

Synthesis of unprecedented gold-silver three-legged luminescent honeycomb aggregates by both solvent-based and solvent-free methods

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Group 11 metal alkynyl complexes continue to receive great attention due in part to their rich emissive properties.^[1] Homometallic derivatives are significantly more numerous than the heteronuclear ones, due probably to the synthetic difficulty in controlling the selective formation of heterometallic arrays.^[2] Synthetic strategies to heteronuclear aggregates include self-assembly reactions involving *i*, direct combination of metal ions and ligands,^[3] and *ii*, preorganized metallo-ligand fragments, such as reactions between $[Ag(C\equiv CC_6H_4R-4)]_n$ and $[Au_2(\mu-dppm)]_2^{2+}$ to give gold-silver clusters.^[4] Self-assembly reactions have also been used to obtain different types of gold aggregates such as catenate complexes $[(AuC\equiv C)_2(P(CH_2)_nP)]$,^[5] or diphosphine-diacetylide derivatives with $R_2P(CH_2)_nPR_2$,^[6] including some based on $[Au_xM_y(C\equiv CR)_{2x}]^{x-y}$ clusters.^[7] In this article, we describe unprecedented polynuclear aggregates based on the latter structural unit. In particular, the metalloligand $[Au(C\equiv CPh)PPh_3]$ is reacted with metallic salts to give unusually large, highly ordered heterometallic materials only supported by acetylide-metal or metal-metal interactions. Interestingly, the nuclearity of the products is controlled through the addition of different donor ligands, with all the new derivatives exhibiting honeycomb metallic cores and strong luminescence. In addition to conventional solvent-based approaches, solventless mechanochemistry^[8] is used for the first time to synthesize this type of gold complexes.

The 1:2 reaction of $[Au(C\equiv CPh)PPh_3]$ with $[Ag(OTf)]$ leads to

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the high nuclearity cluster $[Ag_{12}Au_{10}(C\equiv CPh)_{17}(OTf)_5(PPh_3)_3]$ (1). The X-ray structure shows a central core formed by three hexagonal Ag_6Au_3 prisms, which share the three faces joined by the same central edge (Figure 1). The silver atoms are placed at the ends of longitudinal alternate edges in the hexagonal prisms. The edges that remain free are occupied by bis(acetylide)gold fragments, $Au(C\equiv CPh)_2$, with the gold atoms at the mid-points of the edges. The main core has a metallic composition $Ag_{12}Au_7$, which differs from the previously reported metastable cage $Ag_{13}Au_6$ containing a central silver atom.^[9] Defining the main core are $Au(C\equiv CPh)PPh_3$ fragments, which are coordinated to the silver atoms occupying the non-shared edges. Overall this forms an unprecedented $Ag_{12}Au_{10}$ framework, which is very stable and can serve as suitable starting point for further aggregation.

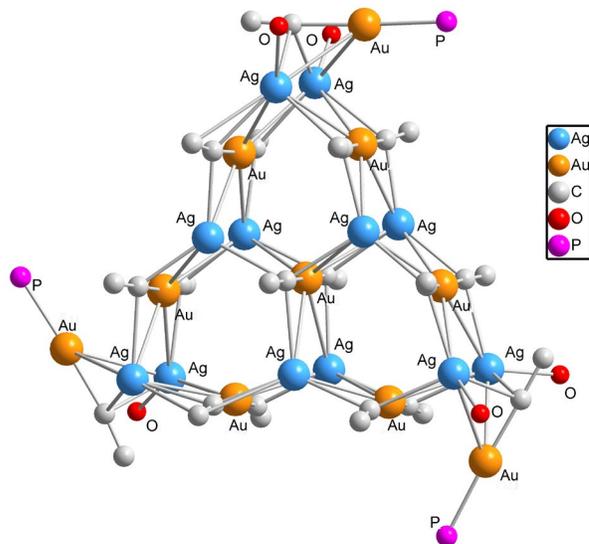


Figure 1.

In order to investigate the influence of additional ligands on the metal coordination environments, the reactivity of $[Au(C\equiv CPh)PPh_3]$ was tested with $[Ag(OTf)(tht)]$ (tht = tetrahydrothiophene). Remarkably, the 1:2 reaction led to the formation of an even higher nuclearity complex $[Ag_{26}Au_{20}(C\equiv CPh)_{34}(OTf)_{12}(PPh_3)_6(tht)_2]$ (2). The X-ray structure, (Figure 2) can be described as a dimer of honeycomb units connected by a bridging $Ag(\mu-tht)_2Ag$ group. The central core of three hexagonal prisms remains unchanged, and the new linking group has been added to one of the terminal $Au(C\equiv CPh)PPh_3$ fragments.

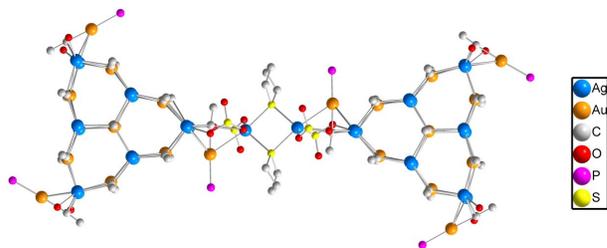


Figure 2.

The reaction between $[Au(C\equiv CPh)PPh_3]$ and $[Ag(OTf)]$ was also done in the presence of pyridine, which, unlike tht, does not usually act as bridging ligand. The product of this reaction is the

new aggregate, $[\text{Ag}_{14}\text{Au}_{10}(\text{C}\equiv\text{CPh})_{17}(\text{OTf})_6(\text{PPh}_3)_3(\text{py})_4]\text{OTf}$ (**3**) whose X-ray structure shows a central core that again remains unchanged. The new $[\text{Ag}(\text{py})_2]$ moieties are coordinated through $\text{Au}\cdots\text{Ag}$ interactions and to the acetylene ligands of the $\text{Au}(\text{C}\equiv\text{CPh})\text{PPh}_3$ fragments located around the heterometallic core.

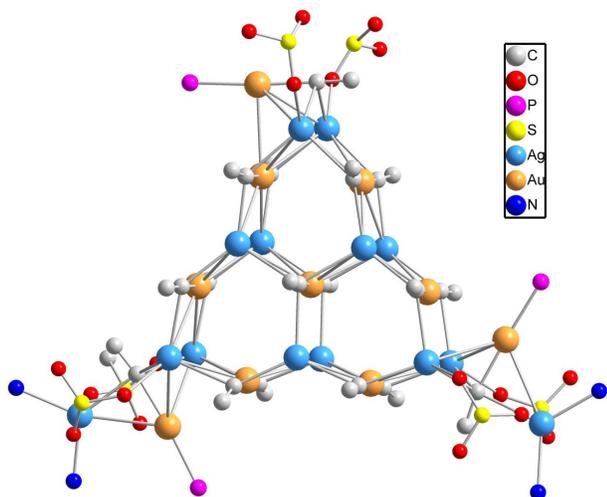
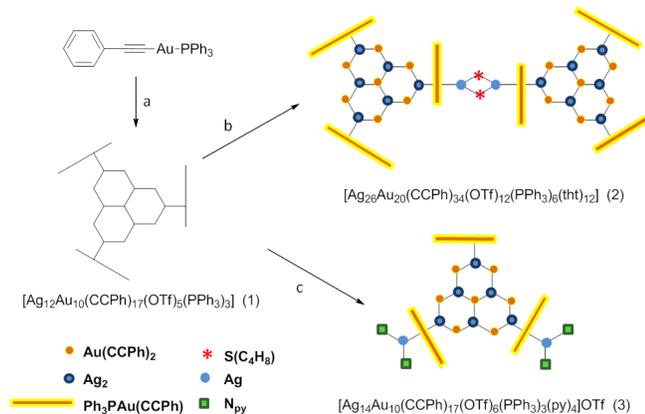


Figure 3.

Following structural elucidation of complexes **1-3**, their syntheses were optimized, as summarized in Scheme 1 (see experimental section included in the supporting information for full synthetic details and spectroscopic data, Figures S1-S15).



Scheme 1.

Interestingly, the hexagonal arrangement of the metal centers for the three derivatives is also reproduced macroscopically, as shown by scanning electron microscopy (see supporting information for micrographs of **1-3** are in the, Figures S16-S21).

The electronic absorption spectra for complexes **1-3** in dichloromethane show intense absorption bands at ca. 220-270 nm and low-energy shoulders tailing to ca. 450 nm (see Table S1 in the supporting information). The high-energy bands below 270 nm are typical for phosphine and alkynyl ligands and are assigned as IL ($\pi \rightarrow \pi^*$) transitions.^[10] The absorptions centered at ~300 nm can be assigned to electronic transitions from the σ ($\text{Au}-\text{P}$) to empty antibonding aryl π^* orbitals. The tails extending down to 450 nm, are not exhibited by the homonuclear starting complexes $[\text{Au}(\text{C}\equiv\text{CPh})\text{PPh}_3]$ or $[\text{Au}(\text{C}\equiv\text{CPh})_2]$, and may arise from cluster centered (Au_xAg_y) transitions or from the $\text{Ag}-\pi$ -(alkynyl) core.¹¹

All compounds exhibit strong luminescence in the solid state and in solution, at both 298 K and 77 K (see Tables S2-S3 and Figures S22-S24 in the supporting information). Upon excitation at $\lambda_{\text{ex}} > 300$ nm, the emission spectra of **1-3** show a band at ≈ 570 nm, red-shifted compared to that of the starting material $[\text{Au}(\text{C}\equiv\text{CPh})\text{PPh}_3]$. The origin of this emission can be assigned as a mixture of MLCT ($\text{Au}_x\text{Ag}_y \rightarrow \text{C}\equiv\text{CPh}$) transitions and metal cluster centered transitions in the heterometallic core.^[12] Although the different nuclearities of the metal cores of **1-3** do not affect the emission, similar excited states in solid and in solution indicate the strong coordination of the metallic core to the alkynyl unit. In glass solution, dual emission is observed for compounds **1** and **3**. In addition to the transitions already described, a structured band appears at ca. 450 nm, likely to originate from IL [$\pi \rightarrow \pi^*$ $\text{C}\equiv\text{CPh}$ and/or phosphine] transitions.

The generally low solubility of metalloligands has been one of the greatest difficulties in self-assembly reactions. Because of this, as well as reasons of reducing environmental contamination,^[8] we carried out preliminary studies using solventless ball-milling synthetic techniques.

Reactions to obtain **1** and **2** were carried out in a shaker mill where $[\text{Au}(\text{C}\equiv\text{CPh})\text{PPh}_3]$ was combined with $[\text{Ag}(\text{OTf})]$ or $[\text{Ag}(\text{OTf})(\text{tht})]$. The colors of the mixtures changed as the grinding took place, from the pale yellow of the starting materials to the characteristic bright yellow of the reaction products. In addition, when the reaction mixtures were placed under UV light, the emission changed from blue, due to the starting material $[\text{Au}(\text{C}\equiv\text{CPh})\text{PPh}_3]$, to orange due to **1** and **2** (pictures taken during solvent-less synthesis of **2**, under both visible and UV-light, can be seen in supporting information, Figure S25).

Reactions were complete after 70 (**1**) or 45 min (**2**) milling. Spectroscopic characterization of the samples by IR, luminescence and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies showed similar results to those obtained in the solvent-based synthesis. It is notable that dimer **2** forms more quickly than complex **1**, suggesting a possible role of the tht as a solvent during the reaction. The presence of small amounts of 'internal solvent' in starting materials, such as coordinated or cocrystallised water, has previously been shown to have an accelerating effect of mechanochemical formation of metal complexes.^[8f]

In conclusion, it is noted that i) unusually large, luminescent, heteronuclear alkynyl clusters with different nuclearities can be prepared through the addition of different donor ligands, ii) the metal cores of the new derivatives adopt a honeycomb structure both at micro- and macroscopic level, and iii) the compounds can be prepared using mechanochemistry as well as solvent-based methods.

Experimental details of this work can be found in the Supporting Information.

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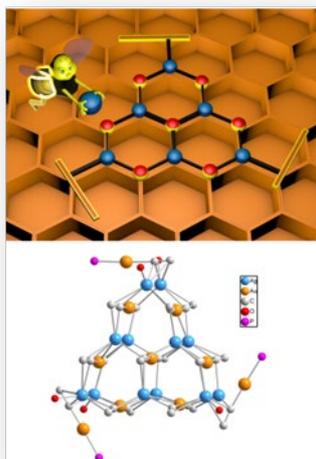
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Luminescent honeycombs

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High nuclearity heterometallic clusters have been synthesized from the metalloligand unit $[\text{Au}(\text{C}\equiv\text{CPh})\text{PPh}_3]$, using both standard solvent-based and solvent-free reactions. The latter are applied for the first time in gold cluster synthesis. The aggregates are stabilized only by acetylide-metal or metal-metal interactions and their nuclearity is controlled through the addition of different donor ligands. As well as their interesting structures, strong luminescence is observed.