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A New Class of Singlet Carbene Ligands

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General: All reactions were carried out in flame-dried glassware under Argon. The solvents were purified by distillation over the drying solvents indicated and were transferred under Argon. THF, Et₂O (Mg-anthracene), CH₂Cl₂ (P₄O₁₀), MeCN (CaH₂), toluene (Na/K). Flash chromatography was performed with silica gel (Merck 60, 230-400 Mesh) or Florisil® (Aldrich, 200 Mesh) and TLC with Polygram® Alox N/UV254 plates. IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 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. Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. Unless stated otherwise, all commercially available compounds (Acros, Fluka, Aldrich) were used as received.

Starting Materials

Compound 3a: PPh₃ (0.82 g, 3.11 mmol) was added to a solution of **2** (0.80 g, 3.11 mmol)¹ in toluene (40 mL) and the resulting mixture was stirred at reflux temperature overnight. The precipitate was filtered off under Argon, washed with dry pentane and dried in vacuo to give the bromide salt as a bright yellow powder. A saturated aqueous solution of NaBF₄ (340 mg, 3.11 mmol) was added to a solution of this material in the minimum amount of H₂O/MeOH (10:1), causing the immediate precipitation of a yellow solid. This product was filtered off, washed with water and EtOH (5 mL) and dried in vacuum to give compound **3a** in analytically pure form (0.91 g, 55 %). M.p. = 173-177 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 6.66 (d, J = 7.6 Hz, 1H), 6.74 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 14 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.80 ppm (m, 18H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 98.8 (CH, d, J = 90.9 Hz), 119.0 (C), 119.9 (C), 121.3 (CH), 121.8 (CH), 123.7 (CH), 128.2 (CH), 128.4 (CH), 129.5 (CH), 131.6 (CH, d, J = 13.1 Hz), 133.9 (C, d, J = 4.5 Hz), 134.0 (CH), 134.4 (CH, d, J = 10.9 Hz), 136.4 (CH, d, J = 2.9 Hz), 138.3 (C, d, J = 17.8 Hz), 141.9 (C), 145.0 ppm (C); ³¹P NMR (162 MHz, CD₂Cl₂): δ = 15.4 ppm; IR (film): $\tilde{\nu}$ = 1576, 1438, 1106, 1049, 996, 840, 786, 741, 725, 688 cm⁻¹; MS (ESI+) m/z (%): 439 (100, [M⁺-BF₄]); HRMS (ESI+) m/z : calcd for C₃₂H₂₄P: 439.16102; found: 439.16119.

Compound 3b: Prepared analogously as a yellow solid (1.38 g, 68 %); m.p. = 185-187 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 6.57 (d, J = 7.8 Hz, 1H), 6.62 (dt, J = 7.8, 0.9 Hz, 1H), 7.06 (d, J = 12.9 Hz, 1H), 7.24 (br t, J = 7.4 Hz, 1H), 7.32 (dt, J = 7.4, 0.9 Hz, 1H), 7.46 (br t, J = 7.5 Hz, 1H), 7.61 (m, 6H), 7.79 (m, 9H), 7.93 (m, 1H), 8.94 ppm (d, J = 4.7 Hz, 1H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 102.4 (CH, d, J = 89 Hz), 122.6 (C, d, J = 89 Hz), 124.7 (CH), 125.2 (CH), 127.6 (CH), 131.5 (CH), 132.0 (CH), 132.60 (CH), 132.64 (CH), 132.9 (CH), 134.6 (CH, d, J = 13 Hz), 137.5 (C, d, J = 4.9 Hz), 138.3 (CH, d, J = 10.6 Hz), 139.5 (CH, d, J =

¹ G. C. Paul, J. J. Gajewski, *Synthesis* **1997**, 524-526.

3.0 Hz), 142.0 (C, d, $J = 18.2$ Hz), 142.4 (CH, d, $J = 10.7$ Hz), 145.1 (C), 148.4 (C, d, $J = 60.0$ Hz), 149.9 (C), 156.9 (CH, d, $J = 19.8$ Hz), 165.3 ppm (C); IR (film): $\tilde{\nu} = 1738, 1438, 1365, 1229, 1217, 1050, 842, 734, 689$ cm^{-1} ; MS (ESI+) m/z (%): 440 (100, $[M^+ - \text{BF}_4]$). HRMS (ESI+) m/z : calcd for $\text{C}_{31}\text{H}_{23}\text{NP}$: 440.15626; found: 440.15612.

Compound 3c: Prepared analogously as a yellow solid (1.63 g, 77 %); m.p. = 288-289 °C; ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 1.37$ (m, 3H), 1.52 (m, 6H), 1.69 (m, 6H), 1.85 (m, 3H), 1.96 (m, 6H), 2.15 (m, 6H), 2.95 (m, 3H), 6.34 (d, $J = 9.9$ Hz, 1H), 7.43 (br t, $J = 7.6$ Hz, 1H), 7.53 (br dd, $J = 7.2, 2.8$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.76 (br d, $J = 7.6$ Hz, 3H), 7.91 ppm (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 26.0$ (CH_2), 27.2 (CH_2), 27.3 (CH_2), 28.37 (CH_2), 28.41 (CH_2), 34.5 (CH, d, $J = 41.3$ Hz), 96.0 (CH, d, $J = 76.1$ Hz), 120.9 (CH), 121.9 (CH), 123.1 (CH), 125.5 (CH), 129.3 (CH), 133.1 (CH), 133.9 (CH), 134.5 (C), 138.8 (C), 140.9 (C), 144.6 (C), 160.8 ppm (C); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 28.6$ ppm; IR (film): $\tilde{\nu} = 2935, 2858, 1581, 1449, 1267, 1047, 786, 729, 700$ cm^{-1} ; MS (ESI+) m/z (%): 457 (100, $[M^+ - \text{BF}_4]$). HRMS (ESI+) m/z : calcd for $\text{C}_{32}\text{H}_{42}\text{P}$: 457.30187; found: 457.30206; elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{42}\text{P}$: C 70.59, H 7.78; found: C 69.58, H 7.51.

Compound 3d: Prepared analogously as a yellow solid (1.47 g, 62 %); ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 2.89$ (d, $J = 10.2$ Hz, 18H), 6.39 (d, $J = 11.8$ Hz, 1H), 7.43 (m, 2H), 7.54 (m, 2H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.74 (d, $J = 7.2$ Hz, 1H), 7.86 ppm (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 37.4$ (CH_3 , d, $J = 4.8$ Hz), 100.3 (CH, d, $J = 163.7$ Hz), 121.0 (CH), 123.3 (CH), 127.4 (CH), 129.2 (CH), 129.4 (CH), 133.2 (CH), 133.6 (CH), 134.7 (C, d, $J = 5.1$ Hz), 138.3 (C, d, $J = 20.9$ Hz), 141.5 (C), 144.6 (C), 158.4 ppm (C); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 47.0$ ppm; MS (ESI+) m/z (%): 340 (100, $[M^+ - \text{BF}_4]$). HRMS (ESI+) m/z : calcd for $\text{C}_{20}\text{H}_{27}\text{N}_3\text{P}$: 340.19371; found: 340.19379.

Compound 10: 1-Methyl-2-formyl-benzimidazole (0.59 g, 3.68 mmol) was added to a solution of compound **9** (1.73 g, 4.05 mmol)² in THF (30 mL) and the resulting mixture was stirred overnight at reflux temperature. For work up, the mixture was allowed to reach ambient temperature before it was diluted with Et_2O (50 mL) and washed with water and brine (30 mL each). The organic layer was dried over Na_2SO_4 and evaporated and the residue purified by flash chromatography, eluting with CH_2Cl_2 (0.90 g, 80 %). M.p. = 232-234 °C; ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 3.83$ (s, 3H), 7.21 (dq, $J = 7.6, 1.2$ Hz, 2H), 7.28 (m, 2H), 7.33 (m, 3H), 7.38 (s, 1H), 7.64 (d, $J = 7.5$ Hz, 2H), 7.78 (m, 2H), 9.03 ppm (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 31.2$ (CH_3), 110.3 (CH), 111.6 (CH); 120.3 (CH), 120.6 (CH), 120.7 (CH), 121.4 (CH), 123.3 (CH), 124.1 (CH), 128.0 (CH), 128.4 (CH), 128.5 (CH), 130.1 (CH), 130.7 (CH), 136.5 (C), 136.8 (C), 140.1 (C), 140.8 (C), 142.4 (C), 142.7 (C), 144.2 (C), 150.0 ppm (C); IR (film): $\tilde{\nu} = 3016, 2970, 1738, 1439, 1366, 1228, 1217, 952, 907, 779, 726$ cm^{-1} ; MS (EI) m/z (%): 308 (33, $[M^+]$), 307 (100), 292 (24, $[M^+ - \text{CH}_4]$); MS

² L. A. Pinck, G. E. Hilbert, *J. Am. Chem. Soc.* **1947**, *69*, 723.

(ESI+) m/z (%): 309 (100, $[M^+ + H]$), 331 (10, $[M^+ + Na]$), 617 (30, $[2M^+ + H]$); HRMS (ESI+) m/z : calcd for $C_{22}H_{16}H_2+Na$: 331.12057; found: 331.12053.

Trimethyloxonium tetrafluoroborate (500 mg, 3.37 mmol) was added to a suspension of this compound (865 mg, 2.8 mmol) in Et_2O (10 mL) at 0 °C and the resulting mixture was stirred overnight at reflux temperature. For work up, the suspension was filtered, the filtrate evaporated, and the residue triturated with Et_2O (2 x 3 mL) before it was recrystallized from CH_2Cl_2/Et_2O to give the title compound as a bright yellow solid (1.13 g, 98 %). M.p. = 248-250 °C; 1H NMR (400 MHz, CD_2Cl_2): δ = 4.03 (s, 6H), 6.42 (d, J = 7.6 Hz, 1H), 7.10 (dt, J = 7.6, 0.8 Hz, 1H), 7.49 (m, 3H), 7.57 (dt, J = 7.6, 0.8 Hz, 1H), 7.78 (m, 4H), 7.88 (m, 2H), 8.07 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 33.6 (CH_3), 101.6 (CH), 113.7 (CH), 121.1 (CH), 121.8 (CH), 123.7 (CH), 123.8 (CH), 128.4 (2 CH), 129.1 (CH), 129.3 (CH), 132.7 (CH), 132.8 (CH), 132.9 (CH), 134.7 (C), 137.3 (C), 141.4 (C), 143.8 (C), 149.2 (C), 151.5 ppm (C); IR (film): $\tilde{\nu}$ = 1640, 1602, 1511, 1468, 1453, 1339, 1033, 944, 768, 757, 739, 725 cm^{-1} ; MS (EI) m/z (%): 323 (100, $[M^+-BF_4]$), 307 (26), 292 (15); HRMS (ESI+) m/z : calcd for $C_{23}H_{19}N_2$: 323.15428; found: 323.15433; elemental analysis calcd (%) for $C_{23}H_{19}N_2$: C 67.34, H 4.67, N 6.83; found: C 67.04, H 4.58, N 6.45.

Compound 14: Ylide **9** (7.5 g, 17.58 mol) was added to a solution of aldehyde **13** (2.1 g, 17.58 mol) in toluene (12 mL) and the resulting mixture was stirred at 100 °C for 12 h. For work up, the mixture was filtered through a pad of Celite, the filtrate was evaporated, and the residue purified by flash chromatography ($EtOAc$ /hexanes, 1:4) to give the resulting olefin, which was immediately used in the next step (2.74 g, 58 %). Triphenylcarbenium tetrafluoroborate (3.6 g, 10.9 mol) was added in portions at 0 °C to a solution of this compound (2.9 g, 10.9 mol) in CH_2Cl_2 (35 mL), and the resulting mixture was stirred at that temperature overnight. The mixture was evaporated and the residue extracted with Et_2O to give product **14** as a solid (2.8 g, 75 %). 1H NMR (400 MHz, CD_2Cl_2): δ = 7.0 (dt, J = 7.6, 0.8 Hz, 1H), 7.27 (dt, J = 7.6, 0.8 Hz, 1H), 7.38 (m, 2H), 7.53 and 7.57 (d, J = 8 Hz, 3H), 7.72 (s, 1H), 7.75 (d, J = 8 Hz, 1H), 8.88 (m, 4H), 9.28 ppm (br d, J = 10.8 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 121.2 (CH), 122.0 (CH), 123.4 (CH), 124.5 (CH), 124.7 (CH), 128.7 (CH), 129.2 (CH), 132.9 (CH), 133.9 (CH), 134.9 (C), 141.4 (C), 144.0 (C), 144.4 (C), 150.1 (C), 152.9 (CH), 153.8 (CH), 154.8 (CH), 167.7 ppm (C); MS (EI) m/z (%): 268 (100), 267 (80, $[M^+-BF_4]$), 165 (10); HRMS (ESI+) m/z : calcd for $C_{21}H_{15}$: 267.11683; found: 267.11672.

Compound 18: Prepared as described in the literature:³ A solution of DDQ (595 mg, 2.62 mmol) in toluene (25 mL) was slowly added over a period of 5 minutes to a solution of compound **17** (875 mg, 2.38 mmol) in toluene (25 mL) at 90 °C. Once the addition was complete, stirring was continued for 10 min before the suspension was cooled to 0 °C. The precipitate was filtered off and discarded while the filtrate was evaporated to dryness. The residue was purified by flash chromatography on silica (toluene/pentanes, 40:60), affording

³ L. Salisbury, *J. Org. Chem.* **1972**, *37*, 4075-4077.

allene **18** as a colorless solid (113 mg, 13 %). ^1H NMR (400 MHz, CD_2Cl_2): δ = 6.84 (s, 2H), 7.16-7.33 (m, 10H), 7.45-7.49 (dm, J = 7.2 Hz, 2H), 7.68 ppm (t, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 119.5 (C), 121.0 (CH), 123.7 (CH), 128.0 (CH), 129.0 (br s, CH), 129.7 (CH), 129.8 (CH), 130.4 (CH), 132.0 (CH), 135.5 (C), 136.0 (C), 138.4 (C), 139.6 (C), 165.4 (C), 207.2 ppm (C); IR (film): $\tilde{\nu}$ = 3018, 1916, 1488, 1446, 1433, 1293, 944, 300, 772, 759, 733 cm^{-1} ; HRMS (EI) m/z : calcd for $\text{C}_{29}\text{H}_{18}$: 366.14060; found: 366.14085; elemental analysis calcd (%) for $\text{C}_{29}\text{H}_{18}$: C 95.05, H 4.95; found C 94.74, H 4.78.

Carbene and Metal-Carbene Complex Formation

Carbene 4d: Compound **3d** (60 mg, 0.14 mmol) was added at $-78\text{ }^\circ\text{C}$ to a solution of KHMDS (28 mg, 0.14 mmol) in $[\text{D}_8]$ -THF (0.6 mL). After stirring for 10 min at that temperature, the mixture was transferred under Ar into a well dried NMR tube. Carbene **4d** showed the following spectral properties: ^1H NMR (300 MHz, $[\text{D}_8]$ -THF, $-80\text{ }^\circ\text{C}$): δ = 2.72 (br d, J = 9.5 Hz, 18H), 7.24 (m, 4H), 7.70 ppm (m, 4H); ^{13}C NMR (75 MHz, $[\text{D}_8]$ -THF, $-80\text{ }^\circ\text{C}$): δ = 3.14 (CH_3), 37.7 (CH_3), 119.6 (CH), 123.0 (CH), 127.5 (CH), 140.4 (CH), 140.8 (CH), 142.2 (CH), 149.6 (CH), 214.1 ppm (C:, d, J = 58 Hz); ^{31}P NMR (122 MHz, $[\text{D}_8]$ -THF, $-80\text{ }^\circ\text{C}$): δ = 56.1 ppm.

Complex 5a: $(\text{Me}_2\text{S})\text{AuCl}$ (88.4 mg, 0.3 mmol) was added to a suspension of compound **3a** (157.8 mg, 0.3 mmol) and KHMDS (60 mg, 0.3 mmol) in THF (3 mL) at $-78\text{ }^\circ\text{C}$, which had been stirred at that temperature for 5 min. Stirring was continued for 1 h before the mixture was slowly warmed to room temperature. After an additional 2 h, the solvents were evaporated, the residue was extracted with dichloromethane (3 mL), and the product crystallized by slowly diffusing pentane into the dichloromethane phase (83 mg, 41 %). ^1H NMR (400 MHz, CD_2Cl_2): δ = 9.77 (d, J = 8.1 Hz, 1H), 7.80-7.71 (m, 6H), 7.63-7.57 (m, 3H), 7.55 (d, J = 7.7 Hz, 1H), 7.50-7.42 (m, 7H), 7.38 (dt, J = 7.5, 0.7 Hz, 1H), 7.25 (dt, J = 7.8, 1.3 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.53 (d, J = 7.8, 1H), 6.32 ppm (dt, J = 7.7, 1.1 Hz, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 159.9, 142.3, 142.0 (d, J = 29.2 Hz), 141.0, 136.3 (d, J = 11.3 Hz), 135.2 (d, J = 26.6 Hz), 134.2 (d, J = 9.2 Hz), 133.9 (d, J = 3.1 Hz), 130.3, 129.7 (d, J = 12.0 Hz), 129.4, 128.2, 128.1, 125.8 (d, J = 85.4 Hz), 125.5, 124.5, 119.8, 119.1 ppm (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 22.9 ppm; IR (film): $\tilde{\nu}$ = 1481, 1433, 1270, 1104, 996, 828, 780, 729, 710, 687 cm^{-1} ; HRMS: calcd for $\text{C}_{32}\text{H}_{23}\text{PAuCl}+\text{Na}$: 693.07836; found 693.07815; elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{23}\text{PAuCl}\cdot\text{CH}_2\text{Cl}_2$: C 52.44, H 3.33; found C 52.88, H 3.12.

Complex 5b: Prepared analogously as a yellow solid by crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (36 mg, 31 %); m.p. = 225-227 $^\circ\text{C}$ (decomp.); ^1H NMR (400 MHz, CD_2Cl_2): δ = 6.28 (br t, J = 7.6 Hz, 1H), 6.41 (dd, J = 7.9, 0.6 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 7.22 (br t, J = 7.6 Hz, 1H), 7.38 (m, 7H), 7.55 (m, 4H), 7.80 (br dd, J = 8.4, 7.4 Hz, 4H), 7.96 (br t, J = 6.7 Hz, 1H), 8.77 (br d, J = 3.9 Hz, 1H), 9.74 ppm (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 119.6

(CH), 120.4 (CH), 124.9 (CH), 126.2 (CH), 126.5 (C, d, $J = 46.8$ Hz), 127.56 (CH), 127.58 (CH), 128.7 (CH, d, $J = 18.0$ Hz), 129.8 (CH), 130.2 (CH, d, $J = 12.5$ Hz), 130.9 (CH), 131.5 (CH, d, $J = 23.2$ Hz), 134.3 (CH, d, $J = 2.6$ Hz), 134.8 (CH, d, $J = 8.8$ Hz), 136.9 (C, d, $J = 10.5$ Hz), 137.7 (CH, d, $J = 10.0$ Hz), 141.5 (C), 142.2 (C, d, $J = 28.5$ Hz), 142.9 (C), 150.0 (C), 151.0 (C), 152.5 (CH, d, $J = 17.2$ Hz), 160.7 ppm (C); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 16.7$ ppm; IR (film): $\tilde{\nu} = 2963, 1738, 1435, 1260, 1096, 1020, 784, 730, 686$ cm^{-1} ; MS (ESI+) m/z (%): 694 (100, $[\text{M}^+\text{Na}]$), 440 (95); HRMS (ESI+) m/z : calcd for $\text{C}_{31}\text{H}_{22}\text{ClIPAu}+\text{Na}$: 694.07361; found: 694.07328.

Complex 5c: Prepared analogously by crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -60 °C. The complex must be stored at -30 °C under Ar. Yellow powder (67 mg, 19 %). ^1H NMR (300 MHz, CD_2Cl_2 , -30 °C): $\delta = 1.12$ (m, 9H), 1.71 (m, 15H), 2.10 (m, 6H), 3.09 (m, 3H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.56 (m, 2H), 7.66 (d, $J = 6.7$ Hz, 1H), 9.78 ppm (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2 , -30 °C): $\delta = 25.7$ (CH_2), 27.2 (CH_2), 27.4 (CH_2), 28.5 (CH_2), 37.8 (CH), 118.9 (CH), 120.2 (CH), 123.5 (CH), 124.2 (CH), 126.0 (CH), 127.6 (CH), 129.3 (CH), 129.4 (CH), 136.7 (C, d, $J = 9.2$ Hz), 138.0 (C), 139.5 (C), 141.7 (C), 159.3 ppm (C); ^{31}P NMR (121 MHz, CD_2Cl_2 , -30 °C): $\delta = 29.5$ ppm; IR (film): $\tilde{\nu} = 2930, 1738, 1440, 1365, 1229, 1217, 898, 846, 778, 727$ cm^{-1} ; MS (ESI+) m/z (%): 688 (7, $[\text{M}^+]$), 652 (18, $[\text{M}^+\text{HCl}]$), 456 (90, $[\text{M}^+\text{AuCl}]$), 209 (100); HRMS (ESI+) m/z : calcd for $\text{C}_{32}\text{H}_{41}\text{AuClIP}+\text{Na}$: 711.21921; found: 711.21932.

Complex 5d: Prepared analogously by crystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -60 °C. The complex must be stored at -30 °C under Ar. Yellow powder (79 mg, 28 %). ^1H NMR (300 MHz, CD_2Cl_2 , -30 °C): $\delta = 2.72$ (dd, $J = 9.6, 1.6$ Hz, 18H), 7.20 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.27 (dt, $J = 7.6, 0.8$ Hz, 1H), 7.33 (br t, $J = 7.2$ Hz, 1H), 7.39 (br t, $J = 7.2$ Hz, 1H), 7.59 (br d, $J = 7.2$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 9.89 ppm (d, $J = 8$ Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2 , -30 °C): $\delta = 15.0$ (CH_3), 36.4 (CH_3), 118.5 (CH), 119.2 (CH), 122.5 (CH), 125.3 (CH), 127.3 (CH), 127.4 (CH), 128.9 (CH), 129.5 (CH), 134.8 (C), 136.5 (C, d, $J = 9.6$ Hz), 139.6 (C), 140.1 (C, d, $J = 29.4$ Hz), 140.9 (C), 158.8 ppm (C, d, $J = 1.8$ Hz); ^{31}P NMR (122 MHz, CD_2Cl_2 , -30 °C): $\delta = 52.6$ ppm; IR (film): $\tilde{\nu} = 2894, 1433, 1286, 1180, 1064, 978, 836, 786, 748, 669$ cm^{-1} ; MS (EI) m/z (%): 571 (16, $[\text{M}^+]$), 338 (60), 252 (100); HRMS (ESI+) m/z (%): calcd for $\text{C}_{20}\text{H}_{26}\text{N}_3\text{AuClIP}+\text{Na}$: 594.11106; found: 594.11162.

Complex 11: Prepared analogously; purification by flash chromatography (Florisol, 1 \rightarrow 5 % MeOH/ CH_2Cl_2) gave **11** as a yellow powder (126 mg, 45 %); m.p. = 251–253 °C (decomp.); ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 3.73$ (s, 6H), 5.69 (d, $J = 8$ Hz, 1H), 6.78 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.18 (dt, $J = 7.6, 0.8$ Hz, 1H), 7.32 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.40 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.57 (br s, 4H), 7.65 (m, 2H), 9.49 ppm (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 32.1$ (CH_3), 112.6 (CH), 119.9 (CH), 121.0 (CH), 121.3 (CH), 123.9 (CH), 126.8 (CH), 128.3 (CH), 128.6 (CH), 129.4 (CH), 130.2 (CH), 132.5 (C), 136.2 (C), 137.8

(C), 140.2 (C), 141.0 (C), 141.3 (C), 147.7 (C), 160.4 ppm (C); IR (film): $\tilde{\nu}$ = 1737m 1581, 1503, 1475, 1443, 1348, 1135, 1026, 951, 763, 657 cm^{-1} ; MS (EI) m/z (%): 554 (15, $[M^+]$), 322 (58, $[M^+-\text{AuCl}]$), 321 (100); HRMS (ESI+) m/z (%): calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{ClAu}+\text{Na}$: 577.07162; found: 577.07199.

Rhodium carbonyl complex 6: Compound **3a** (184 mg, 0.35 mmol) was added at $-78\text{ }^\circ\text{C}$ to a solution of KHMDS (70 mg, 0.35 mmol) in THF (3 mL) and the resulting mixture was stirred for 8 min prior to the addition of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (68 mg, 0.175 mmol). The temperature was then raised to $0\text{ }^\circ\text{C}$ over the course of 5 h before the mixture was filtered through a pad of Celite under Ar. The filtrate was evaporated and the residue purified by flash chromatography (Florisil®, 1→2 % MeOH in CH_2Cl_2) to give complex **6** as a bright orange solid (30 mg, 14 %). A sample suitable for X-ray diffraction analysis was obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. M.p. = $173\text{--}175\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CD_2Cl_2): δ = 6.28 (dt, J = 7.6, 1.1 Hz, 1H), 6.45 (d, J = 8 Hz, 1H), 6.91 (br t, J = 7.3 Hz, 1H), 7.23 (dt, J = 7.5, 1.2 Hz, 1H), 7.30 (dt, J = 7.4, 1.0 Hz, 1H), 7.38 (br dt, J = 7.8, 3.1 Hz, 6H), 7.44 (br d, J = 7.6 Hz, 1H), 7.53 (m, 5H), 7.75 (m, 5H), 9.91 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 119.4 (CH), 120.0 (CH), 125.9 (CH, d, J = 8.4 Hz), 127.6 (CH), 128.5 (CH, d, J = 8.1 Hz), 129.0 (CH), 129.7 (CH, d, J = 11.9 Hz), 130.0 (CH), 131.6 (C, d, J = 13.1 Hz), 134.1 (CH, d, J = 2.5 Hz), 135.7 (CH), 136.0 (CH, d, J = 26.1 Hz), 142.0 (C), 143.0 (C), 143.9 (C), 160.9 (C), 184.5 (C), 185.3 (C), 186.4 (C), 186.9 ppm (C); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 16.9 ppm; IR (film): $\tilde{\nu}$ = 3059, 2056 (CO), 1979 (CO), 1438, 1261, 1100, 823, 730, 692 cm^{-1} ; MS (ESI+) m/z (%): 599 (80), 541 (75), 439 (100); HRMS (ESI+) m/z : calcd for $\text{C}_{34}\text{H}_{23}\text{O}_2\text{PRh}$: 597.04782; found: 597.04764.

Rhodium complex 7: Compound **3a** (263 mg, 0.5 mmol) was added at $-78\text{ }^\circ\text{C}$ to a solution of KHMDS (60 mg, 0.3 mmol) in THF (3 mL) and the resulting mixture was stirred for 10 min before $[\text{Rh}(\text{cod})\text{Cl}]_2$ (147 mg, 0.5 mmol) was added. The mixture was allowed to reach ambient temperature over the course of 4 h before it was filtered through a pad of Celite under Ar. The filtrate was evaporated and the residue purified by flash chromatography (Florisil®, EtOAc/hexanes, 4:1), affording complex **7** (115 mg, 45 %) as a dark red solid. A sample suitable for X-ray diffraction analysis was obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. M.p. = $191\text{--}192\text{ }^\circ\text{C}$ (decomp.); ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.16 (m, 1H), 1.39 (m, 4H), 1.66 (m, 1H), 2.15 (m, 1H), 2.60 (m, 1H), 2.75 (m, 1H), 3.31 (br t, J = 7.0 Hz, 1H), 4.17 (br t, J = 7.0 Hz, 1H), 4.71 (dd, J = 14.8, 6.8 Hz, 1H), 6.22 (m, 2H), 6.85 (dt, J = 7.1, 1.2 Hz, 1H), 7.57 (m, 19H), 11.04 ppm (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 28.2 (CH_2), 29.7 (CH_2), 30.3 (CH_2), 34.4 (CH_2), 66.7 (CH, d, J = 15.5 Hz), 73.3 (CH, d, J = 15.1 Hz), 93.9 (CH, d, J = 7 Hz), 95.3 (CH, d, J = 6.9 Hz), 118.9 (CH), 119.6 (CH), 125.4 (CH), 127.0 (CH), 127.2 (CH), 128.2 (CH), 128.7 (CH), 130.0 (CH), 131.5 (CH), 131.7 (CH), 134.4 (CH, d, J = 10.8 Hz), 135.4 (C, d, J = 12.4 Hz), 141.6 (C), 142.2 (C), 143.4 (C, d, J = 31.2 Hz), 157.3 (C), 162.5 (C), 162.8 ppm (C, d, J = 6.3 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 12.1 ppm; IR (film): $\tilde{\nu}$ = 2858, 1479, 1433, 1117, 1093, 996, 816, 779, 741, 727, 707, 689 cm^{-1} ;

MS (ESI+) m/z (%): 649 (100, $[M^+-Cl]$), 541 (15), 439 (40); HRMS (ESI+) m/z : calcd for $C_{40}H_{35}PRh$: 649.15259; found: 649.15237.

Rhodium complex 12: Prepared analogously as an orange-red solid (42 mg, 28 %). The product was crystallized from CH_2Cl_2/Et_2O under Ar. M.p. $> 300^\circ C$; 1H NMR (400 MHz, CD_2Cl_2): $\delta = 1.66$ (m, 2H), 1.81 (m, 1H), 1.99 (m, 2H), 2.42 (m, 2H), 2.72 (m, 1H), 2.96 (m, 1H), 3.38 (s, 3H), 3.77 (br t, $J = 7.0$ Hz, 1H), 4.26 (s, 3H), 4.98 (m, 1H), 5.10 (m, 1H), 5.64 (d, $J = 7.8$ Hz, 1H), 6.83 (dt, $J = 7.5, 1.0$ Hz, 1H), 7.19 (dt, $J = 7.4, 0.8$ Hz, 1H), 7.49 (dt, $J = 7.4, 0.96$ Hz, 1H), 7.61 (m, 4H), 7.75 (m, 3H), 10.62 ppm (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 28.8$ (CH_2), 30.9 (CH_2), 32.1 (CH_3), 32.4 (CH_2), 34.2 (CH_3), 35.0 (CH_2), 68.9 (CH), 69.0 (CH), 69.7 (CH), 60.8 (CH), 95.2 (CH, d, $J = 7.4$ Hz), 96.8 (CH, d, $J = 7.0$ Hz), 112.4 (CH, d, $J = 6.4$ Hz), 119.5 (CH), 120.5 (CH, d, $J = 2.7$ Hz), 125.9 (CH), 126.2 (CH), 127.1 (CH), 127.4 (CH), 127.9 (CH), 128.0 (C), 128.2 (CH), 128.5 (CH), 129.4 (CH), 132.9 (C), 133.4 (C), 136.9 (C), 140.6 (C), 141.0 (C), 141.8 (C), 161.5 (C), 169.1 ppm (C); IR (film): $\tilde{\nu} = 2937, 1566, 1473, 1443, 1345, 1129, 822, 781, 731$ cm^{-1} ; MS (ESI+) m/z (%): 533 (88, $[M^+-Cl]$), 425 (5), 323 (100); HRMS (ESI+) m/z : calcd for $C_{31}H_{30}N_2Rh$: 533.14586; found: 533.14553.

Rhodium complex 8: Compound **3b** (208 mg, 0.4 mmol) was added at $-78^\circ C$ to a solution of KHMDS (80 mg, 0.4 mmol) in THF (4 mL) and the resulting mixture was stirred for 8 min prior to the addition of $[Rh(cod)Cl]_2$ (99 mg, 0.2 mmol). The mixture was allowed to reach $-20^\circ C$ over the course of 4 h before $AgBF_4$ (78 mg, 0.4 mmol) was introduced, causing an immediate color change from dark brown to red-brown. The mixture was warmed to $0^\circ C$ before it was filtered through a short pad of Celite under Ar. The filtrate was evaporated and the residue purified by flash chromatography (Florisil, 1 \rightarrow 15 % MeOH in CH_2Cl_2), followed by recrystallization from CH_2Cl_2/Et_2O , which furnished complex **8** as a dark orange-red solid (133 mg, 55 %). M.p. = 188-192 $^\circ C$ (decomp.); 1H NMR (400 MHz, CD_2Cl_2): $\delta = 1.04$ (m, 1H), 1.50 (m, 2H), 1.73 (m, 1H), 2.00 (m, 2H), 2.54 (m, 2H), 3.52 (m, 1H), 3.77 (m, 1H), 4.22 (m, 1H), 4.97 (m, 1H), 6.53 (m, 2H), 7.15 (m, 5H), 7.44 (m, 6H), 7.83 (m, 6H), 8.01 (m, 1H), 8.45 (d, $J = 5.3$ Hz, 1H), 9.72 ppm (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 29.47$ (CH_2), 29.54 (CH_2), 31.4 (CH_2), 31.8 (CH_2), 81.5 (CH, d, $J = 11.4$ Hz), 88.3 (CH, d, $J = 13.1$ Hz), 96.4 (CH, d, $J = 7.1$ Hz), 100.1 (CH, d, $J = 6.7$ Hz), 120.2 (CH), 120.6 (CH), 123.5 (C), 126.8 (CH, d, $J = 17.3$ Hz), 127.9 (CH), 129.6 (CH); 129.99 (CH), 130.02 (CH), 130.6 (CH), 130.8 (C, d, $J = 10.9$ Hz), 131.6 (CH, d, $J = 13$ Hz), 133.0 (CH, d, $J = 20.7$ Hz), 133.2 (CH, d, $J = 10.9$ Hz), 135.15 (CH, d, $J = 11.0$ Hz), 135.18 (CH, d, $J = 11.1$ Hz), 140.2 (CH, d, $J = 10.0$ Hz), 141.9 (C), 142.0 (C), 153.2 (CH, d, $J = 11.9$ Hz), 158.3 (C), 160.1 ppm (C); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 6.0$ ppm; IR (film): $\tilde{\nu} = 3058, 1437, 1055, 997, 782, 734, 691$ cm^{-1} ; MS (ESI+) m/z (%): 650 (100, $[M^+-BF_4]$), 542 (15); HRMS (ESI+) m/z : calcd for $C_{39}H_{34}NPRh$: 650.14784; found: 650.14747.

Crystallographic Information

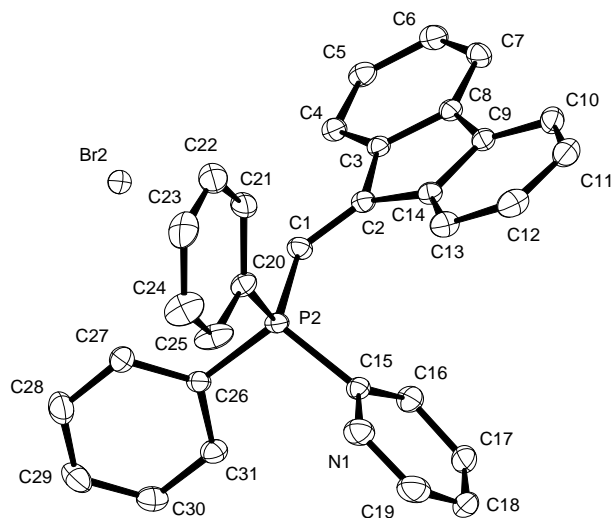


Figure S-1. Structure of compound **3b(Br)** in the solid state. Note that this compound is the bromide rather than the BF_4 salt of the cation present in compound **3b**.

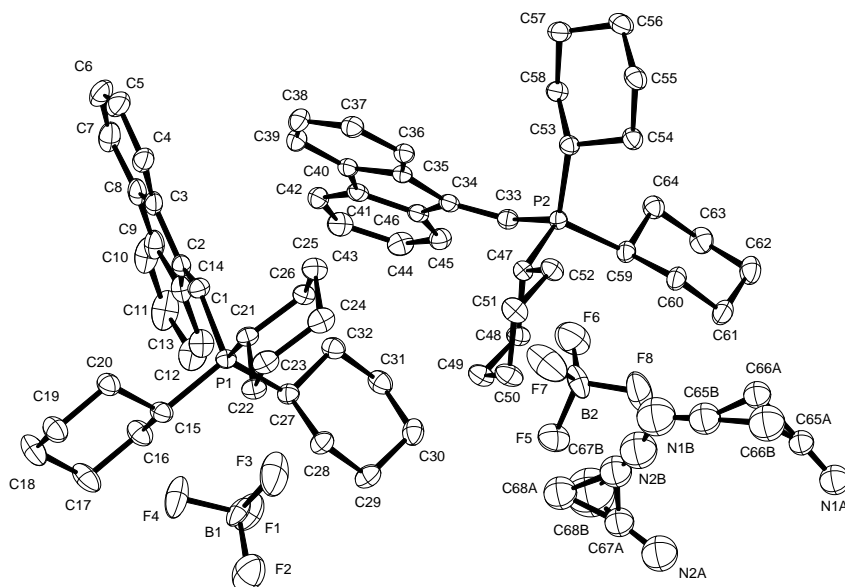


Figure S-2. Structure of compound **3c** in the solid state.

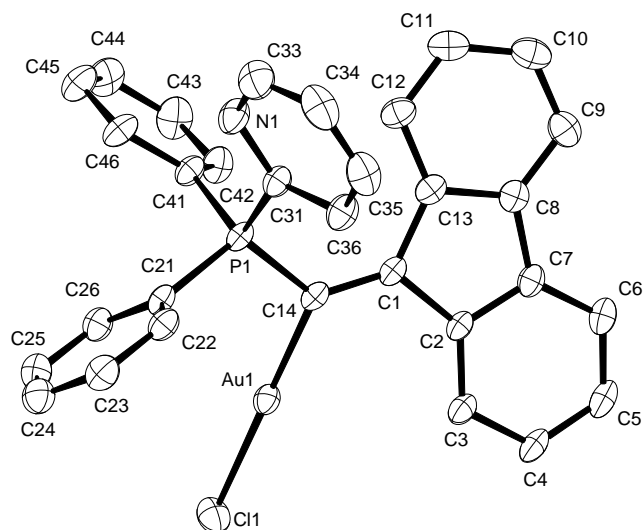


Figure 3. Structure of compound **5b** in the solid state.

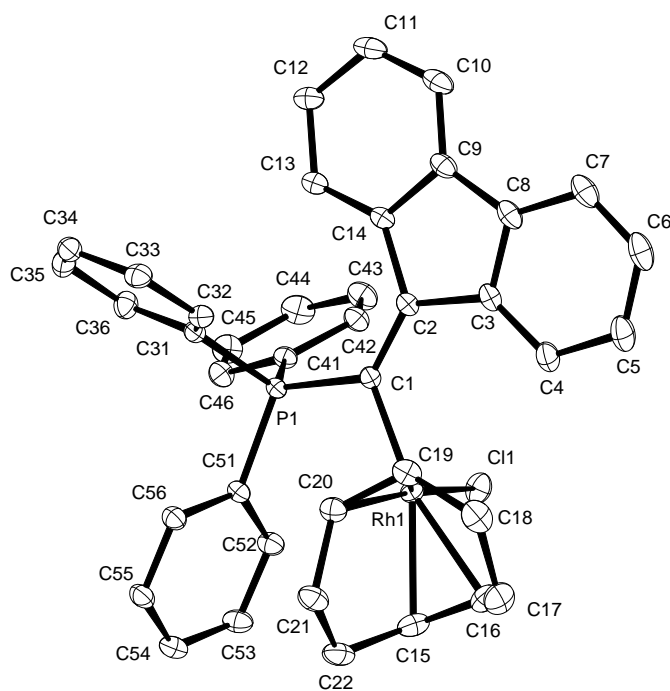


Figure S-4. Structure of complex **7** in the solid state.

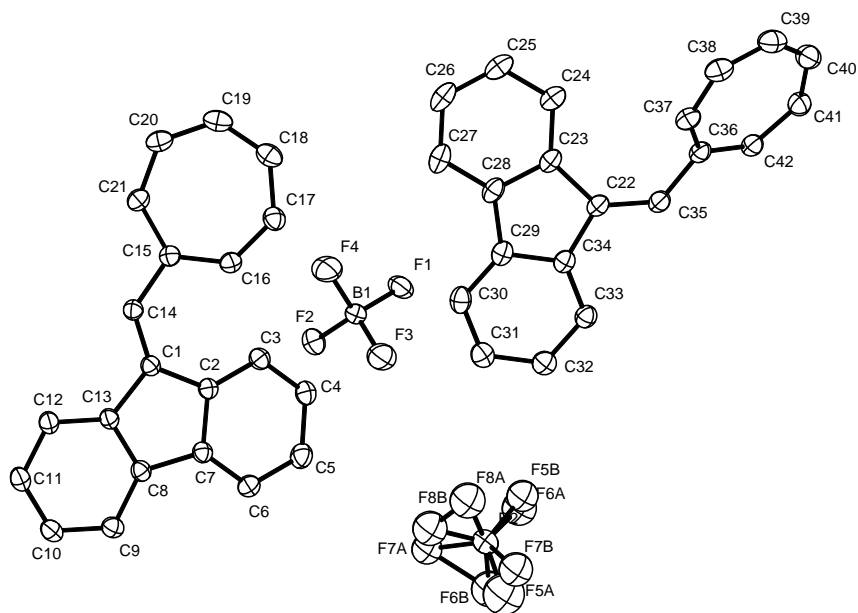
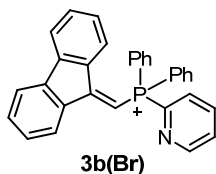


Figure S-5. Structure of compound **14** in the solid state.

For the structure of complex **5a** in the solid state, see ref.⁴

X-ray crystal structure analysis of compound 3b(Br): This compound is the bromide rather than tetrafluoroborate salt of the alkenyl phosphonium cation present in **3b**. $C_{31}H_{23}BrNP$, $M_r = 520.38 \text{ g} \cdot \text{mol}^{-1}$, yellow block, crystal size 0.06 x 0.02 x 0.02 mm, triclinic, space group $P\bar{1}$, $a = 10.1176(12) \text{ \AA}$, $b = 11.7275(14) \text{ \AA}$, $c = 12.2882(15) \text{ \AA}$, $\alpha = 66.841(2)^\circ$, $\beta = 83.877(3)^\circ$, $\gamma = 66.139(2)^\circ$, $V = 1223.6(3) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 2$, $D_{calc} = 1.412 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 1.765 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.85$, $T_{max} = 1.00$), Bruker-AXS APEX-II diffractometer, $2.34 < \theta < 36.55$, 11545 measured reflections, 11545 independent reflections, 9024 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.045 [I > 2\sigma(I)]$, $wR_2 = 0.106$, 307 parameters, H atoms riding, $S = 1.049$, residual electron density $+0.9 / -0.6 \text{ e} \text{ \AA}^{-3}$.



X-ray crystal structure analysis of compound 3c: $C_{34}H_{45}BF_4NP$, $M_r = 585.49 \text{ g} \cdot \text{mol}^{-1}$, yellow block, crystal size 0.36 x 0.28 x 0.16 mm, monoclinic, space group $P2_1/c$, $a = 10.0810(5) \text{ \AA}$, $b = 40.0775(19) \text{ \AA}$, $c = 15.9057(8) \text{ \AA}$, $\beta = 104.946(2)^\circ$, $V = 6208.8(5) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 8$, $D_{calc} = 1.253 \text{ g} \cdot \text{cm}^3$, $\lambda = 1.54178 \text{ \AA}$, $\mu(Cu-K\alpha) = 1.182 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.68$, $T_{max} = 0.84$), Bruker AXS X8 Proteum diffractometer, $3.08 < \theta < 69.54$, 140353 measured reflections, 11548 independent reflections, 10892 reflections

⁴ M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nature Chem.* **2009**, *1*, 295-301.

with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_I = 0.081$ [$I > 2\sigma(I)$], $wR_2 = 0.241$, extinction coefficient = 0.0084(13), 737 parameters, H atoms riding, $S = 1.053$, residual electron density +0.7 / -0.5 e \AA^{-3} .

X-ray crystal structure analysis of compound 5b: $C_{31}H_{22}AuClNP$, $M_r = 671.88$ g \cdot mol $^{-1}$, yellow block, crystal size 0.36 x 0.36 x 0.16 mm, triclinic, space group $P\bar{1}$, $a = 10.3130(3)$ \AA , $b = 11.8401(4)$ \AA , $c = 12.6183(4)$ \AA , $\alpha = 105.5990(10)^\circ$, $\beta = 99.0790(10)^\circ$, $\gamma = 115.5640(10)^\circ$, $V = 1270.53(7)$ \AA^3 , $T = 100$ K, $Z = 2$, $D_{calc} = 1.756$ g \cdot cm 3 , $\lambda = 0.71073$ \AA , $\mu(Mo-K\alpha) = 5.978$ mm $^{-1}$, Empirical absorption correction ($T_{min} = 0.11$, $T_{max} = 0.38$), Nonius KappaCCD diffractometer, $3.35 < \theta < 33.13$, 30573 measured reflections, 9604 independent reflections, 9167 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_I = 0.030$ [$I > 2\sigma(I)$], $wR_2 = 0.082$, 316 parameters, H atoms riding, $S = 1.051$, residual electron density +2.7 / -3.8 e \AA^{-3} .

X-ray crystal structure analysis of compound 5c: $C_{32}H_{41}AuClP$, $M_r = 689.03$ g \cdot mol $^{-1}$, yellow block, crystal size 0.50 x 0.43 x 0.29 mm, monoclinic, space group $P2_1/n$, $a = 12.10270(10)$ \AA , $b = 17.72680(10)$ \AA , $c = 12.88090(10)$ \AA , $\beta = 93.72^\circ$, $V = 2757.67(3)$ \AA^3 , $T = 100$ K, $Z = 4$, $D_{calc} = 1.660$ g \cdot cm 3 , $\lambda = 0.71073$ \AA , $\mu(Mo-K\alpha) = 5.509$ mm $^{-1}$, Empirical absorption correction ($T_{min} = 0.05$, $T_{max} = 0.21$), Nonius KappaCCD diffractometer, $1.94 < \theta < 37.87$, 113431 measured reflections, 14823 independent reflections, 14025 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_I = 0.022$ [$I > 2\sigma(I)$], $wR_2 = 0.067$, extinction coefficient = 0.0084(13), 316 parameters, H atoms riding, $S = 1.295$, residual electron density +1.2 / -3.9 e \AA^{-3} .

X-ray crystal structure analysis of compound 7: $C_{40}H_{35}ClP Rh$, $M_r = 685.01$ g \cdot mol $^{-1}$, colorless block, crystal size 0.20 x 0.20 x 0.02 mm, monoclinic, space group $P2_1/n$, $a = 10.55590(10)$ \AA , $b = 16.9602(2)$ \AA , $c = 17.7817(2)$ \AA , $\beta = 102.8960(10)^\circ$, $V = 3103.16(6)$ \AA^3 , $T = 100$ K, $Z = 4$, $D_{calc} = 1.466$ g \cdot cm 3 , $\lambda = 0.71073$ \AA , $\mu(Mo-K\alpha) = 0.717$ mm $^{-1}$, Gaussian absorption correction ($T_{min} = 0.84$, $T_{max} = 0.98$), Nonius KappaCCD diffractometer, $2.97 < \theta < 33.20$, 80257 measured reflections, 11865 independent reflections, 10746 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_I = 0.054$ [$I > 2\sigma(I)$], $wR_2 = 0.143$, 388 parameters, H atoms riding, $S = 1.048$, residual electron density +0.5 / -1.1 e \AA^{-3} .

X-ray crystal structure analysis of compound 8: $C_{41}H_{34}BF_4NO P Rh$, $M_r = 777.38$ g \cdot mol $^{-1}$, red block, crystal size 0.06 x 0.04 x 0.02 mm, monoclinic, space group $P2_1/c$, $a = 10.6705(10)$ \AA , $b = 11.2395(10)$ \AA , $c = 28.766(3)$ \AA , $\beta = 99.565(2)^\circ$, $V = 3401.9(5)$ \AA^3 , $T = 100$ K, $Z = 4$, $D_{calc} = 1.518$ g \cdot cm 3 , $\lambda = 0.71073$ \AA , $\mu(Mo-K\alpha) = 0.606$ mm $^{-1}$, Empirical absorption correction ($T_{min} = 0.92$, $T_{max} = 1.00$), Bruker-AXS APEX-II diffractometer, $1.94 < \theta < 36.61$, 126787 measured reflections, 16263 independent reflections, 14576 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against

F^2 to $R_1 = 0.033$ [$I > 2\sigma(I)$], $wR_2 = 0.095$, extinction coefficient = 0.0084(13), 450 parameters, H atoms riding, $S = 1.078$, residual electron density +0.9 / -1.3 e Å⁻³.

X-ray crystal structure analysis of compound 18: C₂₉H₁₈, $M_r = 366.43$ g · mol⁻¹, colorless block, crystal size 0.30 x 0.16 x 0.06 mm, orthorhombic, space group $P2_12_12_1$, $a = 7.2673(2)$ Å, $b = 9.2730(2)$ Å, $c = 29.2631(7)$ Å, $V = 1972.03(8)$ Å³, $T = 105$ K, $Z = 4$, $D_{calc} = 1.234$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 0.070$ mm⁻¹, Semi-empirical absorption correction ($T_{min} = 0.56$, $T_{max} = 0.99$), Nonius KappaCCD diffractometer, $3.03 < \theta < 33.13$, 50931 measured reflections, 7480 independent reflections, 5544 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.050$ [$I > 2\sigma(I)$], $wR_2 = 0.118$, absolute structure parameter = -3(10), 262 parameters, H atoms riding, $S = 1.028$, residual electron density +0.2 / -0.2 e Å⁻³.

X-ray crystal structure analysis of compound 14: C₂₁H₁₅BF₄, $M_r = 354.14$ g · mol⁻¹, red block, crystal size 0.18 x 0.12 x 0.03 mm, monoclinic, space group $P2_1/c$, $a = 13.7780(2)$ Å, $b = 7.0662(1)$ Å, $c = 33.5933(6)$ Å, $\beta = 91.723(1)^\circ$, $V = 3269.10(9)$ Å³, $T = 100$ K, $Z = 8$, $D_{calc} = 1.439$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 0.113$ mm⁻¹, Semi-empirical absorption correction ($T_{min} = 0.94$, $T_{max} = 1.00$), Nonius KappaCCD diffractometer, $1.21 < \theta < 33.17$, 75412 measured reflections, 12469 independent reflections, 8061 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.081$ [$I > 2\sigma(I)$], $wR_2 = 0.241$, extinction coefficient = 0.0084(13), 466 parameters, H atoms riding, $S = 1.036$, residual electron density +1.2 / -1.1 e Å⁻³.

CCDC 780346 (**3b**), 780345 (**3c**), 780347 (**5b**), 780350 (**5c**), 780348 (**7**), 780349 (**8**), 780344 (**14**) and 780343 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif.