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Gold(I) Macrocycles and Topologically Chiral [2]Catenanes

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Abstract: The design and synthesis of a new type of topologically chiral [2]catenane is reported. The compounds are formed easily by self-assembly on reaction of the oligomeric digold(I) diacetylide precursor complex $[\{4\text{-BrC}_6H_4CH(4\text{-C}_6H_4OCH_2CCAu)_2\}_n]$ with diphosphine ligands. Reactions with the diphosphines PP = bis(diphenylphosphinophoshino)acetylene, *trans*-1,2-bis(diphenylphosphino)ethylene, bis(diphenylphosphino)ethane, and 1,1′-bis(diphenylphosphino)ferrocene yield simple ring complexes $[4\text{-BrC}_6H_4\text{-}CH(4\text{-C}_6H_4OCH_2CCAu)_2(\mu\text{-PP})]$ as the only products, since the spacer groups in the diphosphines are not long enough or are too bulky to allow catenane formation. Reaction with PP = bis(diphenylphosphino)propane or bis(diphenylphosphino)butane gave [2]catenane complexes $[\{4\text{-BrC}_6H_4CH(4\text{-C}_6H_4OCH_2CCAu)_2\text{-}(\mu\text{-PP})\}_2]$, whose structures are confirmed crystallographically. The macrocyclic ring compounds have C_s symmetry but, as a result of the presence of the unsymmetrical "hinge group" 4-BrC_6H_4CH, the [2]catenanes have C_2 symmetry and so are topologically chiral. In favorable cases, the formation of the [2]catenane can be proved by NMR spectroscopy since catenane formation leads to nonequivalence of most ring atoms. The formation of the [2]catenanes was successfully predicted based on the conformation of the precursor bis(phenol), and it is argued that the methods used should be more generally applicable to the synthesis of functionally substituted supermolecules of interest for application in molecular devices.

Introduction

The chemistry of interlocked molecules—catenanes, rotaxanes, and knots—is enjoying a period of remarkable growth, since the advent of new and improved synthetic strategies allows the isolation and characterization of increasingly intricate structural motifs.[1,2] Self-assembly from simple precursor molecules is the optimum synthetic method for these "supermolecules", and so a fundamental understanding of the self-assembly process is a vital step with respect to the potential application of these new molecules in the development of nanotechnology.[3]

Recent work on the synthesis of organogold(I) rings, oligomers, and polymers[4] led to the discovery of the first family of organometallic catenanes by self-assembly from the components $[\{X(C_6H_4OCH_2CCAu)_2\}_n]$, an oligomeric digold(I) diacetylide, and $Ph_2P(CH_2)_nPPh_2$, a diphosphine ligand.[5] Systematic investigation of this unusual self-assembly system showed that the number of methylene spacer groups *n* in the diphosphine ligand $Ph_2P(CH_2)_nPPh_2$ and the nature of the hinge group X are key factors in determining if the self-assembly will give a simple ring by 1 + 1 assembly, a [2]catenane by 2 + 2 assembly, or a doubly braided [2]catenane by 4 + 4 assembly (Scheme 1).[6] The selectivity is determined by thermodynamic rather than kinetic factors in most cases, and the molar masses are most reliably determined by X-ray structure determinations though

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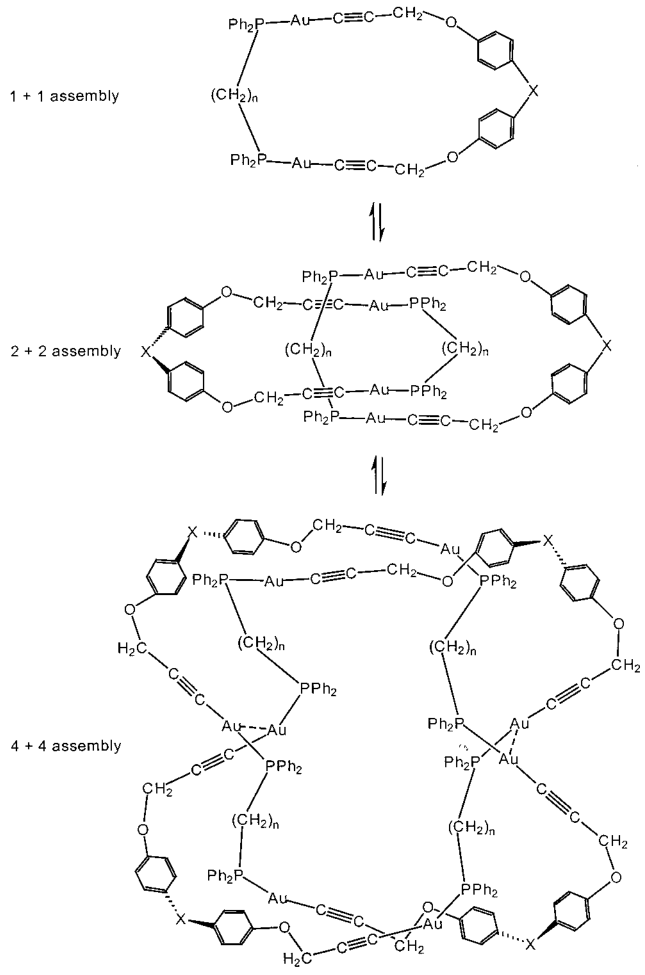
Scheme 1



MALDI-TOF or ESI MS can give useful data in favorable instances.[5,6]

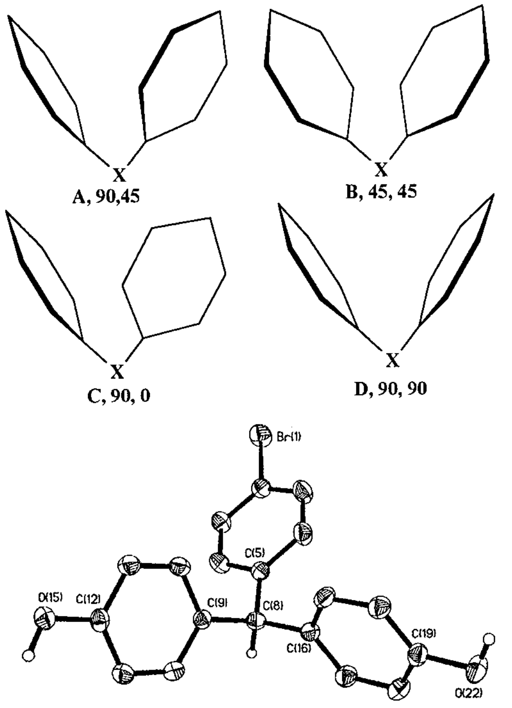


Figure 1. Top: Conformations of $X(C_6H_4O)_2$ groups that, in the digold(I) complexes $[\{X(4\text{-}C_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)\}_x]$, favor [2]-catenane (**A** and **B**), simple ring (**C**), or doubly braided catenane (**D**) formation. Bottom: The structure of the precursor compound **1** in which the corresponding angles are 85° and 54°, close to **A** and so expected to favor [2]catenane formation.

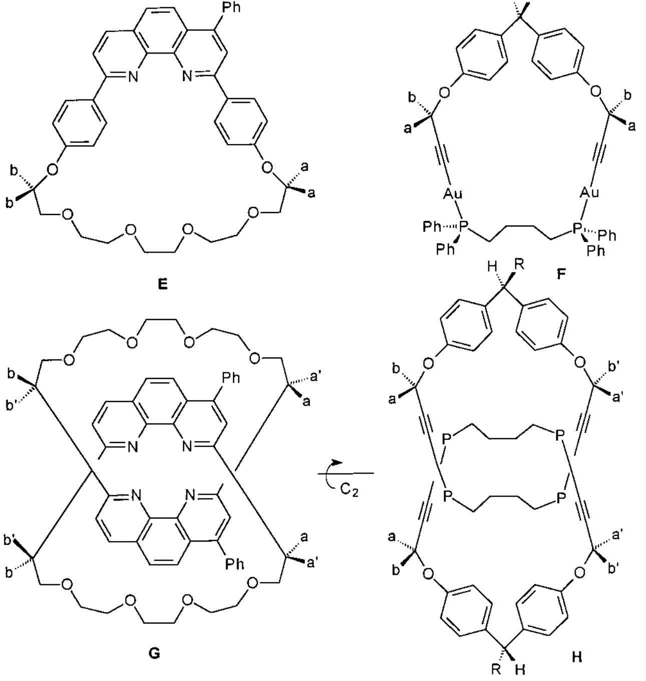


Figure 2. Two rings that can give topologically chiral [2]catenanes. **E** and **F** each have C_s symmetry, but the mirror plane lies in the ring plane in **E** and perpendicular to the ring plane in **F**. **G** and **H** are the corresponding topologically chiral [2]catenanes, each with C_2 symmetry. Nonequivalent CH_2 protons are indicated as a,b or, in the [2]catenanes, a,a′; b,b′.

Formation of the [2]catenane was favored for $n = 3$ or 4, and for hinge groups X which gave conformations of the $X(C_6H_4O)_2$ units close to **A** or **B** (Figure 1, X = CH_2 or CMe_2), rather than **C** (simple ring formation, X = O or S) or **D** (doubly braided [2]catenane formation, X = cyclohexylidene).[6] A key test of the value of this correlation is to determine if it can be used predictively in the design of functional [2]catenanes. This article reports the application to the design of chiral [2]catenanes. Although there is intense interest in chiral supermolecules,[7] the first report of a topologically chiral [2]catenane still represents the state of the art.[8] In that work, the asymmetry resulted from in-plane substitution in the macrocyclic ring **E** (Figure 2), whereas in the present work, out-of-plane substitution is introduced through the unsymmetrical hinge group 4-bromophenylmethylene as shown in **F** (Figure 2). In both cases, the resulting [2]catenane is C_2 symmetric and chiral, whereas a single ring is C_s symmetric and achiral. However, there are important differences in terms of the symmetry of atoms in and out of the ring plane as illustrated in Figure 2 for pairs of CH_2 groups. The two ring types shown in Figure 2 are thus complementary, and each represents a simple way to obtain topologically chiral [2]catenanes.

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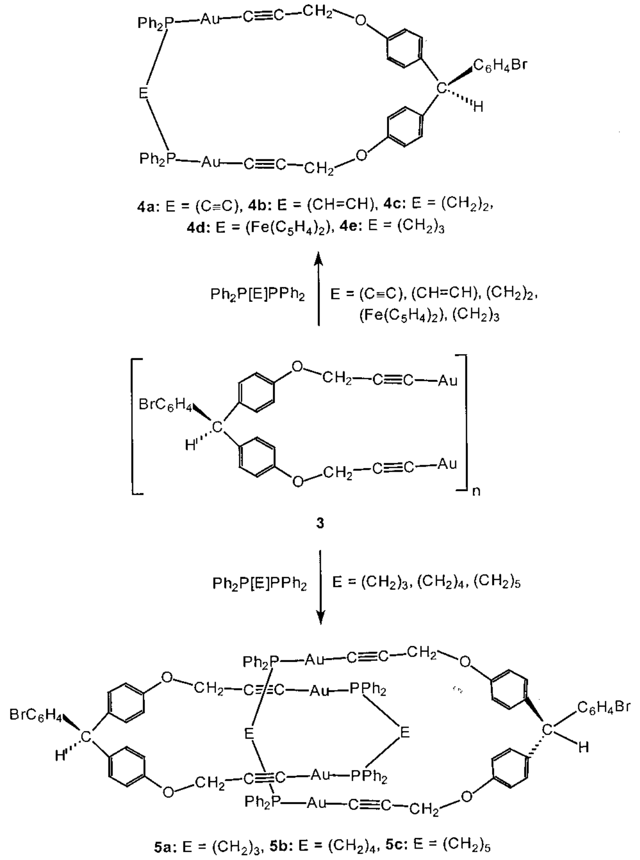
Scheme 2



Results

The Precursor Complexes. The bisphenol derivative (4-bromophenyl)bis(4-hydroxyphenyl)methane (**1**) was synthesized by the acid catalyzed condensation of phenol and 4-bromobenzaldehyde.[9] The structure of **1** is shown in Figure 1. It adopts a propeller conformation, with the two phenol rings twisted at angles of 54 and 85° with respect to the hinge plane (plane defined by the hinge carbon atom and its two bonded *ipso* carbon atoms, Figure 1). On the basis of the empirical correlation previously established,[6] the orientation of the phenol groups in this parent bis(phenol) is close to the ideal conformation **A** (Figure 1) for the formation of singly braided [2]catenanes from the propargylgold(I) derivatives which are formed as shown in Scheme 2. Another important feature of bis(phenol) **1** is the presence of nonequivalent groups on the hinge carbon atom [H and 4-C_6H_4Br], which will give a catenated product with C_2 symmetry.

The synthesis of the bis(propargyl) derivative 4-BrC_6H_4CH-(4-$C_6H_4OCH_2CCH)_2$, **2**, and then the oligomeric digold(I) diacetylide [$\{4\text{-}BrC_6H_4CH(4\text{-}C_6H_4OCH_2CCAu)_2\}_n$], **3**, was straightforward.[5,6] Such gold(I) acetylides are oligomeric or polymeric, with both σ and π bonds from gold to the alkynyl groups, and the resulting insolubility makes structural characterization difficult.[10] Evidence for the proposed structural type is seen in the IR spectrum which shows $\nu(C{\equiv}C) = 2010\ cm^{-1}$, a reduction of 113 cm^{-1} compared to the parent bis(alkyne) **2**, as a consequence of the alkynyl group acting as a π-donor to

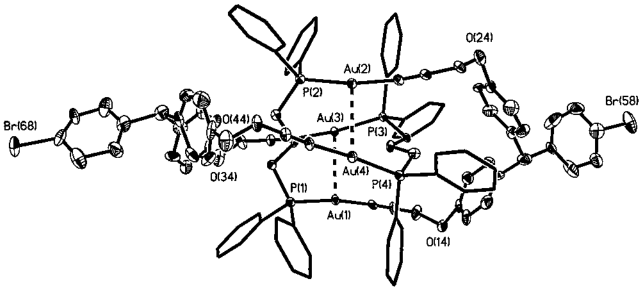


Figure 3. A view of the structure of the [2]catenane complex **5a**. Selected bond distances (Å) and angles (deg): Au(1)−Au(3) 3.1937(6); Au(2)−Au(4) 3.1409(6); Au(1)−C(11) 2.02(1); Au(2)−C(21) 2.00(1); Au(3)−C(31) 2.01(1); Au(4)−C(41) 2.00(1); Au(1)−P(1) 2.272(4); Au(2)−P(2) 2.280-(3); Au(3)−P(3) 2.270(3); Au(4)−P(4) 2.266(4) C; C(11)−Au(1)−P(1) 171.8(3); C(21)−Au(2)−P(2) 171.0(3); C(31)−Au(3)−P(3) 169.7(3); C(41)−Au(4)−P(4) 174.3(3).

the gold(I) centers in **3**. Compound **3** reacted with diphosphine ligands to yield macrocyclic organogold(I) complexes (Scheme 2), by replacement of the gold−alkyne π-bonds by the stronger phosphine donors. The challenge is to determine if the simple ring, **4**, or singly braided [2]catenane, **5**, or other products are formed by the self-assembly process.

Macrocyclic Complexes. Reaction of **3** with the diphosphines bis(diphenylphosphino)acetylene, *trans*-1,2-bis(diphenylphosphino)ethylene, bis(diphenylphosphino)ethane, and 1,1′-bis(diphenylphosphino)ferrocene yield simple ring complexes **4a**−**d** as the only products (Scheme 2). In these cases, the spacer groups are not long enough or are too bulky to allow catenane formation. In each case, the ^{31}P NMR spectrum contains only a singlet resonance, and the ^{1}H and ^{13}C NMR spectra are consistent with the expected C_s symmetry. For example, complex **4c** gave single resonances for the alkynyl carbon atoms at $\delta(^{13}C) = 97.53$ [***C***≡C−Au] and 132.00 [C≡***C***−Au] and the observation of phosphorus−carbon coupling proves the presence of PAuCC units. However, the expected nonequivalence of out-of-ring-plane atoms (Figure 2) was not resolved. For example, the OCH^aH^b protons gave a single resonance $\delta(^{1}H) = 4.78$ [s, 4H, OCH_2] and only one set of phenyl resonances was observed for the PPh^aPh^b groups in the ^{13}C NMR spectrum. The structure of **4a** was confirmed by a partial structure determination, but poor quality data did not allow a full refinement.

[2]Catenanes. Reaction of **3** with bis(diphenylphosphino)propane gave a mixture of products: a simple ring **4e**, a [2]catenane **5a**, and a small amount of a third complex **6**, whose structure is unknown. The $(CH_2)_3$ spacer-group is only just long enough to allow catenation to occur, and an equilibrium exists between the three products. Recrystallization of the reaction mixture gave pure [2]catenane **5a**, whose structure is shown in Figure 3. The two-component 24-membered rings of the catenane are tightly entwined, as evidenced by the presence of two strong intramolecular aurophilic interactions [Au(1)−Au(3) = 3.1937(6) Å; Au(2)−Au(4) = 3.1409(6) Å].[11] The phenol twist angles in the catenane [84.1 and 45.3° in one ring, 93.6 and 47.3° in the other] are comparable to those in the parent bisphenol **1**. This provides further support for the proposal that it is the aryl conformations that direct the self-assembly process and not vice versa. The solid-state structure also illustrates the

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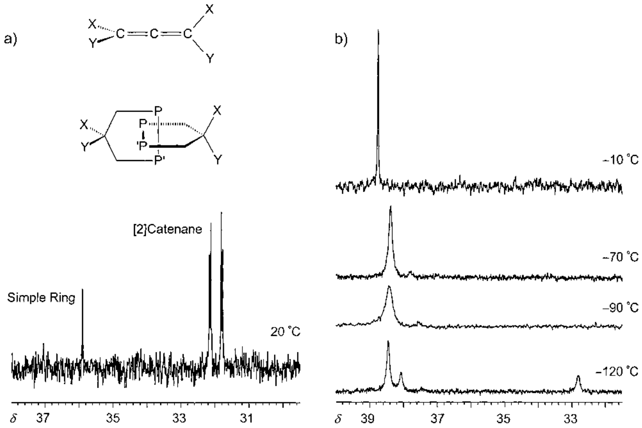

Figure 4. ^{31}P NMR spectra of complexes **5a** and **5b**. (a) The analogy between chiral allene and topologically chiral [2]catenane and the non-equivalence of phosphorus atoms P, P′ in the [2]catenane **5a**. (b) The variable-temperature ^{31}P NMR spectra of [2]catenane **5b**—evidence for two easily equilibrating conformers, one giving a singlet and the other giving two singlets.

approximate C_2 symmetry of the catenane, a result of the presence of inequivalent groups on the hinge carbon atom. The lack of mirror symmetry in **5a** is expected to lead to nonequivalence of ring atoms that would be equivalent in a simple macrocyclic structure, and this is most simply illustrated by the ^{31}P NMR spectrum (Figure 4a). In a solution containing both **4e** and **5a**, a singlet was observed at δ 35.90 for the simple ring **4e** (C_s symmetry) and an AB quartet at δ 31.80 and 32.15 ($^4J_{PP} = 6$ Hz) for the [2]catenane **5a** (C_2 symmetry). This splitting of the phosphorus resonances on [2]catenane formation is not observed when there is a symmetrical hinge such as CMe_2 and so, when it is resolved, the effect confirms that the [2]-catenane structure is maintained in solution. However, in the ^{1}H NMR spectrum, the expected nonequivalence of OCH^aH^b protons or PPh^aPh^b resonances was not resolved. For example, the OCH^aH^b protons appeared as a broad resonance in the 600 MHz ^{1}H NMR spectrum.

The reaction of complex **3** with bis(diphenylphosphino)butane was expected to give a [2]catenane selectively since the $(CH_2)_4$ spacer group in the diphosphine and the conformation of the phenol groups are both optimized for this reaction. Indeed, the reaction occurred selectively to give complex **5b** in high yield, and a structure determination confirmed that the [2]catenane was formed selectively by the self-assembly process (Figure 5). Once again the phenol twist angles (Figure 1) are essentially maintained from the parent bisphenol [84.9 and 35.3° in one ring, 76.2 and 36.5° in the other]. In **5b**, the interlocking of the larger 25-membered rings occurs without formation of any very short Au···Au contacts [the shortest is shown in Figure 5 with Au(1)···Au(4) = 3.47 Å and corresponds to a weak aurophilic attraction[11] while Au(1)···Au(2) = 5.15 Å, Au(2)···Au(3) = 6.54 Å, and Au(3)···Au(4) = 6.54 Å are clearly nonbonding] and so the driving force for [2]catenane formation arises primarily from aryl−aryl attractive forces in this case. The symmetry of the [2]catenane is approximately C_2 and so, as discussed for **5a**, there are expected to be two ^{31}P NMR resonances, as well as a doubling of other ring resonances in the ^{1}H and ^{13}C NMR spectra for **5b**. However, the room temperature ^{31}P NMR spectrum (Figure 4b) contained only one singlet at δ 38.86, not the two signals expected for the C_2 structure. One interpretation of this observation is that the ring atoms are sufficiently remote from the source of asymmetry that the two different phosphorus environments are effectively degenerate. The increased flexibility compared to **5a** might be a factor and, in an attempt to slow these molecular motions, low-temperature ^{31}P NMR of **5b** were recorded in 50:50 $CD_2Cl_2/CHFCl_2$ and are illustrated in Figure 4b. As the solution of **5b** is cooled the singlet broadens but, even at −120 °C, the main resonance does not split. However, at the lowest temperatures two new peaks δ 38.09 and 32.83 grow in, and the original singlet sharpens at −120 °C. It is likely that the new resonances are due to another catenane "conformer", perhaps one that is similar to the structure of **5a,** with closer Au···Au interactions that help to differentiate the ^{31}P environments. The relative intensities of the ^{31}P resonances in the temperature range −100 to −120 °C were independent of the concentration of **5b**, thus showing that the two forms have the same molecular weight. In the ^{1}H NMR spectrum of **5b**, the OCH^aH^b protons appeared as a closely spaced AB quartet, $^2J(H^aH^b) = 17$ Hz, and so it seems that [2]catenane formation causes the resolution since it was not observed for any of the simple ring complexes **4**. However, the further splitting expected for the [2]catenane (Figure 2) was not resolved.

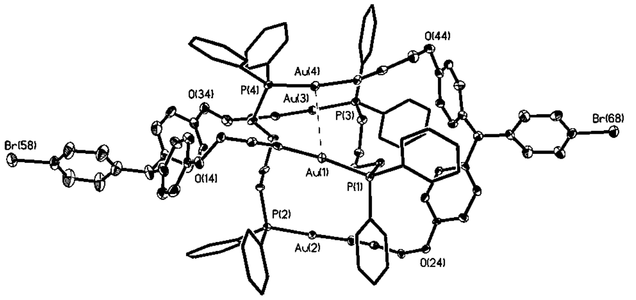

Figure 5. A view of the structure of the [2]catenane complex **5b**. Selected bond distances (Å) and angles (deg): Au(1)−C(11) 2.02(1); Au(2)−C(21) 2.02(1); Au(3)−C(31) 2.01(1); Au(4)−C(41) 1.99(1); Au(1)−P(1) 2.279(2); Au(2)−P(2) 2.270(2); Au(3)−P(3) 2.271(2); Au(4)−P(4) 2.270(2) C; C(11)−Au(1)−P(1) 174.1(3); C(21)−Au(2)−P(2) 178.1(3); C(31)−Au(3)−P(3) 178.3(3); C(41)−Au(4)−P(4) 171.0(3).

Complexes **5a** and **5b** are chiral and are formed as racemic mixtures. In principle, it should be possible to resolve resonances of the enantiomers by using a chiral shift reagent. However, the NMR spectra were not changed in the presence of the lanthanide shift reagent tris[3-{(trifluoromethyl)hydroxymethylene}-+-camphorato]europium(III). It is likely that the phenol oxygen atoms are too sterically hindered to coordinate to the europium ion and so no paramagnetic shifts are observed.

The structures of **5a** and **5b** indicate that aryl−aryl attractions are important in favoring [2]catenane formation.[5,6] In **5b**, there are two phenyl−phenyl offset face-to-face (**off**) interactions, with participating phenyl groups almost parallel, and four phenyl−aryl vertex-to-face (**vf**) interactions, with participating aryl groups essentially orthogonal.[12] The closest gold···gold contact is Au(1)−Au(4) = 3.47 Å, which is probably only weakly attractive, and so the aryl−aryl interactions are the key to [2]catenane formation in this case. In **5a**, the gold···gold attractions are much stronger (Figure 3) but the aryl−aryl attractions appear less favorable. There are again two phenyl−phenyl offset face-to-face (**off**) interactions,[12] with parallel aryl rings separated by 4.0 Å, but four additional weaker aryl−aryl

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interactions have nonideal orientations intermediate between offset face-to-face (**off**) and edge-to-face (**ef**) interactions.[12] Typical aryl−aryl attractions have energies of about 2 kcal/mol, compared to 7−11 kcal/mol for Au···Au interactions. In **5b**, the aryl−aryl attractions are optimized whereas, in **5a**, the weaker aryl−aryl attractions are balanced by the presence of two strong Au···Au attractions. In either case, the sum of these attractive forces is evidently sufficient to overcome the unfavorable entropy associated with [2]catenane formation. Any strain in the macrocyclic rings in **5a** or **5b** is expected to be reflected in distortion at the hinge carbon atoms defined by C(9)−C(8)−C(16) = 107.9° in the precursor bis(phenol) **1** (Figure 1). The corresponding angles in **5a** are 113.8° and 113.6° and in **5b** they are 114.1° and 111.2° in the two rings, only slightly opened up from the natural tetrahedral angle. Thus, there is little angle strain involved in the formation of the [2]catenanes.

The reaction of **3** with bis(diphenylphosphino)pentane gave a single complex. The ^{31}P NMR spectrum contained only a single resonance and the ^{1}H NMR spectrum contained an AB quartet for the OCH^{a}H^{b} protons, very similar to the observations for **5b**. Hence, the structure is expected to be the [2]catenane **5c**, with effectively degenerate ^{31}P NMR chemical shifts as for **5b**, but the data do not disprove the simple ring structure. Attempted characterization of the molar mass by MALDI-TOF MS was unsuccessful in this case.

Discussion

This work has demonstrated that, for this series of organogold macrocycles, it is possible to predict the topology of the self-assembly products through consideration of both the starting organic bis(phenol) fragment and the choice of phosphine ligand. Furthermore, the catenanes are topologically chiral and the synthesis by self-assembly is particularly easy. Topologically chiral [2]catenanes have been prepared previously by the Sauvage group,[8] and this work is complementary since the symmetry planes of the individual rings in the two classes of compounds are perpendicular to one another, and so the NMR properties of the [2]catenanes are distinct. In the case of complex **5a**, the [2]catenane can be identified by ^{31}P NMR spectroscopy in solution as a result of the dissymmetry induced by catenane formation.

The factors that control the self-assembly processes are subtle but this work has shown that, at least within closely related series of compounds, it is possible to predict the nature of the self-assembly and so to use it to prepare functional materials. It is anticipated that further application of the principles outlined here will allow the design and synthesis of more complex molecular structures, in particular, functionalized [2]catenanes and poly-[2]catenanes.

Experimental Section

All gold complexes were protected from light by using darkened reaction flasks. NMR spectra were recorded by using Varian Mercury 400 MHz and Inova 600 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane, and ^{31}P chemical shifts relative to the 85% H_3PO_4 as an external standard. IR spectra were recorded by using a Perkin-Elmer 2000 FTIR as Nujol mulls on KBr plates or as CH_2Cl_2 solutions in solution cells. Mass spectra were recorded with a Finnigan MAT 8200 spectrometer.

(4-BrC$_6$H$_4$)CH(4-C$_6$H$_4$OH)$_2$, 1. A solution of *p*-bromobenzaldehyde (1.50 g, 8.1 mmol) and phenol (1.72 g, 18 mmol) in acetic acid (3 mL) was cooled to 0 °C and a mixture of sulfuric acid (3 mL) and acetic acid (10 mL) was added dropwise with stirring. The mixture was kept at 0 °C for 72 h, and the product was precipitated by addition of ice water, separated by filtration, washed with water, and vacuum-dried overnight, then recrystallized from benzene. Yield: 1.56 g, 54%. IR (Nujol): ν(OH) = 3200−3500 cm^{-1}. NMR (CD$_3$CN, 25 °C): δ(^{1}H) = 5.38 [s, 1H, CH], 6.72 [m, 4H, C$_6$H$_4$O], 6.82 [s, 2H, OH], 6.90 [m, 4H, C$_6$H$_4$O], 7.00 [m, 2H, C$_6$H$_4$Br], 7.42 [m, 2H, C$_6$H$_4$Br]; δ(^{13}C) = 54.4 [s, CH], 115.3 [s, C$_6$H$_4$O], 119.6 [s, C$_6$H$_4$Br], 130.4 [s, C$_6$H$_4$O], 131.3 [s, C$_6$H$_4$Br], 131.4 [s, C$_6$H$_4$Br], 135.5 [s, C$_6$H$_4$O], 144.8 [s, C$_6$H$_4$Br], 155.6 [s, C$_6$H$_4$O]. Mass spectrum: *m/z* 356, 354 (M), 275 (loss of Br), 199 (loss of C$_6$H$_4$Br).

(4-BrC$_6$H$_4$)CH(4-C$_6$H$_4$OCH$_2$C$\equiv$CH)$_2$, 2. Finely ground KOH (0.25 g, 4.50 mmol) and BrCH$_2$C$\equiv$CH (0.50 g, 4.22 mmol) were added to a solution of 4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OH)$_2$ (0.50 g, 1.41 mmol) in acetone (10 mL). The mixture was refluxed for 16 h and the solution was decolorized by activated charcoal and filtered. An oily, viscous yellow liquid was obtained after solvent removal under reduced pressure. Yield: 0.46 g, 75%. IR (Nujol): ν(C$\equiv$C) 2123 (m), 2047 (w) cm^{-1}. NMR (CD$_2$Cl$_2$, 25 °C): δ(^{1}H) = 2.56 [t, ^{4}J(HH) = 2 Hz, 2H, C$\equiv$CH], 4.67 [d, ^{4}J(HH) = 2 Hz, 4H, OCH$_2$], 5.42 [s, 1H, CH], 6.89 [m, 4H, C$_6$H$_4$O], 6.99 [m, 2H, BrC$_6$H$_4$], 7.01 [m, 4H, C$_6$H$_4$O], 7.41 [m, 2H, BrC$_6$H$_4$]; δ(^{13}C) = 54.8 [s, CH], 56.0 [s, OCH$_2$], 75.6 [s, C$\equiv$*C*H], 78.9 [s, *C*$\equiv$CH], 114.9 [s, C$_6$H$_4$O], 120.3 [s, C$_6$H$_4$Br], 130.4 [s, C$_6$H$_4$O], 131.3 [s, C$_6$H$_4$Br], 131.6 [s, C$_6$H$_4$Br], 136. 9 [s, C$_6$H$_4$O], 143.8 [s, C$_6$H$_4$Br], 156.4 [s, C$_6$H$_4$O]. Mass spectrum: *m/z* 432, 430 (M), 393 and 391 (loss of CH$_2$C$\equiv$CH), 377 and 375 (loss of OCH$_2$C$\equiv$CH), 301 and 299 (loss of C$_6$H$_4$OCH$_2$C$\equiv$CH).

4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C$\equiv$CAu)$_2$, 3. To a solution of [AuCl(SMe$_2$)] (0.60 g, 2.03 mmol) in methanol (50 mL) and THF (100 mL) was added a solution of 4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C$\equiv$CH)$_2$ (0.44 g, 1.01 mmol) and NaOAc (0.25 g, 3.05 mmol) in methanol (20 mL) and THF (20 mL). The mixture was stirred for 7 h, then the yellow precipitate of the product was filtered and washed with THF, methanol, diethyl ether, and pentane successively. **CAUTION:** The product is shock sensitive. Yield: 0.58 g, 69%. IR (Nujol): ν (C$\equiv$C) = 2010 cm^{-1}. Anal. Calcd for C$_{25}$H$_{17}$Au$_2$BrO$_2$: C, 36.5; H, 2.1; Br, 9.7. Found: C, 36.1; H, 2.1; Br, 9.4.

[4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C$\equiv$CAu)$_2$(μ-Ph$_2$PC$\equiv$CPPh$_2$)], 4a. A mixture of 4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C$\equiv$CAu)$_2$ (0.15 g, 0.18 mmol) and Ph$_2$PC$\equiv$CPPh$_2$ (0.06 g, 0.16 mmol) in CH$_2$Cl$_2$ (50 mL) was stirred at room temperature in a darkened reaction flask for 2 h. Activated charcoal was added and the mixture was stirred for another 0.5 h. The mixture was filtered, and the solvent was removed under reduced pressure to give the product, which was recrystallized from CH$_2$Cl$_2$/pentane. Yield 62%. IR (CH$_2$Cl$_2$): ν(C$\equiv$C) = 2137 cm^{-1}. NMR (CD$_2$Cl$_2$, 25 °C): δ(^{1}H) = 4.80 [s, 4H, OCH$_2$], 5.41 [s, 1H, CH], 6.99 [m, 2H, C$_6$H$_4$Br], 7.03 [m, 8H, C$_6$H$_4$O], 7.40 [m, 2H, C$_6$H$_4$Br], 7.48−7.76 [m, 20H, Ph]; δ(^{31}P) = 18.7 [s]; δ(^{13}C) = 55.1 [s, CH], 56.6 [s, OCH$_2$], 97.8 [s, *C*$\equiv$CAu], 101.5 [m, C$\equiv$C], 115.3 [s, C$_6$H$_4$O], 120.2 [s, C$_6$H$_4$Br], 128.2 [d, ^{1}J(PC) = 62 Hz, Ph], 129.9 [d, ^{2}J(PC) = 12 Hz, Ph], 130.3 [s, C$_6$H$_4$O], 131.4 [s, C$_6$H$_4$Br], 131.5 [s, C$_6$H$_4$Br], 132.5 [d, ^{2}J(PC) = 155 Hz, C$\equiv$*C*Au], 132.8 [s, Ph], 133.6 [d, ^{3}J(PC) = 11 Hz, Ph], 136.3 [s, C$_6$H$_4$O], 144.4 [s, C$_6$H$_4$Br], 156.7 [s, C$_6$H$_4$O]. Anal. Calcd for C$_{48}$H$_{35}$Au$_2$BrO$_2$P$_2$: C, 48.9; H, 3.0; Br, 6.8. Found: C, 48.3; H, 2.5; Br, 6.4.

Similarly prepared were the following:

[4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C$\equiv$CAu)$_2$(μ-*trans*-Ph$_2$PCH=CHPPh$_2$)], 4b. Yield 60%. IR (CH$_2$Cl$_2$): ν(C$\equiv$C) = 2137 cm^{-1}, ν (C=C) = 1600 cm^{-1}. NMR (CD$_2$Cl$_2$, 25 °C): δ(^{1}H) = 4.79 [s, 4H, OCH$_2$], 5.41 [s, 1H, CH], 6.87 [m, 2H, CH=CH], 7.00 [m, 2H, C$_6$H$_4$Br], 7.04 [m, 8H, C$_6$H$_4$O], 7.40 [m, 2H, C$_6$H$_4$Br], 7.52 [m, 20H, Ph]; δ(^{31}P) = 39.50 [s]; δ(^{13}C) = 55.1 [s, CH], 56.6 [s, OCH$_2$], 97.6 [m, *C*$\equiv$CAu], 115.4 [s, C$_6$H$_4$O], 120.2 [s, C$_6$H$_4$Br], 128.2 [m, Ph], 129.9 [s, Ph], 130.3 [s, C$_6$H$_4$O], 130.6 [m, Cb$\equiv$*C*Au], 131.4 [s, C$_6$H$_4$Br], 131.5 [s, C$_6$H$_4$Br], 132.6 [s, Ph], 134.3 [s, Ph], 136.3 [s, C$_6$H$_4$O], 141.0 [m,

Table 1. Crystal and Structure Refinement Data

	1·1.5C_6H_6	**5a**·C_5H_{12}·H_2O	**5b**·$^1/_2C_4H_{10}O$·$^3/_2CH_2Cl_2$
formula	$C_{28}H_{24}BrO_2$	$C_{57}H_{54.5}Au_2BrO_3P_2$	$C_{56.5}H_{53}Au_2BrCl_3O_{2.5}P_2$
fw	472.38	1323.29	1414.12
temp/K	200(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group cell dimens.	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a/Å	13.8604(4)	20.1462(4)	11.2137(3)
b/Å	18.4059(8)	12.8256(2)	20.7128(7)
c/Å	9.3622(3)	39.3165(7)	24.6213(7)
α/deg	90	90	104.052(2)
β/deg	102.925(2)	99.197(1)	93.098(2)
γ/deg	90	90	102.873(2)
V/Å^3, Z	2327.9(1), 4	10028.3(3), 8	5372.7(3), 4
d(calcd)/mg/m^3	1.348	1.753	1.748
abs. coeff./mm^{-1}	1.787	6.749	6.449
F(000)	972	5148	2744
θ range/deg	2.64−27.48	2.56−27.50	2.58−27.50
no. of reflcns/ind. reflcns	24120/5310	81751/22888	52288/23138
abs. corr.	Integration	Integration	Integration
no. of data/restr/param	5310/0/282	22888/14/1015	23138/41/1108
goof	0.893	0.933	0.946
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.041, 0.086	0.059, 0.146	0.057, 0.132
$R1$, $wR2$ (all data)	0.111, 0.101	0.149, 0.165	0.112, 0.148

C═C], 144.2 [s, C_6H_4Br], 156.7 [s, C_6H_4O]. Anal. Calcd for $C_{48}H_{37}Au_2BrO_2P_2$: C, 48.8; H, 3.2; Br, 6.8. Found: C, 48.8; H, 3.0; Br, 6.5.

[4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C≡CAu)$_2$(μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$)], 4c. Yield: 73%. IR (CH_2Cl_2): ν(C≡C) 2136 cm^{-1}. NMR (CD_2Cl_2, 25 °C): $\delta(^1H) = 2.51$ [m, 4H, CH_2], 4.79 [s, 4H, OCH_2], 5.40 [s, 1H, CH], 7.01 [m, 2H, C_6H_4Br], 7.03 [m, 4H, C_6H_4O], 7.09 [m, 4H, C_6H_4O], 7.39 [m, 2H, C_6H_4Br], 7.44−7.52 [m, 20H, Ph]; $\delta(^{31}P) = 40.4$ [s]; $\delta(^{13}C) = 23.9$ [m, CH_2], 55.2 [s, CH], 56.6 [s, OCH_2], 97.5 [m, *C*≡CAu], 115.5 [s, C_6H_4O], 120.2 [s, C_6H_4Br], 129.3 [m, Ph], 129.7 [m, Ph], 130.2 [s, C_6H_4O], 131.3 [s, C_6H_4Br], 131.5 [s, C_6H_4Br], 132.0 [m, C≡*C*Au], 132.4 [s, Ph], 133.6 [m, Ph], 136.4 [s, C_6H_4O], 144.0 [s, C_6H_4Br], 156.6 [s, C_6H_4O). Anal. Calcd for $C_{48}H_{39}Au_2BrO_2P_2$: C, 48.7; H, 3.3; Br, 6.7. Found: C, 48.6; H, 3.4; Br, 6.4.

[4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C≡CAu)$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Fe}], 4d. Yield 70%. IR (CH_2Cl_2): ν(C≡C) = 2134 cm^{-1}. NMR (CD_2Cl_2, 25 °C): $\delta(^1H) = 4.38$ [m, 10H, C_5H_4], 4.84 [s, 4H, OCH_2], 5.40 [s, 1H, CH], 7.02 [m, 2H, C_6H_4Br], 7.07 [m, 8H, C_6H_4O], 7.40 [m, 2H, C_6H_4Br], 7.44−7.54 [m, 20H, Ph]; $\delta(^{31}P) = 37.1$ [s]; $\delta(^{13}C) = 55.1$ [s, CH], 57.0 [s br, OCH_2], 72.1 [m br, C_5H_4], 75.1 [d, $^3J_{PC} = 8$ Hz, C_5H_4], 75.4 [d, $^2J_{PC} = 13$ Hz, C_5H_4], 97.8 [s, *C*≡CAu], 115.3 [s, C_6H_4O], 120.2 [s, C_6H_4Br], 129.0 [m, Ph], 129.3 [d, $^3J(PC) = 11$ Hz, Ph], 130.4 [s, C_6H_4O], 131.4 [s, C_6H_4Br], 131.5 [s, C_6H_4Br], 131.7 [d, $^2J(PC) = 56$ Hz, C≡*C*Au], 131.8 [s, Ph], 134.0 [d, $^2J(PC) = 15$ Hz, Ph], 136.3 [s, C_6H_4O], 144.3 [s, C_6H_4Br], 157.0 [s, C_6H_4O]. Anal. Calcd for $C_{56}H_{43}Au_2BrFeO_2P_2$: C, 50.2; H, 3.2; Br, 6.0. Found: C, 50.3; H, 3.0; Br, 5.9.

[{4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C≡CAu)$_2$(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)}$_2$], 5a. Yield 64%. IR (CH_2Cl_2): ν(C≡C) = 2134 cm^{-1}. The initial product is a mixture of isomers but recrystallization gave the pure [2]catenane, whose data are given. NMR (CD_2Cl_2, 25 °C): $\delta(^1H) = 1.68$ [m, 8H, CH_2], 2.20 [m, 4H, CH_2], 4.57 [m br, 8H, OCH_2], 5.26 [s, 2H, CH], 6.09 [m, 4H, C_6H_4O], 6.11 [m, 4H, C_6H_4O], 6.54 [m, 8H, C_6H_4O], 6.63 [m, 4H, BrC_6H_4], 7.18 [m, 4H, BrC_6H_4], 7.26−7.50 [m, 40H, Ph]; $\delta(^{31}P) = 31.98$ [AB quartet, $J(PP) = 6$ Hz]. Anal. Calcd for $C_{98}H_{81}Au_4Br_2O_4P_4$: C, 49.1; H, 3.4; Br, 6.7. Found: C, 49.2; H, 3.6; Br, 6.3. The ^{31}P NMR spectrum of the initial product contained additional resonances at $\delta(^{31}P) = 35.90$ [s, simple ring **4e**], and weaker peaks at $\delta(^{31}P) = 31.80$, 32.15 [br, unknown complex **6**]; the pure catenane in solution reverted to the equilibrium mixture over a period of 2 days.

[{4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C≡CAu)$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)}$_2$], 5b. Yield 72%. IR (CH_2Cl_2): ν(C≡C) 2134 cm^{-1}. NMR (CD_2Cl_2, 25 °C): $\delta(^1H) = 1.73$ [m, 8H, CH_2], 2.35 [m, 8H, CH_2], 4.76, 4.80 [AB q, $^2J(HH) = 17$ Hz, 8H, OCH_2], 5.40 [s, 2H, CH], 6.99 [m, 4H, C_6H_4Br], 7.02 [m, 8H, C_6H_4O], 7.07 [m, 8H, C_6H_4O], 7.39 [m, 4H, C_6H_4Br], 7.45−7.62 [m, 40H, Ph]; $\delta(^{31}P) = 38.9$ [s]; $\delta(^{13}C) = 27.6$ [m, CH_2], 28.0 [d, $^1J(PC) = 34$ Hz, CH_2], 55.1 [s, CH], 56.8 [s, OCH_2], 97.5 [d, $^3J(PC) = 27$ Hz, *C*≡CAu], 115.3 [s, C_6H_4O], 120.1 [s, C_6H_4Br], 129.5 [m, Ph], 130.3 [s, C_6H_4O], 130.6 [d, $^1J(PC) = 54$ Hz, Ph], 131.3 [s, C_6H_4Br], 131.5 [s, C_6H_4Br], 131.9 [s, Ph], 132.2 [d, $^2J(PC) = 143$ Hz, C≡*C*Au], 133.6 [m, Ph], 136.2 [s, C_6H_4O], 144.4 [s, C_6H_4Br], 156.8 [s, C_6H_4O]. Anal. Calcd for $C_{100}H_{86}Au_4Br_2O_4P_4$: C, 49.6; H, 3.6; Br, 6.6. Found: C, 49.8; H, 3.6; Br, 7.0.

[4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C≡CAu)$_2$(μ-Ph$_2$P(CH$_2$)$_5$PPh$_2$)], 5c. Yield 77%. IR (CH_2Cl_2): ν(C≡C) = 2134 cm^{-1}. NMR (CD_2Cl_2, 25 °C): $\delta(^1H) = 1.54$ [m, 12H, CH_2], 2.34 [m, 8H, CH_2], 4.76, 4.78 [AB q, $^2J(HH) = 18$ Hz, 8H, OCH_2], 5.42 [s, 2H, CH], 7.01 [m, 4H, C_6H_4Br], 7.03 [m, 16H, C_6H_4O], 7.40 [m, 4H, C_6H_4Br], 7.45−7.65 [m, 40H, Ph]; $\delta(^{31}P) = 37.5$ [s]; $\delta(^{13}C) = 25.8$ [d, $^2J(PC) = 5$ Hz, CH_2], 28.1 [d, $^1J(PC) = 34$ Hz, CH_2], 33.0 [m, CH_2], 55.0 [s, CH], 56.8 [s, OCH_2], 97.5 [d, $^3J(PC) = 26$ Hz, *C*≡CAu], 115.3 [s, C_6H_4O], 120.1 [s, C_6H_4Br], 127.5 [d, $^3J(PC) = 11$ Hz, Ph], 130.3 [s, C_6H_4O], 130.9 [m, Ph], 131.4 [s, C_6H_4Br], 131.5 [s, C_6H_4Br], 131.8 [s, Ph], 132.1 [d, $^2J(PC) = 143$ Hz, C≡*C*Au], 133.6 [d, $^2J(PC) = 13$ Hz, Ph], 136.2 [s, C_6H_4O], 144.4 [s, C_6H_4Br], 156.9 [s, C_6H_4O]. Anal. Calcd for $C_{102}H_{90}Au_4Br_2O_4P_4$: C, 50.0; H, 3.7; Br, 6.5. Found: C, 48.1; H, 3.7; Br, 7.5.

X-ray Structure Determinations. Crystals of [(4-BrC$_6$H$_4$)CH(4-C$_6$H$_4$OH)$_2$]·$^3/_2$benzene, **1**, were grown from benzene solution. An orange prism was mounted on a glass fiber. Data were collected at low temperature (−73 °C) by using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out with use of the Nonius DENZO package. The data were scaled by using SCALEPACK (Nonius, 1998) and no other absorption corrections were applied. The crystal data and refinement parameters are listed in Table 1. The reflection data and systematic absences were consistent with the monoclinic space group $P2(1)/c$. The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve the structure by direct methods, followed by successive difference Fouriers. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Crystals of [{4-BrC$_6$H$_4$CH(4-C$_6$H$_4$OCH$_2$C≡CAu)$_2$(μ-Ph$_2$P(CH$_2$)$_3$-PPh$_2$)}$_2$] ·2pentane·2H$_2$O were grown by slow diffusion of pentane into a CH_2Cl_2 solution, and a colorless crystal was mounted on a glass fiber. Data were collected at low temperature (−123 °C) and treated as above.

The reflection data and systematic absences were consistent with the monoclinic space group $P2(1)/n$. All the non-hydrogen atoms were refined anisotropically. The two pentanes of solvation were modeled isotropically with fixed C−C bond lengths. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The two water molecules were modeled as isotropic oxygen atoms.

Crystals of $[\{4\text{-BrC}_6H_4CH(4\text{-C}_6H_4OCH_2C{\equiv}CAu)_2(\mu\text{-Ph}_2P(CH_2)_4\text{-PPh}_2)\}_2]\cdot 1Et_2O\cdot 3CH_2Cl_2$ were grown by slow diffusion of ether into a CH_2Cl_2 solution. A colorless plate was cut and mounted on a glass fiber. Data were collected at −123 °C and treated as above. The reflection data were consistent with the triclinic space group $P\bar{1}$. All the non-hydrogen atoms were refined anisotropically. The ether of solvation was modeled anisotropically with fixed C−C and C−O bond lengths. Two of the methylene chlorides were modeled anisotropically with fixed C−Cl bond lengths [1.65 Å]. The third methylene chloride was disordered over two sites and was modeled as a 50/50 isotropic mixture with fixed C−Cl bond lengths [1.65 Å] and Cl−Cl bond lengths [2.74 Å]. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

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Supporting Information Available: Tables of X-ray data for compounds **1**, **5a,**and **5b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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