

Supplementary Information

Synthesis

Synthesis of **3**: A solution of 1-propargyl-3-vinylimidazolium hexafluorophosphate (0.15 g, 0.54 mmol) in THF (20 ml) was treated with *n*-BuLi (1M solution in *n*-hexane) (1.0 ml, 1.00 mmol) at -60 °C and stirred over a period of 1.5 h at -55 °C.

Chloro(trimethylphosphine)gold (0.33 g, 1.07 mmol) was added in small portions, and the mixture was then allowed to warm to room temperature over a period of 2 h. After stripping of solvent *in vacuo*, the residue was dissolved in CH₂Cl₂ (20 ml) and filtered. After solvent removal, an off-white microcrystalline material (0.39 g), was obtained. A solution of the crude product in CH₂Cl₂ (8 ml) was layered with Et₂O (1 ml) and stored at -30 °C. Small crystals of **3** (barely) suitable for X-ray diffraction analysis formed over a period of 12 months.

Analysis (NMR assignments for **3** based on spectra of crude product mixture)

m.p.: 145 °C (dec). IR (KBr): 2135 (C≡C) cm⁻¹. ¹H-NMR (600 MHz, CD₂Cl₂, 25°C): δ 7.50 (dd, ³*J*_{trans} = 15.6 Hz, ³*J*_{cis} = 8.8 Hz, 3H, NCH=CH₂), 7.41–7.35 (m, 6H, NCH=CHNCH=CH₂), 5.54 (dd, ³*J*_{trans} = 15.6 Hz, ²*J*_{gem} = 2.7 Hz, 3H, NCH=C(*H*_{trans})*H*_{cis}), 5.20 (dd, ³*J*_{cis} = 8.8 Hz, ²*J*_{gem} = 2.7 Hz, 3H, NCH=C(*H*_{trans})*H*_{cis}), 5.07 (s, 6H, AuC≡CCH₂N), 1.49 (d, ²*J* = 10.2 Hz, 18H, PMe₃). ¹³C-NMR (151 MHz, CD₂Cl₂, 25°C): δ 184.6 (s, Au=C), 133.2 (s, NCH=CH₂), 132.9 (s, AuC≡CCH₂N), 122.7 (s, NCH=CHNCH=CH₂), 117.6 (s, NCH=CHNCH=CH₂), 105.2 (s, NCH=CH₂), 95.3 (s, AuC≡CCH₂N), 43.0 (s, AuC≡CCH₂N), 15.6 (d, ¹*J* = 37.2 Hz, CH₃). ³¹P-NMR (243 MHz, CD₂Cl₂, 25°C): δ 1.43 (s, AuPMe₃), 1.55 (s, AuPMe₃), -143.3 (sp, ¹*J* = 710.5

Hz, PF₆⁻). FAB MS *m/z*: 1333 (M - PF₆, 1%), 1257 (M - PF₆ - PMe₃, 1%), 1181 (M - PF₆ - 2PMe₃, 4%), 985 (M - PF₆ - Au(PMe₃)₂, 4%), 349 (Au(PMe₃)₂, 100%), 273 (AuPMe₃, 44%). ESI-MS *m/z*: [M⁺ - PF₆] calcd for C₃₀H₃₉Au₄N₆P₂, 1333; found, 1333; [M⁺ - PF₆ - PMe₃] calcd for C₂₇H₃₀Au₄N₆P, 1257; found, 1257; [M⁺ - PF₆ - 2PMe₃] calcd for C₂₄H₂₁Au₄N₆, 1181; found, 1181; [C₈H₇N₂ + 2AuPMe₃] calcd for C₁₄H₂₅Au₂N₂P₂, 677; found, 677; [C₈H₇N₂ + AuPMe₃ + Au] calcd for C₁₁H₁₆Au₂N₂P₂, 601; found, 601; [C₈H₈N₂ + AuPMe₃] calcd for C₁₁H₁₇AuN₂P, 405; found, 405; [Au(PMe₃)₂] calcd for C₆H₁₈AuP₂, 349; found, 349.

Note: ¹³C NMR (151 MHz, CD₂Cl₂, 25°C) of **2**, 14.84 (m, PMe₃)

Methods

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Tetrahydrofuran and diethyl ether were distilled under N₂ from sodium benzophenone ketyl radical and dichloromethane from CaH₂. The melting point was determined using a Stuart Scientific Melting Point Apparatus SMP3 and is uncorrected. Mass spectra were recorded on a VG Quattro (ESI, 70 eV, solvent CH₂Cl₂) or a VG 70SEQ (FAB, 70 eV) instrument, the infrared spectra on a Perkin-Elmer 1600 Series or a Nicolet Avatar 330 FT-IR with ATR (attenuated total reflection) accessory (Smart Performer) and NMR spectra on an INOVA 600 MHz spectrometer (δ reported relative to the solvent resonance or external reference 85% H₃PO₄). Determination of ¹H-¹H cosy, ¹H-¹³C ghsqc, ¹H-¹³C long range ghmqc and ¹H-³¹P long range ghmqc NMR spectra allowed unambiguous assignment of the signals in the NMR spectra. The gold(I) starting material chloro(trimethylphosphine)gold was prepared by substitution of tetrahydrothiophene (tht) in ClAu(tht)^{1,2} with the phosphine. Comparison of the characterisation data³ in the literature confirmed the purity. 1-Propargyl-3-vinylimidazolium was prepared according to literature⁴. All other chemicals are commercially available and were used without further purification.

X-ray crystallography

The crystals were of irregular shape and appeared (by visual inspection) to be of rather poor quality. However, a crystal was mounted on a Bruker-Nonius SMART Apex diffractometer and intensity data were collected over a period of 16 hours. Most of the non-hydrogen atoms were located by direct methods (SHELXS) and the remaining atoms were located in difference electron density maps. Only the gold and phosphorus atoms were refined anisotropically. All attempts to refine the remaining non-hydrogen atoms anisotropically resulted in non-positive definite displacement parameters. Several unsuccessful attempts were made (over a period of two years!) to grow more suitable crystals and we eventually decided to use the original data despite the poor quality of the model.

Crystal data for 3: $C_{32.5}H_{44}Au_4Cl_{5.5}F_3N_6P_{2.5}$, $M = 1636.00$, colorless block, $0.10 \times 0.10 \times 0.05 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.232(9)$, $b = 14.873(10)$, $c = 14.917(10) \text{ \AA}$, $\alpha = 119.874(9)$, $\beta = 108.507(12)$, $\gamma = 93.365(12)^\circ$, $V = 2329(3) \text{ \AA}^3$, $Z = 2$, $D_c = 2.333 \text{ g/cm}^3$, $F_{000} = 1510$, Smart APEX, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 100(2) \text{ K}$, $2\theta_{\text{max}} = 56.5^\circ$, 13306 reflections collected, 9938 unique ($R_{\text{int}} = 0.1844$). Final $GooF = 0.958$, $RI = 0.1246$, $wR2 = 0.2550$, R indices based on 3074 reflections with $I > 2\sigma(I)$ (refinement on F^2), 126 parameters, 6 restraints. Lp and absorption corrections applied, $\mu = 13.006 \text{ mm}^{-1}$. See CCDC 740231.

The asymmetric unit of the final crystallographic model consists of the [2]rotaxane with an overall charge of +1 which is balanced by the presence of half of a hexafluorophosphate ion and half a chloride ion. This model is consistent with both the intensity data and charge balance – indeed, chloride ions are present in the solution from

which the complex was isolated. One and a half molecules of dichloromethane are also present in the asymmetric unit (one of these shares a site with the half-occupancy chloride ion). Close inspection of the asymmetric unit and also of a packing diagram reveals the possible presence of a threefold rotation axis. However, the unit cell cannot be reindexed in the trigonal system and the ADDSYM⁵ routine of PLATON⁶ did not indicate the presence of threefold crystallographic symmetry. Therefore we conclude that the structure possesses pseudo-threefold (i.e. non-crystallographic) symmetry.

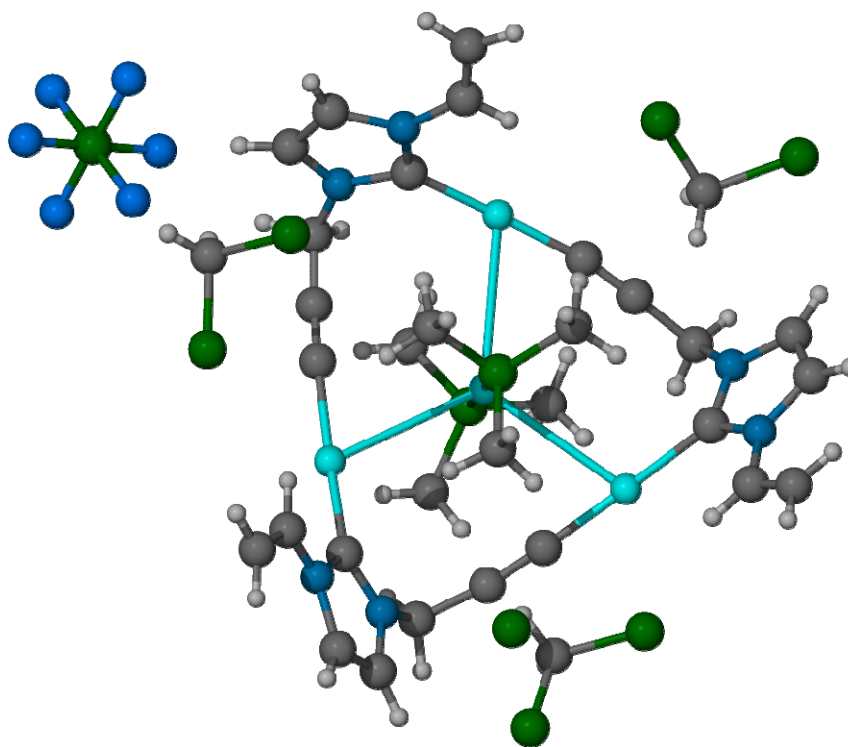


Figure S1 Ball-and-stick image showing the [2]rotaxane, three dichloromethane solvent molecules, PF_6^- and Cl^- . The chloride ion is disordered and shares a site with one of the dichloromethane molecules – each with a 50% site occupancy.

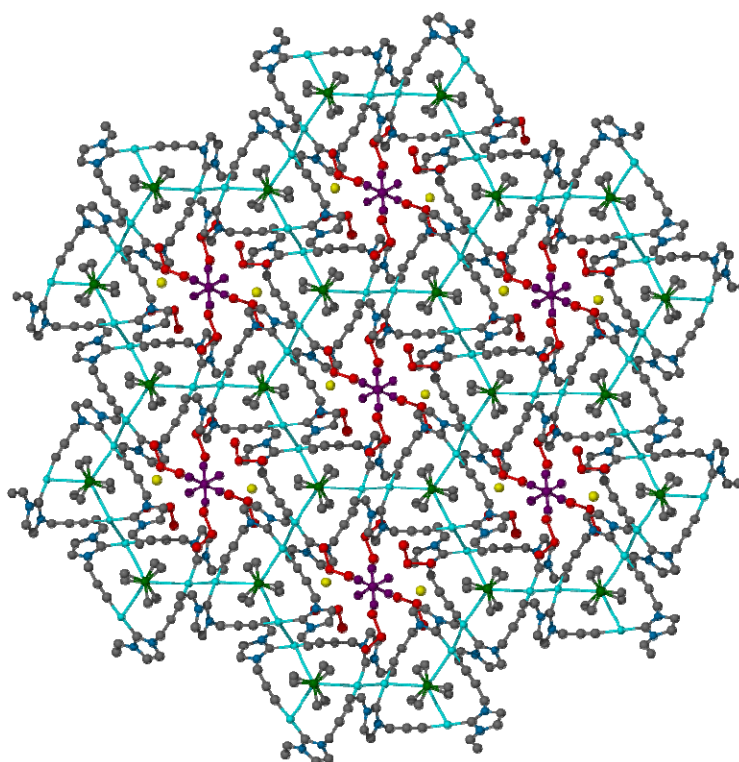


Figure S2 Ball-and-stick image viewed perpendicular to (100) showing the apparent 3-fold symmetry of the structure. The three gold atoms of each metallocycle are each involved in intermolecular Au...Au interactions with neighboring rings to form sheets parallel to (100).

References

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