Supporting Information
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Selective formation of a Supramolecular Coordination Complex in the Nanometre Scale with a Ferrocene-based Phospholane Ligand

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Abstract: A straightforward synthesis of the tetradentate phospholane ligand **1** is reported. The 2:1 [M:L] reaction of **1** with [AuCl(tht)] (tht = tetrahydrothiophene) resulted in a 4:2 [M:L] supramolecular coordination complex **2** where two ligands **1** are bridging four gold(I) cations. The formation of **2** can be rationalised via a geometrical analysis of the ligand. The coordination mode of the gold atoms was evaluated based on a CSD search, revealing the geometrical changes for a transition from linear to trigonal planar coordination environment.

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2. General remarks

All oxygen- and moisture-sensitive experiments were carried out under dry nitrogen using standard Schlenk-technique. Solvents were dried and degassed using an MB SPS-800 Solvent Purification System from MBraun. For reactions including *n*-butyllithium, tetrahydrofuran was used, which was dried and distilled from potassium/benzophenone and kept over molecular sieve (4Å).
1,3,5-Tris[*p*-(diethoxyphosphonylmethyl)phenyl]benzene[1], 1,1´-diformylferrocene[2] and [AuCl(tht)][3] (tht = tetrahydrothiophene) were synthesised according to the literature.

Cyclic voltammetry. Determination of redox potentials was carried out at room temperature using a three-electrode arrangement (glassy carbon working electrode, platinum counter electrode, silver pseudo-reference electrode) on a SP-50 potentiostat from Bio-Logic Science Instruments. A 0.1 M tetrabutylammonium tetrafluoroborate solution in dichloromethane was used as supporting electrolyte. Decamethylferrocene was used as internal standard.[4]

Elemental analysis. Carbon and hydrogen contents of the compounds were determined using a Vario EL Analyser from Heraeus.

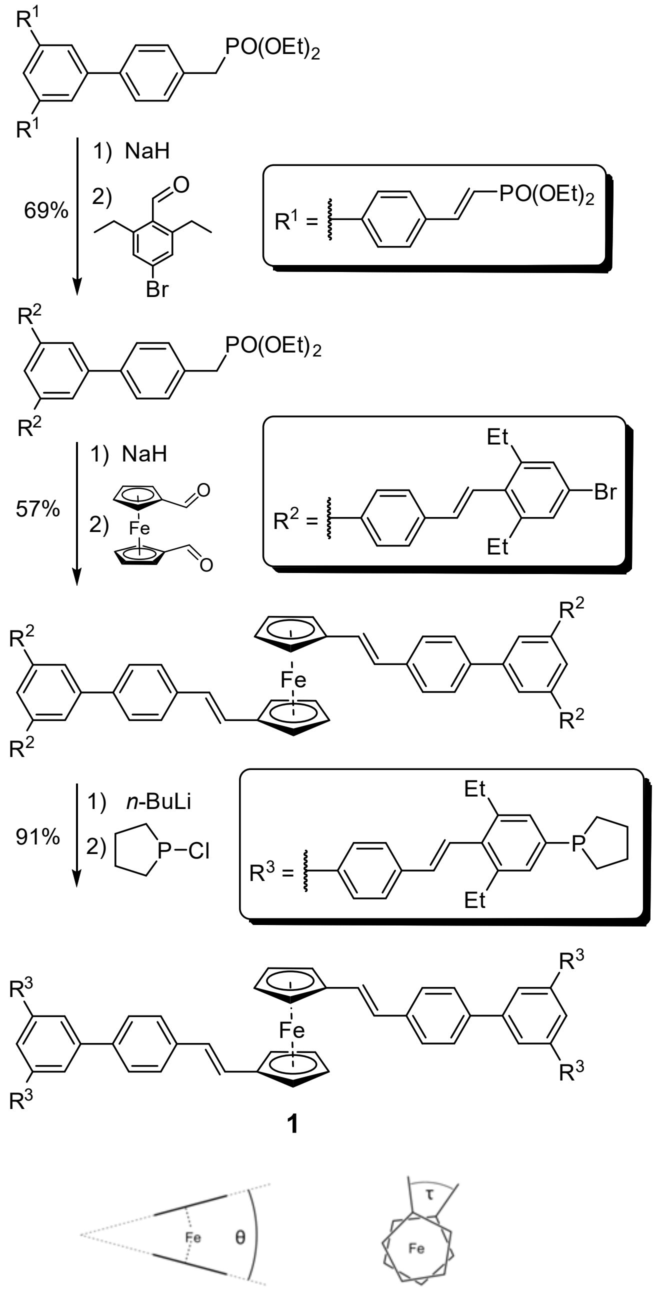
IR spectroscopy. IR spectra were recorded in the range from 4000 to 400 cm^{-1}. ATR spectra were recorded on a Thermofisher Nicolet iS5 ATR spectrometer; KBr pellets were measured on an FT-IR Spektrum 2000 spectrometer from PerkinElmer.

NMR spectroscopy. NMR spectra were recorded at room temperature using a Bruker Avance DRX 400 (^{1}H-NMR 400.13 MHz, ^{13}C-NMR 100.16 MHz, ^{31}P-NMR 161.98 MHz) NMR spectrometer. Tetramethylsilane (TMS) was used as internal standard for ^{1}H-NMR spectra. ^{13}C- and ^{31}P- NMR spectra were referenced to TMS on the Ξ scale.[5] Correlation of ^{1}H and ^{13}C signals was based on 2D-NMR experiments (HMBC, HSQC) and APT spectra when necessary.

Mass spectrometry. ESI mass spectra were recorded on an Impact II and Esquire 3000 Plus mass spectrometer from Bruker Daltonics.

TGA/DSC measurements. The TGA/DSC measurements were performed on a STA 449 F1 Jupiter from Netzsch, using helium as atmosphere and carrier gas. During TGA/DSC, mass fragments could be detected using a QMS 403 C Aeolos from Netzsch. The samples were prepared in alumina crucibles and a heating rate of 10 K/min was applied.

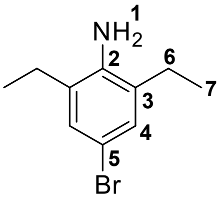
3. Synthetic Procedures



Scheme S1. Synthesis of tetrakis-phospholane **1** including description of geometrical parameters in the ferrocenylene unit.

4-Bromo-2,6-diethylaniline

2,6-Diethylaniline (25 g, 167.5 mmol; 1.0 eq) was dissolved in 200 ml dimethylsulfoxide and cooled to 0 °C. 200 ml of an aqueous HBr solution (40%) was added and the mixture was allowed to warm to room temperature. The mixture was stirred for 7 days at room temperature, then neutralised with aqueous NaOH solution and extracted with diethyl ether (3 x 80 ml). The collected organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure.



Yield: 36.8 g (96%), slightly brown oil.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 7.03 (s, 2H, H^4), 3.56 (s, 2H, H^1), 2.41 (q, $^3J_{HH}$ = 7.5 Hz, 4H, H^6), 1.19 ppm (t, $^3J_{HH}$ = 7.6 Hz, 6H, H^7).

^{13}C{^{1}H}-NMR ($CDCl_3$, 100.16 MHz): δ = 140.7 (s, C^2), 129.6 (s, C^3), 128.4 (s, C^4), 110.1 (s, C^5), 24.1 (s, C^6), 12.7 ppm (s, C^7).

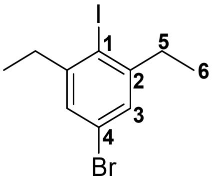
IR (KBr): $\tilde{\nu}$ = 3923 (w), 3485 (s), 3402 (s), 3234 (w), 2966 (s), 2935 (m), 2875 (s), 2732 (w), 2429 (w), 2175 (w), 1739 (m), 1622 (s), 1578 (m), 1451 (s), 1378 (m), 1344 (m), 1303 (w), 1284 (m), 1247 (w), 1210 (s), 1137 (w), 1056 (m), 986 (w), 970 (w), 867 (s), 853 (m), 796 (m), 759 (w), 740 (m), 723 (w), 586 (w), 548 (m), 523 (w), 488 (w), 413 (w) cm^{-1}.

MS (ESI(+), MeCN): *m/z* = 228.1 $[M+H]^+$.

EA for $C_{10}H_{14}BrN$	calculated (%)	C: 52.65	H: 6.19	N: 6.14
M = 228.13 g/mol	found (%)	C: 53.06	H: 6.15	N: 6.33

5-Bromo-1,3-diethyl-2-iodobenzene

4-Bromo-2,6-diethylaniline (73.0 g, 320.0 mmol; 1.0 eq) was suspended in 1.1 l H_2O, 200 ml acetonitrile and 350 ml concentrated aqueous HCl and cooled to –10 °C. $NaNO_2$ (40 g, 580 mmol; 1.8 eq) in 200 ml H_2O were added dropwise, resulting in a pink precipitate, followed by formation of a clear red solution. After the addition, the solution was stirred for 60 min at –10 °C, followed by dropwise addition of a solution of KI (184 g, 902 mmol; 2.8 eq) in 300 ml H_2O. The formation of a yellowish foam was observed. Afterwards, the mixture was carefully allowed to warm up to room temperature. The mixture was stirred overnight, heated to 60 °C for 30 min, cooled to room temperature, and extracted with *n*-hexane (4 x 50 ml). The collected organic phases were stirred over saturated aqueous Na_2SO_3 solution, until the organic phase turned light yellow. The organic phase was separated and dried over $MgSO_4$. After filtration, the solvent removed under reduced pressure.



Yield: 100.0 g (92%), slightly yellow oil.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 7.15 (s, 2H, H^3), 2.73 (q, $^3J_{HH}$ = 7.5 Hz, 4H, H^5), 1.18 ppm (t, $^3J_{HH}$ = 7.4 Hz, 6H, H^6).

^{13}C{^{1}H}-NMR ($CDCl_3$, 100.16 MHz): δ = 148.8 (s, C^2), 128.7 (s, C^3), 122.6 (s, C^4), 105.4 (s, C^1), 35.3 (s, C^5), 14.5 ppm (s, C^6).

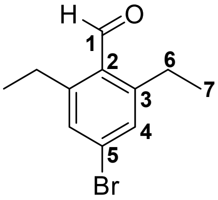
IR (KBr): $\tilde{\nu}$ = 2968 (s), 2931 (m), 2873 (m), 2382 (w), 2347 (w), 1734 (w), 1558 (m), 1460 (s), 1427 (m), 1417 (m), 1397 (w), 1373 (m), 1327 (m), 1271 (w), 1241 (m), 1128 (m), 1075 (w), 1051 (m), 1004 (s), 862 (s), 813 (m), 784 (w), 726 (w), 709 (w), 661 (w), 600 (w), 568 (w), 530 (w), 421 (w) cm^{-1}.

MS (ESI(+), DCM/MeOH): *m/z* = 374.9 $[C_{10}H_{10}BrI+K]^+$.

EA for $C_{10}H_{12}BrI$	calculated (%)	C: 35.46	H: 3.57
M = 339.01 g/mol	found (%)	C: 35.97	H: 3.55

4-Bromo-2,6-diethylbenzaldehyde

5-Bromo-1,3-diethyl-2-iodobenzene (10.0 g, 29.5 mmol; 1.0 eq) was dissolved in 100 ml diethyl ether and cooled to –78 °C. 21.9 ml (33.9 mmol; 1.1 eq) of a 1.55 M *n*-butyllithium solution in *n*-hexane were added in one portion and the mixture was stirred for 90 min at a temperature below –45 °C, resulting in a white precipitate. Afterwards 10.3 ml (132.8 mmol; 4.5 eq) dimethylformamide were added dropwise and the precipitate dissolved. The mixture was allowed to warm to room temperature and was stirred overnight, resulting again in a white precipitate. 20 ml of an aqueous NH_4Cl solution were added carefully and the mixture was extracted with diethyl ether (2 x 25 ml). The collected organic phases were dried over $MgSO_4$ and the solvent removed using the rotary evaporator after filtration. The raw product was filtered over silica using *n*-hexane/EtOH (20:1; $R_f = 0.7$) and subsequently distilled at $2.6 \cdot 10^{-2}$ mbar and 100 °C.



Yield: 6.2 g (87%), colourless oil.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 10.52 (s, 1H, H^1), 7.28 (s, 2H, H^4), 2.93 (q, $^3J_{HH}$ = 7.5 Hz, 4H, H^6), 1.24 ppm (t, $^3J_{HH}$ = 7.6 Hz, 6H, H^7).

^{13}C{^{1}H}-NMR ($CDCl_3$, 100.16 MHz): δ = 192.3 (s, C^1), 149.1 (s, C^3), 131.0 (s, C^4), 130.3 (s, C^2), 127.8 (s, C^5), 26.4 (s, C^6), 16.1 ppm (s, C^7).

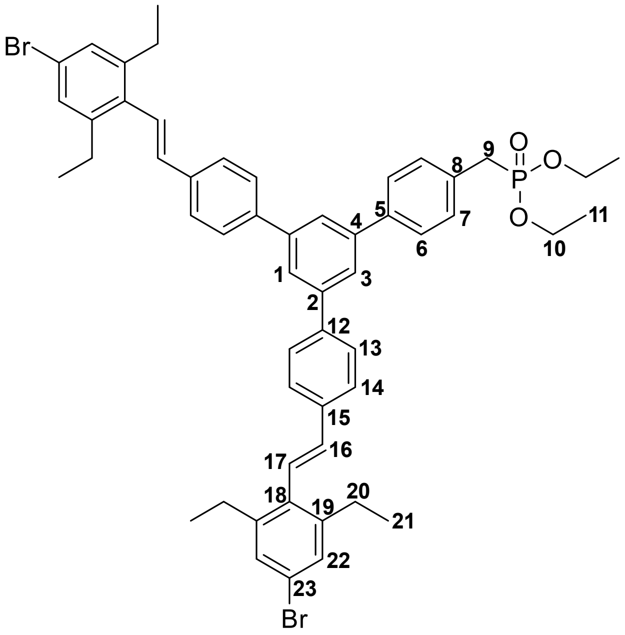
IR (KBr): $\tilde{\nu}$ = 3373 (w), 2970 (s), 2934 (m), 2874 (m), 2767 (m), 1740 (m), 1695 (s), 1574 (s), 1457 (s), 1401 (m), 1377 (m), 1324 (w), 1298 (w), 1264 (m), 1234 (s), 1184 (m), 1158 (m), 1114 (s), 1061 (m), 968 (w), 893 (m), 867 (s), 844 (s), 799 (w), 737 (m), 590 (w), 442 (m) cm^{-1}.

MS (ESI(+), MeCN): *m/z* = 298.3 $[M+CH_3CN+CH_3]^+$.

EA for $C_{11}H_{13}BrO$	calculated (%)	C: 54.79	H: 5.43
M = 241.12 g/mol	found (%)	C: 54.82	H: 5.57

Synthesis of 1-[4-(Diethoxyphosphonylmethyl)phenyl]-3,5-bis{4-[(*E*)-(4-bromo-2,6-diethyl)-styryl]phenyl}benzene

1,3,5-Tris(*p*-(diethoxyphosphonylmethyl)phenyl)benzene (2.54 g, 3.36 mmol; 1.0 eq) was dissolved in 20 ml THF. NaH (0.24 g, 6.0 mmol; 1.8 eq; 60% in mineral oil) was added. The solution was stirred for 3 h followed by addition of 0.81 g (3.36 mmol; 1.0 eq) 4-bromo-2,6-diethylbenzaldehyde in 10 ml THF. The reaction mixture was stirred over night at room temperature, and the additions were repeated once more. 20 ml water was added carefully and the mixture neutralised with hydrochloric acid. All volatiles were removed in vacuum. The resulting oil was dissolved in DCM, washed with brine and water (50 ml each) and dried over $MgSO_4$. The pure product was obtained after column chromatography using *n*-hexane/EtOH (10:1; R_f = 0.4).



Yield: 1.64 g (69%), viscous, slightly yellow oil.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ = 7.81 (s, 1H, H^{1}), 7.80 (s, 2H, H^{3}), 7.73 (d, $^{3}J_{HH}$ = 8.4 Hz, 4H, H^{13}), 7.67 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, H^{6}), 7.62 (d, $^{3}J_{HH}$ = 8.4 Hz, 4H, H^{14}), 7.44 (m, 2H, H^{7}), 7.25 (s, 4H, H^{22}), 7.13 (d, $^{3}J_{HH}$ = 16.8 Hz, 2H, H^{17}), 6.61 (d, $^{3}J_{HH}$ = 16.8 Hz, 2H, H^{16}), 4.07 (m, 4H, H^{10}), 3.23 (d, $^{2}J_{PH}$ = 21.9 Hz, 2H, H^{9}), 2.70 (q, $^{3}J_{HH}$ = 7.6 Hz, H, H^{20}), 1.29 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H, H^{11}), 1.20 ppm (t, $^{3}J_{HH}$ = 7.6 Hz, 12H, H^{21}).

^{13}C{^{1}H}-NMR ($CDCl_3$, 100.16 MHz): δ = 144.7 (s, C^{19}), 142.1 (s, C^{4}), 141.9 (s, C^{2}), 140.4 (s, C^{12}), 139.6 (d, $^{5}J_{PC}$ = 3.7 Hz, C^{5}), 136.6 (s, C^{15}), 135.2 (s, C^{18}), 133.8 (s, C^{16}), 131.1 (d, $^{2}J_{PC}$ = 9.2 Hz, C^{8}), 130.3 (d, $^{3}J_{PC}$ = 6.4 Hz, C^{7}), 128.8 (s, C^{22}), 127.6 (s, C^{13}), 127.4 (d, $^{4}J_{PC}$ = 2.8 Hz, C^{6}), 126.9 (s, C^{14}), 125.7 (s, C^{17}), 124.9 (s, C^{3}), 124.7 (s, C^{1}), 121.1 (s, C^{23}), 62.2 (d, $^{2}J_{PC}$ = 6.7 Hz, C^{10}), 33.5 (d, $^{1}J_{PC}$ = 138.2 Hz, C^{9}), 26.8 (s, C^{20}), 16.4 (d, $^{3}J_{PC}$ = 5.8 Hz, C^{11}), 15.1 ppm (s, C^{21}).

^{31}P{^{1}H}-NMR ($CDCl_3$, 161.98 MHz): δ = 26.3 ppm (s).

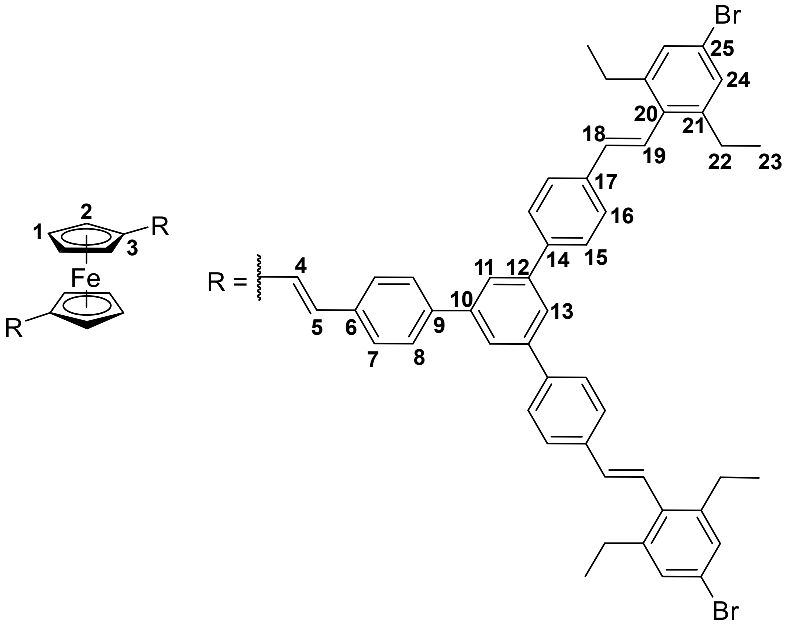
IR (KBr): $\tilde{\nu}$ = 3027 (w), 2966 (s), 2931 (m), 2872 (m), 2346 (w), 1639 (s), 1595 (s), 1575 (s), 1510 (s), 1456 (s), 1394 (m), 1326 (m), 1248 (s), 1182 (m), 1097 (m), 1054 (s), 1027 (s), 968 (s), 850 (s), 811 (s), 767 (w), 739 (w), 704 (m), 646 (w), 612 (w), 597 (w), 574 (w), 543 (s) cm^{-1}.

MS (ESI(+), DCM/MeOH): *m/z* = 953.3 [M+Na]$^{+}$.

EA for $C_{53}H_{55}Br_2O_3P$	calculated (%)	C: 68.39	H: 5.96
M = 930,80 g/mol	found (%)	C: 67.76	H: 5.98

Synthesis of 1,1´-Bis{(*E*)-[4-(3,5-bis{4-[(*E*)-(4-bromo-2,6-diethyl)styryl]phenyl})styryl]}ferrocene

1-[4-(Diethoxyphosphonylmethyl)phenyl]-3,5-bis{4-[(*E*)-(4-bromo-2,6-diethyl)-styryl]phenyl}benzene (3.44 g, 3.70 mmol; 3.0 eq) was dissolved in 200 ml THF. NaH (0.37 g, 9.25 mmol; 7.5 eq; 60% in mineral oil) was added and the mixture was stirred for 90 min. The suspension was warmed to 50 °C for a short period, resulting in an intense dark brown colour. Subsequently, 0.30 g (1.23 mmol; 1.0 eq) of freshly purified (via column chromatography) 1,1´-diformylferrocene was added as a solid in one portion, resulting in a colour change of the solution to red. The reaction mixture was stirred over night at room temperature followed by careful addition of 15 ml water. All volatiles were removed using the rotary evaporator. The pure product was obtained after column chromatography using *n*-hexane/toluene (5:3; R$_f$ = 0.5).



Yield: 1.26 g (57%), intense red, solidifying oil.

^{1}H-NMR (CDCl$_3$, 400.13 MHz): δ = 7.67 (s, 2H, H^{11}), 7.62 (s, 1H, H^{13}), 7.52 – 7.49 (m, 6H, H^8+H^{15}), 7.42 (d, $^3J_{HH}$ = 8.4 Hz 4H, H^{16}), 7.34 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H^7), 7.14 (s, 4H, H^{24}), 6.96 (d, $^3J_{HH}$ = 16.7 Hz, 2H, H^{19}), 6.75 (d, $^3J_{HH}$ = 15.8 Hz, 1H, H^4), 6.61 (d, $^3J_{HH}$ = 15.8 Hz, 1H, H^5), 6.45 (d, $^3J_{HH}$ = 16.7 Hz, 2H, H^{18}), 4.37 (s, 2H, H^2), 4.21 (s, 2H, H^1), 2.56 (q, $^3J_{HH}$ = 7.5 Hz, 8H, H^{22}), 1.08 ppm (t, $^3J_{HH}$ = 7.5 Hz, 12H, H^{23}).

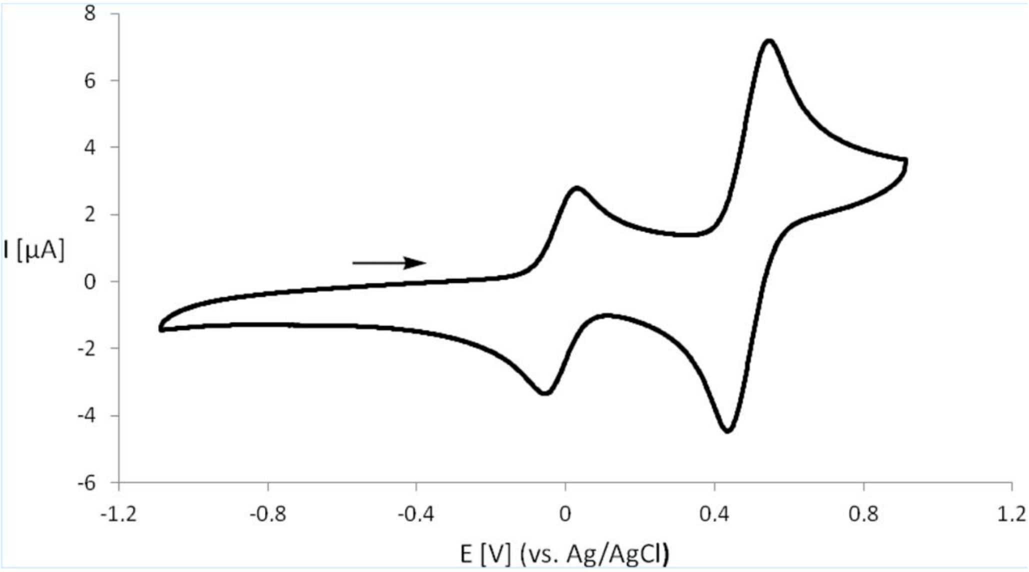
^{13}C{^{1}H}-NMR (CDCl$_3$, 100.16 MHz): δ = 144.5 (s, C^{21}), 142.0 (s, C^{10}), 141.7 (s, C^{12}), 140.3 (s, C^{14}), 139.0 (s, C^9), 137.2 (s, C^6), 136.4 (s, C^{17}), 135.1 (s, C^{20}), 133.7 (s, C^{18}), 128.7 (s, C^{24}), 127.5 (s, C^{15}), 127.3 (s, C^8), 126.7 (s, C^{16}), 126.5 (s, C^4), 126.2 (s, C^7), 125.9 (s, C^5), 125.6 (s, C^{19}), 124.5 (m, C^{11}+C^{13}), 121.0 (s, C^{25}), 84.1 (s, C^3), 70.1 (s, C^1), 68.1 (s, C^2), 26.7 (s, C^{22}), 15.0 ppm (s, C^{23}).

IR (KBr): $\tilde{\nu}$ = 3024 (w), 2964 (m), 2929 (w), 2870 (w), 1631 (m), 1594 (m), 1575 (m), 1558 (w), 1510 (m), 1456 (m), 1394 (w), 1262 (s), 1179 (w), 1096 (s), 1026 (s), 970 (m), 862 (m), 848 (m), 805 (s), 704 (w), 609 (w), 491 (w) cm^{-1}.

MS (ESI(+), DCM/MeCN): *m/z* = 1794.6 [M–H]$^+$.

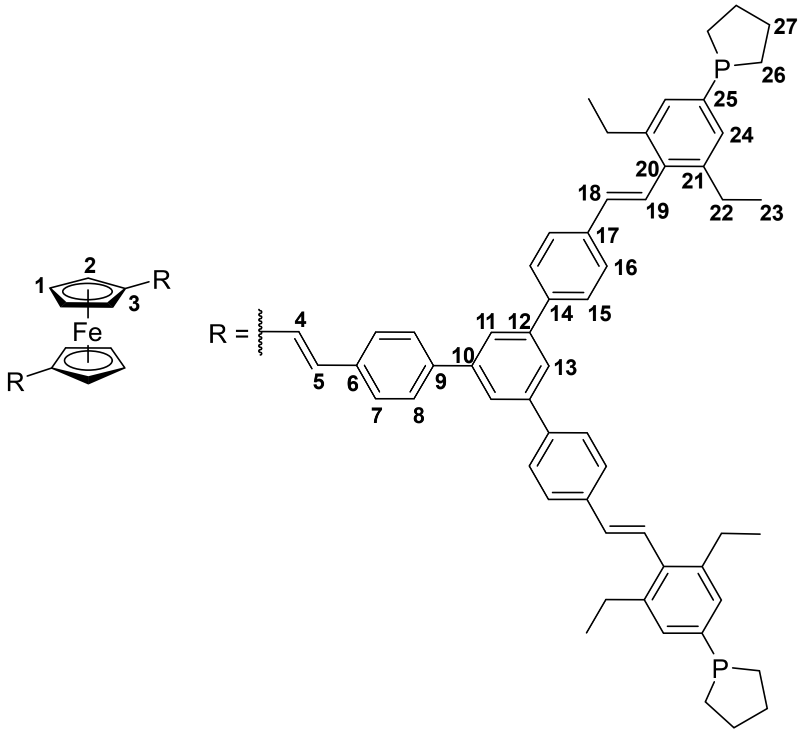
EA for $C_{110}H_{98}Br_4Fe$	calculated (%)	C: 73.50	H: 5.61
M = 1795,46 g/mol	found (%)	C: 73.37	H: 5.68

Cyclic voltammogram:



Synthesis of Ligand 1 (1,1´-Bis{(*E*)-[4-(3,5-bis{4-[(*E*)-(4-phospholane-2,6-diethyl)styryl]phenyl})styryl]}ferrocene)

1,1´-Bis{(*E*)-[4-(3,5-bis{4-[(*E*)-(4-bromo-2,6-diethyl)styryl]phenyl})styryl]}ferrocene (0.46 g, 0.26 mmol; 1.0 eq) was dissolved in 20 ml THF and cooled to –78 °C. To this solution, 0.84 ml (1.28 mmol; 5.0 eq) of a 1.52 M *n*-butyllithium solution in *n*-hexane was quickly added and stirred at –78 °C for 90 min, followed by addition of 0.19 g (1.54 mmol; 6.0 eq) 1-chlorophospholane. The mixture was warmed to room temperature followed by removal of the solvent in vacuum. The remaining solid was dissolved in 10 ml DCM and filtered over a layer of silica (ca. 3 cm thick, inert). Removal of the solvent in vacuum gave the pure product as red oil.



Yield: 0.43 g (91%), intense red, solidifying oil.

^{1}H-NMR (CDCl$_3$, 400.13 MHz): δ = 7.77 (m, 2H, H^{11}), 7.73 (s, 1H, H^{13}), 7.64 – 7.60 (m, 6H, H^{8}+H^{15}), 7.55 (d, $^{3}J_{HH}$ = 8.3 Hz 4H, H^{16}), 7.46 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, H^{7}), 7.18 (d, $^{3}J_{HH}$ = 16.6 Hz, 2H, H^{19}), 7.13 (d, $^{3}J_{HP}$ = 5.5 Hz, 4H, H^{24}), 6.87 (d, $^{3}J_{HH}$ = 16.1 Hz, 1H, H^{4}), 6.72 (d, $^{3}J_{HH}$ = 16.1 Hz, 1H, H^{5}), 6.60 (d, $^{3}J_{HH}$ = 16.6 Hz, 2H, H^{18}), 4.48 (s, 2H, H^{2}), 4.32 (s, 2H, H^{1}), 2.71 (q, $^{3}J_{HH}$ = 7.5 Hz, 8H, H^{22}), 2.02 (m, 8H, H^{26}), 1.82 (m, 8H, H^{27}), 1.20 ppm (t, $^{3}J_{HH}$ = 7.5 Hz, 12H, H^{23}).

^{13}C{^{1}H}-NMR (CDCl$_3$, 100.16 MHz): δ = 142.2 (s, C^{21}+C^{25}), 142.1 (s, C^{10}), 141.9 (s, C^{12}), 140.2 (s, C^{14}), 139.2 (s, C^{9}), 137.2 (s, C^{6}), 136.8 (s, C^{17}), 135.5 (s, C^{20}), 133.3 (s, C^{18}), 128.2 (m, C^{24}), 127.6 (s, C^{15}), 127.4 (s, C^{8}), 126.8 (s, C^{16}), 126.6 (s, C^{4}), 126.5 (s, C^{19}), 126.3 (s, C^{7}), 126.0 (s, C^{5}), 124.7 (s, C^{13}), 124.6 (s, C^{11}), 84.1 (s, C^{3}), 70.3 (s, C^{1}), 68.1 (s, C^{2}), 28.0 (s, C^{26}), 27.1 (s, C^{22}+C^{27}), 15.5 ppm (s, C^{23}).

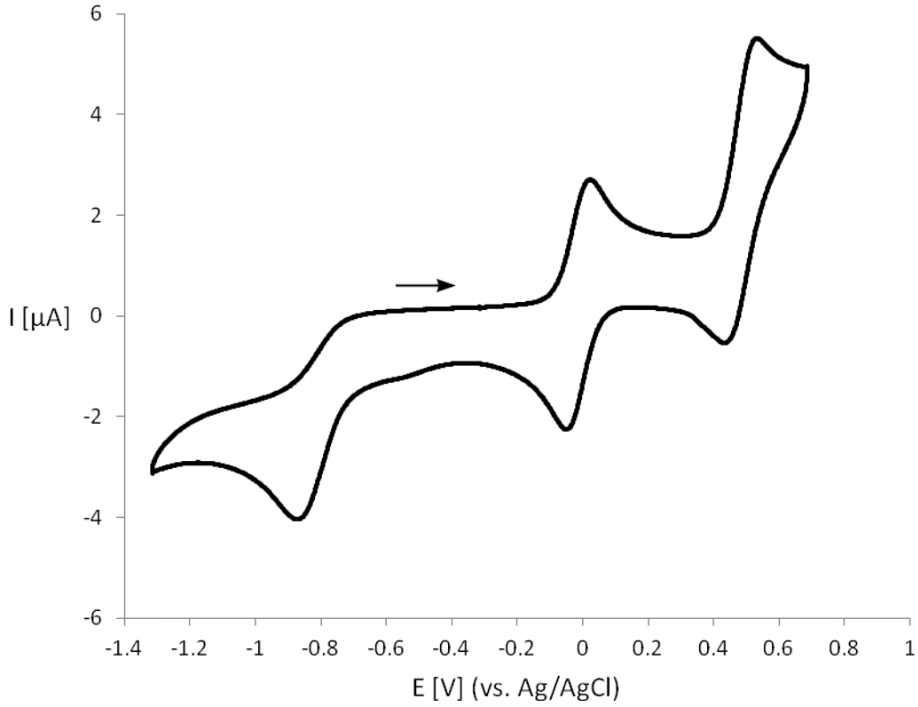
^{31}P{^{1}H}-NMR (CDCl$_3$, 161.98 MHz): δ = –16.3 ppm (s).

IR (KBr): $\tilde{\nu}$ = 3025 (m), 2961 (s), 2931 (s), 2870 (s), 1780 (w), 1632 (m), 1594 (s), 1548 (w), 1510 (s), 1457 (s), 1421 (m), 1395 (m), 1373 (w), 1301 (w), 1261 (s), 1184 (w), 1095 (s), 1045 (s), 1027 (s), 970 (m), 853 (m), 807 (s), 759 (w), 705 (w), 648 (w), 609 (w), 493 (m), 393 (m) cm^{-1}.

MS (ESI(+), CHCl$_3$/MeCN): *m/z* = 912.9 [M+2H]$^{2+}$, 1824.9 [M+H]$^{+}$.

EA for $C_{126}H_{130}FeP_4$	calculated (%)	C: 82.87	H: 7.29
M = 1824.17 g/mol	found (%)	C: 78.94	H: 7.24

Cyclic voltammogram:



Synthesis of Complex 2 (Bis[*μ*-1,1´-bis{(*E*)-[4-(3,5-bis{4-[(*E*)-(4-phospholane-2,6-diethyl)styryl]phenyl})styryl]}ferrocene-*κ*^{4}*P,P´,P´´,P´´´*]tetragold(I)-tetrachloride)

1,1´-Bis{(*E*)-[4-(3,5-bis{4-[(*E*)-(4-phospholane-2,6-diethyl)styryl]phenyl})-styryl]}ferrocene (160 mg, 88 µmol; 2.0 eq) was dissolved in 10 ml DCM followed by addition of 60 mg (187 µmol; 2.1 eq) [AuCl(tht)] in 6 ml DCM. The intense red, clear solution was stirred at room temperature for 15 min followed by filtration via cannula. The resulting solution was diluted with 5 ml *o*-difluorobenzene and 5 ml toluene. Gas-phase diffusion of a 1:1 (v:v) mixture of *n*-pentane/*n*-hexane into this solution at room temperature gave deep red crystals of **2** suitable for X-ray crystallography within a few days.

^{1}H-NMR (CD_2Cl_2, 400.13 MHz): δ = 7.61 – 6.41 (m, 100H, $H^4+H^5+H^7+H^8+H^{11}+H^{13}+H^{15}+H^{16}+H^{18}+H^{19}+H^{24}$), 4.38 (s, 8H, H^2), 4.24 (s, 8H, H^1), 2.58 – 1.01 ppm (m, 144H, $H^{22}+H^{23}+H^{26}+H^{27}$). (Numbering of positions is identical to ligand **1**)

^{31}P{^{1}H}-NMR (CD_2Cl_2, 161.98 MHz): δ = 31.1 ppm (s).

IR (ATR): $\tilde{\nu}$ = 3341 (m), 2962 (s), 2931 (s), 2870 (m), 2362 (w), 2161 (w), 1589 (m), 1506 (s), 1454 (s), 1396 (m), 1265 (m), 1121 (m), 1060 (m), 1028 (w), 970 (s), 846 (m), 808 (m), 760 (m), 689 (m) cm^{-1}.

MS (ESI(+), DCM): L = $C_{126}H_{130}FeP_4$, *m/z* = 1108.9 $[Au_2L]^{2+}$, 1412.9 $[Au_3L_2]^{3+}$, 1418.2 $[Au_3L_2O]^{3+}$, 1490.5 $[Au_4ClL_2]^{3+}$, 1495.8 $[Au_4ClL_2O]^{3+}$, 2137.3 $[Au_3ClL_2]^{2+}$, 2144.7 $[Au_3ClL_2O]^{3+}$, 2253.7 $[Au_4Cl_2L_2]^{2+}$, 2369.7 $[Au_5Cl_3L_2]^{2+}$, 2485.6 $[Au_3Cl_2L]^{+}$.

EA for $C_{252}H_{260}Au_4Cl_4Fe_2P_8 \cdot 3\ CH_2Cl_2$	calculated (%)	C: 63.38	H: 5.55
M = 4832.83 g/mol	found (%)	C: 63.87	H: 5.63

Cyclic voltammogram:

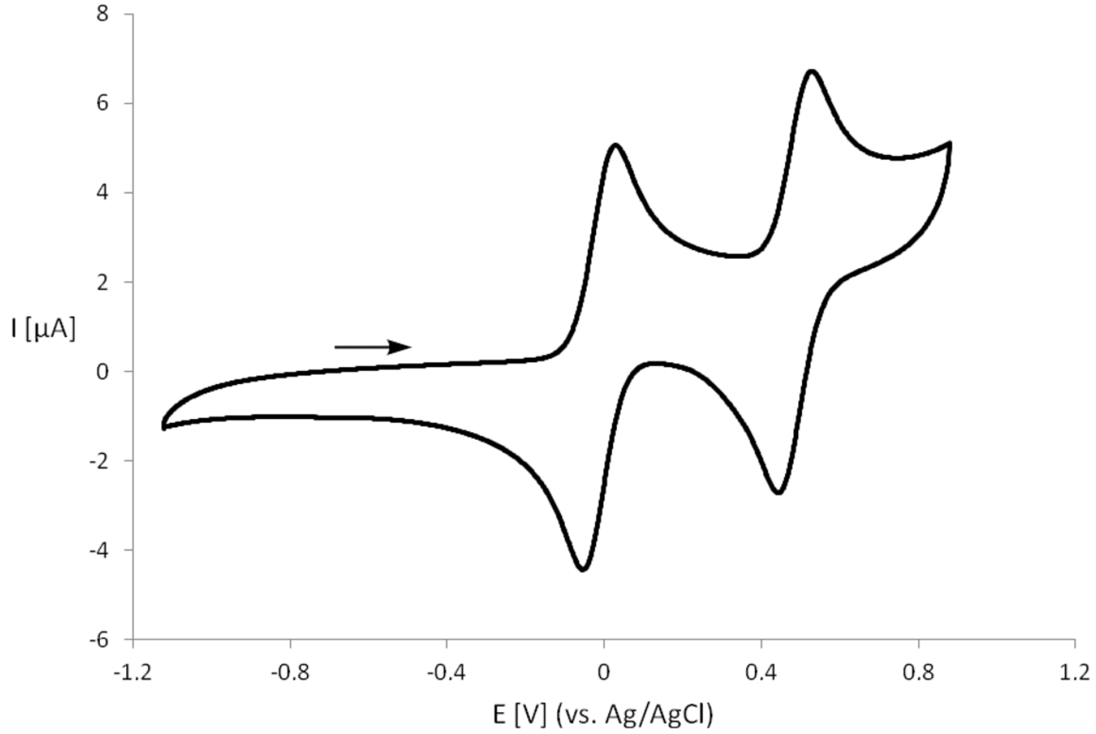


Table 1: Peak and reduction potentials in dichloromethane at room temperature with 50 mV/s speed of **1a**, **1** and **2**.

	$E_{p,c}$ [mV]	$E_{p,a}$ [mV]	ΔE_p [mV]	E_{red} [mV] vs. Ag/AgCl	E_{red} [mV] vs. Fc/Fc$^+$
1a	546	437	109	492	–40
1	532	436	96	484	–48
2	527	438	89	486	–46

4. Single-Crystal X-Ray Diffraction

The data were collected on a Gemini diffractometer (Rigaku Inc.) using Mo-Kα radiation (λ = 0.71073 Å) and ω-scan rotation. Data reduction was performed with CrysAlisPro[6] including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by dual space methods (SHELXT-2014 [7]) and the anisotropic refinement of all non-hydrogen atoms was performed with SHELXL-2018 [8]. All hydrogen atoms were calculated on idealised positions.

Several parts of the ligand are disordered over two positions. This involves two phospholane groups at P3 (0.58(2):0.42(2)) and P4 (0.55(2):0.45(2)), three ethyl groups at C34 (0.80(1):0.20(1)), C36 (0.58(1):0.42(1)) and C97 (0.62(1):0.38(1)), as well as a phenylene group C83-C88 (0.712(6):0.288(6)).

Although it was possible to locate 4 diffusely oriented CH_2Cl_2 solvent molecules of the asymmetric unit (8 for the unit cell), the electron density of all solvent molecules has been removed with the SQUEEZE[9] routine implemented in PLATON. Based on the squeezed electron count, the electron density of approximately 28 poorly defined and diffusely oriented dichloromethane molecules was removed from the unit cell (28 x 42 = 1176 electrons). This value corresponds with the estimated "squeezed" electron density of 1169 electrons. A volume of 94 Å^3 for one dichloromethane molecule (approximately 31 Å^3 for each non-hydrogen atom) is acceptable for loosely packed solvent molecules. The solvent molecules are located in channels along the crystallographic [211] direction (Figure S1). The size of these approximately rectangular channels is 5 Å x 2 Å. CCDC 2095487 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

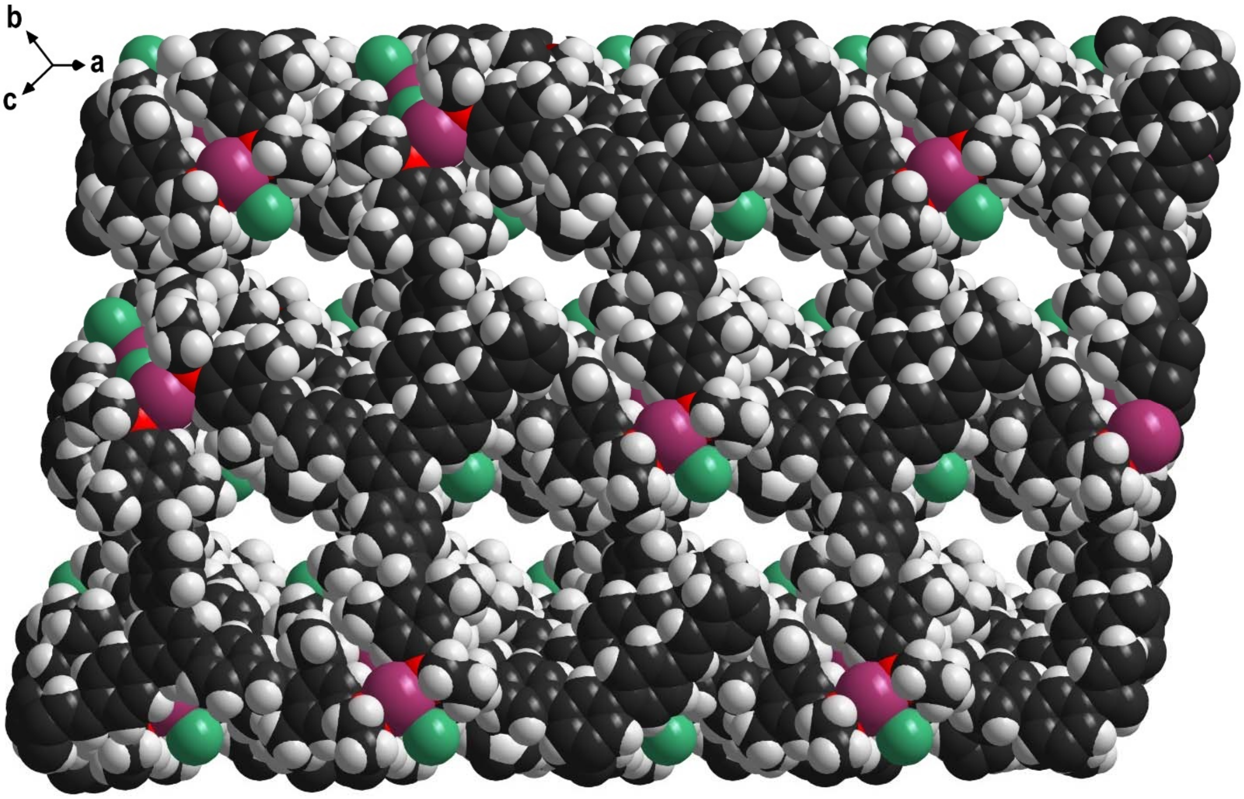


Figure S1. Representation of the rectangular channels along the crystallographic [211] direction.

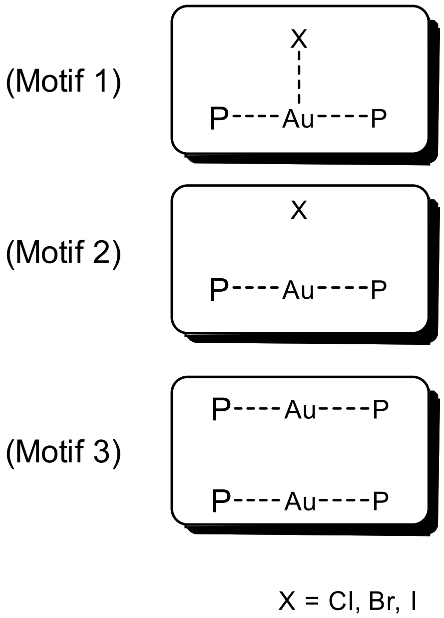
Table S1. Crystallographic data of **2**.

Empirical formula	$C_{280}H_{316}Au_4Cl_{60}Fe_2P_8$	
Molecular formula	$[Au_4Fe_2(C_{63}H_{65}P_2)_4Cl_4]\cdot 28\ CH_2Cl_2$	
Formula weight	6955.64	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 19.259(1) Å	α = 95.215(4)°
	b = 20.133(1) Å	β = 112.055(4)°
	c = 23.4890(9) Å	γ = 113.282(6)°
Volume	7441.2(8) Å^3	
Z	1	
Density (calculated)	1.552 Mg/m^3	
Absorption coefficient	2.693 mm^{-1}	
F(000)	3504	
Crystal size	0.34 x 0.12 x 0.05 mm^3	
Theta range for data collection	1.883 to 28.163°	
Index ranges	$-25 \geq h \geq 24$, $-25 \geq k \geq 26$, $-30 \geq l \geq 30$	
Reflections collected	79657	
Independent reflections	30914 [R(int) = 0.0671]	
Completeness to theta = 25.350°	99.9 %	
Absorption correction	Analytical[10] and semi-empirical from equivalents	
Max. and min. transmission	0.882 and 0.580	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30914 / 53 / 1213	
Goodness-of-fit on F^2	0.976	
Final R indices [I>2sigma(I)]	R_1 = 0.0554, wR_2 = 0.1156	
R indices (all data)	R_1 = 0.1193, wR_2 = 0.1373	
Largest diff. peak and hole	2.277 and -0.745 e·Å^{-3}	

5. CSD Search

Search Parameters

The Cambridge Structural Database (CSD), version 5.42 (November 2020)[11] was used for the crystal structure search. The searches have been performed using the program ConQuest,[12] version 2020.3.0. Three search motifs (Scheme S1) were utilised. Au···X distances from 1.8 to 4 Å were searched. For the remaining parameters, no restrictions were applied.



Scheme S2. Search masks used for the CSD search. Dashed lines represent “any bond” as used in ConQuest.

The search yielded 227 structures. Every search hit was individually checked and excluded from consideration if the vicinity of the halogen atom was coincidental and not the result of an interaction, such as for instance halogenated solvent molecules. If multiple measurement of a structure were present, the measurement with the better R_1 value was chosen (excluding polymorphs). After inspection, 232 hits in 165 structures were selected and sorted in three categories:

- *Category 1*: Complexes with Au atoms coordinated by two P atoms and a halogen (trigonal planar environment) or by two P atoms and an interaction with a halogen.
- *Category 2*: Complexes as in category 1 with an additional aurophilic interaction to a second Au atom. The cut-off for the consideration was set at 3.0 Å.
- *Category 3*: Complexes as in category 1 where the halogen however is not free but part of a molecular counter ion such as for instance $AlCl_4^-$.

Table S2 contains the complete results of the CSD search including the categories, type of halogen as well structural parameters for every search.

Table S2. Complete results of the CSD search including type of halogen (X), category (see above), selected interatomic distances (Å) and angles (°).

Ref. Code	Category	Halogen X	d(Au–X)	d(Au–P1)	d(Au–P2)	<(P–Au–P)
AJEHII	1	Cl	2.662	2.34	2.34	152.69
AJEHUU	3	Cl	3.438	2.322	2.323	166.828
AJEJEG	3	Cl	3.515	2.299	2.291	173.608
AVEBOS	1	Cl	2.953	2.307	2.304	173.478
BAXWOM06	1	Cl	2.544	2.324	2.312	136.813
BAXWOM16	1	Cl	2.528	2.32	2.32	133.205
BEDJEC	1	Cl	2.538	2.317	2.316	148.74
BIBZEU	1	Cl	2.832	2.293	2.297	175.993
BIBZEU	1	Cl	2.85	2.293	2.302	174.168
CABDAL	2	Cl	3.281	2.309	2.306	175.216
CABDAL	2	Cl	2.776	2.327	2.326	166.82
CABDAL	2	Cl	2.873	2.307	2.306	168.478
CABDIT	1	I	2.945	2.322	2.321	155.913
CABDIT	1	I	2.993	2.309	2.331	155.28
CABDIT	1	I	3.053	2.308	2.324	158.237
CABDIT	1	I	3.054	2.322	2.311	158.908
CELSAQ	3	Cl	3.038	2.314	2.321	162.963
CINBUZ	3	Cl	3.252	2.339	2.322	169.104
CINCAG	3	Cl	3.239	2.325	2.297	173.71
CORQEI	1	Cl	2.62	2.311	2.305	151.85
CTPAUB01	1	Cl	2.509	2.313	2.331	132.733
CUJQOO	1	Cl	2.566	2.317	2.317	139.081
CUJROP	1	Cl	2.462	2.333	2.349	116.727
CUJRUV	1	Cl	2.457	2.338	2.318	117.769
CUJRUV	1	Cl	2.475	2.335	2.336	120.617
CUKQII	1	I	2.996	2.342	2.322	157.905
CUKQII	1	I	3.142	2.301	2.318	159.201
DAJRIP	1	Cl	3.436	2.31	2.311	176.516
DALWAR	1	Cl	2.453	2.278	2.401	119.003
DALWEV	1	Cl	2.472	2.33	2.293	119.289
DIFTOE	3	Cl	2.967	2.305	2.308	160.02
DUFWIK	2	Cl	2.808	2.335	2.338	171.419
DUFWOQ	2	Cl	2.964	2.333	2.337	173.08
DUKREG01	2	Cl	3.467	2.302	2.303	176.812
DUKREG01	2	Cl	3.534	2.303	2.302	176.812
DUMJIG	2	Cl	2.949	2.306	2.31	173.244
DUMJIG	2	Cl	2.978	2.308	2.313	170.036
EKOWUY	1	Cl	2.562	2.342	2.303	147.219
EKOWUY	1	Cl	2.677	2.315	2.303	158.072
FAXCAI	1	Br	2.841	2.292	2.302	157.745
FAXCAI	1	Br	2.894	2.317	2.312	162.06
FAXCAI01	1	Br	3.764	2.327	2.305	178.447
FAXCOW	1	Br	2.777	2.323	2.323	147.449
FAXHER	1	I	3.008	2.31	2.315	159.113
FAXJIX	1	I	2.895	2.343	2.328	143.062
FEHBUR01	1	I	2.976	2.314	2.318	152.975
FEHCEC	2	I	3.203	2.306	2.304	163.134
FEYPUU	1	Br	2.625	2.323	2.323	132.458
FEYRAC	1	I	2.754	2.333	2.333	132.131
FILCEL	3	Cl	3.811	2.363	2.293	179.079
FOJDUD	2	Br	2.869	2.312	2.354	156.521
FONFAR	1	Cl	2.709	2.324	2.33	151.768
FONFIZ	1	Cl	3.319	2.305	2.306	171.494
FONFOF	1	Cl	3.197	2.301	2.301	172.766
FONSEJ	3	Cl	2.986	2.32	2.301	168.787
GACTEL	1	Cl	2.6	2.295	2.294	153.274
GACTEL	1	Cl	2.625	2.291	2.293	154.668
GACTIP	1	Cl	2.627	2.292	2.303	151.554
GACTIP	1	Cl	2.639	2.298	2.29	153.177
GACTOV	1	Cl	2.691	2.307	2.3	148.334
GESMEW	2	Cl	2.644	2.334	2.307	145.1
GESMEW	2	Cl	2.695	2.341	2.301	148.388
GITKID	2	Cl	2.964	2.29	2.301	158.513
GITKOJ	2	Br	3.108	2.294	2.304	158.967
HIFGEI	1	Cl	3.227	2.26	2.26	180
IBOLET	1	Cl	2.543	2.315	2.306	128.185

ICUDIV	3	Cl	2.946	2.295	2.3	176.624
ICUDIV	3	Cl	3.005	2.293	2.307	176.914
ICUDIV	3	Cl	3.045	2.299	2.314	177.624
ICUDIV	3	Cl	3.089	2.304	2.317	177.135
IDUMIF	3	Cl	3.04	2.311	2.313	176.679
IDUMIF	3	Cl	3.032	2.301	2.305	177.978
IJAVIA	2	I	3.085	2.336	2.336	158.554
IJAVOG	2	I	3.538	2.329	2.329	168.122
INACOP	2	I	3.1	2.309	2.33	154.475
IYOKOX	1	Br	2.789	2.312	2.31	150.671
IYOKUD	1	Br	2.829	2.31	2.305	156.207
IYOLAK	1	Br	2.803	2.306	2.31	154.191
IYOLEO	1	Br	2.817	2.312	2.31	153.362
IYOLIS	1	Br	2.711	2.3	2.32	139.874
IYOLIS	1	Br	2.725	2.303	2.313	145.104
IYOLOY	1	Br	2.885	2.304	2.303	157.803
IYOLUE	1	Br	2.823	2.305	2.311	155.799
IYOMAL	1	Br	2.713	2.302	2.315	141.485
IYOMAL	1	Br	2.737	2.309	2.315	146.689
IZOCOQ	3	Cl	2.934	2.303	2.307	175.026
IZOCOQ	3	Cl	2.986	2.296	2.317	175.616
IZOCOQ	3	Cl	3.04	2.301	2.319	176.459
IZOCOQ	3	Cl	3.057	2.297	2.308	175.536
IZOCUW	3	Cl	3.107	2.479	2.447	173.991
IZOCUW	3	Cl	3.451	2.021	2.02	176.85
IZODEH	3	Cl	2.949	2.305	2.311	175.671
IZODEH	3	Cl	2.967	2.296	2.305	175.748
IZODEH	3	Cl	2.779	2.296	2.314	166.605
IZODEH	3	Cl	2.744	2.271	2.301	165.452
JAFGOM	2	Cl	3.591	2.304	2.301	177.415
JAFGOM	2	Cl	3.679	2.301	2.304	177.415
JAJMUC	2	Br	3.494	2.305	2.302	176.696
JAJNEN	2	Cl	3.028	2.293	2.286	178.035
JAJNEN	2	Cl	3.022	2.301	2.295	178.192
JAJNIR	2	Br	3.083	2.313	2.298	178.32
JAJNIR	2	Cl	3.112	2.291	2.287	176.478
JAJNOX	2	I	3.151	2.292	2.291	171.608
JAJNOX	2	I	3.277	2.31	2.297	178.578
JAJNOX	2	I	3.331	2.285	2.287	176.024
JAJNOX	2	I	3.267	2.287	2.294	174.027
JAZRAD	1	Cl	2.521	2.31	2.31	134.118
KEPSII06	1	Cl	2.582	2.328	2.346	136.446
KIXGAC	1	Cl	3.955	2.313	2.314	175.899
KIXGAC	1	Cl	3.704	2.322	2.322	178.579
KIXGAC	1	Cl	3.678	2.316	2.305	177.22
KIXGAC	1	Cl	3.659	2.314	2.324	177.842
KOBSIG	2	Cl	2.588	2.306	2.34	141.391
KOCMIZ	3	Cl	3.042	2.304	2.303	165.202
KOQXEW	1	Cl	3.015	2.319	2.317	166.657
KOQXEW	1	Cl	3.296	2.313	2.311	172.946
KUNHAD	1	Cl	2.544	2.323	2.306	137.364
KUNHEH	1	Cl	2.572	2.345	2.355	132.885
KUNHEH	1	Cl	2.591	2.352	2.327	137.801
LAPXOQ	1	Cl	2.847	2.308	2.308	173.221
LEHWAW	2	Cl	3.866	2.321	2.335	173.987
LEHWAW	2	Cl	3.768	2.321	2.335	173.987
LEKGAJ	2	Cl	2.951	2.333	2.299	164.896
MIVMEL	1	Cl	2.788	2.319	2.319	158.314
NAWQAE	1	Cl	2.534	2.313	2.33	135.514
NEKJUL	3	I	3.662	2.302	2.302	180
NELNOK	1	Cl	2.661	2.305	2.309	144.905
NOFJAV	1	Cl	2.902	2.297	2.294	172.768
NOFJEZ	1	Cl	2.924	2.3	2.306	167.356
NOFJEZ	1	Cl	3.038	2.295	2.3	167.621
NOFJEZ	1	Cl	3.05	2.298	2.301	167.746
NOFJEZ	1	Cl	3.268	2.297	2.293	170.066
NOFKEA	1	Cl	2.941	2.296	2.292	175.323
NOFWUC	1	Cl	2.807	2.299	2.299	169.376
NOFWUC	1	Cl	2.845	2.288	2.294	170.157

NUSZAF	3	Cl	3.443	2.309	2.305	144.295
OCUYUH	2	I	3.107	2.317	2.32	166.328
OCUYUH	2	I	3.101	2.31	2.311	164.704
OKACAF	3	Br	3.45	2.305	2.309	172.978
OKACEJ	3	Br	3.481	2.309	2.306	172.898
OKACIN	3	Cl	3.174	2.318	2.32	168.033
OKACOT	3	Br	3.215	2.321	2.32	170.826
OMUFIN01	2	Cl	3.161	2.037	2.393	158.651
OMUFIN01	2	Cl	2.829	2.413	2.324	159.877
OROXEA	3	Cl	2.86	2.294	2.294	156.74
ORULOE	1	Br	2.64	2.303	2.306	164.828
ORULUK	1	Cl	2.554	2.311	2.305	165.479
ORUMAR	1	I	2.798	2.316	2.311	163.691
OSATOT	3	Cl	3.284	2.285	2.269	164.366
PODFOD	1	Cl	2.71	2.293	2.323	155.237
PPEAUC	2	Cl	2.766	2.325	2.284	155.848
PUYKOK	3	Br	3.871	2.303	2.299	153.456
PUYKUQ	3	I	3.95	2.312	2.31	153.317
QABMOX	3	Cl	3.086	2.311	2.308	172.362
QAKPOK	1	Cl	2.633	2.333	2.32	140.279
QAKQOL	1	Cl	2.65	2.322	2.327	139.811
QEZYOL	1	Br	2.645	2.314	2.323	143.532
QEZYOL	1	Br	2.667	2.311	2.315	144.77
QIDZUZ	2	Cl	2.636	2.297	2.288	159.403
QIZKIW	1	Br	3.347	2.309	2.31	169.454
QIZKIW	1	Br	3.489	2.304	2.302	176.131
REDMAO	3	Cl	3.373	2.295	2.32	177.513
REXQUG	1	Cl	2.654	2.316	2.316	139.516
RILSIR	1	Cl	3.511	2.3	2.3	168.09
RILSOX	1	Cl	3.494	2.302	2.306	168.248
RILTEO	1	Cl	2.949	2.307	2.308	177.697
ROMSOB	2	Cl	3.349	2.328	2.321	175.448
ROZRAA	3	Cl	3.037	2.307	2.305	165.209
RUHCAA	1	Cl	2.871	2.291	2.295	173.063
RUTDOC	1	I	2.674	2.319	2.343	115.33
RUTFEU	1	I	2.703	2.321	2.324	117.695
RUTFEU	1	I	2.713	2.331	2.325	117.766
RUTFIY	1	Cl	2.512	2.327	2.327	122.007
RUTGEV	1	I	2.697	2.327	2.327	116.753
SAVROW	2	I	3.343	2.322	2.317	170.115
SAVROW	2	I	3.162	2.31	2.328	171.396
SERBAU	1	I	2.931	2.305	2.322	152.881
SERBIC	1	I	3.001	2.309	2.302	164.632
SERBIC	1	I	3.083	2.309	2.311	172.317
SERBOI	1	I	2.805	2.335	2.3	133.042
SOVPAW	3	Cl	3.257	2.334	2.285	176.367
SUCYOH	1	Cl	2.334	2.673	2.24	97.664
SUCYUN	1	Cl	2.322	2.235	2.629	98.141
SUJBAB	1	Cl	2.577	2.323	2.305	140.14
SUJBIJ	1	Cl	2.602	2.334	2.33	159.908
SUJBOP	1	Cl	2.573	2.346	2.343	159.161
TAXJEH	3	Cl	3.405	2.304	2.306	168.379
TAXJEH	3	Cl	3.509	2.313	2.31	170.104
TAXJEH	3	Cl	3.608	2.313	2.31	170.104
TAXJEH	3	Cl	3.752	2.304	2.306	168.379
TONTUM	1	Cl	2.633	2.313	2.324	145.213
TORGIQ	2	Cl	3.113	2.316	2.302	170.87
UCOXUH	3	Cl	3.288	2.319	2.309	175.032
UCOXUH	3	Cl	3.506	2.31	2.315	176.314
UCOXUH	3	Cl	3.507	2.303	2.303	180
UCOXUH	3	Cl	3.685	2.3	2.3	180
UCOXUH	3	Cl	3.183	2.3	2.3	180
UCOXUH	3	Cl	3.308	2.31	2.315	176.314
UCOXUH	3	Cl	3.423	2.303	2.303	180
UCOXUH	3	Cl	3.495	2.319	2.309	175.032
UCOXUH	3	Cl	3.279	2.31	2.315	176.314
UCOXUH	3	Cl	3.482	2.319	2.309	175.032
UCOXUH	3	Cl	3.268	2.319	2.309	175.032
UCOXUH	3	Cl	3.519	2.31	2.315	176.314

VICBOZ	1	Cl	2.658	2.318	2.305	145.257
VIJHAA	1	Cl	2.309	2.885	2.242	79.473
VIJHEE	1	I	2.594	2.3	2.533	85.215
VUXDUN	1	Cl	2.744	2.324	2.3	158.236
WADLOC	2	Cl	2.897	2.311	2.308	175.904
WEFXOU	1	Cl	2.623	2.298	2.308	143.046
WEFXUA	1	Cl	2.551	2.316	2.315	136.483
WIHXOD	1	Cl	2.462	2.312	2.297	118.38
WIKNIP	1	Cl	2.489	2.341	2.331	174.094
XAXMAK	2	Cl	3.842	2.308	2.307	164.404
XEFKOJ	1	Cl	2.506	2.293	2.294	132.555
XESWAV	1	Cl	2.665	2.302	2.313	147.231
XIBKIF	1	I	2.715	2.359	2.371	115.747
XIBKOL	1	I	2.726	2.347	2.353	119.021
XIDVIR	1	Cl	2.523	2.306	2.306	129.488
XIVFEQ	1	Cl	2.639	2.317	2.325	139.941
XIVFEQ	1	Cl	2.641	2.32	2.333	141.153
XIVFEQ	1	Cl	2.65	2.298	2.362	141.768
XUKKIA	1	Cl	2.588	2.292	2.309	143.163
YAVNOA	1	I	2.719	2.32	2.32	128.491
YAYZAB	1	Cl	2.809	2.309	2.304	160.361
YEXYIL	3	Cl	3.285	2.285	2.294	159.916
YINLEM	1	Cl	2.952	2.3	2.3	173.171
YUTMUW	2	Cl	3.674	2.294	2.298	168.781
YUTNAD	2	Cl	3.526	2.305	2.309	172.18
ZAKXEO	1	Cl	2.437	2.315	2.347	116.127
ZEPYIC	3	Cl	3.134	2.319	2.324	172.777
ZUQFOG	1	Cl	2.824	2.304	2.316	169.968

Conclusions of the Search

The following representations complement the two plots shown in Figure 3 and 4 in the main text. Figures S2 and S3 contain the plot for only category 1, pointing out by comparison with Figures 3 and 4 that the aurophilic interactions of the search hits in category 2 have no significant influence of the dependencies discussed in the main text. To underline this, complexes with the general formula [$Au_2X_2L_2$] are shown in Table S3, where X is a halide (Cl, Br, I) and L is a bisphosphane ligand. Some of these complexes possess aurophilic interaction between the gold atoms while others do not (Au···Au distance is listed). As can be seen from the Table S3, there is no systematic influence of the Au···Au distance on the investigated dependencies.

Table S3. Complete results of the CSD search including type of halogen (X), category (see above), selected interatomic distances (Å) and angles (°).

Ref. Code	Category	Halogen X	d(Au–X)	d(Au–P1)	d(Au–P2)	<(P–Au–P)	d(Au···Au)
AVEBOS	1	Cl	2.953	2.307	2.304	173.478	11.736
CABDAL	2	Cl	3.281	2.309	2.306	175.216	2.992
CABDAL	2	Cl	2.776	2.327	2.326	166.82	2.945
CABDAL	2	Cl	2.873	2.307	2.306	168.478	2.945
CABDIT	1	I	2.945	2.322	2.321	155.913	3.057
CABDIT	1	I	2.993	2.309	2.331	155.28	3.028
CABDIT	1	I	3.053	2.308	2.324	158.237	3.023
CABDIT	1	I	3.054	2.322	2.311	158.908	2.993
CUKQII	1	I	2.996	2.342	2.322	157.905	3.076
CUKQII	1	I	3.142	2.301	2.318	159.201	2.951
DUKREG01	2	Cl	3.467	2.302	2.303	176.812	3.014
DUKREG01	2	Cl	3.534	2.303	2.302	176.812	3.014
DUMJIG	2	Cl	2.949	2.306	2.31	173.244	2.974
DUMJIG	2	Cl	2.978	2.308	2.313	170.036	2.974
FEHBUR01	1	I	2.976	2.314	2.318	152.975	3.395
FONFAR	1	Cl	2.709	2.324	2.33	151.768	6.277
GESMEW	2	Cl	2.644	2.334	2.307	145.1	3.07
GESMEW	2	Cl	2.695	2.341	2.301	148.388	3.002
INACOP	2	I	3.1	2.309	2.33	154.475	2.993
IYOKUD	1	Br	2.829	2.31	2.305	156.207	3.848
IYOLAK	1	Br	2.803	2.306	2.31	154.191	3.568
IYOLIS	1	Br	2.711	2.3	2.32	139.874	3.098
IYOLIS	1	Br	2.725	2.303	2.313	145.104	3.317
IYOLOY	1	Br	2.885	2.304	2.303	157.803	3.514

IYOLUE	1	Br	2.823	2.305	2.311	155.799	3.734
IYOMAL	1	Br	2.713	2.302	2.315	141.485	3.094
IYOMAL	1	Br	2.737	2.309	2.315	146.689	3.325
JAFGOM	2	Cl	3.591	2.304	2.301	177.415	3.019
JAFGOM	2	Cl	3.679	2.301	2.304	177.415	3.019
NOFJEZ	1	Cl	2.924	2.3	2.306	167.356	ca. 6
NOFJEZ	1	Cl	3.038	2.295	2.3	167.621	ca. 6
NOFJEZ	1	Cl	3.05	2.298	2.301	167.746	ca. 6
NOFJEZ	1	Cl	3.268	2.297	2.293	170.066	ca. 6
NOFWUC	1	Cl	2.845	2.288	2.294	170.157	8.504
OCUYUH	2	I	3.107	2.317	2.32	166.328	2.958
OCUYUH	2	I	3.101	2.31	2.311	164.704	2.958
DUFWIK	2	Cl	2.808	2.335	2.338	171.419	2.097
DUFWOQ	2	Cl	2.964	2.333	2.337	173.08	3.002
FEHCEC	2	I	3.203	2.306	2.304	163.134	3.393
FOJDUD	2	Br	2.869	2.312	2.354	156.521	3.015
GITKID	2	Cl	2.964	2.29	2.301	158.513	4.339
GITKOJ	2	Br	3.108	2.294	2.304	158.967	4.346
JAJMUC	2	Br	3.494	2.305	2.302	176.696	3.023
JAJNEN	2	Cl	3.028	2.293	2.286	178.035	2.927
JAJNEN	2	Cl	3.022	2.301	2.295	178.192	2.927
JAJNIR	2	Br	3.083	2.313	2.298	178.32	2.944
JAJNIR	2	Cl	3.112	2.291	2.287	176.478	2.944
JAJNOX	2	I	3.151	2.292	2.291	171.608	2.976
JAJNOX	2	I	3.277	2.31	2.297	178.578	2.976
JAJNOX	2	I	3.331	2.285	2.287	176.024	2.971
JAJNOX	2	I	3.267	2.287	2.294	174.027	2.971
KOBSIG	2	Cl	2.588	2.306	2.34	141.391	3.006
LEKGAJ	2	Cl	2.951	2.333	2.299	164.896	2.994
OMUFIN01	2	Cl	3.161	2.037	2.393	158.651	2.925
OMUFIN01	2	Cl	2.829	2.413	2.324	159.877	3.011
PPEAUC	2	Cl	2.766	2.325	2.284	155.848	2.958
QIDZUZ	2	Cl	2.636	2.297	2.288	159.403	2.893

The same is true, if the hits of category 3 are included which contain a molecular ion with a halogen atom instead of a halide counter ion such as for instance $AlCl_4^-$ (Figures S4 and S5). We did not include this result in the main article, as more thorough investigation would be required. It is displayed here for the sake of completeness.

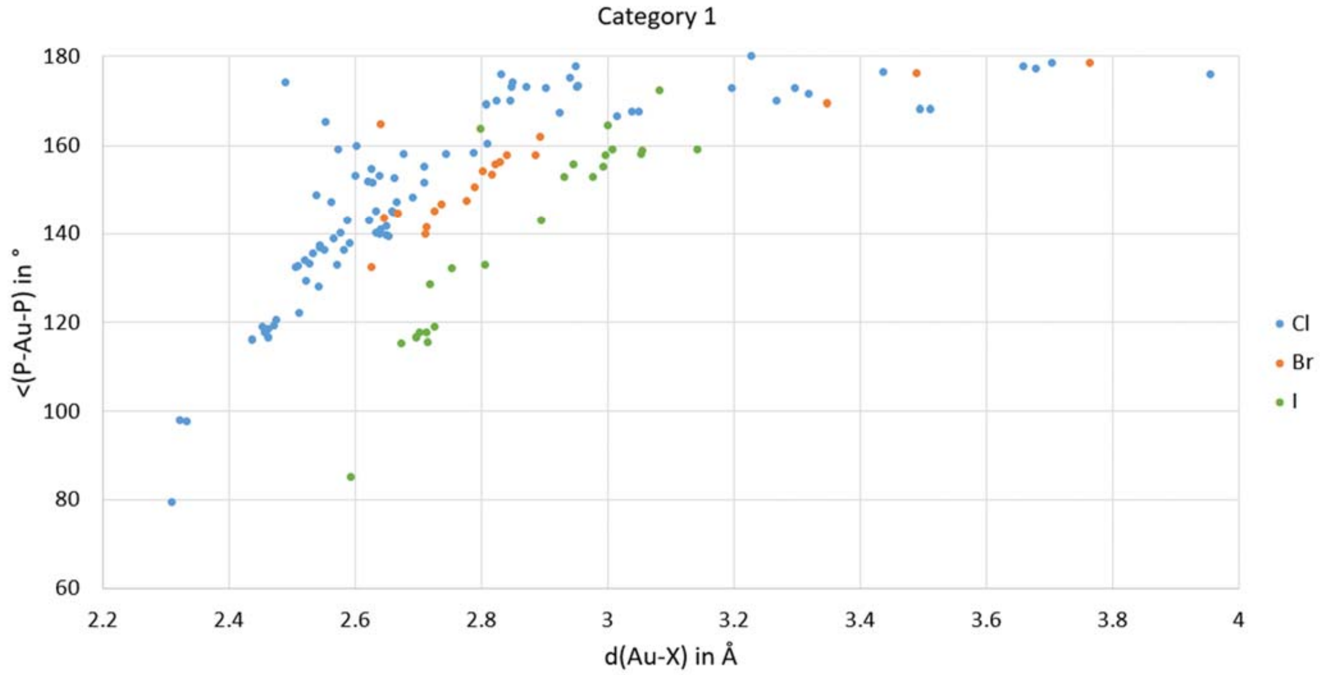


Figure S2. Plot of interatomic distance d(Au–X) versus the angle <(P–Au–P) for the search hit of category 1.

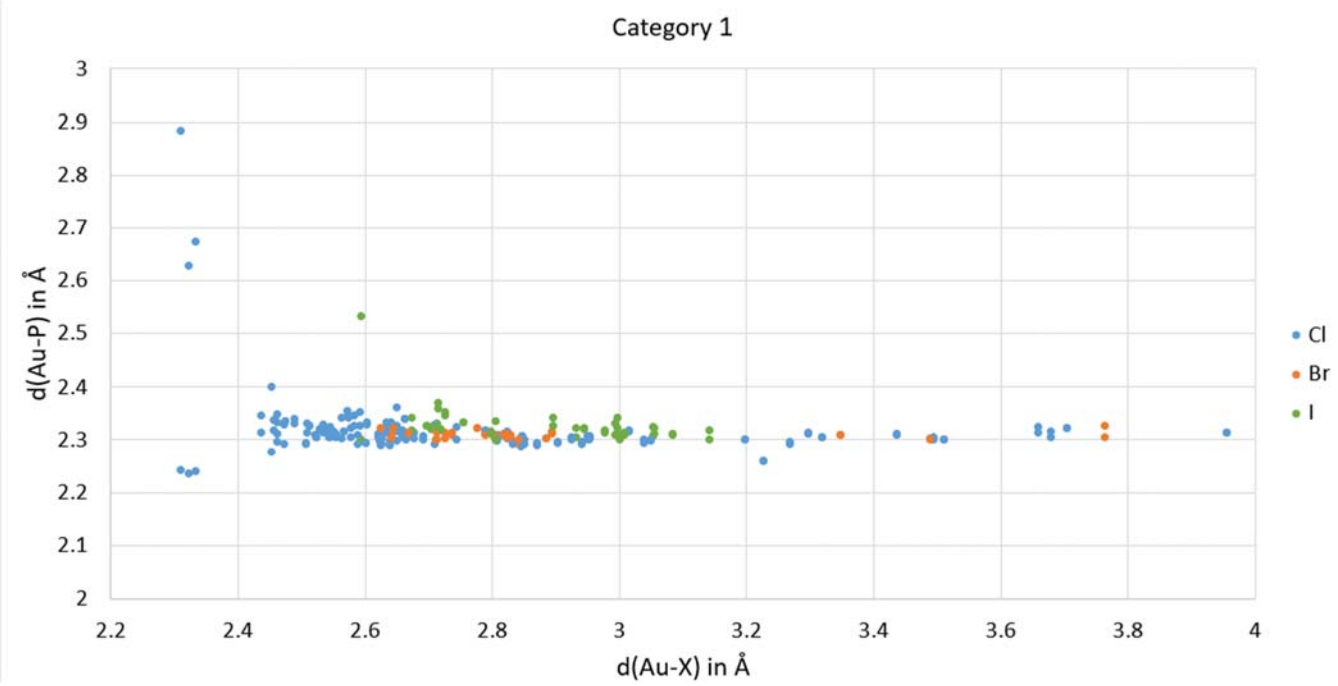


Figure S3. Plot of interatomic distance d(Au–X) versus the distance d(Au–P) for the search hit of category 1.

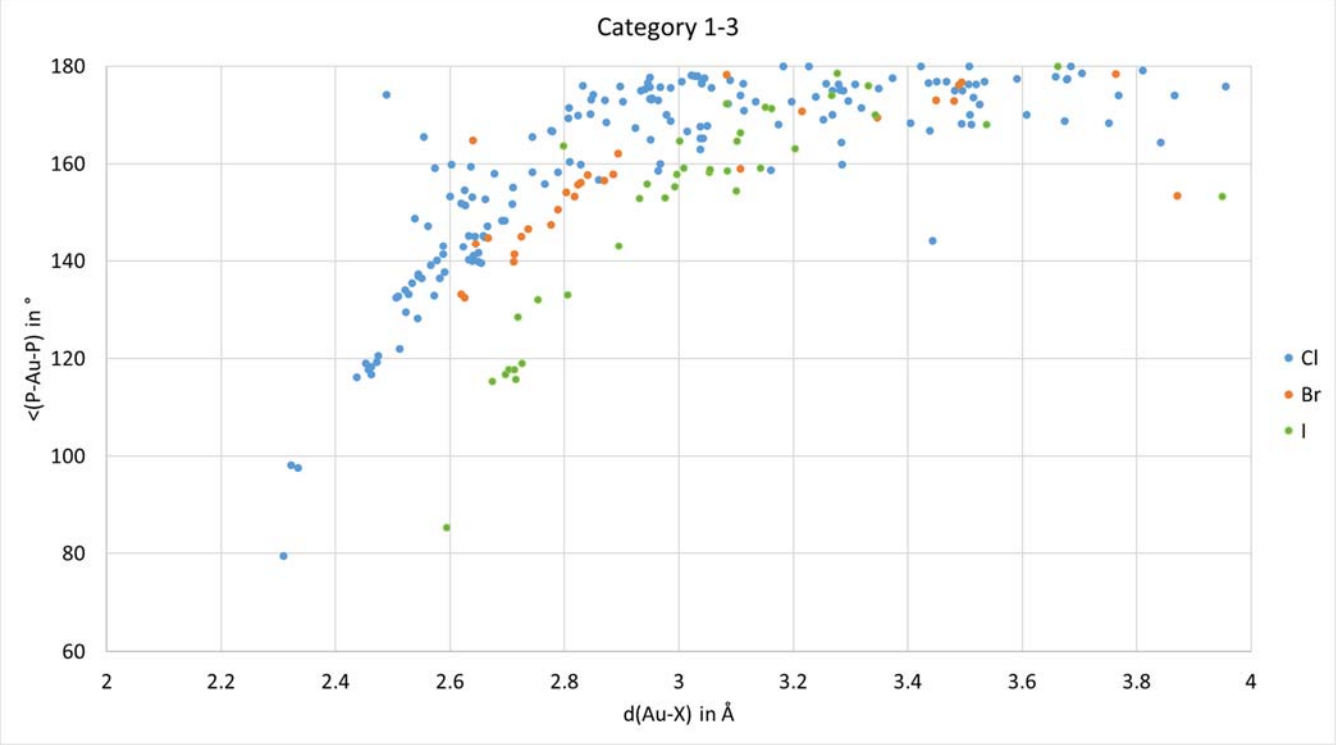


Figure S4. Plot of interatomic distance d(Au–X) versus the angle <(P–Au–P) for the search hit of category 1 to 3.

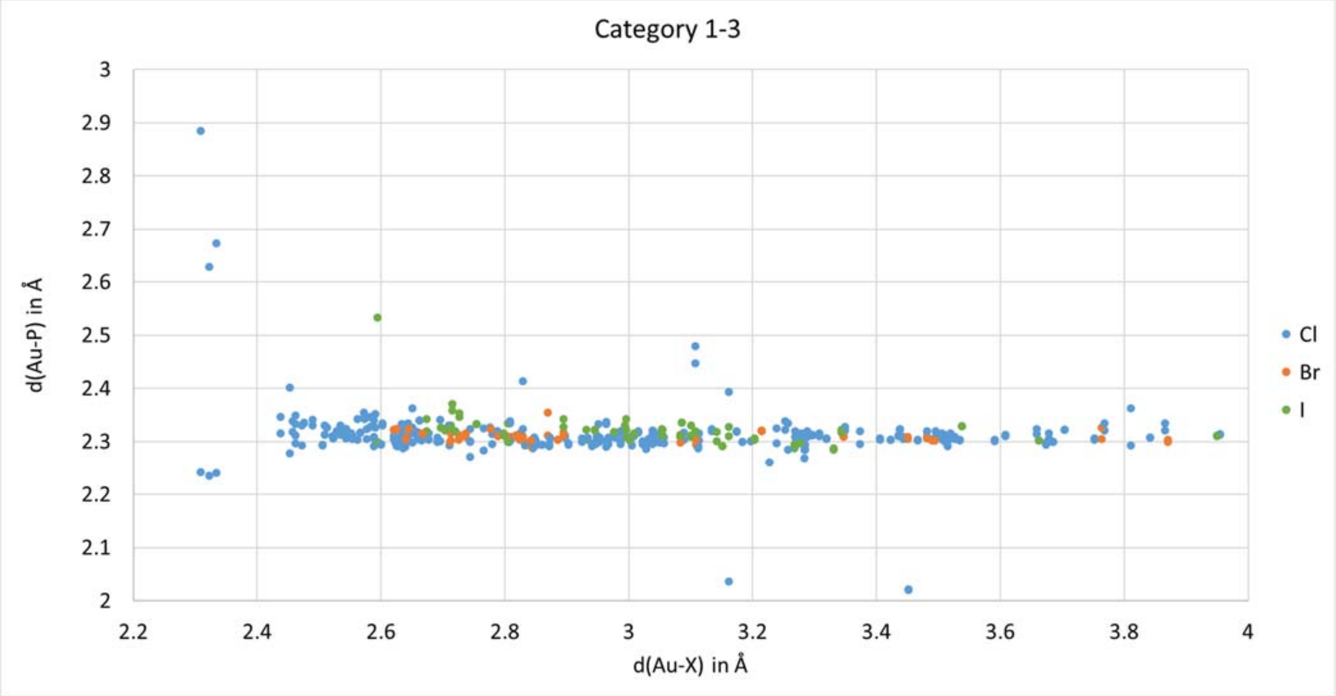


Figure S5. Plot of interatomic distance d(Au–X) versus the distance d(Au–P) for the search hit of category 1 to 3.

6. TGA/DSC measurements

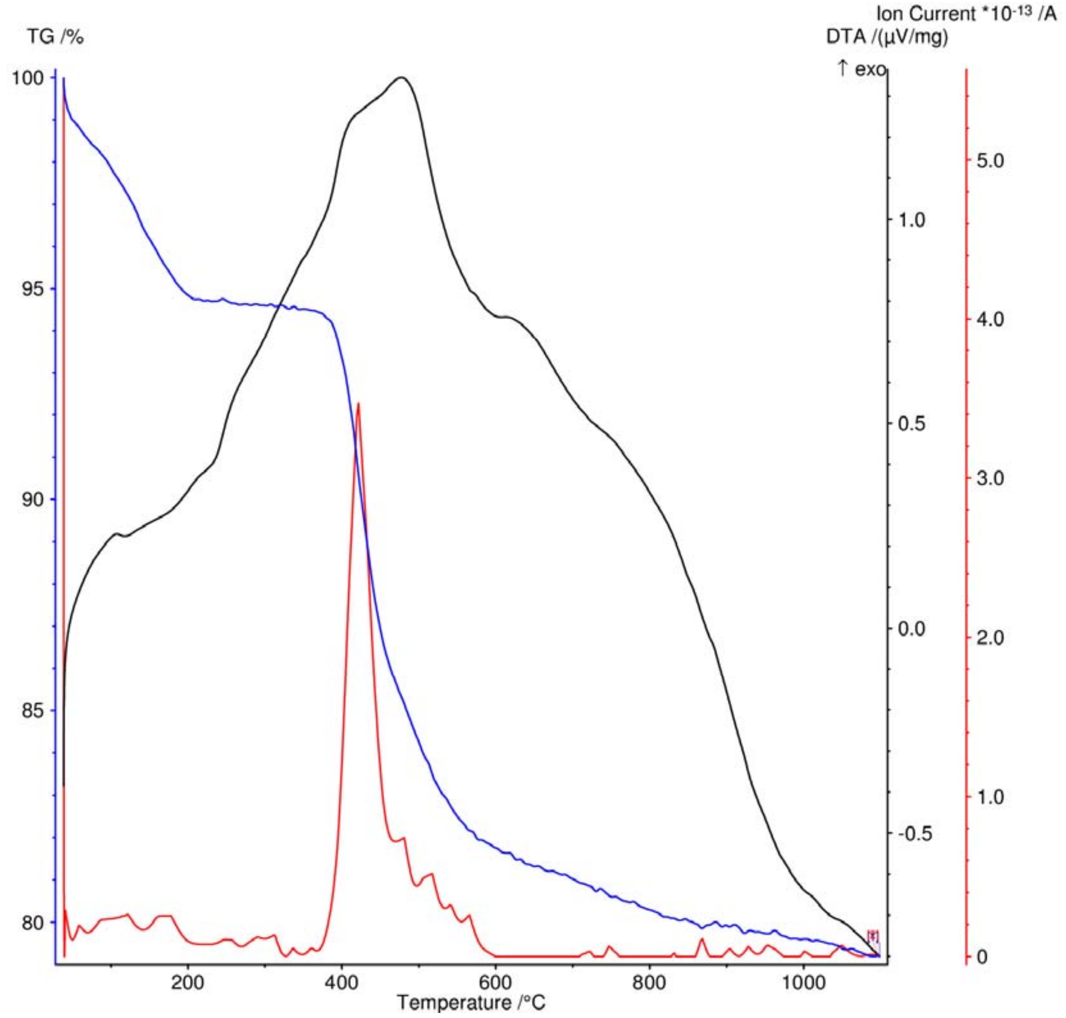


Figure S6. TGA/DSC of **2** in the temperature range from 35 to 1100 °C with a temperature raise of 10 K/min. Blue – mass of the sample; red – mass flow of 26 g/mol; black – heat of reaction.

TGA/DSC-MS measurements were performed on crystals of **2**·28DCM which had been dried in vacuum. As Figure S6 shows, the sample loses 5% of its original weight until 198°C, which is in good accordance with a theoretical mass loss of 5.3% for 3 DCM. Released DCM was identified by mass spectrometry (signals with m/z 84, 86 and 88 (3 isotopic compounds due to ^{35}Cl and ^{37}Cl)). Degradation of **2** starts at 396 °C, correlated with detection of ethyne (identified with m/z 26 in MS) which is released due to decomposition of the aromatic ring in the ligand backbone.

7. References

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