Small Gold(I) and Gold(I)–Silver(I) Clusters by C–Si Auration
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Experimental Procedures

1. General Experimental Methods

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification and all the reactions were carried out under Ar in solvents dried by passing through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Hexanuclear gold clusters 2a-e were synthesized under nitrogen atmosphere, while other gold and gold-silver species of 4-9 were synthesized at air atmosphere. For catalysis part including kinetic studies, deuterated solvents were dried under activated MS 3Å for at least three d and deoxygenated by bubbling argon for 30 min before storing them in the glovebox. All the glassware used was dried in the oven at 100 °C for at least 12 h before use. Analytical TLC was performed on precoated silica gel plates ((Merck 60 F254) and observed under UV light. Preparative TLC was performed on 20 cm × 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech). NMR spectra were recorded at 298 K on BrukerAvance Ultrashield NMR spectrometers (300, 400, 500 and 500 with CryoProbe). Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (J) are reported in hertz (Hz). Mass spectra were recorded on a Waster LCT Premier Spectrometer (ESI and APCI), on an Autoflex Broker Daltonics (MALDI and LDI), or on an AgilentMSD-5975B (GC-MS). UV-Vis measurements were carried out on a Shimadzu UV-1700PC spectrophotometer equipped with a photomultiplier detector, double beam optics, and D2 and W light source. The C, H, N analyses were carried out with a CE instruments EA 1110 elemental analyzer. Single crystal X-ray diffraction data were recorded on a Bruker Kappa APEX II DUO diffractometer equipped with an APPEX 24K CCD area detector, a Microsource with Moka radiation and an Oxford Cryostream 700 low temperature device (T = 100 K).

2. Experimental Details

2.1 Synthesis of phosphine ligands

Diphenyl(2-trimethylsilylphenyl)phosphine, L1-TMS

(2-bromophenyl)diphenylphosphane (1.13 g, 3.31 mmol) was dissolved in degassed Et2O (15 mL) under argon atmosphere. The reaction vessel was flushed to 0 °C and a solution of n-butyllithium (1.338 mL, 3.35 mmol, 2.5 M in hexane) was added dropwise. When the addition was completed, the reaction mixture was stirred at 23 °C for 2 h, then chlorotrimethylsilane (0.467 mL, 3.68 mmol) was added dropwise at 0 °C. The resulting mixture was gradually warmed to 23 °C for 3 h and quenched with a saturated aqueous solution of NH4Cl (10 mL). The mixture was extracted with Et2O (20 mL × 3). The combined organic layers were dried over anhydrous MgSO4, filtered and evaporated under reduced pressure. The solution was concentrated in vacuum, and the residue was subjected to column chromatography on silica gel with hexane to give ligand L1-TMS as white solid in 80% yield. The data of 1H, 13C, 31P(1H) NMR were consistent with those reported in the literature.1

Diphenyl(2-(trimethylsilylnaphthalen-1-yl)phosphine, L2-TMS

2-(Trimethylsilyl)-1-naphthyl triflate was synthesized according to the literature.2 A solution of 2-bromonaphthalen-1-ol (2 g, 8.52 mmol) and bis(trimethylsilyl)amine (1.794 mL, 8.52 mmol) in THF (35 mL) was refluxed for 1.5 h. The solvent was evaporated under reduced pressure and the pale brown residue was subjected to vacuum to remove excess NH3 and unreacted HMDS. The crude product was dissolved in THF (30 mL), the solution was cooled to -80 °C, and n-butyllithium (5.86 mL, 9.37 mmol, 2.5 M in hexane) was added dropwise to afford a yellow solution. The reaction was stirred for 20 min, then Et2O (30 mL) was added, and the trifluoromethanesulfonic anhydride (1.81 mL, 10.65 mmol) were added dropwise. The mixture was stirred at -80 °C for 20 min and then warm to 23 °C overnight. Saturated aqueous NaHCO3 was added, the phases were separated, and the aqueous layer was extracted with EtO. The combined organic layers were dried over anhydrous MgSO4, filtered, and concentrated under reduced pressure affording an orange residue. The residue was purified by column chromatography with cyclohexane to afford a colourless oil (2.10 g, 72%). The data of 1H and 13C NMR were consistent with those reported in the literature.2

To a vial, palladium(II) acetate (0.24 g, 1.05 mmol) and 1,3-bis(diphenylphosphanyl)propane (0.43 g, 1.05 mmol) were added and then dissolved in dry DMSO (3 mL), the mixture was allowed to stir for 30 min at 23 °C. Then 2-(Trimethylsilyl)-1-naphthyl triflate (3.66 g, 10.5 mmol), N,N-Diisopropylethylamine (7.3 mL,
Diphenyl(1-trimethylsilyl)naphthalen-2-yl)phosphine oxide (1.26 g, 3.15 mmol) in dried toluene (15 mL) was added triethylamine (7.97 mL, 57.2 mmol) and trichlorosilane (6.35 mL, 62.9 mmol) at 23 °C. The mixture was heated to 100 °C and stirred for 3 d. On completion, the reaction mixture was cooled to 23 °C and diluted with 20 mL Et2O. The reaction mixture was quenched with aqueous sodium bicarbonate (10 mL) and brine. After the resulting organic layer was dried over anhydrous MgSO4, the solvent was removed under reduced pressure. The resulting dark red residue was purified by column chromatography with cyclohexane/acetone/Et2N (10/1/0.1) to give white solid as diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphine oxide (2.55 g, 61%). 1H NMR (500 MHz, CD2Cl2): δ 8.12 - 8.04 (m, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.69 - 7.64 (m, 4H), 7.58 - 7.57 (m, 1H), 7.54 - 7.41 (m, 4H), 7.39 - 7.35 (m, 1H), 7.10 - 7.07 (m, 1H), 0.43 (s, 9H). 31P NMR (202 MHz, CD2Cl2): δ 33.26 (s). 13C NMR (126 MHz, CD2Cl2): δ 151.80 (d, J = 13.5 Hz), 132.90 (d, J = 100.6 Hz), 131.12 (d, J = 13.5 Hz), 132.31 (s), 132.23 (s), 131.87 (d, J = 2.8 Hz), 131.62 (d, J = 3.4 Hz), 128.88 (d, J = 1.8 Hz), 128.86 (d, J = 12.0 Hz), 127.80 (d, J = 6.7 Hz), 126.12 (d, J = 35.0 Hz), 3.90 (s). HRMS (ESI): calculated m/z for [C25H25OPSiNa]+; [M+Na]+: 423.1304; found: 423.1295.

**Diphenyl(1-trimethylsilyl)naphthalen-2-yl)phosphine, L2-TMS**

1-(Trimethylsilyl)-2-naphthyl triflate was synthesized according to the literature. A solution of 1-bromonaphthalen-2-ol (2.23 g, 9.70 mmol) and bis(trimethylsilyl)amine (2.04 mL, 9.70 mmol) in THF (30 mL) was refluxed for 1.5 h. The solvent was evaporated under reduced pressure and the pale brown residue was subjected to vacuum to remove excess NH3 and unreacted HMDS. The crude product was dissolved in THF (30 mL), the solution was cooled to -80 °C, and n-butyllithium (4.27 mL, 10.67 mmol, 2.5 M in hexane) was added dropwise to afford a yellow solution. The reaction was stirred for 20 min, then Et2O (30 mL) and trifluoromethanesulfonic anhydride (2.06 mL, 12.13 mmol) dropwise were added. The mixture was stirred at -80 °C for 20 min and then warm to 23 °C in 2 h. Saturated aqueous NaHCO3 was added, the phases were separated, and the aqueous layer was extracted with Et2O. The combined organic layers were dried over anhydrous MgSO4, filtered, and concentrated under reduced pressure affording an orange residue. The residue was purified by column chromatography with cyclohexane to afford a colorless oil (2.50 g, 74%). The data of 1H and 13C NMR were consistent with those reported in the literature.

To a solution of 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (1.46 g, 4.18 mmol), 1,2-Bisdiphenylphosphino)ethane nickel(II) chloride (0.11 g, 0.21 mmol) and zinc (0.82 g, 12.55 mmol) in anhydrous DMF (20 mL) was added chlorodiphenylphosphine (1.61 mL, 8.36 mmol). The reaction mixture was heated to 100-110 °C for 1 day. On completion, the resulting mixture was filtered through Celite, and then the solvent was removed under reduced pressure to give brown residue. The residue was purified by column chromatography under nitrogen with cyclohexane to give white solid as diphenyl(1-(trimethylsilyl)naphthalen-2-yl)phosphine, L2-TMS (0.9 g, 56%). 1H NMR (400 MHz, CD2Cl2): δ 8.40 - 8.33 (m, 1H), 7.81 - 7.75 (m, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.53 - 7.44 (m, 2H), 7.35 - 7.19 (m, 11H), 0.63 (d, J = 2.5 Hz, 9H). 31P NMR (162 MHz, CD2Cl2): δ -4.32 (s). 13C NMR (101 MHz, CD2Cl2): δ 148.75 (d, J = 45.0 Hz), 143.49 (d, J = 15.0 Hz), 139.32 (d, J = 14.1 Hz), 138.24 (d, J = 15.6 Hz), 133.87 (s), 133.81 (s), 133.69 (s), 132.03 (s), 129.74 (d, J = 30.3 Hz), 129.29 (s), 128.99 (s), 128.90 (d, J = 28.8 Hz), 126.72 (s), 125.88 (s), 5.88 (d, J = 13.6 Hz). HRMS (ESI): calculated m/z for [C25H25PSi]+; [M+H]+: 385.1536; found: 385.1528.

**Dicyclohexyl(2-trimethylsilylphenyl)phosphine, L4-TMS**
(2-bromophenyl)dicyclohexylphosphine (508 mg, 1.438 mmol) was dissolved in degassed Et\(_2\)O (10 mL) under argon atmosphere. The reaction flask was cooled to 0 °C and a solution of n-butyllithium (0.581 mL, 1.452 mmol, 2.5 M in hexane) was added dropwise. When the addition was complete, the reaction mixture was stirred at 23 °C for 2 h, then chlorotrimethylsilane (0.203 mL, 1.596 mmol) was added at 0°C. The resulting mixture was gradually warmed to ambient temperature for 3 h and quenched with a saturated aqueous solution of NH\(_4\)Cl (10 mL). The mixture was extracted with Et\(_2\)O (10 mL × 3). The combined organic layers were dried over anhydrous MgSO\(_4\), filtered and evaporated under reduced pressure. The solution was concentrated in vacuo, and the residue was subjected to column chromatography on silica gel with cyclohexane to give a white solid as dicyclohexyl(2-trimethylsilyl)phenylphosphine L\(^{TMS}\) (424 mg, 85 %). \(^1\)H NMR (500 Hz, CD\(_2\)Cl\(_2\)) δ 7.60 - 7.56 (m, 2H), 7.36 - 7.29 (m, 2H), 2.03 - 1.97 (m, 2H), 1.91 - 1.83 (m, 2H), 1.81 - 1.77 (m, 2H), 1.68 - 1.61 (m, 2H), 1.45 - 1.39 (m, 2H), 1.36 - 1.15 (m, 8H), 1.12 - 1.02 (m, 2H), 0.42 (d, \(J = 1.6\) Hz, 9H).

\(^31\)P \(^{1}\)H NMR (162 Hz, CD\(_2\)Cl\(_2\)) δ -50.83 (s).

\(^13\)C NMR (101 MHz, CD\(_2\)Cl\(_2\)) δ 151.43 (d, \(J = 7.1\) Hz), 147.24 (d, \(J = 3.0\) Hz), 146.71 (s), 139.77 (s), 135.25 (d, \(J = 2.3\) Hz), 134.68 (d, \(J = 17.6\) Hz), 128.94 (d, \(J = 1.3\) Hz), 128.87 (d, \(J = 1.6\) Hz), 120.38 (d, \(J = 20.0\) Hz), 110.74 (d, \(J = 4.7\) Hz), 0.94 (d, \(J = 9.8\) Hz). HRMS (MALDI, dcb): calculated m/z for [C\(_{21}\)H\(_{36}\)PSi\(^{TMS}\)]\(^{+}\), [M+H\(^{+}\)]\(^{+}\): 347.2318; found: 347.2309.

\([\text{Di}(2\text{-furyl})][2\text{-trimethylsilyl}])\text{phosphine}, L\(^{5}\)-TMS

A solution of n-butyllithium (2.133 mL, 5.33 mmol, 2.5 M in hexane) was added dropwise into the solution of 2-bromophenyltrimethyliance (1 mL, 5.28 mmol) in THF at -78 °C, then the reaction was stirred at -78 °C for 2 h. Then chlorodifuran-2-ylphosphine (0.831 mL, 5.33 mmol) in THF (5 mL) was added dropwise into the reaction at -78 °C. Then the reaction was warmed to 23 °C overnight. The reaction was quenched by column chromatography (eluent: n-pentane) to afford the (2-bromophenyl)trimethylsilane (5.61 g, 72%). The data of \(^1\)H and \(^13\)C NMR were consistent with those reported in the literature.\(^3\)

A solution of n-butyllithium (2.133 mL, 5.33 mmol, 2.5 M in hexane) was added dropwise into the solution of 2-bromophenyltrimethyliance (1 mL, 5.28 mmol) in THF at -78 °C, then the reaction was stirred at -78 °C for 2 h. Then chlorodifuran-2-ylphosphine (0.831 mL, 5.33 mmol) in THF (5 mL) was added dropwise into the reaction at -78 °C. Then the reaction was warmed to 23 °C overnight. The reaction was quenched by NH\(_4\)Cl saturated solution, extracted with Et\(_2\)O, then washed by brine, dried over anhydrous MgSO\(_4\), purified by column chromatography with cyclohexane to obtain a colourless oil as [di(2-furyl)][2-trimethylsilyl]phosphine, L\(^{5}\)-TMS (1.38 g, 83%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) δ 7.80 - 7.75 (m, 1H), 7.76 - 7.54 (m, 3H), 7.37 - 7.33 (m, 2H), 6.58 - 6.57 (m, 2H), 6.43 - 6.41 (m, 2H), 0.40 (d, \(J = 1.8\) Hz, 9H).

\(^31\)P \(^{1}\)H NMR (162 Hz, CD\(_2\)Cl\(_2\)) δ -50.83 (s).

\(^13\)C NMR (101 MHz, CD\(_2\)Cl\(_2\)) δ 151.43 (d, \(J = 7.1\) Hz), 147.24 (d, \(J = 3.0\) Hz), 146.71 (s), 139.77 (s), 135.25 (d, \(J = 2.3\) Hz), 134.68 (d, \(J = 17.6\) Hz), 128.94 (d, \(J = 1.3\) Hz), 128.87 (d, \(J = 1.6\) Hz), 120.38 (d, \(J = 20.0\) Hz), 110.74 (d, \(J = 4.7\) Hz), 0.94 (d, \(J = 9.8\) Hz). HRMS (MALDI, dcb): calculated m/z for [C\(_{21}\)H\(_{20}\)O\(_2\)PSi\(^{TMS}\)]\(^{+}\), [M+H\(^{+}\)]\(^{+}\): 315.0965; found: 315.0950.

### 2.2 Synthesis of mono gold chloride complex 1a-e

General procedure: The synthesis of mono gold chloride complexes was performed under air atmosphere in the absence of light. The equal amount of Me\(_2\)SAuCl was added into the solution of ortho-silylphosphine ligands (1 equiv) TMS-L\(^{1-5}\) in CH\(_2\)Cl\(_2\), respectively, and then the reaction was stirred for 15 min at 23 °C. (Note: the reaction time cannot last longer than 20 min, otherwise the aurated product would be observed). On completion, the resulting solution was filtered through cotton. The solution was condensed to ca. 1 mL, and layered by n-pentane at 5 °C to obtain white crystals as mono gold chloride complexes 1a-e in yield: 95% for 1a, 89% for 1b, 93% for 1c, 92% for 1d, 90% for 1e (based on gold).

**Diphenyl(2-(trimethylsilyl)phenyl)phosphinegold(I) chloride, (L\(^{1}\)-TMS)AuCl, 1a**

\(^1\)H NMR (400 Hz, CD\(_2\)Cl\(_2\)) δ 7.87 (m, 1H), 7.58 - 7.41 (m, 11H), 7.31 - 7.26 (m, 1H), 6.90 - 6.84 (m, 1H), 0.37 (s, 9H).

\(^31\)P \(^{1}\)H NMR (162 Hz, CD\(_2\)Cl\(_2\)) δ 35.17 (s).

\(^13\)C NMR (101 Hz, CD\(_2\)Cl\(_2\)) δ 146.42 (d, \(J = 24.5\) Hz), 137.38 (d, \(J = 16.1\) Hz), 134.63 (d, \(J = 13.4\) Hz), 134.29 (d, \(J = 9.8\) Hz), 133.70 (d, \(J = 60.1\) Hz), 131.88 (d, \(J = 2.6\) Hz), 130.37 (d, \(J = 2.9\) Hz), 130.02 (d, \(J = 62.3\) Hz), 129.26 (d, \(J = 11.8\) Hz), 128.97 (d, \(J = 9.8\) Hz), 2.95 (d, \(J = 1.2\) Hz). HRMS (MALDI, dcb): calculated m/z for [C\(_{21}\)H\(_{23}\)AuPSiClNa\(^{TMS}\)]\(^{+}\),
Solution, layered with ether, and then extracted with CH

Under Argon atmosphere, for C = 4H), 1.88

[M+Na] +: 589.0553; found: 589.0548. Anal. calcld for C21H23AuClPSi: C, 44.49; H, 4.09; Found: C, 44.66; H, 3.99.

Diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphinegold(I) chloride, (L²-TMS)AuCl, 1b

1H NMR (400 MHz, CD2Cl2): δ 8.03 - 8.01 (m, 1H), 7.95 (dd, J = 8.3, 2.9 Hz, 1H), 7.85 (m, 1H), 7.57 - 7.33 (m, 12H), 6.99 - 6.95 (m, 1H), 0.49 (d, J = 0.5 Hz, 9H). 31P NMR (162 MHz, CDCl3): δ 32.27 (s). 13C NMR (101 Hz, CD2Cl2): δ 153.24 (d, J = 26.8 Hz), 134.59 (d, J = 6.8 Hz), 134.44 (d, J = 7.0 Hz), 133.54 (d, J = 13.1 Hz), 132.70 (d, J = 5.8 Hz), 132.50 (d, J = 84.1 Hz), 131.72 (d, J = 2.6 Hz), 131.63 (d, J = 3.3 Hz), 130.64 (d, J = 61.2 Hz), 129.78 (d, J = 11.7 Hz), 129.28, 127.94 (d, J = 7.9 Hz), 126.86 (s), 126.13 (s), 4.23 (d, J = 1.5 Hz). HRMS (ESI): calculated m/z for [C25H25AuClPSi] +, [M+Na] +: 639.0710, found: 639.0718; [C25H25AuClPSi] +, [M-Cl] -: 581.1123, found: 581.1121. Anal. calcld for C25H25AuClPSi: C, 48.67; H, 4.08; Found: C, 48.52; H, 3.95.

Diphenyl(1-(trimethylsilyl)naphthalen-2-yl)phosphinegold(I) chloride, (L¹-TMS)AuCl, 1c

1H NMR (400 MHz, CD2Cl2): 5.839 - 8.35 (m, 1H), 7.85 - 7.81 (m, 1H), 7.72 - 7.69 (m, 1H), 7.59 - 7.45 (m, 12H), 6.96 (dd, J = 11.5, 8.6 Hz, 1H), 0.58 (d, J = 0.6 Hz, 9H). 31P NMR (162 MHz, CD2Cl2): δ 37.78 (s). 13C NMR (101 Hz, CD2Cl2): δ 150.02 (d, J = 25.0 Hz), 138.66 (d, J = 18.1 Hz), 134.94 (d, J = 13.4 Hz), 134.08 (d, J = 2.6 Hz), 133.44 (d, J = 60.9 Hz), 132.35 (d, J = 2.6 Hz), 131.71 (d, J = 60.9 Hz), 130.40 (d, J = 10.9 Hz), 130.23 (s), 130.09 (d, J = 10.2 Hz), 129.91 (d, J = 11.7 Hz), 129.33 (d, J = 1.4 Hz), 128.09 (s), 126.42 (s), 6.24 (d, J = 2.2 Hz). HRMS (ESI): calculated m/z for [C25H25AuClPSi] +, [M+Na] +: 639.0710, found: 639.0727. Anal. calcld for C25H25AuClPSi: C, 48.67; H, 4.08 C, 48.52; H, 3.95.

Dicyclohexyl(2-(trimethylsilyl)phenyl)phosphinegold(I) chloride, (L⁴-TMS)AuCl, 1d

1H NMR (500 Hz, CD2Cl2): 5.781 - 7.78 (m, 1H), 7.60 - 7.55 (m, 1H), 7.49 - 7.46 (m, 2H), 2.28 - 2.10 (m, 4H), 1.88 - 1.83 (m, 2H), 1.75 - 1.61 (m, 6H), 1.41 - 1.21 (m, 8H), 0.68 (s, 9H). 31P (1H) NMR (203 Hz, CD2Cl2): δ 47.10 (s). 13C NMR (126 Hz, CD2Cl2): δ 147.73 (d, J = 20.7 Hz), 137.46 (d, J = 14.5 Hz), 134.05 (d, J = 52.1 Hz), 133.72 (s), 130.64 (d, J = 2.9 Hz), 129.40 (d, J = 8.5 Hz), 38.89 (s), 31.68 (d, J = 3.1 Hz), 30.58 (s), 27.24 (d, J = 12.8 Hz), 27.08 (d, J = 13.8 Hz), 26.29 (d, J = 1.7 Hz), 4.87 (s). HRMS (MALDI, dcb): calculated m/z for [C21H35AuClPSi] +, [M+Na] +: 601.1492; found: 601.1486. Anal. calcld for C21H35AuClPSi: C, 43.56; H, 6.09; Found: C, 42.59; H, 5.83.

[Di(2-furlyl)][2-(trimethylsilyl)phenyl]phosphinegold(I) chloride, (L⁵-TMS)AuCl, 1e

1H NMR (500 Hz, CD2Cl2): δ 7.92 - 7.78 (m, 3H), 7.54 - 7.50 (m, 1H), 7.41 - 7.39 (m, 1H), 7.15 - 7.10 (m, 1H), 6.98 - 6.96 (m, 2H), 6.60 (dd, J = 3.4, 1.7 Hz, 2H), 0.41 (d, J = 0.5 Hz, 9H). 31P (1H) NMR (203 Hz, CD2Cl2): δ - 5.12 (s). 13C NMR (126 Hz, CD2Cl2): δ 150.24 (d, J = 6.5 Hz), 145.73 (d, J = 27.2 Hz), 143.25 (d, J = 92.5 Hz), 137.61 (d, J = 17.5 Hz), 133.73 (d, J = 10.7 Hz), 132.67 (d, J = 69.6 Hz), 131.18 (d, J = 3.1 Hz), 129.56 (d, J = 10.7 Hz), 125.82 (d, J = 22.0 Hz), 112.21 (d, J = 8.4 Hz), 2.77 (s). HRMS (MALDI, dcb): calculated m/z for [C17H19O2PSi] +, [M-Cl] -: 511.0552; found: 511.0554. Anal. calcld for C17H19AuClPSiO2Si: C, 37.34; H, 3.50; Found: C, 37.32; H, 3.38.

2.3 Synthesis of gold or gold-silver clusters

Synthesis of hexanuclear gold clusters 2a-e [Au6(L)4(SbF6)2] (L = L⁵-⁶):

Under Argon atmosphere, a suspension of 1 equiv of AgSbF6 in methanol was added slowly into the solution of (TMS-L)AuCl (1a-e) in CH2Cl2, the mixture was stirred in absence of light at 23 °C for 30 min. On completion, the resulting yellow solution was evaporated to dry under vacuum, washed with diethyl ether, and then extracted with CH2Cl2, then filtered into a tube through a pad of Celite to obtain yellow solution, layered with diethyl ether for slow diffusion, yellow or pale-yellow crystals can be isolated after several d in yield as 65%(2a), 81%(2b), 52%(2c), 65%(2d), 55%(2e), based on gold.

Hexanuclear gold cluster [Au6(L)₄(SbF₆)₂], 2b
Hexanuclear gold cluster \([\text{Au}(L^3)_4(SbF_6)_2]\), 2c

\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.80 - 7.79 (m, 2H), 7.82 (d, \(J = 8.2\) Hz, 1H), 7.76 - 7.73 (m, 2H), 7.56 - 7.46 (m, 6H), 7.33 - 7.21 (m, 4H). 31P NMR (203 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 48.11 (s). \(^{13}\)C NMR (126 Hz, CD\(_2\)Cl\(_2\)): \(\delta\) 151.24, 150.91, 150.58, 149.36, 149.05, 148.85, 148.78, 135.14, 134.18, 133.88, 133.78, 133.58, 133.27, 132.79, 132.62, 130.61, 130.03, 129.86, 129.62, 129.45, 129.37, 128.97, 128.36, 127.93, 127.48. HRMS (MALDI, dcb): calculated m/z for \([\text{C}_{38}\text{H}_{60}\text{Au}_6\text{SbF}_{12}]^+\), \([M-\text{SbF}_6]^+\): 2663.0917; found: 2663.0861. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 2b in CH\(_2\)Cl\(_2\). Anal. calcd for C\(_{17}\)H\(_{20}\)AuClPSi: C, 36.46; H, 2.23. Found: C, 36.39; H, 2.30.

Hexanuclear gold cluster \([\text{Au}(L^3)_4(SbF_6)_2]\), 2d

\(^1\)H NMR (400 Hz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.89 - 7.86 (m, 2H), 7.68 - 7.62 (m, 2H), 2.66 - 2.52 (m, 2H), 2.16 - 2.08 (m, 2H), 1.99 - 1.83 (m, 7H), 1.80 - 1.70 (m, 2H), 1.49 - 1.27 (m, 6H), 1.20 - 1.05 (m, 3H). \(^{31}\)P \(^1\)H NMR (162 Hz, CD\(_2\)Cl\(_2\)): \(\delta\) 71.50 (s). \(^{13}\)C NMR (101 Hz, CD\(_2\)Cl\(_2\)): \(\delta\) 150.54, 150.21, 150.13, 149.81, 147.89, 147.49, 147.06, 146.48, 133.96, 133.88, 133.49, 133.42, 131.09, 37.06, 36.80, 34.09, 33.79, 32.89, 30.91, 29.78, 29.73, 28.27, 27.01, 26.86, 26.60, 26.52, 26.49, 26.39, 26.13, 25.91, 25.76, 25.52. HRMS (MALDI, dcb): calculated m/z for \([\text{C}_{72}\text{H}_{96}\text{Au}_6\text{SbF}_{12}]^+\), \([M-\text{SbF}_6]^+\): 2509.4018, found 2509.4024. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 2d in CH\(_2\)Cl\(_2\). Anal. calcd for C\(_{17}\)H\(_{20}\)AuClPSi: C, 31.48; H, 3.82. Found: C, 31.50; H, 3.67.
Method ii: 1 equiv of silver oxide $\text{Ag}_2\text{O}$ (18.4 mg, 0.079 mmol) (prepared from the reaction of $\text{AgNO}_3$ and $\text{NaOH}$ in water) was added into the solution of ($\text{TMS-}$1$\text{AuCl}$ (1) (45 mg, 0.079 mmol) in $\text{CH}_2\text{Cl}_2$ (1.2 mL)), the mixture was stirred at 23 °C for 30 min. Then a suspension of 1.5 equiv $\text{AgSbF}_6$ (40.9 mg, 0.119 mmol) in methanol (0.2 mL) was added slow into the mixture. The reaction was stirred for another 5 h in absence of light at 23 °C (monitored by $^{31}$PNMR). On completion, the resulting solution was evaporated to dry under vacuum to obtain the crude product. Yellow block-like crystals 4a can be isolated in 29.5 mg, 59% yield (based on gold) by slow diffusion of diethyl ether into the solution of the crude product in $\text{CH}_2\text{Cl}_2$.

Hexanuclear gold-silver cluster $[\text{Au}_4\text{Ag}_2(\text{L})_4(\text{SbF}_6)_2]$, 3a

Method i: 1 equiv of silver oxide $\text{Ag}_2\text{O}$ (18.4 mg, 0.079 mmol) (prepared from the reaction of $\text{AgNO}_3$ and $\text{NaOH}$ in water) was added into the solution of ($\text{TMS-}$1$\text{AuCl}$ (1a) (45 mg, 0.079 mmol) in $\text{CH}_2\text{Cl}_2$ (1.2 mL)), the mixture was stirred at 23 °C for 30 min. Then a suspension of 1.5 equiv $\text{AgSbF}_6$ (40.9 mg, 0.119 mmol) in acetone (0.3 mL) was added slow into the mixture. The reaction was stirred for another 5 h in absence of light at 23 °C (monitored by $^{31}$PNMR spectroscopy). On completion, the resulting solution was evaporated to dry under vacuum to obtain the crude product. Yellow block-like crystals 3a can be isolated in 36 mg, 72% yield (based on gold) by slow diffusion of diethyl ether into the solution of the crude product in acetone.

Method ii: Crystals of 4a (10 mg) were dissolved in acetone (1.5 mL), and the yellow solution was filtered through cotton, and layered by diethyl ether to diffuse slowly, yellow block like crystals 3a can be obtained in several days (crystals isolated yield in 90 %). $^{1}$H NMR (500 Hz, $\text{CD}_2\text{Cl}_2$): $\delta$ 7.80 - 7.44 (m, 1H), 7.70 - 7.65 (m, 1H), 7.58 - 7.54 (m, 1H), 7.48 - 7.43 (m, 1H), 7.41 - 7.36 (m, 1H), 7.28 - 7.24 (m, 1H). $^{31}$P NMR (162 MHz, $\text{CD}_2\text{Cl}_2$): $\delta$ 3.15 (s). $^{13}$C NMR (126 Hz, $\text{CD}_2\text{Cl}_2$): $\delta$ 78.49, 76.43, 76.34, 76.24, 76.15, 76.07. HRMS (MALDI, dctb): calculated m/z for [C$_{36}$H$_{40}$Au$_3$O$_6$Fe$_2$P$_4$Sb$_4$]$^+$, [M-SbF$_6$]$^+$: 2284.9050, found: 2284.9031.
Hexanuclear gold of crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 3a in acetone. Anal. calcd for C_{17}H_{20}AuCIPSi: C, 34.31; H, 2.24; Found: C, 34.25; H, 2.25.

**Configuration rearrangement between cluster 4a and 3a:**

$$\text{Au}_{12}\text{Ag}_{4}(\text{L}^1\text{O})_2(\text{SbF}_6)_4 \rightarrow \text{Au}_{12}\text{Ag}_{4}(\text{L}^2\text{O})_2(\text{SbF}_6)_4$$

i: Cluster 4a was dissolved in acetone, and the solution was measured by $^{31}$P ($^1$H) NMR spectroscopy. The study $^{31}$P ($^1$H) NMR spectrum showed 4a in acetone fully isomerized into 3a.

ii: After drying 3a under vacuum at 25 °C for 48 h, the yellow colour of the crystals turned into pale beige. $^{31}$P ($^1$H) NMR study showed 3a in CD$_2$Cl$_2$ slowly isomerized into 4a. After storing the solution overnight, ca. 45% conversion was observed.

**Hexadecanuclear Heterometallic Cluster Au$_{12}$Ag$_4$(L$^1$O)$_2$(SbF$_6$)$_4$, 5a**

Trace of 5a was formed in the synthesis of 4a. The yield of 5a can be improved by the method showed in below: To the solution of 1a (85 mg, 0.15 mmol) and Et$_2$N (2 equiv) in CH$_2$Cl$_2$ was added a suspension of 1 equiv AgSbF$_6$ was added into the mixture. The reaction was stirred 25 °C for 0.5 h. On completion, the resulting mixture was evaporated to dry and washed by ethyl ether several times, resulting into white crystalline solid as [(L$^1$-TMS)AuNEt$_3$(SbF$_6$)$_4$] (1a$^+$) (127 mg, 89%, based on gold). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.93 - 7.90 (m, 1H), 7.67 - 7.63 (m, 2H), 7.43 - 7.35 (m, 5H), 6.87 (m, 1H), 3.29 - 3.21 (m, 6H), 1.45 (t, J = 7.2 Hz, 9H), 0.32 (m, 1H). $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): δ 31.61 ppm. $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): δ 146.12, 145.94, 145.92, 138.25, 138.12, 135.05, 134.96, 134.80, 134.69, 133.20, 133.18, 131.81, 131.53, 131.51, 131.33, 130.30, 130.21, 129.94, 129.86, 128.79, 128.28, 54.23, 54.02, 53.80, 53.58, 53.37, 52.39, 52.37, 12.21, 3.01.

To the solution of [(L$^1$-TMS)AuNEt$_3$(SbF$_6$)$_4$] (1a$^+$) (30 mg, 0.035mmol) in CH$_2$Cl$_2$ and 0.2 mL water was added a suspension of 2 equiv AgSbF$_6$ was added into the mixture. The reaction was stirred 25 °C for 24 h. On completion, the resulting suspension was filtered into a tube through a pad of Cellite, then layered with diethyl ether for slow diffusion, resulting into yellow star-like crystals as cluster 5a (8 mg, 47%, based on gold). $^1$H NMR (400MHz, CD$_2$Cl$_2$): δ 8.54 (dd, J = 7.3, 3.2 Hz, 1H), 8.11 (d, J = 7.3 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.65 - 7.50 (m, 10H), 7.36 - 7.28 (m, 4H), 7.20 - 7.12 (m, 2H), 7.02 (d, J = 9.6 Hz, 2H), 6.95 (t, J = 8.9 Hz, 1H), 6.66 (t, J = 8.2 Hz, 3H), 6.57 (dd, J = 13.2, 7.3 Hz, 3H). $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): δ 43.35 (d), 34.97 (s). $^{13}$CNMR (126 MHz, CD$_2$Cl$_2$): δ 147.34, 146.82, 144.42, 144.23, 143.82, 143.67, 141.58, 140.95, 135.90, 135.86, 135.78, 134.69, 134.32, 134.14, 134.03, 134.01, 133.90, 133.58, 133.06, 132.74, 132.65, 132.41, 132.34, 132.27, 131.22, 130.25, 130.22, 130.20, 130.15, 130.11, 129.91, 129.82, 129.76, 128.00, 127.49, 126.12, 125.72, 125.24, 124.74, 123.79, 123.55, 123.31. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 5a in CH$_2$Cl$_2$ and MeOH, which was synthesized by the same method for 5a, using AgNTf$_2$ instead.

**Hexanuclear gold-silver cluster Au$_4$Ag$_2$(L$^2$O)$_2$(SbF$_6$)$_3$**, 3b

S9
1 equiv of silver oxide Ag₂O (13.2 mg, 0.057 mmol) (prepared from the reaction of AgNO₃ and NaOH in water) was added into the solution of (TMS-L²)AuCl (1b) (35 mg, 0.057 mmol) in CH₂Cl₂ (1.2 mL), the mixture was stirred at 23 °C for 30 min. Then a suspension of 1.5 equiv AgSbF₆ (29.2 mg, 0.085 mmol) in acetone (0.3 mL) was added slowly into the mixture. The reaction was stirred for another 0.5 h in absence of light at 23 °C (monitored by ³¹P NMR spectroscopy). On completion, the resulting solution was evaporated to dry under vacuum to obtain the crude product. Yellow block-like crystals 3b can be isolated in 17.5 mg, 49% yield by slow diffusion of diethyl ether into the solution of the crude product in CH₂Cl₂:acetone (v/v = 2/1). ¹H NMR (400 Hz, CD₂Cl₂): δ 7.91 - 7.79 (m, 3H), 7.69 - 7.58 (m, 4H), 7.55 - 7.46 (m, 3H), 7.37 - 7.30 (m, 4H), 7.28 - 7.24 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H). ³¹P NMR (162 MHz, CD₂Cl₂): δ 55.84 (t, J = 4.5 Hz). ¹³C NMR (126 Hz, CD₂Cl₂): δ 154.53, 154.22, 154.02, 153.81, 153.56, 145.51, 145.21, 144.91, 138.93, 138.80, 138.68, 135.81, 134.89, 133.34, 133.30, 133.28, 133.25, 133.22, 132.72, 132.16, 130.81, 130.64, 130.60, 130.58, 130.56, 130.52, 130.48, 130.46, 130.43, 129.94, 129.92, 129.90, 129.87, 129.86, 129.80, 128.99, 128.50, 127.15, 126.72, 126.52, 126.31. HRMS (MALDI, dctb): calculated m/z for [C₁₂₈H₂₀₂Au₃Ag₂Cl₄P₂(SbF₆)₄]: 2484.9682, found: 2484.9682. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 3b in a mixed solvent of CH₂Cl₂ and acetone. Anal. calcd for C₁₁₇H₂₀₂AuCl₂PSi: C, 38.85; H, 2.37. Found: C, 38.95; H, 2.70.

Hexanuclear gold-silver cluster Au₄Ag₂(L³)₄(SbF₆)₂, 4c

1 equiv of silver oxide Ag₂O (15.1 mg, 0.065 mmol) (prepared from the reaction of AgNO₃ and NaOH in water) was added into the solution of (TMS-L²)AuCl (1c) (40.1 mg, 0.065 mmol) in CH₂Cl₂ (1.2 mL), the mixture was stirred at 23 °C for 30 min. Then a suspension of 1 equiv AgSbF₆ (22.3 mg, 0.065 mmol) in methanol (0.2 mL) was added slowly into the mixture and another 1 equiv AgSbF₆ in methanol (0.2 mL) was added after 10 min. The reaction was stirred for 2 h in absence of light at 23 °C (monitored by ³¹PNMR). On completion, the resulting solution was evaporated to dry under vacuum to obtain the crude product. Orange-red plate-like crystals 4c can be isolated in 29.2 mg, 66% yield by slow diffusion of diethyl ether into the solution of the crude product in CH₂Cl₂:acetone (v/v = 2/1). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.09 - 8.05 (m, 2H), 7.97 - 7.93 (m, 1H), 7.89 - 7.82 (m, 3H), 7.71 (d, J = 8.1 Hz, 1H), 7.54 - 7.51 (m, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.12 - 7.08 (m, 2H), 7.00 - 6.95 (m, 2H), 6.80 (t, J = 7.5 Hz, 1H), 6.72 - 6.69 (m, 1H). ³¹P NMR (202 MHz, CD₂Cl₂): δ 40.35(d). ¹³C NMR (126 Hz, CD₂Cl₂): δ 154.76, 154.43, 154.08, 153.80, 153.47, 146.53, 146.00, 142.75, 142.66, 142.57, 134.99, 134.77, 134.72, 134.69, 134.66, 134.63, 134.61, 134.55, 133.53, 133.40, 132.93, 132.88, 132.86, 132.82, 132.79, 132.77, 132.62, 132.16, 130.36, 130.30, 130.26, 130.21, 129.89, 129.71, 129.65, 129.60, 129.57, 129.56, 129.28, 128.93, 128.88, 128.83, 128.27, 128.25, 127.82, 127.65, 127.63, 127.23, 127.21. HRMS (MALDI, dctb): calculated m/z for [C₇₇H₅₆Au₄Ag₂F₆P₂(Sb)₆]: [M-SbF₆]⁺: 2484.9682, found: 2485.0043. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 4c in CH₂Cl₂. Anal. calcd for C₁₁₇H₂₀₂AuCl₂PSi: C, 38.85; H, 2.37. Found: C, 38.95; H, 2.70.

Pentanuclear gold(I) cluster [Au₅(L³)₄(SbF₆)₂], 6
To the solution of (TMS-\(L^3\))AuCl (30 mg, 0.049 mmol) in CH\(_2\)Cl\(_2\) (1.5 mL) was added 1 equiv of silver oxide Ag\(_2\)O (15.3 mg, 0.049 mmol) and 3 equiv of NaSbF\(_6\) (38 mg, 0.146 mmol), the mixture was stirred at 23 °C for 3 h in absence of light. On completion, the resulting suspension was filtered through a pad of Celite, then layered with diethyl ether for slow diffusion, resulting into yellow block crystals as cluster 6 in 69% yield, based on gold. \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 8.21 (d, \(J = 8.3\) Hz, 1H), 7.96 - 7.93 (m, 1H), 7.80 (d, \(J = 8.1\) Hz, 1H), 7.72 - 7.67 (m, 1H), 7.63 - 7.45 (m, 1H), 7.41 - 7.25 (m, 6H), 7.21-7.16 (m, 2H), 7.14 - 7.10 (m, 1H), 6.91 - 6.85 (m, 2H), 6.77 - 6.75 (m, 1H), 6.68-6.63 (m, 1H), 6.58 (dd, \(J = 8.5, 3.2\) Hz, 1H), 5.92 (td, \(J = 8.3, 1.7\) Hz, 1H). \(^{31}\)P NMR (162 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 53.53(s), 42.68(s). \(^{13}\)C NMR (126 Hz, CD\(_2\)Cl\(_2\)): \(\delta\) 154.89, 154.44, 154.17, 151.25, 150.76, 148.85, 148.66, 140.45, 140.24, 135.69, 135.32, 135.21, 134.36, 134.11, 134.00, 133.68, 133.63, 133.49, 133.43, 133.39, 133.33, 133.12, 132.96, 132.66, 132.35, 132.26, 131.76, 131.65, 131.09, 130.98, 130.46, 130.42, 130.37, 130.06, 129.97, 129.89, 129.74, 129.37, 129.20, 129.18, 129.10, 128.94, 128.76, 128.68, 128.33, 128.17, 127.36, 126.72, 126.68, 126.60, 126.34, 124.86, 124.79, 124.40. HRMS (MALDI, dctb): calculated m/z for [C\(_{88\text{H}_{64}Au_4P_3}]^+$, [M-(SbF\(_6\))]\(^+\): 2229.2281, found:2229.2301. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 6 in CH\(_2\)Cl\(_2\). Anal. calcd for C\(_{17}\)H\(_20\)AuCIPSi: C, 42.86; H, 2.62; Found: C, 42.96; H, 2.73.

**Pentanuclear gold-silver cluster[Au\(_4\)Ag(L\(^3\))\(_4\)(SbF\(_6\))]**, 7

1 equiv of silver oxide Ag\(_2\)O was added into the solution of (TMS-\(L^3\))AuCl (1c), the mixture was stirred for 30 min. Then a solution of 0.25 equiv of AgSbF\(_6\) in methanol was added dropwise into the suspension. The reaction mixture was stirred overnight in absence of light. Then the resulting suspension was filtered through a pad of Celite to obtain yellow solution, and then the filter was condensed, and then layered with diethyl ether for slow diffusion, resulting into yellow plate-like crystals as cluster 7 in yield of 57%, based on gold. \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 8.31 (d, \(J = 8.3\) Hz, 1H), 7.67 (t, \(J = 6.9\) Hz, 1H), 7.54 - 7.39 (m, 6H), 7.30 - 7.17 (m, 3H), 7.04 (dd, \(J = 12.1, 7.2\) Hz, 2H), 6.88 - 6.80 (m, 2H), 6.17 (t, \(J = 8.4\) Hz, 1H). \(^{31}\)P NMR (162 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 142.53, 142.29, 135.27, 135.13, 134.48, 133.79, 133.72, 133.39, 133.23, 132.87, 131.56, 131.33, 130.34, 129.88, 129.18, 128.23, 127.93, 127.86, 127.70, 127.64, 127.58, 127.53, 127.13, 125.70, 53.96, 53.68, 53.42, 53.15, 52.88. HRMS (MALDI, dctb): calculated m/z for [C\(_{88\text{H}_{64}Au_4AgP_3}]^+$, [M-(SbF\(_6\))]\(^+\): 2141.1686, found:2141.1606. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 7 in CH\(_2\)Cl\(_2\). Anal. calcd for C\(_{17}\)H\(_20\)AuCIPSi: C, 44.47; H, 2.71; Found: C, 44.35; H, 2.83.

**Dinuclear gold(I) complex [Au\(_2\)(μ-1-C\(_{10}\)H\(_{12}\)PPh\(_2\))]**, 8

To the solution of (TMS-\(L^3\))AuCl (1c) (30 mg, 0.049 mmol) in CH\(_2\)Cl\(_2\) (1.5 mL) was added 1 equiv of AgOAc (8.1 mg, 0.049 mmol) in methanol (0.5 mL) and the mixture was stirred at 23 °C for 1.5 h. On
completion, the resulting suspension was filtered into a tube through a pad of Celite. Then several drops of diethyl ether were added into the colorless solution, white plate-like crystals of 8 in 50% yield (based on gold) can be isolated after slow evaporation for several days. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.64 - 8.60 (m, 1H), 7.80 - 7.77 (m, 1H), 7.63 - 7.60 (m, 3H), 7.49 - 7.41 (m, 7H), 7.26 - 7.21 (m, 2H), 7.14 - 7.09 (m, 2H). $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): δ 39.43 (s). $^{13}$C NMR (126 Hz, CD$_2$Cl$_2$): δ 187.26, 186.93, 186.65, 186.37, 186.04, 141.80, 141.69, 141.59, 138.28, 138.23, 137.70, 137.65, 137.24, 134.35, 134.23, 134.12, 134.07, 134.01, 133.91, 133.61, 133.48, 132.95, 132.89, 132.73, 132.70, 132.54, 132.48, 131.93, 131.85, 130.55, 130.40, 129.13, 129.07, 129.01, 128.96, 128.84, 128.80, 128.76, 128.64, 128.50, 128.40, 128.03, 127.95, 127.76, 126.94, 125.98, 125.96, 125.93, 125.13. HRMS (ESI): calculated m/z for [C$_{44}$H$_{33}$Au$_2$P$_2$]$,^+$, [M+H]$^+$: 1017.1383, found: 1017.1397. Suitable crystals for X-ray diffraction analysis were obtained from the slow diffusion of diethyl ether into a solution of 8 in CH$_2$Cl$_2$.

Oxonium trigold cluster [OAu$_3$(TMS-$^1$L)$_3$](SbF$_6$)$_3$ 9

Method i: 1 equiv of silver oxide (prepared from AgNO$_3$ and NaOH in water) and 1 equiv of NaSbF$_6$ were added into the solution of (L-$^1$-TMS)AuCl (1a) (45 mg, 0.079 mmol) in CH$_2$Cl$_2$, the mixture was stirred at 23 °C for 3 h in absence of light. On completion, the resulting mixture was filtered through a pad of Celite to afford colourless solution, and then evaporated to dry to obtain white solid as oxonium trigold cluster [OAu$_3$(L-$^1$-TMS)]$_3$(SbF$_6$)$_3$ (9a) (46 mg, 94 %, based on gold), and the white solid has been confirmed by NMR and mass spectrometry.

Method ii: 1 equiv of silver oxide Ag$_2$O (prepared from the reaction of AgNO$_3$ and NaOH in water) was added into the solution of (L-$^1$-TMS)AuCl (1a) in CH$_2$Cl$_2$, the mixture was stirred at 23 °C for 30 min. Then a suspension of one equiv AgSbF$_6$ in methanol was added slowly into the mixture. After addition, the reaction mixture was filtered immediately through a pad of Celite to afford colourless solution, and then evaporated to dry to obtain white solid 9a. DFT-optimized structure was shown in below.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.86 - 7.83 (m, 1H), 7.53 - 7.46 (m, 3H), 7.40 - 7.25 (m, 9H), 6.83 - 6.78 (m, 1H), 0.30 (s, 9H). $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): 26.83 (s). $^{13}$C NMR (101 Hz, CD$_2$Cl$_2$): δ 146.70 (d, J = 24.0 Hz), 138.10 (d, J = 16.0 Hz), 134.97 (d, J = 13.0 Hz), 134.91 (d, J = 10.1 Hz), 133.80 (d, J = 61.1 Hz), 132.63 (s), 131.18 (s), 130.37 (d, J = 65.7 Hz), 130.01 - 129.72 (m), 129.70 (d, J = 10.0 Hz). HRMS (ESI): calculated m/z for [C$_{63}$H$_{69}$Au$_3$OP$_3$Si$_3$]$,^+$, [M-SbF$_6$]$^+$: 1609.2861, found:1609.2849.

Oxonium trigold cluster [OAu$_3$(TMS-$^4$L)$_3$](BF$_4$)$_3$, 9d
1 equiv of silver oxide (prepared from AgNO₃ and NaOH in water) and 1 equiv of NaBF₄ were added into the solution of (L⁴-TMS)AuCl (30 mg, 0.052 mmol) in CH₂Cl₂, the mixture was stirred at 23 °C for 3 h in absence of light. On completion, the resulting mixture was filtered through a pad of Celite to afford colourless solution, and then evaporated to dry to obtain white solid as oxoni trigold cluster [OAu₃(L⁴-TMS)](BF₄) (26 mg, 80 %, based on gold), and the white solid has been confirmed by NMR and mass spectrometry. Suitable colourless crystals for X-ray analysis was obtained by slow diffusion of hexane into the solution of cluster 9d in CH₂Cl₂ at -20 °C. HRMS (ESI): calculated m/z for [C₆₃H₁₀₅Au₃OP₃Si₃]⁺, [M-BF₄]⁺: 1645.5678, found: 1645.5733; calculated m/z for [BF₄]⁻: 87.0035, found: 87.0027. [OAu₃(L⁴-TMS)](SbF₆) or [OAu₃(L⁴-TMS)](OTf) can be isolated by using NaSbF₆ or NaOTf instead, and have been confirmed by HRMS (ESI): calculated m/z for [C₆₃H₁₀₅Au₃OP₃Si₃]⁺, [M-SbF₆]⁺: 1645.5678, found: 1645.5643; calculated m/z for [SbF₆]⁻: 234.8942, found: 234.8948; calculated m/z for [C₆₃H₁₀₅Au₃OP₃Si₃]⁺, [M-OTf]⁻: 1645.5678, found: 1645.5671; calculated m/z for [OTf]⁻: 148.9527, found: 148.9527.

3. Study of interaction between clusters and solvents/substrates by NMR spectroscopy

3.1 Interaction between gold or gold-silver clusters with acetonitrile

Acetonitrile (12 µL, 0.292 mmol) was added into the solution of gold or gold-silver clusters (0.5 mol%) in CH₂Cl₂ (0.4 mL) at 23 °C. Then the mixture was monitored immediately after the addition of acetonitrile into the gold or gold-silver clusters (0.5 mol%) in CH₂Cl₂ by ³¹P NMR spectroscopy, the records were keeping for 0.5 h, and each measurement is proceeded in the time interval of 2 min.

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Fig. S3.1 ³¹P NMR spectra of the interaction between 2a and acetonitrile in CH₂Cl₂.
Fig. S3.2 $^{31}$P NMR spectra of the interaction between 4a and acetonitrile in CH$_2$Cl$_2$. Note: The last $^{31}$P NMR spectrum corresponds to the recovered product by recrystallization from Et$_2$O and CH$_2$Cl$_2$. The $^{31}$P NMR signal of the sixteenth line at 52.15 ppm indicates the formation of 3a.

Fig. S3.3 $^{31}$P NMR spectra of the interaction between 3b and acetonitrile in CD$_2$Cl$_2$. Note: The last $^{31}$P NMR spectrum corresponds to the recovered product 3b by recrystallization from Et$_2$O and CD$_2$Cl$_2$. 
**Fig. S3.4** $^{31}$P NMR spectra of the interaction between 4c and acetonitrile in CD$_2$Cl$_2$.

**Fig. S3.5** $^{31}$P NMR spectra of the interaction between 6 and acetonitrile in CD$_2$Cl$_2$. Note: The last $^{31}$P NMR spectrum corresponds to the recovered product by recrystallization.
3.2 Interaction between 2a and 1,3,5-trimethoxybenzene

1,3,5-trimethoxybenzene (18 mg, 0.107 mmol) was added into the solution of 2a (2 mol%) in CD$_2$Cl$_2$ (0.4 mL) at 23 °C. The mixture was measured by NMR spectroscopy, which did not show any signal change.

Fig. S3.6 $^{31}$P NMR spectra of the interaction between 7 and acetonitrile in CD$_2$Cl$_2$. Note: The last $^{31}$P NMR spectrum corresponds to the recovered product by recrystallization.

Fig. S3.7 $^1$H NMR spectra of (1) 2a in CD$_2$Cl$_2$; (2) the mixture of 2a and 1,3,5-trimethoxybenzene in CD$_2$Cl$_2$. 
3.3 Interaction between 4a and 1,3,5-trimethoxybenzene

1,3,5-trimethoxybenzene (18 mg, 0.107 mmol) was added into the solution of 4a (2 mol%) in CD₂Cl₂ (0.4 mL) at 23 °C. The mixture was measured by NMR spectroscopy immediately (1) and after keeping it overnight (2). As observed in Figure S3.8, 4a can partially rearranged into 3a through the interaction with 1,3,5-trimethoxybenzene.

Fig. S3.8 ³¹P NMR and ¹H NMR spectra of (1) the mixture of 1,3,5-trimethoxybenzene and 4a in CD₂Cl₂ measured immediately; (2) measured after keeping it overnight.
3.4 Interaction between 3a and 1,3,5-trimethoxybenzene

1,3,5-trimethoxybenzene (18 mg, 0.107 mmol) was added into the solution of catalytically amount of 3a (2 mol%) in CD$_2$Cl$_2$ (0.4 mL) at 23 °C. The mixture was measured by NMR spectroscopy immediately (1) and after keeping it overnight (2). As observed in Figure S3.8, 4a in CD$_2$Cl$_2$ in the presence of 1,3,5-trimethoxybenzene can partially rearrange into 3a.

Fig. S3.9 $^{31}$P NMR and $^1$H NMR spectra of (1) 3a in CD$_2$Cl$_2$ measured immediately; (2) measured after keeping it overnight.
3.5 Interaction between 2a and phenylacetylene

Phenylacetylene (27 µL, 0.245 mmol) was added into the solution of 2a (2.5 mol%) in CD₂Cl₂ (0.4 mL) at 23 °C. As shown in Figure S3.10, obvious signal shifts can be observed in the NMR spectra. By recrystallization, hexagold cluster 2a can be quantitatively recovered from the mixture of phenylacetylene and 2a.

Fig. S3.10 ³¹P NMR and ¹H NMR spectra of (1) the mixture 2a and phenylacetylene in CD₂Cl₂; (2) 2a in CD₂Cl₂. (Note: the minor peak at 6.8 ppm is from the impurity in phenylacetylene.)
3.6 Interaction between 4a and phenylacetylene

Phenylacetylene (13 µL, 0.117 mmol) was added into the solution of catalytically amount of 4a (2 mol%) in CD$_2$Cl$_2$ (0.4 mL) at 23 °C. As shown in FigureS3.11, the spectra of 4 showed 4a partially rearranged into 3a and trace decomposition can be observed overnight.

![Fig. S3.11](image)

3.7 Interaction between 3a and phenylacetylene

Phenylacetylene (13 µL, 0.117 mmol) was added into the solution of catalytically amount of 3a (2 mol%) in CD$_2$Cl$_2$ (0.4 mL) at 23 °C. The mixture was measured by NMR spectroscopy. As shown in FigureS3.12, the spectra of 4 showed 3a partially rearranged into 4a and trace decomposed species was observed after storing for overnight.
Fig. S3.12 $^{31}$P NMR spectra of (1) 3a in CD$_2$Cl$_2$, (2) the mixture of 3a and phenylacetylene in CD$_2$Cl$_2$ measured immediately; (3) measured after 30 min, (4) measured after keeping it overnight.

3.8 Interaction between 4a/3a and methanol

Methanol (20 equiv, 2 µL, 0.05 mmol) was added into the solution of 4a (5.4 mg, 0.002 mmol) in CD$_2$Cl$_2$ (0.4 mL) at 23 ºC. The mixture was measured by NMR spectroscopy. As shown in Figure S3.13, 11a in CD$_2$Cl$_2$ in the presence of MeOH can partially transformed into 3a. As shown in Figure S3.14, minor shift can be observed from the interaction of 3a with methanol.
**Fig. S3.13** $^{31}$P NMR and $^1$H NMR spectra of (1) 4a in CD$_2$Cl$_2$, (2) addition of MeOH to 4a in CD$_2$Cl$_2$ after 2.5 h, (3) addition of MeOH into 4a in CD$_2$Cl$_2$ after 20 h, (4) 3a in CD$_2$Cl$_2$ and MeOH.
**Fig. S3.14** $^{31}$P NMR and $^1$H NMR spectra of (1) 3a in CD$_2$Cl$_2$, (2) addition of MeOH to 3a in CD$_2$Cl$_2$. 
4. General procedure for addition of nucleophiles to 1,6-enynes, scope and kinetic studies

4.1 General procedure

In the glovebox, to the solution of 1,6-enyne (0.07 mmol) and nucleophile (NuH, 2 equiv) in CD$_2$Cl$_2$ (0.4 mL), the catalyst was added. The reaction mixture was stirred at 25 °C and monitored by TLC. On completion, the solvent was evaporated and then the yield of product was determined by $^1$H NMR spectroscopy.

Table S4. Nucleophilic addition of 1,3,5-trimethoxybenzene (NuH) to 1,6-enyne 10 using gold/gold-silver species

| Entry | Catalyst (mol %) | Additive (mol %) | Time (h) | Product (yield, %)$^a$ |
|-------|------------------|------------------|----------|-----------------------|
| S1    | 2a (0.05%)       | -                | 8        | 63 %$^b$              |
| S2    | 2e (0.05%)       | -                | 8        | 48 %$^b$              |
| S3    | CAT-1 (1%)       | -                | 12       | trace                 |
| S4    | CAT-2 (1%)       | -                | 12       | 6%                    |
| S5    | CAT-3 (1%)       | -                | 12       | 0                     |
| S6    | CAT-4 (1%)       | -                | 12       | 0                     |
| S7    | CAT-4 (1%)       | NaBAR$_4$ (10%)  | 12       | 50%                   |
| S8    | PPh$_3$AuCl (3 mol%)/AgSbF$_6$ (3 mol%) | - | 1 | 68% |
| S9    | PPh$_3$AuCl (0.3 mol%)/AgSbF$_6$ (0.3 mol%) | - | 1 | 47% |
| S10   | NaBAR$_4$ (10%)  |                  |          | N.R.                  |

$^a$ Conversion and the product ratios were determined by $^1$H NMR spectroscopy, 1,4-diacetylbenzene was used as internal standard added after the reaction; $^b$ yield of isolated product; $^c$ 80 °C, DCE as solvent.

Scheme S4.1 CAT-1 [Au$_{16}$C]: [Au$_{16}$[PPh$_3$]$_{16}$ (C)][SbF$_6$]$_2$, CAT-2 [Au$_{16}$Ag$_2$C]: [Au$_{16}$Ag$_2$(dppy)$_8$ (C)][SbF$_6$]$_4$, CAT-3 nano-[Au$_8$]: [Au$_8$(L)$_8$](NO$_3$)$_2$ (L = (PPh$_2$(C$_6$H$_4$Me-p))), CAT-4 [Au$_{13}$]: [Au$_{13}$(dppe)$_8$]Cl$_2$Cl$_3$. S24
4.2 Kinetic studies by NMR spectroscopy

To a solution of 1,6-enyne 10 (0.07 mmol), 1,3,5-trimethoxybenzene (2 equiv) and 1,3,5-tris(trifluoromethyl)benzene (internal standard, 0.33 equiv) in CD$_2$Cl$_2$ (0.3 mL), the solution of catalyst in CD$_2$Cl$_2$ (0.1 mL) was added. The reaction mixture was measured immediately and kept being monitored by $^1$H NMR spectroscopy for 8 h (time interval of 2 min), and the final yield of 11a was determined after 12 h or 24 h of the reaction. During the first several h of the reactions, $^{31}$P NMR spectra were monitored (showed in below, X axis: the frequency of $^{31}$P signal, Y axis: the number of records, each spectrum is measured in the time interval of 2 min corresponding to the $^1$H NMR spectrum).

![Kinetic studies by NMR spectroscopy](image)

**Fig. S 4.1** Kinetic studies of the addition of 1,3,5–trimethoxybenzene to a 1,6–enyne reactions with clusters 2a-e, 4a, 3a, 5a. Top–right insertion: final $^{31}$P NMR spectrum of the reaction with cluster 2c.

![31P NMR spectra of reaction with catalyst 2a during the first 3 h.](image)
Fig. S 4.3 $^{31}$P NMR spectra of reaction with catalyst 2b during the first 2.5 h.

Fig. S 4.4 $^{31}$P NMR spectra of reaction with catalyst 2c during the first 2.5 h.
Fig. S 4.5 $^{31}$P NMR spectra of reaction with catalyst $2e$ during the first 2.5 h.

Fig. S 4.6 $^{31}$P NMR spectra of reaction with catalyst $4a$ during the first 5 h.
Fig. S 4.7  $^{31}$P NMR spectra of reaction with catalyst 3a during the first 5 h.

Fig. S 4.8  $^{31}$P NMR spectra of the reaction with catalyst 3b during the first 2.5 h.
Fig. S 4.9 $^{31}$P NMR spectra of reaction with catalyst 4c during the first 5 h.

Fig. S 4.10 $^{31}$P NMR spectra of the reaction with 6/NaBAR$_{4}$ during the first 6 h.
Fig. S 4.11 a) kinetics on nucleophilic addition to 1,6-ene by using 5a (0.5 mol%); b) 31P NMR spectra of the reaction after 1 h and 2 h (signals at 41.46(br) and 33.07(s) are from cluster 5a).

5. General procedure for the formation of indenes from 7-phenylethynyl cycloheptatriene 12[4]

To a solution of 7-alkynyl cycloheptatriene 12 (0.052 mmol) in CD2Cl2 (0.3 mL), the catalyst was added. The reaction was stirred at 25 °C and monitored by TLC to show the conversion. Then the resulting mixture was filtered through Celite, the solvent was evaporated and the crude yield was assessed by 1H NMR analysis (DCls, 1,4-diacetylbenzene used as internal standard).

Table S5: Catalytic studies of various gold/gold-silver species on cycloisomerization of 7-alkynyl cycloheptatrienes

| Entry | Catalyst (2.5 mol%) | Additive (mol%) | Time | Conversion (%) | 13a/13b (ratio) |
|-------|---------------------|----------------|------|---------------|-----------------|
| S1    | 2a                  | -              | 8 h  | >99 %         | 50:50           |
| S2    | 2b                  | -              | 8 h  | >99 %         | 63:37           |
| S3    | 2c                  | -              | 8 h  | >99 %         | 63:37           |
| S4    | 2e                  | -              | 3 h  | >99 %         | 55:45           |
| S5    | 4a                  | -              | 6 h  | >99 %         | 61:39           |
| S6    | 3a                  | -              | 6 h  | >99 %         | 61:39           |
| S7    | 3b                  | -              | 8 h  | 64 %          | 36:28           |
| S8    | 4c                  | -              | 8 h  | >99 %         | 59:41           |
| S9    | 6                   | -              | 15 h | trace         | -               |
| S10   | 7                   | -              | 15 h | trace         | -               |
| S11   | 8                   | -              | 0    | 0             | -               |
a) Conversion and the product ratio were determined by $^1$H NMR spectroscopy (diphenylmethane was used as internal standard).

6. Procedure for [4+2] cycloaddition of 1,6-enyne 14$^{[5]}$

To a solution of 1,6-enyne 14 in 1,2-dichloroethane, the catalyst was added. The reaction was stirred at 60 °C for 12 h, then the solvent was evaporated, and the crude yield was assessed by $^1$H NMR analysis (CDCl$_3$, 1,4-diacetylbenzene as internal standard).

**Table S6: [4+2] cycloaddition of 14 catalyzed by 2a, 2e and 4a**

| Entry | Catalyst (mol %) | Time, h | Temp.(°C) | Conversion (%)$^a$ |
|-------|------------------|---------|-----------|-------------------|
| S1    | 2a (2 %)         | 12      | 25        | 5 %               |
| S2    | 2e (2 %)         | 48      | 65        | 75 %              |
| S3    | 4a (1 %)         | 12      | 60        | 3 %               |

a) Conversion and the product ratios were determined by $^1$H NMR spectroscopy (1,4-diacetylbenzene as internal standard).

![Fig. S6.1 $^{31}$P NMR spectrum of the reaction in Table S6 entry S2 after completion of the reaction.](image)
7. Photophysical spectra of gold and gold-silver clusters

**Fig. 7.1** UV-vis absorption spectrum of 1a in CH$_2$Cl$_2$

**Fig. 7.2** UV-vis absorption spectrum of 1b in CH$_2$Cl$_2$

**Fig. 7.3** UV-vis absorption spectrum of 1c in CH$_2$Cl$_2$
Fig. 7.4 UV-vis absorption spectrum of 1d in CH₂Cl₂

Fig. 7.5 UV-vis absorption spectrum of 1e in CH₂Cl₂

Fig. 7.6 UV-vis absorption spectrum of 2a in CH₂Cl₂
Fig. 7.7 UV-vis absorption spectrum of 2b in CH₂Cl₂

Fig. 7.8 UV-vis absorption spectrum of 2c in CH₂Cl₂

Fig. 7.9 UV-vis absorption spectrum of 2d in CH₂Cl₂
Fig. 7.10 UV-vis absorption spectrum of 2e in CH₂Cl₂

Fig. 7.11 UV-vis absorption spectrum of 4a in CH₂Cl₂

Fig. 7.12 UV-vis absorption spectrum of 3a in CH₂Cl₂
Fig. 7.13 UV-vis absorption spectrum of 3b in CH$_2$Cl$_2$

Fig. 7.14 UV-vis absorption spectrum of 4c in CH$_2$Cl$_2$

Fig. 7.15 UV-vis absorption spectrum of 6 in CH$_2$Cl$_2$
Fig. 7.16 UV-vis absorption spectrum of 7 in CH$_2$Cl$_2$

Fig. 7.17 UV-vis absorption spectrum of 8 in CH$_2$Cl$_2$

Fig. 7.18 UV-vis absorption spectrum of 5a in CH$_2$Cl$_2$
Fig. 7.19 UV-vis absorption spectrum of 5a⁻ in CH₂Cl₂

8. Thermogravimetric analysis of 2a, 2e, 4a, 3a

Fig. S8.1 Thermogravimetric analysis of 2a.
Fig. S8.2 Thermogravimetric analysis of 2e.

Fig. S8.3 Thermogravimetric analysis of 4a.
Fig. S8.4 Thermogravimetric analysis of 3a.

9. NMR characterisation

Fig. S9.1 $^{31}$P NMR spectrum of diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphine oxide in CD$_2$Cl$_2$. 
Fig. S9.2 $^1$H NMR spectrum of diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphine oxide in CD$_2$Cl$_2$

Fig. S9.3 $^{13}$C NMR spectrum of diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphine oxide in CD$_2$Cl$_2$
Fig. S9.4 $^1$H-$^1$H COSY spectrum of diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphine oxide in CD$_2$Cl$_2$

Fig. S9.5 $^1$H-$^{13}$C HSQC spectrum of diphenyl(2-(trimethylsilyl)naphthalen-1-yl)phosphine oxide in CD$_2$Cl$_2$
Fig. S9.6 $^{31}$P NMR spectrum of L$^2$-TMS in CD$_2$Cl$_2$

Fig. S9.7 $^1$H NMR spectrum of L$^2$-TMS in CD$_2$Cl$_2$
Fig. S9.8 $^{13}$C NMR spectrum of L$^2$-TMS in CD$_2$Cl$_2$

Fig. S9.9 $^1$H-$^1$H COSY spectrum of L$^2$-TMS in CD$_2$Cl$_2$
Fig. S9.10 $^1$H-$^{13}$C HSQC spectrum of L$^2$-TMS in CD$_2$Cl$_2$

Fig. S9.11 $^{31}$P NMR spectrum of L$^3$-TMS in CD$_2$Cl$_2$
Fig. S9.12 $^1$H NMR spectrum of $L^3$-TMS in $CD_2Cl_2$

Fig. S9.13 $^{13}$C NMR spectrum of $L^3$-TMS in $CD_2Cl_2$
Fig. S9.14 $^1$H-$^1$H COSY spectrum of L$^3$-TMS in CD$_2$Cl$_2$

Fig. S9.15 $^1$H-$^{13}$C HSQC spectrum of L$^3$-TMS in CD$_2$Cl$_2$
Fig. S9.16 $^3$P NMR spectrum of L$^4$-TMS in CD$_2$Cl$_2$

Fig. S9.17 $^1$H NMR spectrum of L$^4$-TMS in CD$_2$Cl$_2$
Fig. S9.18 $^{13}$C NMR spectrum of $L^4$-TMS in CD$_2$Cl$_2$

Fig. S9.19 COSY spectrum of $L^4$-TMS in CD$_2$Cl$_2$
Fig. S9.20 $^1$H-$^{13}$C HSQC spectrum of $\text{L}^4$-TMS in CD$_2$Cl$_2$

Fig. S9.21 $^{31}$P NMR spectrum of $\text{L}^5$-TMS in CD$_2$Cl$_2$
Fig. S9.22 $^1$H NMR spectrum of $L^5$-TMS in CD$_2$Cl$_2$

Fig. S9.23 $^{13}$C NMR spectrum of $L^5$-TMS in CD$_2$Cl$_2$
Fig. S9.24 $^1$H-$^1$H COSY spectrum of L$^5$-TMS in CD$_2$Cl$_2$

Fig. S9.25 $^1$H-$^{13}$C HSQC spectrum of L$^5$-TMS in CD$_2$Cl$_2$
Fig. S9.26 $^{31}$P NMR spectrum of complex 1a in CD$_2$Cl$_2$.

Fig. S9.27 $^1$H NMR spectrum of complex 1a in CD$_2$Cl$_2$. 
Fig. S9.28 $^{13}$C NMR spectrum of complex 1a in CD$_2$Cl$_2$

Fig. S9.29 $^1$H-$^1$H COSY spectrum of complex 1a in CD$_2$Cl$_2$
Fig. S9.30 $^1$H-$^{13}$C HSQC spectrum of complex 1a in CD$_2$Cl$_2$

Fig. S9.31 $^{31}$P NMR spectrum of complex 1b in CD$_2$Cl$_2$
Fig. S9.32 $^1$H NMR spectrum of complex 1b in CD$_2$Cl$_2$

Fig. S9.33 $^{13}$C NMR spectrum of complex 1b in CD$_2$Cl$_2$
Fig. S9.34 $^1$H-$^1$H COSY spectrum of complex 1b in CD$_2$Cl$_2$

Fig. S9.35 $^1$H-$^{13}$C HSQC spectrum of complex 1b in CD$_2$Cl$_2$
Fig. S9.36 $^{31}$P NMR spectrum of complex 1c in CD$_2$Cl$_2$

Fig. S9.37 $^1$H NMR spectrum of complex 1c in CD$_2$Cl$_2$
Fig. S9.38 $^{13}$C NMR spectrum of complex 1c in CD$_2$Cl$_2$

Fig. S9.39 $^1$H-$^1$H COSY spectrum of complex 1c in CD$_2$Cl$_2$
Fig. S9.40 $^1$H-$^{13}$C HSQC spectrum of complex 1c in CD$_2$Cl$_2$

Fig. S9.41 $^{31}$P NMR spectrum of complex 1d in CD$_2$Cl$_2$
Fig. S9.42 $^1$H NMR spectrum of complex 1d in CD$_2$Cl$_2$

Fig. S9.43 $^{13}$C NMR spectrum of complex 1d in CD$_2$Cl$_2$
**Fig. S9.44** $^1$H-$^1$H COSY spectrum of complex 1d in CD$_2$Cl$_2$

**Fig. S9.45** $^1$H-$^{13}$C HSQC spectrum of complex 1d in CD$_2$Cl$_2$
Fig. S9.46 $^{31}$P NMR spectrum of complex 1e in CD$_2$Cl$_2$

Fig. S9.47 $^1$H NMR spectrum of complex 1e in CD$_2$Cl$_2$
Fig. S9.48 $^{13}$C NMR spectrum of complex 1e in CD$_2$Cl$_2$

Fig. S9.49 $^1$H-$^1$H COSY spectrum of complex 1e in CD$_2$Cl$_2$
**Fig. S9.50** $^1$H-$^{13}$C HSQC spectrum of complex 1e in CD$_2$Cl$_2$

**Fig. S9.51** $^{31}$P NMR spectrum of cluster 2b in CD$_2$Cl$_2$
Fig. S9.52 $^1$H NMR spectrum of cluster 2b in CD$_2$Cl$_2$

Fig. S9.53 $^{13}$C NMR spectrum of cluster 2b in CD$_2$Cl$_2$
Fig. S9.54 $^1$H-$^1$H COSY spectrum of cluster 2b in CD$_2$Cl$_2$

Fig. S9.55 $^1$H-$^{13}$C HSQC spectrum of cluster 2b in CD$_2$Cl$_2$
Fig. S9.56 $^{31}$P NMR spectrum of cluster $2c$ in CD$_2$Cl$_2$

Fig. S9.57 $^1$H NMR spectrum of cluster $2c$ in CD$_2$Cl$_2$
**Fig. S9.58** $^{13}$C NMR spectrum of cluster 2c in CD$_2$Cl$_2$

$^{13}$C NMR DEPTQ135 Experiment

**Fig. S9.59** $^{13}$C NMR DEPTQ135 spectrum of cluster 2c in CD$_2$Cl$_2$
Fig. S9.60 $^1$H-$^1$H COSY spectrum of cluster 2c in CD$_2$Cl$_2$

Fig. S9.61 $^1$H-$^{13}$C HSQC spectrum of cluster 2c in CD$_2$Cl$_2$
Fig. S9.62 $^{31}$P NMR spectrum of cluster 2d in CD$_2$Cl$_2$

Fig. S9.63 $^1$H NMR spectrum of cluster 2d in CD$_2$Cl$_2$
Fig. S9.64 $^{13}$C NMR spectrum of cluster 2d in CD$_2$Cl$_2$

Fig. S9.65 $^1$H-$^1$H COSY spectrum of cluster 2d in CD$_2$Cl$_2$
Fig. S9.66 $^1$H-$^{13}$C HSQC spectrum of cluster 2d in CD$_2$Cl$_2$

Fig. S9.67 $^{31}$P NMR spectrum of cluster 2e in CD$_2$Cl$_2$
Fig. S9.68 $^1$H NMR spectrum of cluster 2e in CD$_2$Cl$_2$

Fig. S9.69 $^{13}$C NMR spectrum of cluster 2e in CD$_2$Cl$_2$
Fig. S9.70 $^1$H-$^1$H COSY spectrum of cluster 2e in CD$_2$Cl$_2$

Fig. S9.71 $^1$H-$^{13}$C HSQC spectrum of cluster 10 in CD$_2$Cl$_2$
**Fig. S9.72** $^{31}$P NMR spectrum of cluster 4a in CD$_2$Cl$_2$

**Fig. S9.73** $^1$H NMR spectrum of cluster 4a in CD$_2$Cl$_2$
Fig. S9.74 $^{13}$C NMR spectrum of cluster 4a in CD$_2$Cl$_2$

Fig. S9.75 $^1$H-$^1$H COSY spectrum of cluster 4a in CD$_2$Cl$_2$
Fig. S9.76 $^1$H-$^{13}$C HSQC spectrum of cluster 4a in CD$_2$Cl$_2$

Fig. S9.77 $^{31}$P NMR spectrum of cluster 3a in CD$_2$Cl$_2$
Fig. S9.78 $^1$H NMR spectrum of cluster 3a in CD$_2$Cl$_2$

Fig. S9.79 $^{13}$C NMR spectrum of cluster 3a in CD$_2$Cl$_2$
Fig. S9.80 $^{13}$C NMR DEPTQ135 spectrum of cluster 3a in CD$_2$Cl$_2$

Fig. S9.81 $^1$H-$^1$H COSY spectrum of cluster 3a in CD$_2$Cl$_2$
**Fig. S9.82** $^1$H-13C HSQC spectrum of cluster 3a in CD$_2$Cl$_2$

**Fig. S9.83** 31P NMR spectrum of cluster 3b in CD$_2$Cl$_2$
Fig. S9.84 $^1$H NMR spectrum of cluster 3b in CD$_2$Cl$_2$

Fig. S9.85 $^{13}$C NMR spectrum of cluster 3b in CD$_2$Cl$_2$
Fig. S9.86 $^1$H-$^1$H COSY spectrum of cluster 3b in CD$_2$Cl$_2$

Fig. S9.87 $^1$H-$^{13}$C HSQC spectrum of cluster 3b in CD$_2$Cl$_2$
Fig. S9.88 $^{31}$P NMR spectrum of cluster 4c in CD$_2$Cl$_2$

Fig. S9.89 $^1$H NMR spectrum of cluster 4c in CD$_2$Cl$_2$
Fig. S9.90 $^{13}$C NMR spectrum of cluster 4c in CD$_2$Cl$_2$

Fig. S9.91 $^1$H-$^1$H COSY spectrum of cluster 4c in CD$_2$Cl$_2$
Fig. S9.92 $^1$H-$^{13}$C HSQC spectrum of cluster 4c in CD$_2$Cl$_2$

Fig. S9.93 $^{31}$P NMR spectrum of cluster 6 in CD$_2$Cl$_2$
Fig. S9.94 $^1$H NMR spectrum of cluster 6 in CD$_2$Cl$_2$

Fig. S9.95 $^{13}$C NMR spectrum of cluster 6 in CD$_2$Cl$_2$
Fig. S9.96 $^1$H-$^1$H COSY spectrum of cluster 6 in CD$_2$Cl$_2$

Fig. S9.96 $^1$H-$^{13}$C HSQC spectrum of cluster 6 in CD$_2$Cl$_2$
Fig. S9.97 $^{31}$P NMR spectrum of cluster 7 in CD$_2$Cl$_2$

Fig. S9.98 $^1$H NMR spectrum of cluster 7 in CD$_2$Cl$_2$
Fig. S9.99 $^{13}$C NMR spectrum of cluster 7 in CD$_2$Cl$_2$

Fig. S9.100 $^1$H-$^1$H COSY spectrum of cluster 7 in CD$_2$Cl$_2$
Fig. S9.101 $^1$H-$^{13}$C HSQC spectrum of cluster 7 in CD$_2$Cl$_2$

Fig. S9.102 $^{31}$P NMR spectrum of complex 8 in CD$_2$Cl$_2$
Fig. S9.103 $^1$H NMR spectrum of complex 8 in CD$_2$Cl$_2$

Fig. S9.104 $^{13}$C NMR spectrum of complex 8 in CD$_2$Cl$_2$
**Fig. S9.105** $^1$H-$^1$H COSY spectrum of complex 8 in CD$_2$Cl$_2$

**Fig. S9.106** $^1$H-$^{13}$C HSQC spectrum of complex 8 in CD$_2$Cl$_2$
Fig. S9.107 $^{31}$P NMR spectrum of $9a \text{[OAu}_3\text{(TMS-L}$-$^1\text{)]}_3\text{(SbF}_6\text{)}$ in CD$_2$Cl$_2$

Fig. S9.108 $^1$H NMR spectrum of $9a \text{[OAu}_3\text{(TMS-L}$-$^1\text{)]}_3\text{(SbF}_6\text{)}$ in CD$_2$Cl$_2$
Fig. S9.109 $^{13}$C NMR spectrum of 9a [OAu$_3$(TMS-$L^1$)$_3$](SbF$_6$) in CD$_2$Cl$_2$.

Fig. S9.110 $^1$H-$^1$H COSY spectrum of 9a [OAu$_3$(TMS-$L^1$)$_3$](SbF$_6$) in CD$_2$Cl$_2$. 
Fig. S9.111 $^1$H-$^{13}$C HSQC spectrum of 9a [OAu$_3$(TMS-L$^1$)$_3$](SbF$_6$) in CD$_2$Cl$_2$

Fig. S9.112 $^{31}$P NMR spectrum of (TMS-L$^1$)Au(OAc) in CD$_2$Cl$_2$
Fig. S9.113 $^1$H NMR spectrum of (TMS-$^1$L$^1$)Au(OAc) in CD$_2$Cl$_2$

Fig. S9.114 $^{13}$C NMR spectrum of (TMS-$^1$L$^1$)Au(OAc) in CD$_2$Cl$_2$
Fig. S9.115 $^1$H–$^1$H COSY spectrum of (TMS-$^1$)Au(OAc) in CD$_2$Cl$_2$

Fig. S9.116 $^{31}$P NMR spectrum of complex [(TMS-$^1$)Au(Et$_3$N)](SbF$_6$) in CD$_2$Cl$_2$. 
Fig. S9.117 $^1$H NMR spectrum of complex [(TMS-L)$^1$Au(Et$_3$N)](SbF$_6$) $1a'$ in CD$_2$Cl$_2$.

Fig. S9.118 $^{13}$C NMR spectrum of complex [(TMS-L)$^1$Au(Et$_3$N)](SbF$_6$) $1a'$ in CD$_2$Cl$_2$. 
Fig. S9.119 $^1$H-$^{13}$C HSQC spectrum of complex $[[\text{TMS-L}^1\text{Au(Et}_3\text{N})](\text{SbF}_6)]$ 1a' in CD$_2$Cl$_2$.

Fig. S9.120 $^1$H-$^1$H COSY spectrum of complex $[[\text{TMS-L}^1\text{Au(Et}_3\text{N})](\text{SbF}_6)]$ 1a' in CD$_2$Cl$_2$. 
Fig. S9.121 $^{31}$P NMR spectrum of complex 5a in CD$_2$Cl$_2$.

Fig. S9.122 $^1$H NMR spectrum of complex 5a in CD$_2$Cl$_2$. 
Fig. S9.123 $^{13}$C NMR spectrum of complex 5a in CD$_2$Cl$_2$.

Fig. S9.124 $^1$H-$^{13}$C HSQC spectrum of complex 5a in CD$_2$Cl$_2$. 
Fig. S9.125 $^1$H-$^1$H COSY spectrum of complex 5a in CD$_2$Cl$_2$.

10. Crystal data by X-ray diffraction crystallography

Fig. S10.1 X-ray analysed structure of monogold chloride complexes 1a-e.

Fig. S10.2 X-ray analysed structure coordinating with acetone of different views, 3a·(CH$_3$COCH$_3$)$_2$: [Au$_4$Ag$_2$(CH$_3$COCH$_3$)$_2$($L^1$)$_4$](SbF$_6$)$_2$. Note: the solvent can be removed under high vacuum.
Fig. S10.3 X-ray analysed structure coordinating with methanol in 3a·(MeOH): [Au₄Ag₂(MeOH)₂(L¹)₃](SbF₆)₂. (SbF₆ anions were omitted for clarity.)

Table S10.1 Crystal data and structure refinement for 1a.

| Item                          | Value                                      |
|-------------------------------|--------------------------------------------|
| Identification code           | 1a                                         |
| Empirical formula             | C₄₂H₄₆Au₂Cl₂P₂Si₂                          |
| Formula weight                | 1133.74                                    |
| Temperature                   | 100(2) K                                   |
| Wavelength                    | 0.71073 Å                                  |
| Crystal system                | Triclinic                                   |
| Space group                   | P-1                                        |
| Unit cell dimensions          | a = 9.0183(3) Å α = 82.9347(19)°.          |
|                              | b = 12.4470(3) Å β = 79.818(2)°.           |
|                              | c = 20.2322(5) Å γ = 69.909(3)°.           |
| Volume                        | 2094.54(11) Å³                             |
| Z                             | 2                                          |
| Density (calculated)          | 1.798 Mg/m³                                |
| Absorption coefficient        | 7.286 mm⁻¹                                 |
| F(000)                        | 1096                                       |
| Crystal size                  | 0.12 x 0.15 x 0.10 mm³                     |
| Theta range for data collection | 1.964 to 29.615°.                        |
| Index ranges                  | -11≤h≤12, -16≤k≤16, -27≤l≤27               |
| Reflections collected         | 34030                                      |
| Independent reflections       | 10315[R(int) = 0.0332]                     |
| Completeness to theta =29.615°| 87.3%                                      |
Table S10.2 Crystal data and structure refinement for 1b.

| Category                                               | Value                                      |
|--------------------------------------------------------|--------------------------------------------|
| Identification code                                    | 1b                                         |
| Empirical formula                                      | C25 H25 Au Cl P Si                         |
| Formula weight                                         | 616.92                                     |
| Temperature                                            | 100(2) K                                   |
| Wavelength                                             | 0.71073 Å                                  |
| Crystal system                                         | Monoclinic                                 |
| Space group                                            | C2/c                                       |
| Unit cell dimensions                                   | 
| \(a = 24.8391(12) \) Å \(\alpha = 90^\circ\).     |                                            |
| \(b = 9.6167(4) \) Å \(\beta = \)                 |                                            |
| \(c = 19.9723(9) \) Å \(\gamma = 90^\circ\).      |                                            |
| Volume                                                 | 4662.0(4) Å\(^3\)                         |
| Z                                                      | 8                                          |
| Density (calculated)                                   | 1.758 Mg/m\(^3\)                          |
| Absorption coefficient                                 | 6.555 mm\(^{-1}\)                         |
| F(000)                                                 | 2400                                       |
| Crystal size                                           | 0.15 x 0.15 x 0.10 mm\(^3\)               |
| Theta range for data collection                        | 2.087 to 28.282°.                         |
| Index ranges                                           | -27<=h<=33, -11<=k<=12, -26<=l<=19         |
| Reflections collected                                  | 22040                                      |
| Independent reflections                               | 5728[R(int) = 0.0398]                      |
| Parameter                                    | Value                                      |
|----------------------------------------------|--------------------------------------------|
| Completeness to theta =29.615°               | 99.1%                                      |
| Absorption correction                        | Multi-scan                                 |
| Max. and min. transmission                   | 0.560 and 0.275                            |
| Refinement method                            | Full-matrix least-squares on F²            |
| Data / restraints / parameters                | 5728/ 0/ 266                               |
| Goodness-of-fit on F²                         | 1.033                                      |
| Final R indices [I>2sigma(I)]                | R1 = 0.0243, wR2 = 0.0585                  |
| R indices (all data)                         | R1 = 0.0277, wR2 = 0.0600                  |
| Largest diff. peak and hole                  | 1.473 and -2.723 e.Å⁻³                    |
Table S10.3 Crystal data and structure refinement for 1c.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | 1c                                        |
| Empirical formula                             | C25 H25 Au Cl P Si                         |
| Formula weight                                | 616.92                                    |
| Temperature                                   | 100(2) K                                  |
| Wavelength                                    | 0.71073 Å                                 |
| Crystal system                                | Monoclinic                                 |
| Space group                                   | P2(1)/c                                   |
| Unit cell dimensions                          | a = 8.79820(10) Å  α = 90°.               |
|                                               | b =15.1425(2) Å  β = 94.5780(10)°.        |
|                                               | c =16.9260(2) Å  γ = 90°.                 |
| Volume                                        | 2247.80(5) Å³                             |
| Z                                             | 4                                         |
| Density (calculated)                          | 1.823Mg/m³                                |
| Absorption coefficient                        | 6.798mm⁻¹                                 |
| F(000)                                        | 1200                                      |
| Crystal size                                  | 0.2 x 0.2 x 0.15 mm³                      |
| Theta range for data collection               | 2.322 to 37.262°.                        |
| Index ranges                                  | -14<=h<=13, -25<=k<=25, -28<=l<=28        |
| Reflections collected                         | 66237                                     |
| Independent reflections                       | 11362[R(int) = 0.0312]                    |
| Completeness to theta =37.262°               | 97.6%                                     |
| Absorption correction                         | Multi-scan                                |
| Max. and min. transmission                    | 0.429 and 0.33                           |
| Refinement method                             | Full-matrix least-squares on F²           |
| Data / restraints / parameters                | 11362/ 12/ 359                           |
| Goodness-of-fit on F²                          | 1.053                                     |
| Final R indices [>2sigma(l)]                  | R1 = 0.0209, wR2 = 0.0411                |
| R indices (all data)                           | R1 = 0.0250, wR2 = 0.0419                |
| Largest diff. peak and hole                   | 1.761 and -2.067 e.Å⁻³                   |
| **Table S10.4 Crystal data and structure refinement for 1d.** |
|---------------------------------------------------------------|
| **Identification code** | 1d |
| **Empirical formula** | C21 H135 Au1 Cl1 P1 Si1 |
| **Formula weight** | 578.96 |
| **Temperature** | 100(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Monoclinic |
| **Space group** | P2(1)/c |
| **Unit cell dimensions** |  |
| | a = 10.8187(4) Å α = 90°. |
| | b = 14.1211(5) Å β = 109.3312(9)°. |
| | c = 15.6127(5) Å γ = 90°. |
| **Volume** | 2250.71(14) Å³ |
| **Z** | 4 |
| **Density (calculated)** | 1.709 Mg/m³ |
| **Absorption coefficient** | 6.782 mm⁻¹ |
| **F(000)** | 1144 |
| **Crystal size** | 0.20 x 0.10 x 0.05 mm³ |
| **Theta range for data collection** | 1.995 to 31.596°. |
| **Index ranges** | -15<=h<=15, -20<=k<=19, -16<=l<=21 |
| **Reflections collected** | 21598 |
| **Independent reflections** | 7150[R(int) = 0.0443] |
| **Completeness to theta = 31.596°** | 94.700005% |
| **Absorption correction** | Multi-scan |
| **Max. and min. transmission** | 0.7462 and 0.3022 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 7150/ 0/ 229 |
| **Goodness-of-fit on F²** | 1.016 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0286, wR2 = 0.0683 |
| **R indices (all data)** | R1 = 0.0376, wR2 = 0.0724 |
| Largest diff. peak and hole | 2.028 and -1.395 eÅ⁻³ |
Table S10.5 Crystal data and structure refinement for 1e.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | 1e                                         |
| Empirical formula               | C17 H19 Au Cl O2 P Si                      |
| Formula weight                  | 546.80                                     |
| Temperature                     | 100(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | Monoclinic                                 |
| Space group                     | P2(1)/c                                    |
| Unit cell dimensions            | a = 11.72842(17) Å α = 90°.                |
|                                 | b = 11.29230(13) Å β = 110.2932(18)°.      |
|                                 | c = 15.6376(3) Å γ = 90°.                  |
| Volume                          | 1942.50(5) Å³                              |
| Z                               | 4                                          |
| Density (calculated)            | 1.870 Mg/m³                                |
| Absorption coefficient          | 7.860mm⁻¹                                  |
| F(000)                          | 1048                                       |
| Crystal size                    | 0.20 x 0.10 x 0.05 mm³                     |
| Theta range for data collection | 2.276 to 25.027°.                          |
| Index ranges                    | -13<=h<=13, -13<=k<=13, -18<=l<=18         |
| Reflections collected           | 25728                                      |
| Independent reflections         | 3425[R(int) = 0.0268]                      |
| Completeness to theta = 25.027° | 100.0%                                     |
| Absorption correction           | Multi-scan                                 |
| Max. and min. transmission      | 0.695 and 0.535                            |
| Refinement method               | Full-matrix least-squares on F²            |
| Data / restraints / parameters  | 3425/0/211                                 |
| Goodness-of-fit on F²           | 1.146                                      |
| Final R indices [I>2sigma(I)]   | R1 = 0.0179, wR2 = 0.0463                  |
| R indices (all data)            | R1 = 0.0187, wR2 = 0.0467                  |
| Largest diff. peak and hole | 2.534 and -1.233 eÅ$^3$ |
**Table S10.6** Crystal data and structure refinement for 2b.

| Property                          | Value                        |
|-----------------------------------|------------------------------|
| Identification code               | 2b                           |
| Empirical formula                 | C95 H80 Au6 Cl2 F12 P4 Sb2   |
| Formula weight                    | 3069.66                      |
| Temperature                       | 100(2) K                     |
| Wavelength                        | 0.71073 Å                    |
| Crystal system                    | Triclinic                    |
| Space group                       | P-1                          |
| Unit cell dimensions              |                              |
| a                                 | 12.4401(6) Å, α = 81.045(4)° |
| b                                 | 15.4396(7) Å, β = 78.332(4)° |
| c                                 | 23.4991(13) Å, γ = 85.784(4)°|
| Volume                            | 4362.2(4) Å³                 |
| Z                                 | 2                            |
| Density (calculated)              | 2.337 Mg/m³                  |
| Absorption coefficient            | 10.866 mm⁻¹                  |
| F(000)                            | 2856                         |
| Crystal size                      | 0.05 x 0.05 x 0.03 mm³       |
| Theta range for data collection   | 2.674 to 25.349°             |
| Index ranges                      | -14 <= h <= 14, -18 <= k <= 18, -28 <= l <= 28 |
| Reflections collected             | 16181                        |
| Independent reflections           | 16181[R(int) = ?]            |
| Completeness to theta = 25.349°   | 99.2%                        |
| Absorption correction             | Multi-scan                   |
| Max. and min. transmission        | 0.736 and 0.566              |
| Refinement method                 | Full-matrix least-squares on F²|
| Data / restraints / parameters    | 16181/1145/1237              |
| Goodness-of-fit on F²             | 1.210                        |
| Final R indices [I>2sigma(I)]     | R1 = 0.0565, wR2 = 0.1615    |
| R indices (all data)              | R1 = 0.0779, wR2 = 0.1692    |
Largest diff. peak and hole
3.584 and -2.523 eÅ⁻³

Table S10.7 Crystal data and structure refinement for 2c.

| Identification code | 2c |
|---------------------|----|
| Empirical formula   | C₄₆H₃₆Au₃Cl₄F₆P₂Sb |
| Formula weight      | 1619.14 |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Triclinic |
| Space group         | P-1 |
| Unit cell dimensions| a = 13.0520(6) Å α = 76.0107(11)°, b = 14.4543(6) Å β = 79.6318(11)°, c = 25.7754(12) Å γ = 83.2951(10)°. |
| Volume              | 4627.8(4) Å³ |
| Z                   | 4 |
| Density (calculated)| 2.324 Mg/m³ |
| Absorption coefficient| 10.416 mm⁻¹ |
| F(000)              | 3008 |
| Crystal size        | 0.40 x 0.05 x 0.05 mm³ |
| Theta range for data collection | 0.824 to 30.594°. |
| Index ranges        | -18<=h<=18, -19<=k<=20, 0<=l<=36 |
| Reflections collected| 24260 |
| Independent reflections| 24260[R(int) = ?] |
| Completeness to theta = 30.594° | 88.6% |
| Absorption correction| Multi-scan |
| Max. and min. transmission | 0.624 and 0.48 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 24260/ 378/ 1208 |
| Goodness-of-fit on F² | 1.030 |
Table S10.8 Crystal data and structure refinement for 2d.

| Identification code | 2d            |
|---------------------|---------------|
| Empirical formula   | C75 H110 Au6 Cl6 F12 P4 Sb2 |
| Formula weight      | 3001.50       |
| Temperature         | 100(2) K      |
| Wavelength          | 0.71073 Å     |
| Crystal system      | Monoclinic    |
| Space group         | P2(1)/n       |
| Unit cell dimensions| a = 15.5210(14) Å, α = 90°, b = 32.453(2) Å, β = 114.1964(17)°, c = 18.7684(17) Å, γ = 90°. |
| Volume              | 8623.2(13) Å³ |
| Z                   | 4             |
| Density (calculated)| 2.312 Mg/m³   |
| Absorption coefficient| 11.109 mm⁻¹  |
| F(000)              | 5624          |
| Crystal size        | 0.20 x 0.20 x 0.20 mm³ |
| Theta range for data collection | 2.227 to 27.614°. |
| Index ranges        | -20<=h<=20, -42<=k<=42, -24<=l<=22 |
| Reflections collected| 122997       |
| Independent reflections| 19660[R(int) = 0.0399] |
| Completeness to theta = 30.594° | 98.1% |
| Absorption correction| Empirical    |
| Max. and min. transmission | 0.215 and 0.165 |
| Refinement method   | Full-matrix least-squares on F² |
Data / restraints / parameters | 19660/ 199/ 1073
Goodness-of-fit on \( F^2 \) | 1.089
Final R indices \( [I>2\sigma(I)] \) | \( R1 = 0.0332, \text{ wR2} = 0.0744 \)
R indices (all data) | \( R1 = 0.0498, \text{ wR2} = 0.0835 \)
Largest diff. peak and hole | 3.014 and -1.255 e.Å\(^{-3}\)

**Table S10.9** Crystal data and structure refinement for **2e**.

| Identification code | 2e |
|---------------------|----|
| Empirical formula   | \( \text{C75 H110 Au6 Cl6 F12 P4 Sb2} \) |
| Formula weight      | 2618.06 |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Monoclinic |
| Space group         | \( \text{C2/m} \) |
| Unit cell dimensions| \( a = 17.026(7) \) Å \( \alpha = 90^\circ \) \( b = 21.542(8) \) Å \( \beta = 114.1964(17)^\circ \) \( c = 12.042(5) \) Å \( \gamma = 90^\circ \) |
| Volume              | 3128(2)Å\(^3\) |
| \( Z \)             | 2 |
| Density (calculated)| 2.780 Mg/m\(^3\) |
| Absorption coefficient| 15.053 mm\(^{-1}\) |
| \( F(000) \)        | 2368 |
| Crystal size        | 0.20 x 0.20 x 0.20 mm\(^3\) |
| Theta range for data collection | 2.392 to 26.284° |
| Index ranges        | \(-21<=h<=21, -26<=k<=26, -14<=l<=14\) |
| Reflections collected| 31006 |
| Independent reflections | 3150[\( R(int) = 0.1136 \)] |
| Completeness to theta = 30.594° | 96.7% |
| Absorption correction| Empirical |
| Max. and min. transmission | 0.153 and 0.118 |
### Refinement method
- Full-matrix least-squares on $F^2$

### Data / restraints / parameters
- 3150/ 490/ 368

### Goodness-of-fit on $F^2$
- 1.066

### Final R indices [$I>2\sigma(I)$]
- $R1 = 0.0880, wR2 = 0.2081$

### R indices (all data)
- $R1 = 0.1462, wR2 = 0.2287$

### Largest diff. peak and hole
- 3.194 and -1.907 e.Å$^3$

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**Table S10.10** Crystal data and structure refinement for 4a.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                          | 4a                                         |
| Empirical formula                            | C74 H60 Ag2 Au4 Cl4 F12 P4 Sb2             |
| Formula weight                                | 2690.00                                    |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Triclinic                                  |
| Space group                                   | P1                                         |
| Unit cell dimensions                          | $a = 13.1207(2)$ Å $\alpha = 90.5527(19)^\circ$  |
|                                              | $b = 18.2607(5)$ Å $\beta = 109.5584(19)^\circ$  |
|                                              | $c = 18.7251(4)$ Å $\gamma = 110.161(2)^\circ$  |
| Volume                                        | 3928.67(16) Å$^3$                          |
| Z                                             | 2                                          |
| Density (calculated)                          | 2.274 Mg/m$^3$                             |
| Absorption coefficient                        | 8.889 mm$^{-1}$                            |
| $F(000)$                                      | 2504                                       |
| Crystal size                                  | 0.20 x 0.20 x 0.20 mm$^3$                  |
| Theta range for data collection               | 1.735 to 28.489°.                          |
| Index ranges                                  | -17<=$h<=$17, -24<=$k<=$24, -24<=$l<=$24     |
| Reflections collected                         | 65623                                      |
| Independent reflections                       | 65623[R(int) = ?]                          |
| Completeness to theta                          | 98.2%                                      |
| Absorption correction                         | Multi-scan                                 |
| Max. and min. transmission                     | 0.349 and 0.269                            |
Table S10.11 Crystal data and structure refinement for 3a·(acetone)₂.

| Property                                      | Value |
|-----------------------------------------------|-------|
| Identification code                          | 3a_acetone |
| Empirical formula                            | C₈₁ H₇₄ Ag₂ Au₄ F₁₂ O₃ P₄ Sb₂ |
| Formula weight                                | 2694.38 |
| Temperature                                   | 100(2) K |
| Wavelength                                    | 0.71073 Å |
| Crystal system                                | Monoclinic |
| Space group                                   | P₂(1)/n |
| Unit cell dimensions                          | a = 17.14436(12) Å α = 90°. |
|                                              | b = 16.27035(11) Å β = 96.3437(6)°. |
|                                              | c = 29.0696(2)Å γ = 90°. |
| Volume                                        | 8059.16(10) Å³ |
| Z                                             | 4 |
| Density (calculated)                          | 2.221 Mg/m³ |
| Absorption coefficient                        | 8.541 mm⁻¹ |
| F(000)                                        | 5056 |
| Crystal size                                  | 0.200 x 0.150 x 0.150 mm³ |
| Theta range for data collection               | 1.731 to 34.524°. |
| Index ranges                                  | -27<=h<=26, -25<=k<=25, -46<=l<=46 |
| Reflections collected                         | 318340 |
| Independent reflections                       | 33289[R(int) = 0.0263] |
| Completeness to theta = 34.524°               | 97.2% |
Absorption correction: Multi-scan
Max. and min. transmission: 0.361 and 0.278
Refinement method: Full-matrix least-squares on $F^2$
Data / restraints / parameters: 33289/ 66/ 1017
Goodness-of-fit on $F^2$: 1.124
Final R indices [I>2sigma(I)]:
R1 = 0.0168, wR2 = 0.0341
R indices (all data):
R1 = 0.0202, wR2 = 0.0346
Largest diff. peak and hole: 1.195 and -0.628 e.Å$^{-3}$

**Table S10.12** Crystal data and structure refinement for 3a·(MeOH)$_2$.

| Identification code | 3a_MeOH |
|---------------------|---------|
| Empirical formula   | C75.31 H67.18 Ag2 Au4 Cl2.44 F12 O2.28 P4 Sb2 |
| Formula weight      | 2694.15 |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Monoclinic |
| Space group         | C2/c |
| Unit cell dimensions| a = 48.689(3) Å $\alpha$ = 90°. 
                          b = 1.4023(7) Å $\beta$ = 118.6312(9)°. 
                          c = 31.887(2) Å $\gamma$ = 90°. |
| Volume              | 15538.2(17) Å$^3$ |
| Z                   | 8 |
| Density (calculated)| 2.303 Mg/m$^3$ |
| Absorption coefficient| 8.941 mm$^{-1}$ |
| F(000)              | 10070 |
| Crystal size        | 0.20 x 0.05 x 0.05 mm$^3$ |
| Theta range for data collection | 1.848 to 30.568°. |
| Index ranges        | -69<=h<=61, -16<=k<=16, -45<=l<=45 |
| Reflections collected| 81920 |
Independent reflections 23745 [R(int) = 0.0338]
Completeness to theta = 30.568° 99.5%
Absorption correction Multi-scan
Max. and min. transmission 0.916 and 0.485

Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 23745/ 184/ 1058
Goodness-of-fit on F^2 1.008
Final R indices [I>2sigma(I)] R1 = 0.0271, wR2 = 0.0675
R indices (all data) R1 = 0.0339, wR2 = 0.0702
Largest diff. peak and hole 1.814 and -1.286 eÅ^-3

Table S10.13 Crystal data and structure refinement for 3b.

| Identification code | 3b |
|---------------------|----|
| Empirical formula   | C199.40 H178.40 Ag4 Au8 F24 O7.20 P8 Sb4 |
| Formula weight      | 5887.78 |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Orthorhombic |
| Space group         | Fdd2 |
| Unit cell dimensions| a = 31.8168(12) Å α = 90°.  
b = 48.8606(19) Å β = 90°.  
c = 25.7045(10) Å γ = 90°. |
| Volume              | 39960(3) Å^3 |
| Z                   | 8 |
| Density (calculated)| 1.957 Mg/m^3 |
| Absorption coefficient | 6.900 mm^-1 |
| F(000)              | 22339 |
| Crystal size        | 0.20 x 0.02 x 0.01 mm^3 |
| Theta range for data collection | 1.528 to 32.098°. |
|-------------------------------|------------------|
| Index ranges                  | -47<=h<=33, -72<=k<=69,-38<=l<=38 |
| Reflections collected         | 131178 |
| Independent reflections       | 34543[R(int) = 0.0617] |
| Completeness to theta =32.098° | 99.6% |
| Absorption correction         | Multi-scan |
| Max. and min. transmission    | 0.934 and 0.718 |
| Refinement method             | Full-matrix least-squares on F^2 |
| Data / restraints / parameters| 34543/ 315/ 1322 |
| Goodness-of-fit on F^2        | 0.948 |
| Final R indices [I>2sigma(I)] | R1 = 0.0324, wR2 = 0.0612 |
| R indices (all data)          | R1 = 0.0507, wR2 = 0.0664 |
| Flack parameter               | x =0.0040(19) |
| Largest diff. peak and hole   | 1.475 and -2.588 e.Å^{-3} |

**Table S10.14** Crystal data and structure refinement for 4c.

| Identification code   | 4c            |
|-----------------------|---------------|
| Empirical formula     | C92 H72 Ag2 Au4 Cl8 F12 P4 Sb2 |
| Formula weight        | 3060.08       |
| Temperature           | 100(2) K      |
| Wavelength            | 0.71073 Å     |
| Crystal system        | Orthorhombic  |
| Space group           | Pbca          |
| Unit cell dimensions  | a = 14.761(2) Å α = 90°. |
|                       | b = 26.214(3)Å β = 118.6312(9)°. |
|                       | c = 47.072(7) Å γ = 90°. |
| Volume                | 18214(4) Å^3  |
| Z                     | 8             |
| Density (calculated)  | 2.232 Mg/m^3  |
| Absorption coefficient| 7.798 mm^{-1} |
Table S10.15 Crystal data and structure refinement for 5a'.

| Property                        | Value                   |
|---------------------------------|-------------------------|
| Identification code             | 5a'                     |
| Empirical formula               | C163.30 H147.20 Ag4 Au12 Cl5 F21 N4 O20.30 P8 S7 |
| Formula weight                  | 6333.95                 |
| Temperature                     | 100(2) K                |
| Wavelength                      | 0.71073 Å               |
| Crystal system                  | Orthorhombic            |
| Space group                     | Pnna                    |
| Unit cell dimensions            | a = 34.2355(9) Å α = 90°. |
|                                 | b = 29.4107(7) Å β = 90°. |
|                                 | c = 19.0523(5)Å γ = 90°. |
| Volume                          | 19183.6(8) Å³          |
| Z                               | 4                       |
| Property                                | Value                        |
|-----------------------------------------|------------------------------|
| Density (calculated)                    | 2.193 Mg/m³                 |
| Absorption coefficient                  | 9.826 mm⁻¹                  |
| F(000)                                  | 11838                        |
| Crystal size                            | 0.12 x 0.1 x 0.03 mm³       |
| Theta range for data collection         | 2.192 to 26.733°            |
| Index ranges                            | -34<=h<=43, -33<=k<=37, -22<=l<=24 |
| Reflections collected                   | 88644                        |
| Independent reflections                 | 20297 [R(int) = 0.0571]     |
| Completeness to theta =26.733°          | 99.6%                        |
| Absorption correction                   | Multi-scan                   |
| Max. and min. transmission              | 0.757 and 0.582              |
| Refinement method                       | Full-matrix least-squares on F² |
| Data / restraints / parameters          | 20297/ 2450/ 1863            |
| Goodness-of-fit on F²                   | 1.230                        |
| Final R indices [I>2sigma(I)]           | R1 = 0.0518, wR2 = 0.1446    |
| R indices (all data)                    | R1 = 0.0917, wR2 = 0.1662    |
| Largest diff. peak and hole             | 2.010 and -1.950 eÅ⁻³        |
Table S10.16 Crystal data and structure refinement for 6.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | 6                                          |
| Empirical formula               | C92.83 H75.76 Au5 Cl1.26 F6 O1.05 P4 Sb    |
| Formula weight                  | 2597.18                                    |
| Temperature                     | 100(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | Monoclinic                                 |
| Space group                     | Cc                                         |
| Unit cell dimensions            | a = 22.5623(3) Å α = 90°. b = 63.5786(8)Å β = 103.3624(14)°. c =31.1124(5) Å γ = 90°. |
| Volume                          | 43421.9(10) Å³                            |
| Z                               | 20                                         |
| Density (calculated)            | 1.986 Mg/m³                                |
| Absorption coefficient          | 8.893 mm⁻¹                                 |
| F(000)                          | 24451                                      |
| Crystal size                    | 0.15 x 0.15 x 0.05 mm³                     |
| Theta range for data collection | 2.210 to 28.747°.                          |
| Index ranges                    | -30<=h<=29, -83<=k<=84, -41<=l<=40          |
| Reflections collected           | 282352                                     |
| Independent reflections         | 94680 [R(int) = 0.0447]                    |
| Completeness to theta = 25.242° | 99.9 %                                     |
| Absorption correction           | Semi-empirical from equivalents            |
| Max. and min. transmission      | 1.000 and 0.378                            |
| Refinement method               | Full-matrix least-squares on F²            |
| Data / restraints / parameters  | 94680 / 12237 / 5885                       |
| Goodness-of-fit on F²           | 0.879                                      |
| Final R indices [I>2sigma(I)]   | R1 = 0.0434, wR2 = 0.1272                  |
| R indices (all data)            | R1 = 0.0689, wR2 = 0.1409                  |
| Parameter                          | Value          |
|-----------------------------------|----------------|
| Absolute structure parameter     | 0.502(7)       |
| Extinction coefficient            | n/a            |
| Largest diff. peak and hole       | 3.929 and -2.101 e.Å⁻³ |
| **Table S10.17** Crystal data and structure refinement for 7. |
|-------------------------------------------------------------|
| **Identification code** | 7 |
| **Empirical formula** | C92.40 H74.40 Ag Au4 Cl2.40 F6 O0.80 P4 Sb |
| **Formula weight** | 2537.96 |
| **Temperature** | 100(2) K |
| **Wavelength** | null Å |
| **Crystal system** | Monoclinic |
| **Space group** | P2(1)/n |
| **Unit cell dimensions** | a = 18.5191(10) Å α = 90°. b = 17.3139(8)Å β = 108.6229(13)°. c = 27.2956(14) Å γ = 90°. |
| **Volume** | 8293.8(7) Å³ |
| **Z** | 4 |
| **Density (calculated)** | 2.033 Mg/m³ |
| **Absorption coefficient** | 7.818 mm⁻¹ |
| **F(000)** | 4816 |
| **Crystal size** | 0.40 x 0.20 x 0.10 mm³ |
| **Theta range for data collection** | 1.415 to 27.484°. |
| **Index ranges** | -24<=h<=22, -17<=k<=22, -35<=l<=35 |
| **Reflections collected** | 76252 |
| **Independent reflections** | 18645[R(int) = 0.0314] |
| **Completeness to theta =27.484°** | 98.1% |
| **Absorption correction** | Multi-scan |
| **Max. and min. transmission** | 0.7467 and 0.4602 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 18645/ 215/ 1128 |
| **Goodness-of-fit on F²** | 1.032 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0253, wR2 = 0.0567 |
| **R indices (all data)** | R1 = 0.0329, wR2 = 0.0600 |
| Largest diff. peak and hole | 1.960 and -2.505 eÅ⁻³ |
| **Table S10.18 Crystal data and structure refinement for 8.** |
|-------------------------------------------------------------|
| **Identification code** | 8 |
| **Empirical formula** | C44 H32 Au2 P2 |
| **Formula weight** | 1016.57 |
| **Temperature** | 100(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Triclinic |
| **Space group** | P-1 |
| **Unit cell dimensions** | a = 9.07630(10) Å α = 76.858(2)°.  
b = 9.19550(10) Å β = 89.488(2)°.  
c = 11.1166(2) Å γ = 72.7040(10)°. |
| **Volume** | 860.93(2) Å³ |
| **Z** | 1 |
| **Density (calculated)** | 1.961 Mg/m³ |
| **Absorption coefficient** | 8.636 mm⁻¹ |
| **F(000)** | 484 |
| **Crystal size** | 0.050 x 0.050 x 0.050 mm³ |
| **Theta range for data collection** | 1.885 to 31.468°. |
| **Index ranges** | -13<=h<=13, -13<=k<=13, -16<=l<=16 |
| **Reflections collected** | 20021 |
| **Independent reflections** | 5678[R(int) = 0.0162] |
| **Completeness to theta =31.468°** | 99.3% |
| **Absorption correction** | Multi-scan |
| **Max. and min. transmission** | 0.672 and 0.517 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 5678/ 0/ 217 |
| **Goodness-of-fit on F²** | 1.073 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0110, wR2 = 0.0264 |
| **R indices (all data)** | R1 = 0.0119, wR2 = 0.0265 |
|                         |       |
|-------------------------|-------|
| Largest diff. peak and hole | 1.000 and -0.305 e.Å⁻³ |
| **Table S10.19** Crystal data and structure refinement for 9. |
|---------------------------------------------------------------|
| **Identification code** | 9 |
| **Empirical formula** | C64.50 H105.25 Au3 B Cl3 F4 O1.50 P3 Si3 |
| **Formula weight** | 1865.97 |
| **Temperature** | 100(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Cubic |
| **Space group** | F-43c |
| **Unit cell dimensions** | a = 40.6274(2) Å α = 90°. |
| | b = 40.6274(2) Å β = 90°. |
| | c = 40.6274(2) Å γ = 90°. |
| **Volume** | 67059.2(10) Å³ |
| **Z** | 32 |
| **Density (calculated)** | 1.479 Mg/m³ |
| **Absorption coefficient** | 5.476 mm⁻¹ |
| **F(000)** | 29448 |
| **Crystal size** | 0.1 x 0.1 x 0.06 mm³ |
| **Theta range for data collection** | 1.736 to 28.080°. |
| **Index ranges** | -52<=h<=52, -51<=k<=52, -45<=l<=53 |
| **Reflections collected** | 110196 |
| **Independent reflections** | 6594 [R(int) = 0.0433] |
| **Completeness to theta =28.080°** | 98.5% |
| **Absorption correction** | Multi-scan |
| **Max. and min. transmission** | 1.00000 and 0.29846 |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 6594/855/517 |
| **Goodness-of-fit on F²** | 1.247 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0508, wR2 = 0.1473 |
| **R indices (all data)** | R1 = 0.0693, wR2 = 0.1598 |
| Parameter                          | Value                        |
|----------------------------------|------------------------------|
| Flack parameter                  | $x = 0.019(5)$              |
| Largest diff. peak and hole      | $1.064$ and $-1.275 \text{ e.A}^{-3}$ |
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