

Table of contents

General	S-2
Synthesis and Characterization of Compounds 2-10	S-6
Single crystal X-ray structure analyses	S-7

General: All reactions were carried out in flame-dried glassware under Ar. All the solvents were purified by distillation over the drying agents indicated and were transferred under Ar. CH₂Cl₂ (CaH₂), *n*-pentane, toluene, benzene (Na/K). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 400 or a AV 600 spectrometer in the solvents indicated; ¹H and ¹³C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. All commercially available compounds (Acros, ABCR, Fluka, Lancaster, Alfa Aesar, Aldrich) were used as received unless stated otherwise. 2,4,6-Tris(isopropyl)phenylphosphine ¹ and 1-chloro-2,3-(diisopropylamino)cyclopropenium tetrafluoroborate² were prepared according to literature procedures.

Compound 2: A mixture containing (PhO)₃PO (25.4 g, previously melted and dried in vacuum at 60 °C for 3 h), bromide **1** (7.4 g, 16.97 mmol) and 2-pyridyldiphenylphosphine (4.49 g, 17.05 mmol) was stirred overnight at 120 °C. Once cooled to rt, toluene (100 mL) was added and the suspension stirred for three hours. After filtration of the organic solvents, the remaining residue was washed with toluene three times, re-dissolved in MeOH (30 mL) and precipitated with Et₂O (40 mL). Finally, the light grey solid thus obtained was dried in vacuum affording the desired product (2.84 g, 24%). ¹H-NMR (400 MHz, CD₂Cl₂): δ = 8.22-8.07 (m, 11H), 8.02-7.91 (m, 4H), 7.66-7.57 (m, 5H), 7.50-7.46 (m, 1H), 7.46-7.36 ppm (m, 10H); ¹³C-NMR (100 MHz, CD₂Cl₂): δ = 150.7 (d, *J* = 20 Hz), 142.3 (d, *J* = 119 Hz), 138.4 (d, *J* = 11 Hz), 135.3 (d, *J* = 3 Hz), 135.2 (d, *J* = 11 Hz), 135.1, 134.7 (d, *J* = 11 Hz), 134.2 (d, *J* = 26 Hz), 130.1 (d, *J* = 14 Hz), 130.0 (d, *J* = 13 Hz), 129.0 (d, *J* = 3 Hz), 118.0 (d, *J* = 89 Hz), 117.1 (d, *J* = 89 Hz), 16.8 ppm (t, *J* = 47 Hz); ³¹P-NMR (162 MHz, CD₂Cl₂): δ = 21.5 (d, *J* = 18 Hz), 16.3 ppm (d, *J* = 18 Hz); MS (ESI+): *m/z* (%): 538.3 (100); HRMS (ESI+): *m/z*: calcd. for C₃₆H₃₀NP₂: 538.1848; found: 538.1854.

Compound 3: NH₃ (45 mL) was condensed in a 100 mL two neck round-bottom flask containing compound **2** (1.14 g, 1.63 mmol) and NaNH₂ (410 mg, 10.51 mmol), and the mixture stirred for 7 h at -35 °C. After that, the NH₃ was allowed to slowly evaporate before toluene (15 mL) was added to the reaction mixture. The yellow organic phase was filtered and the remaining solid washed at rt with toluene (2x10 mL). Evaporation of the combined organic phases afforded the desired compound as a yellow solid (770 mg, 88 %). ¹H-NMR (600 MHz, d₈-THF): δ = 8.45 (m, 1H), 8.38 (m, 1H), 7.64 (m, 4H), 7.63 (m, 6H), 7.62 (m, 1H), 7.26 (m, 3H), 7.19 (m,

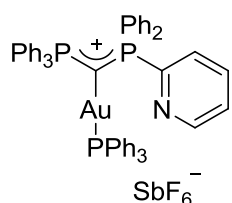
¹ Y. van den Winkel, H. M. M. Bastiaans, F. Bickelhaupt, *J. Organomet. Chem.* **1991**, 405,183.

² R. Weiss, K. G. Wagner, C. Priesner, J. Macheleid, *J. Am. Chem. Soc.* **1985**, 107, 4491.

2H), 7.18 (m, 6H), 7.16 (m, 1H), 7.10 ppm (m, 4H); ^{13}C -NMR (150 MHz, d_8 -THF): δ = 161.7 (dd, J = 119, 10 Hz), 149.4 (d, J = 18 Hz), 138.4 (dd, J = 89, 7 Hz), 138.2 (dd, J = 88, 6 Hz), 135.7 (d, J = 9 Hz), 133.2 (d, J = 10 Hz), 133.0 (d, J = 10 Hz), 129.9 (d, J = 3 Hz), 129.6 (d, J = 3 Hz), 129.1 (d, J = 22 Hz), 128.2 (d, J = 11 Hz), 127.8 (d, J = 11 Hz), 123.8 (d, J = 3 Hz), 11.8 ppm (dd, J = 122, 119 Hz).

^1H -NMR (600 MHz, C_6D_6): δ = 8.64 (m, 1H), 8.31 (m, 1H), 8.04 (m, 4H), 7.90 (m, 6H), 7.02 (m, 1H), 7.00 (m, 9H), 6.99 (m, 6H); 6.46 ppm (m, 1H); ^{13}C -NMR (150 MHz, C_6D_6): δ = 161.3 (dd, J = 119, 10 Hz), 148.9 (d, J = 18 Hz), 137.9 (dd, J = 89, 7 Hz), 137.6 (dd, J = 88, 6 Hz), 134.9 (d, J = 9 Hz), 132.9 (d, J = 10 Hz), 132.6 (d, J = 10 Hz), 129.4 (d, J = 2 Hz), 129.3 (d, J = 3 Hz), 128.7 (d, J = 22 Hz), 127.8 (d, J = 11 Hz), 127.6 (d, J = 11 Hz), 122.9 (d, J = 3 Hz), 12.3 ppm (dd, J = 118, 115 Hz); ^{31}P -NMR (162 MHz, C_6D_6): δ = -2.14 (d, J = 85 Hz), -5.55 ppm (d, J = 85 Hz); IR (neat): ν_{max} = 3050, 1571, 1476, 1433, 1298, 1270, 1173, 1097, 1026, 970, 741, 691 cm^{-1} ; MS (EI): m/z (%): 536 (100), 459 (43), 352 (12), 262 (34), 183 (33), 165 (21); HRMS (EI): m/z calcd. for $\text{C}_{36}\text{H}_{29}\text{NP}_2$: 537.1775; found: 537.1770; elemental analysis calcd. (%) for $\text{C}_{36}\text{H}_{29}\text{NP}_2$: C 80.43, H 5.44, N 2.61; found: C 79.76, H 5.74, N 1.92.

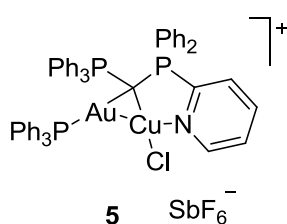
Compound 4: [Ph_3PAuCl] (70 mg, 0.142 mmol) was added to a precooled solution of compound



3 (75 mg, 0.140 mmol) in THF (3 mL) at 0 °C and the resulting mixture stirred for 1 h at the same temperature. Subsequently, NaSbF_6 (36.3 mg, 0.140 mmol) was added and the suspension stirred for an additional hour. Evaporation of the volatile materials afforded a white solid that was re-dissolved in CH_2Cl_2 (2 mL) and filtered.

Concentration of the organic phase in vacuum afforded the desired product as a white solid (168 mg, 97 %). ^1H -NMR (600 MHz, CD_2Cl_2): δ = 8.44 (m, 1H), 7.80 (m, 4H), 7.71 (m, 6H), 7.50-7.42 (m, 10H), 7.32 (m, 6H), 7.30 (m, 4H), 7.26 (m, 6H), 7.22 (m, 1H), 7.01 ppm (m, 6H); ^{13}C -NMR (150 MHz, CD_2Cl_2): δ = 156.0 (dt, J = 114, 3 Hz), 150.4 (d, J = 18 Hz), 136.4 (d, J = 9 Hz), 134.1 (d, J = 14 Hz), 133.6 (d, J = 10 Hz), 133.3 (d, J = 10 Hz), 132.2 (d, J = 3 Hz), 132.1 (dd, J = 91, 4 Hz), 132.0 (d, J = 3 Hz), 131.8 (d, J = 2 Hz), 131.7 (dd, J = 92, 5 Hz), 130.0 (d, J = 55 Hz), 129.3 (d, J = 11 Hz), 128.8 (d, J = 12 Hz), 128.6 (d, J = 23 Hz), 125.4 (d, J = 3 Hz), 24.5 ppm (dt, J = 86, 84 Hz); ^{31}P -NMR (162 MHz, CD_2Cl_2): δ = 41.28 (t, J = 6 Hz), 19.70 (dd, J = 30, 7 Hz), 15.03 ppm (dd, J = 30, 7 Hz); IR (neat): ν_{max} = 3059, 1571, 1481, 1435, 1312, 1184, 1127, 1099, 1068, 1027, 998, 844, 744, 691, 656 cm^{-1} ; MS (ESI+): m/z (%): 996.3 (100); HRMS (ESI+): m/z calcd. for $\text{C}_{54}\text{H}_{44}\text{AuNP}_3$: 996.2347; found: 996.2347; elemental analysis calcd. (%) for $\text{C}_{54}\text{H}_{44}\text{AuNP}_3\cdot\text{SbF}_6$: C 52.62, H 3.60, N 1.14; found: C 50.16, H 3.29, N 0.92.

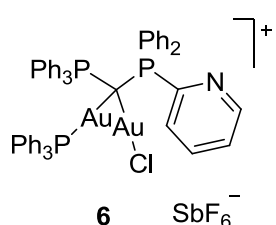
Compound 5: CuCl (4.8 mg, 0.0485 mmol) was added to a solution of **4** (48 mg, 0.0390 mmol) in



CH_2Cl_2 at 0 °C and the mixture stirred at this temperature overnight. Removal of the solvent in vacuum provided the desired compound as an orange solid (49.3 mg, 95 %). ^1H -NMR (600 MHz, CD_2Cl_2): δ = 9.06 (m, 1H), 7.97 (dd, J = 12, 8 Hz, 2H), 7.85 (tdt, J = 8, 5, 2 Hz, 1H), 7.75 (m, 6H), 7.67 (m, 1H), 7.63 (m, 1H), 7.54 (m, 3H), 7.48 (m, 1H), 7.45 (m, 3H), 7.40 (m, 6H), 7.30 (m, 2H), 7.25 (m, 6H),

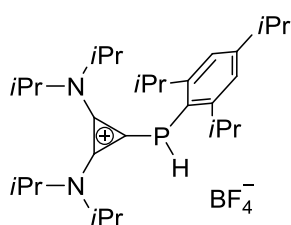
7.24 (m, 2H), 7.16 (ddq, $J = 8, 5, 1$ Hz, 1H), 7.11 (m, 6H), 6.94 ppm (m, 2H); ^{13}C -NMR (150 MHz, CD_2Cl_2): $\delta = 152.8$ (dd, $J = 130, 15$ Hz), 150.2 (d, $J = 16$ Hz), 138.9 (d, $J = 9$ Hz), 134.1, 134.0 (d, $J = 14$ Hz), 133.89 (d, $J = 10$ Hz), 133.83, 133.5 (d, $J = 10$ Hz), 133.2 (d, $J = 10$ Hz), 133.1 (d, $J = 3$ Hz), 132.2 (d, $J = 2$ Hz), 129.9 (d, $J = 12$ Hz), 129.8 (d, $J = 12$ Hz), 129.6 (d, $J = 12$ Hz), 129.4 (d, $J = 24$ Hz), 129.2 (d, $J = 12$ Hz), 128.9 (d, $J = 58$ Hz), 128.5 (dd, $J = 89, 5$ Hz), 128.0 (d, $J = 2$ Hz), 126.4 (dd, $J = 76, 3$ Hz), 124.2 (d, $J = 79$ Hz), 17.5 ppm (ddd, $J = 68, 58, 52$ Hz); ^{31}P -NMR (122 MHz, CD_2Cl_2): $\delta = 39.7$ (m), 26.2 ppm (ddd, $J = 49, 23, 9$ Hz); IR (neat): $\nu_{\text{max}} = 3050, 2956, 1575, 1481, 1435, 1311, 1262, 1185, 1161, 1096, 991, 741, 689, 650$ cm^{-1} ; MS (ESI⁺): m/z (%): 1094.2 (60); HRMS (ESI⁺): m/z : calcd. for $\text{C}_{54}\text{H}_{44}\text{AuClCuNP}_3$: 1094.1331; found: 1094.1354; elemental analysis calcd. (%) for $\text{C}_{54}\text{H}_{44}\text{AuClCuNP}_3 \cdot \text{SbF}_6$: C 48.71, H 3.33, N 1.05; found: C 47.01, H 3.47, N 0.95.

Compound 6: $[(\text{Me}_2\text{S})\text{AuCl}]$ (13.5 mg, 0.0458 mmol) was added to a cooled (0 °C) solution of **4**



(54 mg, 0.0438 mmol) in CH_2Cl_2 (1 mL) and the mixture was stirred 2 h at this temperature. Evaporation in vacuum of all volatile materials afforded **6** as a white solid (54.5 mg, 85 %). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane in CH_2Cl_2 solutions of the product. ^1H -NMR (600 MHz, CD_2Cl_2): $\delta = 8.05$ (m, 1H), 7.99 (m, 2H), 7.89 (m, 6H), 7.80 (m, 2H), 7.75 (m, 1H), 7.59 (m, 3H), 7.58 (m, 1H), 7.52 (m, 1H), 7.47 (m, 3H), 7.46 (m, 6H), 7.41 (m, 1H), 7.34 (m, 1H), 7.32 (m, 2H), 7.27 (m, 6H), 7.19 (m, 6H), 7.15 ppm (m, 2H); ^{13}C -NMR (150 MHz, CD_2Cl_2): $\delta = 152.0$ (dt, $J = 117, 3$ Hz), 150.2 (d, $J = 19$ Hz), 138.1 (d, $J = 9$ Hz), 134.5 (d, $J = 10$ Hz), 134.3 (d, $J = 10$ Hz), 134.12 (d, $J = 14$ Hz), 134.11 (d, $J = 10$ Hz), 133.9 (d, $J = 3$ Hz), 133.6 (d, $J = 3$ Hz), 133.3 (d, $J = 3$ Hz), 132.5 (d, $J = 2$ Hz), 129.82 (d, $J = 12$ Hz), 129.81 (d, $J = 23$ Hz), 129.52 (d, $J = 12$ Hz), 129.49 (d, $J = 12$ Hz), 129.1 (d, $J = 12$ Hz), 129.0 (d, $J = 58$ Hz), 127.3 (dd, $J = 89, 3$ Hz), 127.2 (d, $J = 3$ Hz), 126.5 (dd, $J = 89, 6$ Hz), 125.4, (d, $J = 87$ Hz), 14.2 ppm (ddd, $J = 66, 42, 40$ Hz); ^{31}P -NMR (162 MHz, CD_2Cl_2): $\delta = 35.4$ (m), 27.5 (m), 21.9 ppm (t, $J = 7.1$ Hz); IR (neat): $\nu_{\text{max}} = 3057, 2963, 1586, 1572, 1481, 1435, 1311, 1260, 1187, 1094, 1024, 998, 944, 798, 740, 711, 689$ cm^{-1} ; MS (ESI⁺): m/z (%): 1228.3 (100); HRMS (ESI⁺): m/z : calcd. for $\text{C}_{54}\text{H}_{44}\text{Au}_2\text{ClNP}_3$: 1228.1701; found: 1228.1695.

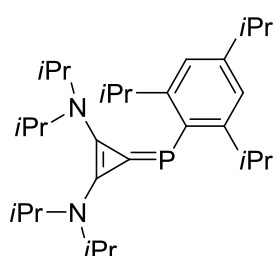
Compound 7: 2,4,6-Tris(isopropyl)phenylphosphine (1.63 g, 6.90 mmol) was added to a mixture



of chlorocyclopropenium salt (1.24 g, 3.45 mmol) in bis(2-methoxyethyl)ether (15 mL) and the resulting mixture was heated at 135 °C for 24 hours. After cooling to room temperature, the solvent was removed in vacuum at 40°C, the residue dissolved in dichloromethane (20 mL) and washed with a saturated solution of NaBF_4 (3 × 15 mL). Once dried over MgSO_4 , the organic phase was concentrated and the residue purified by flash column chromatography (1:9, acetone : dichloromethane), affording the desired compound as a white solid (1.20g, 62%). ^1H NMR (400 MHz, CDCl_3) $\delta = 1.10$ (dd, $J = 14.0, 6.8$ Hz, 12H), 1.19 (dd, $J = 13.4, 6.8$ Hz, 12H), 1.20 (d, $J = 6.5$ Hz, 6H), 1.32 (dd, $J = 6.6, 2.5$ Hz, 12H), 2.87 (m, 1H), 3.44 (m, 2H), 3.57 (m, 2H), 4.04 (m, 2H), 5.47 (d, $J = 238$ Hz, 1H), 7.07 (d, $J = 2.8$

Hz, 2H); ^{31}P NMR (162 MHz, CDCl_3) δ = -100.80 ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 21.1, 21.3 (d, J = 4.9 Hz), 22.0, 23.7 (d, J = 3.8 Hz), 24.0 (d, J = 20.9 Hz), 33.5 (d, J = 14.5 Hz), 34.5, 51.2, 53.9, 106.9, 119.3, 122.4, 136.9, 153.6, 154.7 ppm (d, J = 13.6 Hz). IR (neat) ν_{max} = 688, 882, 1032, 1047, 1152, 1357, 1459, 1542, 1711, 1876, 2955 cm^{-1} ; HRMS calcd. for $\text{C}_{30}\text{H}_{52}\text{N}_2\text{P}^+$: 471.386759; found: 471.386263.

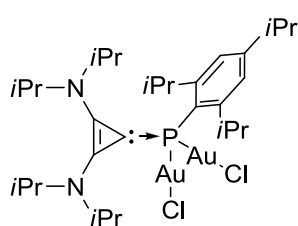
Compound 8: KHMDS (46.1 mg, 0.231 mmol) was added to a cooled (-80 °C) suspension of **7**



(129.0 mg, 0.231 mmol) in dry toluene (15 mL). The resulting mixture was allowed to reach rt and stirred for additional 2 h. The suspension thus formed was filtered under argon atmosphere and the organic phase concentrated in vacuum.

The desired phosphinidene is stable at room temperature only for a few hours. ^1H NMR (400 MHz, d_8 -THF) δ = 0.92 (d, J = 6.6 Hz, 12H), 1.16 (dd, J = 31.7, 7.0 Hz, 12H), 1.23 (d, J = 6.8 Hz, 6H), 1.35 (d, J = 6.6 Hz, 12H), 2.81 (m, 1H), 3.16 (m, 2H), 3.86 (m, 2H), 4.36 (m, 2H), 6.91 ppm (d, J = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 23.4 (d, J = 7.2 Hz), 23.7, 24.6, 25.5 (d, J = 1.8 Hz), 33.6 (d, J = 10.4 Hz), 35.0, 49.4, 124.6, 128.4, 129.3, 147.2, 155.0 (d, J = 6.6 Hz) ppm. ^{31}P NMR (162 MHz, d_8 -THF) δ = -83.33 ppm; HRMS calcd. for $\text{C}_{30}\text{H}_{52}\text{N}_2\text{P}^+$: 470.379141; found: 470.378989.

Compound 9: A solution of **8** in toluene was prepared from **7** (84.0 mg, 0.150 mmol) and

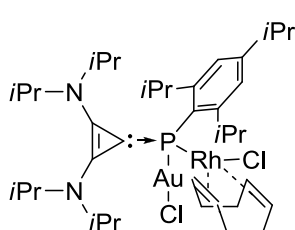


KHMDS (29.9 mg, 0.150 mmol) as described above. This solution was cooled to -78 °C before $(\text{Me}_2\text{S})\text{AuCl}$ (176.6 mg, 0.300 mmol) was added. The resulting mixture was allowed to slowly reach ambient temperature during 16 h.

Removal of the solvent in vacuum and purification of the residue by flash chromatography (1:9, acetone:dichloromethane), afforded the desired compound as a white solid (117 mg, 83%).

^1H NMR (400 MHz, CD_2Cl_2) δ = 1.13 (d, J = 6.9 Hz, 12H), 1.16 (d, J = 6.9 Hz, 6H), 1.20 (m(br), 12H), 1.23 (d, J = 6.9 Hz, 12H), 2.79 (m, 1H), 3.81 (m, 2H), 3.90 (m, 2H), 4.28 (m, 2H), 7.01 ppm (d, J = 4.3 Hz, 2H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ = -54.00 ppm. ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 20.7, 21.2, 22.7, 23.5, 33.0, 33.1, 33.5, 110.8 (d, J = 9.0 Hz), 122.5, 122.8, 122.9, 123.0, 133.8, 150.8, 151.7 ppm (d, J = 9.2 Hz); IR (neat) ν_{max} = 679, 894, 1031, 1142, 1358, 1454, 1543, 1711, 1866, 2963 cm^{-1} ; HRMS calcd. for $\text{C}_{30}\text{H}_{51}\text{Au}_2\text{Cl}_2\text{N}_2\text{PNa}^+$: 957.238922; found 957.239014.

Compound 10: A solution of **8** in toluene (15 mL) was prepared from **7** (65.0 mg, 0.116 mmol)



and KHMDS (29.9 mg, 0.150 mmol) as described above. This solution was cooled to -78 °C before $[(\text{Me}_2\text{S})\text{AuCl}]$ (34.3 mg, 0.116 mmol) was added followed by $[\text{RhCl}(\text{cod})]_2$ (28.6 mg, 0.058 mmol). The resulting mixture was allowed to come to room temperature and was stirred for additional 16 h. Finally, the obtained suspension was filtered and dried in vacuum to afford the desired product as a yellow solid (60 mg, 54%).

^{31}P -NMR indicated this compound to be contaminated with 8% of **9**. ^1H NMR (400 MHz, CD_2Cl_2) δ = 1.15 (d, J = 6.9 Hz, 12H), 1.20 (d, J = 6.9 Hz, 12H), 1.26 (d, J = 6.9

Hz, 6H), 1.33 (m(br), 12H), 1.88 (m(br), 2H), 2.00 (m(br), 2H), 2.41 (m, 2H), 2.78 (m, 1H), 3.64 (m, 2H), 4.16 (m, 2H), 4.90 (m(br), 2H), 5.21 (m(br), 1H), 5.52 (m(br), 1H), 6.98 (d, $J = 3.1$ Hz, 2H) ppm. ^{31}P NMR (161 MHz, CD_2Cl_2) $\delta = -30.94$ (d, $J = 122$ Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2) $\delta = 20.7, 21.2, 22.7, 23.5, 33.0, 33.1, 33.5, 110.8$ (d, $J = 9.0$ Hz), 122.5, 122.8, 122.9, 123.0, 133.8, 150.8, 151.7 (d, $J = 9.2$ Hz) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2) $\delta = 21.7, 23.9, 25.7, 29.0, 29.9, 31.3, 32.4, 34.0, 34.5, 80.1, 97.8, 98.7, 117.7, 124.1, 124.2, 129.4, 150.4, 152.6$ (d, $J = 8.0$ Hz) ppm. IR (neat) $\nu_{\text{max}} = 678, 883, 1036, 1139, 1349, 1447, 1518, 1855, 2948\text{ cm}^{-1}$. HRMS calcd. for $\text{C}_{38}\text{H}_{63}\text{AuClN}_2\text{PRh}$: 913.313556, found 913.313689.

Single crystal X-ray structure analyses

Crystal structure analysis of 3

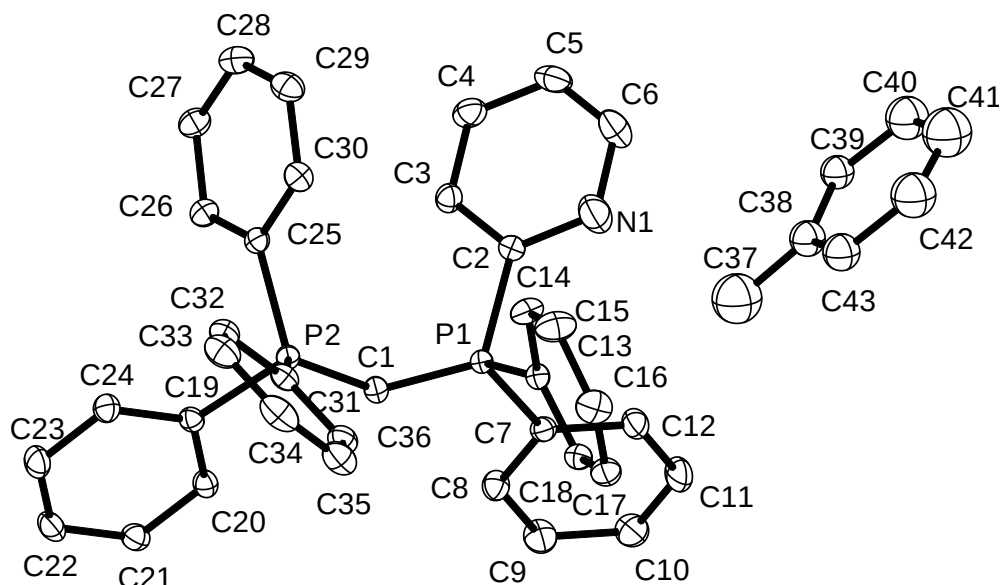


Figure S-1. Molecular structure of $3 \cdot \frac{1}{2}(\text{C}_7\text{H}_8)$.

Crystal data for $3 \cdot \frac{1}{2}\text{C}_7\text{H}_8$: Chemical formula $2 [\text{C}_{36} \text{H}_{29} \text{N} \text{P}_2] \cdot \text{C}_7 \text{H}_8$, $F_w = 1167.22 \text{ g mol}^{-1}$, yellow needle from toluene, crystal size $0.05 \times 0.02 \times 0.02 \text{ mm}^3$, crystal system triclinic, space group $P\bar{1}$, $a = 10.5881(12)$, $b = 11.7546(14)$, $c = 13.4581(16) \text{ Å}$, $\alpha = 73.849(2)$, $\beta = 73.626(2)$, $\gamma = 78.953(2)^\circ$, $V = 1531.9(3) \text{ Å}^3$, $T = 100 \text{ K}$, $\rho_c = 1.265 \text{ Mg m}^{-3}$, $Z = 1$, $\lambda = 0.71073 \text{ Å}$, $\mu = 0.172 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\min} = 0.99209$, $T_{\max} = 0.99724$), scaling SADABS, Bruker AXS Mach3 ApexII diffractometer equipped with Helios multilayer X-ray optics, $5.10 < \theta < 32.04^\circ$, 47413 reflections collected, 10542 unique reflections ($R_{\text{int}} = 0.0715$), 7527 reflections with $I > 2\sigma(I)$. Intensity statistics:

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	R(int)	Rsigma
Inf - 1.80	538	557	96.6	6.09	52.2	47.23	0.0261	0.0150
1.80 - 1.44	551	551	100.0	6.38	19.8	33.89	0.0376	0.0198
1.44 - 1.26	538	538	100.0	6.17	17.9	31.46	0.0440	0.0222
1.26 - 1.14	578	578	100.0	5.78	16.7	27.07	0.0477	0.0254
1.14 - 1.06	545	545	100.0	5.44	9.7	19.27	0.0666	0.0366
1.06 - 1.00	546	546	100.0	5.09	8.0	15.84	0.0770	0.0442
1.00 - 0.95	545	545	100.0	4.88	8.4	16.06	0.0818	0.0459
0.95 - 0.91	531	531	100.0	4.64	6.8	13.50	0.1001	0.0564
0.91 - 0.87	662	662	100.0	4.43	6.5	12.65	0.1040	0.0619
0.87 - 0.84	563	563	100.0	4.23	5.7	10.34	0.1252	0.0721
0.84 - 0.81	653	653	100.0	4.06	4.7	8.90	0.1492	0.0884
0.81 - 0.78	749	749	100.0	3.93	4.2	7.77	0.1694	0.1054
0.78 - 0.76	571	571	100.0	3.78	3.9	6.91	0.1795	0.1164
0.76 - 0.74	663	663	100.0	3.59	3.8	6.36	0.1964	0.1288
0.74 - 0.72	720	720	100.0	3.51	3.1	5.23	0.2394	0.1593
0.72 - 0.70	799	799	100.0	3.35	2.7	4.59	0.2607	0.1983
0.70 - 0.68	820	886	92.6	2.80	2.5	3.81	0.2832	0.2555
0.68 - 0.67	2	13	15.4	0.15	1.2	0.38		2.4259
Inf - 0.67	10574	10670	99.1	4.46	9.6	14.78	0.0656	0.0484

Solution by direct methods (*SHELXS*-97), refinement by full-matrix least-squares on F^2 (*SHELXL*-97, G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), H atoms riding. The position of the N atom in the pyridyl group could not be located by refining the structure with C atoms in all the 6-membered rings, which indicates that the pyridyl group may be disordered over several positions in the molecule. Nevertheless, a lack of electron density in a region where the H atom of a C-H group would be expected suggests that N1 is the likely position of the N atom. The crystal contains a toluene molecule that is disordered about a crystallographic centre of symmetry. Disordered atoms were refined with isotropic atomic displacement parameters and half occupancy. Reflections above 4 Å resolution were affected by the beamstop and removed from the final refinement cycles. $R_1 = 0.053$ [$I > 2\sigma(I)$], $wR_2 = 0.152$ (all data), 381 parameters, $S = 1.042$, residual electron density +0.90 / -0.71 e Å⁻³ [in the vicinity of C42 (0.57 Å) and C37 (0.53 Å), respectively]. CCDC 914763.

Crystal structure analysis of 4

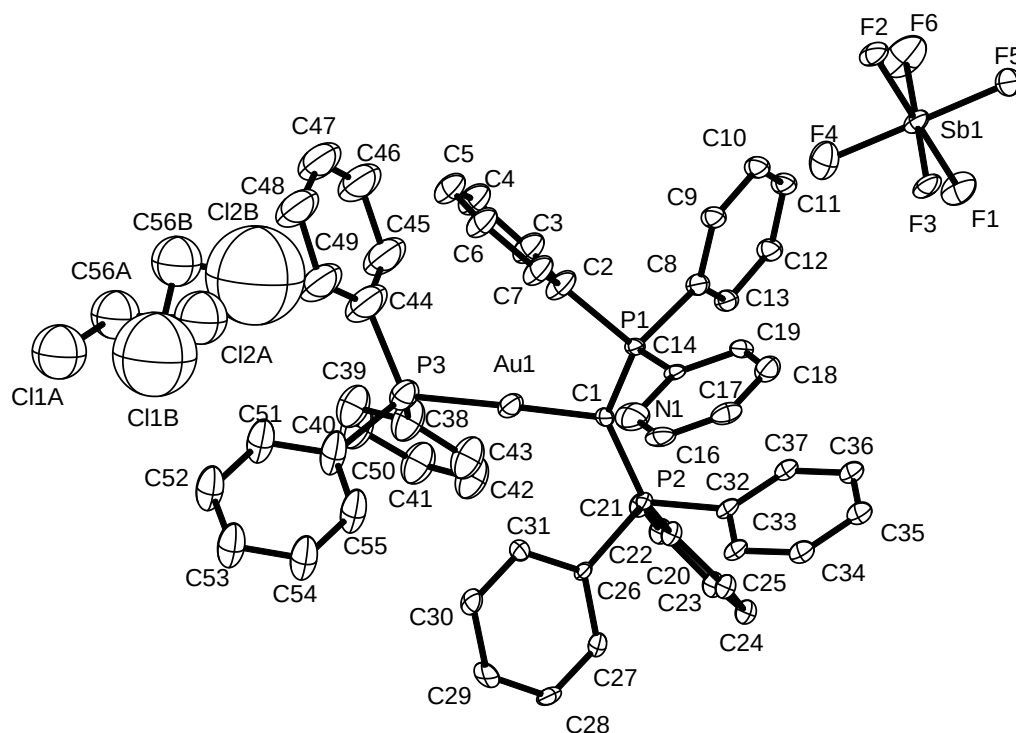


Figure S-2. Molecular structure of **4**·CH₂Cl₂.

Crystal data for 4·CH₂Cl₂: Chemical formula [C₅₄ H₄₄ Au N P₃]⁺ [F₆ Sb]⁻· C₂ H₂ Cl₂, *F_w* = 1317.45 g mol⁻¹, colourless plate from dichloromethane/pentane, crystal size 0.010 x 0.010 x 0.004 mm³, crystal system triclinic, space group *P* $\bar{1}$, *a* = 12.0585(17), *b* = 15.106(2), *c* = 16.288(2) Å, α = 63.058(2), β = 68.541(3), γ = 83.121(3)°, *V* = 2457.9(6) Å³, *T* = 100 K, ρ_c = 1.780 Mg m⁻³, *Z* = 2, λ = 0.71073 Å, μ = 3.800 mm⁻¹, Gaussian absorption correction (*T*_{min} = 0.95624, *T*_{max} = 0.98694), scaling *SADABS*, Brucker AXS Mach3 ApexII diffractometer equipped with Helios multilayer X-ray optics, 1.82 < θ < 23.44°, 34062 reflections collected, 7175 unique reflections (*R*_{int} = 0.0705), 5917 reflections with *I* > 2σ(*I*). Intensity statistics:

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	R(int)	Rsigma
Inf - 2.44	360	361	99.7	5.57	78.5	38.26	0.0327	0.0196
2.44 - 1.93	371	374	99.2	5.52	52.9	32.13	0.0418	0.0243
1.93 - 1.68	369	369	100.0	5.55	44.9	28.36	0.0451	0.0265
1.68 - 1.52	373	373	100.0	5.44	36.9	25.27	0.0518	0.0300
1.52 - 1.42	365	365	100.0	5.46	35.9	24.49	0.0532	0.0313
1.42 - 1.33	409	409	100.0	5.37	30.1	21.00	0.0609	0.0361
1.33 - 1.26	382	382	100.0	5.28	23.7	17.94	0.0772	0.0436
1.26 - 1.20	421	421	100.0	5.08	22.4	16.21	0.0798	0.0484
1.20 - 1.15	428	428	100.0	4.87	20.2	14.86	0.0929	0.0550
1.15 - 1.11	388	388	100.0	4.81	16.7	12.61	0.1043	0.0653
1.11 - 1.07	464	464	100.0	4.56	18.4	13.18	0.1039	0.0648
1.07 - 1.04	373	373	100.0	4.49	14.9	10.91	0.1257	0.0785
1.04 - 1.01	437	437	100.0	4.29	14.1	9.98	0.1286	0.0852
1.01 - 0.98	501	501	100.0	4.29	13.6	9.38	0.1338	0.0912
0.98 - 0.96	362	362	100.0	4.02	13.0	8.59	0.1466	0.0986
0.96 - 0.94	392	392	100.0	4.05	11.4	7.53	0.1597	0.1132
0.94 - 0.92	424	424	100.0	3.93	10.0	6.76	0.1749	0.1287
0.92 - 0.89	359	392	91.6	2.80	8.9	5.35	0.1843	0.1889
Inf - 0.89	7178	7215	99.5	4.72	25.2	16.46	0.0705	0.0483

Solution by direct methods (*SHELXS*-97), refinement by full-matrix least-squares on F^2 (*SHELXL*-97, G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), H atoms riding. The crystal appears to be twinned about (0 0 1) $[-2 \ -2 \ 5]$ with a rotation matrix of $[-1 \ 0 \ 0 \ 0 \ -1 \ 0 \ -0.854 \ -0.895 \ 1.0]$ (according to *PLATON*, A. L. Spek, *Acta Cryst.* **2009**, D65, 148-155). The refined fractional contribution of the second component was 0.09987(154). The crystal diffracted so poorly that the possible non-merohedral intensity data of this minor second component could not be collected. It cannot be ruled out that the reflections for which the measured intensities were significantly higher than the calculated ones based on the model, are not a result of loss of solvent from the crystal and corresponding crystallinity with retention of the gold contribution. The probable position of the N atom was determined by refining atomic displacement parameters of all atoms in the 6-membered rings as C atoms. The C atom, with the smallest atomic displacement parameter and no adjacent electron density that could be construed as an H atom, was chosen to be N. Subsequent refinement cycles with atomic displacement parameters of all ring atoms restrained to be similar with a standard uncertainty of 0.001 (252 restraints) suggested that this choice was likely, but not certain. We cannot rule out that the N atom is disordered over several pyridyl rings. Assuming that the final model is correct, the larger than unity goodness-of-fit of 1.835 at the end of refinement suggests that the weights attributed to the measured intensities were underestimated. $R_1 = 0.054$ [$I > 2\sigma(I)$], $wR_2 = 0.103$ (all data), 620 parameters, $S = 1.835$, residual electron density $+2.37 / -1.22 \text{ e } \text{\AA}^{-3}$ [in the vicinity of Au1 (1.07 Å and 0.74 Å, respectively)]. CCDC 914764.

Crystal structure analysis of 5

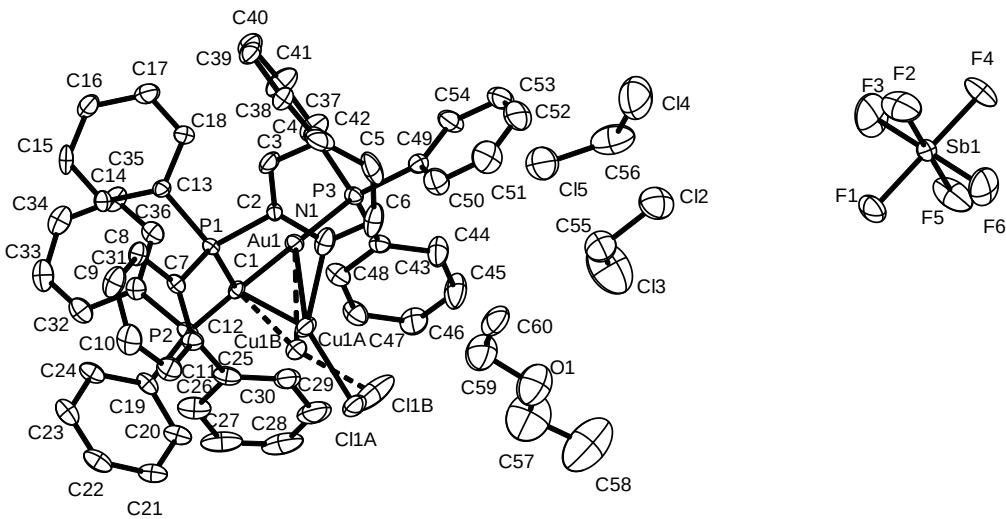


Figure S-3. Molecular structure of 5·C₄H₁₀O·1.26(CH₂Cl₂).

Crystal data for 5·C₄H₁₀O·1.26(CH₂Cl₂): Chemical formula [C₅₄ H₄₄ Au Cl Cu N P₃]⁺ [F₆ Sb][−] · C₄ H₁₀ O · 1.26(C₂ H₂ Cl₂), *F_w* = 1512.60 g mol^{−1}, yellow needle from dichloro-methane/diethylether/hexane, crystal size 0.100 x 0.020 x 0.010 mm³, crystal system monoclinic, space group *C2/c*, *a* = 31.703(8), *b* = 11.136(3), *c* = 38.620(11) Å, *β* = 114.233(4)°, *V* = 12433(6) Å³, *T* = 100 K, *ρ_c* = 1.616 Mg m^{−3}, *Z* = 8, *λ* = 0.71073 Å, *μ* = 3.410 mm^{−1}, Gaussian absorption correction (*T_{min}* = 0.73288, *T_{max}* = 0.96823), scaling *SADABS*, Brucker AXS Mach3 ApexII diffractometer equipped with Helios multilayer X-ray optics, 2.42 < *θ* < 27.88°, 94800 reflections collected, 14815 unique reflections (*R_{int}* = 0.0946), 12024 reflections with *I* > 2σ(*I*). Intensity statistics:

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	R(int)	Rsigma
Inf - 2.07	844	852	99.1	7.56	84.4	26.19	0.0522	0.0309
2.07 - 1.63	843	844	99.9	8.05	52.4	23.84	0.0567	0.0326
1.63 - 1.42	850	850	100.0	8.14	45.8	22.77	0.0617	0.0336
1.42 - 1.28	917	917	100.0	7.82	35.3	20.86	0.0708	0.0376
1.28 - 1.18	931	931	100.0	7.38	25.8	17.83	0.0883	0.0444
1.18 - 1.11	873	873	100.0	6.86	24.6	16.32	0.0930	0.0500
1.11 - 1.05	929	929	100.0	6.60	20.0	14.47	0.1138	0.0589
1.05 - 1.00	953	953	100.0	6.31	17.6	12.67	0.1237	0.0674
1.00 - 0.96	950	950	100.0	6.00	16.6	11.57	0.1327	0.0751
0.96 - 0.92	1100	1100	100.0	5.75	14.2	10.56	0.1472	0.0866
0.92 - 0.89	929	929	100.0	5.63	12.8	9.39	0.1694	0.0978
0.89 - 0.86	1078	1078	100.0	5.33	11.2	8.52	0.1745	0.1119
0.86 - 0.84	849	849	100.0	5.20	9.8	7.42	0.1995	0.1305
0.84 - 0.82	878	878	100.0	5.10	9.2	7.23	0.2180	0.1412
0.82 - 0.80	981	981	100.0	4.85	8.5	6.38	0.2291	0.1614
0.80 - 0.78	1111	1111	100.0	4.84	7.5	5.79	0.2490	0.1787
0.78 - 0.76	1222	1223	99.9	4.55	6.6	4.94	0.2926	0.2166
0.76 - 0.74	595	812	73.3	1.97	5.7	3.25	0.2989	0.3080
Inf - 0.74	16833	17060	98.7	5.95	21.8	12.53	0.0947	0.0638

Solution by direct methods (*SHELXS-97*), refinement by full-matrix least-squares on F^2 (*SHELXL-97*, G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), H atoms riding. The Cu and Cl atoms in the cation are each disordered over two positions with refined occupancy of 0.802(7):0.198(7). Bond distances, angles and vectors indicate that in the major component (80%), Cu1A is bonded to N1 of the pyridyl group with a Cu1A-N1 bond distance of 2.267(6) Å. As a result, the Cl atom, Cl1A, which bonded to Cu1A, is bent away from N1 in the plane of Au1, Cu1A, N1, such that the C1-Cu1A-Cl1A bond angle is 148.3(2)°. Bond angles around the Cu atom of the minor component indicate that Cu1B undergoes interaction with an N atom of a minor pyridyl ring component near to the position of C20. Due to the partial occupancy of solute and the presence of Au, Cu and Cl in the structure, it was not possible to locate the exact position of this pyridyl group, but it is probably bonded to P2. In addition, the large anisotropic atomic displacement parameter of Cl1B indicate that the partial pyridyl group is itself disordered. The crystal contains both solute ether and dichloromethane. Both dichloromethane molecules are present with refined partial occupancy of 62.9(4)%. Several low angle reflections were shaded by the beamstop and were not used in the final refinement cycles. Assuming that the final model is correct, the larger than unity goodness-of-fit of 1.319 at the end of refinement suggests that the weights attributed to the measured intensities were slightly underestimated. $R_1 = 0.052$ [$I > 2\sigma(I)$], $wR_2 = 0.120$ (all data), 734 parameters, $S = 1.319$, residual electron density +1.88 / -2.68 e Å⁻³ [in the vicinity of Au1 (0.91 Å and 0.05 Å, respectively)]. CCDC 914765.

Crystal structure analysis of 6

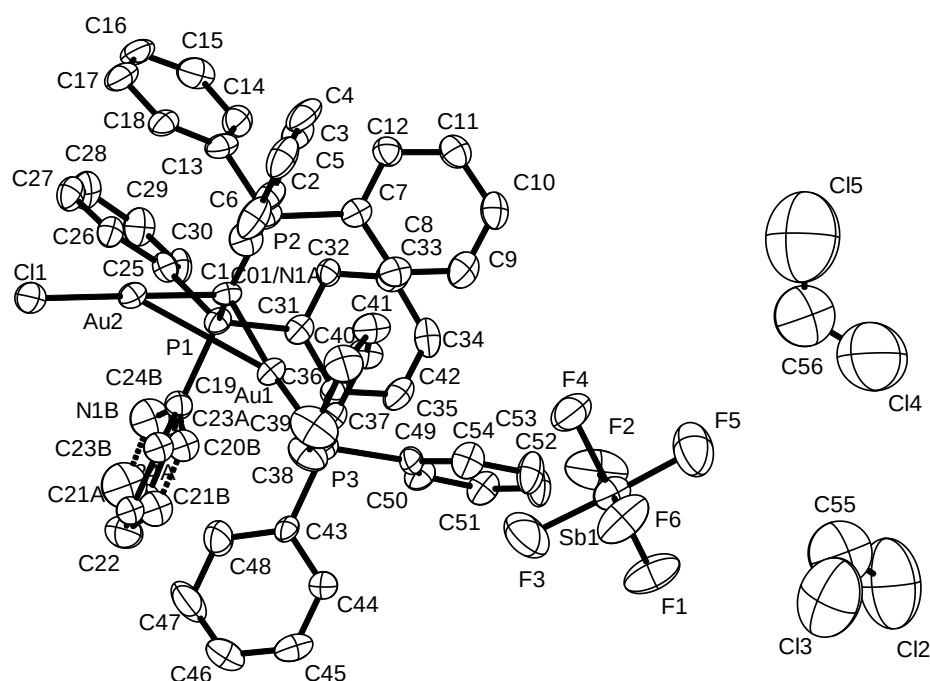


Figure S-4. Molecular structure of **6**·2(CH₂Cl₂).

Crystal data for 6·2(CH₂Cl₂): Chemical formula [C₅₄ H₄₄ Au₂ Cl N P₃]⁺ [F₆ Sb]⁻ · 2(C₂ H₂ Cl₂), *F_w* = 1634.80 g mol⁻¹, colourless plate from dichloro-methane/diethylether, crystal size 0.036 x 0.036 x 0.010 mm³, crystal system triclinic, space group *P* $\bar{1}$, *a* = 11.0964(17), *b* = 16.611(3), *c* = 17.876(3) Å, *α* = 63.214(2), *β* = 74.097(3), *γ* = 71.051(3)°, *V* = 2750.0(7) Å³, *T* = 100 K, *ρ_c* = 1.974 Mg m⁻³, *Z* = 2, *λ* = 0.71073 Å, *μ* = 6.199 mm⁻¹, Gaussian absorption correction (*T*_{min} = 0.77426, *T*_{max} = 0.94267), scaling *SADABS*, Brucker AXS Mach3 ApexII diffractometer equipped with Helios multilayer X-ray optics, 2.18 < *θ* < 26.78°, 58526 reflections collected, 11609 unique reflections (*R*_{int} = 0.0799), 8203 reflections with *I* > 2σ(*I*). Intensity statistics:

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	R(int)	Rsigma
Inf - 2.15	584	586	99.7	6.34	56.0	34.91	0.0289	0.0221
2.15 - 1.72	583	583	100.0	6.27	30.3	28.06	0.0374	0.0258
1.72 - 1.49	614	614	100.0	6.20	26.3	25.79	0.0443	0.0281
1.49 - 1.35	614	614	100.0	6.13	21.7	23.01	0.0514	0.0312
1.35 - 1.25	620	620	100.0	5.99	15.9	19.20	0.0669	0.0382
1.25 - 1.18	594	594	100.0	5.78	12.9	16.30	0.0791	0.0461
1.18 - 1.12	588	588	100.0	5.52	10.3	13.16	0.0963	0.0569
1.12 - 1.07	641	641	100.0	5.30	10.6	13.04	0.1004	0.0601
1.07 - 1.03	582	582	100.0	5.12	8.8	10.75	0.1174	0.0725
1.03 - 0.99	695	695	100.0	4.99	8.1	9.60	0.1319	0.0818
0.99 - 0.96	600	600	100.0	4.75	7.8	9.14	0.1395	0.0888
0.96 - 0.93	673	673	100.0	4.62	6.4	7.59	0.1648	0.1100
0.93 - 0.90	795	795	100.0	4.46	5.2	6.08	0.1962	0.1374
0.90 - 0.87	868	868	100.0	4.28	4.6	5.24	0.2198	0.1633
0.87 - 0.85	662	662	100.0	4.27	3.6	4.13	0.2832	0.2073
0.85 - 0.83	737	737	100.0	4.10	3.5	3.93	0.2782	0.2280
0.83 - 0.81	795	795	100.0	3.95	2.9	3.19	0.3276	0.2842
0.81 - 0.79	368	474	77.6	2.43	2.8	2.78	0.3292	0.3520
Inf - 0.79	11613	11721	99.1	4.99	12.6	12.61	0.0762	0.0585

Solution by direct methods (*SHELXS*-97), refinement by full-matrix least-squares on F^2 (*SHELXL*-97, G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), H atoms riding. One of the phenyl/pyridyl groups attached to P was rotationally disordered over two positions about C19. The location of the single 2-pyridyl group attached to P could not be determined with certainty. However, refinement of all the six-membered ring atoms as C resulted in smaller than average C atomic displacement parameters for C01 and C20A, indicating that these positions are the preferential locations of N. Position C20A and half of position C01 were refined as N atoms (N1A and N1B, respectively). Distances of these two N atoms to the Au atom Au2 (N1A...Au2 3.31(1) and N1B...Au2 3.41(1) Å) indicate that the 2-pyridyl group is not bonded to Au2. This is confirmed by the almost linear C1-Au2-Cl1 angle of 178.8(2)°. The crystal contains two solute dichloromethane molecules. The atomic displacement parameter of one Cl atom (Cl4) is somewhat anisotropic. Attempts to model the disorder of this atom by two atoms with half occupancy were unsuccessful, since the close proximity of a centre of symmetry, and associated symmetry related molecule, prevented an otherwise chemically sensible interpretation of the disorder. Several low angle reflections were shaded by the beamstop and were not included in the final refinement cycles. $R_1 = 0.051$ [$I > 2\sigma(I)$], $wR_2 = 0.139$ (all data), 648 parameters, $S = 1.270$, residual electron density +3.23 / - 1.98 e Å⁻³ [in the vicinity of Au2 (0.92 Å) and Cl4 (0.74 Å), respectively]. CCDC 914766.

Crystal structure analysis of 9

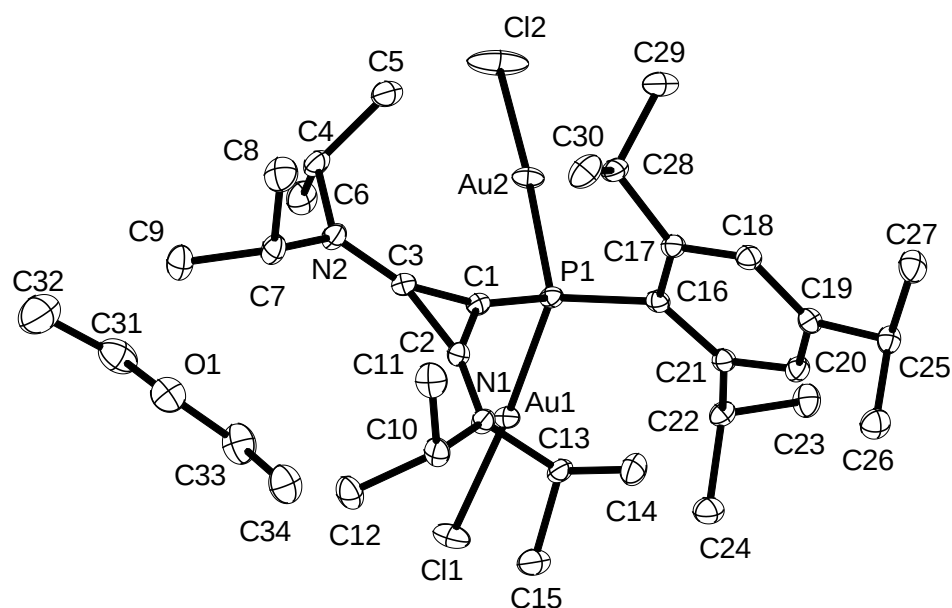


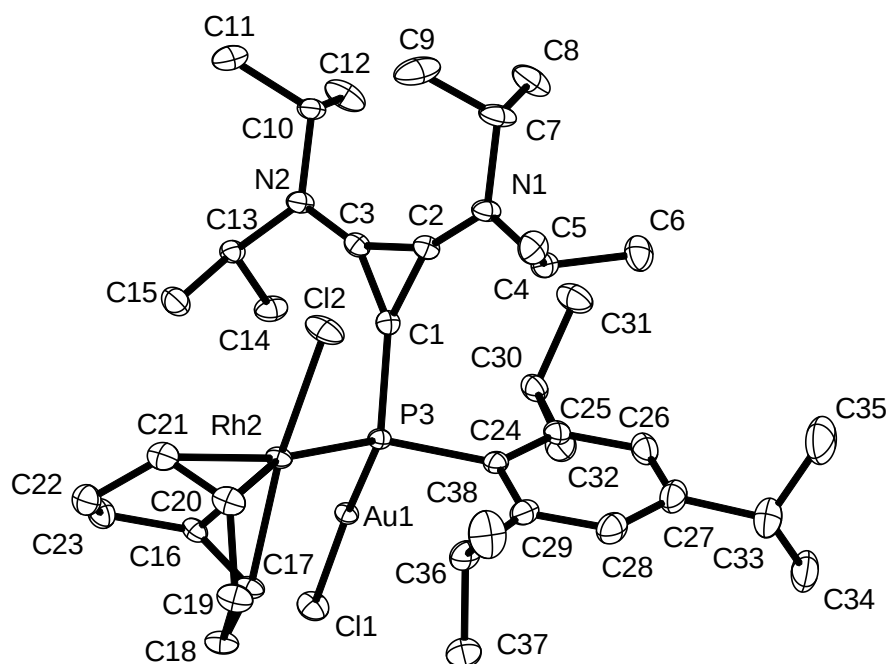
Figure S-5. Molecular structure of **9**·C₄H₁₀O.

Crystal data for 9·C₄H₁₀O: Chemical formula [C₃₀ H₅₁ Au₂ Cl₂ N₂ P] · (C₄ H₁₀ O), $F_w = 1009.65 \text{ g mol}^{-1}$, colourless prism from dichloromethane/diethylether, crystal size 0.110 x 0.100 x 0.060 mm³, crystal system monoclinic, space group $P2_1/n$, $a = 12.2004(15)$, $b = 18.010(2)$, $c = 17.840(2) \text{ Å}$, $\beta = 96.719(2)^\circ$, $V = 3893.2(8) \text{ Å}^3$, $T = 100 \text{ K}$, $\rho_c = 1.723 \text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073 \text{ Å}$, $\mu = 7.733 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{\min} = 0.35063$, $T_{\max} = 0.67230$), scaling *SADABS*, Bruker AXS Mach3 ApexII diffractometer equipped with Helios multilayer X-ray optics, $1.61 < \theta < 31.02^\circ$, 112428 reflections collected, 12388 unique reflections ($R_{\text{int}} = 0.0279$), 11258 reflections with $I > 2\sigma(I)$. Intensity statistics:

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.88	192	195	98.5	11.00	133.0	107.25	0.0178	0.0074
2.88 - 1.90	452	452	100.0	12.05	88.5	104.04	0.0167	0.0071
1.90 - 1.50	640	640	100.0	12.14	73.2	98.63	0.0179	0.0074
1.50 - 1.31	636	636	100.0	11.95	49.5	85.15	0.0212	0.0083
1.31 - 1.18	685	685	100.0	11.55	43.0	77.13	0.0224	0.0092
1.18 - 1.10	605	605	100.0	10.90	41.2	71.55	0.0240	0.0097
1.10 - 1.03	690	690	100.0	10.31	34.0	62.01	0.0267	0.0109
1.03 - 0.98	616	616	100.0	9.74	29.2	56.13	0.0287	0.0124
0.98 - 0.93	760	760	100.0	9.39	25.6	50.59	0.0314	0.0136
0.93 - 0.90	532	532	100.0	8.89	24.4	47.99	0.0337	0.0147
0.90 - 0.87	603	603	100.0	8.77	21.2	43.00	0.0380	0.0163
0.87 - 0.84	721	721	100.0	8.35	19.4	40.25	0.0391	0.0179
0.84 - 0.81	796	796	100.0	8.09	16.6	34.55	0.0466	0.0206
0.81 - 0.79	628	628	100.0	7.79	16.0	32.99	0.0474	0.0220
0.79 - 0.77	666	666	100.0	7.60	13.0	27.66	0.0565	0.0259
0.77 - 0.76	369	369	100.0	7.38	13.9	27.77	0.0516	0.0255
0.76 - 0.74	791	791	100.0	7.16	12.6	25.91	0.0590	0.0283
0.74 - 0.72	875	875	100.0	7.00	12.8	24.82	0.0573	0.0291
0.72 - 0.71	485	485	100.0	6.58	11.4	22.83	0.0666	0.0335
0.71 - 0.70	510	510	100.0	6.68	10.3	21.42	0.0724	0.0361
0.70 - 0.69	503	546	92.1	5.45	11.2	20.29	0.0685	0.0390
Inf - 0.69	12755	12801	99.6	8.92	29.3	49.28	0.0277	0.0135

Solution by direct methods (*SHELXS*-97), refinement by full-matrix least-squares on F^2 (*SHELXL*-97, G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), H atoms riding. $R_1 = 0.0148$ [$I > 2\sigma(I)$], $wR_2 = 0.0351$ (all data), 395 parameters, $S = 1.029$, residual electron density +1.93 / -1.22 e Å⁻³ [in the vicinity of Au2 (0.68 Å) and Cl2 (0.73 Å), respectively]. CCDC 914767.

Crystal structure analysis of 10



Solution by direct methods (*SHELXS-97*), refinement by full-matrix least-squares on F^2 (*SHELXL-97*, G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112-122), H atoms riding. Reflections above 9 Å resolution were shaded by the beamstop and removed from the final least-squares refinement cycles. $R_1 = 0.020$ [$I > 2\sigma(I)$], $wR_2 = 0.049$ (all data), 420 parameters, $S = 1.228$, residual electron density +1.56 / -1.04 e Å⁻³ [in the vicinity of Rh2 (0.92 Å) and Au1 (0.76 Å), respectively]]. CCDC 914768.