Controlled Self-Assembly of Cyclic Gold(I) Complexes: The First Family of Organometallic Catenanes**

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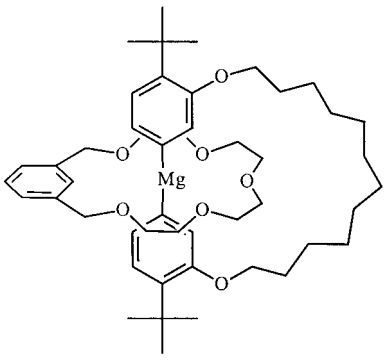
The synthesis of catenanes for potential application in molecular devices has been achieved through several very clever strategies,[1, 2] such as "metal ion templating",[3, 4] and methods have recently been devised for synthesis of catenanes with metal atoms incorporated into the macrocycles.[5] However, there appear to be only two isolated examples in which organometallic centers are present, namely the organomagnesium compound **A** (with metal in one ring only) and the gold(I) acetylide **B** (R = *t*Bu).[6, 7] For different reasons, neither



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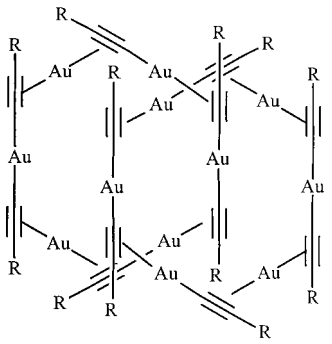

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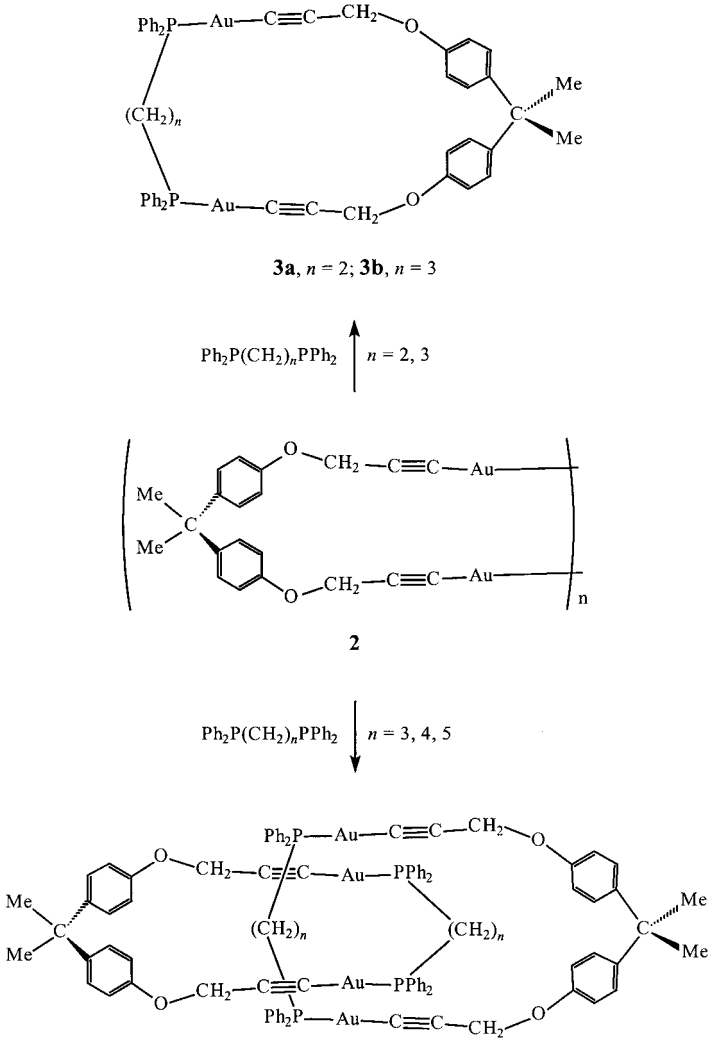
synthetic method is easily adapted to the planned synthesis of a wide range of catenanes, but the method reported below leads to easy self-assembly of organometallic catenanes with different ring sizes and so allows systematic study of such complexes.

We have previously reported the synthesis of digold(I) diacetylide complexes $[(AuC{\equiv}C{-}R{-}C{\equiv}CAu)_x]$ **1**, having linear spacer groups R (e.g. $R = C_6H_4$), and their use as precursors for the preparation of rigid-rod polymers or organogold ring complexes.[8] However, the complexation of **1** with neutral bidentate ligands such as diphosphanes gives ring complexes with cavities that are too small to allow formation of catenanes.[8] The digold(I) diacetylide complex **2** is longer and more flexible than **1** and so can form rings having a larger cavity; **2** reacts with the diphosphane ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 2-5$) to give the interesting ring structures **3** and **4** (Scheme 1). The new ring complexes **3** and [2]catenanes **4** are formed in good yield; they are colorless, air-stable solids which are soluble in organic solvents such as dichloromethane.[9]



Scheme 1. Synthesis of the new ring complexes **3a** and **3b** and the new catenane complexes **4a–c**. See Supporting Information for experimental details.

The beauty of the synthetic method shown in Scheme 1 is that the ring size can be varied easily by changing the number of methylene spacer groups in the diphosphane ligand $Ph_2P(CH_2)_nPPh_2$. As *n* increases, the cavity size increases and then catenanes can form by simple self-assembly. Thus, the reaction of **2** with $Ph_2P(CH_2)_nPPh_2$ yields only the simple

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ring complex **3a** when $n = 2$, and only the catenanes **4b** and **4c** when $n = 4$ or 5, respectively. The crossover between these reaction types occurs when $n = 3$ where a mixture of the simple ring complex **3b**, the catenane **4a**, and a third "isomer" of undetermined structure is formed.[10] Slow crystallization of this mixture gives pure **4a** which reverts to the above mixture of isomers over a period of days when dissolved in CD_2Cl_2, as monitored by NMR spectroscopy.[9] The catenane formation is clearly reversible in this case.

The new compounds were characterized by their spectroscopic properties and by structure determinations for **3a**, **4a**, and **4b**.[9, 11] Complex **3a** is shown to be formed as a single isomer by the observation of a single sharp resonance at $\delta =$ 40.26 in the ^{31}P NMR spectrum. The complex exists as a simple ring (Figure 1, top), which is strongly puckered as a

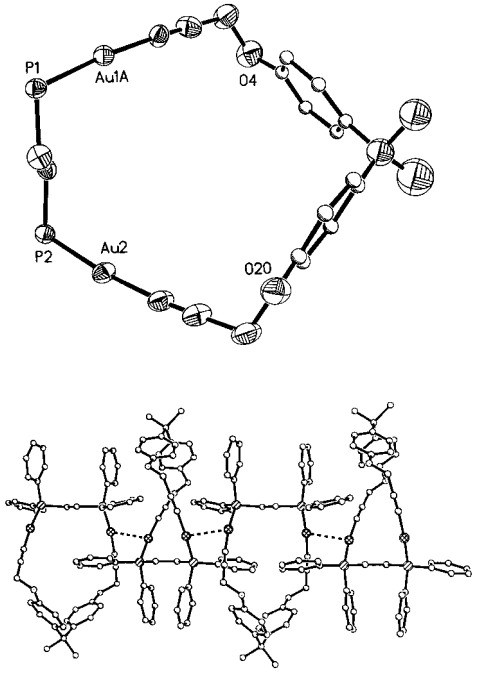

Figure 1. Top) A view of the structure of **3a**, showing the single ring form. Phenyl groups are omitted and other aryl carbon atoms are shown as small spheres for clarity. Bottom) A part of the infinite chains formed by intermolecular Au ··· Au bonding. Note the twisted ring conformation.

result of the need to bring the two gold atoms close enough together that they can be bridged by the ligand $Ph_2PCH_2CH_2PPh_2$ with its relatively small bite distance. The molecular packing within the crystal lattice is interesting; adjacent molecules, which are held together by short Au ··· Au contacts,[12] adopt an *anti* arrangement to minimize steric interactions. The intermolecular gold–gold distance of 2.9668(8) Å indicates that there is a significant aurophilic attraction between neighboring gold(I) centers and results in a loose polymeric structure (Figure 1, bottom).

The structures of the organometallic catenanes **4a** and **4b** are shown in Figure 2, with phenyl substituents removed to show the interlocking rings more clearly. In each case, the rings interlock symmetrically across the polymethylene chain of the diphosphane ligand, but there are also significant differences between the two structures. For **4a** the large unit cell contains two inequivalent catenanes; in one of these there

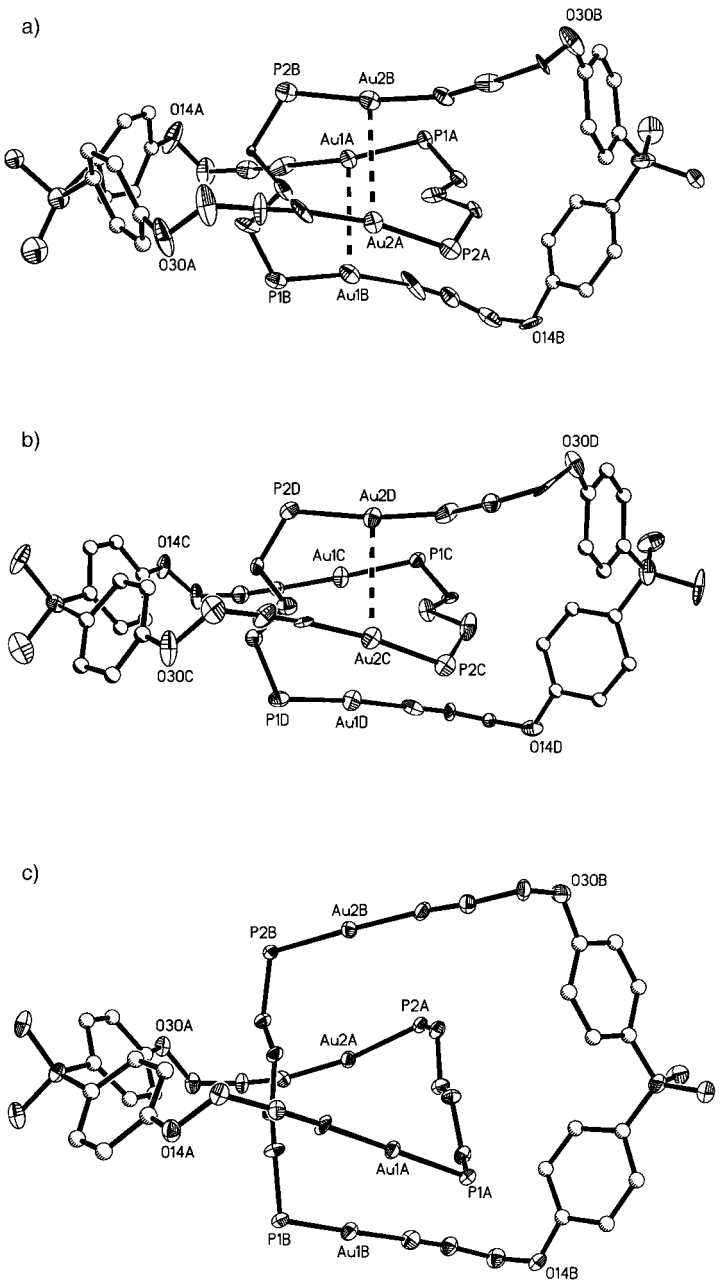

Figure 2. A view of the structures of the [2]catenanes with inter-ring Au ··· Au interactions indicated by dotted lines. Phenyl groups are omitted and other aryl carbon atoms are shown as small spheres for clarity. a) and b) the independent molecules of **4a;** c) the complex **4b**. Note the larger cavity of **4b** compared to **4a** and the absence of Au ··· Au bonding in **4b**.

are two close inter-ring Au ··· Au contacts (3.216(2) Å and 3.357(2) Å), while in the other there is only one Au ··· Au distance that is short enough to be considered an aurophilic interaction (3.231(2) Å), as the other Au ··· Au distance (3.686(2) Å) is outside the normal range of 2.75–3.40 Å for such bonds. The structure of **4b** differs most obviously from **4a** by having no short Au ··· Au contacts. The shortest distances are Au1A ··· Au1B 4.993(1) and Au2A ··· Au2B 5.219(1) Å, and these are both beyond the range for any bonding interaction. The reason for this difference is clear by examination of Figure 2. In **4a** the short trimethylene chain leads to a small 24-membered ring and, in turn, this leads to

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significant steric congestion and to short inter-ring Au ··· Au distances; since the Au ··· Au interaction is attractive,[12] it is naturally present. However, in **4b** the longer tetramethylene chain leads to a 25-membered ring, and the observed conformation with the tetramethylene chains passing through the ring centers naturally leads to minimum steric congestion but longer Au ··· Au distances than in **4a**. The complex could distort to give shorter Au ··· Au distances but this would cause greater steric hindrance; the steric effects are clearly dominant in this case.

In summary, it is established that gold(I) catenanes with diacetylide and diphosphane ligands can be formed easily by self-assembly, that the transition from simple ring to [2]catenane can be controlled by simple ligand design and that, in at least one case, it is possible for the simple ring and [2]catenane to interconvert. While aurophilic attractions may enhance catenane formation they are clearly not a necessary feature, and the low steric hindrance associated with the linear gold(I) acetylide units appears to be more important in allowing the easy formation of catenanes. Attractive inter-aryl forces also favor catenane formation. It follows that the principles outlined here may also be useful in the design of more complex molecular topologies, such as rotaxanes and knots with organometallic functionality, and that these systems are well suited for studies of the mechanisms and energetics of catenane formation.

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[9] Synthetic procedures are similar to those described in ref. [8], with gold complexes protected from light by using darkened flasks throughout. Selected data: **2:** Yield: 94 % from [AuCl(SMe$_2$)]. IR (Nujol): $\tilde{\nu} = 2000$ (w, C≡C) cm^{-1}. **3a:** Yield: 70 %. IR (Nujol): $\tilde{\nu} = 2130$ (w, C≡C) cm^{-1}; ^{1}H NMR (CD_2Cl_2, 25 °C): $\delta = 1.65$ (s, 6H; 2 CH_3), 2.51 (m, 4H; 2 CH_2), 4.75 (s, 4H, 2 OCH_2), 7.01 (m, 4H; 2 C_6H_4), 7.23 (m, 4H; 2 C_6H_4), 7.42 – 7.52 (m, 20H; 4 C_6H_5); ^{31}P NMR (CD_2Cl_2, 25 °C): $\delta = 40.26$ (s). **4a:** Yield of mixture with **3b** and third isomer: 81 %. Recrystallization from CH_2Cl_2/Et_2O gave pure **4a**. ^{31}P NMR (CD_2Cl_2, 25 °C): $\delta = 31.67$ (s); IR (Nujol): $\tilde{\nu} = 2132$ (w, C≡C) cm^{-1}. **3b**: ^{31}P NMR (CD_2Cl_2, 25 °C): $\delta = 35.61$ (s). Third isomer: ^{31}P NMR (CD_2Cl_2, 25 °C): $\delta = 34.56$ (s), 34.47 (s). **4b**: Yield 68 %; IR (Nujol): $\tilde{\nu} = 2132$ (w, C≡C) cm^{-1}; ^{31}P NMR (CD_2Cl_2, 25 °C): $\delta = 38.73$ (s). **4c:** Yield 70 %; IR (Nujol): $\tilde{\nu} = 2130$ (w, C≡C) cm^{-1}; ^{31}P NMR (CD_2Cl_2, 25 °C): $\delta = 37.36$ (s).

[10] The identity of the third isomer is not established at this stage. It could be a more complex catenane or an oligomer. Note that the bulky Ph_2P groups will act as a barrier to prevent free motion of interpenetrating rings.

[11] X-ray data; Enraf-Nonius diffractometer equipped with a CCD detector; refinement used SHELX software; crystals were small and of only adequate quality but the structures are well-defined; partial occupation of lattice vacancies by solvent molecules is responsible for the unusual stoichiometries: Complex **3a** · 0.75 CH_2Cl_2: $C_{47.75}H_{43}Au_2Cl_{1.50}O_2P_2$, $M_r = 1157.87$, $T = 293$ K, monoclinic, $P2_1/n$, $a = 17.9418(7)$, $b = 14.4752(6)$, $c = 20.1253(6)$ Å, $\beta = 111.736(2)°$, $V = 4855.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.584$ Mg m^{-3}, $\mu = 6.218$ mm^{-1}, 33078 reflections, 9880 independent reflections, $\theta_{max} = 26.41°$, refinement by full-matrix least-squares on F^2, 505 parameters, $R1 = 0.0817$, $wR2 = 0.1091$. Complex **4a** · 0.125 $C_2H_4Cl_2$: $C_{48.25}H_{44.5}Au_2Cl_{0.25}O_2P_2$, $M_r = 1121.07$, $T = 150(2)$ K, $\lambda = 0.71073$ Å, monoclinic, $P2_1/n$, $a = 12.4526(3)$, $b = 45.006(2)$, $c = 30.538(1)$ Å, $\beta = 98.570(2)°$, $V = 16924(1)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.760$ Mg m^{-3}, $\mu = 7.056$ mm^{-1}, 27409 reflections, 18686 independent reflections, $\theta_{max} = 26.38°$, refinement by full-matrix least-squares on F^2, 1450 parameters, $R1 = 0.0889$, $wR2 = 0.1726$. Complex **4b** · 2.5 $CHCl_3$: $C_{50.25}H_{47.25}Au_2Cl_{3.75}O_2P_2$, $M_r = 1271.94$, $T = 200(2)$ K, $\lambda = 0.71073$ Å, triclinic, $P\bar{1}$, $a = 15.7561(4)$, $b = 16.1929(5)$, $c = 21.2826(7)$ Å, $\alpha = 106.545(1)$, $\beta = 97.842(1)$, $\gamma = 102.660(1)°$, $V = 4962.5(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.702$ Mg m^{-3}, $\mu = 6.209$ mm^{-1}, 70232 reflections, 34852 independent reflections, $\theta_{max} = 32.70°$, 1103 parameters, $R1 = 0.0957$, $wR2 = 0.2390$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120855 – 120857. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Specific Alkylation of Guanine Opposite to a Single Nucleotide Bulge: A Chemical Probe for the Bulged Structure of DNA

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Drug interactions at nucleotide bulges have been intensively studied because the stabilization of the bulged structure by intercalators is thought to enhance frameshift mutation of DNA.[1] Furthermore, the drugs bound to RNA bulges has

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