Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

SUPPORTING INFORMATION

Carbenes Stabilized by Ylides: Pushing the Limits

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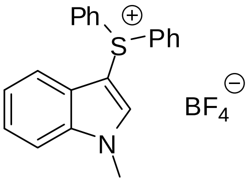
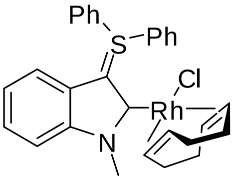
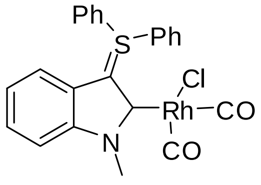
General : All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the drying agents indicated and were transferred under Ar. THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). 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 DMX 600 spectrometer in the solvents indicated; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS (the solvent signals were used as references and the chemical shifts converted to the TMS scale). ^{31}P chemical shifts are reported in ppm relative H_3PO_4, coupling constants (J) in Hz. Melting points: Büchi melting point apparatus B-540 (corrected); elemental analyses: H. Kolbe, Mülheim/Ruhr. Unless stated otherwise, all commercially available compounds (Acros, Fluka, Lancaster, Aldrich) were used as received.



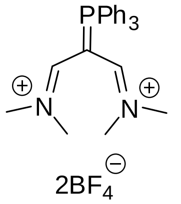
Compound 2: A solution of trifluoroacetic acid anhydride (840 mg, 3.96 mmol) in CH_2Cl_2 (5 mL) was added during 15 min to a stirred solution of methylindole **1** (530 mg, 3.96 mmol) and diphenylsulfoxide (834 mg, 3.96 mmol) in CH_2Cl_2 (5 mL) at −30 °C. After reaching ambient temperature, the mixture was shaken with a saturated solution of sodium tetrafluoroborate (10 mL) and the aqueous phase extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried and evaporated. The residue was triturated with Et_2O (3 x 10 mL) before it was disolved in MeOH and layered with more Et_2O, causing product **2** to crystallize in form of white needles (702 mg, 44 %). M.p. = 130-132 °C. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.54 (s, 1H), 7.86-7.70 (m, 11H), 7.42 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 3.98 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 140.1, 138.1, 133.6, 131.1, 129.7, 126.7, 124.5, 124.2, 123.0, 118.1, 112.6, 88.0, 34.0 ppm; IR (neat): $\tilde{\upsilon}$ = 3112, 1578, 1516, 1476, 1453, 1377, 1033, 977, 764, 742, 681 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{18}BF_4NS$: C 62.55, H 4.50, N 3.47; found: C 62.40, H 4.31, N 3.34.



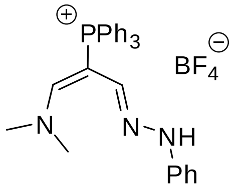
Compound 3: KHMDS (40 mg, 0.2 mmol) was added to a suspension of compound **2** (80.6 mg, 0.2 mmol) and $[RhCl(cod)]_2$ (49 mg, 0.1 mmol) in THF (2 mL) at −78 °C. After stirring for 1 h, the mixture was slowly warmed to ambient temperature and stirring continued for 3 h. The solvents were evaporated and the residue purified by flash chromatography (2 % MeOH in CH_2Cl_2) to afford complex **3** as a yellow solid (20.2 mg, 18 %). M.p. = 166-167 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.71 (d, J = 8.1 Hz, 2H), 7.59-7.47 (m, 5H), 7.39-7.32 (m, 3H), 7.09 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 6.9 Hz, 1H), 6.65 (t, J = 6.8 Hz, 1H), 6.56 (d, J = 7.4 Hz, 1H), 4.83 (bs, 2H), 4.15 (s, 3H), 3.21 (bs, 1H), 2.86 (bs, 1H), 2.43-2.17 (m, 3H), 2.03-1.90 (m, 1H), 1.85-1.72 (m, 3H), 1.70-1.56 ppm (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 144.2, 133.2, 132.2, 131.4, 130.7, 130.6, 130.2, 129.6, 128.1, 120.7, 115.3, 109.8, 98.6 (d, J = 6.3 Hz), 98.3 (d, J = 6.2 Hz), 69.7 (d, J = 15.2 Hz), 67.0 (d, J = 14.8 Hz), 37.3, 33.8, 33.6, 29.7 ppm; MS (EI): m/z (%): 454 (M^+-cod). IR (neat): $\tilde{\upsilon}$ = 3456, 2970, 1738, 1442, 1366, 1270, 1229, 1216, 1064, 977, 750, 689 cm^{-1}; elemental analysis calcd (%) for $C_{29}H_{30}ClNSRh$: C 61.87, H 5.37, N 2.49; found: C 61.80, H 5.43, N 2.29.



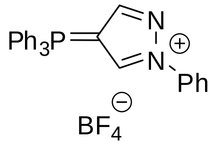
Compound 4: CO was bubbled for 5 min through a solution of compound **3** (56 mg, 0.1 mmol) in THF (2 mL). The solvents were then removed, and the remaining solid was washed with pentane and dried to give complex **4** as a yellow solid (26.5 mg, 52 %). Characteristic data: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.70-7.35 (m, 10H), 7.28 (d, J = 8.4 Hz, 1H), 7.04 (t, J = 8.1 Hz, 1H), 6.83 (t, J = 8.1 Hz, 1H), 6.75 ppm (d, J = 7.8 Hz, 1H); IR (neat): $\tilde{\upsilon}$ = 2052, 1975 cm^{-1}; HRMS: *m/z*: calcd for: $C_{23}H_{17}NClO_2SRh$: 508.97236; found: 508.97192.



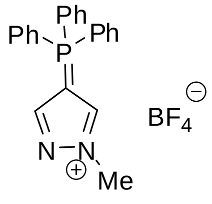
3-Dimethylamino-*N,N*-dimethyl-2-triphenylphosphoniopropeniminium tetrafluoroborate (9): 2-(Dimethylaminovinyl)-triphenylphosphonium bromide **8** (2.06 g, 5 mmol)[1] was added in small portions to a solution of phosphoryl chloride (2.30 g, 15 mmol) in DMF (3.65 g, 50 mmol). After stirring for 30 min at ambient temperature, the mixture was heated to 70 °C for 2 h. For work up, the mixture was allowed to cool to ambient temperature before it was poured into a chilled saturated aqueous solution of sodium tetrafluoroborate, causing the desired product **9** to precipitate as a light brown crystalline solid (2.27 g, 81 %). M.p. = 205-208 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.95 (dt, J = 2.4, 7.3 Hz, 3H), 7.83-7.64 (m,14H), 3.45 (s, 6H), 3.11 ppm (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ = 164.9 (d, J = 16.8 Hz), 134.9 (d, J = 3.0 Hz), 134.0 (d, J = 10.8 Hz), 129.9 (d, J = 13.1 Hz), 117.1 (d, J = 90.4 Hz), 70.0 (d, J = 106.2 Hz), 47.7, 42.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.1 ppm; IR (neat): $\tilde{\upsilon}$ = 1630, 1604, 1439, 1360, 1106, 1030, 995, 919, 822, 749, 724, 688 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{29}B_2F_8N_2P$: C 53.42, H 5.20, N 4.98; found: C 53.64, H 5.18, N 5.10.



Compound 10a: Phenylhydrazine (108 mg, 1 mmol) was added to a solution of compound **9** (562 mg, 1 mmol) in MeCN (10 mL) and the resulting mixture was refluxed overnight. When allowed to cool to ambient temperature, product **10a** crystallized as orange prisms which were collected by filtration, washed with Et_2O and dried in vacuo (365 mg g, 68 %). ^{1}H NMR (300 MHz, CD_3CN): δ = 8.36 (s, 1H), 8.25 (d, J = 17.8 Hz, 1H), 7.82-7.70 (m, 9H), 7.70-7.55 (m, 6H), 6.88 (t, J = 7.4 Hz, 2H), 6.57 (t, J = 6.7 Hz, 1H), 6.16 (d, J = 25.3 Hz, 1H), 6.14 (s, 2H), 3.15 ppm (s, 6H); ^{13}C NMR (75 MHz, CD_3CN): δ = 153.7 (d, J = 23.6 Hz), 144.6, 134.1 (d, J = 2.6 Hz), 133.9 (d, J = 10.5 Hz), 133.4 (d, J = 2.6 Hz), 129.2 (d, J = 12.8 Hz), 128.4, 121.3 (d, J = 91.5 Hz), 118.4, 111.1, 76.0 (d, J = 108.6 Hz), 43.9 ppm; ^{31}P NMR (121 MHz, CD_3CN): δ = 26.3 ppm; HRMS: *m/z*: calcd for: $C_{29}H_{29}N_3P$: 450.20936; found: 450.20986; elemental analysis calcd (%) for $C_{29}H_{29}BF_4N_3P$: C 64.82, H 5.44, N 7.82; found: C 65.05, H 5.40, N 7.98.



Compound 11a: Phenylhydrazine (108 mg, 1 mmol) was added to a solution of 3-dimethylamino-*N,N*-dimethyl-2-triphenylphosphoniopropeniminium tetrafluoroborate **9** (562 mg, 1 mmol) in MeCN (10 mL) and the resulting mixture was heated for 1 h in a sealed tube at 180 °C in a microwave oven. After reaching ambient temperature, the solvents were evaporated and the remaining oil purified by flash chromatography (MeOH:CH_2Cl_2, 1:10) to afford the desired product **11a** as a white solid (433 mg, 88 %). M.p. = 75-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.92-7.61 (m, 16H), 7.51 (t, J = 7.1 Hz, 2H), 7.33 ppm (t, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0 (d, J = 10.6 Hz), 138.2, 135.7 (d, J = 20.6 Hz), 135.2 (d, J = 3.0 Hz), 133.5 (d, J = 11.2 Hz), 130.3 (d, J = 13.1 Hz), 129.4, 128.3, 120.0, 118.2 (d, J = 92.5 Hz), 97.9 ppm (d, J = 115.3 Hz); ^{31}P NMR (162 MHz): δ = 13.2 ($CDCl_3$); 14.4 (THF-d_8) ppm; IR (neat): $\tilde{\upsilon}$ =1595, 1513, 1436, 1171, 1112, 1093, 1049, 770, 760, 724, 689 cm^{-1}. HRMS: *m/z*: calcd for: $C_{27}H_{22}N_2P$: 405.15151; found: 405.15180; elemental analysis calcd (%) for $C_{27}H_{22}BF_4N_2P$: C 65.88, H 4.50, N 5.69; found: C 65.75, H 4.46, N 5.73.



Compound 11b: Methylhydrazine (47 mg, 1 mmol) was added to a solution of 3-dimethylamino-*N,N*-dimethyl-2-triphenylphosphoniopropeniminium tetrafluoroborate **9** (562 mg, 1 mmol) in MeCN (10 mL) and the resulting mixture stirred at reflux temperature overnight. After reaching ambient temperature, the solvents were evaporated and the remaining oil purified by flash chromatography (MeOH:CH_2Cl_2, 1:10) to afford product **11b** as a white solid (292 mg, 68 %). M.p. = 225-227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 7.90-7.79 (m, 3H), 7.78-7.66 (m, 6H), 7.65-7.52 (m, 7H), 4.12 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1 (d, J = 11.2 Hz), 139.5 (d, J = 20.5 Hz), 135.0 (d, J = 2.9 Hz), 133.3 (d,

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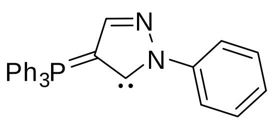
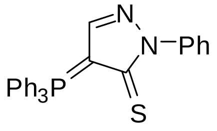
[1] R. Gompper, E. Kujath, H.-U. Wagner, *Angew. Chem.* **1982**, *94*, 559-560; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 543-544.

J = 11.1 Hz), 130.2 (d, J = 13.1 Hz), 118.6 (d, J = 92.6 Hz), 94.9 (d, J = 117.4 Hz), 39.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 13.0 ppm; HRMS: *m/z*: calcd for: $C_{22}H_{20}N_2P$: 343.13586; found: 343.13569; elemental analysis calcd (%) for $C_{22}H_{20}BF_4N_2P$: C 61.42, H 4.69, N 6.51; found: C 61.57, H 4.74, N 6.73.

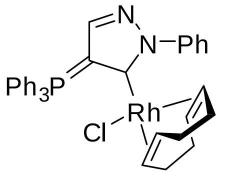
Carbene 12: A solution of KHMDS (24.3 mg, 0.121 mmol) in d_8-THF (0.4 mL) at −78 °C was added to a suspension of compound **11a** (57 mg, 0.116 mmol) in d_8-THF (0.4 mL) at the same temperature. The spectroscopic data of the resulting carbene **12** are as follows: ^{1}H NMR (300 MHz, d_8-THF, −78 °C): δ = 8.44 (d, J = 7.7 Hz, 2H), 8.02-7.84 (m, 6H), 7.73-7.50 (m, 9H), 7.33-7.18 (t, J = 7.3 Hz, 2H), 7.07 ppm (bs, 2H); ^{13}C NMR (75 MHz, d_8-THF, −78 °C): δ = 218.8 (d, J = 51.2 Hz), 147.1, 144.6 (d, J = 24.7 Hz), 135.1 (d, J = 10.1 Hz), 134.0, 130.1 (d, J = 12.3 Hz), 128.8, 126.4, 125.3, 124.5, 119.9, 101.0 ppm (d, J = 131.9 Hz); ^{31}P NMR (121 MHz, d_8-THF, −78 °C): δ = 10.2 ppm.



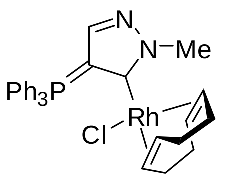
Compound 13: KHMDS (40 mg, 0.2 mmol) was added to a suspension of compound **11a** (98.4 mg, 0.2 mmol) and sulfur (9.6 mg, 0.3 mmol) in THF (2 mL) at −78 °C. After stirring for 30 min, the mixture was slowly warmed to ambient temperature and stirring continued for 2 h. The solvents were then evaporated and the remaining oil purified by flash chromatography (5 % acetone in CH_2Cl_2) to afford product **13** as a white solid (57 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 6.5 Hz, 2H), 7.80-7.35 (m, 15H), 7.30 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 6.95 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0 (d, J = 14.9 Hz), 140.3, 133.9 (d, J = 10.6 Hz), 133.4, 130.2, 129.1 (d, J = 12.9 Hz), 127.8, 126.2, 124.7, 121.0 ppm (d, J = 94.2 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 12.0 ppm; IR (neat): $\tilde{\nu}$ = 1595, 1498, 1434, 1340, 1305, 1107, 937, 755, 711 cm^{-1}; HRMS: *m/z*: calcd for: $C_{27}H_{22}N_2PS$: 437.12359; found: 437.12392.



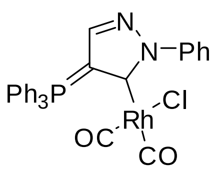
Compound 14a: KHMDS (40 mg, 0.2 mmol) was added to a suspension of compound **11a** (98.4 mg, 0.2 mmol) and $[RhCl(cod)]_2$ (49 mg, 0.1 mmol) in THF (2 mL) at −78 °C. After stirring for 30 min, the mixture was slowly warmed to ambient temperature and stirring continued for additional 2 h. The solvents were then evaporated and the residue purified by flash chromatography (2 % MeOH in CH_2Cl_2) to afford complex **14a** as a yellow solid (114 mg, 88 %). M.p. = 221-223 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.61 (d, J = 7.4 Hz, 2H), 7.85-7.77 (m, 6H), 7.77-7.65 (m, 3H), 7.57-7.50 (m, 6H), 7.42-7.29 (m, 3H), 7.28-7.22 (m, 1H), 4.85-4.81 (m, 1H), 4.21-4.14 (m, 1H), 2.45-2.35 (m, 2H), 2.02-1.97 (s, 1H), 1.56-1.47 (m, 2H), 1.25-1.02 (m, 4H), 0.85-0.80 ppm (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 188.0 (dd, J = 41.0, 36.8 Hz), 147.2 (d, J = 16.5 Hz), 146.2, 135.7 (d, J = 10.3 Hz), 134.4 (d, J = 2.8 Hz), 130.0 (d, J = 12.5 Hz), 128.5, 127.1, 125.6, 124.0 (d, J = 90 Hz), 96.7 (d, J = 7.1 Hz), 92.7 (d, J = 7.1 Hz), 68.8 (d, J = 15.3 Hz), 68.5 (d, J = 15.0 Hz), 33.2, 31.5, 29.9, 27.7 ppm; ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 16.6 ppm; HRMS: *m/z*: calcd for: $C_{35}H_{33}N_2PRh$: 615.14309; found: 615.14362; elemental analysis calcd (%) for $C_{35}H_{33}ClN_2PRh$: C 64.58, H 5.11, N 4.30; found: C 64.65, H 5.06, N 4.26.



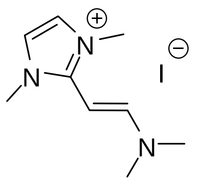
Compound 14b: Prepared analogously as a yellow solid (108 mg, 92 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90-7.56 (m, 15H), 7.23 (s, 1H), 4.83 (q, J = 7.5 Hz, 1H), 4.57 (s, 3H), 4.44 (q, J = 7.2 Hz, 1H), 3.22-3.16 (m, 1H), 2.46-2.33 (m, 2H), 2.23-2.13 (m, 1H), 1.77-1.70 (m, 1H), 1.60-1.50 (m, 3H), 1.26-1.12 (m, 1H), 1.11-0.96 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.8 (dd, J = 43.3, 35.6 Hz), 145.4 (d, J = 18.7 Hz), 134.8 (d, J = 10.3 Hz), 134.1 (d, J = 3.0 Hz), 129.8 (d, J = 12.6 Hz), 129.0, 123.6 (d, J = 91.5 Hz), 96.6 (d, J = 7.1 Hz), 93.5 (d, J = 6.8 Hz), 69.9 (d, J = 15.5 Hz), 65.3 (d, J = 15.2 Hz), 43.9, 34.3, 31.4, 28.8, 28.4 ppm; ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 15.1 ppm; MS (ESI): *m/z:* 553.2 (M^+ -Cl).



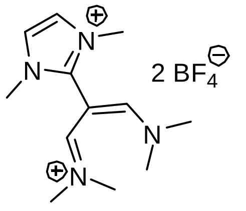
Compound 15: CO was bubbled for 5 min through a solution of complex **14a** (33 mg, 0.05 mmol) in THF (2 mL). The solvents were then evaporated and the remaining solid washed with pentane and dried to give complex **15** as a yellow solid. (24 mg, 79 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.08 (d, J = 7.5 Hz, 2H), 7.83-7.42 (m, 15H), 7.32 (t, J = 8 Hz, 2H), 7.23 ppm (t, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 187.4 (d, J = 43.1 Hz), 184.9 (d, J = 53.7 Hz), 146.7 (d, J = 16.8 Hz), 145.3, 135.7 (d, J = 10.1 Hz), 134.7 (d, J = 2.7 Hz), 130.2 (d, J = 13.0 Hz), 129.3, 128.9, 127.7, 125.5, 122.6 ppm (d, J = 92.4 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 15.5 ppm; IR (neat): ν = 2052, 1965 cm^{-1}.



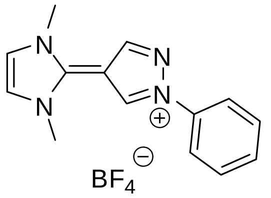
Compound 18: A suspension of 1,2,3-trimethyl imidazolium chloride (4.76 g. 20 mmol) in dimethyl formamide diethylacetal (8.6 mL, 50 mmol) was stirred under reflux for 4 d. After reaching ambient temperature, the precipitate was filtered off and washed with ether to afford product **18** as a light brown solid (5.50 g, 94 %). ^{1}H NMR (300 MHz, CD$_3$CN): δ = 7.20 (d, J = 13.6 Hz, 1H), 7.06 (s, 2H), 4.69 (d, J = 13.6 Hz, 1H), 3.66 (s, 6H), 3.01 ppm (s, 6H); ^{13}C NMR (75 MHz, CD$_3$CN): δ = 149.7, 146.1, 120.1, 72.7, 35.3 ppm; HRMS: *m/z*: calcd for: C$_9$H$_{16}$N$_3$: 166.13442; found: 166.13431; elemental analysis calcd (%) for C$_9$H$_{16}$N$_3$I: C 36.87, H 5.50, N 14.33; found: C 36.98, H 5.64, N 14.21.



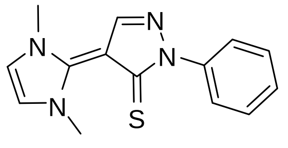
Compound 19: Salt **18** (5.53 g, 18.9 mmol) was added in small portions to a solution of phosphoryl chloride (9.20 g, 60 mmol) in DMF (14.6 g, 200 mmol). After stirring for 30 min, the mixture was heated to 70 °C for 2 h. For work up, the mixture was allowed to cool before it was poured into an chilled (0 °C) saturated aqueous solution of sodium tetrafluoroborate. The brown suspension was concentrated to one third of its original volume and the precipitated excess of NaBF$_4$ filtered off. The remaining oil was kept at 0 °C overnight, causing the product to precipitate as a beige solid (5.46 g, 73 %). M.p. = 219-221 °C. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 7.89 (s, 2H), 7.63 (s, 2H), 3.77 (s, 6H), 3.39 (s, 6H), 2.42 ppm (s, 6H); ^{13}C NMR (100 MHz, CD$_3$CN): δ = 164.1, 124.5, 48.9, 37.5, 35.4 ppm; IR (neat): $\tilde{\nu}$ = 3145, 1614, 1408, 1290, 1210, 1020, 825, 777 cm^{-1}. MS (EI): *m/z* (%): 705.4 (2 M^+ -BF$_4$).



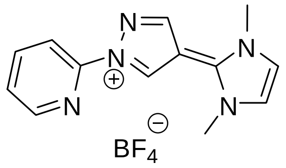
Compound 20: Phenylhydrazine (346 mg, 3.2 mmol) was added to a solution of compound **19** (1.19 g, 3 mmol) in MeCN (10 mL) and the resulting mixture heated for 1 h in a sealed tube at 180 °C in a microwave oven. After reaching ambient temperature, the solvents were evaporated and the residue purified by flash chromatography (MeOH:CH$_2$Cl$_2$, 1:10) to afford salt **20** as a white solid (792 mg, 81 %). M.p. = 143-145 °C. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 8.64 (s, 1H), 8.10 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 8.0 Hz, 2H), 7.50-7.40 (m, 3H), 3.81 ppm (m, 6H); ^{13}C NMR (100 MHz, CD$_3$CN): δ = 140.7, 138.9, 130.1, 129.5, 127.7, 122.9, 119.4, 103.6, 35.5 ppm; IR (neat): $\tilde{\nu}$ = 3146, 1611, 1595, 1524, 1508, 1254, 1049, 1029, 955, 768, 758, 707, 693 cm^{-1}; HRMS: *m/z*: calcd for: C$_{14}$H$_{15}$N$_4$: 239.129133; found: 239.128993.

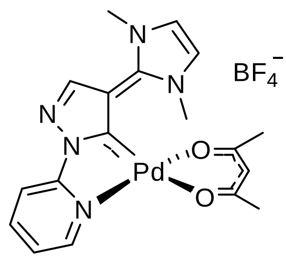


Compound 22: A solution of KHMDS (181 mg, 0.905 mmol) in THF (4.5 mL) was slowly added to a suspension of compound **20** (296.0 mg, 0.907 mmol) and sulphur (31 mg, 0.967 mmol) in THF (9 mL) at –78 °C. After stirring for 30 min, the mixture was slowly warmed to ambient temperature and stirring continued for 8 h. The solvents were then evaporated and the residue purified by flash chromatography (gradient 2 % → 4 % MeOH in CH$_2$Cl$_2$) to afford product **22** as a brownish solid (135 mg, 55 %). M.p. = 188-190 °C. ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ = 8.08 (m, 2H), 7.54 (s, 1H), 7.43 (m, 2H), 7.28 (m, 1H), 7.19 (s, 2H), 3.90 ppm (s, 6H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ = 161.2, 145.1, 141.8, 139.1, 128.2, 126.4, 125.3, 122.0, 101.6, 36.8 ppm; HRMS: *m/z*: calcd for: C$_{14}$H$_{14}$N$_4$NaS: 239.08314; found: 239.08292.



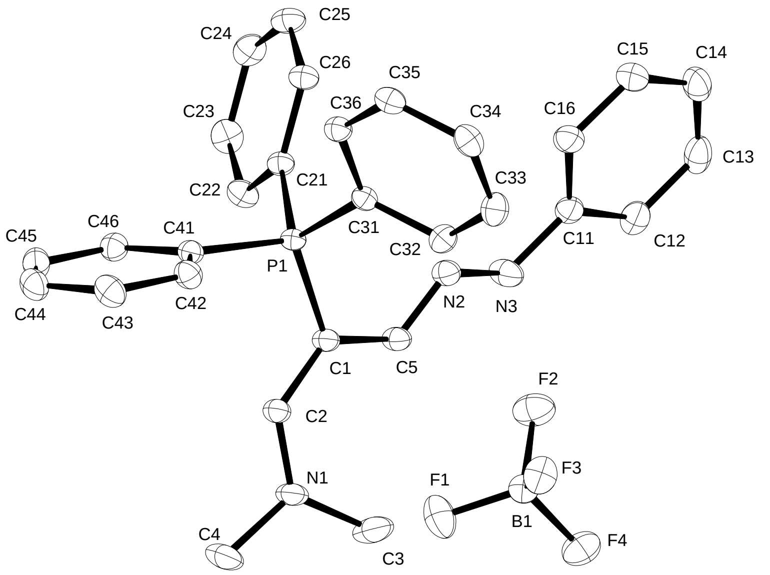
Compound 23. 1-Hydrazinopyridine (96 µL, 0.88 mmol) was added to a solution of compound **19** (350 mg, 0.88 mmol) in MeCN (3 mL) and the resulting mixture heated for 1 h. in a sealed tube at 180 °C in a microwave oven. After reaching ambient temperature, the solvents were evaporated and the residue purified by flash chromatography (MeOH:CH$_2$Cl$_2$, 1:20) to afford salt **23** as a beige solid (220 mg, 76 %). ^{1}H NMR (400 MHz, d$_6$-DMSO): δ = 9.37 (s, 1H), 8.59-8.54 (m, 1H), 8.41 (d, J = 0.4 Hz, 1H), 8.14-8.07 (m, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.84 (s, 2H), 7.50 (ddd, J = 1.2, 4.8, 7.2 Hz, 1H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, d$_6$-DMSO): δ = 150.0, 148.6, 142.3, 140.1, 130.2, 123.4, 123.3, 112.6, 104.5, 35.8; IR (neat): $\tilde{\nu}$ = 3153, 1597, 1524, 1455, 1253, 1066, 1015, 959, 778, 711; MS (EI): *m/z* (%): 240 (M^+ -BF$_4$)*;* HRMS: *m/z*: calcd for: C$_{13}$H$_{14}$N$_5$: 240.1244; found 240.1245.

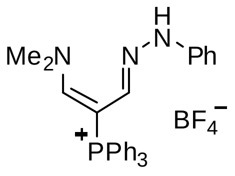




Compound 24. A degassed solution of compound **23** (180 mg, 0.55 mmol) and Pd(acac)$_2$ (168 mg, 0.552 mmol) in chlorobenzene (1.5 mL) was stirred for 18h at 160 °C. For work up, the mixture was passed through a short pad of silica, which was carefully rinsed with CH_2Cl_2 (4 x 2 mL) and hot MeCN (2 x 4 mL), the combined filtrates were evaporated and the residue purified by flash chromatography (4 % MeOH in CH_2Cl_2) to give complex **24** as a brown solid (170 mg, 58 %). M.p. = 280 °C (decomp.). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 8.62 (ddd, J = 0.7, 1.6, 5.7 Hz, 1H), 8.12 (ddd, J = 1.6, 2.5, 8.3 Hz, 1H), 7.85 (ddd, J = 0.8, 1.2, 8.3 Hz, 1H), 7.80 (s, 1H), 7.46 (s, 2H), 7.35 (ddd, J = 1.3, 5.7, 7.5 Hz, 1H), 5.48 (s, 1H), 3.78 (s, 6H), 2.11 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 189.2, 186.1, 154.7, 153.7, 146.5, 142.7, 142.2, 142.1, 122.9 (2C), 121.6, 111.8, 106.3, 101.4, 36.3 (2C), 27.6, 26.8; IR (neat): $\tilde{\nu}$ = 3142, 2921, 2850, 1608, 1562, 1518, 1494, 1381, 1051, 1024, 944, 785, 733, 715; MS (ESI): *m/z* (%): 444 (M^+–BF_4); HRMS: *m/z*: calcd for: $C_{18}H_{20}N_5O_2Pd$: 444.0659; found: 444.0653.

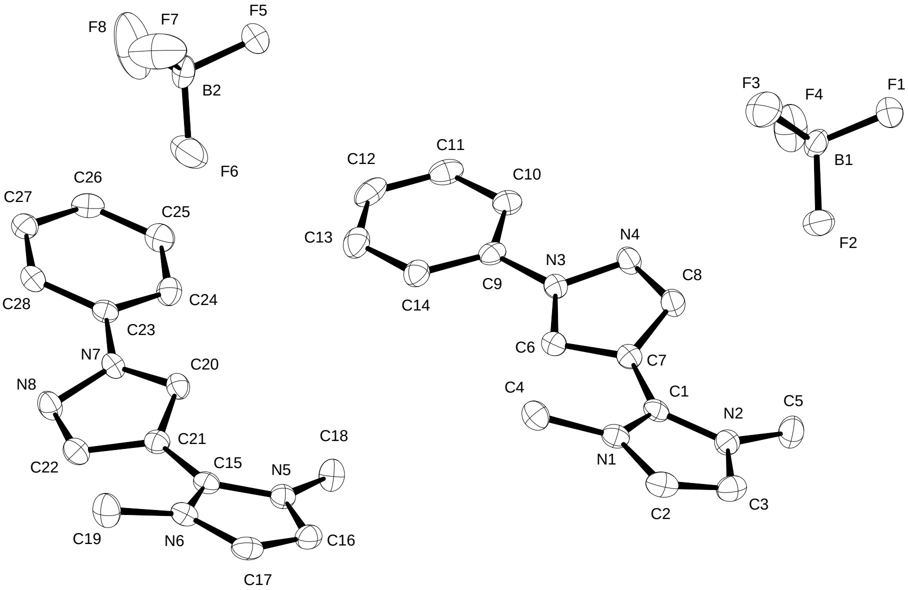
ADDITIONAL CRYSTALLOGRAPHIC INFORMATIONS





10a

Figure S-1. Structure of the salt **10a** in the solid state.



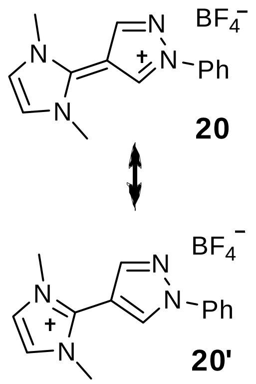


Figure S-2. Structure of salt **20** in the solid state, showing two crystallographically independent molecules in the unit cell.

X-ray Crystal Structure Analysis of 2: $C_{21}H_{18}BF_4NS$, $M_r = 403.23$ g · mol^{-1}, colorless plate, crystal size 0.34 x 0.34 x 0.08 mm, monoclinic, space group $P2_1/c$, $a =$ 10.8888(2) Å, $b =$ 10.9330(2) Å, $c =$ 16.1552(3) Å, $\beta =$ 93.0600(10)°, $V =$ 1920.49(6) Å^3, $T =$ 100 K, $Z = 4$, $D_{calc} =$ 1.395 g·cm^3, $\lambda =$ 0.71073 Å, $\mu(Mo\text{-}K_\alpha) =$ 0.212 mm^{-1}, Empirical absorption correction ($T_{min} = 0.48$, $T_{max} = 0.75$), Nonius KappaCCD diffractometer, $2.97 < \theta < 33.13°$, 53680 measured reflections, 7298 independent reflections, 6229 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.041$ [$I > 2\sigma(I)$], $wR_2 =$ 0.119, 254 parameters, H atoms riding, $S =$ 1.093, residual electron density 0.6 / -0.8 e Å^{-3}. CCDC-692803.

X-ray Crystal Structure Analysis of 3: $C_{29}H_{29}ClNO_{0.25}RhS$, $M_r = 565.95$ g · mol^{-1}, yellow plate, crystal size 0.20 x 0.18 x 0.08 mm, monoclinic, space group $P2_1/c$, $a =$ 8.42670(10) Å, $b =$ 14.9555(2) Å, $c =$ 20.3091(2) Å, $\beta =$ 95.2580(10)°, $V =$ 2548.69(5) Å^3, $T =$ 100 K, $Z = 4$, $D_{calc} =$ 1.475 g·cm^3, $\lambda =$ 0.71073 Å, $\mu(Mo\text{-}K_\alpha) =$ 0.876 mm^{-1}, Empirical absorption correction ($T_{min} = 0.51$, $T_{max} = 0.78$), Nonius KappaCCD diffractometer, $2.90 < \theta < 37.80°$, 104721 measured reflections, 13658 independent reflections, 11424 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.034$ [$I > 2\sigma(I)$], $wR_2 =$ 0.090, 303 parameters, H atoms riding, $S =$ 1.038, residual electron density 1.1 / -1.6 e Å^{-3}. CCDC-692804.

X-ray Crystal Structure Analysis of 10a (R = Ph): $C_{29}H_{29}BF_4N_3P$, $M_r = 537.33$ g · mol^{-1}, pale yellow plate, crystal size 0.58 x 0.27 x 0.20 mm, monoclinic, space group $P2_1/c$, $a =$ 8.6892(2) Å, $b =$ 16.7981(3) Å, $c =$ 19.0914(3) Å, $\beta =$ 98.6410(10)°, $V =$ 2754.99(9) Å^3, $T =$ 100 K, $Z = 4$, $D_{calc} =$ 1.295 g·cm^3, $\lambda =$ 0.71073 Å, $\mu(Mo\text{-}K_\alpha) =$ 0.150 mm^{-1}, Empirical absorption correction ($T_{min} = 0.45$, $T_{max} = 0.97$), Nonius KappaCCD diffractometer, $2.96 < \theta < 33.13°$, 44691 measured reflections, 10469 independent reflections, 8045 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.045$ [$I > 2\sigma(I)$], $wR_2 =$ 0.129, 349 parameters, H atoms riding, $S =$ 1.032, residual electron density 0.5 / -0.4 e Å^{-3}. CCDC-692800.

X-ray Crystal Structure Analysis of 11: $C_{27}H_{22}BF_4N_2P$, $M_r = 492.25$ g · mol^{-1}, colorless plate, crystal size 0.22 x 0.15 x 0.12 mm, monoclinic, space group Cc, $a =$ 17.0477(5) Å, $b =$ 7.4791(2) Å, $c =$ 19.9077(6) Å, $\beta =$ 112.0130(10)°, $V =$ 2353.22(12) Å^3, $T =$ 100 K, $Z = 4$, $D_{calc} =$ 1.389 g·cm^3, $\lambda =$ 0.71073 Å, $\mu(Mo\text{-}K_\alpha) =$ 0.168 mm^{-1}, Empirical absorption correction ($T_{min} = 0.\ 66$, $T_{max} = 0.\ 98$), Nonius KappaCCD diffractometer, $3.01 < \theta < 33.08°$, 20324 measured reflections, 8203 independent reflections, 7757 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.036$ [$I > 2\sigma(I)$], $wR_2 =$ 0.103, 316 parameters, H atoms riding, $S =$ 1.111, absolute structure parameter = 0.23(5), residual electron density 0.5 / -0.6 e Å^{-3}. CCDC-692801.

X-ray Crystal Structure Analysis of 14: $C_{35}H_{33}ClN_2PRh$, $M_r = 650.96$g · mol^{-1}, yellow plate, crystal size 0.06 x 0.04 x 0.02 mm, monoclinic, space group $C2/c$, $a =$ 16.898(3) Å, $b =$ 14.613(3) Å, $c =$ 23.847(5) Å, $\beta =$ 90.121(4)°, $V =$ 5888(2) Å^3, $T =$ 100 K, $Z = 8$, $D_{calc} =$ 1.469 g·cm^3, $\lambda =$ 0.71073 Å, $\mu(Mo\text{-}K_\alpha) =$ 0.753 mm^{-1}, Empirical absorption correction ($T_{min} = 0.68$, $T_{max} =$ 0.88), Nonius KappaCCD diffractometer, $1.71 < \theta < 25.10°$, 53762 measured reflections, 5214 independent reflections, 4022 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.043$ [$I > 2\sigma(I)$], $wR_2 =$ 0.166, 361 parameters, H atoms riding, $S =$ 1.288, residual electron density 1.2 / -1.6 e Å^{-3}. CCDC-692805.

X-ray Crystal Structure Analysis of 20: $C_{14}H_{15}BF_4N_4$, $M_r = 326.11$ g · mol^{-1}, colorless plate, crystal size 0.41 x 0.17 x 0.02 mm, orthorhombic, space group $Pbca$, $a =$ 13.683(2) Å, $b =$ 13.794(2) Å, $c =$ 30.960(4) Å, $V =$ 5843.5(15) Å^3, $T =$ 100 K, $Z =$ 16, $D_{calc} =$ 1.483 g·cm^3, $\lambda =$ 0.71073 Å, $\mu(Mo\text{-}K_\alpha) =$ 0.126 mm^{-1}, Semi-empirical absorption correction ($T_{min} = 0.\ 36$, $T_{max} = 0.\ 75$), Nonius KappaCCD diffractometer, $3.55 < \theta < 25.61°$, 96080 measured reflections, 5493 independent reflections, 4175 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 =$ 0.048 [$I > 2\sigma(I)$], $wR_2 =$ 0.116, 419 parameters, H atoms riding, $S =$ 1.050, absolute structure parameter = 0.23(5), residual electron density 0.5 / -0.5 e Å^{-3}. CCDC-692802.