

SUPPORTING INFORMATION

Metal complexes with carbene ligands stabilized by lateral enamines

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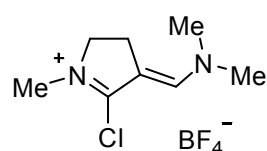
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General : All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O (Mg-anthracene), CH₂Cl₂, CHCl₃, MeCN, Et₃N, Me₂NH, MeNO₂ (CaH₂), MeOH (Mg), hexane, toluene (Na/K). IR: Nicolet FT-7199 spectrometer, wavenumbers 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, AV 400 or AV 600 spectrometer in the solvents indicated; ¹H and ¹³C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) are given in Hz and are not averaged; aromatic systems were invariably analyzed as ‘first order’ coupling pattern. 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. All commercially available compounds (Acros, Fluka, Lancaster, Aldrich) were used as received unless stated otherwise.

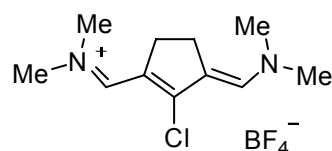
Starting Materials

The chloro vinamidinium salts **3**,¹ **6**,² **10**,³ **12**⁴ and **14**⁵ were prepared in analogy to literature procedures as described below:

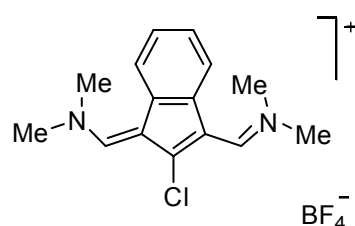
Compound 3: POCl₃ (9.13 mL, 100 mmol) was slowly added to a cooled (0 °C) mixture of N-methylpyrrolidone (4.81 mL, 50 mmol) and DMF (11.6 mL, 150 mmol) in CH₂Cl₂ (40 mL). Once the addition was complete, the mixture was stirred for 6 h at ambient temperature before it was poured into a sat. aq. solution of NaBF₄. The organic layer was separated, dried over MgSO₄ and evaporated to give compound **3** as a yellow solid (5.72 g, 44%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.43 (s, 1H), 4.04 (t, *J* = 8.8 Hz, 2H), 3.36 (t, *J* = 8.8 Hz, 2H), 3.32 (s, 3H), 3.29 (s, 3H), 3.27 ppm (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 163.5, 153.5, 101.7, 55.4, 48.7, 39.9, 36.1, 25.6 ppm; MS (ESI+): *m/z* (%): 173.0 (100).



Compound 6: POCl₃ (16.0 mL, 175 mmol) was slowly added to a cooled (0 °C) solution of DMF (19.6 mL, 253 mmol) in CH₂Cl₂ (40 mL). Once the addition was complete, the mixture was stirred for 1 h before cyclopentanone (4.4 g, 50 mmol) was introduced. The resulting mixture was stirred for 5 h at reflux temperature. For work up, the mixture was cooled to ambient temperature and poured into a solution of NaBF₄ (17.9 g, 163 mmol) in water (400 mL). The precipitates were filtered off and washed with H₂O and MeOH to afford the desired product as a red solid (6.45 g, 43%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.47 (s, 2H), 3.27 (s, 12H), 3.07 (s, 4H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 164.2, 152.6, 115.6, 49.1, 40.6, 28.5 ppm; HRMS (ESI+): *m/z*: calcd for C₁₁H₁₈N₂Cl: 213.11530; found: 213.11512.



Compound 10: A solution of 2-indanone (380 mg, 2.88 mmol) in CH₂Cl₂ (1.5 mL) was added to a solution of chloromethylene-*N,N*-dimethyl ammonium chloride (1.24 g, 9.70 mmol) in CH₂Cl₂ (4.7 mL) at 0 °C, and the resulting mixture was stirred for 3.5 h at ambient temperature. A sat. aq. solution of NaBF₄ was added and stirring continued for 30 min. The aqueous phase was extracted with CH₂Cl₂ (4 x 5 mL), the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue was recrystallized by slowly diffusing Et₂O into a solution of the compound in CH₂Cl₂ at 4 °C. Yellow crystals (750 mg, 75 %). ¹H NMR (400



¹ S. Yanagisawa, K. Oya, K. Shigeno, Jpn. Kokai Tokkyo Koho, **2006**, JP 2006162853.

² H. Hartmann, C. Heyde, I. Zug, *Synthesis* **2000**, 6, 805-808.

³ Z. Arnold, *Coll. Czech. Chem. Commun.* **1965**, 30, 2783-2792.

⁴ Y. Lin, S. A. Lang, *J. Org. Chem.* **1980**, 45, 4857-4860.

⁵ C. Heyde, I. Zug, H. Hartmann, *Eur. J. Org. Chem.* **2000**, 3273-3278.

MHz, CD₂Cl₂): δ = 8.25 (s, 2H), 7.48 (dd, J = 6.0, 3.2 Hz, 2H), 7.30 (dd, J = 6.0, 3.2 Hz, 2H), 3.65 (s, 6H), 3.59 ppm (s, 6H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 159.0 (CH), 146.7 (C), 131.8 (C), 124.3 (CH), 121.5 (CH), 111.8 (C), 49.1 (CH₃), 45.0 (CH₃) ppm; MS (ESI⁺): m/z (%): 261.1 (100).

Compound 14: A solution of oxalyl chloride (0.515 mL, 6.09 mmol) in CHCl₃ (3.0 ml) was added over the course of 30 min to a stirred solution of DMF (0.945 mL, 12.21 mmol) in CHCl₃ (3.0 mL), keeping the temperature between 15 °C and 20 °C. The mixture was stirred at 40 °C for 15 min before it was cooled to 0 °C. A solution of 4-methoxy-but-3-en-1-yne (500 mg, 6.09 mmol) in CHCl₃ (3.0 mL) was then introduced over 30 minutes at such a rate as to keep the bath temperature between 0 °C and 5 °C. After stirring at room temperature for 30 min, a solution of Me₂NH·HBF₄ (810 mg, 6.095 mmol) and Me₂NH (0.450 mL, 6.79 mmol) in MeNO₂ (4.5 mL) was added at 0 °C over 40 min and the mixture was allowed to stand at ambient temperature overnight. The resulting precipitate was filtered off, washed with CH₂Cl₂ (2 x 2 mL), dried in vacuo and recrystallized by slowly diffusing Et₂O into a solution of the crude product in MeCN. Yellow crystals (670 mg, 40 %). ¹H NMR (600 MHz, [D₆]-DMSO): δ = 8.07 (d, J = 11.5 Hz, 2H), 6.14 (d, J = 11.5 Hz, 2H), 3.35 (s, 6H), 3.10 ppm (s, 6H); ¹³C NMR (150 MHz, [D₆]-DMSO): δ = 157.6 (CH), 157.4 (C), 100.6 (CH), 46.2 (CH₃), 38.8 (CH₃) ppm; MS (ESI⁺): m/z (%): 187 (100).

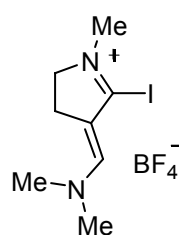
Compound 12: POCl₃ (2.40 mL, 26 mmol) was slowly added to a cooled (0 °C) solution of 3-dimethylamino-1-phenyl-prop-2-en-1-one (4.54 g, 26 mmol) in CH₂Cl₂ (25 mL). The mixture was stirred for 6 h at ambient temperature before it was poured into sat. aq. NaBF₄ at 0 °C. The organic layer was dried over MgSO₄ and evaporated, affording compound **12** as a pale brown solid (6.08 g, 82%). ¹H NMR (400 MHz, CD₃CN): δ = 8.75 (d, J = 9.2 Hz, 1H), 8.05-8.00 (m, 2H), 7.71 (app. t, J = 6.8 Hz, 1H), 7.62 (app. t, J = 7.2 Hz, 2H), 7.36 (d, J = 10.0 Hz, 1H), 3.74 (s, 3H), 3.55 ppm (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 166.8, 163.7, 135.4, 135.1, 130.1, 129.6, 114.5, 51.4, 43.4 ppm; HRMS (ESI⁺): m/z : calcd for C₁₁H₁₃NCl: 194.07310; found: 194.07288.

Compound 16: POCl₃ (804 mg, 5.24 mmol) was added to a solution of 1,9-(dimethylamino)-nona-1,3,6,8-tetraen-5-one (930 mg, 4.22 mmol)⁶ in CH₂Cl₂ (25 mL) at 0 °C. After 5 min the solution was allowed to reach ambient temperature and stirring continued for 3 h. Evaporation of all volatile materials afforded a residue that was dissolved in CH₂Cl₂ (30 mL). The solution was washed with sat.

⁶ Z. H. Krasnaya, T. S. Stytsenko, E. P. Prokofev, V. A. Petukhov, V. F. Kucherov, *Izv. Akad. Nauk, Seriya Khimicheskaya* **1976**, *3*, 595-600.

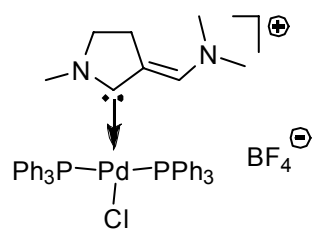
aq. NaBF₄, the aqueous phase was extracted with CH₂Cl₂ (5 x 30 mL), and the combined organic layers were dried over Na₂SO₄ and evaporated to give the product as a dark blue solid (350 mg, 25%). ¹H NMR (600 MHz, [D₆]-DMSO): δ = 7.91 (d, *J* = 11.8 Hz, 2H), 7.56 (t, *J* = 12.6 Hz, 2H), 6.39 (d, *J* = 12.6 Hz, 2H), 6.03 (t, *J* = 12.1 Hz, 2H), 3.26 (s br, 6H), 3.11 ppm (s br, 6H); ¹³C NMR (150 MHz, [D₆]-DMSO): 161.0 (CH), 150.9 (CH), 149.7 (C), 116.0 (CH), 107.1 (CH), 46.0 (CH₃), 38.3 (CH₃) ppm; IR (neat): $\tilde{\nu}$ = 3022, 2929, 1659, 1628, 1533, 1488, 1426, 1412, 1393, 1293, 1209, 1182, 1156, 1029, 987, 847, 688, 664 cm⁻¹; MS (ESI+): *m/z* (%): 239 (100); HRMS (ESI+): *m/z*: calcd for C₁₃H₂₀ClN₂: 239.1310; found: 239.1308.

Compound 18: KI (5.1 g, 30.72 mmol) was added to a suspension of **3** (800 mg, 3.07 mmol) in acetone (15 mL) and the suspension stirred in the dark for 5 days. Solid materials were then filtered off and carefully washed with CH₂Cl₂ (50 mL). The combined filtrates were washed twice with sat. aq. NaBF₄, dried and evaporated to afford **18** as a light yellow solid (1.0 g, 93%). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.37 (s, 1H), 4.01 (m, 2H), 3.42 (s, 3H), 3.26 ppm (s, 8H); ¹³C NMR (150 MHz, CD₂Cl₂): δ = 157.1 (CH), 152.7 (C), 109.3 (C), 57.0 (CH₂), 48.1 (CH₃), 41.2 (CH₃), 39.6 (CH₃), 26.6 (CH₂) ppm; IR (neat) $\tilde{\nu}$ = 2983, 2926, 2808, 1625, 1538, 1469, 1435, 1401, 1346, 1298, 1261, 1221, 1124, 1082, 1048, 951, 911, 835, 751 cm⁻¹; MS (ESI+): *m/z* (%): 265 (100); HRMS (ESI+): *m/z*: calcd for C₈H₁₄IN₂: 265.0196; found: 265.0195.



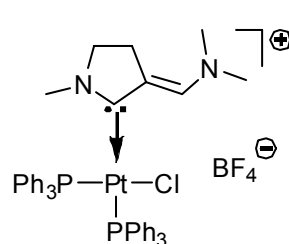
Metal Carbene Complexes

Representative procedure for the preparation of metal carbene complexes by oxidative insertion into chloro vinamidinium salts. Complex 4:



A neat mixture of the compound **3** (56.5 mg, 0.250 mmol) and Pd(PPh₃)₄ (289 mg, 0.250 mmol) was evacuated for 10 min. The flask was then flushed with Ar before toluene (12 mL) was added and the resulting suspension stirred at 100 °C for 3h. After reaching ambient temperature, the solid was filtered off and washed with pentanes (3 x 15 mL) to remove residual PPh₃. The crude product was then recrystallized by slow diffusion of diethyl ether into a solution of the material in the minimum amount of CH₂Cl₂. Yellow solid (192 mg, 96 %). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.83 (s, 1H), 7.80-7.70 (m, 12H), 7.65-7.48 (m, 18H), 3.30 (s, 3H), 2.79 (s, 6H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.31 ppm (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 212.4 (s), 153.0, 135.1 (t, *J* = 6.2 Hz), 132.5, 130.0, 129.6 (d, *J* = 10.2 Hz), 114.5, 57.1, 53.7, 41.1, 26.6 ppm; ³¹P NMR (162 MHz, CD₂Cl₂): δ = 23.1 ppm; MS (EI+): *m/z* (%): 805.2 (100), 625.5 (5), 541.5 (23); HRMS (ESI+): *m/z*: calcd for C₄₄H₄₄ClN₂P₂Pd: 803.17121; found: 803.17100; elemental analysis calcd (%) for C₄₄H₄₄BClF₄N₂P₂Pd: C 59.28, H 4.97, N 3.14; found: C 59.41, H 5.05, N 3.02.

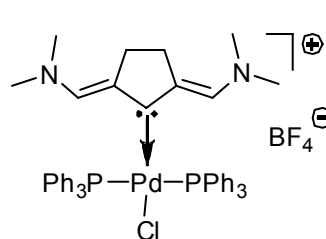
Complex 5. Prepared analogously as a yellow solid (144 mg, 96 %). ^1H NMR (400 MHz,



CD_2Cl_2): δ = 7.96 (s, 1H), 7.50-7.20 (m, 30H), 3.48-3.40 (m, 1H), 3.38 (s, 3H), 3.07 (s, 6H), 2.91-2.76 (m, 2H), 2.29-2.18 ppm (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 207.3 (C) (dd, J = 122.5, 8.4 Hz), 152.5 (CH), 135.0 (CH) (d, J = 10.2 Hz), 134.2 (CH) (d, J = 11.3 Hz), 132.5 (CH), 131.3 (CH), 129.6 (C) (d, J = 52 Hz), 128.9 (CH) (d, J = 11.6 Hz), 128.7 (CH) (d, J = 10.3 Hz), 114.1 (C), 57.9 (CH₂)

(d, J = 7.2 Hz), 43.5-41.5 (CH₃) (br s), 40.4 (CH₃), 26.1 ppm (CH₂) (d, J = 4.7 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 16.6 ($^1J(\text{Pt-P})$ = 1980, $^2J(\text{P-P})$ = 17.8 Hz), 11.8 ppm ($^1J(\text{Pt-P})$ = 3852, $^2J(\text{P-P})$ = 17.8 Hz); IR (neat) $\tilde{\nu}$ = 3055, 2940, 1636, 1533, 1481, 1434, 1400, 1335, 1298, 1228, 1091, 1046, 1035, 999, 917, 758, 742, 694 cm^{-1} ; MS (ESI⁺): m/z (%): 893 (100), 631 (80); HRMS (ESI⁺): m/z : calcd for $\text{C}_{44}\text{H}_{44}\text{ClN}_2\text{P}_2\text{Pt}$: 892.2311; found: 892.2304; elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{44}\text{BClF}_4\text{N}_2\text{P}_2\text{Pt}\cdot\text{CH}_2\text{Cl}_2$: C 50.75, H 4.35, N 2.64; found: C 51.00, H 4.53, N 2.72.

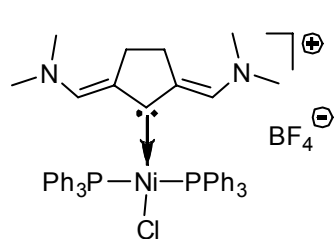
Complex 7. Prepared analogously as an orange solid (170 mg, 70%). ^1H NMR (600 MHz,



CD_2Cl_2): δ = 7.71 (br s, 2H), 7.70-7.66 (m, 12H), 7.55-7.52 (m, 6H), 7.50-7.46 (m, 12H), 2.84 (s, 12H), 1.96 ppm (s, 4H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 223.3 (C) (t, J = 5.9 Hz), 157.1 (CH), 134.7 (CH) (t, J = 6.3 Hz), 131.5 (CH), 130.2 (C) (t, J = 24.2 Hz), 128.8 (CH) (t, J = 5.3 Hz), 127.2 (C) (t, J = 2.3 Hz), 45-38 (CH₃) (very br.), 28.8 ppm (CH₂); ^{31}P NMR (162 Hz, CD_2Cl_2):

δ = 24.7 ppm; IR (neat): $\tilde{\nu}$ = 3053, 2927, 1569, 1480, 1435, 1415, 1353, 1325, 1269, 1111, 1091, 1052, 998, 925, 761, 745, 694 cm^{-1} ; MS (ESI⁺): m/z (%): 843 (40), 581 (100); HRMS (ESI⁺): m/z : calcd for $\text{C}_{47}\text{H}_{48}\text{ClN}_2\text{P}_2\text{Pd}$: 843.2026; found: 843.2028; elemental analysis calcd (%) for $\text{C}_{47}\text{H}_{48}\text{BClF}_4\text{N}_2\text{P}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$: C 56.72, H 4.96, N 2.76; found: C 56.78, H 5.11, N 2.61.

Complex 8. $[\text{Ni}(\text{cod})_2]$ (34 mg, 0.1236 mmol) was added to a solution of PPh_3 (65 mg, 0.2478

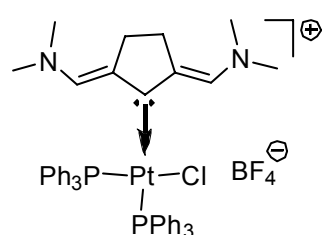


mmol) in THF (3.4 mL) and the mixture was stirred for 15 min before compound **6** (37 mg, 0.1231 mmol) was introduced. The suspension was stirred overnight, the precipitated solid was allowed to settle, the supernatant solution was siphoned off, and the solid was dried in vacuo to afford complex **8** as an orange-red solid (40 mg, 37 %). Crystals suitable for X-ray analysis were

formed by slowly diffusing Et_2O into a solution of the complex in CH_2Cl_2 . ^1H NMR (600 MHz, CD_2Cl_2): δ = 8.45 (s, 2H), 7.72 (m, 12H), 7.53 (m, 6H), 7.46 (m, 12H), 2.91 (br s, 12H), 1.82 ppm (s, 4H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 230.0 (C) (t, J = 30.8 Hz), 156.8 (CH), 134.6 (CH) (t, J = 5.3 Hz), 131.3 (CH), 130.5 (C) (t, J = 22.8 Hz), 129.7 (C), 128.6 (CH) (t, J = 4.9 Hz), 45-41 (CH₃) (very br.), 29.1 ppm (CH₂); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 23.2 ppm; IR (neat): $\tilde{\nu}$ = 3053, 2921, 1567, 1508, 1463, 1415, 1376, 1349, 1318, 1268,

1089, 1046, 1035, 952, 922, 761, 745, 696 cm^{-1} ; MS (ESI+): m/z (%): 795 (10), 533 (100), 271 (30); HRMS (ESI+): m/z : calcd for $\text{C}_{47}\text{H}_{48}\text{ClN}_2\text{NiP}_2$: 795.2329; found: 795.2328.

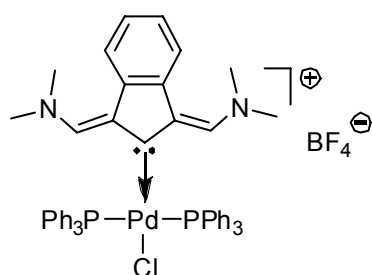
Complex 9. Prepared analogously as an orange solid (80 mg, 59 %). ^1H NMR (600 MHz,



CD_2Cl_2): δ = 8.21 (s, 2H), 7.46-7.18 (m, 30H), 3.18 (s, 12H), 2.70 (m, 2H), 2.10 ppm (m, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 219.1 (C) (dd, J = 111.0, 8.0 Hz), 157.4 (CH), 134.9 (CH) (d, J = 9.8 Hz), 134.4 (CH) (d, J = 10.5 Hz), 132.0 (CH), 130.9 (CH), 130.4 (C) (d, J = 48.5 Hz), 129.2 (C) (br d, J = 63 Hz), 128.5 (CH) (d, J = 7.5 Hz), 128.4 (d, J = 7.5 Hz), 127.99 (C), 127.96

(C), 48-41 (CH₃) (very br.), 29.83 (CH₂), 29.78 ppm (CH₂); ^{31}P NMR (122 MHz, CD_2Cl_2): δ = 20.5 ($^1J(\text{Pt-P})$ = 1774, $^2J(\text{P-P})$ = 17.1 Hz), 15.6 ppm ($^1J(\text{Pt-P})$ = 4058, $^2J(\text{P-P})$ = 17.1 Hz); IR (neat) $\tilde{\nu}$ = 3054, 2928, 1637, 1558, 1480, 1434, 1415, 1348, 1315, 1259, 1214, 1088, 1048, 999, 924, 754, 741, 693 cm^{-1} ; MS (ESI+): m/z (%): 933 (100), 671 (90); HRMS (ESI+): m/z : calcd for $\text{C}_{47}\text{H}_{48}\text{ClN}_2\text{P}_2\text{Pt}$: 932.2619; found: 932.2626; elemental analysis calcd (%) for $\text{C}_{47}\text{H}_{48}\text{BClF}_4\text{N}_2\text{P}_2\text{Pt}\cdot\text{CH}_2\text{Cl}_2$: C 52.17, H 4.56; found: C 52.21, H 4.41.

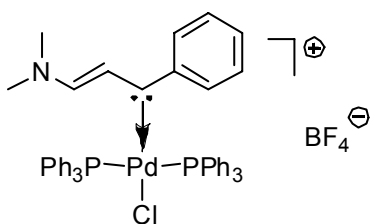
Complex 11. Prepared analogously as a yellow-green solid (125 mg, 90 %). ^1H NMR (400



MHz, CD_2Cl_2): δ = 8.03 (s, 2H), 7.50-7.38 (m, 18H), 7.31-7.25 (m, 12H), 7.00-6.95 (m, 2H), 6.89-6.84 (m, 2H), 3.01 ppm (br s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 202.4 (C) (s), 161.4 (CH), 136.9 (C), 134.4 (CH) (t, J = 6.3 Hz), 131.4 (CH), 129.8 (C) (t, J = 24.3 Hz), 128.8 (CH) (t, J = 5.2 Hz), 124.0 (C), 122.7 (CH), 120.9 (CH), 47.5 (CH₃) (br s), 43.5 ppm (CH₃) (br s); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 23.6 ppm; IR

(neat): $\tilde{\nu}$ = 3058, 2967, 2930, 1592, 1480, 1435, 1418, 1373, 1322, 1255, 1156, 1115, 1090, 1048, 1033, 998, 923, 759, 740, 693 cm^{-1} ; MS (ESI+): m/z (%): 891 (100), 629 (40); HRMS (ESI+): m/z : calcd for $\text{C}_{51}\text{H}_{48}\text{ClN}_2\text{P}_2\text{Pd}$: 891.2027; found: 891.2023; elemental analysis calcd (%) for $\text{C}_{51}\text{H}_{48}\text{BClF}_4\text{N}_2\text{P}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$: C 58.67, H 4.73, N 2.63; found: C 59.27, H 5.02, N 2.51.

Complex 13. Prepared analogously as a yellow solid (113 mg, 81 %). ^1H NMR (400 MHz,

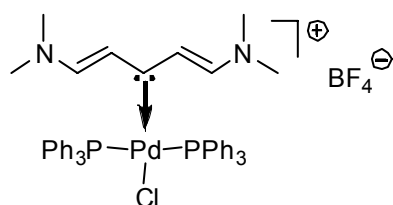


CD_2Cl_2): δ = 8.38 (d, J = 10.8 Hz, 1H), 7.50-7.41 (m, 12H), 7.40-7.48 (m, 8H), 7.32-7.28 (m, 12H), 7.14 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 8.4 Hz, 2H), 6.02 (d, J = 10.8 Hz, 1H), 3.17 (s, 3H), 2.90 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 186.1 (s), 161.4, 143.5, 135.3 (t, J = 6.0 Hz), 132.8, 132.0, 130.8, 130.2, 130.0 (d, J = 2.4 Hz), 129.3, 120.8, 49.4, 41.3 ppm; ^{31}P NMR

(162 MHz, CD_2Cl_2): δ = 23.8 ppm; MS (ESI+): m/z (%): 824.2 (58), 564 (100). HRMS (ESI+): m/z : calcd for $\text{C}_{47}\text{H}_{43}\text{ClN}_2\text{Pd}$: 824.16039; found: 824.16076; elemental analysis

calcd (%) for $C_{47}H_{43}BClF_4N_2P_2Pd \cdot CH_2Cl_2$: C 57.80, H 4.53, N 1.40; found: 57.46, H 4.76, N 1.21.

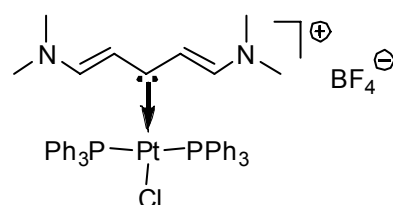
Complex 15a. Prepared analogously as a yellow-green solid (193 mg, 98 %). 1H NMR (600



MHz, CD_2Cl_2): δ = 7.81 (d, J = 12.0 Hz, 2H), 7.67 (m, 12H), 7.52 (m, 6H), 7.44 (m, 12H), 4.80 (d, J = 12.0 Hz, 2H), 2.89 (s, 6H), 2.50 ppm (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 215.7 (C) (s), 162.5 (CH), 134.8 (CH) (t, J = 6.2 Hz), 131.5 (CH), 129.8 (C) (t, J = 24.0 Hz), 128.7 (CH) (t, J = 5.2 Hz), 113.2 (CH), 46.1 (CH₃), 38.0 (CH₃) ppm; ^{31}P NMR (162

MHz, CD_2Cl_2): δ = 24.5 ppm; IR (neat): $\tilde{\nu}$ = 3057, 2931, 1636, 1570, 1492, 1409, 1368, 1235, 1202, 1090, 1050, 1037, 997, 866, 755, 744, 707, 693 cm^{-1} ; MS (ESI⁺): m/z (%): 817 (30), 557 (100); HRMS (ESI⁺): m/z : calcd for $C_{45}H_{46}ClN_2P_2Pd$: 817.1869; found: 817.1868.

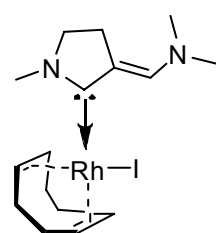
Compound 15b: Obtained analogously as yellow crystals (130 mg, 95 %). 1H NMR (600



MHz, CD_2Cl_2): δ = 7.92 (d, J = 12.0 Hz, 2H), 7.66 (m, 12H), 7.52 (m, 6H), 7.45 (m, 12H), 4.97 (d, J = 12.0 Hz, 2H), 2.85 (s, 6H), 2.46 ppm (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 198.7 (C) (t, J = 7.3 Hz), 162.5 (CH), 134.8 (CH) (t, J = 5.9 Hz), 131.6 (CH), 128.9 (C) (t, J = 29.0 Hz), 128.6 (CH) (t, J = 5.3 Hz), 114.1 (CH), 46.0 (CH₃), 38.0 ppm (CH₃); ^{31}P

NMR (122 MHz, CD_2Cl_2): δ = 22.0 ppm ($^1J(Pt-P)$ = 2834 Hz); IR (neat) $\tilde{\nu}$ = 3053, 2903, 2800, 1635, 1564, 1482, 1435, 1412, 1361, 1236, 1188, 1093, 1047, 998, 867, 742, 692 cm^{-1} ; MS (ESI⁺): m/z (%): 907 (90), 645 (100); HRMS (ESI⁺): m/z : calcd for $C_{45}H_{46}ClN_2P_2Pt$: 906.2471; found: 906.2482; elemental analysis calcd (%) for $C_{45}H_{46}BClF_4N_2P_2Pt \cdot CH_2Cl_2$: C 51.20, H 4.48, N 2.60; found: C 52.20, H 4.47, N 2.67.

Complex 19: Phenylmagnesium bromide (1.29 M in THF, 0.210 mL, 0.271 mmol) was added

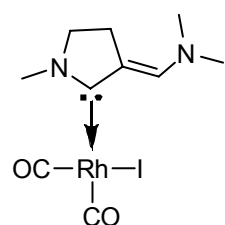


to a suspension of **18** (92 mg, 0.261 mmol) in CH_2Cl_2 (0.7 mL) and Et_2O (1.4 mL). The resulting clear yellow solution was stirred for 15 min before solid $[Rh(cod)Cl]_2$ (64.0 mg, 0.130 mmol) was introduced. Stirring was continued overnight, the solvent was evaporated and the residue purified by rapidly passing it through a column of Florisil, using $CH_2Cl_2/MeOH$ (98:2) as the eluent, to give complex **19** as a yellow solid (82 mg, 66 %), which

can be recrystallized from CH_2Cl_2/Et_2O . 1H NMR (400 MHz, CD_2Cl_2): δ = 8.00 (t, J = 1.6 Hz, 1H), 4.99 (m, 2H), 3.61 (s, 3H), 3.60-3.56 (m, 2H), 3.41 (m, 2H), 3.07 (s, 6H), 3.03-2.93 (m, 1H), 2.90-2.79 (m, 1H), 2.36-2.16 (m, 4H), 2.02-1.94 (m, 1H), 1.91-1.82 (m, 1H), 1.82-1.71 ppm (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 237.4 (C) (d, J = 39.8 Hz), 153.8 (CH), 117.4 (C), 96.3 (CH) (d, J = 6.1 Hz), 96.0 (CH) (d, J = 6.1 Hz), 73.7 (CH) (d, J = 14.5 Hz), 71.1 (CH) (d, J = 14.5 Hz), 58.5 (CH₂), 42.2 (CH₃), 41.5 (CH₃), 33.1 (CH₂), 32.1 (CH₂), 30.1 (CH₂), 29.3 (CH₂), 26.3 ppm (CH₂); IR (neat) $\tilde{\nu}$ = 2926, 2908, 2864, 2825, 1637, 1514, 1459,

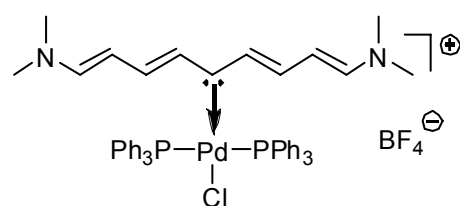
1427, 1386, 1317, 1293, 1254, 1227, 1185, 1107, 1073, 1050, 994, 912, 859, 800, 765 cm^{-1} ; MS (EI): m/z (%): 476 (85) [M^+], 368 (51), 366 (51), 349 (100), 239 (39), 197 (21), 139 (92), 137 (62); HRMS (EI): m/z : calcd for $\text{C}_{16}\text{H}_{26}\text{IN}_2\text{Rh}$: 476.0189; found: 476.0188; elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{26}\text{IN}_2\text{Rh}$: C 40.36, H 5.50, N 5.88; found: C 39.98, H 5.64, N 5.63.

Complex 20. CO was bubbled during 30 min through a solution of complex **19** (10.4 mg, 0.0218 mmol) in CH_2Cl_2 . Evaporation of the volatiles afforded the desired



compound as a red-brown solid (9.2 mg, quant.) ^1H NMR (600 MHz, CD_2Cl_2): δ = 7.55 (s, 1H), 3.80-3.69 (m, 2H), 3.36 (s, 3H), 3.09-3.05 (m, 2H), 3.06 ppm (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 221.0 (C) (d, J = 32.9 Hz), 189.4 (C) (d, J = 52.8 Hz), 183.6 (C) (d, J = 80.5 Hz), 154.1 (CH), 118.5 (C) (d, J = 2.1 Hz), 58.8 (CH_2) (d, J = 1.4 Hz), 42.7-42.0 (CH_3) (br), 42.0 (CH_3) (d, J = 1.4 Hz), 26.6 ppm (CH_2); IR (neat) $\tilde{\nu}$ = 2916, 2055, 1981, 1632, 1519, 1437, 1397, 1326, 1294, 1259, 1230, 1115, 1080, 1018, 912, 798, 761 cm^{-1} ; MS (EI): m/z (%): 396 (89), 368 (100), 297 (23), 239 (62), 197 (45), 137 (94), 94 (21), 42 (18), 28 (82); HRMS (ESI+): m/z : calcd for $\text{C}_{10}\text{H}_{14}\text{IN}_2\text{O}_2\text{RhNa}$: 446.9047; found: 446.9048.

Complex 17. A mixture of compound **16** (48.0 mg, 0.147 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (189 mg,

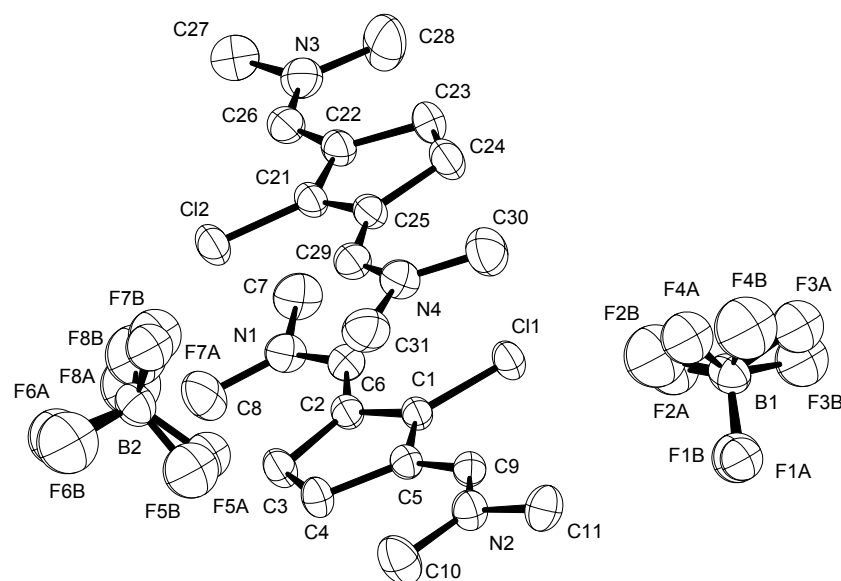


0.164 mmol) was evacuated for 5 min. The flask was then filled with Ar, toluene (6 mL) was added and the suspension stirred at ambient temperature for 30 h. The solid material was allowed to settle and the supernatant mother liquor was removed via canula. The residue was then triturated with toluene and dried in vacuo to afford the desired complex as an iridescent blue solid (72 mg, 51%). ^1H NMR (600 MHz, CD_2Cl_2): δ = 7.72-7.69 (m, 2H), 7.68-7.64 (m, 12H), 7.50-7.46 (m, 6H), 7.43-7.39 (m, 12H), 6.69 (d, J = 11.9 Hz, 2H), 5.32 (m, 2H), 5.15 (t, J = 12.2 Hz, 2H), 3.30-3.02 (br s, 6H), 3.02-2.80 ppm (br s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 213.5 (C) (t, J = 4 Hz), 160.8 (CH), 157.0 (CH), 135.0 (CH) (t, J = 6.3 Hz), 131.5 (CH), 131.1 (CH), 130.5 (C) (t, J = 23.4 Hz), 128.4 (CH) (t, J = 5.1 Hz), 104.5 (CH), 46.2 (CH_3) (br), 38.0 ppm (CH_3) (br); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 24.8 ppm; IR (neat): $\tilde{\nu}$ = 3054, 2921, 1614, 1573, 1516, 1470, 1401, 1371, 1279, 1175, 1141, 1024, 969, 842, 744, 691 cm^{-1} ; MS (ESI+): m/z (%): 871.3 (30), 609 (100); HRMS (ESI+): m/z : calcd for $\text{C}_{49}\text{H}_{50}\text{ClIN}_2\text{P}_2\text{Pd}$: 869.2183; found: 869.2178; elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{50}\text{BClIN}_2\text{F}_4\text{P}_2\text{Pd}\cdot\text{CH}_2\text{Cl}_2$: C 57.61, H 5.03, N 2.69; found: C 58.22, H 5.72, N 2.71.

Supporting Crystallographic Information

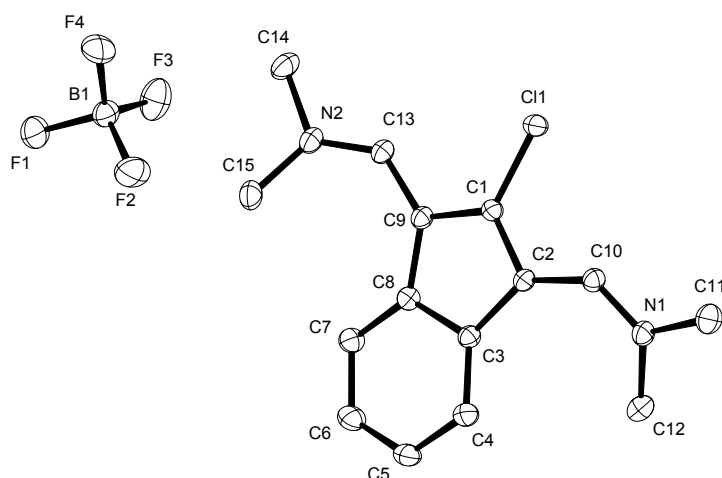
Chloro Vinamidinium Salts

Crystal structure X-ray analysis of compound 6.



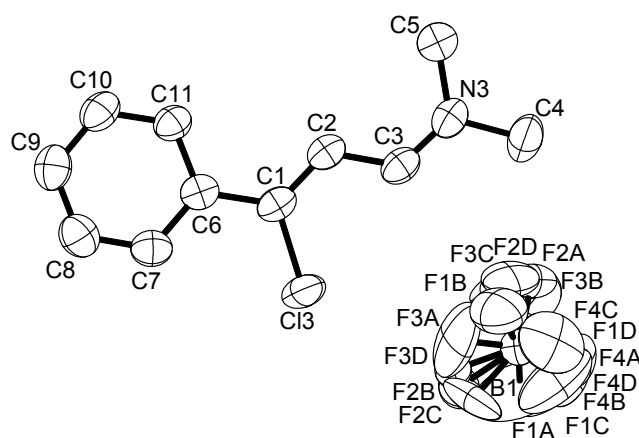
Chemical formula $[\text{C}_{11} \text{H}_{18} \text{Cl} \text{N}_2]^+ [\text{B} \text{F}_4]^-$, $F_w = 300.53 \text{ g mol}^{-1}$, red prism from acetonitrile/diethylether, crystal size $0.05 \times 0.05 \times 0.02 \text{ mm}^3$, crystal system *triclinic*, space group $P\bar{1}$, $a = 7.6530(7)$, $b = 12.1577(11)$, $c = 16.2528(14) \text{ \AA}$, $\alpha = 106.620(2)$, $\beta = 91.767(2)$, $\gamma = 102.890(2)^\circ$, $V = 1405.2(2) \text{ \AA}^3$, $T = 100 \text{ K}$, $\rho_c = 1.421 \text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.304 \text{ mm}^{-1}$, empirical absorption correction ($T_{\min} = 0.91$, $T_{\max} = 1.00$), $1.80 < \theta < 30.70^\circ$, 40284 reflections collected, 8636 unique reflections ($R_{\text{int}} = 0.0383$), 6051 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The two independent tetrafluoroborate anions are rotationally disordered. Fluorine atoms were split and refined with isotropic atomic displacement parameters. $R_1 = 0.086 [I > 2\sigma(I)]$, $wR_2 = 0.286$ (all data), 343 parameters, $S = 1.019$, residual electron density $+1.3 / -1.0 \text{ e \AA}^{-3}$ (in the vicinity of F4A and F6A, respectively).

Crystal structure X-ray analysis of compound 10.



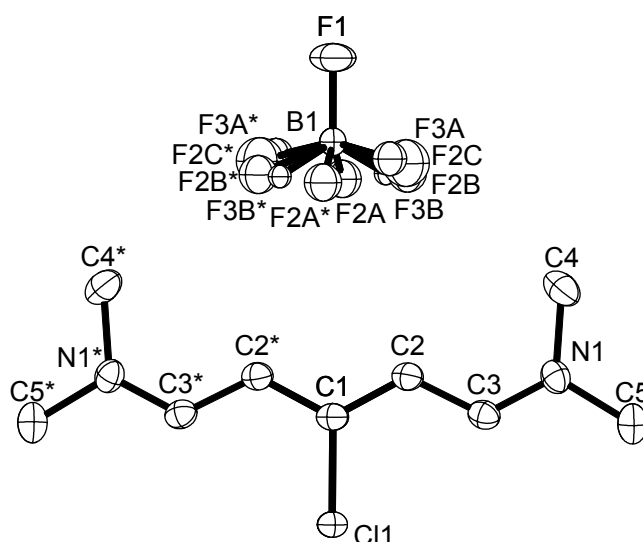
Chemical formula [C₁₅ H₁₈ Cl N₂]⁺ [B F₄]⁻, $F_w = 348.57 \text{ g mol}^{-1}$, yellow block from dichloromethane/diethylether, crystal size $0.32 \times 0.31 \times 0.29 \text{ mm}^3$, crystal system *monoclinic*, space group *Cc*, $a = 12.1625(5)$, $b = 17.6971(7)$, $c = 7.3078(3) \text{ \AA}$, $\beta = 96.479(2)^\circ$, $V = 1562.89(11) \text{ \AA}^3$, $T = 100 \text{ K}$, $\rho_c = 1.481 \text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.285 \text{ mm}^{-1}$, Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, empirical absorption correction ($T_{\min} = 0.69$, $T_{\max} = 0.87$), $3.31 < \theta < 33.90$, 23107 reflections collected, 5992 unique reflections ($R_{\text{int}} = 0.0288$), 5742 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. $R_1 = 0.034$ [$I > 2\sigma(I)$], $wR_2 = 0.093$ (all data), 212 parameters, $S = 1.165$, absolute structure parameter = $0.03(3)$, residual electron density $+0.8 / -0.9 \text{ e \AA}^{-3}$.

Crystal structure X-ray analysis of compound 12.



Chemical formula $[\text{C}_{11} \text{H}_{13} \text{Cl} \text{N}]^+ [\text{B} \text{F}_4]^-$, $F_w = 281.48 \text{ g mol}^{-1}$, pale-yellow plate from acetonitrile/diethylether, crystal size $0.11 \times 0.15 \times 0.45 \text{ mm}^3$, crystal system *monoclinic*, space group $P2_1/c$, $a = 6.8239(4)$, $b = 10.3513(5)$, $c = 18.4709(9) \text{ \AA}$, $\beta = 98.289(2)^\circ$, $V = 1291.1(1) \text{ \AA}^3$, $T = 200 \text{ K}$, $Z = 4$, $\rho_c = 1.421 \text{ Mg m}^{-3}$, $\lambda = 1.54178 \text{ \AA}$, $\mu = 2.926 \text{ mm}^{-1}$, Bruker-AXS ProteumX8 diffractometer, Gaussian absorption correction ($T_{\min} = 0.36356$, $T_{\max} = 0.75043$), $4.84 < \theta < 69.18^\circ$, 28914 reflections collected, 2381 unique reflections ($R_{\text{int}} = 0.0549$), 2059 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The tetrafluoroborate anion is badly rotationally disordered. Each fluorine atom was modelled over four positions. H atoms riding. $R_1 = 0.045 [I > 2\sigma(I)]$, $wR_2 = 0.127$ (all data), 273 parameters, $S = 1.062$, residual electron density $+0.16 / -0.26 \text{ e \AA}^{-3}$.

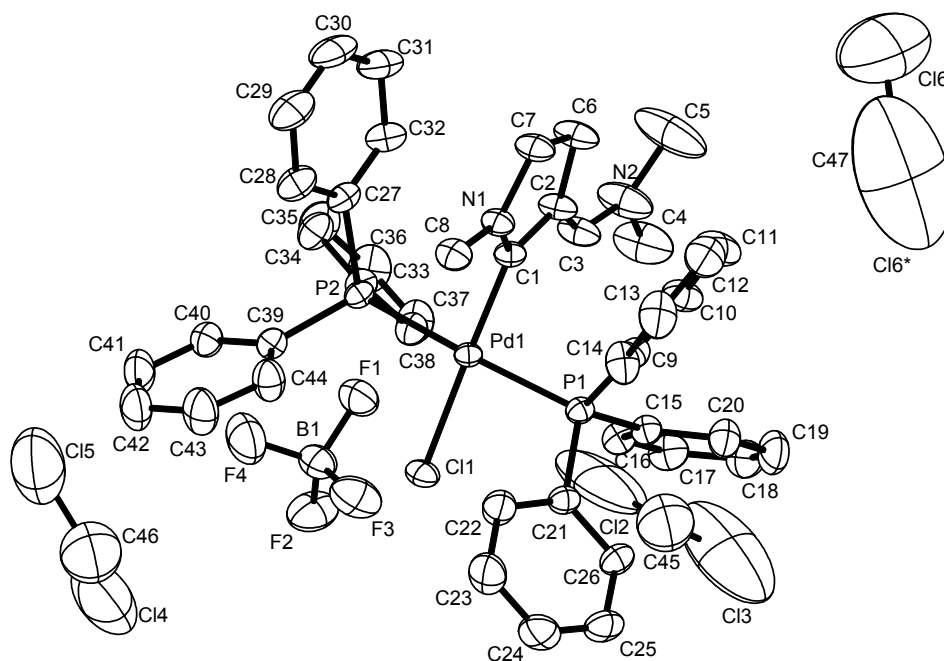
Crystal structure X-ray analysis of compound 14.



Chemical formula $[\text{C}_9 \text{H}_{16} \text{Cl} \text{N}_2]^+ [\text{B} \text{F}_4]^-$, $F_w = 274.50 \text{ g mol}^{-1}$, yellow block from acetonitrile/diethylether, crystal size $0.09 \times 0.10 \times 0.21 \text{ mm}^3$, crystal system *monoclinic*, space group $C2/c$, $a = 10.2205(8)$, $b = 12.2695(9)$, $c = 9.9747(7) \text{ \AA}$, $\beta = 97.135(4)^\circ$, $V = 1241.2(2) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $\rho_c = 1.469 \text{ Mg m}^{-3}$, $\lambda = 1.54178 \text{ \AA}$, $\mu = 3.042 \text{ mm}^{-1}$, Bruker-AXS Proteum X8 diffractometer, empirical absorption correction ($T_{\min} = 0.48$, $T_{\max} = 0.79$), $5.66 < \theta < 66.29^\circ$, 17533 reflections collected, 1080 unique reflections ($R_{\text{int}} = 0.0359$), 1042 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The tetrafluoroborate anion is rotationally disordered about one B-F bond. The disordered fluorine atoms were refined with isotropic atomic displacement parameters. $R_1 = 0.033 [I > 2\sigma(I)]$, $wR_2 = 0.084$ (all data), 92 parameters, $S = 1.059$, residual electron density $+0.32 / -0.22 \text{ e \AA}^{-3}$.

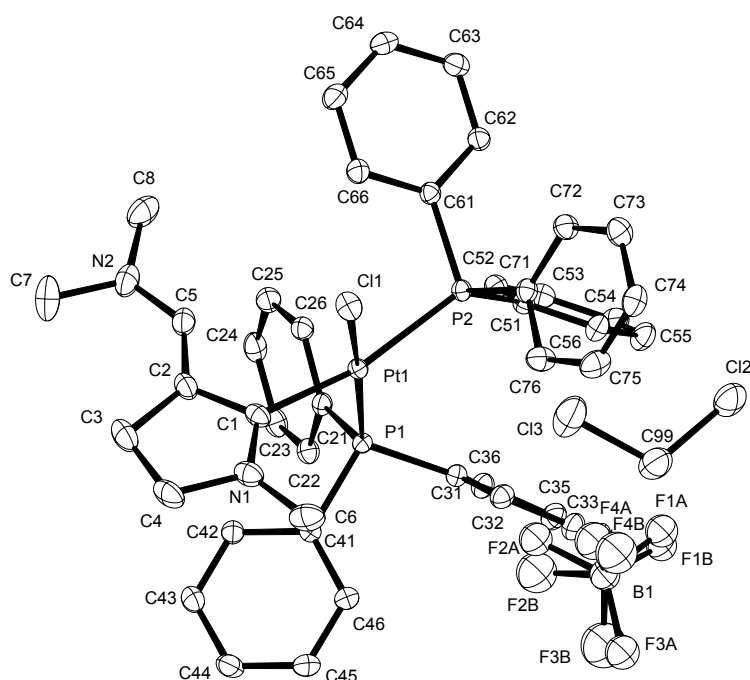
Metal Carbene Complexes

Crystal structure X-ray analysis of complex 4.



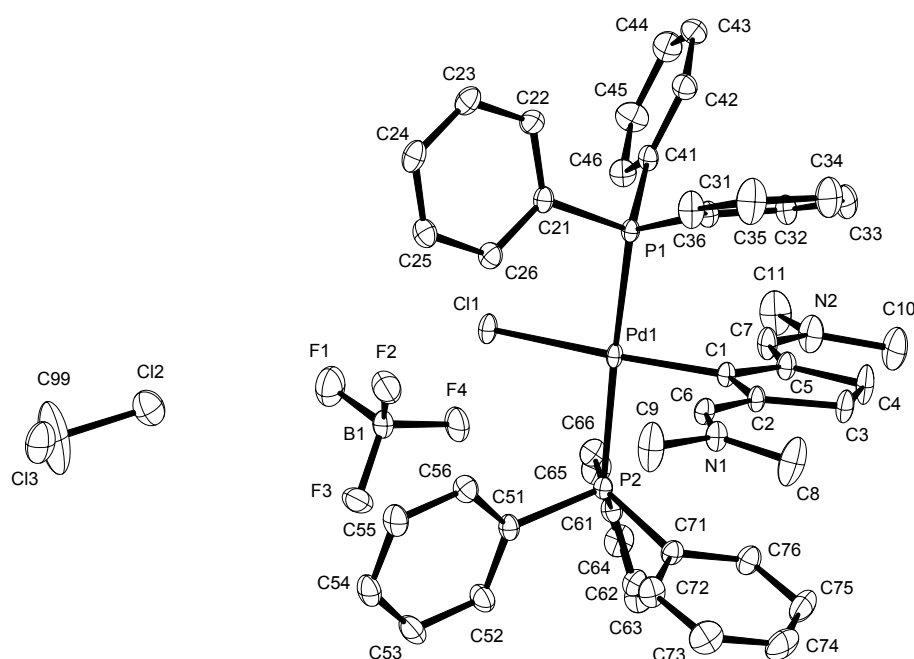
Chemical formula $2[\text{C}_{44}\text{H}_{44}\text{Cl}\text{N}_2\text{P}_2\text{Pd}]^+ 2[\text{B}\text{F}_4]^- 5[\text{C}\text{H}_2\text{Cl}_2]$, $F_w = 2207.45\text{ g mol}^{-1}$, pale-yellow prism from dichloromethane/diethylether, crystal size $0.050 \times 0.050 \times 0.065\text{ mm}^3$, crystal system *monoclinic*, space group *C2/c*, $a = 32.7088(4)$, $b = 16.8288(2)$, $c = 23.4760(3)\text{ \AA}$, $\beta = 125.390(1)^\circ$, $V = 10534.7(2)\text{ \AA}^3$, $T = 160\text{ K}$, $Z = 4$, $\rho_c = 1.392\text{ Mg m}^{-3}$, $\lambda = 0.71073\text{ \AA}$, $\mu = 0.764\text{ mm}^{-1}$, Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, Gaussian absorption correction ($T_{\min} = 0.76729$, $T_{\max} = 0.87787$), $6.81 < \theta < 33.19^\circ$, 115104 reflections collected, 19883 unique reflections ($R_{\text{int}} = 0.0393$), 16131 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. There are voids of 172 \AA^3 in the solvent region of the structure, but little or no residual electron density in this area, indicating loss of dichloromethane from the crystal lattice. The methylene C atoms in the three solute dichloromethane were refined using isotropic atomic displacement parameters, in order to better locate the true atom positions. H atoms riding. $R_1 = 0.070 [I > 2\sigma(I)]$, $wR_2 = 0.220$ (all data), 554 parameters, $S = 1.038$, residual electron density $+2.3 / -1.9\text{ e \AA}^{-3}$ (both in the vicinity of Cl2).

Crystal structure X-ray analysis of complex 5.



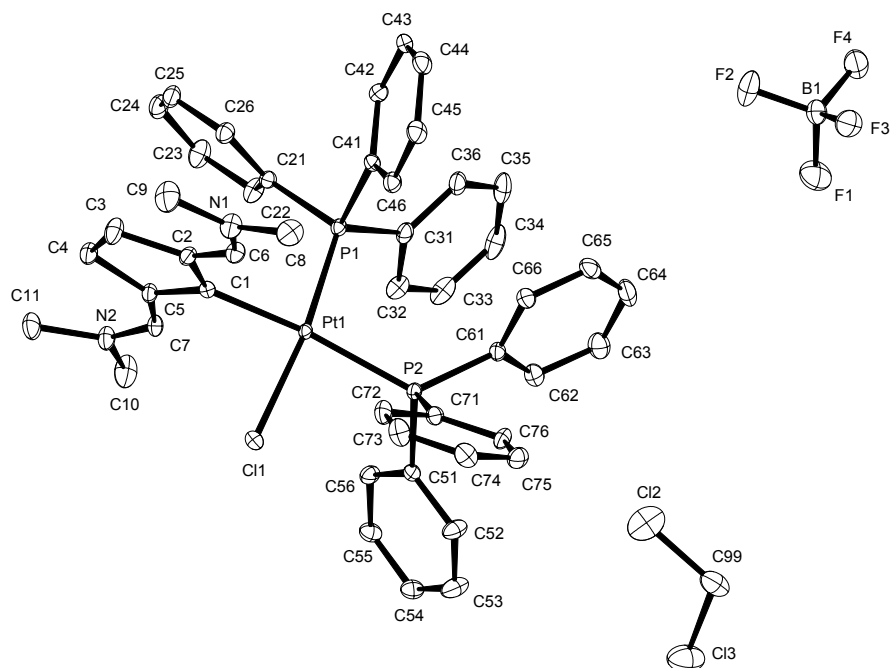
Chemical formula $[\text{C}_{44}\text{H}_{44}\text{Cl}\text{N}_2\text{P}_2\text{Pt}]^+ [\text{B}\text{F}_4]^- [\text{CH}_2\text{Cl}_2]$, $F_w = 1065.03\text{ g mol}^{-1}$, colourless block from dichloromethane/diethylether, crystal size $0.15 \times 0.15 \times 0.08\text{ mm}^3$, crystal system *monoclinic*, space group $P2_1/c$, $a = 15.5910(1)$, $b = 15.9173(1)$, $c = 17.8073(2)\text{ \AA}$, $\beta = 99.450(1)^\circ$, $V = 4359.26(6)\text{ \AA}^3$, $T = 100\text{ K}$, $\rho_c = 1.623\text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073\text{ \AA}$, $\mu = 3.528\text{ mm}^{-1}$, Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, empirical absorption correction ($T_{\min} = 0.74$, $T_{\max} = 0.88$), $2.94 < \theta < 33.31^\circ$, 105582 reflections collected, 16693 unique reflections ($R_{\text{int}} = 0.039$), 14813 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The tetrafluoroborate anion is rotationally disordered. The disorder was modelled by splitting the fluorine atoms. Disordered atom components were refined using isotropic atomic displacement parameters $R_1 = 0.031$ [$I > 2\sigma(I)$], $wR_2 = 0.081$ (all data), 523 parameters, $S = 1.047$, residual electron density $+1.6 / -2.8\text{ e \AA}^{-3}$ (in the vicinity of F3B and Pt1, respectively).

Crystal structure X-ray analysis of complex 7.



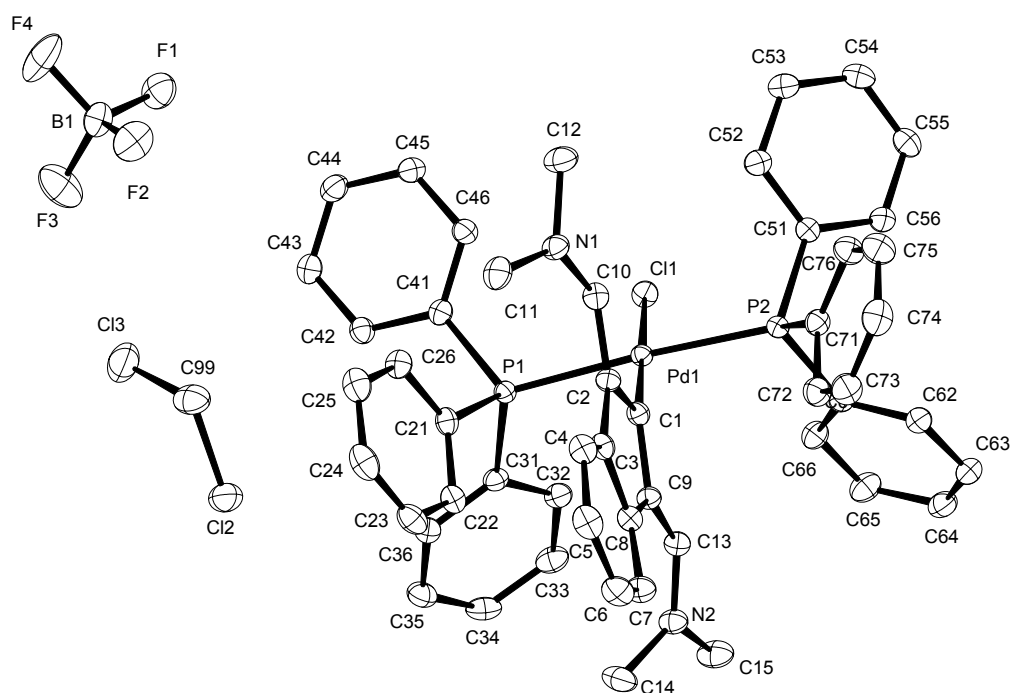
Chemical formula $[\text{C}_{47} \text{H}_{46} \text{Cl} \text{N}_2 \text{P}_2 \text{Pd}]^+ [\text{B} \text{F}_4]^- [\text{C} \text{H}_2 \text{Cl}_2]$, $F_w = 1016.40 \text{ g mol}^{-1}$, orange prism from dichloromethane/diethylether, crystal size $0.050 \times 0.050 \times 0.050 \text{ mm}^3$, crystal system *monoclinic*, space group $P2_1/c$, $a = 15.114(3)$, $b = 19.533(3)$, $c = 21.575(3) \text{ \AA}$, $\beta = 134.308(8)^\circ$, $V = 4557.9(13) \text{ \AA}^3$, $T = 100 \text{ K}$, $\rho_c = 1.478 \text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.706 \text{ mm}^{-1}$, empirical absorption correction ($T_{\min} = 0.62$, $T_{\max} = 0.75$), Bruker-AXS Kappa Mach3 Apex-II diffractometer, $1.89 < \theta < 37.12^\circ$, 251840 reflections collected, 23291 unique reflections ($R_{\text{int}} = 0.0622$), 18801 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The crystal was non-merohedrally twinned $[-1 \ 0 \ 0 \ 0 \ -1 \ 0 \ 0 \ -1 \ 2]$. The methylene group of the solute dichloromethane is disordered over two positions with an occupancy of 0.6:0.4. Disordered atoms were refined with isotropic atomic displacement parameters. The standard uncertainties of the Pd atom parameters are probably underestimated, which results in high standard uncertainties in the differences of the components of the anisotropic displacement parameters along the Pd1-P1 and Pd1-P2 bonds (Hirshfeld test). The relatively large anisotropy in the atomic displacement parameters for C8, C9, C10 and C11 indicate that either the associated N atoms are slightly pyramidal or there is some flexibility in these parts of the molecule. $R_1 = 0.045 [I > 2\sigma(I)]$, $wR_2 = 0.125$ (all data), 554 parameters, $S = 1.072$, residual electron density $+2.8 / -2.3 \text{ e \AA}^{-3}$ (in the vicinity of Pd1).

Crystal structure X-ray analysis of complex 9.



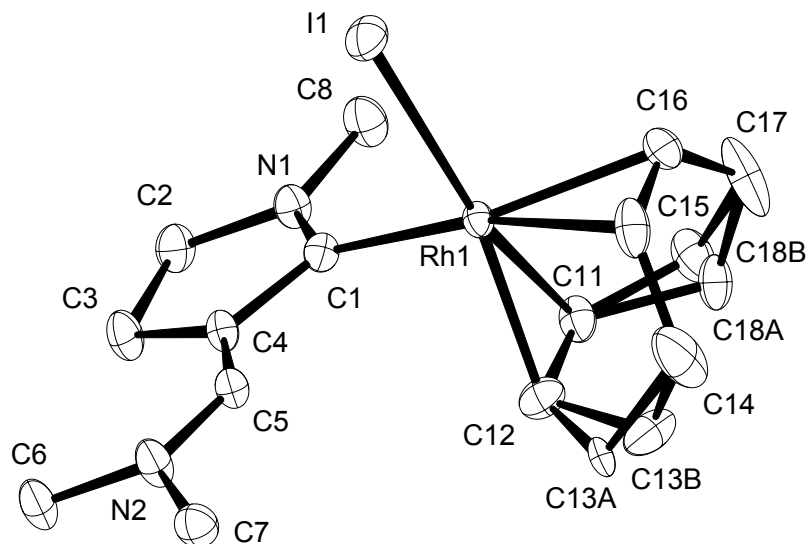
Chemical formula $[\text{C}_{47} \text{H}_{48} \text{Cl} \text{N}_2 \text{P}_2 \text{Pt}]^+ [\text{B} \text{F}_4]^- [\text{C} \text{H}_2 \text{Cl}_2]$, $F_w = 1105.09 \text{ g mol}^{-1}$, orange prism from dichloromethane/diethylether, crystal size $0.11 \times 0.04 \times 0.04 \text{ mm}^3$, crystal system *monoclinic*, space group $P2_1/c$, $a = 15.912(2)$, $b = 14.967(2)$, $c = 18.753(2) \text{ \AA}$, $\beta = 96.182(2)^\circ$, $V = 4440.0(8) \text{ \AA}^3$, $T = 100 \text{ K}$, $\rho_c = 1.653 \text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 3.468 \text{ mm}^{-1}$, empirical absorption correction ($T_{\min} = 0.34$, $T_{\max} = 0.75$), Bruker-AXS Kappa Mach3 Apex-II diffractometer, $1.74 < \theta < 30.95^\circ$, 121603 reflections collected, 13894 unique reflections ($R_{\text{int}} = 0.1008$), 11476 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The standard uncertainties of the Pt atom parameters from the refinement are probably underestimated, leading to unexpectedly high standard uncertainties on the Hirshfeld test for the Pt1-Cl1 and Pt1-P1 bonds. $R_1 = 0.029 [I > 2\sigma(I)]$, $wR_2 = 0.089$ (all data), 554 parameters, $S = 1.024$, residual electron density $+2.0 / -1.2 \text{ e \AA}^{-3}$ (in the vicinity of Pt1 and H6, respectively).

Crystal structure X-ray analysis of complex 11.



Chemical formula $[\text{C}_{51} \text{H}_{48} \text{Cl} \text{N}_2 \text{P}_2 \text{Pd}]^+ [\text{B} \text{F}_4]^- [\text{CH}_2 \text{Cl}_2]$, $F_w = 1064.44 \text{ g mol}^{-1}$, yellow block from dichloromethane/diethylether, crystal size $0.30 \times 0.09 \times 0.07 \text{ mm}^3$, crystal system *monoclinic*, space group $P2_1/c$, $a = 15.6561(2)$, $b = 15.0722(1)$, $c = 20.3553(2) \text{ \AA}$, $\beta = 94.510(1)^\circ$, $V = 4788.39(8) \text{ \AA}^3$, $T = 100 \text{ K}$, $\rho_c = 1.481 \text{ Mg m}^{-3}$, $Z = 4$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.676 \text{ mm}^{-1}$, empirical absorption correction ($T_{\min} = 0.83$, $T_{\max} = 0.98$), $2.94 < \theta < 33.20^\circ$, 129686 reflections collected, 16091 unique reflections ($R_{\text{int}} = 0.0615$), 13526 reflections with $I > 2\sigma(I)$. The crystal lost solute of crystallisation during data collection, resulting in a lower than ideal coverage (88%) of data to θ_{\max} of 33.20° . Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. $R_1 = 0.045$ [$I > 2\sigma(I)$], $wR_2 = 0.113$ (all data), 591 parameters, $S = 1.197$, extinction coefficient = $0.00375(17)$, residual electron density $+1.1 / -1.3 \text{ e \AA}^{-3}$ (in the vicinity of P2 and Pd1, respectively).

Crystal structure X-ray analysis of complex 19.



Chemical formula $[C_{16} H_{26} I N_2 Rh]$, $F_w = 476.20 \text{ g mol}^{-1}$, yellow block from dichloromethane/diethylether, crystal size $0.14 \times 0.08 \times 0.08 \text{ mm}^3$, crystal system *monoclinic*, space group $C2/c$, $a = 18.3031(3)$, $b = 13.9665(2)$, $c = 13.7001(2) \text{ \AA}$, $\beta = 103.708(1)^\circ$, $V = 3402.40(9) \text{ \AA}^3$, $T = 100 \text{ K}$, $\rho_c = 1.859 \text{ Mg m}^{-3}$, $Z = 8$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 2.812 \text{ mm}^{-1}$, Bruker-AXS Enraf-Nonius Kappa CCD diffractometer, empirical absorption correction ($T_{\min} = 0.75$, $T_{\max} = 0.89$), $3.06 < \theta < 33.20^\circ$, 48120 reflections collected, 6515 unique reflections ($R_{\text{int}} = 0.033$), 5815 reflections with $I > 2\sigma(I)$. Solution by direct methods (SHELXS-97), refinement by full-matrix least-squares on F^2 (SHELXL-97), H atoms riding. The methylene groups of the cyclooctadiene ligand show signs of disorder. C13 and C18 were refined using split atoms with half occupancy (C13A, C13B, C18A and C18B). The standard uncertainties of the Rh and I atom parameters from the refinement are probably underestimated, resulting in an unexpectedly high standard uncertainty on the Hirshfeld test for the Rh1-I1 bond. $R_1 = 0.033 [I > 2\sigma(I)]$, $wR_2 = 0.084$ (all data), 203 parameters, $S = 1.064$, extinction coefficient = $0.00057(6)$, residual electron density $+2.2 / -2.1 \text{ e \AA}^{-3}$ (in the vicinity of Rh1).