Polynuclear Complexes

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A Bis(Diphosphanyl N-Heterocyclic Carbene) Gold Complex: A Synthon for Luminescent Rigid $AuAg_2$ Arrays and Au_5 and Cu_6 Double Arrays

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Dedicated to Professor Todd B. Marder on the occasion of his 60th birthday

Abstract: *A mononuclear bis(NHC)/Au^I (NHC = N-heterocyclic carbene) cationic complex with a rigid bis(phosphane)-functionalized NHC ligand ($PC_{NHC}P$) was used to construct linear Au_3 and Ag_2Au arrays, a Au_5 cluster with two intersecting crosslike Au_3 arrays, and an unprecedented Cu_6 complex with two parallel Cu_3 arrays. The impact of metallophilic interactions on photoluminescence was studied experimentally.*

Numerous spectacular developments in gold chemistry have been driven by rational syntheses based on the isolobal analogy between Au^+ and $[Au\text{-}L]^+$ (L = two-electron donor ligand) with H^+ and the carbocations R^+, respectively,[1] and by a fast growing range of applications.[2] These achievements have triggered structural and theoretical studies, in particular, on the propensity of gold(I) centers to participate in attractive d^{10}–d^{10} interactions.[3] Metallophilic interactions are crucial in mediating metal cooperativity and reactivity, and have also been broadly correlated to photoemission properties.[3a,4] Additional key factors for reactivity and photophysical properties include metal core nuclearity and structure, metal coordination numbers, and ligand rigidity and donor properties.[5] Supporting short-bite-type ligands, such as $Ph_2PCH_2PPh_2$, have thus become ubiquitous in the study of d^{10}–d^{10} interactions.[4d,6] Within the exponential development of N-heterocyclic carbenes (NHCs), which have a major impact in gold chemistry[2c,7] and photophysics,[4b] functionalized NHC hybrid ligands, including phosphane-functionalized NHCs, offer novel opportunities for the fine-tuning of properties.[8] Polynuclear complexes with isoelectronic copper(I), featuring halide bridges, in particular iodides, and phosphane and/or NHC donor environments are emerging as promising, inexpensive triplet emitters in optoelectronics.[9]

To further study the interfaces between metallophilicity, short-bite ligands, and P-functionalized NHC donors, we have introduced the heterofunctional ligand $PC_{NHC}P$ having a double short-bite architecture (Scheme 1), which can stabilize linear M_3 arrays (M = Au, Ag, Cu, Pd) with short intermetallic distances.[8d,j] The inherent rigidity of $PC_{NHC}P$ and the N–P bond facilitate direct electronic communication between the donors. We reasoned that $PC_{NHC}P$ could serve as a wide-scope platform for ordered homo- and heteronuclear arrays if selective metal complexation methodology could be developed. Herein, we describe a mononuclear homoleptic bis(NHC)/Au^I complex which fulfills this criteria, and demonstrate its use to access homo- and heteronuclear, linear one-dimensional arrays, and either perpendicular or parallel two-dimensional double arrays. The emergence of d^{10}–d^{10} interactions with diverse topology[3a,b,4d,10] stimulated preliminary luminescence studies.

Au1 was prepared by the reaction of the imidazolium salt PCHP with 1 equivalent of $[Au\{N(SiMe_3)_2\}(PC_{NHC}P)]$ (Scheme 1). The latter was formed cleanly from $[Au\{N(SiMe_3)_2\}(PPh_3)]$ and $PC_{NHC}P$ (see the Supporting Information). Even though it is isolable, it was conveniently reacted in situ with PCHP to yield **Au1**. Spectroscopic data (see the Supporting Information) support uncoordinated $PtBu_2$ and gold-coordinated C_{NHC} donors. Interestingly, this is the first time that $[Au\{N(SiMe_3)_2\}(PPh_3)]$ has been used as a synthon for the nonsynchronous coordination of two NHC ligands by sequential reactions (substitution, aminolysis). The irreversible formation of Au–C_{NHC} is crucial for the synthesis of $[Au\{N(SiMe_3)_2\}(PC_{NHC}P)]$ and **Au1**. The nature of the gold(I) precursors has a major impact on the reaction products.[8d,e] The scope of the present strategy is extended to other nonsymmetrical NHC/Au complexes (e.g. Au1′ with $PC_{NHC}P$ and $^{Dipp}C_{NHC}P$, given in the Supporting Information).

The structure of **Au1** (Figure 1, left) features a linear homoleptic gold center with the two P-κ^1C_{NHC}-P ligands, and the planes of the NHC heterocycles are staggered. The metalloligand nature of **Au1** suggested its use as precursor to homo- or heteronuclear complexes by P-coordination. Initial proof of concept was obtained by accessing the homotrinuclear **Au3**[8d] from the reaction of 2 equivalents of $[Au(tht)_2](CF_3SO_3)$ with **Au1** (Scheme 1). When 4 equivalents of [AuCl(tht)] were used instead, the unique pentanu-

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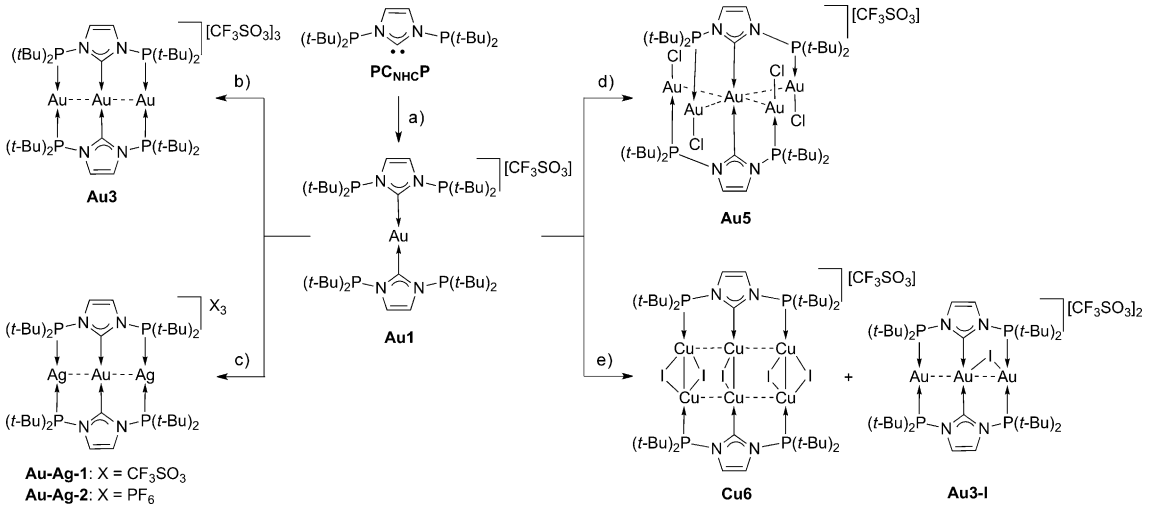


Scheme 1. Reagents and conditions: a) 1 equiv [Au{N(SiMe$_3$)$_2$}(PPh$_3$)] and 1 equiv PCHP, THF, 2 d, RT; b) 2 equiv [Au(tht)$_2$](CF$_3$SO$_3$), THF, 3 h, RT; c) 2 equiv Ag(O$_3$SCF$_3$) or 3 equiv AgPF$_6$, MeCN, 2 h, RT; d) 4 equiv [AuCl(tht)], CH$_2$Cl$_2$, 3 h, RT; e) 2 equiv CuI, THF, 12 h, RT. THF = tetrahydrofuran, tht = tetrahydrothiophene.

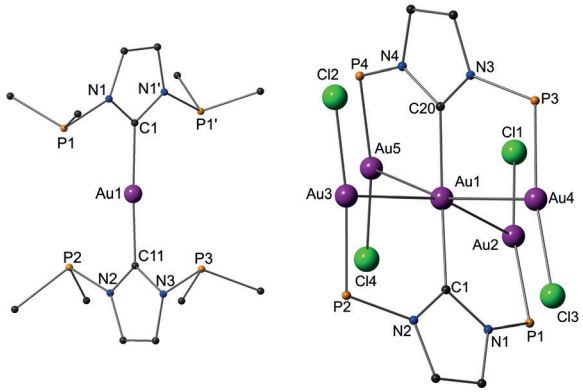


Figure 1. Structure of the cations in **Au1** (left) and **Au5** (right). H atoms, the *t*Bu methyl groups in **Au1** and the *t*Bu groups in **Au5** are omitted for clarity. Metrical data are included in the Supporting Information.

clear **Au5** (Figure 1, right) was isolated and it displays a rare perpendicular, crosslike arrangement of two Au$_3$ arrays sharing one bis(NHC) hexacoordinated gold center as a common intersection. Each chain (Au2-Au1-Au3 and Au4-Au1-Au5) is spanned by one μ_3-PC$_{NHC}$P-($\kappa P,\kappa C,\kappa P$). The five gold atoms are almost coplanar (max. deviation 0.446 Å for Au2), and aurophilic interactions are implied between each of the peripheral and the central gold atoms (average Au–Au distance 3.1271 Å),[3,11] but not between the peripheral gold atoms (average 4.416 Å). The planes of the two NHC heterocycles are at 88.08°. Although substructures with five gold atoms have been observed in higher nuclearity gold clusters or in pentanuclear complexes, they show severe pyramidalization, unlike the structure of **Au5**.[2a,12]

The synthetic scope of **Au1** was extended towards heterometallics by reacting it with 2 equivalents of [AgO$_3$SCF$_3$] in MeCN, thus affording **Au-Ag-1** (Scheme 1). The two ^{31}P{^{1}H} NMR doublets centered at $\delta = 118.3$ ppm ($^1J_{P\text{-}109Ag} = 527.3$ Hz, $^1J_{P\text{-}107Ag} = 457.5$ Hz) support P*t*Bu$_2$ coordination to silver. Its solid-state structure confirmed the silver inclusion in the P-pockets of **Au1** (see Figure S1 in the Supporting Information). Satisfactory refinement of the structure was hampered by persistent disorder in the P(*t*Bu)$_2$ groups and one triflate. With AgPF$_6$ as the silver source, **Au-Ag-2**·2 MeCN was obtained with a cation, analogous to that in **Au-Ag-1** (NMR evidence, see the Supporting Information), containing a centrosymmetric, linear Ag-Au-Ag array with d^{10}–d^{10} interactions[3b,c] (Ag–Au distance 2.8039(7) Å) (Figure 2, left). One MeCN is coordinated to each of the outer silver atoms, thus resulting in deviation of the P1-Ag1-P2 angle from linearity (152.70(9)°).

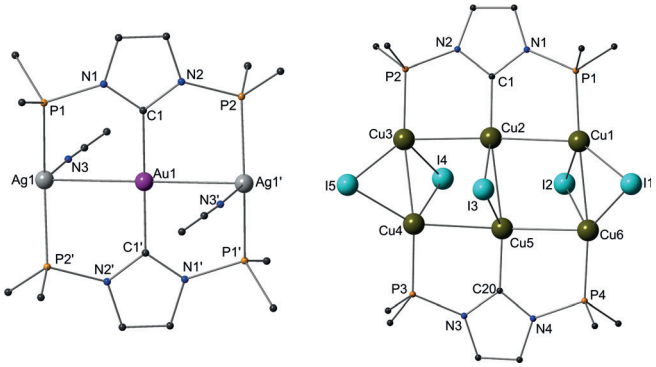
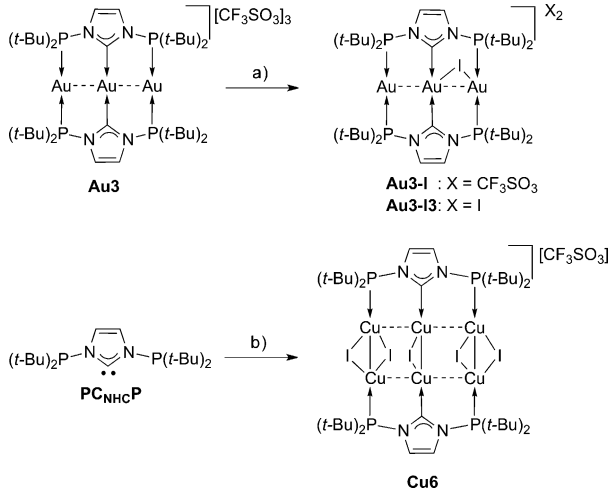


Figure 2. Structure of the cations of **Au-Ag-2**·2 MeCN (left) and **Cu6** (right). H atoms and the *t*Bu groups are omitted for clarity. Metrical data included in the Supporting Information.

With the initial objective to access Au-Cu complexes, **Au1** was treated with CuI in 1:6 ratio in THF, but an unusual transmetallation reaction from gold(I) to copper(I) occurred, and thus led to a mixture of two complexes: 1) the novel hexanuclear copper(I) complex **Cu6** with two parallel homonuclear Cu$_3$ arrays bridged by five iodide ligands; 2) the trinuclear gold(I) iodide complex **Au3-I** with two uncoordi-

nated triflate anions (Scheme 1). In alternative, optimized procedures, a yellow powder of pure **Au3-I** was obtained by adding 1 equivalent of NaI to a solution of **Au3** in MeCN (Scheme 2). The use of 3 equivalents of NaI resulted in



Scheme 2. Reagents and conditions: a) 1 or 3 equiv NaI in MeCN, 0.5 h, RT; b) 1 equiv $[CuO_3SCF_3]_2$·toluene and 5 equiv CuI in THF, 2 d, RT.

complete replacement of the triflates, thus giving **Au3-I3** as yellow microcrystals. Similarly, an alternative, optimized synthesis of **Cu6** involved reaction of $PC_{NHC}P$ with one equivalent of $[Cu(O_3SCF_3)]_2$·toluene and 5 equivalents of CuI in THF for two days (Scheme 2). The structurally similar cations in **Au3-I** and **Au3-I3** (see Figures S2 and S3) show a noticeable difference in the position of the nonsymmetrically bridging iodide (see the Supporting Information).

The structure of **Cu6** (Figure 2, right) comprises two parallel Cu_3 arrays (max. deviation from planarity of 0.265 Å for Cu5), each spanned by one μ_3-$PC_{NHC}P$,κ*P*,κ*C*,κ*P* ligand. This arrangement results in two types of Cu–Cu separations, that is, between opposing copper atoms of different arrays and between adjacent copper atoms of the same array, all falling within the range 2.669(2)–2.872(2) Å, and consistent with d^{10}–d^{10} interactions. Five iodides are bridging six copper atoms in an μ_2 fashion with Cu–I distances in the range of 2.533(2)–2.680(2) Å, which is comparable to typical bond lengths in copper clusters having doubly-bridging iodides (see the Supporting Information).[9c] To the best of our knowledge, the Cu_6 arrangement in **Cu6** is unprecedented and presumably originates from the unique donor characteristics and rigidity of the $PC_{NHC}P$ ligand.

The current interest in the photophysics of polynuclear coinage metal complexes and the novelty of the structures observed here prompted us to study the luminescence of the new complexes in solution and as powders (see Tables S1 and S2 and Figures S4–S6). The absorption spectra for dilute ($c = 1.0\times10^{-5}$ M) solutions of **Au1** in CH_2Cl_2 and **Au-Ag-2** in MeCN display an intense ($\varepsilon = 1.9$–0.6×10^4 M^{-1} cm^{-1}) absorption band in the UV region, and is typical of either phosphine/Au (or Ag) or NHC/Au (or Ag) complexes,[13] whereas solutions of **Au5** exhibited two intense bands with $\varepsilon = 1.5\times10^4$ and 1.6×10^4 M^{-1} cm^{-1} at lower wavelengths ($\lambda_{abs} = 311$ and 344 nm, respectively). The former is attributable to the spin and optically allowed singlet manifold metal-metal-to-ligand charge transfer, ^{1}MMLCT, and the latter to a ^{1}[5dσ*→6pσ] transition with strong metal centered (^{1}MC) character, respectively.[13a,14] In CH_2Cl_2, **Cu6** displayed a featureless absorption spectrum which can be attributed to a convolution of singlet-manifold cluster centered (^{1}CC) and metal-to-ligand charge-transfer transitions (^{1}MLCT; see Table S2 and Figure S4).[5c,d,15]

Upon photoexcitation at $\lambda = 300$–380 nm, **Au-Ag-2** in MeCN displayed an irradiation time-dependent emission spectrum, whose intensity decreases with increasing irradiation time, thus indicating photodecomposition of the complex. In contrast, samples of **Au1** and **Au5** in CH_2Cl_2 were photostable and displayed broad, featureless, weak emissions centered at $\lambda = 553$ nm for **Au1**, and, remarkably, at $\lambda = 760$ nm (i.e. NIR region) for **Au5** (Figure 3). Such radiative

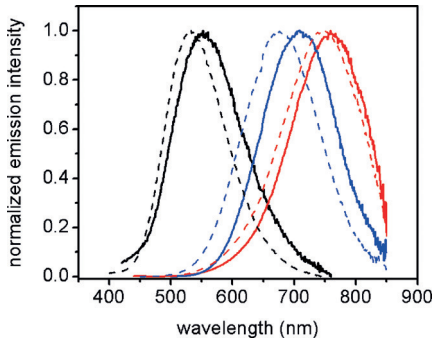


Figure 3. Normalized emission spectra of complex **Au1** (black), **Au5** (red), and **Cu6** (blue) in CH_2Cl_2 at a concentration of 1×10^{-5} M (solid traces) and in the solid state as neat powder (dashed traces) at room temperature. Samples were excited at $\lambda_{exc} = 300$ nm for **Au1** and **Au5**, and $\lambda_{exc} = 350$ nm for **Cu6**.

processes can be attributed to an emitting excited state with triplet ^{3}MLCT and ^{3}MMLCT character for **Au1** and **Au5,** respectively. Such an assignment is also in agreement with the observed long excited-state lifetimes (see Table S1).[14d] Lastly, **Cu6** displayed a moderate emission (photoluminescence quantum yield, PLQY = 6 %) centered at $\lambda = 710$ nm, and is tentatively attributed to an excited state with ^{3}CC character on the basis of similarities with the $[CuIpy]_4$ cubane-like complexes.[5c,d,15]

In the solid state, **Au-Ag-2** remained photo-unstable but a sizeable increase of the PLQY was interestingly observed for **Au1** and **Cu6**, and reached values as high as 31 and 29 %, respectively. This increase was accompanied by a slight hypsochromic shift of the emission maximum and an elongation of the emitting excited-state lifetime (Figure 3 and see Table S3), which is attributable to a rigidochromic effect. Importantly, **Au5** remains emissive in the NIR region, as observed in solution ($\lambda_{em,}$ maximum at 749 nm, PLQY of 6 %). Halide-quenching of luminescence occurred in **Au3-I** and **Au3-I3**, despite the Au–Au distances being shorter than in the strongly luminescent **Au3**.[14c,d,16]

In conclusion, accessing **Au1** by a rational substitution aminolysis route from $[Au\{N(SiMe_3)_2\}(PPh_3)]$ opened the way to novel homo- or hetero-trinuclear and homo-polynuclear complexes displaying metallophilic interactions. Besides their unprecedented structures, the latter serve as probes to test the structure–photophysics relationships towards the rational design of functional molecules.

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