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

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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, electronic and luminescent 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 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 design as well as examples of oligmeric 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$_2$Cl$_2$(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$_5$H$_4$CO$_2$H) to give a yellow powder of [Au$_6$(isonic)$_3$(dppf)$_3$(OTf)$_3$, 3. $^1$H NMR and ESI-MS data ($m/z$ 1070.0 assignable to [Au$(isonic)$(dppf)]$^+$ and 1946.7 to [Au$_6$(isonic)$_3$(dppf)$_3]$) support ionic and phosphine coordination.

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$_5$–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 ionic ligands to form the cascading edges of the triangle.

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

Fig. 1 ORTEP plot of 3 showing a triangular framework of three Au$_2$ moieties, (hydrogen atoms omitted for clarity).
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, NC₅H₄CO₂H) gives NMR data that suggest phosphine and pyridyl coordination but no definitive structural information. The ESI-MS spectrum shows a fragment peak of [Au₂(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 [Au₂(dppf)(NicH₂)]²⁺ (Fig. 2). For the two Au(t) 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 Au₂ 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 systems⁴ 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 metallo-ligand of Au₂. Work is ongoing to construct new hetero-trimetallic {Au₂M} assemblies from 4. Earlier results from our laboratory suggested that a suitable oxophilic metal for such attachment could be Ag⁺.⁴⁵

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 [Au₂(dppf)(PyAcrH)_2](OTf)₂, 5, whose crystal structure † suggests a similar Au₂ 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 Au₂ 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 [Au₂(dppf)(PyAcr)]⁺.

Compound 5 unexpectedly decomposes upon attempted recrystallization from CHCl₃ by abstracting sulfide from triflate and releasing pyridyl acrylate to give [Au₂(μ₄-S)(dppf)₂](OTf)₂, 6. Crystallographic analysis † reveals an Au₄-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

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Fig. 2 ORTEP diagram of 4 showing only the Au₂ cation, with an inversion centre at Fe.

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

Fig. 4 ORTEP diagram of 6 showing the square base of the {Au₄S}. Phenyl rings and hydrogen atoms removed for clarity.
2.8994(6) Å (Fig. 4). This complex is analogous to [AuS(PPh3)2-
(dppf)]7− and [Au2S2(PPh3)3]2+, the latter of which was crystal-
lographically established. The only other all-dppf sulfide complex
of gold is a Au6 cluster. 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°).50

Complex 2 also reacts with other pyridyl carboxylates such as
PyRCO2− (R = CH3, 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-PyBzCO2H (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 carboxy-
late 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
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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 CHCl3. 6 was obtained in the CDC13 solution
used for NMR of 5.

Crystal data. 3: C_{22}H_{10.4}Au_{2}Fe_{2}N_{4.4}O_{2}P_{5}S_{3}; rhombohedral, space

| Group | a = 19.0071(4), c = 123.338(5) Å, γ = 120°. 4: C_{22}H_{20}Au_{2}Cl_{2}Fe_{2}N_{2}O_{2}P_{2}S; monoclinic, space group P2_{1}/c, a = 15.975(5), b = 14.3238(9), c = 15.982(10) Å, β = 103.661(2)°. 5: C_{74}H_{57}Au_{2}Cl_{2}Fe_{2}O_{2}PS; monoclinic, space group P2_{1}/c, a = 15.171(12), b = 14.393(12), c = 32.609(3) Å, β = 100.997(7)°. 6: C_{9}H_{10}Au_{2}Cl_{2}Fe_{2}N_{2}O_{2}P_{2}S; monoclinic, space group P2_{1}/c, a = 8.59(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 crystal-
lographic data in CIF or other electronic format see DOI: 10.1039/b618309e


