Eur. J. Inorg. Chem. **2008** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2008 · ISSN 1434–1948

SUPPORTING INFORMATION

Title: Pyrazole-Bridged NHC Ligands and Their Dimetallic (Allyl)palladium Complexes
Author(s): Ulrich J. Scheele, Michael John, Sebastian Dechert, Franc Meyer*
Ref. No.: I200701230

1 Experimental section

1.1 General remarks

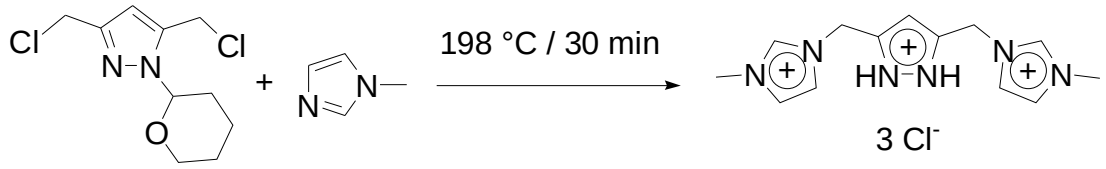
Melting points/ decomposition temperatures were determined on an OptiMelt system (Stanford Research Systems, Inc.) using open capillaries, values are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded either on a Bruker Avance 500 or on a Bruker Avance 300 spectrometer. ^{13}C resonances were obtained with broad-band proton decoupling, spectra were recorded at 300 K if not indicated otherwise. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced internally to solvent signals (CD_3CN: δ_H = 1.94 ppm, δ_C = 1.24 ppm, DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.43 ppm). Peak assignments are based on 2D NMR experiments where necessary. IR spectra from KBr pellets were recorded on a Digilab Excalibur Series FTS 3000 spectrometer. Mass spectra were recorded using an Applied Biosystems API 2000 system (LR-ESI), a Finnigan MAT LCQ (HR-ESI) or a Finnigan MAT 95 (FAB, 3-nitrobenzyl alcohol as matrix). Elemental analyses were performed by the analytical laboratory of the Institut für Anorganische Chemie der Universität Göttingen using a Heraeus CHN-O-RAPID instrument or an Elementar vario EL III instrument.

3,5-Bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole,[1] aryl-substituted imidazoles[2] and (meth-)allylpalladium(II) chloride dimer[3] were prepared by literature procedures. Any other materials are commercially available from various suppliers and were used without further purification. **CAUTION:** 3,5-Bis(chloromethyl)-1*H*-pyrazole hydrochloride (which is used in the preparation of 3,5-Bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole) has to be handled with extreme care! This compound may be a health hazard, especially on repeated and prolonged contact. According to our experiences it should be considered as sensitizing (R42/ R43) and/ or cumulative (R 33).

1.2 Experimental procedures and analytical data

1.2.1 Ligand precursors $[H_4L]Cl_3$

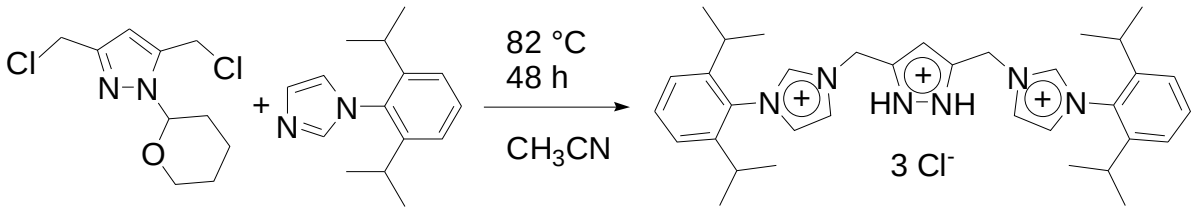
1.2.1.1 3,5-Bis[3-methylimidazolium-1-ylmethyl]-1*H*-pyrazole hydrochloride ($[H_4L^1]Cl_3$)



$C_{10}H_{14}Cl_2N_2O$ 249.14 | $C_4H_6N_2$ 82.10 | $C_{13}H_{19}Cl_3N_6$ 365.69 $[H_4L^1]Cl_3$

A mixture of 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole (6.23 g, 25.0 mmol, 1.0 eq) and 1-methylimidazole (8.21 g, 100 mmol, 4.0 eq) was heated to reflux for 30 minutes. Water (100 mL) and dichloromethane (200 mL) were added to the reaction mixture, phases were separated and the aqueous layer was extracted with dichloromethane (2 × 100 mL). Under reduced pressure water was removed from the aqueous phase, the residue was dried under vacuum. The crude product was then dissolved in ethanol (10 mL) and treated with ethanolic HCl, and the solution was stirred overnight at RT. Addition of diethyl ether (1.0 l) gave a white precipitate, which was collected by filtration, washed with diethyl ether (200 mL) and dried in vacuum at 90 °C. $[H_4L^1]Cl_3$ (5.98 g, 16.4 mmol, 65 %) was obtained as a white solid. M.p. 151 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.86 (s, 6 H, CH_3), 5.50 (s, 4 H, CH_2), 6.51 (s, 1 H, CH^{Pz}), 6.55 (s (br), NH, H_2O), 7.73 (dd, $^3J_{H,H} = {}^4J_{H,H}$ = 1.7 Hz, 2 H, C$H^{Im4/5}$), 7.88 (dd, $^3J_{H,H} = {}^4J_{H,H}$ = 1.7 Hz, 2 H, C$H^{Im4/5}$), 9.48 (dd, $^4J_{H,H}$ = 1.7 Hz, 2 H, CH^{Im2}) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 35.8 (CH_3), 44.2 (CH_2), 105.0 (CH^{Pz}), 122.4 ($CH^{Im4/5}$), 123.7 ($CH^{Im4/5}$), 136.8 (CH^{Im2}), 141.6 (C^{Pz}) ppm; IR (KBr): $\tilde{\nu}$ = 3385 (s), 3199 (vs), 3087 (vs), 3021 (vs), 2934 (s), 2878 (m), 2509 (s, br), 1734 (m), 1638 (s), 1580 (vs), 1561 (vs), 1454 (m), 1416 (m), 1391 (m), 1364 (m), 1346 (m), 1290 (m), 1260 (m), 1213 (m), 1173 (vs), 1093 (m), 1012 (m), 966 (m), 863 (s), 775 (vs) cm^{-1}; MS (FAB$^+$): m/z (%) = 293 (8, $[M\text{-}H\text{-}2Cl]^+$), 257 (27, $[M\text{-}2H\text{-}3Cl]^+$), 175 (100, $[M\text{-}2H\text{-}3Cl\text{-}MeIm]^+$), 83 (20, $[MeIm]^+$); $C_{13}H_{19}Cl_3N_6$ (365.69): calcd.: C 42.70, H 5.24, N 22.98, Cl 29.09; found: C 42.68, H 5.46, N 22.42, Cl 29.10.

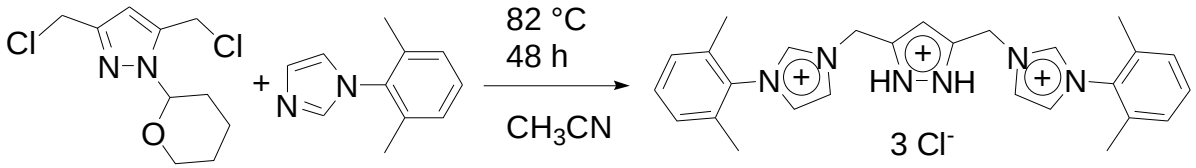
1.2.1.2 3,5-Bis[3-(2,6-diisopropylphenyl)imidazolium-1-ylmethyl]-1*H*-pyrazole hydrochloride ($[H_4L^2]Cl_3$)



$C_{10}H_{14}Cl_2N_2O$ 249.14 | $C_{15}H_{20}N_2$ 228.33 | $C_{35}H_{47}Cl_3N_6$ 658.15 $[H_4L^2]Cl_3$

A solution of 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole (4.98 g, 20.0 mmol, 1.0 eq) and 1-(2,6-diisopropylphenyl)imidazole (13.7 g, 60.0 mmol, 3.0 eq) in acetonitrile (80 mL) was heated to reflux for 48 hours. Afterwards the solvent was removed under reduced pressure and the residue was dissolved in a mixture of water (200 mL) and light petroleum (200 mL). The phases were separated and the aqueous layer was extracted with light petroleum (3 × 100 mL). From the combined organic phases the excess of 1-(2,6-diisopropylphenyl)imidazole could be recovered. Under reduced pressure water was removed from the aqueous phase, the residue was dissolved in ethanol (20 mL) and treated with ethanolic HCl. Precipitation of a white solid was completed by addition of diethyl ether (1.0 l). After filtration and washing with diethyl ether (0.5 l) the product was dried under vacuum at 90 °C. $[H_4L^2]Cl_3$ (11.9 g, 18.1 mmol, 91 %) was obtained as a white solid. M.p. 157 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 1.12 (d, $^3J_{H,H}$ = 6.8 Hz, 24 H, CH_3^{iPr}), 2.24 (sept, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH^{iPr}), 4.31 (s (br), 15 H, N*H*, H_2O), 5.70 (s, 4 H, CH_2), 6.59 (s, 1 H, CH^{Pz}), 7.44 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, C$H^{Ar3,5}$), 7.62 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, CH^{Ar4}), 8.10 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 2 H, C$H^{Im4/5}$), 8.20 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 2 H, C$H^{Im4/5}$), 9.95 (dd, $^4J_{H,H}$ = 1.7 Hz, 2 H, CH^{Im2}) ppm; ^{13}C NMR (125 MHz, DMSO-d$_6$): δ = 23.6 (*C*H$_3^{iPr}$), 23.8 (*C*H$_3^{iPr}$), 28.0 (*C*H^{iPr}), 44.8 (*C*H$_2$), 104.6 (*C*H^{Pz}), 123.3 (*C*H$^{Im4/5}$), 124.3 (*C*H^{Ar3,5}), 125.0 (*C*H$^{Im4/5}$), 130.5 (*C*^{Ar1}), 131.4 (*C*H^{Ar4}), 138.3 (*C*H^{Im2}), 141.6 (*C*^{Pz}), 145.0 (*C*^{Ar2,6}) ppm; IR (KBr): $\tilde{\nu}$ = 3415 (s, br), 3118 (s), 3080 (s), 3015 (s), 2967 (vs), 2934 (s), 2871 (s), 1629 (m), 1561 (s), 1546 (vs), 1460 (s), 1368 (s), 1310 (m), 1186 (vs), 1067 (s), 1000 (m), 807 (s), 760 (s), 671 (m), 629 (m), 556 (m), 460 (m) cm^{-1}; MS (FAB$^+$): m/z (%) = 549 (14, [M-2H-3Cl]$^+$), 321 (100, [M-2H-3Cl-*i*Pr$_2$ArIm]$^+$), 229 (13, [*i*Pr$_2$ArIm]$^+$); $C_{35}H_{47}Cl_3N_6$ (658.15): calcd.: C 63.87, H 7.20, N 12.77; found: C 63.10, H 7.30, N 12.74.

1.2.1.3 3,5-Bis[3-(2,6-dimethylphenyl)imidazolium-1-ylmethyl]-1*H*-pyrazole hydrochloride ($[H_4L^3]Cl_3$)



$C_{10}H_{14}Cl_2N_2O$
249.14

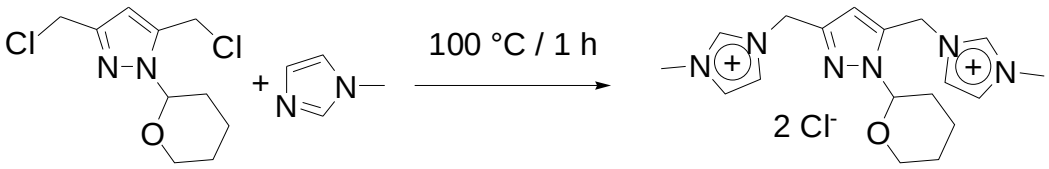
$C_{11}H_{12}N_2$
172.23

$C_{27}H_{31}Cl_3N_6$
545.93
$[H_4L^3]Cl_3$

A solution of 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole (16.9 g, 67.8 mmol, 1.0 eq) and 1-(2,6-dimethylphenyl)imidazole (35.1 g, 204 mmol, 3.0 eq) in acetonitrile (120 mL) was heated to reflux for 48 hours. Afterwards the solvent was removed under reduced pressure and the residue was dissolved in a mixture of water (200 mL) and light petroleum (200 mL). The phases were separated and the aqueous layer was extracted with light petroleum (3 × 150 mL). From the combined organic phases the excess of 1-(2,6-dimethylphenyl)imidazole could be recovered. Under reduced pressure water was removed from the aqueous phase, the residue was dissolved in ethanol (60 mL) and treated with ethanolic HCl. Precipitation of a white solid was completed by addition of diethyl ether (1.5 l). After filtration and washing with diethyl ether (0.5 l) the product was dried under vacuum at 90 °C. $[H_4L^3]Cl_3$ (36.2 g, 66.3 mmol, 98 %) was obtained as a white solid. M.p. 130 °C (decomposition); ^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 2.05 (s, 12 H, C$H_3^{Ar2,6}$), 5.68 (s, 4 H, CH_2), 6.64 (s, 1 H, CH^{Pz}), 6.90 (s (br), 3 H, NH, H_2O), 7.33 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, C$H^{Ar3,5}$), 7.44 (dd, $^3J_{H,H}$ = 7.8 Hz, 2 H, CH^{Ar4}), 8.02 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 2 H, C$H^{Im4/5}$), 8.19 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 2 H, C$H^{Im4/5}$), 9.91 (dd, $^4J_{H,H}$ = 1.7 Hz, 2 H, CH^{Im2}) ppm; ^{13}C NMR (125 MHz, DMSO-d$_6$): δ = 17.0 (*C*H$_3^{Ar2,6}$), 44.8 (*C*H$_2$), 105.0 (*C*H^{Pz}), 123.2 (*C*H$^{Im4/5}$), 123.8 (*C*H$^{Im4/5}$), 128.8 (*C*H^{Ar3,5}), 130.5 (*C*H^{Ar4}), 133.5 (*C*^{Ar1}), 134.6 (*C*^{Ar2,6}), 137.8 (*C*H^{Im2}), 141.6 (*C*^{Pz}) ppm; IR (KBr): $\tilde{\nu}$ = 3397 (vs, br), 3125 (vs), 3079 (vs), 2965 (vs), 2866 (s), 1629 (m), 1604 (m), 1550 (vs), 1475 (s), 1445 (m), 1385 (m), 1366 (m), 1321 (m), 1261 (s), 1193 (vs), 1099 (vs), 1065 (s), 1028 (s), 955 (m), 795 (vs), 664 (s) cm^{-1}; MS (FAB$^+$): m/z (%) = 473 (4, [M-H-2Cl]$^+$), 437 (22, [M-2H-3Cl]$^+$), 265 (100, [M-2H-3Cl-Me$_2$ArIm]$^+$), 173 (21, [Me$_2$ArIm+H]$^+$); $C_{27}H_{31}Cl_3N_6$ (545.93): calcd.: C 59.40, H 5.72, N 15.39, Cl 19.48; found: C 60.02, H 6.03, N 15.23, Cl 18.59.

1.2.2 Ligand precursors $[H_2(THP)L]Cl_2$

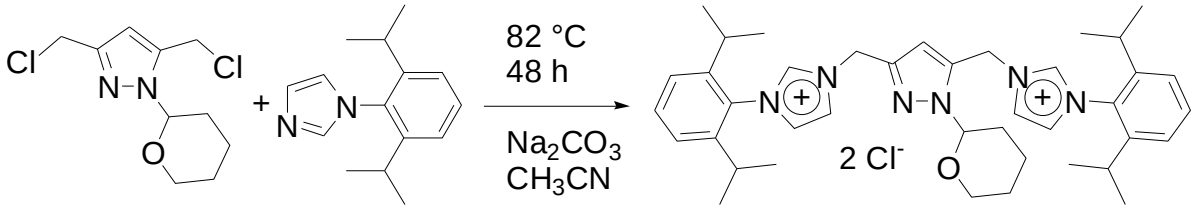
1.2.2.1 3,5-Bis[3-methylimidazolium-1-ylmethyl]-1-(tetrahydropyran-2-yl)pyrazole dichloride ($[H_2(THP)L^1]Cl_2$)



$C_{10}H_{14}Cl_2N_2O$ 249.14 | $C_4H_6N_2$ 82.10 | $C_{18}H_{26}Cl_2N_6O$ 413.34 $[H_2(THP)L^1]Cl_2$

A mixture of 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole (1.99 g, 8.00 mmol, 1.0 eq) and 1-methylimidazole (2.63 g, 32.0 mmol, 4.0 eq) was heated to 100 °C for 60 minutes. The reaction mixture was left to cool to RT and then dichloromethane (100 mL) was added, giving a cloudy yellow solution. After filtration and washing with dichloromethane (50 mL) a white solid could be obtained. Drying under vacuum at RT yielded $[H_2(THP)L^1]Cl_2$ (3.19 g, 7.72 mmol, 96 %) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.48 (m, 2 H, CH_2^{THP}), 1.69 (m, 1 H, CH_2^{THP}), 1.92 (m, 2 H, CH_2^{THP}), 2.18 (m, 1 *H*, CH_2^{THP}), 3.70 (m, 2 H, CH_2^{THP}), 3.90 (s, 6 H, CH_3), 5.45 (s, 2 H, Pz-CH_2), 5.70 (d, $^2J_{H,H}$ = 15.6 Hz, 1 H, Pz-CH_2), 5.76 (dd, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 2.4 Hz, 1 H, CH^{THP}), 5.84 (d, $^2J_{H,H}$ = 15.6 Hz, 1 H, Pz5-CH_2), 6.69 (s, 1 H, CH^{Pz}), 7.78 (m, 2 H, C$H^{Im4/5}$), 7.83 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 1 H, C$H^{Im4/5}$), 7.86 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 1 H, C$H^{Im4/5}$), 9.53 (s, 1 H, CH^{Im2}), 9.66 (m, 1 H, CH^{Im2}) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.5 (*C*H_2^{THP}), 24.4 (*C*H_2^{THP}), 28.5 (*C*H_2^{THP}), 35.6 (*C*H_3), 35.7 (*C*H_3), 42.1 (Pz-*C*H_2), 45.8 (Pz-*C*H_2), 66.2 (*C*H_2^{THP}), 83.6 (*C*H^{THP}), 108.1 (*C*H^{Pz}), 122.3 (*C*H$^{Im4/5}$), 122.4 (*C*H$^{Im4/5}$), 123.4 (*C*H$^{Im4/5}$), 123.6 (*C*H$^{Im4/5}$), 136.7 (*C*H^{Im2}), 137.0 (*C*H^{Im2}), 138.1 (C^{Pz}), 144.8 (C^{Pz}) ppm; IR (KBr): $\tilde{\nu}$ = 3420 (vs, br), 3145 (s), 3082 (vs), 2948 (s), 2863 (s), 2067 (m), 1631 (s), 1570 (vs), 1447 (s), 1384 (m), 1338 (m), 1321 (m), 1291 (m), 1262 (m), 1204 (m), 1167 (vs), 1084 (s), 1059 (m), 1041 (vs), 1007 (s), 939 (m), 916 (s), 883 (m), 847 (s), 817 (m), 766 (s) cm^{-1}; MS (FAB$^+$): m/z (%) = 377 (76, [M-Cl]$^+$), 341 (100, [M-H-2Cl]$^+$), 175 (29, [M-2Cl-THP-MeIm]$^+$); $C_{18}H_{26}Cl_2N_6O$ (413.34): calcd.: C 52.30, H 6.34, N 20.33, Cl 17.15; found: C 52.20, H 6.44, N 20.09, Cl 17.44.

1.2.2.2 3,5-Bis[3-(2,6-diisopropylphenyl)imidazolium-1-ylmethyl]-1-(tetrahydropyran-2-yl)pyrazole dichloride ($[H_2(THP)L^2]Cl_2$)



$C_{10}H_{14}Cl_2N_2O$ 249.14

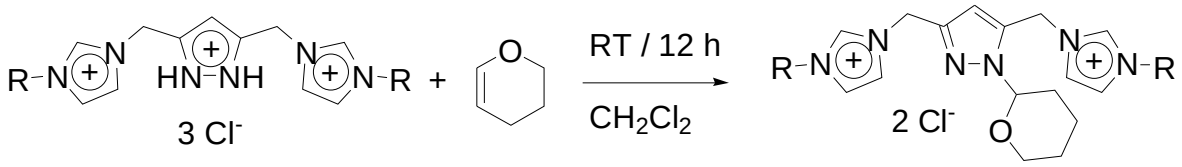
$C_{15}H_{20}N_2$ 228.33

$C_{40}H_{54}Cl_2N_6O$ 705.80 $[H_2(THP)L^2]Cl_2$

A solution of 3,5-bis(chloromethyl)-1-(tetrahydropyran-2-yl)pyrazole (2.49 g, 10.0 mmol, 1.0 eq), 1-(2,6-diisopropylphenyl)imidazole (6.85 g, 30.0 mmol, 3.0 eq) and sodium carbonate (3.18 g, 30.0 mmol, 3.0 eq) in acetonitrile (30 mL) was heated to reflux for 48 hours. The mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in a mixture of water (100 mL) and light petroleum (500 mL). The phases were separated and the aqueous layer was extracted with light petroleum (3 × 100 mL). From the combined organic phases the excess of 1-(2,6-diisopropylphenyl)imidazole could be recovered. Under reduced pressure water was removed from the aqueous phase, and the product was dried under vacuum at RT. $[H_2(THP)L^2]Cl_2$ (5.50 g, 7.79 mmol, 78 %) was obtained as a slightly brownish solid. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.14 (m, 24 H, CH_3^{iPr}), 1.52 (m, 2 H, CH_2^{THP}), 1.71 (m, 1 H, CH_2^{THP}), 1.90 (m, 2 H, CH_2^{THP}), 2.16 (m, 1 *H*, CH_2^{THP}), 2.17 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH^{iPr}), 2.30 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH^{iPr}), 3.71 (m, 2 H, CH_2^{THP}), 5.69 (s, 2 H, Pz-CH_2), 5.87 (dd, $^3J_{H,H}$ = 9.2 Hz, $^3J_{H,H}$ = 2.6 Hz, 1 H, CH^{THP}), 5.91 (d, $J_{H,H}$ = 15.5 Hz, 1 H, Pz-CH_2), 6.07 (d, $J_{H,H}$ = 15.5 Hz, 1 H, Pz-CH_2), 6.82 (s, 1 H, CH^{Pz}), 7.44 (m, 4 H, C$H^{Ar3,5}$), 7.62 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH^{Ar4}), 7.63 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH^{Ar4}), 8.12 (m, 2 H, C$H^{Im4/5}$), 8.19 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 1 H, C$H^{Im4/5}$), 8.24 (dd, $^3J_{H,H}$ = $^4J_{H,H}$ = 1.7 Hz, 1 H, C$H^{Im4/5}$), 9.97 (dd, $^4J_{H,H}$ = 1.7 Hz, 2 H, CH^{Im2}), 10.11 (dd, $^4J_{H,H}$ = 1.7 Hz, 2 H, CH^{Im2}) ppm; ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 23.5 (*C*H$_3^{iPr}$), 27.7 (*C*H^{iPr}), 21.3 (*C*H$_2^{THP}$), 24.4 (*C*H$_2^{THP}$), 28.5 (*C*H$_2^{THP}$), 42.3 (Pz-*C*H$_2$), 46.3 (Pz-*C*H$_2$), 66.0 (*C*H$_2^{THP}$), 83.2 (*C*H^{THP}), 108.0 (*C*H^{Pz}), 123.1 (*C*H$^{Im4/5}$), 123.6 (*C*H$^{Im4/5}$), 124.1 (*m*-*C*$_6$H$_2$), 124.7 (*C*H$^{Im4/5}$), 124.8 (*C*H$^{Im4/5}$), 130.3 (*C*^{Ar1}), 130.4 (*C*^{Ar1}), 131.2 (*C*H^{Ar4}), 137.6 (*C*^{Pz}), 138.1 (*C*H^{Im2}), 138.3 (*C*H^{Im2}), 144.8 (*C*^{Ar2,6}), 144.8 (*C*^{Ar2,6}), 144.8 (*C*^{Ar2,6}), 144.9 (*C*^{Ar2,6}), 144.9 (*C*^{Pz}) ppm; IR (KBr): $\tilde{\nu}$ = 3422 (vs), 3124 (s), 3072 (s), 2965 (vs), 2932 (vs), 2870 (s), 1653 (m), 1628 (m), 1590 (w), 1564 (s), 1546 (s), 1508 (w), 1461 (vs), 1414 (w), 1387 (m), 1367

(s), 1337 (m), 1319 (m), 1291 (w), 1262 (m), 1245 (w), 1203 (s), 1185 (vs), 1149 (w), 1109 (m), 1083 (s), 1070 (s), 1059 (vs), 1041 (vs), 1016 (s), 1007 (s), 958 (w), 937 (w), 917 (m), 885 (m), 849 (m), 808 (s), 760 (s), 671 (m), 629 (w), 555 (m), 520 (w), 459 (w) cm^{-1}; MS (FAB^+): m/z (%) = 669.4 (33, $[M\text{-}Cl]^+$), 633.4 (100, $[M\text{-}H\text{-}2Cl]^+$), 321.2 (34, $[M\text{-}2Cl\text{-}THP\text{-}i Pr_2ArIm]^+$), 229.2 (32, $[iPr_2ArIm+H]^+$); $C_{40}H_{54}Cl_2N_6O$ (705.80): calcd. C 68.07, H 7.71, N 11.91, Cl 10.05; found C 66.12, H 7.85, N 11.68, Cl 10.50.

1.2.2.3 3,5-Bis[3-(2,6-dimethylphenyl)imidazolium-1-ylmethyl]-1-(tetrahydropyran-2-yl)pyrazole dichloride ($[H_2(THP)L^3]Cl_2$)



R = 2,6-Dimethylphenyl

$C_{27}H_{31}Cl_3N_6$	C_5H_8O	$C_{32}H_{38}Cl_2N_6O$
545.93	84.12	593.59
$[H_4L^3]Cl_3$		$[H_2(THP)L^3]Cl_2$

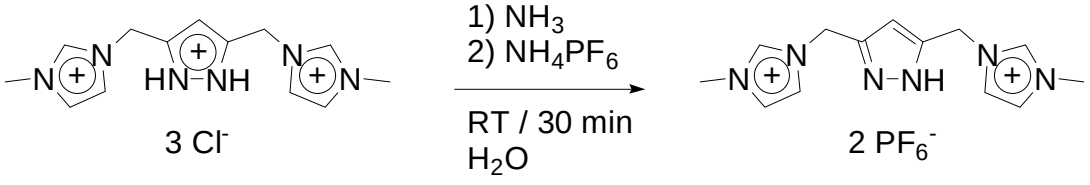
A mixture of $[H_4L^3]Cl_3$ (14.1 g, 25.7 mmol, 1.0 eq) and 3,4-dihydro-2*H*-pyran (6.49 g, 77.2 mmol, 3.0 eq) in dichloromethane (500 mL) was stirred at RT for 12 hours. A solution of sodium carbonate (14.0 g, 132 mmol, 5.1 eq) in water (80 mL) was added, the phases were separated and the organic layer was washed with water (2 × 200 mL). Water was removed from the combined aqueous phases under reduced pressure and the residue was dried under vacuum. The crude product was taken up in absolute acetonitrile. After filtration, the solvent was removed under reduced pressure and the residue dried under vacuum. $[H_2(THP)L^3]Cl_2$ (15.1 g, 25.4 mmol, 99 %) was obtained as a white solid. ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 1.49 (m, 2 H, CH_2^{THP}), 1.74 (m, 1 H, CH_2^{THP}), 1.90 (m, 2 H, CH_2^{THP}), 2.07 (m, 12 H, CH_3), 2.19 (m, 1 *H*, CH_2^{THP}), 3.67 (m, 2 H, CH_2^{THP}), 5.68 (s, 2 H, Pz-CH_2), 5.90 (d, $^2J_{H,H}$ = 15.6 Hz, 1 H, Pz-CH_2), 5.95 (m, 1 H, CH^{THP}), 6.08 (d, $^2J_{H,H}$ = 15.6 Hz, 1 H, Pz-CH_2), 6.84 (s, 1 H, CH^{Pz}), 7.34 (d, $^3J_{H,H}$ = 7.1 Hz, 4 H, C$H^{Ar3,5}$), 7.15 (t, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH^{Ar4}), 8.06 (m, 2 H, C$H^{Im4/5}$), 8.20 (s, 1 H, C$H^{Im4/5}$), 8.24 (s, 1 H, C$H^{Im4/5}$), 9.95 (s, 1 H, CH^{Im2}), 10.15 (s, 1 H, CH^{Im2}) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 16.9 (*C*H$_3$), 16.9 (*C*H$_3$), 21.5 (*C*H$_2^{THP}$), 24.5 (*C*H$_2^{THP}$), 28.6 (*C*H$_2^{THP}$), 42.4 (Pz-*C*H$_2$), 46.4 (Pz-*C*H$_2$), 66.2 (*C*H$_2^{THP}$), 83.3 (*C*H^{THP}), 107.8 (*C*H^{Pz}), 123.1 (*C*H$^{Im4/5}$), 123.6 (*C*H$^{Im4/5}$), 123.6 (*C*H$^{Im4/5}$), 123.6 (*C*H$^{Im4/5}$),

128.7 (CH^{Ar3,5}), 128.7 (CH^{Ar3,5}), 130.4 (CH^{Ar4}), 130.4 (CH^{Ar4}), 133.4 (C^{Ar1}), 133.5 (C^{Ar1}), 134.4 ($C^{Ar2,6}$), 134.5 ($C^{Ar2,6}$), 137.7 (CH^{Im2}), 137.9 (C^{Pz}), 138.0 (CH^{Im2}), 145.1 (C^{Pz}) ppm; IR (KBr): $\tilde{\nu}$ = 3393 (vs), 3123 (s), 3071 (s), 2946 (vs), 2864 (s), 1634 (m), 1564 (s), 1548 (vs), 1510 (m), 1474 (vs), 1447 (s), 1412 (m), 1384 (m), 1364 (m), 1345 (m), 1337 (m), 1321 (m), 1290 (m), 1261 (m), 1190 (vs), 1144 (w), 1101 (s), 1083 (s), 1060 (s), 1041 (vs), 1007 (s), 955 (m), 939 (w), 917 (m), 885 (m), 849 (m), 815 (w), 784 (s), 655 (m), 626 (w), 559 (w), 535 (w) cm^{-1}; MS (FAB$^+$): m/z (%) = 557.4 (34, [M-Cl]$^+$), 521.4 (100, [M-H-2Cl]$^+$), 265.2 (47, [M-2Cl-THP-Me$_2$ArIm]$^+$), 173.1 (32, [Me$_2$ArIm+H]$^+$); $C_{32}H_{38}Cl_2N_6O$ (593.59): calcd. C 64.75, H 6.45, N 14.18, Cl 11.95; found C 62.29, H 6.97, N 12.79, Cl 11.66.

1.2.3 Ligand precursors $[H_3L](PF_6)_2$

General procedure: The minimum amount of water was added to $[H_4L]Cl_3$ (1.0 eq) in order to obtain a clear solution. Ammonium hydroxide (25 %, 3.0 eq) was added and the solution was stirred at RT for some minutes. Then a concentrated solution of ammonium hexafluorophosphate (2.2 eq) in water was added and the reaction mixture was stirred for 30 minutes. The white precipitate formed was collected by filtration, washed with water and dried under vacuum. The residue was dissolved in absolute acetonitrile, filtered again and the solution was evaporated to dryness to give $[H_3L](PF_6)_2$ as an (off-)white solid.

1.2.3.1 3,5-Bis[3-methylimidazolium-1-ylmethyl]-1*H*-pyrazole bishexafluorophosphate ($[H_3L^1](PF_6)_2$)



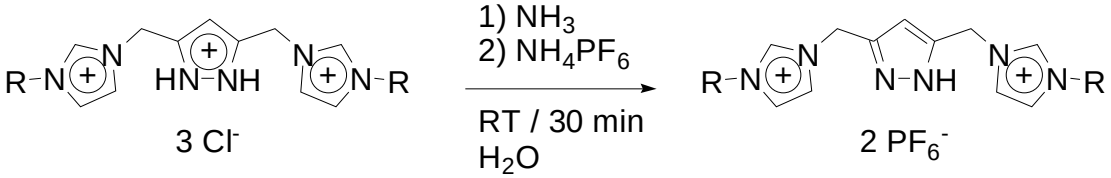
$C_{13}H_{19}Cl_3N_6$
365.69
$[H_4L^1]Cl_3$

$C_{13}H_{18}F_{12}N_6P_2$
548.25
$[H_3L^1](PF_6)_2$

Starting from $[H_4L^1]Cl_3$ (3.00 g, 8.20 mmol) and applying the general procedure, $[H_3L^1](PF_6)_2$ (3.41 g, 6.22 mmol, 76 %) was obtained. M.p. 141 °C (decomposition); ^{1}H-NMR (300 MHz, CD_3CN): δ = 3.83 (s, 6 H, N-CH_3), 5.35 (s, 4 H, Pz-CH_2), 6.51 (s, 1 H, CH^{Pz}), 7.35 (dd, $^3J_{H,H} = {}^4J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4/5}$), 7.38 (dd, $^3J_{H,H} = {}^4J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4/5}$), 8.44 (m,

2 H, C*H*^{Im2}), 11.42 (s (br), 1 H, N*H*) ppm; ^{13}C-NMR (75 MHz, CD_3CN): δ = 37.0 (N-*C*H_3), 45.9 (Pz-*C*H_2), 107.1 (*C*H^{Pz}), 123.3 (*C*H$^{Im4/5}$), 124.9 (*C*H$^{Im4/5}$), 137.1 (*C*H^{Im2}) ppm; IR (KBr): $\tilde{\nu}$ = 3411 (s), 3171 (s), 3136 (m), 3030 (s), 2973 (w), 1632 (w), 1576 (s), 1482 (w), 1460 (w), 1419 (w), 1384 (w), 1338 (s), 1320 (w), 1267 (w), 1231 (w), 1166 (s), 1145 (s), 1118 (w), 1107 (w), 1092 (w), 1027 (w), 1001 (m), 834 (vs), 793 (s), 762 (s), 754 (s), 742 (m), 686 (w), 622 (s), 613 (m), 558 (vs) cm^{-1}; MS (FAB$^+$): m/z (%) = 403.1 (100, [M-PF_6]$^+$), 175.1 (98, [M-H-2PF_6-MeIm]$^+$), 147.0 (15), 73.0 (62); MS (FAB$^-$): m/z (%) = 145 (100, [PF_6]$^-$); $C_{13}H_{18}F_{12}N_6P_2$ (548.25): calcd. C 28.48, H 3.31, N 15.33; found C 28.77, H 3.22, N 15.50.

1.2.3.2 3,5-Bis[3-(2,6-diisopropylphenyl)imidazolium-1-ylmethyl]-1*H*-pyrazole bishexafluorophosphate ($[H_3L^2](PF_6)_2$)



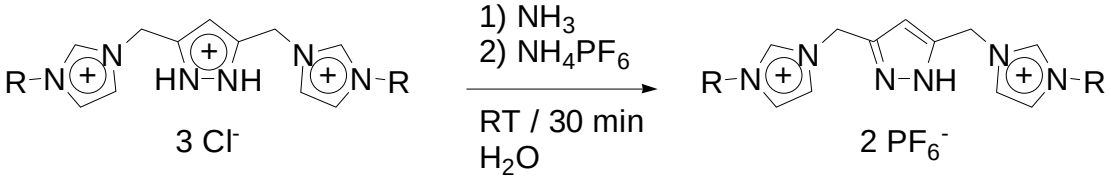
R = 2,6-Diisopropylphenyl

$C_{35}H_{47}Cl_3N_6$	$C_{35}H_{46}F_{12}N_6P_2$
658.15	840.71
$[H_4L^2]Cl_3$	$[H_3L^2](PF_6)_2$

Starting from $[H_4L^2]Cl_3$ (2.20 g, 3.34 mmol) and applying the general procedure, $[H_3L^2](PF_6)_2$ (2.43 g, 2.89 mmol, 87 %) was obtained. M.p. 275 °C (decomposition); ^{1}H-NMR (300 MHz, CD_3CN): δ = 1.13 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3^{iPr}), 1.16 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3^{iPr}), 2.31 (sept, $^3J_{H,H}$ = 6.8 Hz, 4 H, C*H*^{iPr}), 5.53 (s, 4 H, Pz-CH_2), 6.64 (s, 1 H, C*H*^{Pz}), 7.42 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, C*H*^{Ar3,5}), 7.55 (dd, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 2 H, C*H*$^{Im4/5}$), 7.60 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, C*H*^{Ar4}), 7.66 (dd, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 2 H, C*H*$^{Im4/5}$), 8.68 (dd, $^4J_{H,H}$ = 1.6 Hz, 2 H, C*H*^{Im2}), 11.50 (s (br), 1 H, N*H*) ppm; ^{13}C-NMR (75 MHz, CD_3CN): δ = 24.2 (*C*H_3^{iPr}), 29.3 (*C*H^{iPr}), 46.5 (Pz-*C*H_2), 107.3 (*C*H^{Pz}), 124.3 (*C*H$^{Im4/5}$), 125.5 (*C*H^{Ar3,5}), 126.1 (*C*H$^{Im4/5}$), 131.2 (*C*^{Ar1}), 132.8 (*C*H^{Ar4}), 137.8 (*C*H^{Im2}), 142.3 (br, *C*^{Pz}), 146.5 (*C*^{Ar2,6}) ppm; IR (KBr): $\tilde{\nu}$ = 3410 (s), 3162 (m), 3103 (w), 2969 (s), 2935 (m), 2876 (m), 1563 (s), 1553 (s), 1462 (m), 1390 (m), 1369 (m), 1313 (w), 1259 (w), 1185 (s), 1153 (w), 1103 (s), 1073 (s), 1059 (m), 994 (m), 960 (w), 940 (w), 843 (vs), 757 (m), 740 (m), 672 (w), 636 (w), 558 (vs) cm^{-1}; MS (FAB$^+$): m/z (%) = 695.1 (37, [M-PF_6]$^+$), 549.2 (10, [M-H-2PF_6]$^+$), 389.0

(8), 367.0 (10), 339.0 (18), 321.0 (100, [M-H-2Cl-*i*Pr$_2$ArIm]$^+$), 228.9 (16, [*i*Pr$_2$ArIm+H]$^+$), 138 (10); MS (FAB$^-$): m/z (%) = 144.7 (100, [PF$_6$]$^-$); $C_{35}H_{46}F_{12}N_6P_2$ (840.71): calcd. C 50.00, H 5.52, N 10.00; found C 50.06, H 5.25, N 10.50.

1.2.3.3 3,5-Bis[3-(2,6-dimethylphenyl)imidazolium-1-ylmethyl]-1*H*-pyrazole bishexafluorophosphate ([H$_3$L^3](PF$_6$)$_2$)



R = 2,6-Dimethylphenyl

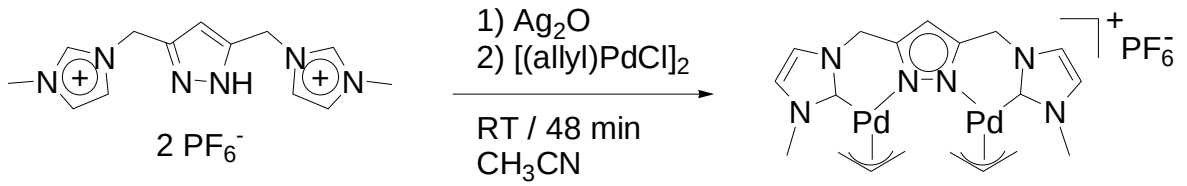
$C_{27}H_{31}Cl_3N_6$	$C_{27}H_{30}F_{12}N_6P_2$
545.93	728.50
[H$_4$L^3]Cl$_3$	[H$_3$L^3](PF$_6$)$_2$

Starting from [H$_4$L^3]Cl$_3$ (1.09 g, 2.00 mmol) and applying the general procedure, [H$_3$L^3](PF$_6$)$_2$ (1.44 g, 1.98 mmol, 99 %) was obtained. M.p. 227 °C (decomposition); ^{1}H-NMR (300 MHz, CD_3CN): δ = 2.06 (s, 12 H, C*H*$_3^{Me}$), 5.52 (s, 4 H, Pz-C*H*$_2$), 6.63 (s, 1 H, C*H*^{Pz}), 7.30 (m, 4 H, C*H*^{Ar3,5}), 7.43 (m, 2 H, C*H*^{Ar4}), 7.49 (dd, $^3J_{H,H} = {}^4J_{H,H} = 1.8$ Hz, 2 H, C*H*$^{Im4/5}$), 7.67 (dd, $^3J_{H,H} = {}^4J_{H,H} = 1.8$ Hz, 2 H, C*H*$^{Im4/5}$), 8.66 (dd, $^4J_{H,H} = 1.6$ Hz, 2 H, C*H*^{Im2}), 11.76 (s (br), 1 H, N*H*) ppm; ^{13}C-NMR (75 MHz, CD_3CN): δ = 17.4 (*C*H$_3^{Me}$), 46.5 (Pz-*C*H$_2$), 107.3 (*C*H^{Pz}), 124.3 (*C*H$^{Im4/5}$), 125.0 (*C*H$^{Im4/5}$), 129.9 (*C*H^{Ar3,5}), 132.0 (*C*^{Ar4}), 134.3 (*C*H^{Ar1}), 136.1 (*C*^{Ar2,6}), 137.4 (*C*H^{Im2}), 142.3 (br, *C*^{Pz}) ppm; IR (KBr): $\tilde{\nu}$ = 3410 (s), 3163 (s), 3105 (w), 3032 (w), 2985 (w), 2931 (w), 2874 (w), 1552 (s), 1477 (m), 1388 (w), 1370 (w), 1192 (s), 1103 (m), 1067 (m), 1035 (m), 998 (m), 957 (m), 838 (vs), 788 (s), 761 (s), 740 (m), 664 (m), 623 (w), 558 (vs) cm^{-1}; MS (FAB$^+$): m/z (%) = 583.1 (48, [M-PF$_6$]$^+$), 437.1 (7, [M-H-2PF$_6$]$^+$), 265.0 (100, [M-H-2PF$_6$-Me$_2$ArIm]$^+$), 173.0 (21, [Me$_2$ArIm+H]$^+$); MS (FAB$^-$): m/z (%) = 145 (100, [PF$_6$]$^-$); $C_{27}H_{30}F_{12}N_6P_2$ (728.50): calcd. C 44.51, H 4.15, N 11.54; found C 44.60, H 4.19, N 11.63.

1.2.4 Palladium complexes $[(allyl)_2Pd_2L](PF_6)$ (1) and $[(methallyl)_2Pd_2L](PF_6)$ (2)

General procedure: A mixture of the ligand precursor $[H_3L](PF_6)_2$ (1.0 eq) and silver(I)oxide (2.5 eq) in acetonitrile (approx. 20 mL per mmol $[H_3L](PF_6)_2$) was stirred under exclusion of light at RT for 24 hours. Activated charcoal was added and the mixture was filtered over Celite® 545. The solvent was removed from the filtrate and the brownish crude product was dried under vacuum. This product was used without further purification. It was dissolved in acetonitrile and a solution of allylpalladium(II) chloride dimer or methallylpalladium(II) chloride dimer in acetonitrile was added (2.0 eq). This mixture was again stirred under exclusion of light at RT for 24 hours and then filtered using activated charcoal and Celite® 545. Most of the solvent was removed from the filtrate, the remaining concentrated solution was poured into diethyl ether and the precipitate that formed was collected by filtration and dried under vacuum yielding $[(allyl)_2Pd_2L](PF_6)$ (**1a-c**) or $[(methallyl)_2Pd_2L](PF_6)$ (**2c**). Crystalline material could be obtained at RT by diffusion of diethyl ether into acetonitrile solutions of the corresponding complexes.

1.2.4.1 $[(allyl)_2Pd_2L^1](PF_6)$ (**1a**)



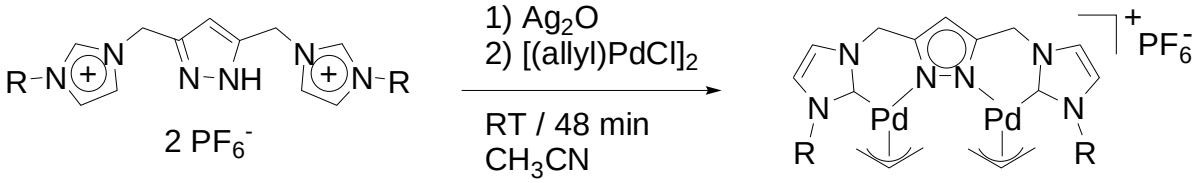
$C_{13}H_{18}F_{12}N_6P_2$
548.25
$[H_3L^1](PF_6)_2$

$C_{19}H_{25}F_6N_6PPd_2$
695.25
1a

Following the general procedure, **1a** (706 mg, 1.02 mmol, 94 %) was obtained as a white solid. M.p.150 °C (decomposition); ^{1}H-NMR (500 MHz, CD_3CN): δ = 2.49 (d, J = 12.3 Hz, 2 H, C$H_2^{anti\text{-allyl, }cis\text{ to carbene, B}}$), 2.67 (d, J = 12.1 Hz, 2 H, C$H_2^{anti\text{-allyl, }cis\text{ to carbene, A}}$), 3.12 (d, $^3J_{H,H}$ = 13.8 Hz, 4 H, C$H_2^{anti\text{-allyl, }trans\text{ to carbene, A, B}}$), 3.77 (s, 6 H, N-C$H_3^{B}$), 3.79 (s, 6 H, N-C$H_3^{A}$), 3.82 (ddd, $^3J_{H,H}$ = 7.0 Hz, J = 2.2 Hz, J = 2.2 Hz, 2 H, C$H_2^{syn\text{-allyl, }cis\text{ to carbene, A}}$), 3.90 (ddd, $^3J_{H,H}$ = 7.0 Hz, J = 2.2 Hz, J = 2.2 Hz, 2 H, C$H_2^{syn\text{-allyl, }cis\text{ to carbene, B}}$), 4.26 (dd, $^3J_{H,H}$ = 7.6 Hz, J = 2.2 Hz, 2 H, C$H_2^{syn\text{-allyl, }trans\text{ to carbene, A}}$), 4.34 (dd, $^3J_{H,H}$ = 7.6 Hz, J = 2.2 Hz, 2 H, C$H_2^{syn\text{-allyl, }trans\text{ to carbene, B}}$), 5.00 (d, $^2J_{H,H}$ = 15.4 Hz, 2 H, Pz-CH_2^{A}), 5.09 (d,

$^{2}J_{H,H}$ = 15.4 Hz, 2 H, Pz-CH_2^{B}), 5.11 (d, $^{2}J_{H,H}$ = 15.4 Hz, 2 H, Pz-CH_2^{A}), 5.14 (d, $^{2}J_{H,H}$ = 15.4 Hz, 2 H, Pz-CH_2^{B}), 5.46 (dddd, $^{3}J_{H,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 12.3 Hz, $^{3}J_{H,H}$ = 7.6 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 2 H, C$H^{allyl, A}$), 5.59 (dddd, $^{3}J_{H,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 12.3 Hz, $^{3}J_{H,H}$ = 7.6 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 2 H, C$H^{allyl, B}$), 6.30 (s, 1 H, C$H^{Pz, A}$), 6.33 (s, 1 H, C$H^{Pz, B}$), 7.12 (d, $^{3}J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4, A}$), 7.13 (d, $^{3}J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4, B}$), 7.24 (d, $^{3}J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im5, A}$), 7.26 (d, $^{3}J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im5, B}$) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ = 38.9 (N-CH_3), 39.0 (N-CH_3), 47.8 ($CH_2^{allyl,\ cis\ to\ carbene}$), 48.1 ($CH_2^{allyl,\ cis\ to\ carbene}$), 48.4 (Pz-$CH_2$), 48.4 (Pz-$CH_2$), 70.8 ($CH_2^{allyl,\ trans\ to\ carbene}$), 71.5 ($CH_2^{allyl,\ trans\ to\ carbene}$), 102.3 (C$H^{Pz}$), 102.4 (C$H^{Pz}$), 118.4 (C$H^{allyl}$), 118.6 (C$H^{allyl}$), 122.5 (C$H^{Im4/5}$), 122.6 (C$H^{Im4/5}$), 123.0 (C$H^{Im4/5}$), 123.2 (C$H^{Im4/5}$), 145.8 ($C^{Pz}$), 145.9 ($C^{Pz}$), 177.2 ($C^{Im2}$) ppm; IR (KBr): $\tilde{\nu}$ = 3436 (m), 3165 (m), 3160 (m), 2962 (w), 2917 (w), 1635 (w), 1567 (w), 1521 (w), 1487 (w), 1465 (m), 1447 (w), 1404 (m), 1375 (w), 1351 (w), 1336 (w), 1302 (m), 1246 (m), 1185 (w), 1153 (w), 1128 (w), 1086 (w), 1073 (w), 1041 (w), 1034 (w), 1013 (w), 959 (m), 904 (m), 847 (vs), 823 (s), 792 (m), 779 (m), 745 (m), 730 (m), 662 (m), 558 (vs), 495 (w) cm^{-1}; MS (ESI$^+$, CH_3CN): m/z (%) = 551.0 (100, [M-PF_6]$^+$), 535.0 (27, [M-PF_6-CH_3]$^+$), 508.9 (64, [M-PF_6-C_3H_5]$^+$), 428.9 (45, [M-PF_6-Pd-CH_3]$^+$), 321.0 (12, [M-PF_6-allyl-Pd-MeIm]$^+$), 146.9 (96, [allylPd]$^+$); MS (ESI$^-$, CH_3CN): m/z (%) = 144.9 (100, [PF_6]$^-$); HRMS calcd. for $C_{19}H_{25}N_6Pd_2$ ([M-PF_6]$^+$): 545.02155, found 545.02148; $C_{19}H_{25}F_6N_6PPd_2 \cdot CH_3CN$ (695.25): calcd. C 34.26, H 3.93, N 13.32; found C 34.43, H 3.93, N 13.44.

1.2.4.2 [(allyl)$_2$Pd$_2$L^2](PF_6) (**1b**)

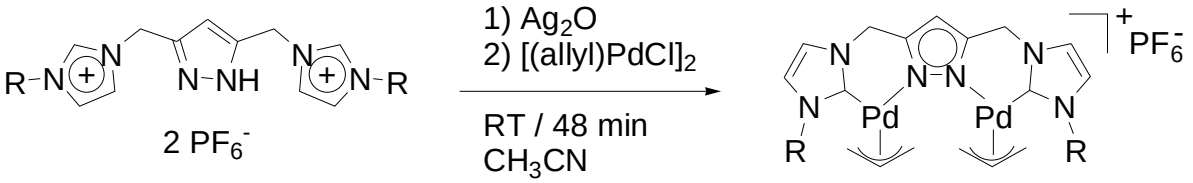


$C_{35}H_{46}F_{12}N_6P_2$	$C_{41}H_{53}F6N_6PPd_2$
840.71	987.70
$[H_3L^2](PF_6)_2$	**1b**

Following the general procedure, **1b** (178 mg, 0.18 mmol, 76 %) was obtained as a slightly yellow solid. M.p.135 °C (decomposition); ^{1}H-NMR (500 MHz, CD_3CN): δ = 0.94 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{iPr, A}$), 1.05 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{iPr, B}$), 1.07 (d, $^{3}J_{H,H}$ = 6.8 Hz,

6 H, C$H_3^{i\mathrm{Pr,\,B}}$), 1.15 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{i\mathrm{Pr,\,A}}$), 1.17 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{i\mathrm{Pr,\,A}}$), 1.20 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{i\mathrm{Pr,\,A}}$), 1.22 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{i\mathrm{Pr,\,B}}$), 1.23 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, C$H_3^{i\mathrm{Pr,\,B}}$), 1.87 (d, J = 12.1 Hz, 2 H, CH_2 *anti*-allyl, *cis* to carbene, B), 2.03 (d, J = 12.1 Hz, 2 H, CH_2 *anti*-allyl, *cis* to carbene, A), 2.14 (dd, $^3J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.9 Hz, 2 H, CH_2 *syn*-allyl, *cis* to carbene, A), 2.38 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C$H^{i\mathrm{Pr,\,A}}$), 2.51 (m, 2 H, C$H^{i\mathrm{Pr,\,B}}$), 2.51 (m, 2 H, CH_2 *syn*-allyl, *cis* to carbene, B), 2.63 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C$H^{i\mathrm{Pr,\,A}}$), 2.63 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C$H^{i\mathrm{Pr,\,B}}$), 2.85 (d, $^3J_{H,H}$ = 13.4 Hz, 2 H, CH_2 *anti*-allyl, *trans* to carbene, B), 2.98 (d, $^3J_{H,H}$ = 13.4 Hz, 2 H, CH_2 *anti*-allyl, *trans* to carbene, A), 4.03 (dd, $^3J_{H,H}$ = 7.4 Hz, J = 2.2 Hz, 2 H, CH_2 *syn*-allyl, *trans* to carbene, B), 4.19 (dd, $^3J_{H,H}$ = 7.4 Hz, J = 2.2 Hz, 2 H, CH_2 *syn*-allyl, *trans* to carbene, A), 5.03 (m, 4 H, C$H^{\mathrm{allyl,\,A,\,B}}$), 5.24 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, CH_2^{B}), 5.33 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, CH_2^{B}), 5.34 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, CH_2^{A}), 5.39 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, CH_2^{A}), 6.46 (s, 1 H, C$H^{\mathrm{Pz,\,B}}$), 6.50 (s, 1 H, C$H^{\mathrm{Pz,\,A}}$), 7.28 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{\mathrm{Im4,\,A}}$), 7.39 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{\mathrm{Im4,\,B}}$), 7.36 (m, 8 H, C$H^{\mathrm{Ar3,5,\,A,\,B}}$), 7.48 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{\mathrm{Im5,\,B}}$), 7.51 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{\mathrm{Im5,\,A}}$), 7.53 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, C$H^{\mathrm{Ar4,\,B}}$), 7.54 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, C$H^{\mathrm{Ar4,\,A}}$) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ = 23.1 (*C*$H_3^{i\mathrm{Pr,\,A}}$), 23.1 (*C*$H_3^{i\mathrm{Pr,\,B}}$), 23.2 (*C*$H_3^{i\mathrm{Pr,\,A}}$), 23.2 (*C*$H_3^{i\mathrm{Pr,\,B}}$), 25.0 (*C*$H_3^{i\mathrm{Pr,\,A}}$), 25.4 (*C*$H_3^{i\mathrm{Pr,\,B}}$), 25.5 (*C*$H_3^{i\mathrm{Pr,\,B}}$), 25.7 (*C*$H_3^{i\mathrm{Pr,\,A}}$), 29.0 (*C*$H^{i\mathrm{Pr,\,B}}$), 29.1 (*C*$H^{i\mathrm{Pr,\,A}}$), 29.1 (*C*$H^{i\mathrm{Pr,\,A,\,B}}$), 47.7 (*C*$H_2^{\mathrm{allyl,}}$ *cis* to carbene, A), 48.9 (Pz-*C*H_2^{B}), 49.0 (Pz-*C*H_2^{A}), 49.2 (*C*$H_2^{\mathrm{allyl,}}$ *cis* to carbene, B), 70.6 (*C*$H_2^{\mathrm{allyl,}}$ *trans* to carbene, B), 72.6 (*C*$H_2^{\mathrm{allyl,}}$ *trans* to carbene, A), 102.9 (*C*$^{\mathrm{Pz,\,B}}$), 103.3 (*C*$^{\mathrm{Pz,\,A}}$), 117.9 (*C*$H^{\mathrm{allyl,\,A}}$), 118.0 (*C*$H^{\mathrm{allyl,\,B}}$), 123.0 (*C*$H^{\mathrm{Im5,\,B}}$), 123.2 (*C*$H^{\mathrm{Im5,\,A}}$), 124.5 (*C*$H^{\mathrm{Ar3,5,\,A}}$), 124.7 (*C*$H^{\mathrm{Ar3,5,\,B}}$), 124.7 (*C*$H^{\mathrm{Ar3,5,\,B}}$), 124.8 (*C*$H^{\mathrm{Ar3,5,\,A}}$), 124.9 (*C*$H^{\mathrm{Im4,\,B}}$), 125.0 (*C*$H^{\mathrm{Im4,\,A}}$), 131.2 (*C*$H^{\mathrm{Ar4,\,A,\,B}}$), 137.5 (*C*$^{\mathrm{Ar1,\,A,\,B}}$), 146.3 (*C*$^{\mathrm{Ar2,6,\,A}}$), 146.3 (*C*$^{\mathrm{Ar2,6,\,B}}$), 146.3 (*C*$^{\mathrm{Ar2,6,\,A}}$), 146.5 (*C*$^{\mathrm{Ar2,6,\,B}}$), 146.9 (*C*$^{\mathrm{Pz,\,B}}$), 147.3 (*C*$^{\mathrm{Pz,\,A}}$), 178.9 (*C*$^{\mathrm{Im2,\,A}}$), 179.1 (*C*$^{\mathrm{Im2,\,B}}$) ppm; IR (KBr): $\tilde{\nu}$ = 3436 (m), 3176 (w), 3149 (w), 3072 (w), 2963 (s), 2928 (m), 2869 (m), 1624 (w), 1469 (m), 1460 (m), 1416 (m), 1406 (m), 1384 (w), 1362 (w), 1324 (w), 1287 (m), 1258 (w), 1232 (w), 1184 (w), 1121 (w), 1107 (w), 1077 (w), 1058 (w), 1041 (w), 1021 (w), 960 (w), 936 (w), 845 (vs), 805 (m), 791 (m), 776 (m), 761 (m), 740 (m), 685 (w), 558 (s), 499 (w) cm^{-1}; MS (ESI$^+$, CH_3CN): m/z (%) = 843.2 (100, $[M\text{-}PF_6]^+$); MS (ESI$^-$, CH_3CN): m/z (%) = 145.0 (100, $[PF_6]^-$); HRMS calcd. for $C_{41}H_{53}N_6Pd_2$ ($[M\text{-}PF_6]^+$): 837.24065, found 837.24121; $C_{41}H_{53}F6N_6PPd_2$ (987.70): calcd. C 49.86, H 5.41, N 8.51; found C 48.88, H 5.39, N 9.29.

1.2.4.3 $[(allyl)_2Pd_2L^3](PF_6)$ (**1c**)



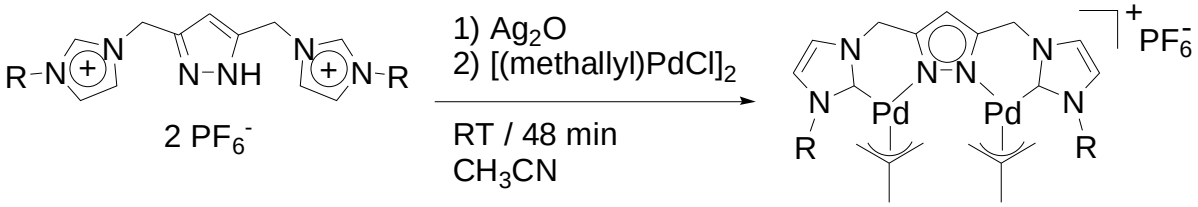
R = 2,6-Dimethylphenyl

$C_{27}H_{30}F_{12}N_6P_2$	$C_{33}H_{37}F_6N_6PPd_2$
728.50	875.49
$[H_3L^3](PF_6)_2$	**1c**

Following the general procedure, **1c** (84.0 mg, 95.9 µmol, 60 %) was obtained as a white solid. M.p.170 °C (decomposition); ^{1}H-NMR (500 MHz, CD_3CN): δ = 1.83 (d, $^3J_{H,H}$ = 12.3 Hz, 2 H, C$H_2^{anti\text{-allyl, }cis\text{ to carbene, B}}$), 1.92 (s, 9 H, C$H_3^{Me, A}$), 2.05 (d, $^3J_{H,H}$ = 12.3 Hz, 2 H, C$H_2^{anti\text{-allyl, }cis\text{ to carbene, A}}$), 2.06 (s, 6 H, C$H_3^{Me, B}$), 2.07 (s, 6 H, C$H_3^{Me, B}$), 2.16 (s, 3 H, C$H_3^{Me, A}$), 2.30 (dd, $^3J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.9 Hz, 2 H, C$H_2^{syn\text{-allyl, }cis\text{ to carbene, A}}$), 2.61 (dd, $^3J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.9 Hz, 2 H, C$H_2^{syn\text{-allyl, }cis\text{ to carbene, B}}$), 2.83 (d, $^3J_{H,H}$ = 13.8 Hz, 2 H, C$H_2^{anti\text{-allyl, }trans\text{ to carbene, B}}$), 2.95 (d, $^3J_{H,H}$ = 13.8 Hz, 2 H, C$H_2^{anti\text{-allyl, }trans\text{ to carbene, A}}$), 3.95 (dd, $^3J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 2.3 Hz, 2 H, C$H_2^{syn\text{-allyl, }trans\text{ to carbene, B}}$),4.05 (dd, $^3J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 2.3 Hz, 2 H, C$H_2^{syn\text{-allyl, }trans\text{ to carbene, A}}$), 5.00 (ddddd, $^3J_{H,H}$ = 13.8 Hz, $^3J_{H,H}$ = 12.3 Hz, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, C$H^{allyl, A, B}$), 5.21 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, Pz-CH_2^B), 5.30 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, Pz-CH_2^B), 5.31 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, Pz-CH_2^A), 5.34 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, Pz-CH_2^A), 6.44 (s, 1 H, C$H^{Pz, B}$), 6.47 (s, 1 H, C$H^{Pz, A}$), 7.17 (d, $^3J_{H,H}$ = 1.8 Hz, 4 H, C$H^{Im4, A}$), 7.17 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4, B}$), 7.25 (m, 8 H, C$H^{Ar3,5, A, B}$), 7.34 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, C$H^{Ar4, A}$), 7.36 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, C$H^{Ar4, B}$), 7.49 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im5, B}$), 7.51 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im5, A}$) ppm; ^{13}C-NMR (125 MHz, CD_3CN): δ = 17.7 (C$H_3^{Me, A}$), 18.0 (C$H_3^{Me, B}$), 18.1 (C$H_3^{Me, A, B}$), 46.9 (C$H_2^{allyl,\ cis\ to\ carbene, A}$), 48.0 (C$H_2^{allyl,\ cis\ to\ carbene, B}$), 48.8 (Pz-C$H_2^B$), 48.9 (Pz-C$H_2^A$), 70.0 (C$H_2^{allyl,\ trans\ to\ carbene, B}$), 71.3 (C$H_2^{allyl,\ trans\ to\ carbene, A}$), 102.7 (C$^{Pz, B}$), 102.8 (C$^{Pz, A}$), 118.2 (C$H^{allyl, A/B}$), 118.4 (C$H^{allyl, A/B}$), 122.5 (C$H^{Im4, B}$), 122.6 (C$H^{Im4, A}$), 123.6 (C$H^{Im5, B}$), 123.8 (C$H^{Im5, A}$), 129.0 (C$H^{Ar3,5, A/B}$), 129.2 (C$H^{Ar3,5, A/B}$), 129.2 (C$H^{Ar3,5, A/B}$), 129.3 (C$H^{Ar3,5, A/B}$), 130.3 (C$H^{Ar4, B}$), 130.4 (C$H^{Ar4, A}$), 136.5 (C$^{Ar2,6, A/B}$), 136.6 (C$^{Ar2,6, A/B}$), 136.7 (C$^{Ar2,6, A/B}$), 139.9 (C$^{Ar1, B}$), 140.0 (C$^{Ar1, A}$), 146.1 (C$^{Pz, B}$), 146.1 (C$^{Pz, A}$), 178.0 (C$^{Im2, A}$), 178.2 (C$^{Im2, B}$) ppm; IR (KBr): $\tilde{\nu}$ = 3443 (s), 3167 (w), 3140 (w), 3077 (w), 2965 (w), 2921 (w), 2863 (w), 1640 (m), 1485 (m), 1458 (w), 1406 (m), 1383 (w), 1362 (w), 1349 (w), 1320 (w), 1290 (m), 1262 (w), 1246 (w), 1189

(w), 1114 (m), 1075 (w), 1038 (m), 1020 (w), 958 (w), 843 (vs), 784 (m), 739 (m), 683 (m), 623 (w), 557 (s), 498 (w) cm^{-1}; MS (ESI^+, CH_3CN): m/z (%) = 731.0 (100, $[M\text{-}PF_6]^+$), 689.0 (6, $[M\text{-}PF_6\text{-}C_3H_6]^+$), 519.0 (20, $[M\text{-}PF_6\text{-}C_3H_5\text{-}Me_2ArIm]^+$), 411.0 (7), 265.2 (11), 219.2 (10), 173.1 (17, $[Me_2ArIm+H]^+$); MS (ESI^-, CH_3CN): m/z (%) = 145.0 (100, $[PF_6]^-$); HRMS calcd. for $C_{33}H_{37}N_6Pd_2$ ($[M\text{-}PF_6]^+$): 725.11512, found 725.11545; $C_{33}H_{37}F_6N_6PPd_2 \cdot 0.5\ CH_3CN$ (875.49): calcd. C 45.58, H 4.33, N 10.16; found C 45.10, H 4.34, N 10.50.

1.2.4.4 [(methallyl)$_2$Pd$_2$L^3](PF$_6$) (**2c**)



$C_{27}H_{30}F_{12}N_6P_2$
728.50
$[H_3L^3](PF_6)_2$

$C_{35}H_{41}F_6N_6PPd_2$
903.54
2c

Following the general procedure, **2c** (142 mg, 0.16 mmol, 86 %) was obtained as a yellow solid. M.p.130 °C (decomposition); ^{1}H-NMR (500 MHz, CD_3CN): δ = 1.52 (s, 6 H, C$H_3^{allyl, A}$), 1.60 (s, 6 H, C$H_3^{allyl, B}$), 1.70 (d, J = 1.6 Hz, 2 H, C$H_2^{anti\text{-}allyl,\ cis\ to\ carbene, B}$), 1.85 (d, J = 1.6 Hz, 2 H, C$H_2^{anti\text{-}allyl,\ cis\ to\ carbene, A}$), 2.03 (s, 6 H, C$H_3^{Me, B}$), 2.06 (s, 12 H, C$H_3^{Me, A}$), 2.12 (s, 6 H, C$H_3^{Me, B}$), 2.54 (dd, J = 3.0 Hz, J = 1.6 Hz, 2 H, C$H_2^{syn\text{-}allyl,\ cis\ to\ carbene, A}$), 2.63 (m, 2 H, C$H_2^{anti\text{-}allyl,\ trans\ to\ carbene, B}$), 2.66 (dd, J = 3.0 Hz, J = 1.6 Hz, 2 H, C$H_2^{syn\text{-}allyl,\ cis\ to\ carbene, B}$), 2.80 (m, 2 H, C$H_2^{anti\text{-}allyl,\ trans\ to\ carbene, A}$), 3.65 (d, J = 3.0 Hz, 2 H, C$H_2^{syn\text{-}allyl,\ trans\ to\ carbene, A}$), 3.66 (d, J = 3.0 Hz, 2 H, C$H_2^{syn\text{-}allyl,\ trans\ to\ carbene, B}$), 5.17 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, Pz-CH_2^B), 5.21 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, Pz-CH_2^A), 5.27 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, Pz-CH_2^B), 5.28 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, Pz-CH_2^A), 6.42 (s, 1 H, C$H^{Pz, B}$), 6.43 (s, 1 H, C$H^{Pz, A}$), 7.16 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4, A}$), 7.16 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, C$H^{Im4, B}$), 7.24 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, C$H^{Ar3,5, A}$), 7.26 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, C$H^{Ar3,5, B}$), 7.34 (dd, $^3J_{H,H}$ = 7.6 Hz, 2 H, C$H^{Ar4, B}$), 7.35 (dd, $^3J_{H,H}$ = 7.6 Hz, 2 H, C$H^{Ar4, A}$), 7.48 (d, $^3J_{H,H}$ = 1.9 Hz, 2 H, C$H^{Im5, B}$), 7.49 (d, $^3J_{H,H}$ = 1.9 Hz, 2 H, C$H^{Im5, A}$); ^{13}C-NMR (125 MHz, CD_3CN): δ = 18.0 (*C*$H_3^{Me, B}$), 18.1 (*C*$H_3^{Me, A}$), 18.2 (*C*$H_3^{Me, A}$), 18.4 (*C*$H_3^{Me, B}$), 23.7 (*C*$H_3^{allyl, A}$), 23.9 (*C*$H_3^{allyl, B}$), 48.8 (Pz-*C*$H_2^{A, B}$), 49.5 (*C*$H_2^{allyl,\ cis\ to\ carbene, A}$), 50.3 (*C*$H_2^{allyl,\ cis\ to\ carbene, B}$), 66.0 (*C*$H_2^{allyl,\ trans\ to\ carbene, B}$),

66.9 ($CH_2^{allyl,\ trans\ to\ carbene,\ A}$), 102.7 ($C^{Pz,\ B}$), 102.8 ($C^{Pz,\ A}$), 122.5 ($CH^{Im4,\ A,\ B}$), 123.3 ($CH^{Im5,\ B}$), 123.4 ($CH^{Im5,\ A}$), 129.2 ($CH^{Ar3,5,\ B}$), 129.2 ($CH^{Ar3,5,\ A}$), 130.3 ($CH^{Ar4,\ A,\ B}$), 133.0 ($CH^{Ar1,\ B}$), 133.4 ($CH^{Ar4,\ A}$), 136.5 ($C^{Ar2,6,\ A}$), 136.5 ($C^{Ar2,6,\ B}$), 136.6 ($C^{Ar2,6,\ B}$), 136.7 ($C^{Ar2,6,\ A}$), 139.9 ($C^{allyl,\ A}$), 140.0 ($C^{allyl,\ B}$), 146.3 ($C^{Pz,\ A}$), 146.4 ($C^{Pz,\ B}$), 178.8 ($C^{Im2,\ A}$), 178.9 ($C^{Im2,\ B}$) ppm; IR (KBr): $\tilde{\nu}$ = 3434 (s), 3171 (m), 3142 (m), 3064 (w), 2964 (m), 2924 (m), 2866 (w), 1603 (m), 1484 (s), 1454 (s), 1416 (m), 1407 (s), 1384 (m), 1350 (w), 1326 (w), 1292 (m), 1262 (m), 1245 (w), 1189 (w), 1169 (w), 1114 (m), 1080 (w), 1033 (m), 959 (m), 843 (vs), 781 (s), 739 (s), 682 (m), 623 (w), 558 (vs) cm^{-1}; MS (ESI^+, CH_3CN): m/z (%) = 759.0 (100, $[M\text{-}PF_6]^+$); MS (ESI^-, CH_3CN): m/z (%) = 144.9 (100, $[PF_6]^-$); HRMS calcd. for $C_{35}H_{41}N_6Pd_2$ ($[M\text{-}PF_6]^+$): 753.14675, found 753.14589; $C_{35}H_{41}F_6N_6PPd_2$ (903.54): calcd. C 46.52, H 4.57, N 9.30; found C 44.59, H 4.58, N 8.94.

2 X-ray crystallography

The crystal data and details of the data collections for $[H_3L^2]Cl_2$, $[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$, **1a, 1b, 1c** and **2c** are given in Tables S1 and S2. X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å) by use of ω scans at –140 °C. The structures were solved by direct methods and refined on F^2 using all reflections with SHELX-97.[4,5] Most non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 $Å^2$. The positional and isotropic thermal parameters of the imidazolium-C^2 bound hydrogen atoms in $[H_3L^2](PF_6)_2$ and $[H_3L^3](PF_6)_2$, and the nitrogen-bound hydrogen-atom in $[H_3L^3](PF_6)_2$ were refined without any restraints or constraints. The PF_6^- anions in $[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$, **1b** and **1c** are disordered. SADI and FLAT restraints and in most cases EADP constraints ($[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$, **1b**) were used to control the geometry and displacement parameters. In all H_3L ($[H_3L^2]Cl_2$, $[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$) the central pyrazole moiety is disordered about a special position ($[H_3L^2]Cl_2$, $[H_3L^2](PF_6)_2$: inversion center; $[H_3L^3](PF_6)_2$: two-fold axis) and was refined at half occupancy. A SADI restraint (d(C1–C2/C3)) was used to model the disorder in $[H_3L^2](PF_6)_2$. The allyl ligands in the Pd-containing compounds **1a** and **1b** are disordered about two positions involving all atoms in **1a** (occupancy factors 0.810(6)/0.190(6)) and only the middle carbon atoms in **1b** (occupancy factors 0.613(7)/0.387(7) and 0.815(8)/0.185(8)). SADI restraints (d(C8–C9)/d(C9–C10)) were used in case of **1a** and EADP constraints were used for both compounds. A partial disorder of the ligand was found in $[H_3L^2]Cl_2$ and **1c**. The disorder of the *i*Pr-group ($[H_3L^2]Cl_2$, occupancy factors 0.620(12)/0.380(12)) and the 2,6-$(CH_3)_2$-C_6H_3 side-arm (**1c**, occupancy factors 0.561(12)/0.439(12)) was modeled by using SADI restraints (d(C–C)/d(C–N). Several disordered solvent molecules were found in $[H_3L^2]Cl_2$ (EtOH), **1c** (MeCN), and **2c** (Et_2O) and were refined in the usual manner. Face-indexed absorption corrections for $[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$, **1a, 1b, 1c** and **2c** were performed numerically with the program X-RED.[6]

CCDC 667625, 667626, 667627, 667628, 667629, 667630, and 667631 contain the supplementary crystallographic data for $[H_3L^2]Cl_2$, $[H_3L^2](PF_6)_2$, $[H_3L^3](PF_6)_2$, **1a, 1b, 1c** and **2c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

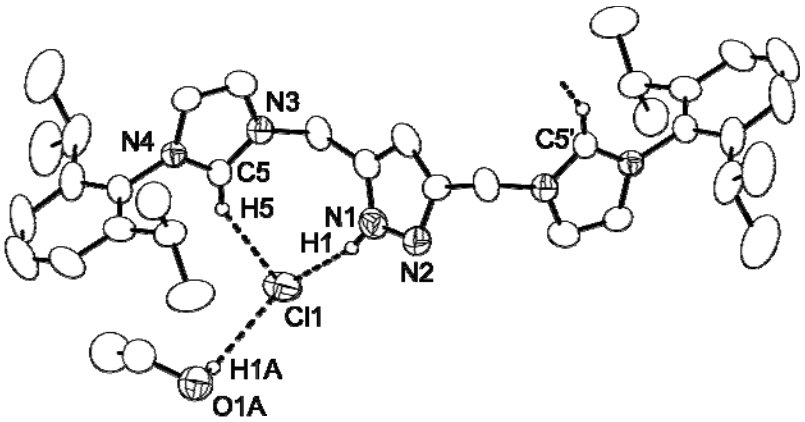


Figure S1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of $[H_3L^2]Cl_2$ emphasizing the hydrogen bonding (dashed lines). For the sake of clarity most hydrogen atoms, disorder, one anion and one solvent molecule have been omitted. Selected bond lengths (Å) and angles (°): N3–C5 1.321(6), N4–C5 1.342(5), N1···Cl1 3.15(1), C5···Cl1 3.37(1), O1A···Cl1 3.17(1); N3–C5–N4 107.2(4), N1–H1···Cl1 162, C5–H5···Cl1 151, O1A–H1A···Cl1 144. Symmetry transformation used to generate equivalent atoms (’): 1–*x*, 1–*y*, 1–*z*.

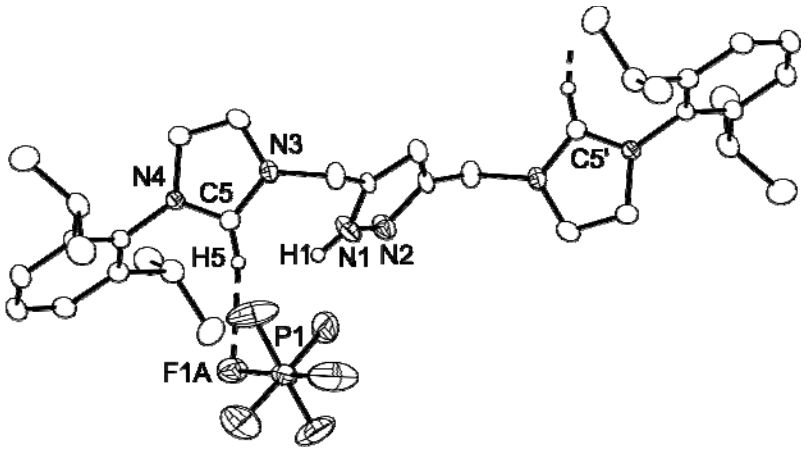


Figure S2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of $[H_3L^2](PF_6)_2$ emphasizing the hydrogen bonding or close contact of the imidazolium-C^2–H to fluorine atom F1A (dashed line). For the sake of clarity most hydrogen atoms, disorder, and one PF_6^- have been omitted. Selected bond lengths (Å) and angles (°): N3–C5 1.336(4), N4–C5 1.325(4), C5···F1A/B 3.27(1)/3.22(1); N3–C5–N4 108.7(3), C5–H5···F1A/B 166(4)/170(4). Symmetry transformation used to generate equivalent atoms (’): –*x*, 1–*y*, 1–*z*.

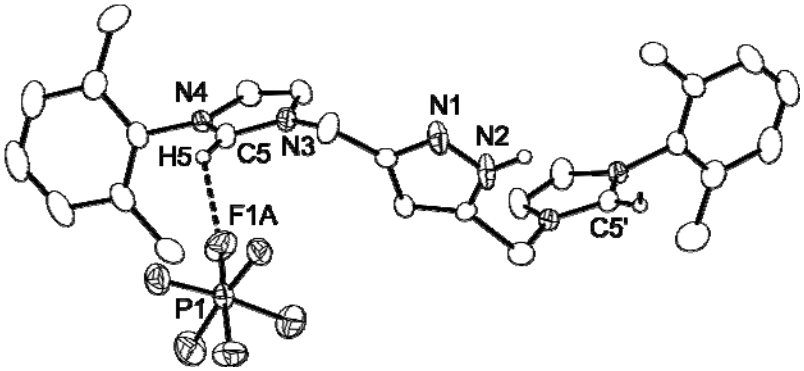


Figure S3. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of $[H_3L^3](PF_6)_2$ emphasizing the hydrogen bonding or close contact of the imidazolium-C^2–H to fluorine atom F1A (dashed line). For the sake of clarity most hydrogen atoms, disorder, and one PF_6^- have been omitted. Selected bond lengths (Å) and angles (°) Selected bond lengths (Å) and angles (°): N3–C5 1.326(5), N4–C5 1.325(5), C5···F1A/B 2.86(1)/3.39(1); N3–C5–N4 109.2(4), C5–H5···F1A/B 130(4)/157(4). Symmetry transformation used to generate equivalent atoms (’): 1–*x*, *y*, 1/2–*z*.

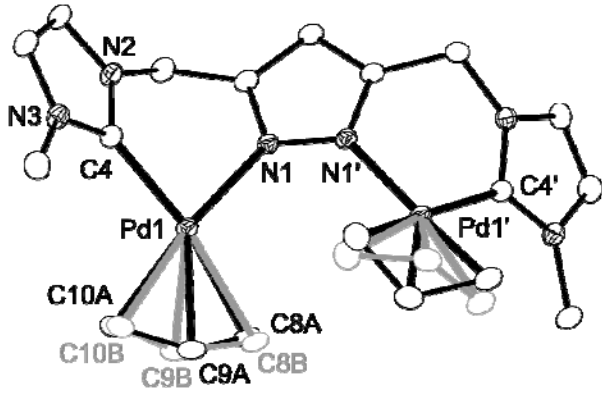


Figure S4. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **1a**. For the sake of clarity all hydrogen atoms, solvent molecules, and PF_6^- have been omitted. Selected bond lengths (Å) and angles (°): Pd1–N1 2.085(2), Pd1–C4 2.042(2), Pd1–C8A 2.174(6), Pd1–C9A 2.138(3), Pd1–C10A 2.114(4), Pd1···Pd1’ 4.0454(4), C8A–C9A 1.381(5), C9A–C10A 1.408(4), N2–C4 1.350(3), N3–C4 1.351(3); N1–Pd1–C4 86.53(7), N1–Pd1–C8A 101.93(14), N1–Pd1–C9A 135.52(9), N1–Pd1–C10A 167.14(12), C4–Pd1–C8A 167.36(14), C4–Pd1–C9A 137.10(10), C4–Pd1–C10A 102.12(12), C8A–C9A–C10A 118.8(4), N2–C4–N3 104.44(17). Symmetry transformation used to generate equivalent atoms (’): 1–*x*, *y*, 1/2–*z*.

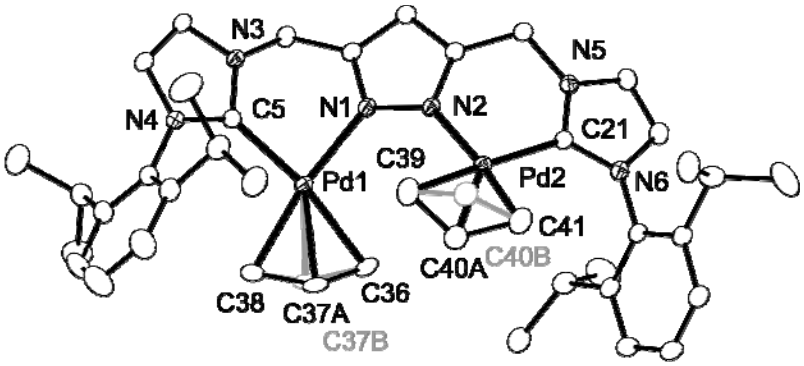


Figure S5. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **1b**. For the sake of clarity all hydrogen atoms, the solvent molecule, and PF_6^- have been omitted. Selected bond lengths (Å) and angles (°): Pd1–N1 2.081(3), Pd1–C5 2.040(3), Pd1–C36 2.189(3), Pd1–C37A 2.156(5), Pd1–C38 2.128(4), Pd2–N2 2.085(3), Pd2–C21 2.043(3), Pd2–C39 2.193(4), Pd2–C40A 2.144(4), Pd2–C41 2.116(3), Pd1···Pd2 4.0241(3), C36–C37A 1.373(7), C37A–C38 1.423(8), C39–C40A 1.372(6), C40A–C41 1.398(6), N3–C5 1.352(4), N4–C5 1.357(4), N5–C21 1.350(4), N6–C21 1.357(4); N1–Pd1–C5 87.36(11), N1–Pd1–C36 102.32(13), N1–Pd1–C37A 133.44(19), N1–Pd1–C38 169.79(13), C5–Pd1–C36 169.87(14), C5–Pd1–C37A 135.55(19), C5–Pd1–C38 102.38(13), N2–Pd2–C21 87.62(11), N2–Pd2–C39 101.64(13), N2–Pd2–C40A 133.98(15), N2–Pd2–C41 169.06(13), C21–Pd2–C39 168.13(15), C21–Pd2–C40A 136.82(16), C21–Pd2–C41 102.02(14), C36–C37A–C38 118.9(5), C39–C40A–C41 121.3(5), N3–C5–N4 104.0(3), N5–C21–N6 104.1(3).

Table S1. Crystal data and refinement details for $[H_3L^2]Cl_2$, $[H_3L^2](PF_6)_2$ and $[H_3L^3](PF_6)_2$.

	$[H_3L^2]Cl_2$	$[H_3L^2](PF_6)_2$	$[H_3L^3](PF_6)_2$
Empirical formula	$C_{35}H_{42}N_6^{2+}$, 2 Cl^-, 3 C_2H_5OH	$C_{35}H_{46}N_6^{2+}$, 2 PF_6^-	$C_{27}H_{30}N_6^{2+}$, 2 PF_6^-,
Formula weight	755.85	840.72	728.51
Crystal size [mm]	0.32 x 0.29 x 0.24	0.50 x 0.33 x 0.23	0.50 x 0.49 x 0.47
Cystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a [Å], α [°]	8.5929(12), 90	8.0071(4), 90	14.2667(8), 90
b [Å], β [°]	15.5448(14), 99.483(11)	18.0675(10), 95.887(4)	13.7559(6), 90.551(4)
c [Å], γ [°]	16.494(2), 90	13.5872(7), 90	15.8098(8), 90
V [Å^3]	2173.1(4)	1955.27(18)	3102.6(3)
Z	2	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.155	1.428	1.560
F(000)	812	872	1488
μ (Mo-K$_\alpha$) [mm^{-1}]	0.191	0.203	0.243
T_{min} / T_{max}	-	0.7806 / 0.9553	0.8104 / 0.9150
hkl range	–9 – 10, –17 – 18, ±19	–9 – 10, –22 –23, ±17	±18, –14 – 17, –19 – 20
θ range [°]	1.81 – 24.84	1.88 – 27.04	2.06 – 26.94
Measured refl.	12309	18080	13719
Unique refl. [R_{int}]	3688 [0.0861]	4234 [0.0455]	3372 [0.0267]
Obs. refl. (I>2σ(I))	1673	3097	2886
Param. / Restraints	279 / 14	298 / 71	264 / 69
Goodness-of-fit	1.036	1.052	1.074
R1 (I>2σ(I))	0.0897	0.0748	0.0797
wR2 (all data)	0.2468	0.2172	0.2206
Resid. el. dens. [e Å^{-3}]	0.297 / –0.341	1.061 / –0.736	0.941 / –0.876

Table S2. Crystal data and refinement details for **1a**, **1b**, **1c** and **2c**.

	1a	**1b**	**1c**	**2c**
Empirical formula	$C_{19}H_{25}N_6Pd_2^+$, PF_6^-, 2 CH_3CN	$C_{41}H_{53}N_6Pd_2^+$, PF_6^-, CH_3CN	$C_{33}H_{37}N_6Pd_2^+$, PF_6^-, 0.5 CH_3CN	$C_{35}H_{41}N_6Pd_2^+$, PF_6^-, 0.5 $C_4H_{10}O$
Formula weight	777.33	1028.72	895.98	940.57
Crystal size [mm]	0.50 x 0.34 x 0.18	0.50 x 0.48 x 0.34	0.44 x 0.35 x 0.27	0.50 x 0.50 x 0.25
Cystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a [Å], α [°]	11.2146(7), 90	13.0051(3), 90	13.8967(4), 90	28.5908(6), 90
b [Å], β [°]	13.8090(6), 90.295(5)	22.4086(4), 106.026(2)	19.7181(6), 109.936(2)	13.5718(2), 91.380(2)
c [Å], γ [°]	18.7798(12), 90	16.4497(4), 90	14.5953(5), 90	20.1813(4), 90
V [Å^3]	2908.2(3)	4607.56(17)	3759.7(2)	7828.7(3)
Z	4	4	4	8
$\rho_{calcd.}$ [g cm^{-3}]	1.775	1.483	1.583	1.596
F(000)	1544	2096	1796	3800
μ (Mo-K$_\alpha$) [mm^{-1}]	1.359	0.877	1.062	1.025
T_{min} / T_{max}	0.5745 / 0.7350	0.6480 / 0.7715	0.6486 / 0.7705	0.5802 / 0.6812
hkl range	±14, –15 – 17, ±23	±16, ±28, –20 – 19	–16 – 17, ±24, –16 – 18	±35, –14 – 16, ±24
θ range [°]	2.17 – 26.97	1.58 – 26.72	1.81 – 26.60	1.42 – 25.96
Measured refl.	13128	53736	36477	78679
Unique refl. [R_{int}]	3168 [0.0266]	9762 [0.0302]	7855 [0.0667]	14942 [0.0495]
Obs. refl. (I>2σ(I))	2935	9016	6669	13464
Param. / Restraints	194 / 2	568 / 70	419 / 40	949 / 11
Goodness-of-fit	1.047	1.041	1.071	1.037
*R*1 (I>2σ(I))	0.0217	0.0397	0.0525	0.0355
*wR*2 (all data)	0.0564	0.1122	0.1593	0.0876
Resid. el. dens. [e Å^{-3}]	0.425 / –0.550	2.582 (near P2) / –1.469	2.406 (near P2) / –1.006	2.302 (near Pd11) / –1.468

3 NMR spectroscopy

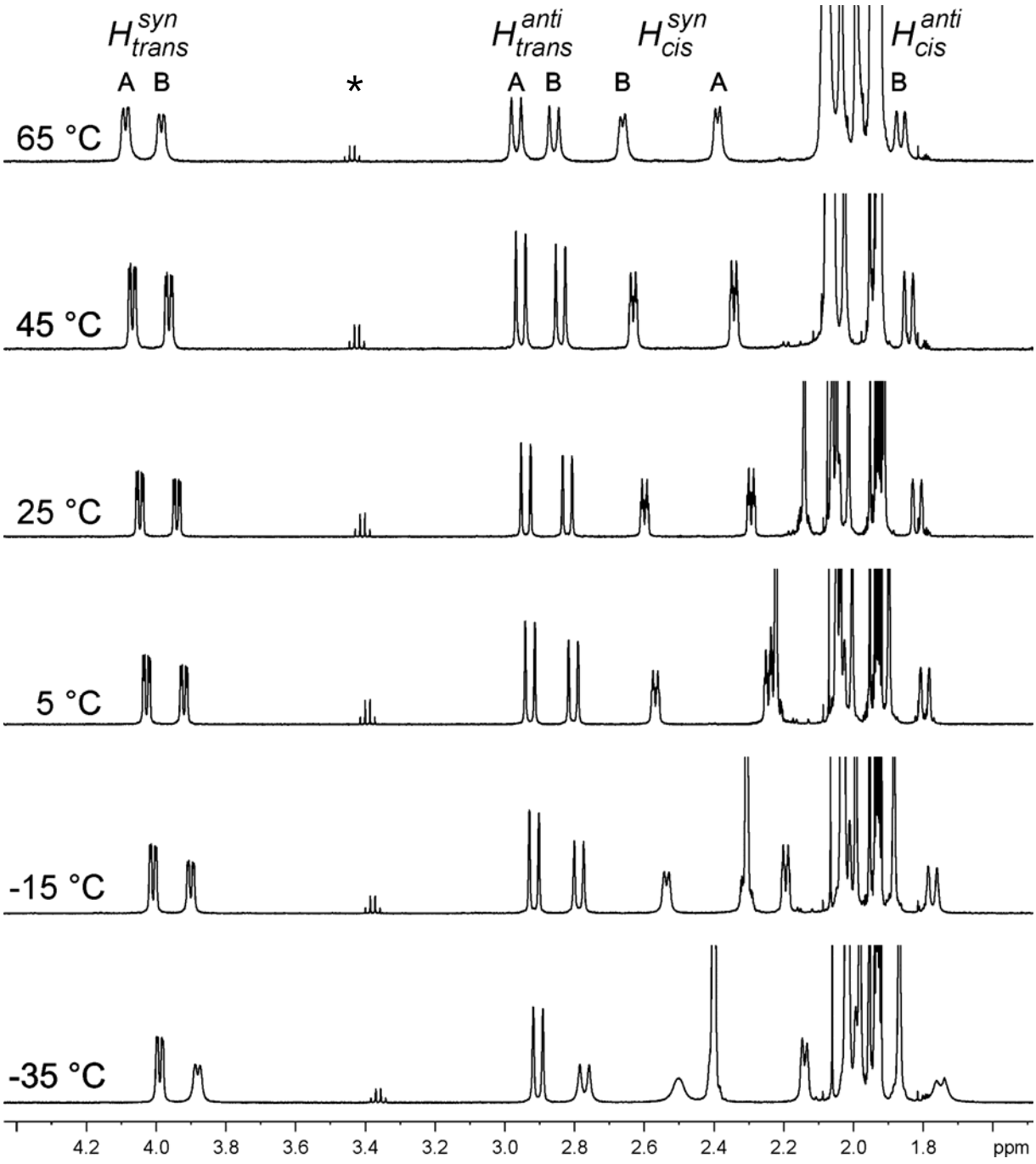


Figure S6. Selected area of temperature dependant ^{1}H-NMR spectra of **1c** in CD_3CN, illustrating the difference in population with temperature for species **1cA** and **1cB**. The asterisk (*****) marks residual diethyl ether.

4 References

[1] J. C. Röder, F. Meyer, H. Pritzkow, *Organometallics* **2001**, *20*, 811-817.
[2] U. J. Scheele, S. Dechert, F. Meyer, *Tetrahedron Lett.* **2007**, *48*, 8366-8370.
[3] Y. Tatsuno, T. Yoshida, S. Otsuka, *Inorg. Synth.* **1988**, *28*, 342-343.
[4] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement,* University of Göttingen, **1997**.
[5] G. M. Sheldrick, *SHELXS-97: Program for Crystal Structure Solution,* University of Göttingen, **1997**.
[6] STOE & CIE GmbH, *X-RED,* Darmstadt, **2002**.