Photochemical Disproportionation of an Au^{II} Pincer Complex: Synthesis and Structure of an $Au^{I}_{4}Au^{III}_{4}$ Macrocycle

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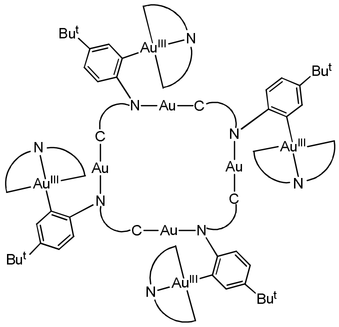


ABSTRACT. The Au(II) C^N^C pincer complex $[(C^\wedge N^\wedge C)Au]_2$ is stable under thermal conditions but disproportionates on irradiation in solution to give an $Au(I)_4Au(III)_4$ mixed-valence aggregate with a 20-membered macrocyclic structure, consisting of four linear Au(I) C-Au-N building blocks, each of which is decorated with a square planar (C^N^C)Au(III) substituent. In the crystal, the rings are stacked to form solvent-filled channels with an internal diameter of 8.3 Å and a cross-channel $Au^{I}\cdots Au^{I}$ distance of 7.7 Å.

Gold in the oxidation state +II is relatively uncommon and, due to partial occupation of its high-lying $d_{x2\text{-}y2}$ orbital, prone to disproportionation into Au(I) and Au(III).[1-3] The stability of Au(II) complexes is improved by forming binuclear complexes with Au^{II}-Au^{II} bonds, particularly if this bond is supported by bridging ligands. Although a significant number of Au(II) compounds have been isolated, the tendency towards disproportionation is a characteristic feature of their chemistry. The nature of the ligand set plays a crucial role. For example, Bennett and others have demonstrated the fine balance between Au(II)-Au(II) and Au(I)-Au(III) compounds.[3-6] More recently, Zopes and co-workers described an Au(II) compound with an unsupported Au-Au bond and a C-N-C ligand set, $Au_2(CF_3)_4(py)_2$; in this case the compound was formed under photochemical conditions but underwent spontaneous disproportionation in solution under ambient conditions.[7] Similarly, another "unsupported"

Au(II) compound, $Au_2(C_6F_5)_4(tht)_2$, was characterized in the solid state but its existence in solution was doubtful.[8] By contrast, as part of a study on Au(III) pincer complexes[9] we reported another example of a C-N-C ligand set with unsupported Au-Au bond, (C^N^C)Au-Au(C^N^C) (**1**). In this case the ligands forma rigid pincer, and as a result, this Au(II) complex proved to be thermally unusually stable both in solution and the solid state. For example, not only was there no observable tendency to disproportionation of **1** in toluene solution on heating to 60 °C,[10] the Au(II) compound could even be generated as the stable end product from the gold(III) precursor (C^N^C)Au(μ-κ*C*:κ*O*-CO_2)Au(C^N^C) by reductive CO_2 elimination on heating to 80 – 120 °C in the solid state.[11]

The originally reported[10] crystal structure of **1** was for the dichloromethane solvate, **1**·CH_2Cl_2, which gave crystals of modest quality from which an Au-Au distance of slightly less than 2.5 Å was determined. We have now obtained better-quality crystals from benzene, **1**·$(C_6H_6)_2$, and have redetermined the structure (Figure 1). The compound shows a slightly longer Au-Au distance of 2.5169(4) Å. This compares well with the metal-metal distance of 2.5062(9) Å in $Au_2(CF_3)_4(py)_2$[7] and suggests that although the *t*Bu substituents of the pincer ligand system in **1** might be expected to exert steric repulsion, the effect on the Au-Au bond strength is small. This is borne out by determinations of the energies of these unsupported Au^{II}-Au^{II} bonds by electrochemical and computational methods.[12,13] Compounds with unsupported Au-Au bonds can show great variability in intermetallic distances, with values up to 2.6405(8) Å in $[Au_2(dppn)_2I_2](PF_6)_2$[14] (dppn = 1,8-bis-(diphenylphosphino)-naphthalene), whereas Au-Au bonds reinforced by bridging ligands can be as short as 2.447(2) Å.[15]

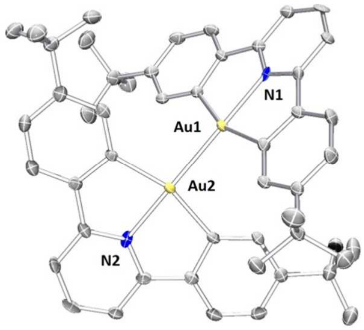


Figure 1. Molecular structure of **1**·$2C_6H_6$. Hydrogen atoms and crystallization solvent molecules (benzene) have been removed for clarity. Selected bond distances [Å] and angles [°]: N1-Au1 2.071(4) ; Au1-Au2 2.5169(4) ; N1-Au1-Au2 178.97(11).

The gold-gold bond in **1** fails to react with dioxygen under 4 bar pressure (even though O_2 insertion is exothermic[12]) and even resists heating with sulfur in toluene. However, we noted that solutions of **1** darken on prolonged exposure to daylight and decided to explore this aspect further.

Irradiating benzene solutions of **1** with UV light (λ = 365 nm) in an NMR tube in the presence of air for 24 h resulted in a color change from yellow to orange-brown. Monitoring the reaction by ^{1}H NMR spectroscopy showed that full conversion of **1** was achieved after 24 h, to give a new product **2** (Figure 2). By comparison, exposing a sample of **1** in C_6D_6 to ambient laboratory lighting resulted in only 30 % conversion over a period of 48 h. The ^{1}H NMR spectrum of the resulting products (CD_2Cl_2) revealed the disappearance of the *tert*-butyl signal of **1** at δ 1.01, which was replaced by two new singlets at δ 1.08 and 1.33 in an approximate 1:1 ratio. There were concomitant changes in the aromatic region, notably the disappearance of the characteristic aryl singlet of **1** at δ 8.14. While it was not possible to assign a specific structure on the basis of the NMR data, the formation of a product of solvent activation, such as (C^N^C)AuPh, could be ruled out.

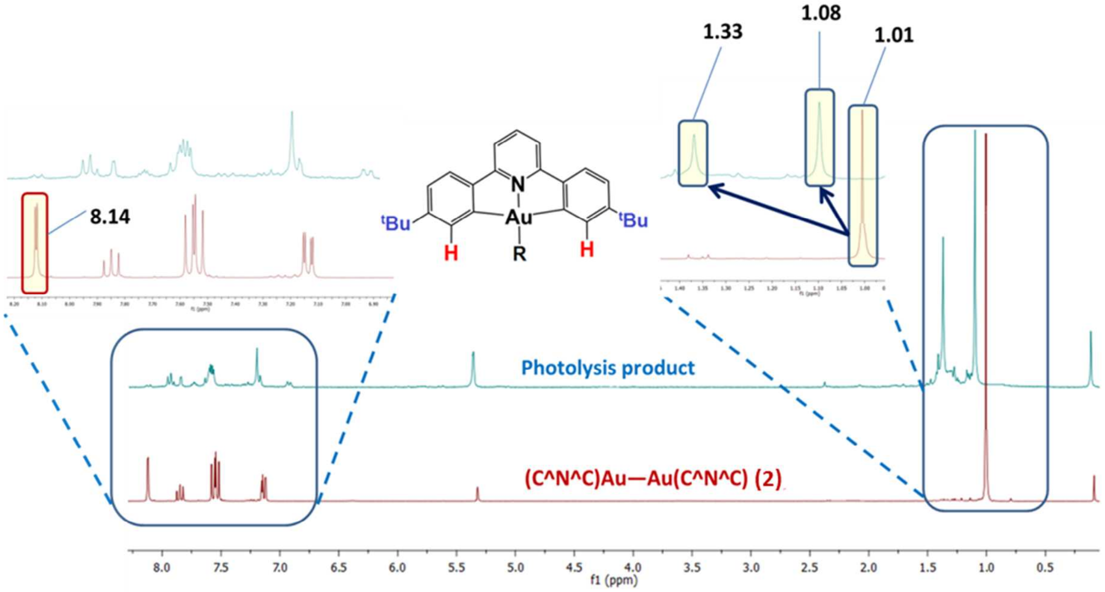
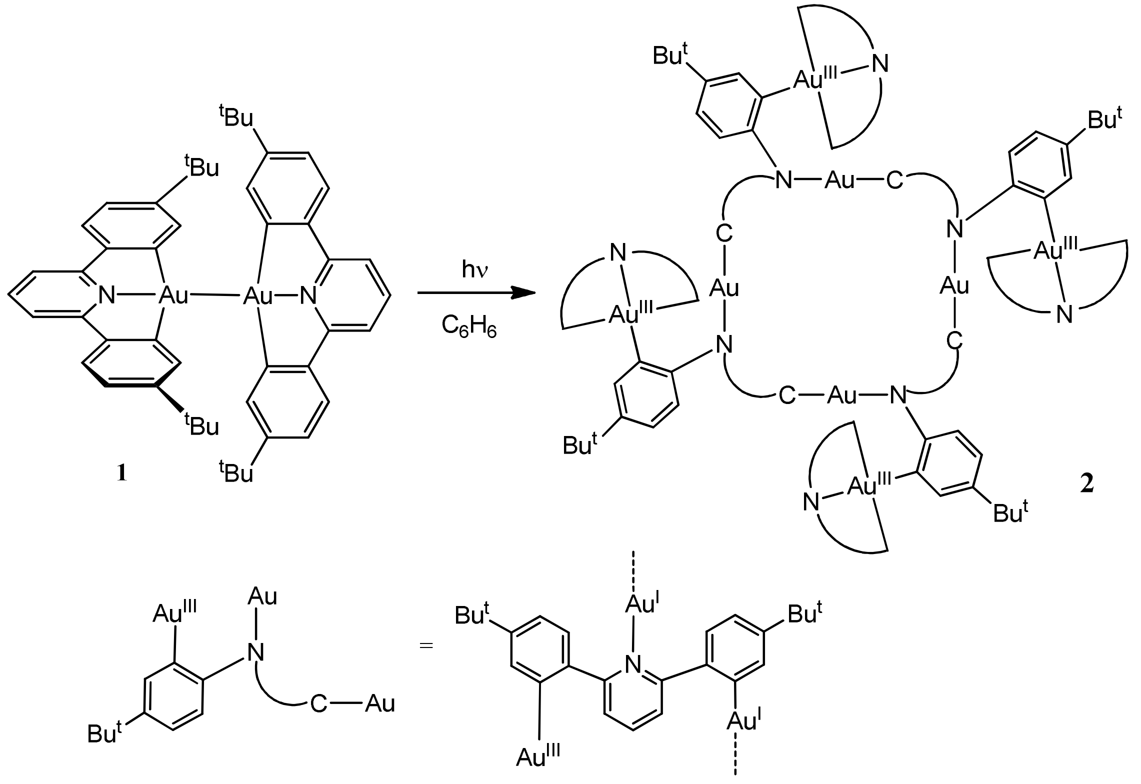


Figure 2. ^{1}H NMR spectra of **1** and of the photolysis product **2**.

Crystallization of the resulting product from dichloromethane allowed the isolation of **2** as yellow crystals (Scheme 1). Since the NMR spectra were not diagnostic, the compound was identified by single crystal X-ray crystallography. As the molecular structure shows, **2** consists of a 20-membered metallacycle formed by four pyridine-Au-aryl moieties of the cyclometallated 2,6-diarylpyridine ligand, with one $C_6H_3Bu^t$ moiety per building block being decorated with a (C^N^C)Au^{III} substituent (Figure 3).

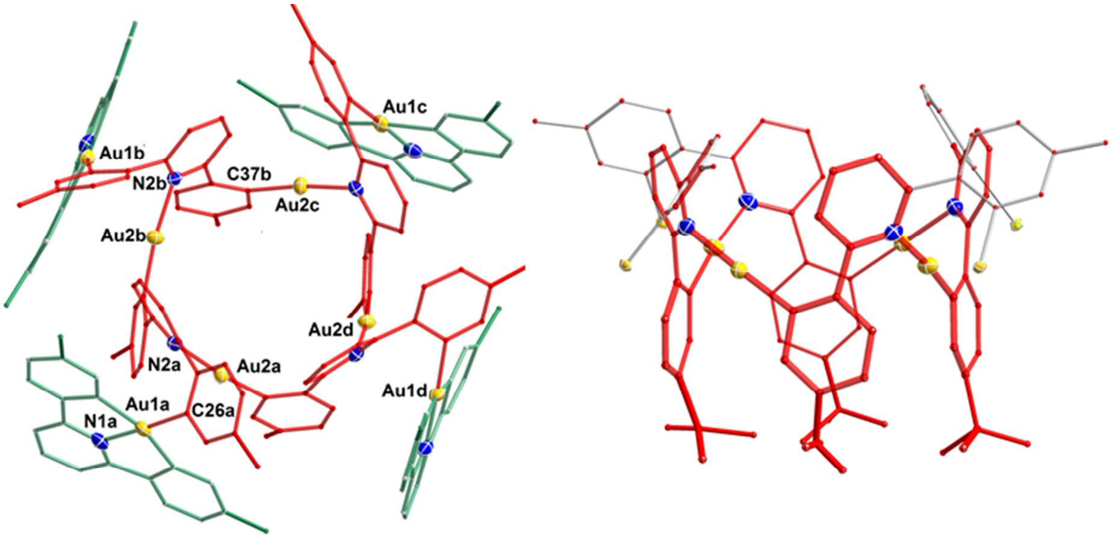
Gold(I) macrocycles are generally made by the addition of bidentate ligands to Au(I) precursors. Those with four or more gold centers show a number of structural types; for example, bridging anionic ligands like amidinates tend to generate Au^I_4 cycles based on near-linear L-Au-X moieties (where L and X represent neutral and anionic donors, respectively),[16] held together by Au···Au aurophilic interactions, as do tetrameric Au(I) thiolates[17] and a recently reported carbide-bridged Au_4 cycle, $[Au\{\mu\text{-}C{\equiv}W(CO)_2(Tp^*)\}]_4$.[18] On the other hand, such interactions are absent in a number of other Au(I) ring structures, including those based on phosphido[19] or acetylide ligands (as in $[Au(\mu\text{-}C{\equiv}CBu^t)]_6$),[20] or compounds with rigid P donors[21] and large macrocyles.[22] In the case of **2**, the formation of a macrocycle is most easily explained by assuming photochemical ring-opening of one of the pincer ligands in **1** and transfer of a phenyl radical from one gold center to another to form an Au(III) aryl moiety. The formation of **2** is therefore an illustration of the general importance of photochemical processes in gold chemistry, even under ambient lighting conditions.[23]



Scheme 1

Complex **2** shows linear pyridine-Au-aryl units (angle C(37b)—Au(2c)—N(2c) 172.98(12)°), as expected for Au(I). The Au^{I}—N bond lengths are significantly longer than the Au^{III}—N bond lengths in the (C^N^C)Au^{III} fragments, viz. Au(2a)—N(2a) 2.138(4) Å, compared to Au(1a)—N(1a) of 2.048(2) Å in the exterior (C^N^C)Au^{III} fragment). The four py-Au^{I}-aryl links of the macrocycle are connected such that they form a zigzag chain, so that the pyridine moieties can be said to make up the "upper" rim and the $C_6H_3{}^{t}Bu$ units the "lower" edge. As a result, the four ${}^{t}Bu$ substituents cause a narrowing of the lower part of the cavity to 3.9 Å (Figure 3b). Overall, the molecule is cup-shaped, with a maximum cavity diameter (as defined by the N(2a) - N(2c) distance) of 8.3 Å and a cross-channel $Au^{I}\cdots Au^{I}$ distance of 7.7 Å. In the crystal, the cavity of **2** is probably occupied by disordered solvent molecules, although attempts to model the residual electron density were unsuccessful. A stacked view depicting the solvent-accessible channel is presented in Figure 4.

The intramolecular $Au^{I}\cdots Au^{III}$ distances of 3.604(5) Å are longer than the sum of the van der Waals radii of two gold atoms (3.4 Å) and slightly longer than the range for which aurophilic interactions can be assumed (2.5 – 3.5 Å).[24] The molecule also displays long intramolecular $\mathrm{Au^{I}\cdots Au^{I}}$ distances (5.471 Å) between two neighboring metal centers, likely due to geometrical constraints. Contacts of comparable length can also be measured between gold(III) centers of neighboring molecules ($\mathrm{Au^{III}\cdots Au^{III}}$ 5.425 Å), similar to other gold(III) compounds bearing the cyclometallated diphenylpyridine ligand. A view of the crystal packing reveals that the $\mathrm{(C^\wedge N^\wedge C)Au^{III}}$ planes are arranged in a head-to-tail fashion, possibly to minimize repulsion between the t-butyl substituents. Complex **2** is only weakly photoluminescent, in accord with an absence of Au···Au interactions.



(a) (b)

Figure 3. (a) Molecular structure of **2**. Components of the macrocycle are colored red. Hydrogen atoms and methyl groups of *t*-butyl fragments have been omitted for clarity. Selected bond distances [Å] and angles [^{0}]: Au(1a)-Au(2a) 3.6036(6); Au(2a)-Au(2b) 5.4708(6); Au(2a)-Au(2c) 7.7369(6); N(2a)-N(2c) 8.772(11); C37b-Au2b-N2a 173.0(4); Au(1b), Au(1c) and Au(1d) are the crystallographic equivalent of Au(1a). Au(2b), Au(3b), Au(4b) are the crystallographic equivalent of Au(2a). (b) View of **2** showing the zigzag arrangement of the py-Au-aryl ribbon forming the cavity and the channel formed by the *tert*-butyl substituents. The (C^N^C)Au(III) fragments have been omitted for clarity.

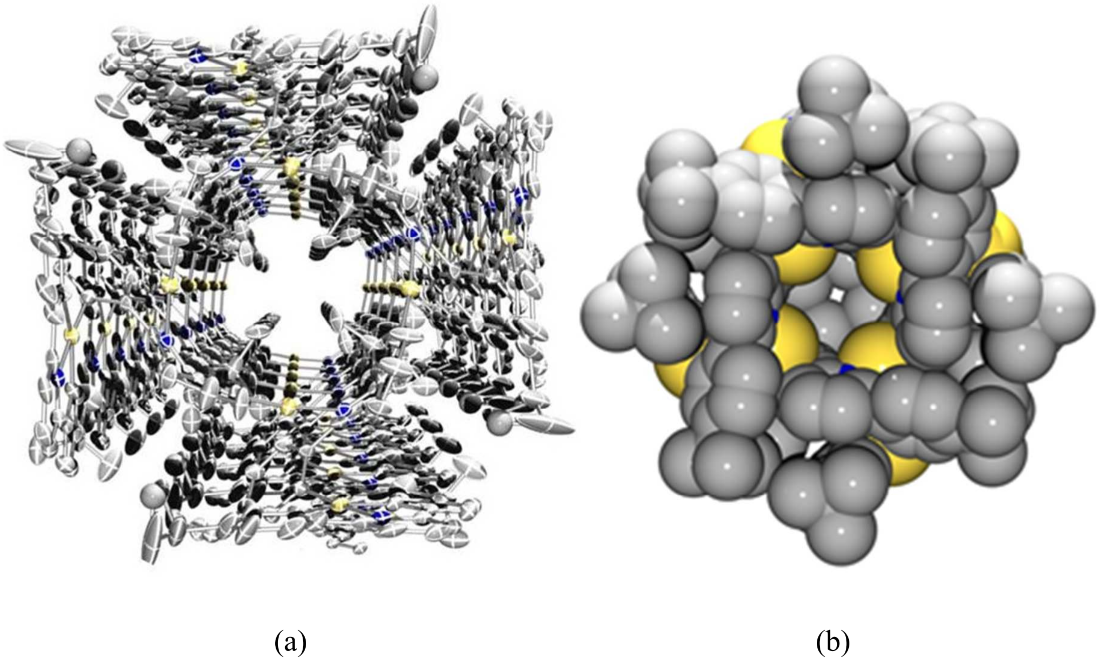


Figure 4. (a) Stacked view comprising of molecules of **2** showing the solvent-accessible channel. (b) Space filling view along *c* axis showing narrowing of the channel by the *t*-butyl substituents which reduce the “lower” opening to 3.9 Å (as defined by the distance between two opposite C atoms in the lower rim).

In summary, the results demonstrate the unusual case of a photochemically, rather than thermally, induced disproportionation of an Au(II) complex. The reaction proceeds slowly even under diffuse daylight and underlines the importance of light-induced processes in gold chemistry. In this case is a mixed-valence product is formed, with a macrocyclic core based on Au(I) building blocks, each of which is decorated with an Au(III) pincer moiety. There are no detectable aurophilic interactions either between the Au(I) or between Au(I) and Au(III) centers. The disproportionation of binuclear Au(II) complexes has, as far as we are aware, previously only been seen as the result of thermal processes. The formation of macrocyles such as **2** by photo-induced disproportionation adds another facet to the interesting reactivity spectrum of Au(II) compounds.

EXPERIMENTAL SECTION

Synthesis of 2. [(C^N^C)Au]$_2$ (**1**) (15 mg, 13.8 μmol) was placed in a J-Young NMR tube and dissolved in 0.5 mL $C_6D_{6.}$ The solution was then placed under a UV lamp (365 nm) for 24 h. The color of the mixture changed from pale yellow to orange-brown. The solvent was removed *in vacuo* and the residue obtained as a dark-orange powder in 70% yield. This product was dissolved in CH_2Cl_2 (3 mL). Layering with light petroleum (3 mL, bp 40-60 °C) and cooling to -20 °C gave **2** as yellow blocks which were characterized by X-ray crystallography.

X-Ray Crystallography. Crystals were mounted in oil on glass fibres and fixed in the cold nitrogen stream on a diffractometer. Diffraction intensities for compounds **1**·$2C_6H_6$ were recorded at 140(2)K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Data were processed using the CrystAlisPro-CCD and –RED software.[25] Intensities for compound **2** were collected at 100(2)K on a Bruker-Nonius Roper CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator at the EPSRC National Crystallography service, Southampton, UK.[26] Data were processed using CrystalClear-SM Expert 3.1 b21 (Rigaku, 20112) programs. The structures of all samples were determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods on F^2 in SHELXL.[27] Non-hydrogen atoms were generally refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions. No missed symmetry was reported by PLATON.[28] Computer programs used in this analysis were run through WinGX.[29] Scattering factors for neutral atoms were taken from reference.[30]

Compound **1**·$2C_6H_6$: Crystals (yellow plates) were obtained by slow evaporation of a benzene solution of **1** at room temperature. *Crystal Data:*$C_{50}H_{54}Au_2N_2$, $2(C_6H_6)$, M =1233.11. Monoclinic, space group $P2_1/c$, a = 12.609(2), b = 26.9775(15), c = 17.476(2) Å, α = 90, β = 121.135(8), γ = 90 °, V = 5088.3(10) $Å^3$, Z = 4, D_c = 1.610 Mg/m^{-3}, T = 140(2) K, μ(Mo-Kα) = 5.798 mm^{-1}, λ(Mo-Kα) = 0.71069 Å. Two benzene solvent molecules are present in the crystal lattice. The LAuAuL molecule is well resolved with no disorder. The N1-Au1-Au2-N2 torsion angles is -168.1(1)° and the Au(1)-Au(2) bond length is 2.5169(4) Å.

Compound **2**: *Crystal Data:* $C_{200}H_{202}Au_8N_8$, M = 4293.66. Tetragonal, space group $P4/n$, a = 26.9936(10), b = 26.9936(10), c = 12.952(5) Å, α = 90, β = 90, γ = 90 °, V = 9438(4) $Å^3$, Z = 2, D_c = 1.436 Mg/m^{-3}, T = 100(2) K, μ(Mo-Kα) = 6.239 mm^{-1}, λ(Mo-Kα) = 0.71069 Å. The diameter of the upper rim of the cavity (8.722(11) Å) is defined by the distance between two opposite nitrogen atoms. The diameter of the lower rim, defined by the distance between the methyl carbons of two opposite *tert*-butyl groups, is 3.971(3) Å. The cavity contains solvent-accessible voids but electron density peaks appeared very diffuse and were not reliably resolved. There was some degree of disorder related to a number of *tert*-butyl groups. The largest electron density peak appears to be in the center of the cavity *ca*. 5 Å from Au(1).

ASSOCIATED CONTENT

Supporting Information

CIF files for **1**·(benzene)$_2$ and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Complete details of the X-ray analyses reported herein have also been deposited at the Cambridge Crystallographic Data Centre (CCDC numbers 1430033 (compound **1**) and 1430032 (compound **2**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, U.K.; fax + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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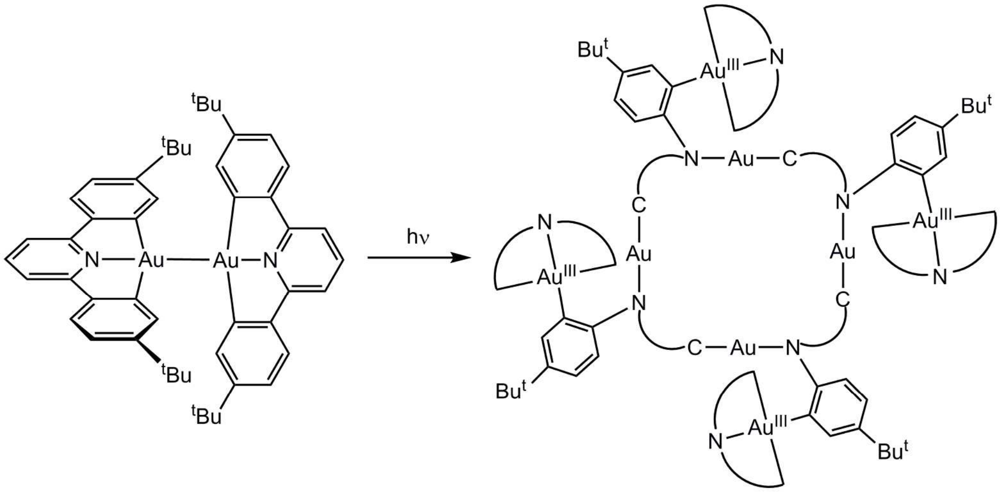

Photolysis of Au(II) dimer leads to Au(I)/Au(III) macrocycle
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