

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

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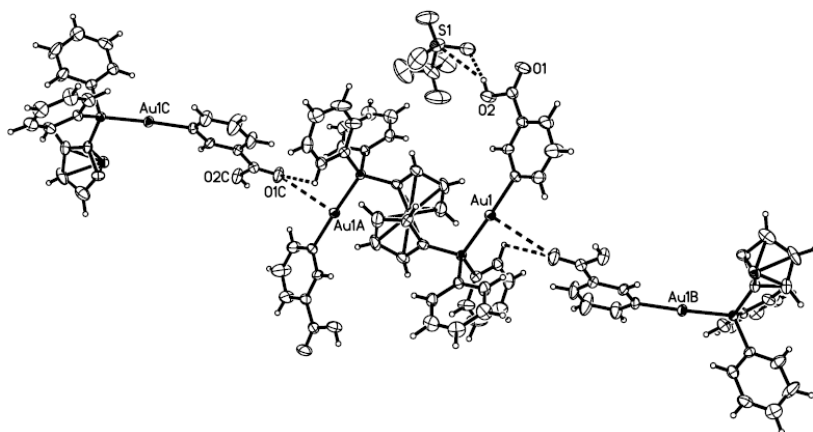
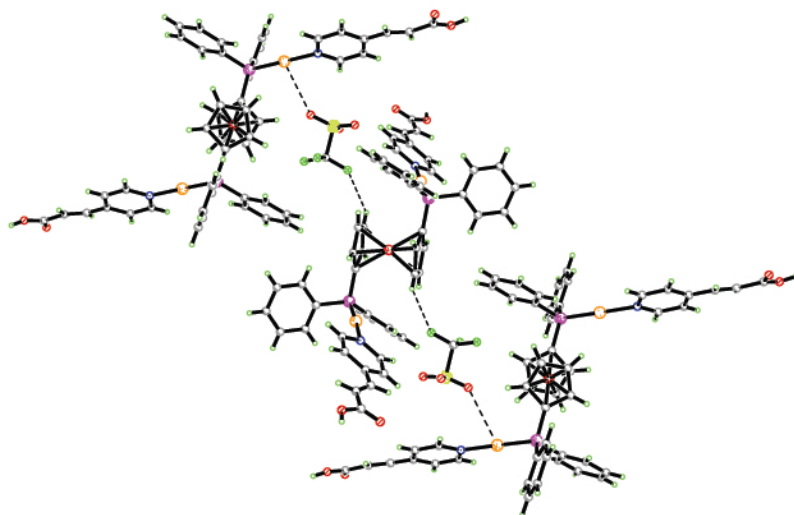


Fig a: ORTEP drawing (30% probability ellipsoids) of **4**, showing the inter-ionic linkages of each diatation of **4** with its neighboring anion and cation. Symmetry transformations used to generate equivalent atoms: A: $-x+1, y+0.5, -z+1.5$; B: $-x+2, y+0.5, -z+1.5$; C: $x-1, -y+0.5, z-0.5$.



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Fig b: ORTEP drawing (50% probability ellipsoids) of **5**, showing the connecting role of the anions among the cations through hydrogen bonding and secondary Au...O interactions.

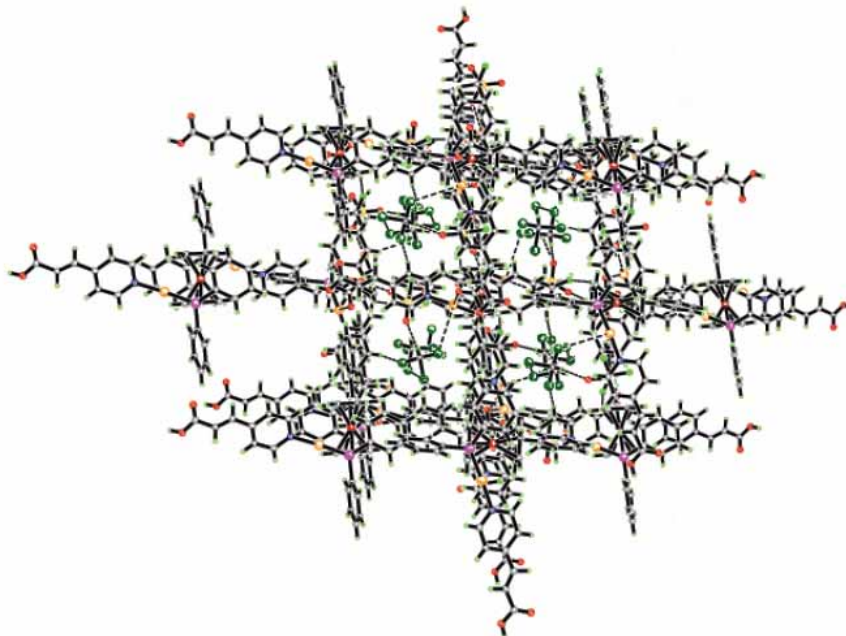


Fig c: Molecular packing diagram of **5**, showing cavities filled by chloroform solvate.

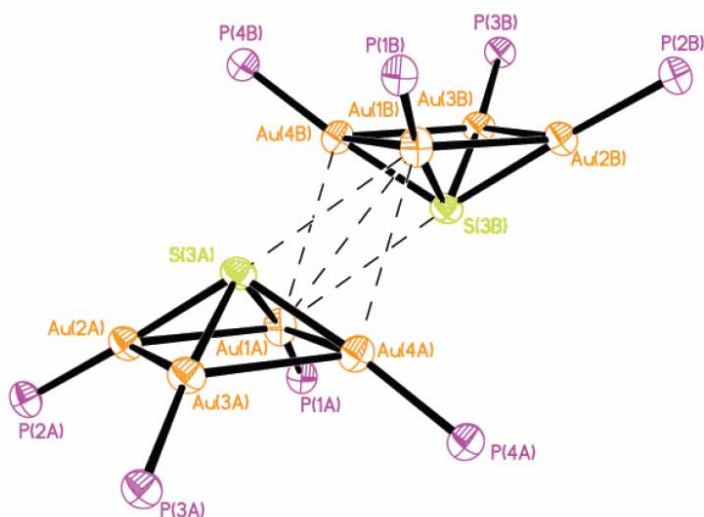


Fig d: An Ortep plot of **6** showing two Au₄S inverting pyramids interacting face-to-face.

Experimental

General procedures

All reactions were performed under pre-purified dry nitrogen using standard Schlenk techniques. The products are air-stable and hence recrystallizations were performed in air. All reagents used were of reagent grade quality obtained from commercial sources and were used as received. Commercial reagents MeCN, CH₂Cl₂ and CHCl₃ were distilled from CaH₂. Au₂Cl₂dppf, **1**, is prepared according to literature procedures⁶.

All ¹H NMR(δ (TMS)=0.0ppm) and ³¹P{¹H} NMR(δ(85% H₃PO₄) = 0.0 ppm) were recorded at *ca.* 300K at operating frequencies of 500.13 and 202.45 MHz respectively on a Bruker AVANCE 500MHz. ESIMS were obtained with a Finnigan / MAT LCQ mass spectrometer coupled with TSP4000 HPLC system and the crystal 310 CE systems. Samples were injected via a Rheodyne valve fitted with a 5 μL sample loop. The capillary temperature was 70°C for obtaining of the spectra of all complexes. The capillary voltage was 17V. Peaks were assigned from the m/z values and from the isotopic distribution patterns. The m/z values given are for the most intense peak in the envelopment in each case. Samples used for elemental analyses were generally those from the bulk whereas crystals for X-Ray diffraction studies were single-crystals grown from the bulk sample. The X-ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo-Kα sealed tube at -50°C. The program SMART⁷ was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT for integration of the intensity of reflections and scaling, SADABS⁸

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for absorption correction and SHELXTL⁹ for space group and structure determination and least-squares refinements on F.

Complex **2** was synthesized by dissolving AgOTf (0.0385g, 0.15mmol) in MeCN (3 ml) to give a colourless solution, followed by the addition of CH₂Cl₂ (20 ml). Complex **1** (0.0765 g, 0.075 mmol) was added and the mixture stirred for 1 h to give a clear yellow solution of [Au₂(dppf)(MeCN)₂](OTf)₂. The mixture was filtered and the filtrate used immediately for syntheses of **3-9**. ³¹P{¹H} NMR: δ = 41.3 (NMR recorded *in situ* on the filtrate upon 1:1 dilution with CD₂Cl₂). Complexes **3-5** and **9** were synthesized by the following method: To an aliquot of **2** was added isonicH (**3**), NicH (**4**), PyAcrH (**5**) or 3PyBzCO₂H (**9**) (0.15 mmol) and the mixture stirred for 5 h. The mixture was then filtered and the filtrate was concentrated to *ca.* 3ml. Et₂O was added to induce precipitation (yellow). The mixture was filtered and dried in vacuum. For **7** and **8**, commercial form of pyridyl carboxylic acid (as HCl adduct) was used.

[Au₆(dppf)₃(isonic)₃](OTf)₃, **3**. ³¹P{¹H} NMR: δ = 24.1 (300K); 25.9, 22.1 (maj), 21.9, 23.3, 23.5, 23.7, 24.0, 26.3 (min) (228K); ²J_{P-P} = 17.4Hz. ¹H NMR: δ = 8.9, 8.0, (s) (pyridyl H), 7.5-7.6 (m) (dppf phenyl H), 4.5, 4.6, 4.7 (s) (dppf Cp H) (300K). ESI: m/z = 1070.0 ([Au₃(dppf)₃(isonic)₂]⁺) (100%), 1946.7 ([Au₆dppf(isonic)]⁺) (25%). IR /cm⁻¹: ν(COO)_{asym}, 1725, 1648; ν(COO)_{sym}, 1266. Anal. Cal. For **3**.6CHCl₃: C, 35.38; H, 2.33; N, 0.96. Found: C, 35.22; H, 2.24; N, 0.98. Crystal data: M = 3669.41, C₁₂₆H_{100.50}Au₆F₉Fe₃N_{4.50}O₁₇P₆S₃. Rhombohedral crystals, space group R-3c; crystal size 0.20X0.10X0.08. a = 19.0071(4), b = 19.0071(4), c = 123.338(5); α = β = 90°, γ = 120°. Z = 12, V = 38588.6(19), D_{calc} = 1.95mg/m³. Final R = 0.0792, wR² = 0.2321. Au(1)-N(1): 2.107(17)Å; Au(1)-Au(2):

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3.0072(12)Å; Au(2)-O(1): 2.075(15); F(2)-H(10): 2.488Å; N(1)-Au(1)-P(1): 172.8(6)°;
N(1)-Au(1)-Au(2): P(1)-Au(1)-Au(2): 100.99(13)°; O(1)-Au(2)-P(2): 177.1(5)°; O(1)-
Au(2)-Au(1): 80.5(4)°; P(2)-Au(2)-Au(1): 101.82(15)°.

Au₂(dppf)(NicH)₂](OTf)₂, 4. ³¹P{¹H} NMR: δ = 22.6, 24.2 (300K); 24.2, 22.3 (maj),
23.7, 23.0, 21.3 (min) (228K); ¹H NMR: δ= 9.6, 9.2, 8.2 (s) (pyridyl H), 7.4-7.6 (m)
(dppf phenyl H), 4.5, 4.6, 4.7 (s) (dppf Cp H) (300K). ESI: m/z = 1072.4 ([Au₂(dppf)
(Nic)]⁺) (25%), 983.1 ([Au₂Cldppf]⁺) (100%). IR /cm⁻¹: ν(COO)_{asym}, 1735, 1640;
ν(COO)_{sym}, 1273; ν(OH), 3448. Anal. Cal. For **4**: C, 40.35; H, 2.68; N, 1.96. Found: C,
39.76; H, 2.42; N, 0.68. Crystal data: M= 1612.02, C₄₉H₃₉Au₂Cl₃F₆FeN₂O₁₀P₂S₂.
Monoclinic crystals, space group P2(1)/c; crystal size 0.20X0.06X0.06. a=8.596(3), b=
15.116(6), c= 21.344(8); α=γ=90, β= 91.555(10). Z=2, V= 2772.4(7), D_{calc}= 1.931mg/m³.
Final R= 0.0593, wR²= 0.1179. Au(1)-N(1): 2.086(7)Å; Au(1)-P(1): 2.243(2)Å; Au(1)-
O(1): 3.404Å; O(1)-H(2b): 2.398Å; H(4a)-Cl(2): 2.806Å; N(1)-Au(1)-P(1): 177.3(2)°.

[Au₂(dppf)(PyAcrH)₂](OTf)₂, 5. ³¹P{¹H} NMR: δ = 23.2 (300K); 21.7, 24.0 (maj), 23.4,
27.7 (min) (203K); ¹H NMR: δ= 8.8 (s) (pyridyl H), 7.4-7.6 (m) (dppf phenyl H), 4.5, 4.7
(s) (dppf Cp H) (300K). ESI: m/z = 1096.0 ([Au₂(dppf)(PyAcr)]⁺) (100%), 983.1
([Au₂Cldppf]⁺) (20%). IR /cm⁻¹: ν(COO)_{asym}, 1616; ν(COO)_{sym}, 1261; ν(OH), 3466;
ν(C=C), 2367. Anal. Cal. For **5**.CH₂Cl₂: C, 39.79; H, 2.75; N, 1.82. Found: C, 40.07; H,
2.41; N, 0.98. Crystal data: M= 1990.13, C₅₆H₄₆Au₂Cl₁₂F₆FeN₂O₁₀P₂S. Monoclinic
crystals, space group P2(1)/c; crystal size 0.20X0.10X0.04. a=15.9755(10), b=
14.3238(9), c= 15.9882(10); α=γ=90, β= 103.61(2). Z=2, V= 3555.1(4), D_{calc}=

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1.859mg/m³. Final R= 0.0858, wR²= 0.2540. Au(1)-N(1): 2.063(8)Å; Au(1)-O(1): 3.640Å; Au(1)-O(5): 3.370Å; H(1)-O(4): 1.819Å; H(4)-F(1): 2.488Å; N(1)-Au(1)-P(1): 177.0(4)^o.

5 will decompose in CHCl₃ to give **6**. As **6** is a decomposed product, no spectroscopic data was obtainable yet. Crystal data for **6**: M= 2346.14, C₇₁H₅₇Au₄Cl₃F₆Fe₂O₆P₄S₃. Monoclinic crystals, space group P2(1)/c; crystal size 0.30X0.26X0.10. a=15.1716(12), b= 14.9383(12), c= 32.609(3); α=γ=90, β= 100.997(2). Z=4, V= 7254.8(10), D_{calc}= 2.148mg/m³. Final R= 0.0562, wR²= 0.1208. Au(1)-S(3): 2.406(3) Å; Au(1)-Au(2): 2.8618(6) Å; Au(1)-Au(4): 2.9541(6) Å; Au(2)-S(3): 2.398(2) Å; Au(2)-Au(3): 2.8446(6) Å; Au(3)-S(3): 2.428(2) Å; Au(3)-Au(4): 2.8970(6) Å; Au(4)-S(3): 2.360(2)Å; P(1)-Au(1)-S(3): 173.63(9)^o; Au(2)-Au(1)-Au(4): 88.507(15)^o; P(2)-Au(2)-S(3): 175.90(8)o; Au(3)-Au(2)-Au(1): 92.206(16)o; P(3)-Au(3)-S(3): 175.52(9)^o; Au(2)-Au(3)-Au(4): 89.972(15)^o; P(4)-Au(4)-S(3): 175.07(9)^o; Au(3)-Au(4)-Au(1): 89.293(15)^o.

Synthesis of 7. PyOAcH.HCl (0.0260g, 0.15mmol) was first reacted with AgNO₃ (0.0255g, 0.15mmol) in water added and the mixture filtered. The filtrate was evaporated in vacuum to give a white solid. An aliquot of **2** was then added to the white solid and the mixture stirred for 5h. The mixture was then filtered and the filtrate was concentrated to ca. 3ml. Diethyl ether was added and a yellow precipitate formed. The mixture was filtered and dried in vacuum to give a yellow solid product. The yellow solid turns purple after 7 days in air. A solution of **7** in a range of solvents turns purple in 48h. ³¹P{¹H} NMR: δ = 22.0 (broad), 24.0 (sharp) (300K); 21.5, 25.1 (maj), 22.3, 23.3, 23.5, 23.6 (min)

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(203K); $^2J_{P-P} = 7.5\text{ Hz}$ ^1H NMR: $\delta = 8.8, 8.5, 7.9$ (s) (pyridyl H), 7.4-7.6 (m) (dppf phenyl H), 3.9, 4.1, 4.6, 4.7 (s) (dppf Cp H) (300K). ESI: $m/z = 1084.1$ ($[\text{Au}_2(\text{dppf})(\text{PyOAc})]^+$) (100%), 983.1 ($[\text{Au}_2\text{Cl}(\text{dppf})]^+$) (65%). IR $/\text{cm}^{-1}$: $\nu(\text{COO})_{\text{asym}}$, 1621; $\nu(\text{COO})_{\text{sym}}$, 1275; $\nu(\text{OH})$, 3464.

For **8**, synthesis is same as that of **7**. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 26.1$ (broad) (300K); 25.2 (maj), 27.6, 26.4, 26.0, 21.6, 21.0 (min) (193K). ^1H NMR: $\delta = 9.0, 8.3, 8.0$ (s) (pyridyl H), 7.9, 7.8 (PyBzCO₂ phenyl), 7.5-7.6 (m) (dppf phenyl H), 4.3, 4.5 (s) (dppf Cp H). ESI: $m/z = 983.1$ ($[\text{Au}_2\text{Cl}(\text{dppf})]^+$) (100%). IR $/\text{cm}^{-1}$: $\nu(\text{COO})_{\text{asym}}$, 1622; $\nu(\text{COO})_{\text{sym}}$, 1271; $\nu(\text{OH})$, 3464, $\nu(\text{phenyl})$, 1436.

For **9**, $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 22.6, 24.1$. ^1H NMR: $\delta = 8.9, 8.1$ (s) (pyridyl H), 7.9, 7.7 (3-PyBzCO₂ phenyl), 7.4-7.6 (m) (dppf phenyl H), 4.2, 4.4, 4.6, 4.7 (s) (dppf Cp H) (300K). ESI: $m/z = 1072.3$ ($[\text{Au}_4(\text{dppf})_2(3\text{-PyCO}_2)_2]^{2+}$) (25%), 1217.2 ($[\text{Au}_2\text{dppf}(3\text{-PyBzCO}_2)\text{Cl}_2 + \text{H}^+]^+$) (15%), 1146.4 ($[\text{Au}_2\text{dppf}(3\text{-PyBzCO}_2)]^+$) (6%), 983.1 ($[\text{Au}_2\text{Cl}(\text{dppf})]^+$) (75%). IR $/\text{cm}^{-1}$: $\nu(\text{COO})_{\text{asym}}$, 1719, 1617; $\nu(\text{COO})_{\text{sym}}$, 1259; $\nu(\text{OH})$, 3467; $\nu(\text{phenyl})$, 1438.

Crystallographic analysis

For complex **3**, the crystal is trigonal, space group R-3c. The data set was poor. At 2-theta max at 48 degrees, $R_{\text{int}} = 0.144$. The structure is that of the expected complex cation (containing 6 Au), 3 OTf anions and probably some solvent. The asymmetric unit

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contains one third of the cation. The whole cation can be obtained by the 3-fold symmetry. One of the OTf is normal. The second one is disordered (flipped over). The third one cannot be completely resolved as it is situated in a void around the 3-fold axis with a large number of residual peaks. We had assigned positions for one S for this OTf and one partially occupied acetonitrile, both at half occupancy. These assignments may not be correct. However, with this model, the R values were much lowered. Final R values are $R_1=0.0792$ and $wR_2=0.2321$. During the final refinement cycles, the phenyl rings were refined as fixed hexagons. Restraints were applied so that some of the atoms with poor thermal parameters and positions can retain the expected geometry. These included the atoms of the second OTf and the acetonitrile solvent. For complex **4**, the crystal is monoclinic, space group $P2(1)/c$. The asymmetric unit contains one half of the cation and one OTf anion. There is one half of solvent disordered at the centre of symmetry. The whole cation can be generated through the centre of symmetry. The crystal used for data collection for **5** was small, resulting in poor data set. The thermal parameters were all very high. Restraints for thermal parameters and bond lengths were used to many of the atoms. Final R values for 2-theta max of 45degrees are reasonable. The asymmetric unit contained one half of the complex cation, one OTf anion and two chloroform molecules. The asymmetric unit of **6** contains one Au complex cation, two OTf anions and one chloroform molecule. The S in the cation could also be assigned as Cl but S was chosen on charge balance considerations. One of the OTf was disordered flipping with 70:30 occupancies).