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Photoreactive gold(I) macrocycles with diphosphine and *trans,trans*-muconate ligands†

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A pair of *trans,trans*-muconate ligands have been successfully aligned in two novel Au(I) macrocycles by design from phosphino metal precursors that undergo photochemical cycloaddition reactions quantitatively, resulting in the formation of cyclooctadiene derivatives.

The solid-state topochemical photodimerization reaction *via* metal–ligand directed assembly has attracted attention due to its environmentally benign synthetic strategy, high efficiency and selectivity to a particular isomer that may otherwise be inaccessible in solution.¹ In recent years, template-controlled synthesis has been found to be a reliable method to align pairs of C=C bonds to satisfy Schmidt's criteria for solid-state photochemical dimerization.² Discrete metallo-macrocycles can be designed using metallophilic interactions and/or multi-topic bridging ligands to preorganise the system for photochemical [2+2] cycloaddition reactions.³ In this respect, dinuclear complexes have been used as 'clips' to anchor C=C bond pairs closely, and to explore their photoreactivity.⁴ Puddephatt's group synthesized a series of tetranuclear Au(I) macrocycles by the combination of binuclear complexes bridged by flexible diphosphine ligands and linear spacer subunits.⁵ Photoreactivity has been observed in these Ag(I)/Au(I) rectangular macrocycles containing the *trans*-1,2-bis(4-pyridyl)ethene (bpe) ligand.⁶

However, parallel orientation of a pair of conjugated C=C bonds in the solid-state still remains a challenge.^{7,8}

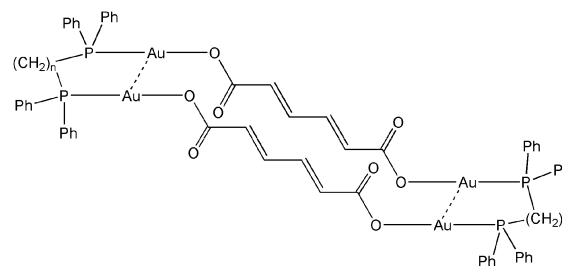


Fig. 1 Self-assembled macrocycles: **1**, $n = 1$, **2**, $n = 2$.

MacGillivray *et al.* have demonstrated the use of hydrogen bonds to align several conjugated C=C bonds.^{8a} Interestingly, most of the photodimerization reactions have been carried out on pyridine based ligands,^{6a} while dicarboxylate systems are largely unexplored. These considerations prompted us to attempt to align the conjugated double bonds of the muconate ligand, where H₂muco = *trans,trans*-muconic acid (1,3-butadiene-1,4-dicarboxylic acid), in two Au(I) macrocycles, and then to test their photoreactivity.

The compounds [Au₄(dppm)₂(muco)₂·2MeOH, **1**,§ and [Au₄(dppe)₂(muco)₂·2CH₂Cl₂·MeOH, **2**] (dppm = diphenylphosphinomethane; dppe = diphenylphosphinoethane), shown in Fig. 1, were synthesized from the precursors [Au₂(dppm)Cl₂] and [Au₂(dppe)Cl₂].^{6c} Addition of silver trifluoroacetate to a suspension of [Au₂(dppm)Cl₂] or [Au₂(dppe)Cl₂] in THF results in the formation of the soluble bis(trifluoroacetate) complexes. Removal of silver chloride and treatment with Na₂muco furnished the neutral complexes [Au₄(dppm)₂(muco)₂] and [Au₄(dppe)₂(muco)₂], respectively, by displacement of the weakly coordinating trifluoroacetate anions. Single crystals of **1** and **2** were obtained by dissolving these complexes in C₂H₄Cl₂/MeOH (2 : 1) and CH₂Cl₂/MeOH (1 : 1), respectively, and layering with *n*-hexane.

The asymmetric units of both complexes contain half of the formula unit, the remainder of the molecule being related by a crystallographic inversion center. In **1** the coordination geometry at the Au(I) center is approximately linear with O1–Au1–P1 and O3–Au2–P2 angles of 175.0(2)° and 175.2(2)°, respectively, as expected for Au(I) complexes. Complex **1** comprises a 26-membered ring containing four Au(I) centers (Fig. 2). The short bridging dppm ligand brings the two Au(I) atoms close together for aurophilic interactions as evidenced by the transannular

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† Electronic supplementary information (ESI) available: Syntheses, UV irradiation experimental details, X-ray data for **1** and **2** and NMR spectral data. CCDC 836596 (**1**) and 836597 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14442a

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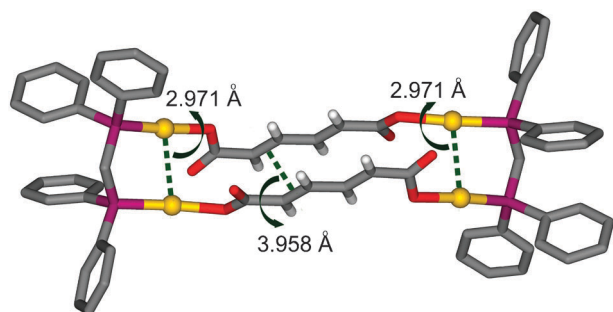


Fig. 2 Molecular structures of **1**. Solvent molecules, and hydrogen atoms of dppm are omitted for clarity.

Au(i)··Au(i) interaction (Au1–Au2, 2.9709(4) Å) which is comparable to the distances observed in (dppm)Au₂ structures.⁵ The muco²⁻ ligand coordinates to each Au(i) centre in a monodentate fashion *via* the carboxylate oxygens (Au1–O1, 2.055(5) and Au2–O3, 2.059(5) Å), and the non-coordinated C=O groups of adjacent muco ligands adopt *anti* orientations.

Most importantly, the C=C bonds of the adjacent muco ligands are now aligned parallel under the influence of (dppm)Au₂ clips. The distance between the centroids of the double bonds is 3.958 Å, thus satisfying Schmidt's geometric criteria for a solid-state [2+2] cycloaddition reaction;² hence the complex is likely to be photoreactive.

Compound **2** forms a similar structure to **1**, but the asymmetric unit contains two symmetry independent halves of the 28-membered rings each containing four Au(i) centers, wherein two dppm ligands bridge two pairs of Au(i) centers linked by muco²⁻ anions (Fig. S1, ESI†). The intra-molecular Au(i)··Au(i) interactions (Au1–Au2, 3.0372(5) and Au3–Au4, 3.3619(5) Å) present in the molecule are in the expected range for (dppm)Au₂ structures.⁵ As in **1**, muco²⁻ ligands coordinate to Au(i) atoms in a monodentate fashion *via* carboxylate oxygens (Au1–O1, 2.047(5); Au2–O3, 2.038(6); Au3–O5, 2.064(5) and Au4–O7, 2.053(5)), and the non-coordinated C=O groups of adjacent muco ligands adopt *anti* orientations. The two CCO₂ groups are also twisted relative to the (CH)₄ plane, but in one unit the dihedral angles (3.34° and 5.16°) are noticeably smaller than in the other unit (10.82° and 11.80°).

The two 28-membered macrocyclic units exhibit slightly different geometries: one has a shorter Au(i)··Au(i) distance of 3.0372(5) Å, but a larger separation of 4.254 Å between the centroids of the double bonds (Fig. S1 left, ESI†), while the other unit exhibits a longer Au(i)··Au(i) interaction of 3.362 Å but a shorter distance of 4.207 Å between the alkene centroid bonds (Fig. S1 right, ESI†).

As in **1**, the olefinic bonds of the adjacent muco ligands in complex **2** are aligned in a parallel fashion, but the distances between the C=C bonds only marginally meet Schmidt's criteria to be photoreactive. However, there are many examples of aligned olefinic bonds with distances of more than 4.2 Å that undergo dimerization upon UV irradiation,⁷ and so the photoreactivity of complexes **1** and **2** has been examined. Each complex, in powder form, was packed between two Pyrex glass slides and UV irradiated using a xenon light source for 1 h on each side of the glass slide. The colourless compounds turned

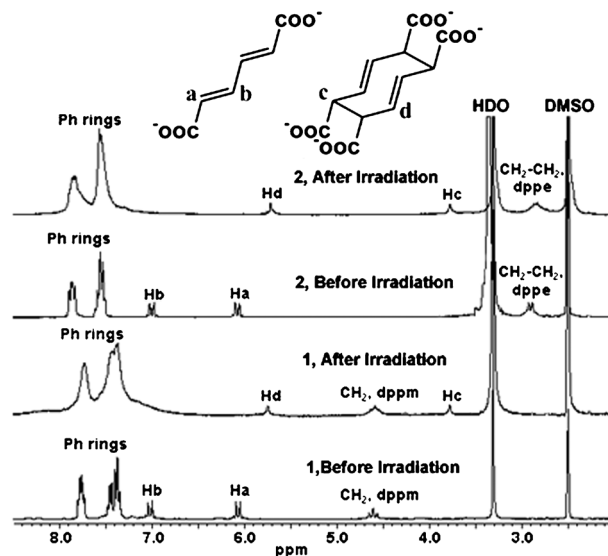
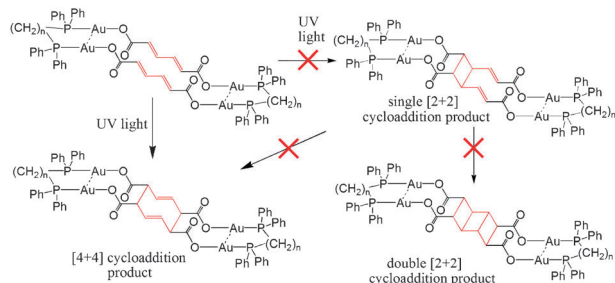


Fig. 3 ¹H NMR spectra of complexes **1** and **2** in *d*₆-DMSO before and after UV irradiation.

orange-brown after 2 h of irradiation, and were then characterized by NMR spectroscopy in *d*₆-DMSO solution. As shown in Fig. 3, the ¹H NMR spectra of **1** and **2** show complete disappearance of the olefinic proton signals of the muconate ligand ($\delta = 6.0$ and 7.0 ppm) and appearance of two new peaks ($\delta = 3.7$ and 5.7), indicating that 100% photodimerization had taken place. However, the ¹H NMR data indicate that there is no ladderane formation for which the cyclobutane protons should emerge in the range $\delta = 3.0$ –4.3 ppm.^{8,9} Instead, the observed chemical shifts correspond clearly to the formation of 1,5-cyclooctadiene derivatives.^{8b,10a}

¹H NMR data were collected at various time intervals to monitor the progress of reaction for **2**, and the stack plot (see ESI†, Fig. S2) indicates the gradual disappearance of the olefinic protons of the muconate ligands with concomitant appearance of cyclooctadiene peaks at 3.7 and 5.7 ppm. Crucially, no peaks were observed corresponding to the intermediate [2+2] cyclobutane dimer obtained by single cycloaddition.

The cyclooctadiene products obtained upon UV irradiation of **1** and **2** are quite different from those observed by MacGillivray and Frišćić^{11a} and by Biradha and Santra,^{11b} whereby [2+2] cycloaddition reactions of non-adjacent double bonds proceeded in a stepwise manner. Indeed, the photodimerization of muconic acid was studied as early as 1967 by Lahav and Schmidt,^{10b} and it was revealed that only one of the two pairs underwent the dimerization reaction, probably attributable to non-alignment of the second C=C bond pair after the formation of the first cyclobutane ring. Similarly, Matsumoto *et al.* noted that a single pair of C=C bonds underwent cyclization in the solid state and subsequently thermally isomerized to the 1,5-cyclooctadiene.^{8b} On the other hand, partial double dimerization occurs when the muconate ligand is present in a 3D porous coordination polymer. However, ¹H-NMR analysis of an alkaline D₂O solution of the irradiated product showed the presence of a mixture containing single dimer, cyclooctadiene dimer and ladderane in the ratio of 10:5:1, along with the unreacted



Scheme 1 Possible reaction products obtained for Au(I) macrocycles **1** and **2** under UV light.

ligand possibly attributable to decomposition of the strained ladderane in alkaline solution.^{8c}

Since there was no evidence for the formation of the single dimer or ladderane even after very long exposure of samples of **1** and **2** to UV light, it appears that the photodimerization reaction occurs either in a single-step concerted [4+4] cycloaddition process,^{8b} or by initial formation of a single cycloaddition product (a *cis*-divinylcyclobutane) which undergoes a fast Cope rearrangement to a 1,5-cyclooctadiene in the solid state.^{8e} We found that the irradiation of **1** in *d*₆-DMSO solution as well as freshly dissolved irradiated product gave the ¹H-NMR spectra similar to the above discussed and hence we conclude that [4+4] cycloaddition appears to occur in these solids as depicted in Scheme 1. A single peak observed in the solid-state ³¹P NMR spectroscopic studies of **1** also indicates the formation of a symmetrical, *i.e.*, [4+4], product not any other intermediates.

Attempts to obtain single-crystal to single-crystal (SCSC) photodimerization at various temperatures were unsuccessful as crystal mosaicity was not preserved after UV irradiation. In addition, despite many attempts to grow single crystals of the photodimers derived from **1** and **2**, they were not of X-ray quality.

In summary, we have successfully designed and synthesized two photoreactive neutral gold(I) macrocycles using a combination of diphosphine and muco²⁻ anions. Such gold(I) macrocycles incorporating dicarboxylic acids have not been reported before. Furthermore, we have shown that a (P–P)Au₂ group acting as a clipping agent in gold(I) macrocyclic rings is capable of aligning conjugated C=C bonds between two dicarboxylic acid molecules for photochemical cycloaddition reactions, which may otherwise be difficult to achieve by conventional synthetic routes. Interestingly, the synthesized gold(I) macrocycles undergo 100% photo-conversion of C=C bonds under UV light in the solid state, as well as in solution. This indicates that parallel alignment of the C=C bonds in the macrocycles is maintained, thus confirming that the solid-state structure is retained in solution. To apply topochemical principles in solution, a stable structure in solution must be found to replace the crystal lattice as an ordering principle.^{9a} The formation of 1,5-cyclooctadienes is likely to proceed through a concerted [4+4] cycloaddition and not by rapid Cope rearrangement after a single [2+2] cycloaddition.

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Notes and references

§ Crystal data for **1**: C₆₄H₆₀Au₄O₁₀P₄, *M*_r = 1900.87, monoclinic space group *P*2₁/*c*, *a* = 11.275(1), *b* = 16.295(1), *c* = 16.219(1) Å, β = 103.224(2)°, *V* = 3078.7(5) Å³, *Z* = 2, ρ_{calcd} = 2.051 g cm⁻³, *T* = 223(2) K, *R*₁ = 0.0432, *wR*₂ = 0.0885, GOF = 0.987 for 5412 reflections with *I* > 2σ(*I*), Mo-Kα (λ = 0.71073 Å) (CCDC 836596).

¶ Crystal data for **2**: C₆₇H₆₄Au₄Cl₄O₉P₄, *M*_r = 2066.73, triclinic space group *P*1, *a* = 13.1309(8), *b* = 14.7191(8), *c* = 18.2436(11) Å, α = 80.685(1)°, β = 81.181(1)°, γ = 87.496(1)°, *V* = 3437.8(3) Å³, *Z* = 2, ρ_{calcd} = 1.997 g cm⁻³, *T* = 223(2) K, *R*₁ = 0.0547, *wR*₂ = 0.1412, GOF = 0.978 for 15638 total reflections of which 12074 reflections have *I* > 2σ(*I*), Mo-Kα (λ = 0.71073 Å) (CCDC 836597).

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