

A strategy for synthesis of large gold rings

Michael J. Irwin, Louis M. Rendina, Jagadese J. Vittal and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

26- and 34-membered rings containing four gold(I) centres are prepared by using a synthetic strategy based on the orienting effects of intramolecular gold...gold attractions in binuclear precursors.

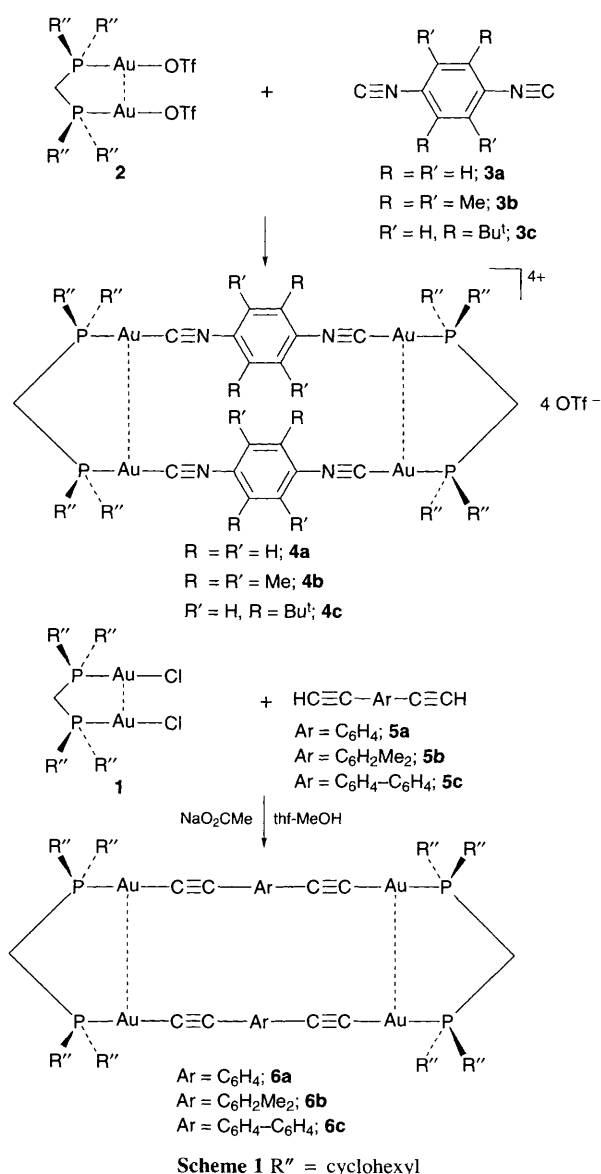
Although the literature is rich in examples of 8- to 12-membered rings containing up to three linear gold(I) centres, it has been difficult to prepare larger macrocycles. The largest rings containing gold atoms appear to be 16- and 18-membered rings containing two trigonal gold(I) or square planar gold(III) centres respectively.¹⁻⁴ This article describes a strategy for the easy synthesis of 26- and 34-membered macrocycles containing four linear gold(I) centres. The strategy is based on the orienting effects of weak intramolecular gold(I)...gold(I) attractions in binuclear precursor molecules. Intermolecular gold...gold interactions have been used recently to prepare interesting network structures and catenanes,^{1,3,5} and this article complements these advances in showing the synthetic promise of intramolecular gold...gold attractions.

The effects of weak intra- and inter-molecular bonding interactions between gold(I) centres on molecular conformations and crystal packing in gold complexes are well established.^{1,5,6} For example, the complexes [(AuX)₂(μ-dppm)] (dppm = Ph₂PCH₂PPh₂, X = Cl or C≡CBu^t) are described as U-shaped,^{6,7} and the conformation of dppm in the complexes is quite different from that in the free ligand, with the difference attributed to the favourable formation of a short intramolecular Au...Au separation in the complexes. The effect is to orient the AuX groups in the same direction, in a conformation which should promote ring formation on reaction with bifunctional ligands such as aryldiisocyanides or aryldiacetylides. This is indeed the case as illustrated in Scheme 1.

The reaction of [AuCl(SMe₂)] with bis(dicyclohexylphosphinomethane) (dcypm), gave [(AuCl)₂(μ-dcypm)] **1**, which reacted with 2 equiv. of silver triflate to yield [(AuOTf)₂(μ-dcypm)] **2**.[†] Reaction of **2** with an equimolar amount of diisocyanide ligand **3a**, **b** or **c** in methylene chloride at room temperature occurred with displacement of triflate to give the cationic tetragold rings **4a**, **b** or **c** respectively (Scheme 1).[‡] Similarly, the reaction of **1** with the diacetylides **5a**, **b** or **c** in the presence of sodium acetate as base gave the neutral tetramers **6a**, **b** or **c** respectively (Scheme 1).[‡] Complexes **4** and **6** are white, air-stable solids, which are soluble in organic solvents such as dichloromethane and acetone.[‡]

The analytical and spectroscopic data for **4** and **6** are consistent with the proposed ring structures shown in Scheme 1[‡] but do not completely disprove the alternative polymeric structure. Complex **4a** was therefore also characterized by an X-ray structure determination,[‡] which confirms the presence of a 26-membered ring containing four gold(I) centres (Fig. 1). As expected,^{5,6} intramolecular gold...gold attractions are present with an Au^I...Au^I separation of 3.133(3) Å. The non-bonded P...P distance of each dcypm ligand is slightly larger at 3.215 Å, and this supports the presence of a weak bonding interaction between Au^I centres. In addition to the Au...Au attractions, there is also evidence for π stacking of the arene rings of the two diisocyanide ligands, which lie parallel to one another but offset such that C(6) lies directly across from the centroid of the adjacent arene ring at a distance of 3.54 Å.

It is clear that macrocyclic 26-membered (**4a-c**, **6a, b**) and 34-membered rings (**6c**) have been prepared in high yield by this simple strategy. These are the largest ring compounds containing gold yet known.¹⁻⁴ The importance of the gold...gold attractions on ring formation is clear since, if the precursor binuclear gold(I) complex is not preorganized for ring formation, as in [(AuCl)₂{μ-C₆H₄(PR₂)_{2-1,4}}] (R = Prⁱ, Ph) for which intramolecular Au...Au interactions are not possible, the reaction with diacetylenes gives polymers rather than rings.⁹ The high selectivity for ring formation in the reactions shown in Scheme 1 relies on the U-shaped conformations of the precursor molecules **1** and **2** being maintained in solution [this is probable based on estimations of the Au...Au bonding forces of 7-8



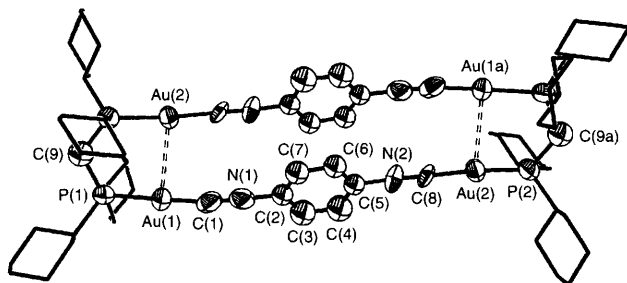


Fig. 1 A view of the structure of the cation **4a**. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.309(9), Au(2)–P(2) 2.313(9), Au(1)–C(1) 1.88(4), Au(2)–C(8) 1.94(3); C(1)–Au(1)–P(1) 178.9(10), C(8)–Au(2)–P(2) 171.1(8), N(1)–C(1)–Au(1) 171(3) N(2)C(8)Au(2) 173(3).

kcal mol⁻¹ (cal = 4.184 J)]¹⁰ leading to kinetic control, and also on the presence of favourable intramolecular Au...Au interactions and π stacking in the products, which probably ensures the thermodynamic stability of **4** and **6**. It has recently been suggested that aurophilicity is a driving force in the formation of the remarkable [2]catenane ring system in $[\{Au(C\equiv CBu^t)_6\}]_2$ and the knitted polymer $[(AuCl)_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}]$ but the present work is believed to be the first in which a planned ring synthesis by self-assembly based on aurophilic attractions has been accomplished.^{3,5} The strategy is clearly applicable to the synthesis of more complex ring systems.

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Footnote

The ligand dcypm was used in place of dpmm to enhance solubility of the products. Satisfactory analytical data were obtained for new complexes. *Selected spectroscopic data* (NMR in CD₂Cl₂, IR as Nujol mull): **1**: δ (³¹P) 47.68 (s), δ (¹H) 56.32 (s). **4a**: δ (³¹P) 53.12 (s), δ (¹H) 7.87 (s, 8 H, Ph), 2.53 [t, 4 H, ²J(PH) 23.6 Hz, CH₂] IR: 2917s cm⁻¹. **4b**: NMR, δ (³¹P) 53.08 (s), δ (¹H) 2.53 [t, 4 H, ²J(PH) 24.3 Hz, CH₂], 2.33 (s, 24 H, CH₃). IR: 2202s

cm⁻¹. **4c**: NMR, δ (³¹P) 53.68 (s), δ (¹H) 7.88 (s, 4 H, Ph), 2.56 [t, 4 H, ²J(PH) 23.9 Hz, CH₂], 1.42 (s, 36 H, Bu^t). IR: 2194s cm⁻¹. **6a**: δ (³¹P) 50.82 (s), δ (¹H) 7.22 (s, 8 H, Ph). IR: 2106w cm⁻¹. **6b**: δ (³¹P) 49.73 (s), δ (¹H) 7.27 (s, 4 H, Ph), 2.43 (s, 12 H, CH₃). IR: 2099 cm⁻¹. **6c**: δ (³¹P) 50.23 (s), δ (¹H) 7.24 (m, 16 H, Ph). IR: 2096w cm⁻¹.

Crystallographic data for 4a: *M* = 2466.71; crystal system, tetragonal, space group *P4/n*; *a* = 29.93(2), *c* = 11.011(10) Å; *U* = 9885(14) Å³, *D_c* = 1.658 cm⁻³ for *Z* = 4 at 23 °C; *R* = 0.0848, *R_w* = 0.1578. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/51.

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