to the component macrocycles follows the sequence **2a*** > **12** > **3a***, indicating that the hinge group effect favoring catenation is Me_2C > Ph_2C. A similar effect was observed in the equilibrium between **2a***, **4a***, and **14** (Scheme 3).

In contrast to the above observations for complexes with Z = $(CH_2)_3$, no new resonances were observed in the ^{1}H or ^{31}P NMR spectra of mixtures of pairs of alkynylgold(I) complexes with diphosphine ligands Ph_2-PZPPh_2 with Z = $(CH_2)_4$. For example, the ^{31}P NMR spectrum of a solution obtained by dissolving equimolar amounts of the solid [2]catenane complexes **1b*** (X = CH_2) and **2b*** (X = CMe_2) contained only two singlet resonances at δ = 38.93 and 39.00, which are assigned to the dissociated macrocycles **1b** and **2b**. The spectrum was unchanged after two weeks in solution. Similar observations were made for mixtures of **2b*** with **3b**, **4b***, **5b**** (this complex crystallizes as a doubly braided [2]catenane),[3] and **6b**. These observations are not consistent with the presence of [2]catenanes in solution, but add support to the conclusion that the complexes with Z = $(CH_2)_4$ exist *in solution* almost exclusively as the simple macrocyclic complexes, even though many of them crystallize as the [2]catenanes.

Chiral [2]Catenanes. The use of C_{2v}-symmetrically substituted hinge groups X (**1**−**6**) results in gold(I) macrocycles and [2]catenanes that are achiral. For each of these achiral molecules, only a single resonance in the ^{31}P NMR spectrum is expected and observed since the phosphorus atoms are in chemically equivalent positions. When the hinge group X has a prochiral carbon such as when X = CHMe (**7**), CMePh (**8**), or 1,1-indanylidene (**9**), the resulting gold(I) macrocycles are still achiral, but the [2]catenanes are chiral with C_2 symmetry. This results in nonequivalent phosphorus atoms P^a and P^b within each ring and contrasts with the case of the unsymmetrical [2]catenanes **12**−**17**, in which the nonequivalent phosphorus atoms P^a and P^b are in the two different rings (Scheme 4). The chiral [2]-catenanes exhibit axial chirality, similar to the allene

Scheme 4. (a) Unsymmetrical [2]Catenane with Different Hinge Groups; (b and c) *aR* and *aS* Enantiomers of the C_2-Chiral [2]Catenane with a Prochiral Hinge Group



and spirane systems.[18] The chiral axis passes diagonally through the center of the [2]catenane, with the arrangement of the R_1 and R_2 substituents determining the configuration of the [2]catenane (stereochemical descriptors a*R* and a*S*).[18,19] The [2]catenanes reported here, as well as the reported [2]catenane with X = CH(4-C_6H_4Br),[12] are not topologically chiral; each enantiomer can be transformed into the other by deformation of the prochiral carbon atom in topological space.[19,20] Previous examples of Euclidean chiral inorganic [2]catenanes have been based on pre-existing chiral elements in the rings, such as axially chiral binaphthyl units.[21]

The gold(I) compounds containing a prochiral carbon at the hinge group X and with Z = $(CH_2)_3$ show three resonances in their ^{31}P NMR spectra: an AB multiplet and a singlet (Table 2). For example, the gold(I) compound with hinge group X = CHMe (**7a**, **7a***) gave an AB multiplet at δ = 31.97 and 32.10 ($^4J_{PP}$ = 6 Hz) due to the chiral [2]catenane **7a*** and a singlet at δ = 35.98 due to the macrocycle **7a** (Figure 8). Similar observations were made for the other gold(I) compounds containing a prochiral carbon at the hinge group, and data are listed in Table 2. In contrast, when Z = $(CH_2)_4$, all complexes gave a singlet in the ^{31}P NMR spectrum, as expected if they exist as the achiral macrocycle only.

Discussion

The self-assembly process that occurs when digold(I) diacetylide units and diphosphine ligands react together can give isomers that form by [1+1] self-assembly to give simple macrocycles, by [2+2] self-assembly to give a [2]catenane and, in some cases, a double ring (Scheme 1), by [4+4] self-assembly to give a doubly braided [2]catenane, or by less defined forms of self-assembly to give higher oligomers or polymers.[3,10−13,22] For complexes [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2)$}$_n$], there appear to be only small energy differences between isomers, so tailoring of the ligands can lead to different products. In this work, it is shown that systems can be designed in which the [2]catenanes have nonequivalent phosphorus atoms while the simple macrocycles do not, and then the structures in solution can be studied by using ^{31}P NMR spectroscopy. The catenanes are unsymmetrical if they contain two different diacetylide groups [{X(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2)$}{X′(4-$C_6H_4$-$OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2)$] or if the hinge group contains a prochiral carbon center [{RR′C(4-C_6H_4-$OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2PZPPh_2)$}$_2$]. By use of this structural probe, it is shown that many of the complexes with Z = $(CH_2)_3$ exist to a major extent as [2]catenanes in solution but that the complexes with Z = $(CH_2)_4$ exist very largely as the simple macrocycles in solution. In both cases, the crystalline samples may exist as [2]catenanes. Thus, the initial assumption[3] that larger rings would be more likely to give [2]catenanes is disproved. Instead, there is a "Goldilocks" effect in which the 24-membered rings with Z = $(CH_2)_3$ appear optimum, and [2]catenanes are less favored with either smaller or larger rings. The hinge group X has a significant effect on the stability of the gold(I) [2]catenanes in solution. Sterically bulky substituents (X = $(CF_3)_2C$ or Ph_2C) or substituents that can conjugate to the aryl groups (X = O, S, C=O) disfavor the [2]catenane structure in solution compared to smaller groups that do not π-bond (X = CH_2, CHMe, CMe_2, C_6H_{10}, SO_2]. In cases in which the [2]catenane is present in solution in only very low concentration, either the simple macrocycle or the [2]catenane may crystallize depending on the magnitude of the equilibrium constant and the relative solubilities of the macrocycle and the [2]catenane, but the [2]catenane is relatively favored in the solid state through the entropy factor. Structural studies indicate that the secondary bonding forces that favor catenation can be any combination of aurophilic attractions, aryl···aryl attractions, and, possibly, CH···Au attractions. The aurophilic attractions are strongest when Z = $(CH_2)_3$, and the tight interlocking of the component macrocycles with the diphosphine ligand

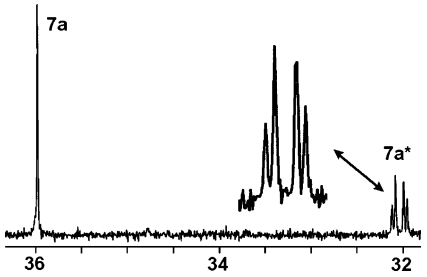


Figure 8. ^{31}P NMR spectrum of an equilibrium mixture of the macrocycle **7a** and the chiral [2]catenane **7a***.

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$Ph_2P(CH_2)_3PPh_2$ appears to add both thermodynamic and kinetic stability to the [2]catenane structure.

Experimental Section

General Procedures. NMR spectra were recorded by using Varian Mercury 400 and Varian Inova 400 spectrometers. ^1H and ^{13}C NMR chemical shifts are referenced to TMS, and ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4 as external standard. 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. The complexes $[AuCl(SMe_2)]$, $[Au_2Cl_2(\mu\text{-}Ph_2PZPPh_2)]$, with Z = $(CH_2)_3$ or $(CH_2)_4$, and several known [2]catenane molecules were prepared according to the literature.[3,10−12,14] Reactions involving gold compounds were protected from light by use of darkened reaction flasks. ***Caution***: Gold acetylides are potentially explosive; they should be prepared in small quantities and not subjected to shock.

$Ph_2C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$. This was prepared from the diphenol $Ph_2C(4\text{-}C_6H_4OH)_2$ according to a general procedure established previously[23] and was isolated as a cream powder. Yield: 97%. IR (KBr disk): ν(C≡C) 2125 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H)$ 2.52 [t, 2H, $^4J_{HH}$ = 2 Hz, C≡C*H*]; 4.66 [d, 4H, $^4J_{HH}$ = 2 Hz, OCH_2]; 6.85 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.10 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.16−7.24 [m, 10H, C*Ph*$_2$]; $\delta(^{13}C)$ 53.72 [*C*Ph$_2$]; 55.73 [O*C*H$_2$]; 75.45 [C≡*C*H]; 78.63 [*C*≡CH]; 113.53, 125.86, 127.38, 131.02, 132.12, 139.98, 147.00, 155.55 [C_6H_4 and *Ph*]. EI-MS (*m/z*): calcd for $C_{31}H_{24}O_2$ 428.1776, found 428.1767.

The following were prepared similarly.

$(F_3C)_2C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$: yellow oil. Yield: 99%. IR (Nujol mull): ν(C≡C) 2126 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H)$ 2.56 [t, 2H, $^4J_{HH}$ = 2 Hz, C≡C*H*]; 4.71 [d, 4H, $^4J_{HH}$ = 2 Hz, OCH_2]; 6.97 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.33 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; $\delta(^{13}C)$ 55.67 [O*C*H$_2$]; 63.52 [m, $^2J_{CF}$ = 25 Hz, *C*(CF$_3$)$_2$]; 75.90 [C≡*C*H]; 78.06 [*C*≡CH]; 114.32, 126.21, 131.42, 157.70 [C_6H_4]; 124.29 (q, $^1J_{CF}$ = 284 Hz, *C*F$_3$]. EI-MS (*m/z*): calcd for $C_{21}H_{14}F_6O_2$, 412.0897, found 412.0891.

$MeHC(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$: yellow liquid. Yield: 65%. IR (Nujol mull): ν(C≡C) 2121 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H)$ 1.61 [d, 3H, $^3J_{HH}$ = 7 Hz, CH*Me*); 2.53 [t, 2H, $^4J_{HH}$ = 2 Hz, C≡C*H*]; 4.09 [q, 1H, $^3J_{HH}$ = 7 Hz, C*H*Me]; 4.67 [d, 4H, $^4J_{HH}$ = 2 Hz, OCH_2]; 6.92 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.16 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4); $\delta(^{13}C)$ 22.14 [CH*Me*]; 43.07 [*C*HMe]; 55.73 [O*C*H$_2$]; 75.36 [C≡*C*H]; 78.69 [*C*≡CH]; 114.61, 128.41, 139.65, 155.72 [C_6H_4]. EI-MS (*m/z*): calcd for $C_{20}H_{18}O_2$ 290.1306, found 290.1314.

$MePhC(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$: cream solid. Yield: 74%. IR (KBr disk): ν(C≡C) 2118 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H)$ 2.16 [s, 3H, C*Me*Ph]; 2.53 [t, 2H, $^4J_{HH}$ = 2 Hz, C≡C*H*]; 4.68 [d, 4H, $^4J_{HH}$ = 2 Hz, OCH_2]; 6.89 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.04 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.11 [m, 2H, CMe*Ph*]; 7.18−7.30 [m, 3H, CMe*Ph*]; $\delta(^{13}C)$ 30.59 [C*Me*Ph]; 51.24 [*C*MePh]; 55.71 [O*C*H$_2$]; 75.42 [C≡*C*H]; 78.65 [*C*≡CH]; 113.96, 129.65, 142.25, 155.61 [C_6H_4]; 125.87, 127.79, 128.55, 149.33 [CMe*Ph*]. EI-MS (*m/z*): calcd for $C_{26}H_{22}O_2$ 366.1619, found 366.1618.

1,1-Indanylidene$(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$: orange oil. Yield: 0.88 g (70%). IR (Nujol mull): ν(C≡C) 2122 cm^{-1}. NMR in $CDCl_3$: $\delta(^1H)$ 2.51 [t, 2H, $^4J_{HH}$ = 2 Hz, C≡C*H*]; 2.76 [t, 2H, $^3J_{HH}$ = 6 Hz, indan-CH_2]; 2.86 [t, 2H, $^3J_{HH}$ = 6 Hz, indan-CH_2]; 4.66 [d, 4H, $^4J_{HH}$ = 2 Hz, OCH_2]; 6.87 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.03 [dd, 1H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, indan-C_6H_4]; 7.08 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.16−7.22 [m, 2H, indan-C_6H_4]; 7.27 [dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, indan-C_6H_4]; $\delta(^{13}C)$ 30.51, 43.71 [indan-CH_2]; 55.76 [O*C*H$_2$]; 60.55 [indan-spiro-*C*]; 75.39 [C≡*C*H]; 78.69 [*C*≡CH]; 114.07, 129.48, 140.29, 155.76 [C_6H_4]; 124.60, 125.91, 126.22, 126.75 [indan-aryl-*C*H]; 143.63, 149.66 [indan-aryl-*C*]. EI-MS (*m/z*): calcd for $C_{27}H_{22}O_2$ 378.1619, found 378.1620.

$[\{Ph_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2\}_n]$. This was prepared from $Ph_2C(4\text{-}C_6H_4OCH_2C{\equiv}CH)_2$ following an established procedure[3] and isolated as a brown solid. Yield: 51%. IR (Nujol): ν(C≡C) 2008 cm^{-1}. Anal. Calcd for $C_{31}H_{22}Au_2O_2$: C, 45.38; H, 2.70. Found: C, 45.30; H, 2.85.

The following were prepared similarly.

$[\{MePhC(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2\}_n]$: yellow solid. Yield: 83%. IR (Nujol): ν(C≡C) 2008 cm^{-1}. Anal. Calcd for $C_{26}H_{20}Au_2O_2$: C, 41.18; H, 2.66. Found: C, 40.79; H, 2.32.

$[\{C_9H_8(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2\}_n]$: C_9H_8 = 1,1-indanylidene, yellow solid. Yield: 82%. IR (Nujol): ν(C≡C) 2014 cm^{-1}. Anal. Calcd for $C_{27}H_{20}Au_2O_2$: C, 42.10; H, 2.62. Found: C, 41.91; H, 2.60.

$[H_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]$, 1a, and $[H_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]_2$, 1a*. This was prepared by reaction of the digold(I) diacetylide $[\{H_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2\}_n]$ with the diphosphine ligand $Ph_2P(CH_2)_3PPh_2$ according to the literature procedure[3] and isolated as a cream solid. Yield: 84%. IR (KBr disk): ν(C≡C) 2130 cm^{-1}. Anal. Calcd for $C_{46}H_{40}Au_2O_2P_2$: C, 51.12; H, 3.73. Found: C, 51.38; H, 3.60. **1a***: NMR in CD_2Cl_2: $\delta(^1H)$ 1.81 [br m, 4H, PCH$_2$CH_2]; 2.45 [br m, 8H, PCH_2]; 3.46 [s, 4H, CH_2]; 4.61 [br, 8H, OCH_2]; 6.07 [d, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 6.67 [d, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.42−7.75 [m, 40H, P*Ph*]; $\delta(^{31}P)$ 32.00 [s]. **1a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.81 [br m, 2H, PCH$_2$CH_2]; 2.45 [br m, 4H, PCH_2]; 3.83 [s, 2H, CH_2]; 4.76 [s, 4H, OCH_2]; 6.97 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.14 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.43−7.75 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 35.98 [s].

The following were prepared similarly.

$[Ph_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]$, 3a, and $[Ph_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]_2$, 3a*: recrystallized from CH_2Cl_2/pentane to give white needles. Yield: 86%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{58}H_{48}Au_2O_2P_2$: C, 56.50; H, 3.92. Found: C, 56.22; H, 3.51. **3a***: NMR in CD_2Cl_2: $\delta(^1H)$ 1.85 [br, 4H, PCH$_2$CH_2]; 2.48 [br, 8H, PCH_2]; 4.58 [s, 8H, OCH_2]; 6.10 [d, 8H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 6.73 [d, 8H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.08−7.29 [m, 20H, C*Ph*]; 7.37−7.59 [m, 40H, P*Ph*]; $\delta(^{31}P)$ 32.07 [s]. **3a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.85 [br m, 2H, PCH$_2$CH_2]; 2.50 [m, 4H, PCH_2]; 4.78 [s, 4H, OCH_2]; 6.99 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.13 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.18−7.24 [m, 10H, C*Ph*]; 7.43−7.59 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 35.78 [s].

$[Ph_2C(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2]$, 3b: cream solid. Yield: 76%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{59}H_{50}Au_2O_2P_2$: C, 56.83; H, 4.04. Found: C, 56.47; H, 3.80. NMR in CD_2Cl_2: $\delta(^1H)$ 1.76 [br s, 4H, PCH$_2$CH_2]; 2.38 [br s, 4H, PCH_2]; 4.78 [s, 4H, OCH_2]; 6.99 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.14 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.18−7.26 [m, 10H, C*Ph*]; 7.44−7.64 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 38.91 [s].

$[C_6H_{10}(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]$, 5a, and $[C_6H_{10}(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]_2$, 5a*: cream solid. Yield: 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: $\delta(^1H)$ 1.29 [br s, 12H, C_6H_{10}]; 1.82 [m, 4H, PCH$_2$CH_2]; 1.97 [br s, 8H, C_6H_{10}]; 2.46 [m, 8H, PCH_2]; 4.61 [br m, 8H, OCH_2]; 6.09 [d, 8H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 6.77 [d, 8H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.39−7.58 [m, 40H, P*Ph*]; $\delta(^{31}P)$ 32.17 [s]. **5a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.47 [br, 6H, C_6H_{10}]; 1.82 [br m, 2H, PCH$_2$CH_2]; 2.24 [br s, 4H, C_6H_{10}]; 2.46 [br m, 4H, PCH_2]; 4.75 [s, 4H, OCH_2]; 6.97 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.23 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.39−7.58 [m, 20H, P*Ph*]. $\delta(^{31}P)$ = 35.92 [s].

$[MePhC(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]$, 8a, and $[MePhC(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2]_2$, 8a*: cream solid. Yield: 83%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{53}H_{46}Au_2O_2P_2$: C, 54.37; H, 3.96. Found: C, 54.86; H, 3.88. **8a***: NMR in CD_2Cl_2: $\delta(^1H)$ 1.80

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Table 3. Crystallographic Data and Experimental Parameters for X-ray Structure Determinations

	1a*·2CH_2Cl_2	**7a***·CH_2Cl_2	**4b***′	**3b**·1/2Cl$(CH_2)_2$Cl	**10**·2CH_2Cl_2	**11**·MeCN
formula	$C_{47}H_{42}Au_2Cl_2O_2P_2$	$C_{48}H_{44}Au_2Cl_2O_2P_2$	$C_{49}H_{40}Au_2F_6O_2P_2$	$C_{59.5}H_{51}Au_2Cl_{0.5}O_2P_2$	$C_{46}H_{36}Au_2Cl_4O_2P_2S$	$C_{49}H_{45}Au_2NO_3P_2$
fw	1165.58	1179.60	1230.68	1271.60	1250.48	1151.73
T, K	200	150	150	150	150	150
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a, Å	12.6303(2)	12.5812(2)	11.7901(4)	11.5787(2)	15.1745(3)	13.1872(5)
b, Å	22.1259(5)	22.3998(3)	13.3497(5)	11.8408(3)	14.0174(4)	13.3599(6)
c, Å	30.8281(5)	31.2783(4)	30.933(1)	18.8233(4)	21.8130(5)	14.2729(3)
α, deg	90	90	93.601(2)	93.407(2)	90	65.537(2)
β, deg	96.8120(10)	97.7630(10)	95.965(2)	93.663(1)	105.383(1)	70.290(2)
γ, deg	90	90	110.796(2)	96.339(1)	90	81.152(2)
V, Å^3	8554.3(3)	8734.0(2)	4500.7(3)	2553.9(1)	4473.5(2)	2154.5(1)
Z	8	8	4	2	4	2
d_{calcd}, g cm^{-3}	1.810	1.794	1.816	1.654	1.857	1.775
μ, mm^{-1}	7.090	6.945	6.646	5.869	6.946	6.919
F(000)	4496	4560	2368	1241	2400	1116
no. of reflns	62 619	121 572	35 844	24 675	50 067	23 187
no. of data/restr/params	19 299/0/895	15 406/0/850	12 818/0/1003	11 706/3/498	13 009/6/466	9831/0/448
θ range, deg	2.59−27.49	2.55−25.03	2.66−23.26	2.57−27.51	2.67−30.06	2.65−27.51
GOF on F^2	0.952	0.980	1.021	1.029	0.999	0.949
R, R_w ($I > 2\sigma(I)$)	0.058, 0.142	0.040, 0.084	0.053, 0.105	0.047, 0.103	0.058, 0.144	0.045, 0.104

[s, 6H, C*Me*Ph]; 1.86 [br m, 4H, PCH_2CH_2]; 2.36 [br m, 8H, PCH_2]; 4.62 [br s, 8H, OCH_2]; 6.22 [t, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 6.67−6.72 [m, 12H, C_6H_4 and CMe*Ph*]; 7.09−7.58 [m, 46H, CMe*Ph* and P*Ph*]; $\delta(^{31}P)$ 32.07, 32.36 [AB multiplet, $^4J_{PP}$ = 6 Hz]. **8a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.82 [br m, 2H, PCH_2CH_2]; 2.13 [s, 3H, C*Me*Ph]; 2.48 [br m, 4H, PCH_2]; 4.77 [s, 4H, OCH_2]; 6.99 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.03 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.09 [d, 1H, CMe*Ph*]; 7.15−7.27 [m, 4H, CMe*Ph*]; 7.42−7.58 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 35.84 [s].

[MePhC(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$], 8b: cream solid. Yield: 81%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{54}H_{48}Au_2O_2P_2$: C, 54.74; H, 4.08. Found: C, 54.48; H, 3.73. NMR in CD_2Cl_2: $\delta(^1H)$ 1.72 [br s, 4H, PCH_2CH_2]; 2.11 [s, 3H, *Me*]; 2.35 [br s, 4H, PCH_2]; 4.77 [s, 4H, OCH_2]; 6.97−7.25 [m, 13H, C*Ph* and C_6H_4]; 7.42−7.63 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 38.90 [s].

[C_9H_8(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$], 9a, and [$C_9H_8$(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$]$_2$, 9a*: cream solid. Yield: 79%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{54}H_{46}Au_2O_2P_2$: C, 54.83; H, 3.92. Found: C, 54.64; H, 3.88. **9a***: NMR in CD_2Cl_2: $\delta(^1H)$ 2.28 [m, 8H, PCH_2]; 2.50 [m, 8H, PCH_2CH_2 and indan-CH_2]; 2.62 [t, 4H, $^3J_{HH}$ = 7 Hz, indan-CH_2]; 4.51 [br s, 8H, OCH_2]; 6.16 [m, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 6.71 [d, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 6.95 [d, 2H, $^3J_{HH}$ = 6 Hz, indan-C_6H_4]; 7.10−7.13 [m, 4H, indan-C_6H_4]; 7.15 [m, 2H, indan-C_6H_4]; 7.21−7.46 [m, 40H, P*Ph*]; $\delta(^{31}P)$ 31.92, 32.01 [AB multiplet, $^4J_{PP}$ = 6 Hz]. **9a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.82 [m, 2H, PCH_2CH_2]; 2.49 [m, 4H, PCH_2]; 2.76 [t, 2H, $^3J_{HH}$ = 6 Hz, indan-CH_2]; 2.84 [t, 2H, $^3J_{HH}$ = 6 Hz, indan-CH_2]; 4.75 [s, 4H, OCH_2]; 6.84 [t, 1H, $^3J_{HH}$ = 8 Hz, indan-C_6H_4]; 7.00 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.10 [m, 5H, C_6H_4 and indan-C_6H_4]; 7.19 [m, 1H, indan-C_6H_4]; 7.25 [m, 1H, indan-C_6H_4]; 7.41−7.59 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 35.86 [s].

[C_9H_8(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$], 9b: cream solid. Yield: 77%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{55}H_{48}Au_2O_2P_2$: C, 55.19; H, 4.04. Found: C, 54.84; H, 3.92. NMR in CD_2Cl_2: $\delta(^1H)$ 1.76 [br s 4H, PCH_2CH_2]; 2.37 [br s, 4H, PCH_2]; 2.75 [t, 2H, $^3J_{HH}$ = 6 Hz, indan-CH_2]; 2.81 [t, 2H, $^3J_{HH}$ = 6 Hz, indan-CH_2]; 4.76 [s, 4H, OCH_2]; 6.83−6.89 [m, 1H, indan-C_6H_4]; 6.99 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.04−7.09 [m, 1H, indan-C_6H_4]; 7.12 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.17−7.19 [m, 1H, indan-C_6H_4]; 7.24−7.26 [m, 1H, indan-C_6H_4]; 7.44−7.52 [m, 12H, P*Ph*]; 7.59−7.64 [m, 8H, P*Ph*]; $\delta(^{31}P)$ 38.93 [s].

[S(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2PC{\equiv}CPPh_2$], 10: cream solid. Yield: 73%. IR (KBr disk): ν(C≡C) 2135 cm^{-1}. Anal. Calcd for $C_{44}H_{32}Au_2O_2P_2S$: C, 48.90; H, 2.98. Found: C, 48.71; H, 3.08. NMR in CD_2Cl_2: $\delta(^1H)$ 4.78 [s, 4H, OCH_2]; 6.99 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.29 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.45−7.65 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 39.55 [s].

[O(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_5PPh_2$)], 11: cream solid. Yield: 80%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{47}H_{42}Au_2O_3P_2$: C, 50.82; H, 3.81. Found: C, 50.49; H, 3.73. NMR in CD_2Cl_2: $\delta(^1H)$ 1.60 [br, 6H, CH_2]; 2.38 [br, 4H, PCH_2]; 4.75 [s, 4H, OCH_2]; 6.95 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.06 [d, 4H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.40−7.69 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 37.45 [s].

[$(CF_3)_2$C(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)], 4a, and [$(CF_3)_2$C(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)]$_2$, 4a*. To a solution of [Au_2Cl_2(μ-$Ph_2P(CH_2)_3PPh_2$)] (0.505 g, 0.576 mmol) in CH_2Cl_2 (20 mL) was added AgO_2CCF_3 (0.254 g, 1.15 mmol). The mixture was stirred for 2 h, then filtered through Celite into a cooled (−78 °C) solution of $(CF_3)_2$C(4-$C_6H_4OCH_2C{\equiv}CH)_2$ (0.237 g, 0.576 mmol) and triethylamine (3.2 mL) in CH_2Cl_2 (40 mL). The reaction mixture was stirred at −78 °C for 2 h, then for a further 1 h with the cold bath removed. Water (50 mL) was added, then the organic phase was separated, dried ($MgSO_4$), and filtered. The filtrate was concentrated (∼8 mL), then pentane (80 mL) was added. The resulting light orange solid was isolated by filtration, then washed with pentane and ether. Recrystallization from CH_2Cl_2/pentane gave white needles. Yield: 0.538 g (77%). IR (KBr disk): ν(C≡C) 2133 cm^{-1}. Anal. Calcd for $C_{48}H_{38}Au_2F_6O_2P_2$: C, 47.38; H, 3.15. Found: C, 46.90; H, 2.85. **4a***: NMR in CD_2Cl_2: $\delta(^1H)$ 1.83 [br m, 4H, PCH_2CH_2]; 2.49 [br m, 8H, PCH_2]; 4.50 [s, 8H, OCH_2]; 6.24 [d, 8H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 6.89 [d, 8H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.21−7.39 [m, 40H, P*Ph*]; $\delta(^{31}P)$ 31.57 [s]. **4a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.86 [br m, 2H, PCH_2CH_2]; 2.54 [br m, 4H, PCH_2]; 4.81 [s, 4H, OCH_2]; 7.11 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.36 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.43−7.63 [m, 20H, P*Ph*]; $\delta(^{31}P)$ = 35.69 [s].

The following were similarly prepared.

[$(CF_3)_2$C(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_4PPh_2$)], 4b: light orange solid. Yield: 80%. IR (KBr disk): ν(C≡C) 2133 cm^{-1}. Anal. Calcd for $C_{49}H_{40}Au_2F_6O_2P_2$: C, 47.82; H, 3.28. Found: C, 47.40; H, 2.99. NMR in CD_2Cl_2: $\delta(^1H)$ 1.75 [br s, 4H, PCH_2CH_2]; 2.37 [br m, 4H, PCH_2]; 4.83 [s, 4H, OCH_2]; 7.13 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.36 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.43−7.63 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 38.81 [s].

[MeHC(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)], 7a, and [MeHC(4-$C_6H_4OCH_2C{\equiv}CAu)_2$(μ-$Ph_2P(CH_2)_3PPh_2$)]$_2$, 7a*: cream solid. Yield: 61%. IR (KBr disk): ν(C≡C) 2130 cm^{-1}. Anal. Calcd for $C_{47}H_{42}Au_2O_2P_2$: C, 51.57; H, 3.87. Found: C, 51.26; H, 3.56. **7a***: NMR in CD_2Cl_2: $\delta(^1H)$ 1.33 [d, 6H, $^3J_{HH}$ = 7 Hz, CH*Me*]; 1.82 [br m, 4H, PCH_2CH_2]; 2.44 [br m, 8H, PCH_2]; 3.67 [q, 2H, $^3J_{HH}$ = 7 Hz, C*H*Me]; 4.62 [br,

8H, OCH_2]; 6.09 [d, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 6.70 [d, 8H, $^3J_{HH}$ = 8 Hz, C_6H_4]; 7.43−7.55 [m, 40H, P*Ph*]; $\delta(^{31}P)$ 31.97, 32.10 [AB multiplet, $^4J_{PP}$ = 6 Hz]. **7a**: NMR in CD_2Cl_2: $\delta(^1H)$ 1.59 [d, 3H, $^3J_{HH}$ = 7 Hz, CH*Me*]; 1.82 [br m, 2H, PCH_2CH_2]; 2.46 [br m, 4H, PCH_2]; 4.06 [q, 1H, $^3J_{HH}$ = 7 Hz, C*H*Me]; 4.76 [s, 4H, OCH_2]; 6.98 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.17 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.43−7.63 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 35.98 [s].

[MeHC(4-$C_6H_4OCH_2C{\equiv}CAu)_2(\mu$-$Ph_2P(CH_2)_4PPh_2)$], 7b: cream solid. Yield: 63%. IR (KBr disk): ν(C≡C) 2132 cm^{-1}. Anal. Calcd for $C_{48}H_{44}Au_2O_2P_2$: C, 52.00; H, 4.00. Found: C, 51.68; H, 3.90. NMR in CD_2Cl_2: $\delta(^1H)$ 1.57 [d, 3H, $^3J_{HH}$ = 7 Hz, CH*Me*]; 1.72 [br, 4H, PCH_2CH_2]; 2.33 [br m, 4H, PCH_2]; 4.04 [q, 1H, $^3J_{HH}$ = 7 Hz, C*H*Me]; 4.76 [s, 4H, OCH_2]; 6.99 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.18 [d, 4H, $^3J_{HH}$ = 9 Hz, C_6H_4]; 7.42−7.61 [m, 20H, P*Ph*]; $\delta(^{31}P)$ 38.98 [s].

Mixed Ligand [2]Catenanes. A mixture of complexes **2a*** (5 mg, X = CMe_2) and **5a*** (5.1 mg, X = C_6H_{10}) was dissolved in CD_2Cl_2 (0.5 mL) in an NMR tube. The ^1H and ^{31}P NMR spectra were obtained immediately and then periodically over a period of 1 week, until equilibrium was reached. The ^{31}P NMR spectrum at equilibrium is shown in Figure 7, and data for the mixed ligand [2]catenane **15** (X = CMe_2, X′ = C_6H_{10}) are listed in Table 2. The other reactions were studied similarly and data are in Table 2.

X-ray Crystal Structure Determinations. Crystals of **1a***·$2CH_2Cl_2$, **4b***, and **7a***·CH_2Cl_2, were grown by slow diffusion of pentane or petroleum ether into a solution of the corresponding complex in CH_2Cl_2. Similarly, crystals of **10**·$2CH_2Cl_2$ were obtained from CH_2Cl_2/ether, and crystals of **3b**·$1/2Cl(CH_2)_2Cl$ and **11** from 1,2-$C_2H_4Cl_2$/MeCN. Data were collected by using a Nonius Kappa-CCD diffractometer with Mo Kα radiation with COLLECT (Nonius B.V., 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out with the DENZO (Nonius B.V., 1998) package. The data were scaled using SCALEPACK (Nonius B.V., 1998). The SHELXTL-NT (G. M. Sheldrick, Madison, WI) package was used to solve the structures, followed by successive difference Fourier transformations, and refined with full-matrix least-squares on F^2. Non-hydrogen atoms were refined anisotropically, unless otherwise specified. The hydrogen atoms were calculated geometrically, riding on their respective carbon atoms. Crystal data and refinement parameters are listed in Table 3.

7a*. The molecule showed disorder at the hinge group CHMe and the associated aryl groups. One was modeled as a 65/35 and the other as a 57/43 isotropic mixture.

3b. The 1,2-dichloroethane solvent molecule, which was located on a symmetry element, was disordered and modeled at half-occupancy. The distances were fixed as C−C = 1.50 Å and C−Cl = 1.70 Å.

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Supporting Information Available: Tables of X-ray data in cif format are available free of charge via the Internet at http://pubs.acs.org.

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