

SUPPORTING INFORMATION

Metal complexes with carbene ligands stabilized by lateral enamines

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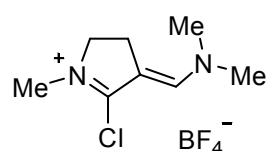
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General : All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O (Mg-anthracene), CH₂Cl₂, CHCl₃, MeCN, Et₃N, Me₂NH, MeNO₂ (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.

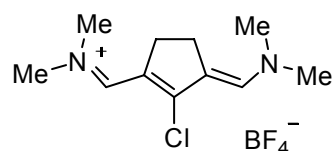
Starting Materials

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:

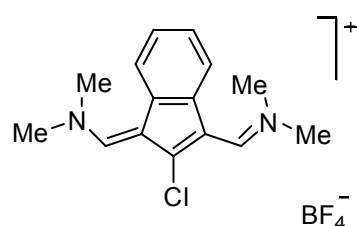
Compound 3: POCl₃ (9.13 mL, 100 mmol) was slowly added to a cooled (0 °C) mixture of N-methylpyrrolidone (4.81 mL, 50 mmol) and DMF (11.6 mL, 150 mmol) in CH₂Cl₂ (40 mL). Once the addition was complete, the mixture was stirred for 6 h at ambient temperature before it was poured into a sat. aq. solution 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).

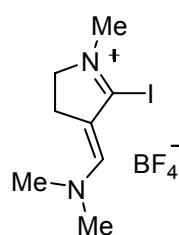
Compound 12: POCl₃ (2.40 mL, 26 mmol) was slowly added to a cooled (0 °C) solution of 3-dimethylamino-1-phenyl-prop-2-en-1-one (4.54 g, 26 mmol) in CH₂Cl₂ (25 mL). The mixture was stirred for 6 h at ambient temperature before it was poured into sat. aq. NaBF₄ at 0 °C. The organic layer was dried over 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.

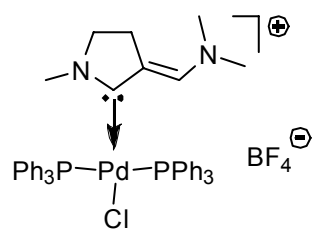
aq. NaBF₄, the aqueous phase was extracted with CH₂Cl₂ (5 x 30 mL), and the combined organic layers were dried over Na₂SO₄ and evaporated to give the product as a dark blue solid (350 mg, 25%). ¹H NMR (600 MHz, [D₆]-DMSO): δ = 7.91 (d, *J* = 11.8 Hz, 2H), 7.56 (t, *J* = 12.6 Hz, 2H), 6.39 (d, *J* = 12.6 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.



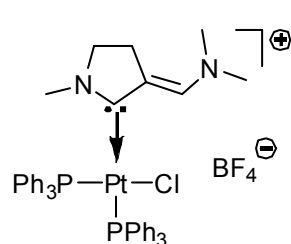
Metal Carbene Complexes

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.

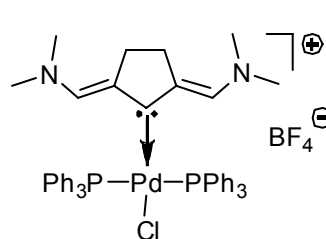
Complex 5. Prepared analogously as a yellow solid (144 mg, 96 %). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.96$ (s, 1H), 7.50-7.20 (m, 30H), 3.48-3.40 (m, 1H), 3.38 (s, 3H), 3.07 (s, 6H), 2.91-2.76 (m, 2H), 2.29-2.18 ppm (m, 1H);



^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 207.3$ (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): $\delta = 16.6$ ($^1J(\text{Pt-P}) = 1980$, $^2J(\text{P-P}) = 17.8$ 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.

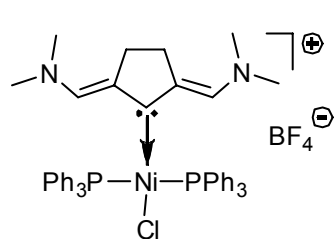
Complex 7. Prepared analogously as an orange solid (170 mg, 70%). ^1H NMR (600 MHz, CD_2Cl_2): $\delta = 7.71$ (br s, 2H), 7.70-7.66 (m, 12H), 7.55-7.52 (m, 6H), 7.50-7.46 (m, 12H), 2.84 (s, 12H), 1.96 ppm (s, 4H); ^{13}C



NMR (150 MHz, CD_2Cl_2): $\delta = 223.3$ (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):

$\delta = 24.7$ 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

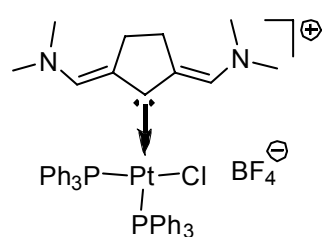


mmol) in THF (3.4 mL) and the mixture was stirred for 15 min before compound **6** (37 mg, 0.1231 mmol) was introduced. The suspension was stirred overnight, the precipitated solid was allowed to settle, the supernatant solution was siphoned off, and the solid was dried in vacuo to afford complex **8**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

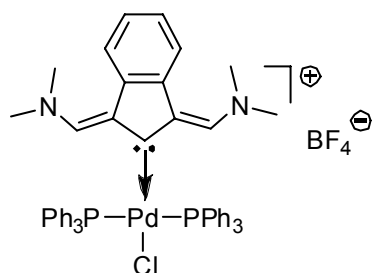
formed by slowly diffusing Et_2O into a solution of the complex in CH_2Cl_2 . ^1H NMR (600 MHz, CD_2Cl_2): $\delta = 8.45$ (s, 2H), 7.72 (m, 12H), 7.53 (m, 6H), 7.46 (m, 12H), 2.91 (br s, 12H), 1.82 ppm (s, 4H); ^{13}C NMR (150 MHz, CD_2Cl_2): $\delta = 230.0$ (C) (t, $J = 30.8$ Hz), 156.8 (CH), 134.6 (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): $\delta = 23.2$ 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.

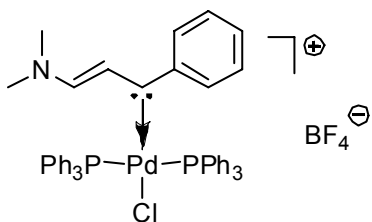
Complex 9. Prepared analogously as an orange solid (80 mg, 59 %). ^1H NMR (600 MHz, CD_2Cl_2): δ = 8.21 (s, 2H), 7.46-7.18 (m, 30H), 3.18 (s, 12H), 2.70 (m, 2H), 2.10 ppm (m, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 219.1 (C) (dd, J = 111.0, 8.0 Hz), 157.4 (CH), 134.9 (CH) (d, J = 9.8 Hz), 134.4 (CH) (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.

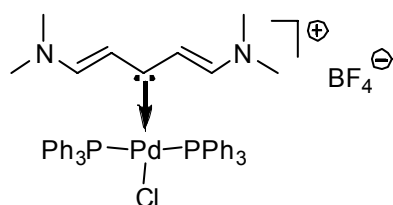


Complex 13. Prepared analogously as a yellow solid (113 mg, 81 %). ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.38 (d, J = 10.8 Hz, 1H), 7.50-7.41 (m, 12H), 7.40-7.48 (m, 8H), 7.32-7.28 (m, 12H), 7.14 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 8.4 Hz, 2H), 6.02 (d, J = 10.8 Hz, 1H), 3.17 (s, 3H), 2.90 ppm (s, 3H); ^{13}C 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 $\text{C}_{47}\text{H}_{43}\text{ClN}_2\text{P}_2\text{Pd}$: 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.

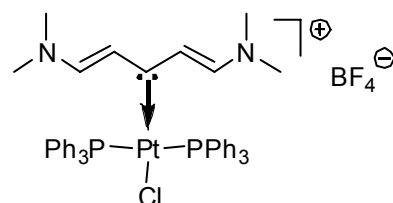
Complex 15a. Prepared analogously as a yellow-green solid (193 mg, 98 %). 1H NMR (600



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.

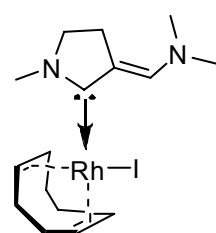
Compound 15b: Obtained analogously as yellow crystals (130 mg, 95 %). 1H NMR (600



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

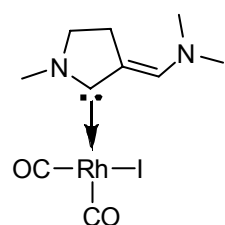


to a suspension of **18** (92 mg, 0.261 mmol) in CH_2Cl_2 (0.7 mL) and Et_2O (1.4 mL). The resulting clear yellow solution was stirred for 15 min before solid $[Rh(cod)Cl]_2$ (64.0 mg, 0.130 mmol) was introduced. Stirring was continued overnight, the solvent was evaporated and the residue purified by 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,

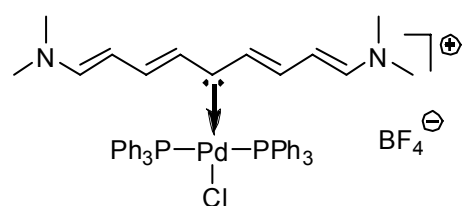
1427, 1386, 1317, 1293, 1254, 1227, 1185, 1107, 1073, 1050, 994, 912, 859, 800, 765 cm^{-1} ; MS (EI): m/z (%): 476 (85) [M^+], 368 (51), 366 (51), 349 (100), 239 (39), 197 (21), 139 (92), 137 (62); HRMS (EI): m/z : calcd for $\text{C}_{16}\text{H}_{26}\text{IN}_2\text{Rh}$: 476.0189; found: 476.0188;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

