Assembly of gold rings and chains with pyridyl carboxylate as directional spacer†

Peili Teo, L. L. Koh and T. S. Andy Hor*

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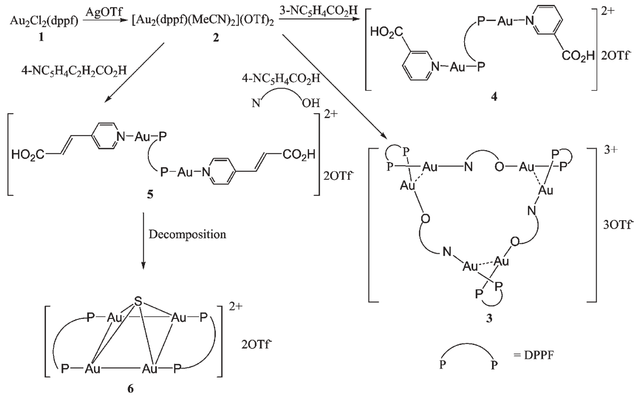
The combinative use of Au(I), a skeletally flexible diphosphine and a bifunctional spacer of pyridyl carboxylate with tunable directional and donor properties has resulted in a series of structurally distinctive ensembles and Au_2 metalloligands with O-donicity.

Self assemblies of Au(I) phosphine complexes have attracted considerable interest in view of their intriguing bonding, structural,[1] electronic[2] and luminescent[3] characteristics. Further development of these complexes as advanced or functional materials will hinge on the ability to design systems and syntheses that provide a mechanism to control the structure-related and other materials properties. Our approach is to use co-ligands that are bifunctional and directional. The former leads to materials with the needed hybrid and tunable characters whereas the latter helps in atomic alignment and nuclearity control. This approach is illustrated in the use of pyridyl carboxylates[5] to support the assembly of Au(I) phosphines. We present herein the isolation of a metalloligand that can be used as precursor for other Au-based designs as well as examples of oligomeric and polymeric complexes that have been isolated using this approach.

A schematic representation of all the key preparations is given in Scheme 1. Reaction of $Au_2Cl_2(dppf)$, **1**, with AgOTf in MeCN gives $[Au_2(dppf)(MeCN)_2](OTf)_2$, **2**, which, upon removal of AgCl, further reacts *in situ* with isonicH (isonicH = $NC_5H_4CO_2H$) to give a yellow powder of $[Au_6(isonic)_3(dppf)_3](OTf)_3$, **3**. ^1H NMR and ESI-MS data {*m*/*z* 1070.0 assignable to $[Au(isonic)(dppf)]^+$ and 1946.7 to $[Au_3(isonic)_2(dppf)_3]^+$} support isonic and phosphine coordination.



Scheme 1 A schematic representations of the formation of **3–6** from **1** through **2**.

X-Ray single-crystal crystallographic analysis revealed a novel hexagold ring (Fig. 1).‡ This tricationic chiral complex is assembled by three pairs of Au_2 interconnected by three O,N-donating isonic spacers without Au–Au interaction. Within each pair of Au atoms, they are bridged by dppf and supplemented by aurophilic interactions (Au···Au 3.007(1) Å). An alternative view is a triangular arrangement of three Au_2 units. Additional H-bonding interactions between the triflate and the C_5 ring (F···H 2.488 Å) are evident.

Self-assembly of the triangular topology is directed by the conformational and geometrical properties of the ligands and metal. The flexible $C_5 \cdots C_5$ twist of dppf permits the bulky diphosphine to juxtapose the two Au(I) in close proximity to support the inherent aurophilicity in conjunction with the T-shape geometry of Au(I) (d^{10}). Very significantly, the torsional twist of the ferrocenyl moiety moves the two neighbouring P–Au–L (L = O and N) axes to bisect at *ca.* 60° to meet the angular demand of an internal angle of a triangle. The three Au–Au axes are projected out of the triangular plane, thus allowing the three isonic ligands to form the cascading edges of the triangle.

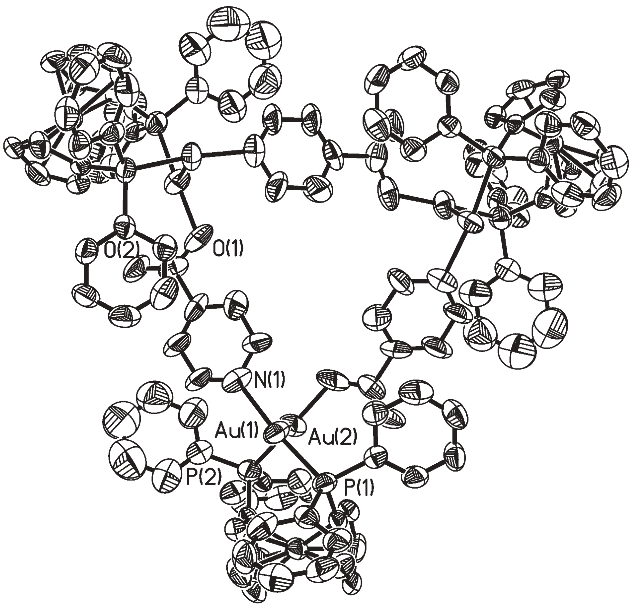


Fig. 1 ORTEP plot of **3** showing a triangular framework of three Au_2 moieties, (hydrogen atoms omitted for clarity).

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543. E-mail: andyhor@nus.edu.sg; peiliteo@nus.edu.sg; Fax: 65 65162663; Tel: 65 65162679

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The directional property of the spacer, or more precisely, the relative positions of the donors, is a major force in dictating the outcome of the assembly. This is further evident when isonicotinate (isonic) is replaced by nicotinate, whereby the carboxyl group is angular (*i.e.* 3-position) instead of *trans* (*i.e.* 4-position) to the pyridyl N. A ring-structure would not be expected since the donors would no longer be favourably directed at the corners of any feasible polygons. The product (**4**) isolated from a mixture of **2** with nicotinic acid (NicH, $NC_5H_4CO_2H$) gives NMR data that suggest phosphine and pyridyl coordination but no definitive structural information. The ESI-MS spectrum shows a fragment peak of $[Au_2(Nic)(dppf)]^+$ at *m*/*z* 1072.4, among others. Single-crystal X-ray crystallographic analysis‡ reveals a digold core bridged by dppf and terminated by N-bonded nicotinic acid $[Au_2(dppf)(NicH)_2]^{2+}$ (Fig. 2). For the two Au(I) to form a dication, the carboxylate ends need to be electronically neutral *i.e.* protonated. Another difference from **3** is that the dppf moves the two gold atoms to *anti* positions, thus precluding any intramolecular aurophilic interactions. Instead, there is a range of weak intermolecular and inter-ionic interactions, *viz.* between the carboxylic acid proton and the S and O of triflate, and between carboxylic O and the metal [Au···O(Nic) ~3.404 Å] and phenyl proton (of dppf). These secondary forces help to align the Au_2 units in a polymer-like chain in the solid-state network. A key feature of the difunctional spacer here is that the pyridyl end participates in covalent intramolecular bonding while the carboxylic acid end engages in electrostatic intermolecular interactions. These complementary roles are not found in other systems[4] and resulted in a unique form of assembly that is not seen elsewhere.

In solution, the secondary intermolecular interactions are likely replaced by solvent interactions, which is consistent with ESI analysis. Complex **4** therefore is a potential O-donating metalloligand of Au_2. Work is ongoing to construct new hetero-trimetallic $\{Au_2M\}$ assemblies from **4**. Earlier results from our laboratory suggested that a suitable oxophilic metal for such attachment could be Ag^+.[4c]

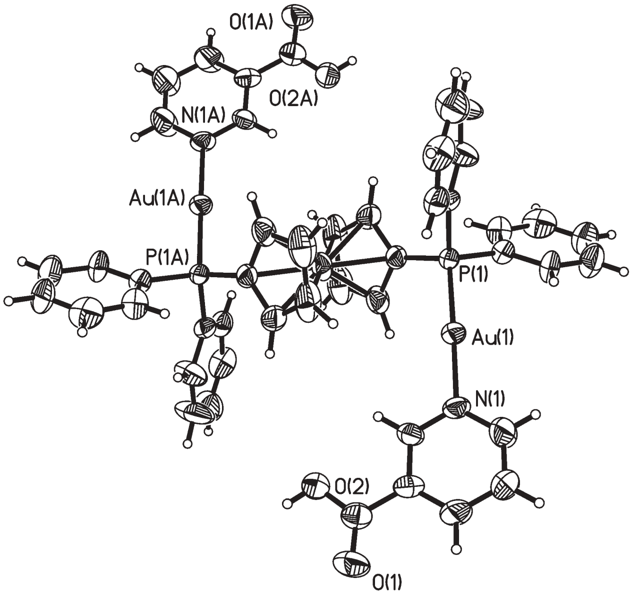

Fig. 2 ORTEP diagram of **4** showing only the Au_2 cation, with an inversion centre at Fe.

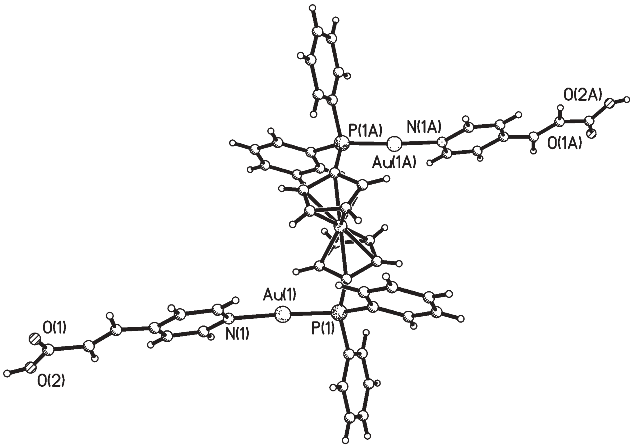

Fig. 3 Ball-and-stick model of **5**, showing one dication, with an inversion centre at Fe.

Formation of **3** and **4** is governed by the different directional properties of the spacers. Can one keep this (directional) characteristic unchanged but introduce additional spacer flexibility through backbone elongation? How would this affect the network assembly? The answers to these are found by using pyridyl acrylic acid as substrate, which has two extra CH separating the pyridyl and carboxylic sites in isonic acid. Its reaction with **2** leads to $[Au_2(dppf)(PyAcrH)_2](OTf)_2$, **5**, whose crystal structure‡ suggests a similar Au_2 metalloligand structure as **4** (Fig. 3). However, the solid-state network structure is completely different. As a result of the expanded intermolecular space created by the elongated spacer, the carboxylate oxygen can no longer bring together the cations without creating big voids. A different type of polymer-like chain is formed by inter-ionic interactions. The triflate uses its O, F dibasic function to align discrete Au_2 entities [Au···O (~3.370 Å) and F···H (Cp) (~2.488 Å)]. The resultant porous crystal network contains solvate-filled square-shaped cavities lined mainly by the pyridyl acrylate and the ferrocene. ESI-MS analysis of a solution of **5** also suggests discrete digold moieties of $[Au_2(dppf)(PyAcr)]^+$.

Compound **5** unexpectedly decomposes upon attempted recrystallization from $CHCl_3$ by abstracting sulfide from triflate and releasing pyridyl acrylate to give $[Au_4(\mu_4\text{-}S)(dppf)_2](OTf)_2$, **6**. Crystallographic analysis‡ reveals an Au_4-based square-pyramidal structure with an "inverted umbrella" completed by an apical sulfide. Each dppf bridges across two of the Au atoms (av. Au–Au

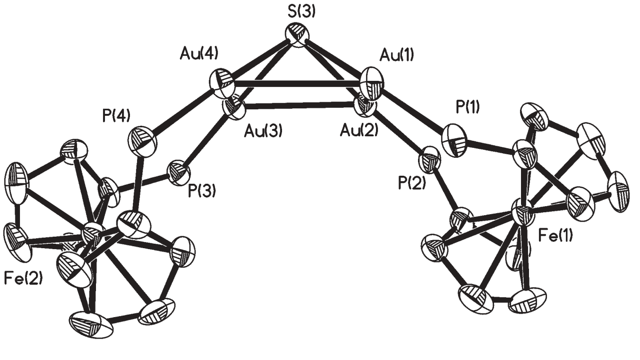

Fig. 4 ORTEP diagram of **6** showing the square base of the $\{Au_4S\}$. Phenyl rings and hydrogen atoms removed for clarity.

2.8994(6) Å) (Fig. 4). This complex is analogous to $[Au_4S(PPh_3)_2(dppf)]^{2+}$ and $[Au_4S(PPh_3)_4]^{2+}$, the latter of which was crystallographically established.[5] The only other all-dppf sulfide complex of gold is a Au_6 cluster.[5a] In the solid state, weak Au···S (av. 3.593 (2) Å) interactions are observed between adjacent inverting pyramids. The crystal lattice therefore contains a series of mutually interacting gold pyramids. However, in **6**, the pyramid base is near-square and planar (Au–Au–Au angles 88.51(2)–92.21(2)°), as compared to the rhombic form reported (*cf.* Au–Au–Au 75 and 100°).[5b]

Complex **2** also reacts with other pyridyl carboxylates such as $PyRCO_2^-$ (R = CH_2, **7**; R = Bz, py = 4-pyridyl, **8** or 3-pyridyl, **9**) but the products decompose readily in solution to give colloidal gold. The product with 3-$PyBzCO_2H$ (3-pyridyl benzoic acid), **9**, is more stable but insofar we are unable to obtain suitable single crystals for analysis.

Although the geometric characteristics of the pyridyl carboxylate play a key role on determining the gold assemblies, the supporting role of dppf is also evident. It is one of the few ligands that could bridge across strongly interacting metals (M–M ~2.85 Å), and those that are non-interacting (M–M >10 Å). Both could even co-exist within a singular structure or have a dynamic equilibrium between them. The dimetal core hence inherits the needed flexibility to adjust to different stereogeometric demands, thus resulting in a myriad of structures dictated by the spacers. These, together with the inherent geometric variation of Au(I) make this one of the most attractive systems for self-assemblies. The isolation of **4** and **5** as metalloligands also creates new opportunities for other hetero metallic assemblies.

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Notes and references

‡ Crystals for **3–5** are obtained by the slow diffusion of diethyl ether into a solution of the complexes in $CHCl_3$. **6** was obtained in the $CDCl_3$ solution used for NMR of **5**.

Crystal data: **3**: $C_{126}H_{100.5}Au_6F_9Fe_3N_{4.5}O_{17}P_6S_3$, rhombohedral, space group $R\bar{3}c$, a = 19.0071(4), c = 123.338(5) Å, γ = 120°. **4**: $C_{56}H_{46}Au_2Cl_{12}F_6FeN_2O_{10}P_2S$, monoclinic, space group $P2_1/c$, a = 15.9755(10), b = 14.3238(9), c = 15.9882(10) Å, β = 103.661(2)°. **5**: $C_{71}H_{57}Au_4Cl_3F_6Fe_2O_6P_4S_3$, monoclinic, space group $P2_1/c$, a = 15.1716(12), b = 14.9383(12), c = 32.609(3) Å, β = 100.997(2)°. **6**: $C_{49}H_{39}Au_2Cl_3F_6FeN_2O_{10}P_2S_2$, monoclinic, space group $P2_1/c$, a = 8.596(3), b = 15.116(6), c = 21.344(8) Å, β = 91.555(10)°.

Refinement and solution.[7–9]

CCDC numbers of complexes **3–6** are 632232–632235. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618309c

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