Supramolecular Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201603688
Internationale Ausgabe: DOI: 10.1002/anie.201603688

Template Synthesis, Metalation, and Self-Assembly of Protic Gold(I)/(NHC)$_2$ Tectons Driven by Metallophilic Interactions

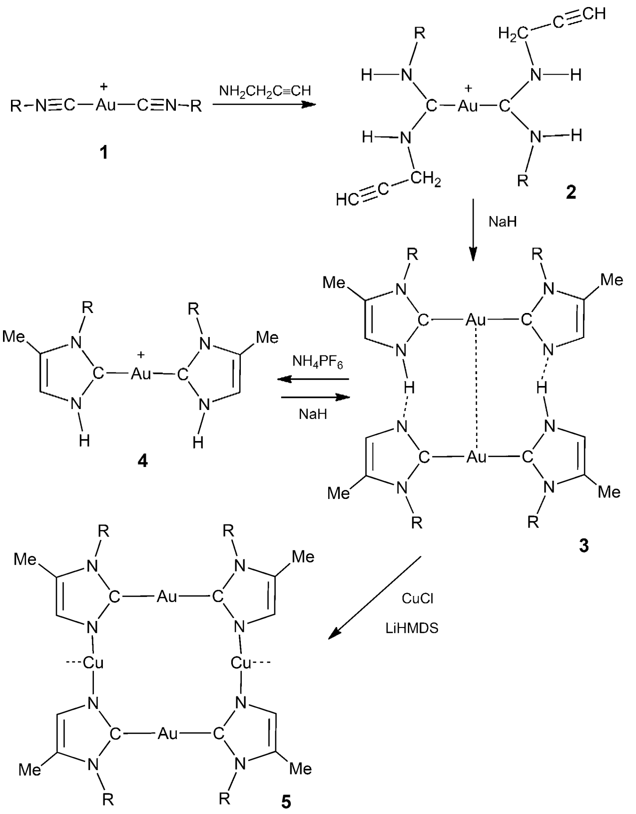
Javier Ruiz, Lucía García, Daniel Sol, and Marilín Vivanco*

Abstract: *A new protocol for the synthesis of protic bis(N-heterocyclic carbene) complexes of* Au^I *by a stepwise metal-controlled coupling of isocyanide and propargylamine is described. They are used as tectons for the construction of supramolecular architectures through metalation and self-assembly. Notably a unique polymeric chain of* Cu^I *with alternate* Au^I*/bis(imidazolate) bridging scaffolds and strong unsupported* Cu^I*–*Cu^I *interactions has been generated, as well as a 28-metal-atoms cluster containing a nanopiece of* Cu_2O *trapped by peripheral* Au^I*/bis(imidazolate) moieties.*

The last two decades have witnessed tremendous development in the chemistry of N-heterocyclic carbenes (NHCs) and their transition-metal complexes,[1] in part owing to the fundamental interest of finding stable molecules containing divalent carbon centers, but especially by the important applications they show in areas such as homogeneous catalysis,[2] medicine,[3] and materials science,[4] and is currently one of the most active fields of research in chemistry.[5] Among NHC complexes, those containing an NH moiety (so called protic NHCs or PNHCs) have been little studied, although they offer additional reactivity patterns such as easy post-functionalization, formation of hydrogen bonds for supramolecular assembly, and substrate recognition in cooperative catalysis.[6] In the specific case of gold, complexes of formula $[Au(NHC)_2]^+$ are attracting increasing interest[7,8] because of their applications as anticancer agents,[3,9] liquid crystals,[10] and luminescent materials,[11] with the additional possibility of exploiting intermolecular aurophilic interactions to build up more complex supramolecular structures. In this context here we describe a new experimental approach for the synthesis of homoleptic gold(I) PNC complexes involving metal-assisted double-coupling of isocyanide and propargylamine, and their use as robust building blocks for the construction of unique supramolecular architectures through metalation and subsequent self-assembly driven by metallophilic interactions. Remarkably, a linear infinite chain of copper(I) ions with alternate gold(I)/bis(imidazolate) bridging scaffolds and unsupported cuprophilic interactions has been generated, as well as a 28-metal-atom cluster containing a nanopiece of Cu_2O trapped by peripheral gold(I)/bis(imidazolate) tectons.

Reaction of $[Au(CNxylyl)_2]PF_6$ ([**1**]PF_6) with two equivalents of propargylamine at room temperature afforded the bis(diaminocarbene)gold(I) complex **2** (Scheme 1), which resulted from nucleophilic addition of the amine to both coordinated isocyanide ligands.[12] The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **2** at room temperature are rather complex, and show up to eight groups of signals for the xylyl and propargyl substituents, very likely because of the formation of various conformers arising from restricted rotation around the two $C_{carbene}$−N bonds in each diaminocarbene ligand.

Colorless crystals of [**2**]PF_6 suitable for an X-ray diffraction study were grown by slow diffusion of diethyl ether and *n*-hexane into a dichloromethane solution of the compound.[13] Rather surprisingly, only one isomer was present in the crystals (up to seven different crystals were used and they all shown the same structure), and corresponds to that having the two N−H protons located at inner positions in both carbene ligands (Figure 1). The PF_6^- anions are involved in N−H⋯F charge-assisted hydrogen-bonding with the four



Scheme 1. Stepwise generation of protic gold(I)/(NHC)$_2$ complexes by the coupling of propargylamine and isocyanide, and subsequent metalation with copper(I) to afford **5**. R = xylyl.

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[*] Prof. J. Ruiz, Dr. L. García, D. Sol, Dr. M. Vivanco
Departamento de Química Orgánica e Inorgánica
Universidad de Oviedo, Facultad de Química, 33006 Oviedo (Spain)
E-mail: jruiz@uniovi.es

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201603688.

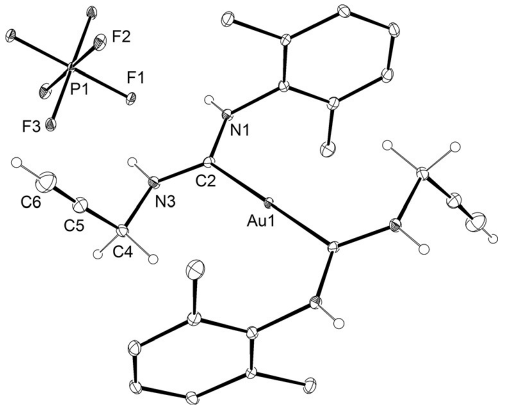

Figure 1. Crystal structure of [**2**]PF_6 shown with thermal ellipsoids set at 50% probability. Hydrogen atoms of the xylyl substituents are omitted for clarity. Selected bond lengths [Å]: C2–N1 1.326(4), C2–N3 1.330(4), C2–Au1 2.036(3).

N−H hydrogen atoms of **2** (H···F distances ranging from 2.20 to 2.46 Å), thus giving a self-assembled infinite chain, and it might be the driving force which induces the formation of just one conformer of **2** in the solid state. This single conformer is maintained on dissolving crystals of [**2**]PF_6 at low temperature (203 K), as deduced from the ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra which reveal the presence of just one set of signals for the xylyl and propargyl groups and a sole singlet signal at $\delta = 208.2$ ppm for the carbene carbon atom. When the temperature of the solution was raised to 293 K, the mixture of different conformers was readily generated, and was once again totally transformed into the preferred conformer upon crystallization.

The reaction of [**2**]PF_6 with NaH in CH_2Cl_2 led to the formation of the neutral complex **3**, whose structure was confirmed by single-crystal X-ray diffraction analysis. As shown in Scheme 1 and Figure 2, each gold atom is surrounded by two imidazole-2-ylidene ligands, one of them present in its deprotonated form. This arrangement allows the formation of a self-assembled dinuclear aggregate with both equivalent molecular units being connected to each other through two N−H···N hydrogen bonds and a gold–gold interaction. The complex **3** results from two intramolecular cyclization processes of the diaminocarbene ligands involving base-promoted hydroamination of the terminal alkynes followed by 1,3 H-shifts.[14,15] The ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra of **3** showed only one set of signals for the imidazole groups, thus proving the chemical equivalence of the four imidazole moieties in the dimeric structure of **3**. In the $^{13}C\{^1H\}$ NMR spectrum the carbene carbon atoms appear in the expected low-field region (singlet at $\delta = 184.4$ ppm), whereas in the proton spectrum the newly formed methyl groups give a singlet at $\delta = 1.79$ ppm. The two hydrogen atoms involved in the N−H···N hydrogen bonds were not observed, most probably because of the existence of a dynamic translocation process of both protons between the nitrogen atoms, thus rendering the four imidazole moieties equivalent on the NMR time scale. This process could not be stopped even by performing the NMR experiments at low temperature. In the crystal structure of **3** a short Au···Au contact of 3.219 Å is observed. The high steric hindrance of the peripheral xylyl groups avoid the formation of extended intermolecular aurophilic interactions within the crystal, as frequently found in other gold(I)/NHC complexes.[7] The two C-Au-C skeletons are almost linear [174.6(7) and 174.5(7)°], but twisted from each other around the Au–Au axis to accommodate the N−H···N hydrogen bonds in the appropriate geometry (C-Au-Au-C torsion angle ca. 65°). The values of the N−H···N and N···N distances are around 1.80 Å and 2.68 Å, respectively, with an average N−H···N bond angle near to 170°, thus showing the strong nature of the hydrogen-bonding pattern.[16]

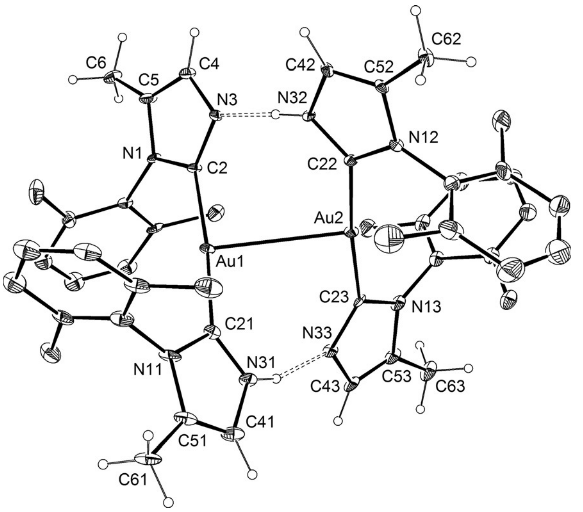

Figure 2. Crystal structure of **3** shown with thermal ellipsoids set at 50% probability. Hydrogen atoms of the xylyl substituents are omitted for clarity. Selected bond lengths [Å]: Au1–Au2 3.2190(12), C2–Au1 2.017(16); C21–Au1 1.971(18), C2–N1 1.36(2), C2–N3 1.34(2).

As expected, the reaction of **3** with NH_4PF_6 readily afforded the cationic complex **4**, containing two protic NHC ligands, which on treatment with base regenerates **3** (Scheme 1). This behavior means that the self-assembled dimeric structure of **3** can be reversibly formed by a simple acid/base protocol. In the ^{1}H NMR spectrum of **4** the N−H proton is clearly observed at room temperature ($\delta = 9.99$ ppm), and is in contrast to that occurring with **3**. Apart from this difference, most of the signals in the NMR spectra of **4** are very similar to those of **3**, including that corresponding to the carbene carbon atom ($\delta = 181.9$ ppm), which is only slightly affected by the protonation degree of the imidazole cycle.

Interestingly, the two N−H proton atoms in **3** can be substituted by copper(I) ions giving the neutral heterometallic gold(I)/copper(I) complex **5** (Scheme 1).[17] The reaction proceeds by treatment of **3** with LiHMDS in the presence of CuCl. The observation of a high-field signal at $\delta = 188$ ppm in the $^{13}C\{^1H\}$ NMR spectrum of **5** proves that the bis(carbene) skeleton of the gold(I)/$(NHC)_2$ units is maintained (see the Supporting Information for full spectroscopic characterization). Colorless crystals of **5** suitable for an X-ray study were grown by slow diffusion of *n*-hexane into a solution of the compound in THF. A view of the structure of **5** is present in Figure 3 (top) together with selected bond distances and

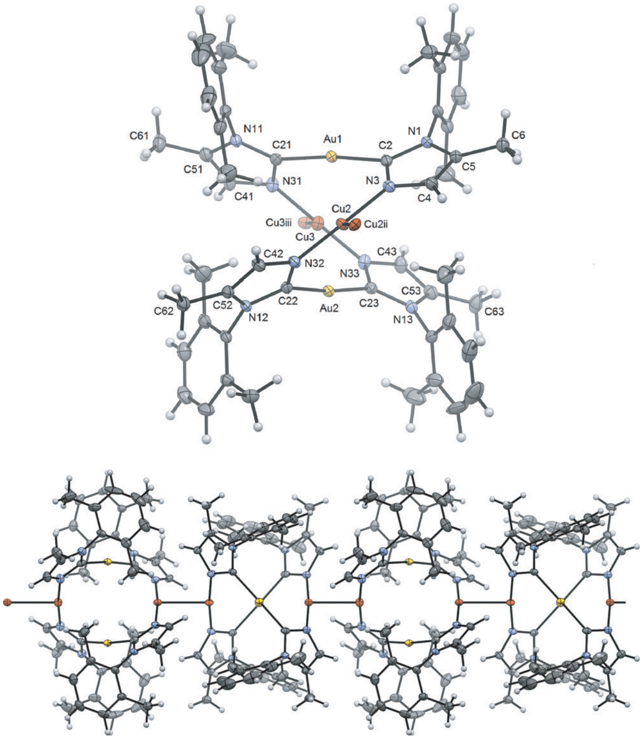

Figure 3. Top: view of the molecular structure of **5**, additionally showing two copper–copper intermolecular contacts. Selected bond lengths [Å] and angles [°]: Au1–C2 2.017(3), Au1–C21 2.021(3), C2–N1 1.372(3), C2–N3 1.339(4), N3–Cu2 1.872(2), N31–Cu3 1.859(2), Cu2–Cu2ii 2.6212(11), Cu3–C3iii 2.590(11); C2-Au1-C21 174.09(11), N3-Cu2-N32 172.91(15), N1-C2-N3 107.6(2). Bottom: crystal structure of **5** showing the one-dimensional self-assembly through cuprophilic interactions. Color code: Au yellow; Cu orange; N blue; C grey.

angles. The new molecule consists of a twisted twelve-membered metallacycle containing two gold and two copper atoms, all featuring almost linear coordination geometry. The four metal atoms within the cycle are coplanar, but lacking intramolecular Cu···Cu (5.072 Å) and Au···Au (4.152 Å) interactions, though the Cu···Au distances (3.267 and 3.287 Å) are close to the sum of the van der waals radii (3.06 Å). The breaking of the Au–Au contact occurs with parallel formation of rather strong Cu–Cu intermolecular bonds (2.590 and 2.621 Å, that is, only slightly longer than those existing in metallic copper, 2.556 Å), thus generating a perfectly linear self-organized infinite chain (Figure 3, bottom) with the copper atoms being located on a crystallographic fourfold inversion axis (−4). This structural feature yields a one-dimensional aggregation of copper atoms connected by alternating cuprophilic interactions and bridging gold(I)/bis(imidazolate) scaffolds, so that **5** can be considered as a sort of molecular wire of copper(I) with alternate disruption of the metal–metal bond. The existence of short copper–copper bonds without reinforcing bridging ligands between the copper atoms must be emphasized. Although a few cases of ligand-unsupported copper(I)–copper(I) contacts have been described,[18] usually leading to two- and three-dimensional networks, to our knowledge the Cu–Cu distances in **5** are the shortest described so far in the literature.

In looking for more complex supramolecular architectures containing gold(I)/bis(imidazolate) tectons, we carried out the reaction of **3** with an excess of CuCl and LiHMDS. Under these reaction conditions **5** was also obtained as the major product but, additionally, a small amount of yellow crystals of a new compound (**6**) suitable for an X-ray study were formed as well. To our surprise the structure of **6** (Figure 4, top) is a cluster of 28 metal atoms (8 Au and 20 Cu) maintaining the gold(I)/bis(imidazolate) moieties, thus proving to be strong and stable scaffolds for the construction of rather sophisticated structures.

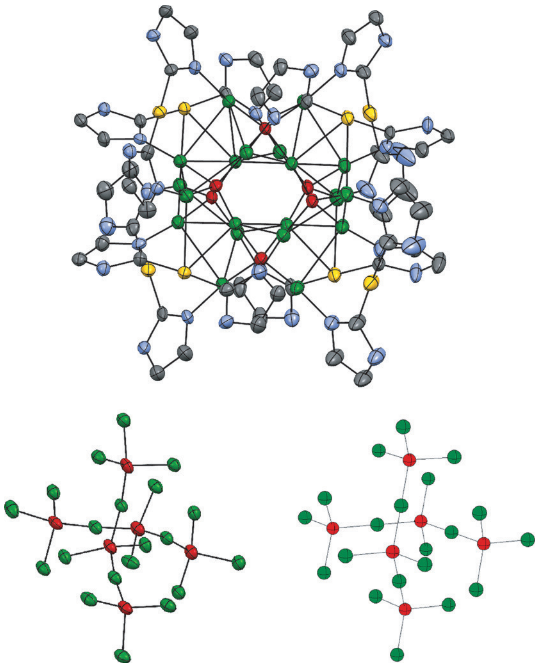

Figure 4. Top: view of the molecular structure of **6**. Xylyl, methyl, and hydrogen substituents of the imidazole cycles are omitted for clarity. Bottom: a view of the $Cu_{20}O_6$ core in the crystal structure of **6** (left) and a similar portion extracted from the cuprite structure (right). Color code: Au yellow; Cu green; O red; N blue; C grey.

The compound **6** can be considered to be formed by four units of **5** which are opened to accommodate six formula units of Cu_2O ($4\times\mathbf{5}+6\times Cu_2O\rightarrow\mathbf{6}$). Very likely, the formation of Cu_2O arises from hydrolysis with traces of water of the tetramer $[CuHMDS]_4$,[19] which was spectroscopically detected in the reaction mixture. In the structure of **6** the six oxygen atoms lead to a distorted octahedron which resembles their disposition in the cuprite structure (Figure 4, bottom).[20] As in bulk Cu_2O the oxygen atoms are surrounded by four copper atoms, but feature a distorted tetrahedral coordination geometry, and the copper atoms are bonded to two oxygen atoms in an almost linear mode. The 24 Cu–O bond distances, ranging from 1.827 to 1.870 Å, are close to those existing in the cuprite structure (1.85 Å), whereas most of the 44 Cu–Cu contacts (ranging from 2.602 to 3.066 Å) are shorter than in cuprite (3.01 Å), and is in accordance with theoretical calculations on Cu_nO_m nanoclusters.[21] Furthermore, there are several peripheral Au···Cu metallophilic contacts (average value 2.93 Å) which stabilize the whole cluster structure. Interestingly, the structure of **6** can be viewed as being formed from a $Cu_{12}O_6$ nanoparticle ("a small piece of Cu_2O") trapped by peripheral units of **5**. Though so far we have not been able to accomplish a selective synthesis of **6**, this result is noteworthy, considering the importance of Cu_2O nanoparticles and clusters in materials science with applications in areas such as battery electrodes,[22] photovoltaic cells,[23] and catalysis,[24] and could stimulate future research aiming to stabilize metal-oxide nanoclusters by using gold(I) imidazolates or other related scaffolds, an attractive synthetic challenge which we will face in the near future in our laboratory.

In summary, we have reported herein an easy reaction pathway to synthesize protic gold(I)/$(NHC)_2$ complexes and its neutral self-assembled dinuclear derivative, by base-promoted double-coupling of isocyanide and propargylamine, simply starting from gold(I)/$(CNR)_2$. We have proved that they behave as robust tectons for the construction of remarkable supramolecular structures on metalation, as shown with the formation of **5** and **6**, containing a copper(I) one-dimensional polymeric chain and a Cu_2O nanocluster, respectively, stabilized by the presence of gold(I) bis(imidazolate) scaffolds. These results are in close connection with applied areas such as molecular wires and metal oxide nanoclusters, thus opening new avenues in the amazing chemistry of NHCs.

Acknowledgments

This work was supported by the Spanisch Ministerio de Economía *y* Competitividad (Projects CTQ2012-32239 and CTQ2015-66959-P). D.S. thanks the Principado de Asturias for a scholarship.

Keywords: copper · gold · heterometallic complexes · N-heterocyclic carbenes · self-assembly

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 8386–8390
Angew. Chem. **2016**, *128*, 8526–8530

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Received: April 15, 2016