

The complex coordination landscape of a di-Au(I) U-shaped metalloligand

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We would like to dedicate this article to Bob Crabtree, on the occasion of his 70th birthday

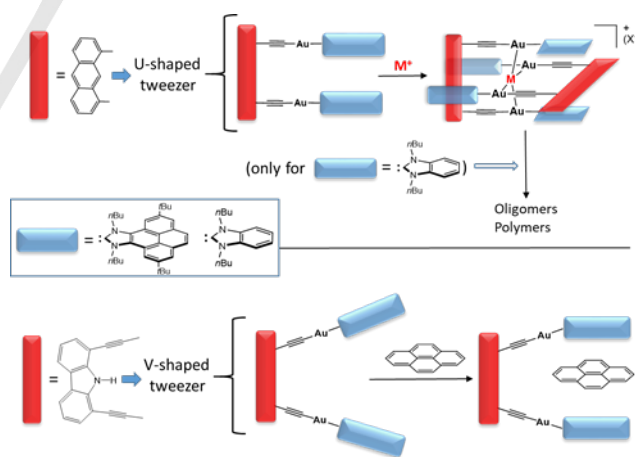
Abstract: A U-shaped di-gold metallotweezer with two pyrene-imidazolylidene edges and a xanthenyl-bis-alkynyl connector was prepared. This metallotweezer acts as metalloligand in the presence of Cu^+ , Tl^+ or Ag^+ , showing three clearly distinct coordination patterns, depending on the cation used. The coordination to Cu^+ , leads to a complex in which the metalloligand is coordinated in a pincer form. The reaction with Tl^+ affords a complex in which the ligand is acting as a K^2 -(trans)-chelate ligand. The reaction with Ag^+ leads to a self-assembled structure, with two silver cations encased inside the cavity of a duplex structure formed by two self-assembled metallotweezers.

Most of the applications of designed functional materials are architecture dependent. This makes that one of the major challenges of synthetic chemists is to find ways to predictable architectures resulting from the assembly of pre-formed building blocks, so that materials with tailor-made applications can be rationally designed.^[1] A convenient approach to materials with ordered architectures is the use of metalloligands, which offer structural rigidity by placing the auxiliary functional groups at pre-organized conformations.^[2] Metalloligands also provide facile access to heterometallic supramolecular structures, which are usually difficult to achieve by using other routes. Molecular tweezers integrating metal centers in their structures are gaining interest in the last few years.^[3] Some authors have provided interesting examples of the use of non-covalent complexation between tweezers and metal-containing guests as a strategy for enforcing short-range metal-metal interactions,^[4] thus opening the possibility to use metallotweezers as a new type of metalloligands.

Due to the high tendency of Au(I) complexes to show linear geometry, and to establish attractive $\text{Au}\cdots\text{Au}$ and $\text{Au}\cdots\text{M}$ interactions,^[5] Au(I)-based metalloligands (or *auroligands*) have gained significant attention in the last few years.^[6] Among auroligands, gold alkynyls^[7] are recently being regarded as an interesting type of supramolecular scaffolds due to the combined binding abilities provided by the alkynyl ligand and by the aurophilic/metallophilic interactions.

By incorporating gold-alkynyl units in the core of molecular tweezers, we were recently able to prepare a series of di-gold metallo-tweezers for the recognition of 'naked' metal cations^[8] and polycyclic aromatic hydrocarbons (PAHs).^[9] The recognition properties of this type of metallotweezers are highly dependent on the nature of the rigid connector, and of the ancillary ligands

that constitute the arms of the tweezer (Scheme 1). For 'U-shaped' tweezers combining a rigid polyaromatic connector with polyaromatic functionalities at the arms of the tweezer, we observed that the recognition abilities are highly influenced by the tendency of the tweezer to self-aggregate forming duplex complexes. These are formed by the combined action of the π - π -stacking interactions of the complementary polyaromatic functionalities, the coordination abilities of the added metal cation to the alkynyl ligands of the tweezer, and the aurophilic/metallophilic interactions between the metals involved in the formation of the inclusion duplex structure. The self-aggregation of these 'U-shaped' molecules can be minimized if the arms of the tweezer are formed by ligands lacking polyaromatic functionalities, so that the π - π -stacking interactions are less likely to be produced. Under these circumstances we found that the molecule may self-aggregate, but the process is reversible and may also give rise to more complex structures, such as oligomers and polymers.^[8b] On the other hand, 'V-shaped' metallotweezers do not self-aggregate because the arms of the tweezer diverge from the connector, therefore reducing the self-complementarity character of the molecule, and allowing the system to be used as receptor of PAHs, such as pyrene, as shown in Scheme 1.^[9] All these findings allowed us to slowly unravel the complex supramolecular landscape of this new class of metallotweezers.



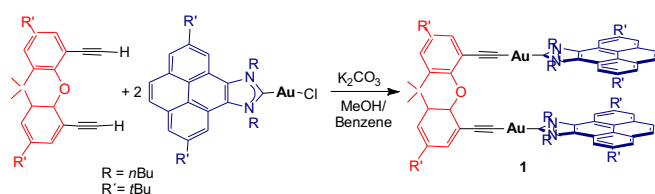
Scheme 1. Supramolecular landscape of U-shaped and V-shaped gold(I) metallotweezers

Based on these previous findings, we now became interested in designing a new metallotweezer based on a xanthen connector. The xanthen linker provides the structural requirements for accessing to a U-shaped metallotweezer, but prevents the self-association of the molecule due to the disruption of the conjugation by the central heterocycle, which minimizes the ability of the connector to participate in π - π -stacking events.

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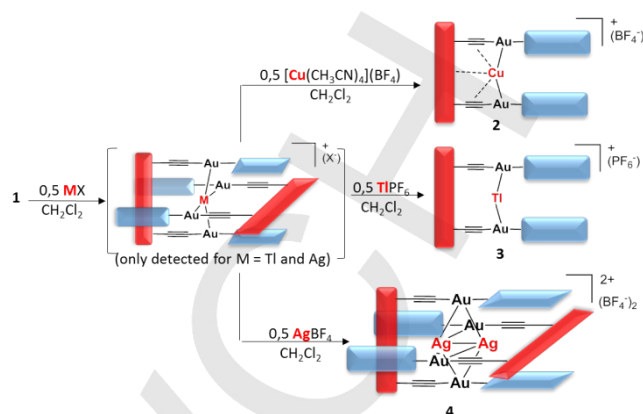
Under these circumstances, the coordination behavior of this potential metalloligand should be determined by the ability of a metal cation to bind to the oxygen of the xanthene linker, the alkyne of the arms, and/or the gold (I) atoms, all these constituting the three possible binding sites of this tweezer.

The xanthene-derived metallo-tweezer **1** was obtained by reaction of 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene with $[\text{Au}(\text{NHC})\text{Cl}]^{[10]}$ (NHC = di-*tert*-butyl-pyrene-imidazolyidene) in a mixture of methanol/benzene (1:1) in the presence of K_2CO_3 . Both the ^1H and ^{13}C NMR spectra of the complex were consistent with the pseudo- C_{2v} geometry of the molecule. The ^{13}C NMR spectrum revealed the resonance due to the two equivalent metallated Au-C_{carbene} carbons at 193.7 ppm.



Scheme 2. Synthesis of the gold metallotweezer **1**

As we recently did for other related U-shaped di-gold metallotweezers,^[8] we were interested in studying the reaction of **1** with metal cations such as Cu^+ , Tl^+ and Ag^+ . The addition of one equivalent of MX (MX = TlPF_6 , AgBF_4 and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$) to a CH_2Cl_2 solution of **1**, allowed the isolation of three different species, whose elemental analyses and mass spectra were consistent with the formation of 1:1 (or 2:2) adducts between **1** and M (Scheme 3). The addition of substoichiometric amounts of MX (0.5 equivalents) did not allow the isolation of the self-aggregated complexes with the metal cation in the inner cavity of the duplex complex ($\text{M}@1_2$ species), although for the case of the reaction with TlPF_6 and AgBF_4 , these species were detected by mass spectrometry. This observation is consistent with the lower ability of **1** to self-aggregate as a consequence of the disruption of the aromaticity of the xanthene connector by the presence of the oxygen-containing ring, thus minimizing the capacity of this part of the molecule to participate in π -stacking events. The 1:1 (or 2:2) adducts were obtained quantitatively when one (in total) equivalent of the metal cation was added to a solution of **1**. The nature of the complexes formed (**2-4**, Scheme 3) was elucidated by combining NMR and mass spectrometric studies. The ^1H NMR spectrum of the Ag-containing adduct **4** shows that the signals due to the protons of the xanthene linker are significantly upfield shifted compared to the signals of the same fragment in **2** and **3** (see Supplementary material for details), and also of the starting complex **1**. In addition, the resonances due to the protons of the methylene group bound to the nitrogen of the imidazolyidene are diastereotopic in **4**, while are magnetically equivalent in **2** and **3**. These observations are an indication that complexes **2** and **3** may contain monomer tweezers of the type $\text{M}@1$, while the silver-containing complex **4** is likely containing a 1_2 dimer.



Scheme 3. Different coordination modes of the metallotweezer/metalloligand **1** with three metal cations

The analysis of the complexes by time-of-flight-mass spectrometry (TOFMS) provides further evidences about the nature of complexes **2-4**. The mass spectra of **2** and **3** revealed main peaks at m/z 1758.7 and 1899.7, respectively. These peaks are consistent with mono-cationic species containing a molecule of **1** plus one metal cation, in agreement with the molecular structure depicted for **2** and **3** in Scheme 3. On the other hand, the mass spectrum of **4**, revealed one peak at m/z 1803.7, which is assigned to a dicationic species containing two molecules of **1** and two silver cations, of the type $[\text{Ag}^+]_2@1_2$. The UV-vis spectrum of **1** in CH_2Cl_2 solution shows a broad intense band between 230-300 nm with local maxima at 245, 267 and 288 nm, which are attributed to the intraligand (IL) π - π^* transitions of the alkyne ligands.^[11]^[12] The spectrum also shows the bands assigned to the absorption of the pyrene fragment, between 300 and 360 nm. The emission spectrum of **1** is dominated by a vibronically-resolved band with a peak maximum at 381 nm, which is coincident with the monomer emission band of pyrene in related pyrene-based-NHC ligands.^[8a, 13] The electronic spectra of complexes **2-4** (see Electronic Supporting Information) show similar bands as those shown by complex **1**. However, in the case of the spectra of complexes **2** and **4** (with Cu^+ and Ag^+ , respectively) the broad band assigned to the IL π - π^* transitions of the alkyne ligands is shifted to lower energy, likely as a consequence of the interaction of the triple bonds of the alkynes with Cu and Ag (the π^* C \equiv C orbital decreases in energy upon coordination to M).^[11] This interpretation is supported by our previous published results that indicate that Cu and Ag tend to coordinate to the triple bonds of alkyne ligands of analogue gold metallotweezers, while Tl is less prone to show this type of interaction. The lack of bonding between thallium and the alkyne in **3** is also supported by infrared spectroscopy. The IR spectrum of **3** shows the band of the alkyne ligand at $\nu(\text{C}\equiv\text{C}) = 2096.4 \text{ cm}^{-1}$, not very different to the frequency shown by **1** (2112.6 cm^{-1}). The IR spectra of **2** and **4**, show their $\nu(\text{C}\equiv\text{C})$ bands at 2040.3 and 2083.7 cm^{-1} , respectively, at lower frequencies than **1** and **3**, as expected for a situation in which a $\text{M}(\eta^2\text{-C}\equiv\text{C})$ interaction is taking place.

The molecular structures of **2** and **4** were unequivocally confirmed by single crystal X-ray diffraction studies. The structure of **2** (Figure 1), consists of a metalloligand **1** that is coordinated to a copper cation. The metalloligand is coordinated in a situation that clearly resembles a *palindromic* pincer coordination form,^[14] in which the copper is bound to the two alkynyls and to the oxygen of the xanthene linker. The copper (I) atom is also at a very close distance to one of the Au atoms [Cu(1)-Au(2)=2.73 Å], indicating a strong metallophilic interaction. The distance between the copper and the other Au atom is much longer (3.43 Å), thus indicating negligible Au-Cu metallophilic interaction with this second gold centre. Interestingly, the average distance between the two pyrene hands of the molecule is 3.5 Å, therefore indicating a strong intramolecular π - π -stacking interaction.

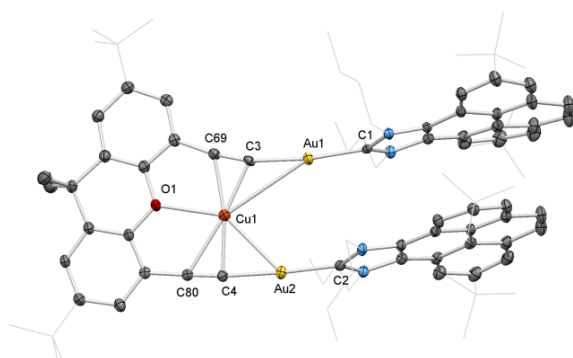


Figure 1. X-ray molecular structure of **2**. Hydrogen atoms, solvent (fluorobenzene) and counter anion (BF_4^-) have been omitted for clarity. *Tert*-butyl and *n*-butyl groups are represented in the wireframe form for clarity. Ellipsoids at 30 % probability. Selected bond distances (Å) and angles ($^\circ$): Au(1)-C(1) 2.029(10), Au(1)-C(3) 1.996(10), Au(2)-C(2) 2.016(10), Au(2)-C(4) 1.993(10), Cu(1)-Au(1) 3.429(13), Cu(1)-Au(2) 2.7320(13), Cu(1)-O(1) 2.361(7), Cu(1)-C(3) 2.031(9), Cu(1)-C(69) 2.104(10), Cu(1)-C(4) 2.053(10), Cu(1)-C(80) 2.375(10), C(3)-Au(1)-C(1) 172.2(4), C(4)-Au(2)-C(2) 175.9(4).

The molecular structure of complex **4** (Figure 2), consists of a self-assembled structure formed by two molecules of **1**, with two Ag^+ cations encased by the four $\text{Au}\equiv\text{C}$ fragments. The two molecules of **1** are assembled in a way that the two pyrene edges of each metallotweezer are sandwiching the xanthene tether of the complementary molecule. The structure resembles a duplex structure that we published recently,^[8a] although in that case only one Ag^+ cation was trapped inside the cavity. In the structure of **4**, each silver cation is η^2 -bound to two alkynyl ligands of the same tweezer, and to three gold atoms, with Ag-Au distances ranging from 2.95-3.22 Å. The distance between the two silver cations is 3.024 Å, thus indicating a significant argentophilic interaction.^[5c] Interestingly, the average distance between the plane formed by each xanthene linker and the pyrene fragments of the complementary molecule, is of ca. 4.8 Å, thus exceeding by far the optimum distance for an effective π - π -stacking interaction (3.5 Å). This observation indicates that the reason that explains the formation of this self-assembled structure must be found in the core of the molecule, in which the silver cations are optimizing all possible interactions with the binding sites of the metallotweezers (alkynyls, and gold centres),

with a further stabilization produced by the formation of an argentophilic bond. This situation contrasts with our previously reported tetra-gold duplex structures, for which π - π -stacking interactions were playing a crucial role.^[8a]

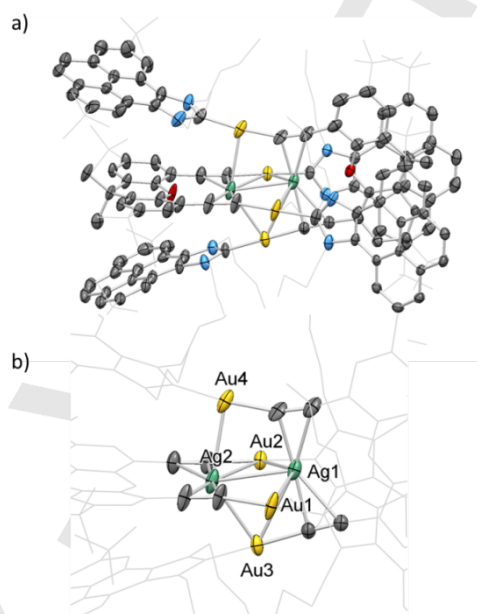


Figure 2. a) Molecular structure of **4** (BF_4^- anions omitted for clarity). b) Central part of the molecule, where the interactions between the metal centres and the ligands are more clearly observed. Selected bond distances (Å): Ag(1)-Au(1) 2.9546(15), Ag(1)-Au(2) 2.9501(13), Ag(1)-Au(3) 3.1907(17), Ag(1)-Ag(2) 3.0241(18), Ag(2)-Au(2) 3.2208(14), Ag(2)-Au(3) 2.9654(17), Ag(2)-Au(4) 2.980(2).

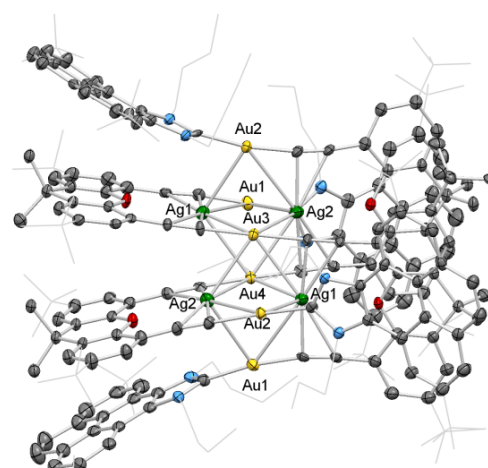
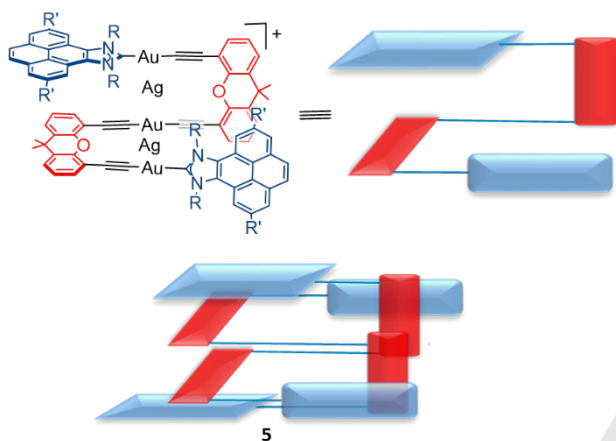


Figure 3. Molecular structure of **5** (BF_4^- anions omitted for clarity). Ellipsoids at 50% probability.

Remarkably, long-standing (> 1 week) CH_2Cl_2 solutions of **4** evolve to a new species (**5**) with concomitant formation of $[\text{Au}(\text{NHC})_2](\text{BF}_4)$ (NHC = pyrene-imidazolylidene). We believe that the stability of this cationic di-NHC gold complex triggers the formation of the heterometallic species **5**. We observed recently a similar type of rearrangement for a previously reported

anthracenyl-connected NHC-based di-gold metallotweezer.^[8b] The X-ray diffraction structure of **5** consists of two self-assembled trigold-units, which are held together due to multiple Au-Ag interactions, and by the bonds formed by four silver cations with the alkynyl ligands. Each tri-gold unit contains two bis-alkynyl-xanthenyl linkers, and two pyrene-imidazolylidenes at the edges (see schematic view in Scheme 4). The self-assembled structure shows that two xanthenyl linkers are sandwiched between two pyrene-imidazolylidenes, on each side of the molecule. Each silver cation shows metallophilic interactions with four gold centres, with distances ranging from 3.08 to 3.24 Å.



Scheme 4. Schematic view of **5**.

In conclusion, we prepared a U-shaped di-Au metalloligand with two pyrene-imidazolylidene hands and a xanthenyl linker. We studied the coordination abilities of this species to three metal cations that are prone to giving metallophilic interactions with the gold centres of the metalloligand. We found that the coordination abilities of the U-shaped ligand are highly dependent on the metal used. All coordination modes are highly influenced by $M^{\text{III}}\text{Au}$ interactions. Our studies not only help to unravel the rich coordination chemistry of a new type of metallotweezer, but also pave the way for materials with predictable sophisticated architectures by controlling the non-covalent interactions that lead to complex self-organized structures.

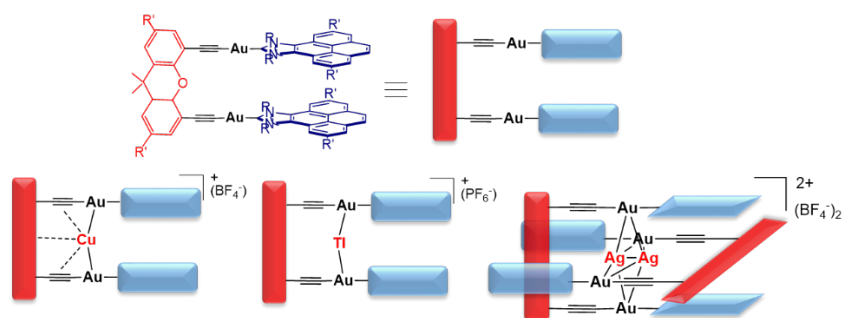
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Keywords: Metallotweezer • metalloligand • N-Heterocyclic carbene • gold • self-assembly

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