Supporting Information

Synthesis of zwitterionic phosphapalladacycles: unusual reactivity pattern of six-membered P,N-chelates

László Szi-Ferenc,[a] Zsófia Császár,[a] György Lendvay,[b,c] Attila Bényei,[d] Szabolcs Balogh,[e] Balázs Nánási,[f] Gergely Farkas,[a*] and József Bakos[a*]

[a]*Department of Organic Chemistry, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary.*
[b]*Department of General and Inorganic Chemistry, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary.*
[c]*Institute of Materials and Environmental Chemistry, Hungarian Academy of Sciences, Magyar tudósok krt. 2., H-1117 Budapest, Hungary.*
[d]*Department of Physical Chemistry, University of Debrecen, Egyetem tér 1, H-4032 Debrecen, Hungary*
[e]*NMR Laboratory, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary*
[f]*Egis Pharmaceuticals PLC, 1106 Budapest, Keresztúri út 30-38., Hungary*

General experimental details

All manipulations were carried out under argon using Schlenk techniques. Solvents were purified, dried and deoxygenated by standard methods. Compounds $[Pd(COD)Cl_2]$,[1] $[Pd(COD)Br_2]$[2] and **1b-d**[3] were prepared according to literature methods. All other starting materials were purchased from Sigma Aldrich and used without further purification, except for benzoquinone that was carefully purified by sublimation in vacuum prior to use.[4] $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$- and ^1H-NMR measurements were carried out on a Bruker Avance 400 spectrometer (NMR Laboratory, University of Pannonia) operating at 161.98, 100.61 and 400.13 MHz respectively. The ^1H NMR and ^{13}C NMR signals were assigned from their related ^1H-^1H COSY and ^{13}C-^1H HMQC spectra, respectively. X-ray data for compounds **2a** and **2b** were collected on a Bruker-Nonius MACH3 or on a Bruker D8 Venture diffractometer. EI and ESI mass spectra were recorded on a Shimadzu GCMS QP2010 SE spectrometer or on an Agilent 1100 LC/MSD SL Quadrupole mass spectrometer (Department of Earth and Environmental Sciences, University of Pannonia), respectively.

(2*S*,4*S*)-4-(diphenylphosphino)-2-dimethylaminopentane (1a)

Dimethylamine in THF (20 mL, 2 M) was added to (*R*,*R*)-4,6-dimethyl-1,3,2-dioxathiane 2,2-dioxide (cyclic sulfate of (*R,R*)-pentane-2,4-diol) (4 g, 24.1 mmol) and the mixture was stirred

for 48 h at room temperature. Next, ether (20 mL) was added to the mixture. The suspension formed was stirred for 30 min and then filtered. The solid was washed two times with ether and dried with azeotropic destillation using toluene. The residual solvent was evaporated by vacuum to give (2*S*,4*R*)-2-dimethylamino-4-sulfatopentane as a white powder. Yield: 90%. Mp. 202 – 205 °C. ^{1}H NMR (400 MHz, DMSO): δ = 4.25 (dqd, *J* = 12.4, 6.2, 2.4 Hz, 1H, CH), 3.49 (m, 1H, CH), 2.68 (s, 6H, $N(CH_3)_2$), 1.84 (ddd, *J* = 14.8, 10.3, 4.8 Hz, 1H, diast. C*H*H), 1.59 (ddd, *J* = 14.1, 8.8, 2.4 Hz, 1H, diast. CH*H*), 1.23 (d, *J* = 6.5 Hz, 3H, CH_3), 1.22 (d, *J* = 6.2 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, DMSO): δ = 70.80 (s, 1C), 59.79 (s, 1C), 39.40 (br. m, 2C), 38.51 (s, 1C), 22.66 (s, 1C), 13.37 (s, 1C) ppm. $LiPPh_2$·1,4-dioxane adduct (26.5 g, 94.5 mmol) was dissolved in THF (50 mL) under argon and the solution was cooled to -10 °C. (2*S*,4*R*)-dimethylamino-4-sulfatopentane (4 g, 18.9 mmol) was added to the red solution in small portions. The reaction mixture was stirred at room temperature for 48 h. The color of the reaction mixture remained red. After evaporation of the solvent, deoxygenated water (80 mL) and ether (60 mL) were added to the residue and the mixture was stirred until the two phases became clear solutions. The pH of the mixture was then adjusted to 1 with 10% deoxygenated HCl solution. The two phases were then separated and the water phase was washed three times with 40 mL portions of ether. The pH was then adjusted to about 9-10 with dropwise addition of a dilute solution of Na_2CO_3. The product was extracted four times with 40 mL portions of ether. After drying with $MgSO_4$ the solvent was evaporated to give (2*S*,4*S*)-2-diphenylphosphino-4-dimethylaminopentane as a transparent oil. Yield: 5 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.44 (m, 4H, aromatic), 7.32 – 7.28 (m, 6H, aromatic), 2.68 (m, 1H, CH), 2.32 (m, 1H, CH), 2.15 (s, 6H, $N(CH_3)_2$), 1.47 (m, 1H, diast. C*H*H), 1.36 (m, 1H, diast. CH*H*), 1.02 (dd, ^{3}J(P,H) = 14.8 Hz, ^{3}J(H,H) = 6.8 Hz, 3H, CH_3(PCH)), 0.92 (d, ^{3}J(H,H) = 6.5 Hz, 3H, CH_3(NCH)) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 137.39 (d, *J*(P,H) = 13.7 Hz, 1C, aromatic), 137.25 (d, *J*(P,H) = 14.7 Hz, 1C, aromatic), 134.01 (d, *J*(P,H) = 19.3 Hz, 2C, aromatic), 133.73 (d, *J*(P,H) = 18.8 Hz, 2C, aromatic), 128.96 (s, 1C, aromatic), 128.88 (s, 1C, aromatic), 128.54 (d, *J*(P,H) = 4.9 Hz, 2C, aromatic), 128.47 (d, *J*(P,H) = 5.2 Hz, 2C, aromatic), 57.00 (d, *J*(P,H) = 12.3 Hz, 1C), 40.55 (s, 2C, $N(CH_3)_2$), 36.34 (d, *J*(P,H) = 17.9 Hz, 1C), 27.37 (d, *J*(P,H) = 9.8 Hz, 1C), 16.53 (d, *J*(P,H) = 15.1 Hz, 1C), 13.93 (s, 1C) ppm. ^{31}P{^{1}H} NMR (162 MHz, DMSO): δ = 0.33 (s) ppm. MS (EI) m/z calculated for $C_{19}H_{26}NP$ $[M]^+$ 299.18, found 299. Anal. calcd. for $C_{19}H_{26}NP$: C, 76.22; H, 8.75; N, 4.68. Found: C, 76.26; H, 8.69; N, 4.30.

(2*R*,3*R*)-3-(diphenylphosphino)-2-dimethylaminobutane (1e)

Dimethylamine in THF (10 mL, 2 M) was added to (4*S*,5*S*)-4,5-dimethyl-1,3,2-dioxathiolane 2,2-dioxide (cyclic sulfate of (*S,S*)-butane-2,3-diol) (2.5 g, 16.4 mmol) and the mixture was stirred for 48 h at room temperature. Next, acetone (20 mL) was added to the mixture. The suspension formed was stirred for 30 min and then filtered. The solid was washed two times with acetone and dried with azeotropic destillation using toluene. The residual solvent was evaporated by vacuum to give (2*R*,3*S*)-2-dimethylamino-3-sulfatobutane as a white powder. Yield: 40%. Mp. 218 – 220 °C. ^{1}H NMR (400 MHz, DMSO): δ = 4.63 (qd, *J* = 6.4 (3), 1.7 Hz, 1H, CH), 3.25 (dq, *J* = 6.8 (3), 1.7 Hz, 1H, CH), 2.78 (s, 6H, $N(CH_3)_2$), 1.18 (d, *J* = 6.6 Hz, 3H, CH_3), 1.16 (d, *J* = 7.0 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, DMSO): δ = 69.68 (s, 1C), 64.00 (s, 1C), 40.22 (s, 2C), 18.21 (s, 1C), 7.77 (s, 1C) ppm. $LiPPh_2$·1,4-dioxane adduct (8.4 g, 30 mmol) was dissolved in THF (30 mL) under argon and the solution was cooled to -10 °C. (2*R*,3*S*)-2-dimethylamino-3-sulfatobutane (1.2 g, 6 mmol) was added to the red solution in small portions. The reaction mixture was stirred at room temperature for 48 h. The color of the reaction mixture remained red. After evaporation of the solvent, deoxygenated water (60 mL) and ether (40 mL) were added to the residue and the mixture was stirred until the two phases became clear solutions. The pH of the mixture was then adjusted to 1 with 10% deoxygenated HCl solution. The two phases were then separated and the water phase was washed three times with 40 mL portions of ether. The pH was then adjusted to about 9-10 with dropwise addition of a dilute solution of Na_2CO_3. The product was extracted four times with 40 mL portions of ether. After drying with $MgSO_4$ the solvent was evaporated. The crude product mixture was purified by column chromatography (Al_2O_3, eluent: hexane/EtOAc 6/1, Rf: ~ 0.4) to give (2*R*,3*R*)-3-(diphenylphosphino)-2-dimethylaminobutane as a transparent oil. Yield: 0.5 g, 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.55 (m, 4H, aromatic), 7.38 – 7.32 (m, 6H, aromatic), 2.81 (br. m, 1H, CH), 2.37 (br. m, 1H, CH), 2.26 (br. s, 6H, $N(CH_3)_2$), 1.16 (d, ^{3}J(H,H) = 6.7 Hz, 3H, CH_3(NCH)), 1.02 (dd, ^{3}J(P,H) = 12.5 Hz, ^{3}J(H,H) = 7.0 Hz, 3H, CH_3(PCH)) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 137.79 (br. s, 1C, aromatic), 136.60 (br. s, 1C, aromatic), 134.29 (d, *J*(P,C) = 20.5 Hz, 2C, aromatic), 133.31 (d, *J*(P,C) = 19.2 Hz, 2C, aromatic), 128.89 (s, 1C, aromatic), 128.44 (s, 1C, aromatic), 128.34 (d, *J*(P,C) = 6.5 Hz, 2C, aromatic), 128.20 (d, *J*(P,C) = 7.4 Hz, 2C, aromatic), 61.23 (d, *J*(P,C) = 16.6 Hz, 1C), 41.79 (s, 2C, $N(CH_3)_2$), 33.40 (br. s, 1C), 11.90 (d, *J*(P,C) = 12.3 Hz, 1C), 11.41 (d, *J*(P,C) = 9.2 Hz, 1C) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = – 4.47 (s) ppm. MS (EI) m/z calculated for $C_{18}H_{24}NP$ $[M]^+$ 285.16, found 285. Anal. calcd. for $C_{18}H_{24}NP$: C, 75.76; H, 8.48; N, 4.91. Found: C, 75.43; H, 8.17; N, 4.97.

(2*R*,5*R*)-5-(diphenylphosphino)-2-dimethylaminohexane (1f)

Dimethylamine in THF (4.2 mL, 2 M) was added to (4*S*,7*S*)-4,7-dimethyl-1,3,2-dioxathiepane 2,2-dioxide (cyclic sulfate of (*S,S*)-hexane-2,5-diol) (1 g, 5.55 mmol) and the mixture was stirred for 48 h at room temperature. Next, acetone (10 mL) was added to the mixture. The suspension formed was stirred for 30 min and then filtered. The solid was washed two times with acetone and dried with azeotropic destillation using toluene. The residual solvent was evaporated by vacuum to give (2*R*,5*S*)-2-dimethylamino-5-sulfatohexane as a white powder. Yield: 42%. Mp. 199 – 200 °C. ^{1}H NMR (400 MHz, DMSO): δ = 4.17 (m, 1H, CH), 3.31 (m, 1H, CH), 2.63 (s, 6H, $N(CH_3)_2$), 1.74 (m, 1H, diast. CHH), 1.47 (m, 3H, diast. CHH), 1.16 (d, *J* = 6.3 Hz, 3H, CH_3), 1.15 (d, *J* = 6.7 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, DMSO): δ = 71.71 (s, 1C), 60.59 (s, 1C), 39.16 (s, 2C), 32.77 (s, 1C), 26.49 (s, 1C), 21.53 (s, 1C), 13.30 (s, 1C) ppm. $LiPPh_2$·1,4-dioxane adduct (1.96 g, 7 mmol) was dissolved in THF (30 mL) under argon and the solution was cooled to -10 °C. (2*R*,5*S*)-2-dimethylamino-5-sulfatohexane (0.5 g, 2.2 mmol) was added to the red solution in small portions. The reaction mixture was stirred at room temperature for 48 h. The color of the reaction mixture remained red. After evaporation of the solvent, deoxygenated water (50 mL) and ether (30 mL) were added to the residue and the mixture was stirred until the two phases became clear solutions. The pH of the mixture was then adjusted to 1 with 10% deoxygenated HCl solution. The two phases were then separated and the water phase was washed three times with 40 mL portions of ether. The pH was then adjusted to about 9-10 with dropwise addition of a dilute solution of Na_2CO_3. The product was extracted four times with 40 mL portions of ether. After drying with $MgSO_4$ the solvent was evaporated to give (2*R*,5*R*)-5-(diphenylphosphino)-2-dimethylaminohexane as a transparent oil. Yield: 330 mg, 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.49 (m, 4H, aromatic), 7.37 – 7.32 (m, 6H, aromatic), 2.45 (m, 1H, CH), 2.35 (m, 1H, CH), 2.26 (s, 6H, $N(CH_3)_2$), 1.63-1.48 (m, 3H, diast. CH_2), 1.29 (m, 1H, diast. CH_2), 1.06 (dd, ^{3}J(P,H) = 14.8 Hz, ^{3}J(H,H) = 6.9 Hz, 3H, CH_3(PCH)), 0.88 (d, ^{3}J(H,H) = 6.5 Hz, 3H, CH_3(NCH)) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 137.55 (d, *J*(P,C) = 10.9, 1C, aromatic), 137.41 (d, *J*(P,C) = 11.7, 1C, aromatic), 133.86 (d, *J*(P,C) = 19.4 Hz, 2C, aromatic), 133.52 (d, *J*(P,C) = 18.8 Hz, 2C, aromatic), 128.78 (s, 1C, aromatic), 128.70 (s, 1C, aromatic), 128.42 (d, *J*(P,C) = 7.0 Hz, 2C, aromatic), 128.34 (d, *J*(P,C) = 7.2 Hz, 2C, aromatic), 59.29 (s, 1C), 40.53 (s, 2C, $N(CH_3)_2$), 31.10 (d, *J*(P,C) = 11.8 Hz, 1C), 30.62 (d, *J*(P,C) = 17.6 Hz, 1C), 30.30 (d, *J*(P,C) = 9.4 Hz, 1C), 16.34 (d, *J*(P,C) = 16.1 Hz, 1C), 13.38 (s, 1C) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = – 2.08 (s) ppm. MS (EI) m/z calculated for $C_{20}H_{28}NP$ $[M]^+$ 313.2, found 313. Anal. calcd. for $C_{20}H_{28}NP$: C, 76.64; H, 9.00; N, 4.47. Found: C, 76.62; H, 8.99; N, 4.47.

Complex 2a

Ligand **1a** (105 mg, 0.35 mmol) dissolved in acetone (5 mL) was added dropwise to a solution of [Pd(COD)Cl_2] (100 mg, 0.35 mmol) and benzoquinone (38 mg, 0.35 mmol) in acetone (5 mL). The mixture was refluxed for 3h. The resulting yellow precipitation was filtered, washed with acetone (4 x 5 mL). (Alternatively it was dissolved in a mixture of $CHCl_3$-MeOH (4:1). The yellow solution was then passed through a short pad of celite and concentrated.) Finally, the residue was titurated with ether to give **2a** (119 mg) as a bright yellow solid. Yield: 72%. Mp. 218-220 °C (decomp.). ^{1}H NMR (400 MHz, DMSO): δ = 7.92 – 7.88 (m, 2H, aromatic), 7.72 – 7.67 (m, 2H, aromatic), 7.62 – 7.60 (m, 2H, aromatic), 7.56 – 7.53 (m, 4H, aromatic), 3.53 (m, 1H, CH, partially overlapped with the next signal), 3.48 (s, 3H, diast. N(C*H*$_3$)CH_3, partially overlapped with the previous and the next signal), 3.46 (d, ^2J(H,H) = 4.9 Hz, 1H, diast. PdC*H*H, partially overlapped with the previous signal), 3.15 (s, 3H, diast. N(CH_3)C*H*$_3$), 2.78 (d, ^2J(H,H) = 4.9 Hz, 1H, diast. PdCH*H*, overlapped with the previous signal), 2.75 (ddd, ^3J(P,H) = 48 Hz, ^2J(H,H) = 18.6 Hz, ^3J(H,H) = 3.3 Hz, 1H, diast. (equatorial) C*H*H), 2.04 (dt, ^2J(H,H) = 18.7 Hz, ^3J(P,H) = ^3J(H,H) = 11.8 Hz, 1H, diast. (axial) CH*H*), 0.86 (dd, ^3J(P,H) = 12.3 Hz, ^3J(H,H) = 6.6 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ = 184.81 (d, ^3J(P,C) = 5.6 Hz, 1C, C=N), 135.83 (d, *J*(P,C) = 11.3 Hz, 2C, aromatic), 132.66 (d, *J*(P,C) = 8.7 Hz, 2C, aromatic), 131.68 (d, *J*(P,C) = 2.4 Hz, 1C, aromatic), 131.01 (d, *J*(P,C) = 2.8 Hz, 1C, aromatic), 128.54 (d, *J*(P,C) = 10.5 Hz, 2C, aromatic), 128.18 (d, *J*(P,C) = 11.0 Hz, 2C, aromatic), 127.74 (d, *J*(P,C) = 51.8 Hz, 1C, aromatic), 125.01 (d, *J*(P,C) = 52.1 Hz, 1C, aromatic), 43.21 (s, 1C, diast. N(*C*H_3)CH_3), 41.98 (s, 1C, diast. N(CH_3)*C*H_3), 35.99 (s, 1C, CH_2), 25.74 (d, ^1J(P,C) = 29.4 Hz, 1C, CH), 24.63 (s, 1C, PdCH_2), 14.38 (d, ^2J(P,C) = 6.9 Hz, 1C, CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz, DMSO): δ = 42.44 (s) ppm. IR (KBr, cm^{-1}): 524, 545, 652, 693, 705, 746, 940, 1103, 1349, 1433, 1591 (vs, ν(C=N)), 2874, 2918, 2969, 3050. Anal. calcd. for $C_{19}H_{24}Cl_2NPdP$: C, 48.07; H, 5.10; N, 2.95. Found: C, 48.08; H, 5.07; N, 2.89.

Complex 2b

Synthesis of complex **2b** was performed as described for complex **2a**. Yield: 75%. Mp. 198-200 °C. ^{1}H NMR (400 MHz, DMSO): δ = 7.92 – 7.81 (m, 2H, aromatic), 7.80 – 7.70 (m, 2H, aromatic), 7.67 – 7.45 (m, 4H, aromatic), 4.23 (m, 1H), 3.77 (m, 1H), 3.69 (ddd, *J* = 12.5, 9.5, 2.8 Hz, 1H), 3.59 (m, 1H), 3.55 (d, ^2J(H,H) = 5.1 Hz, 1H, diast. PdC*H*H), 3.41 (m, 1H, partially buried by the signal of residual water), 2.86 (d, ^2J(H,H) = 5.1 Hz, 1H, diast. PdCH*H*, partially overlapped with the next signal), 2.80 (ddd, ^3J(P,H) = 45.8 Hz, ^2J(H,H) = 19.1 Hz,

^{3}J(H,H) = 4.9 Hz, 1H, diast. (equatorial) C*H*H, partially overlapped with the previous signal), 2.05 (m, 1H, diast. (axial) CH*H*), 1.88 – 1.76 (m, 2H, CH_2), 1.76 – 1.51 (m, 4H, CH_2), 0.90 (dd, ^{3}J(P,H) = 12.3, ^{3}J(H,H) = 6.6 Hz, 3H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO): δ = 182.52 (d, ^{3}J(P,C) = 5.7 Hz, 1C, C=N), 136.19 (d, J(P,C) = 11.2 Hz, 2C, aromatic), 132.64 (d, J(P,C) = 8.7 Hz, 2C, aromatic), 131.85 (d, J(P,C) = 1.7 Hz, 1C, aromatic), 130.93 (d, J(P,C) = 2.4 Hz, 1C, aromatic), 128.51 (d, J(P,C) = 10.4 Hz, 2C, aromatic), 128.16 (d, J(P,C) = 10.9 Hz, 2C, aromatic), 127.99 (d, J(P,C) = 51.4 Hz, 1C, aromatic), 124.81 (d, J(P,C) = 51.7 Hz, 1C, aromatic), 51.13 (s, 1C, diast. NCH_2), 50.07 (s, 1C, diast. NCH_2), 35.53 (s, 1C, CH_2), 25.83 (d, ^{1}J(P,C) = 29.9 Hz, 1C, CH), 25.82 (s, 1C, CH_2), 25.58 (s, 1C, CH_2), 23.77 (d, J = 1.1 Hz, 1C, $PdCH_2$), 22.99 (s, 1C, CH_2), 14.53 (d, ^{2}J(P,C) = 7.1 Hz, 1C, CH_3) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO): δ = 39.60 (s) ppm. IR (KBr, cm^{-1}): 524, 540, 692, 705, 745, 944, 1101, 1330, 1436, 1572 (vs, ν(C=N)), 2851, 2929, 3051. Anal. calcd. for $C_{22}H_{28}Cl_2NPPd$: C, 51.33; H, 5.48; N, 2.72. Found: C, 51.38; H, 5.44; N, 2.68.

Complex 2c

Synthesis of complex **2c** was performed as described for complex **2a**. Yield: 65%. Mp. 207-209 °C. ^{1}H NMR (400 MHz, DMSO): δ = 7.86 – 7.91 (br. m, 2H, aromatic), 7.71 – 7.76 (br. m, 2H, aromatic), 7.53 – 7.65 (br. m, 6H, aromatic), 4.17 – 4.25 (br. m, 1H), 3.92 – 3.99 (br. m, 1H), 3.92 – 3.99 (br. m, 1H), 3.68 – 3.87 (br. m, 5H), 3.51 – 3.65 (br. m, 2H), 3.57 (d, ^{2}J(H,H) = 5.1 Hz, 1H, diast. CH*H*Pd, buried by other signals), 2.92 (d, ^{2}J(H,H) = 5.1 Hz, 1H, diast. C*H*HPd), 2.78 (ddd, ^{3}J(H,P) = 24.7, ^{3}J(H,H) = 18.7, ^{3}J(H,H) = 5.1 Hz, 1H, diast. (equatorial) CH*H*CH), 2.19 (dt, ^{3}J(H,H) = 18.7, ^{3}J(H,H) = ^{3}J(H,P) = 12.1 Hz, 1H, diast. (axial) C*H*HCH), 0.88 (dd, ^{3}J(H,P) = 12.4 Hz, ^{3}J(H,H) = 6.6 Hz, 3H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO): δ = 182.50 (d, ^{3}J(P,C) = 5.5 Hz, 1C, C=N), 136.00 (d, J(P,C) = 11.0 Hz, 2C, aromatic), 132.66 (d, J(P,C) = 8.6 Hz, 2C, aromatic), 131.82 (d, J(P,C) = 2.1 Hz, 1C, aromatic), 131.09 (d, J(P,C) = 3.0 Hz, 1C, aromatic), 128.58 (d, J(P,C) = 10.5 Hz, 2C, aromatic), 128.24 (d, J(P,C) = 11.1 Hz, 2C, aromatic), 127.67 (d, J(P,C) = 52.3 Hz, 1C, aromatic), 124.78 (d, J(P,C) = 52.1 Hz, 1C, aromatic), 65.74 (s, 1C, diast. OCH_2), 65.54 (s, 1C, diast. OCH_2), 50.34 (s, 1C, diast. NCH_2), 49.24 (s, 1C, diast. OCH_2), 35.50 (s, 1C, CH_2), 25.73 (d, ^{1}J(P,C) = 30.04 Hz, 1C, CH), 25.05 (d, ^{2}J(P,C) = 2.1 Hz, 1C, $PdCH_2$), 14.42 (d, ^{2}J(P,C) = 6.9 Hz, 1C, CH_3) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO): δ = 41.04 (s) ppm. IR (KBr, cm^{-1}): 528, 546, 693, 759, 944, 1108, 1118, 1334, 1435, 1546, 1570 (vs, ν(C=N)), 2872, 2929, 2969, 3051. Anal. calcd. for $C_{21}H_{26}Cl_2NOPPd$: C, 48.81; H, 5.07; N, 2.71. Found: C, 48.72; H, 5.27; N, 2.56.

Complex 2d

Synthesis of complex **2d** was performed as described for complex **2a**. Yield: 75%. Mp. 219-221 °C. ^{1}H NMR (400 MHz, DMSO): δ = 7.92 – 7.87 (m, 2H, aromatic), 7.72 – 7.67 (m, 2H, aromatic), 7.63 – 7.60 (m, 2H, aromatic), 7.57 – 7.52 (m, 4H, aromatic), 4.29 (m, 1H), 3.58 – 3.46 (m, 3H), 3.41 (d, ^{2}J(H,H) = 4.6 Hz, 1H, diast. PdC*H*H), 3.24 (m, 1H), 2.82 (ddd, ^{3}J(P,H) = 47.3 Hz, ^{2}J(H,H) = 18.4 Hz, ^{3}J(H,H) = 4.0 Hz, 1H, diast. (equatorial) C*H*H), 2.81 (d, ^{2}J(H,H) = 4.6 Hz, 1H, diast. PdCH*H*), 2.13 – 1.86 (m, 5H, 2 CH_2 and diast. (axial) C*H*H), 0.86 (dd, ^{3}J(P,H) = 12.4 Hz, ^{3}J(H,H) = 6.7 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, DMSO): δ = 181.66 (d, ^{3}J(P,C) = 6.0 Hz, 1C, C=N), 135.85 (d, J(P,C) = 11.2 Hz, 2C, aromatic), 132.67 (d, J(P,C) = 8.6 Hz, 2C, aromatic), 131.70 (d, J(P,C) = 2.4 Hz, 1C, aromatic), 131.0 (d, J(P,C) = 2.3 Hz, 1C, aromatic), 128.54 (d, J(P,C) = 10.3 Hz, 2C, aromatic), 128.22 (d, J(P,C) = 10.8 Hz, 2C, aromatic), 127.81 (d, J(P,C) = 51.7 Hz, 1C, aromatic), 125.20 (d, J(P,C) = 51.9 Hz, 1C, aromatic), 51.49 (s, 1C, diast. NCH_2), 50.78 (s, 1C, diast. NCH_2), 36.76 (s, 1C, CH_2), 25.73 (d, ^{1}J(P,C) = 29.7 Hz, 1C, CH), 25.34 (s, 1C, $PdCH_2$), 24.66 (s, 1C, CH_2), 23.98 (s, 1C, CH_2), 14.35 (d, ^{2}J(P,C) = 7.0 Hz, 1C, CH_3) ppm. ^{31}P NMR (162 MHz, DMSO): δ = 42.98 (s) ppm. IR (KBr, cm^{-1}): 524, 537, 660, 695, 708, 758, 943, 1101, 1321, 1446, 1569 (vs, ν(C=N)), 2868, 2917, 2953, 3050. Anal. calcd. for $C_{21}H_{26}Cl_2NPPd$: C, 50.37; H, 5.23; N, 2.80. Found: C, 50.70; H, 5.21; N, 2.67.

Complex 3a

Synthesis of complex **3a** was performed as described for complex **2a**. The complex was isolated as an acetone solvate with a composition of **3a** · 0.5 $(CH_3)_2CO$ as indicated by ^{1}H NMR and elemental analysis. Yield: 80%. Mp. 203-205 °C. ^{1}H NMR (400 MHz, DMSO): δ = 7.95 – 7.83 (m, 2H, aromatic), 7.73 – 7.63 (m, 2H, aromatic), 7.63 – 7.45 (m, 4H), 3.65 (d, ^{2}J(H,H) = 4.9 Hz, 1H, diast. PdC*H*H), 3.52 (m, 1H, CH), 3.45 (s, 3H, diast. $N(CH_3)C\mathit{H}_3$), 3.08 (s, 3H, diast. $N(C\mathit{H}_3)CH_3$), 2.88 (d, ^{2}J(H,H) = 4.9 Hz, 1H, diast. PdCH*H*), 2.71 (ddd, ^{3}J(P,H) = 47.4 Hz, ^{2}J(H,H) = 20.2 Hz, ^{3}J(H,H) = 4.6 Hz, 1H, diast. (equatorial) C*H*H), 1.94 (dt, ^{2}J(H,H) = 18.3 Hz, ^{3}J(P,H) = ^{3}J(H,H) = 11.7 Hz, 1H, diast. (axial) CH*H*), 0.82 (dd, ^{3}J(P,H) = 12.4 Hz, ^{3}J(H,H) = 6.6 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO): δ = 185.04 (d, ^{3}J(P,C) = 3.0 Hz, 1C, C=N), 136.04 (d, J(P,C) = 11.3 Hz, 2C, aromatic), 132.76 (d, J(P,C) = 8.5 Hz, 2C, aromatic), 131.74 (d, J(P,C) = 1.5 Hz, 1C, aromatic), 131.02 (d, J(P,C) = 2.2 Hz, 1C, aromatic), 128.44 (d, J(P,C) = 10.5 Hz, 2C, aromatic), 128.16 (d, J(P,C) = 10.6 Hz, 2C, aromatic), 127.92 (d, J(P,C) = 52.1 Hz, 1C, aromatic), 125.49 (d, J(P,C) = 51.8 Hz, 1C, aromatic), 43.55 (s, 1C, diast. $N(\mathit{C}H_3)CH_3$), 42.00 (s, 1C, diast. $N(CH_3)\mathit{C}H_3$), 35.82 (s, 1C,

CH_2), 30.69 (s, 1C, $PdCH_2$), 26.36 (d, ^1J(P,C) = 29.2 Hz, 1C, CH), 14.51 (d, ^2J(P,C) = 7.3 Hz, 1C, CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, DMSO): δ = 42.85 (s) ppm. IR (KBr, cm^{-1}): 522, 534, 545, 651, 697, 753, 933, 1102, 1346, 1430, 1437, 1580 (vs, ν(C=N)), 2869, 2913, 2974, 3051. Anal. calcd. for $C_{19}H_{24}Br_2NPPd \cdot 0.5\ (CH_3)_2CO$: C, 41.55; H, 4.59; N, 2.36. Found: C, 41.65; H, 4.61; N, 2.11.

Complex 4e

Ligand **1e** (50 mg, 0.1752 mmol) was dissolved in CH_2Cl_2 (5 mL) was added dropwise to a solution of $[Pd(COD)Cl_2]$ (50 mg, 0.1752 mmol) in CH_2Cl_2. The resulting orange solution was stirred for 60 min, filtered through a short pad of celite and concentrated to ca. 2 mL. The solution was then treated with ether (5 mL) to precipitate a yellow powder that was filtered and washed with ether (3 x 5 mL) to give 69 mg of complex **4e**. Yield: 85%. Mp. 268-270 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.12 – 8.06 (m, 2H, aromatic), 7.76 – 7.71 (m, 2H, aromatic), 7.69 – 7.62 (m, 2H, aromatic), 7.60 – 5.51 (m, 4H, aromatic), 3.21 (s, 3H, diast. NCH_3), 2.92 (m, 1H, CH), 2.89 (s, 3H, diast. NCH_3), 2.67 (m, 1H, CH), 1.11 (d, *J* = 6.5 Hz, 3H, CH_3), 1.00 (dd, *J* = 12.9, 7.0 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 136.26 (d, *J* = 11.5 Hz, 2C, aromatic), 132.58 (d, *J* = 2.9 Hz, 1C, aromatic, overlapped with the next signal), 132.58 (d, *J* = 8.7 Hz, 2C, aromatic, overlapped with the previous signal), 131.69 (d, *J* = 3.3 Hz, 1C, aromatic), 128.53 (d, *J* = 6.4 Hz, 2C, aromatic), 128.42 (d, *J* = 6.2 Hz, 2C, aromatic), 126.48 (d, *J* = 63.5 Hz, 1C, aromatic), 125.45 (d, *J* = 59.9 Hz, 1C, aromatic), 69.34 (d, *J* = 7.2 Hz, 1C), 50.72 (s, 1C), 39.45 (d, *J* = 28.3 Hz, 1C), 12.36 (d, *J* = 7.3 Hz, 1C), 10.35 (d, *J* = 18.8 Hz, 1C). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 52.56 (s) ppm. MS (ESI) m/z calculated for $C_{18}H_{24}Cl_2NPPd$ $[M - Cl]^+$ 428.04, found 427.8. Anal. calcd. for $C_{18}H_{24}Cl_2NPPd$: C, 46.73; H, 5.23; N, 3.03. Found: C, 46.95; H, 5.41; N, 2.65.

Complex 4f

Synthesis of complex **4f** was performed as described for complex **4e**. (Some representative ^1H signals of the major component: ^1H NMR (400 MHz, $CDCl_3$) δ 2.66 (broad s, 6H, NMe_2), 1.15 (d, *J* = 6.4 Hz, 3H, CH_3), 0.89 (dd, *J* = 15.2, 6.9 Hz, 3H, CH_3, overlapped with the corresponding signals of minor components).) ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.29 (s) (2.8%), 37.98 (s) (2.9%), 37.63 (s) (47.3%), 37.30 (s) (16.7%), 37.09 (s) (15.6%), 32.35 (s) (6.4%), 32.17 (s) (3.2%), 31.95 (s) (3.3%), 28.41 (s) (1.8%).Yield: 68%. Anal. calcd. for $C_{20}H_{28}Cl_2NPPd$: C, 48.95; H, 5.75; N, 2.85. Found: C, 48.48; H, 5.78; N, 2.60.

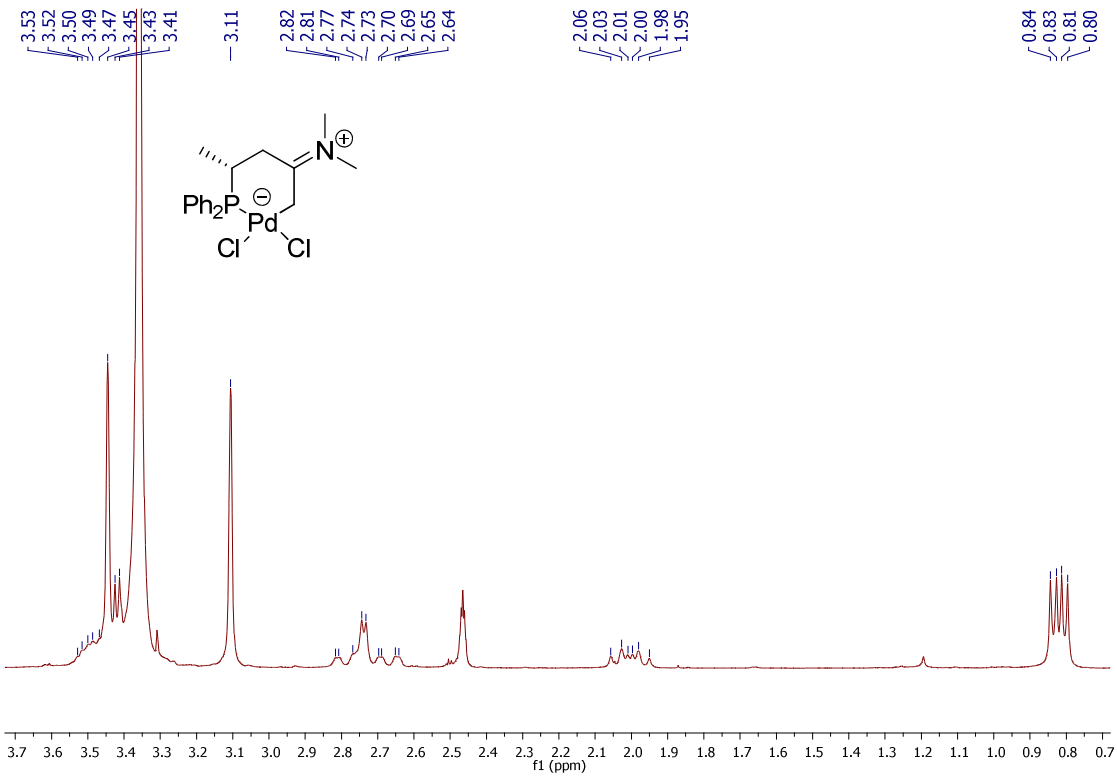

Figure S1 ^{1}H NMR spectrum of **2a** recorded in DMSO-d6 (aliphatic region)

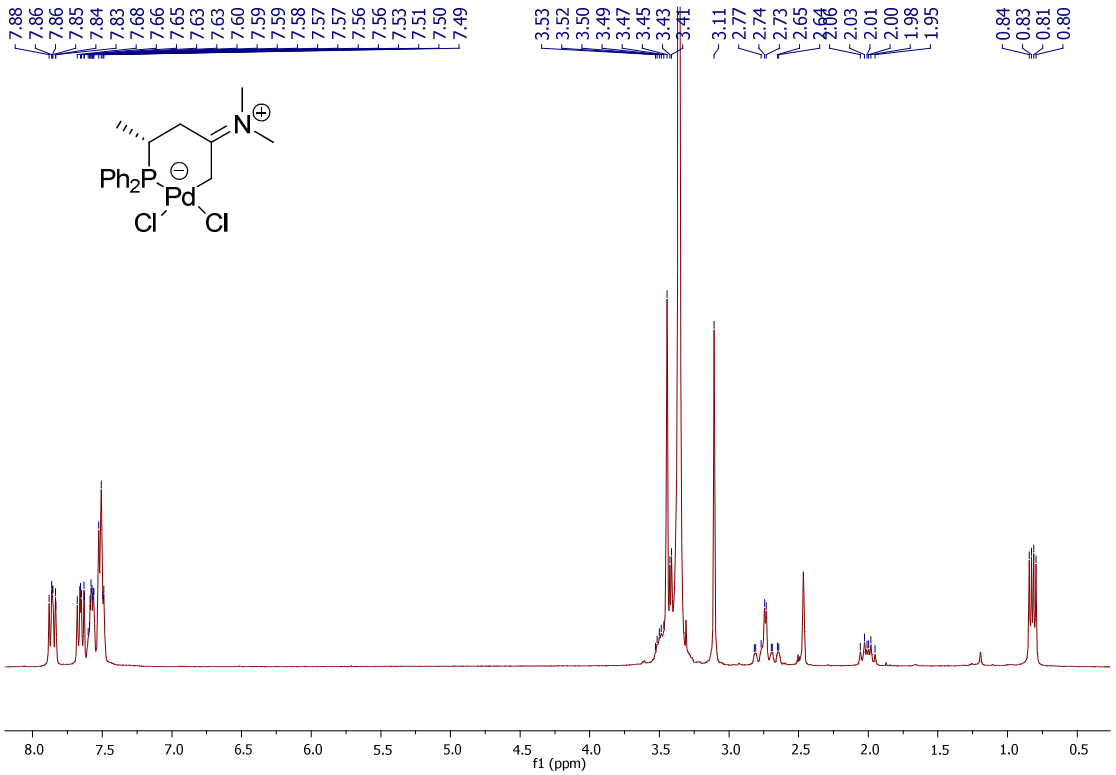

Figure S2 ^{1}H NMR spectrum of **2a** recorded in DMSO-d6 (full spectrum)

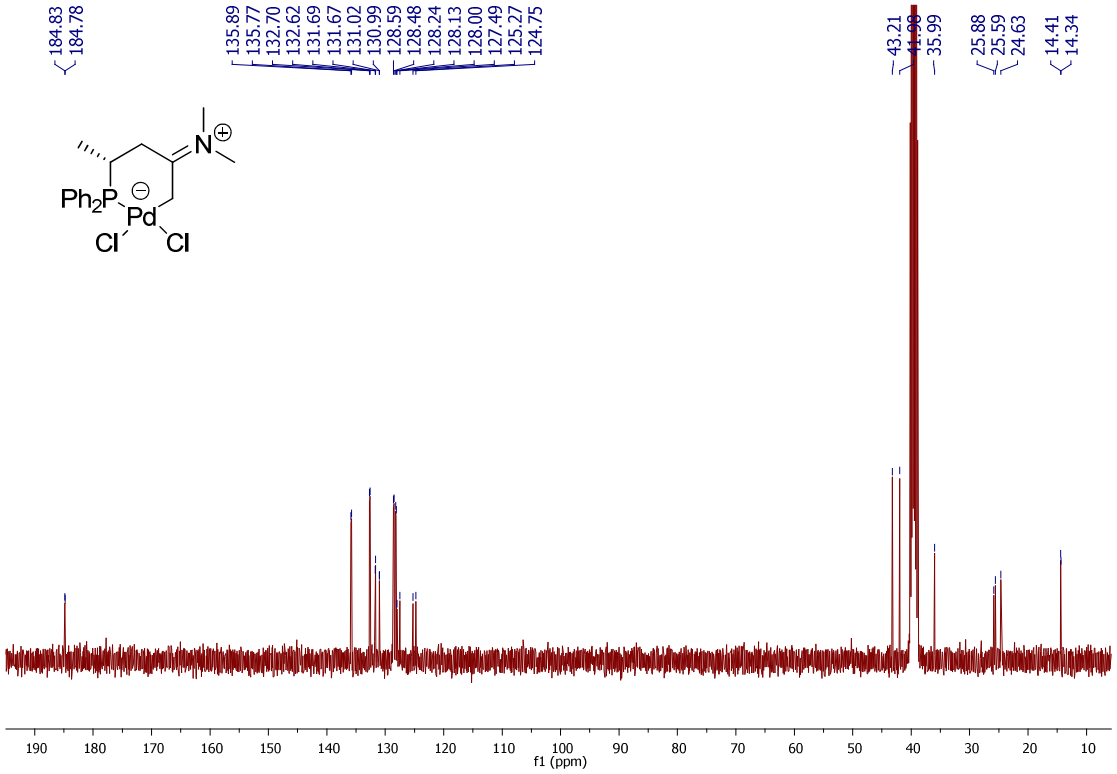

Figure S3 $^{13}C\{^{1}H\}$ NMR spectrum of **2a** recorded in DMSO-d6

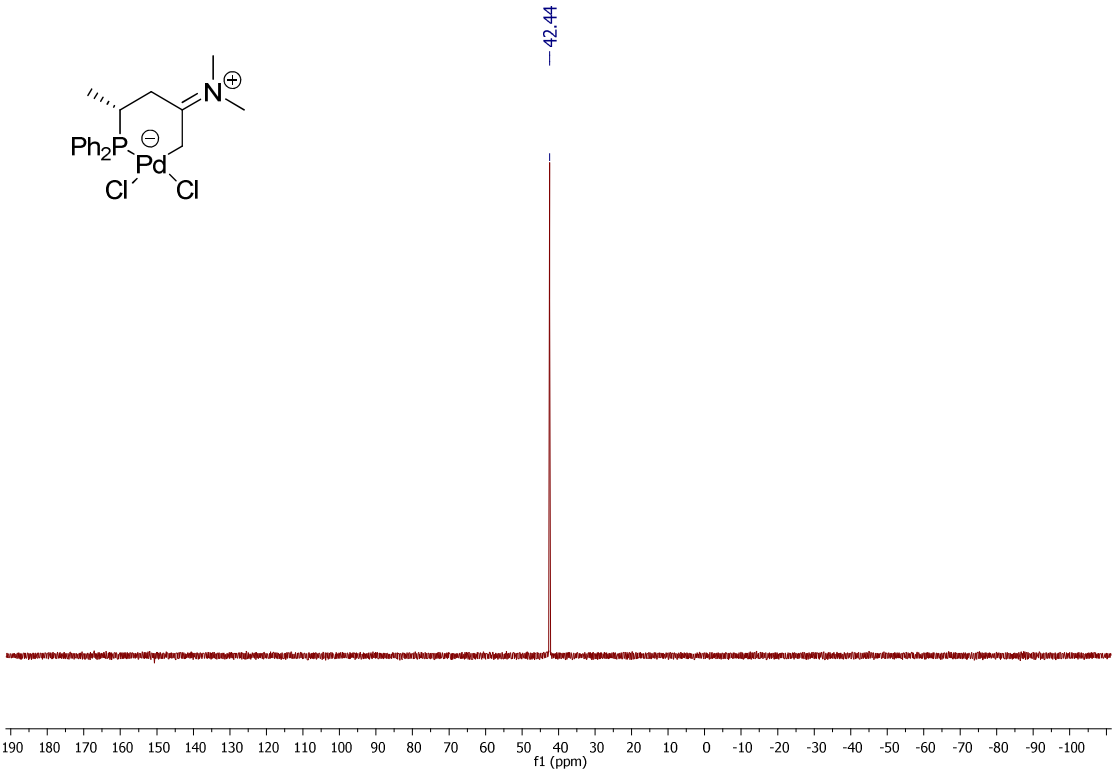

Figure S4 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** recorded in DMSO-d6

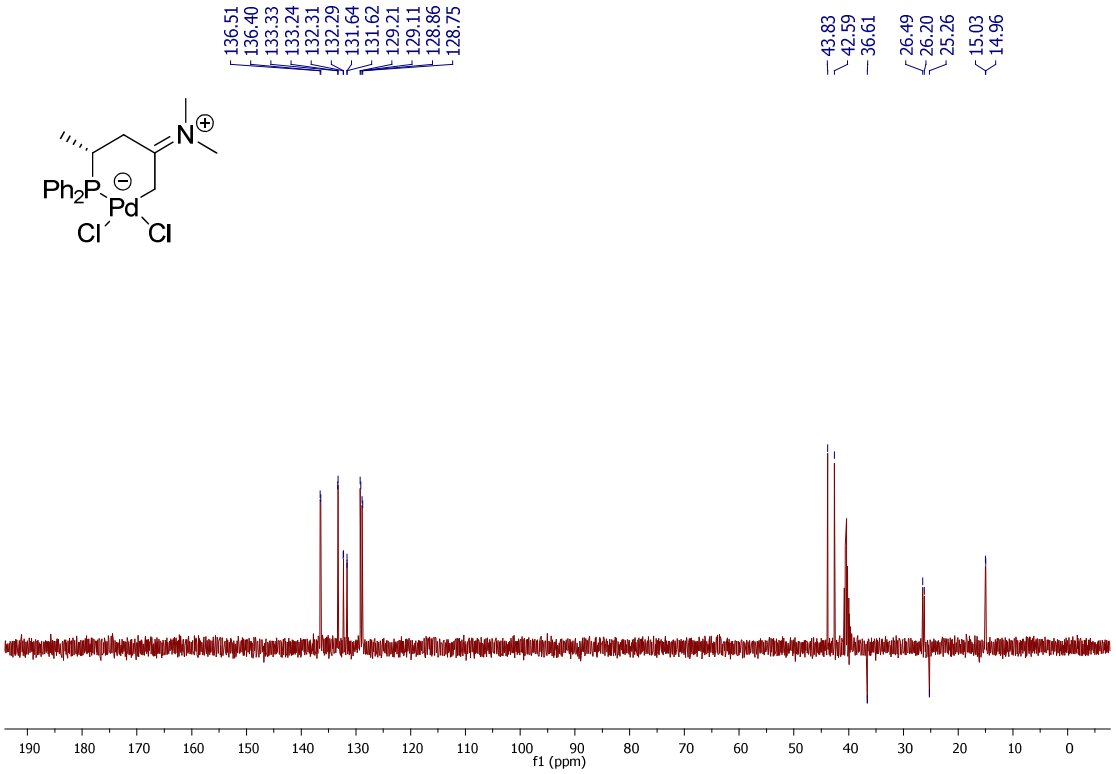

Figure S5 ^{13}C DEPT-135 NMR spectrum of **2a** recorded in DMSO-d6

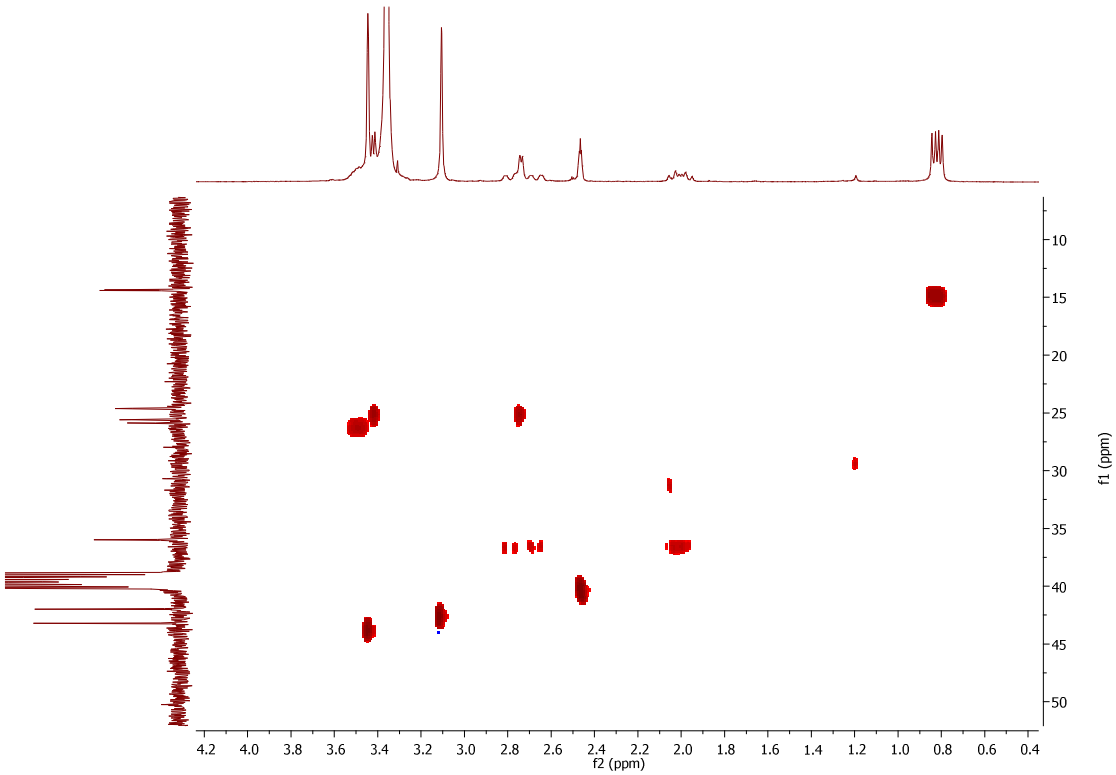

Figure S6 HSQC spectrum of **2a** recorded in DMSO-d6 (aliphatic region)

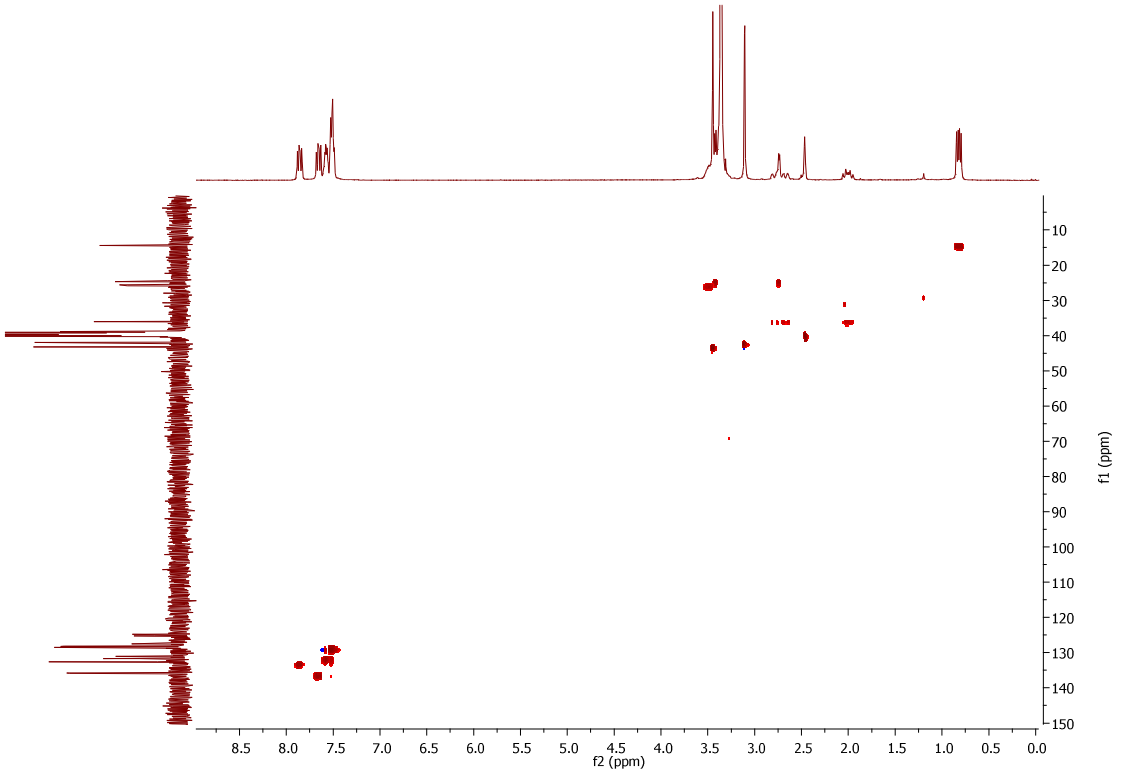

Figure S7 HSQC spectrum of **2a** recorded in DMSO-d6 (full spectrum)

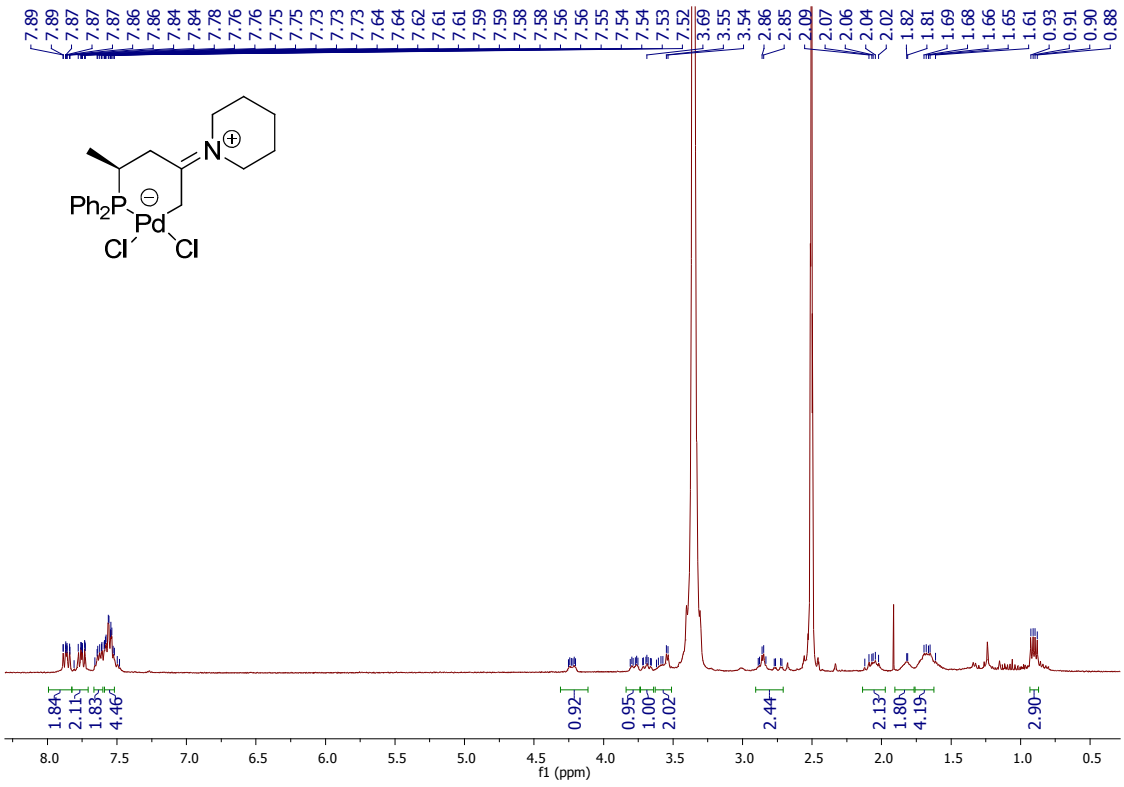

Figure S8 ^{1}H NMR spectrum of **2b** recorded in DMSO-d6

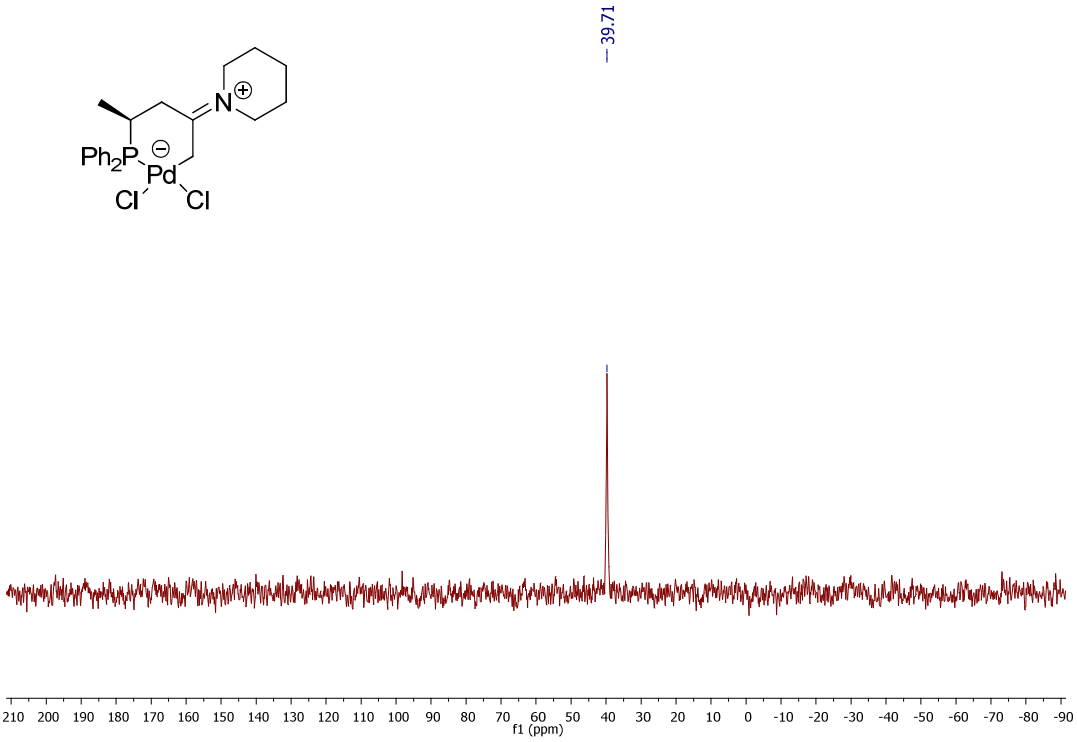

Figure S9 $^{31}P\{^{1}H\}$ NMR spectrum of **2b** recorded in DMSO-d6

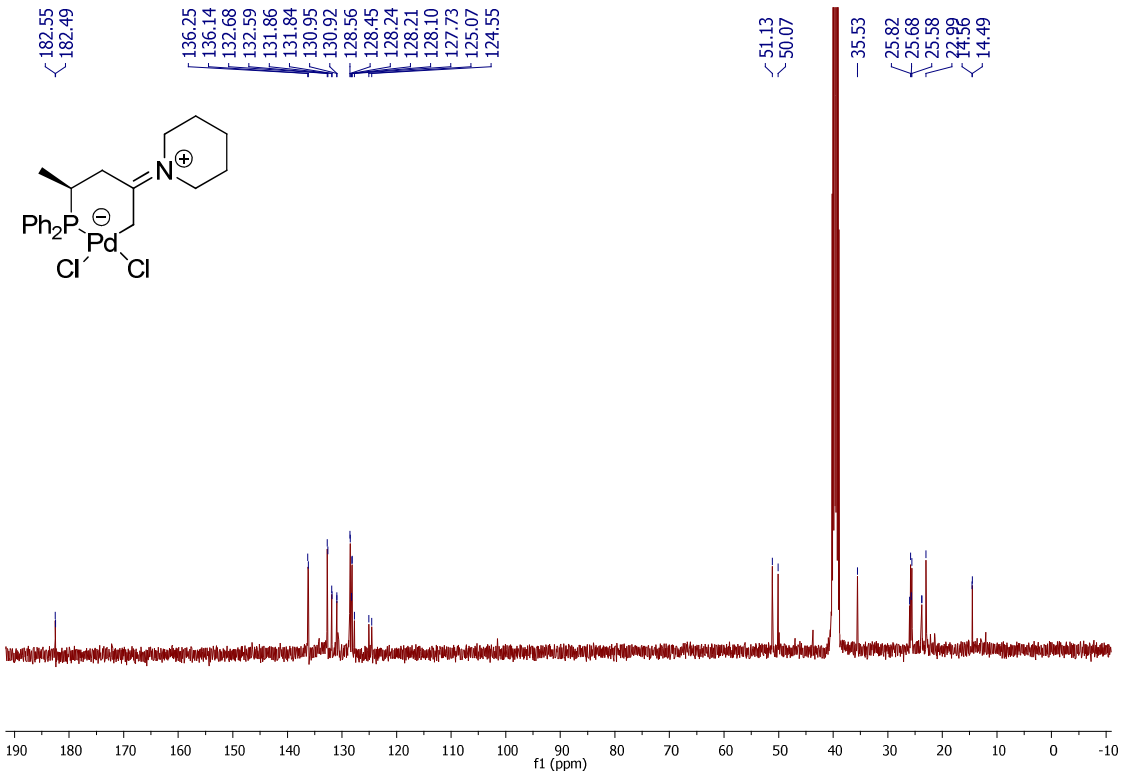

Figure S10 $^{13}C\{^{1}H\}$ NMR spectrum of **2b** recorded in DMSO-d6

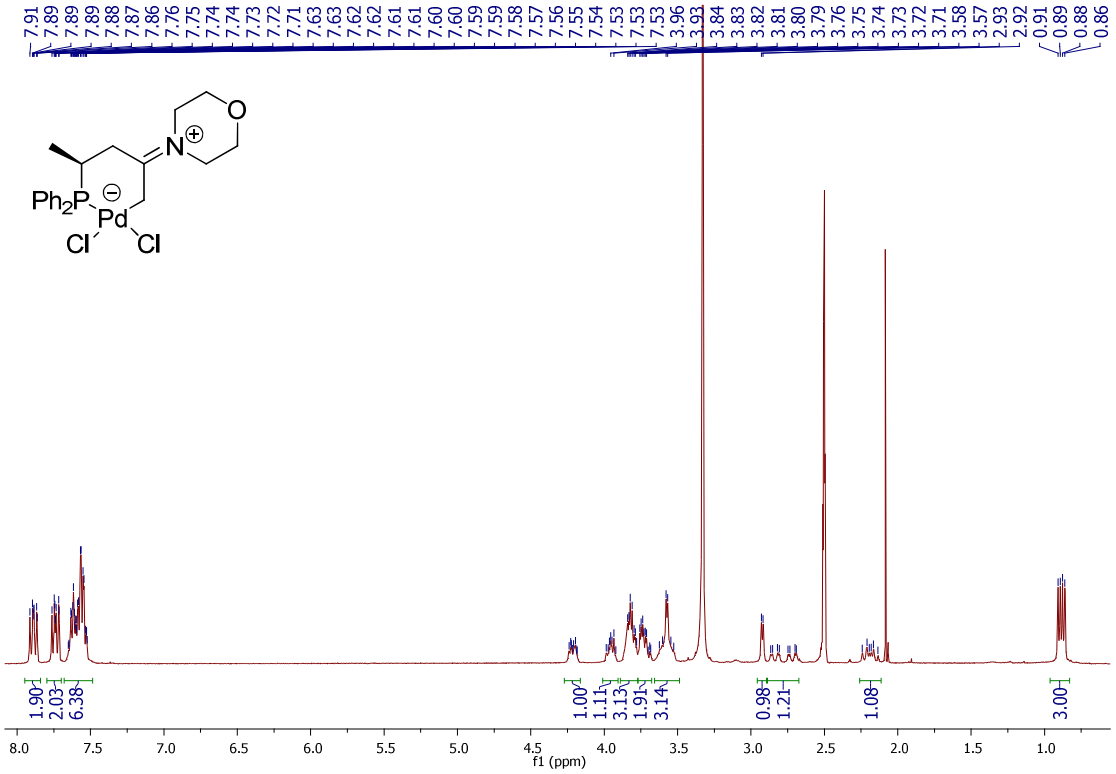

Figure S11 ^{1}H NMR spectrum of **2c** recorded in DMSO-d6

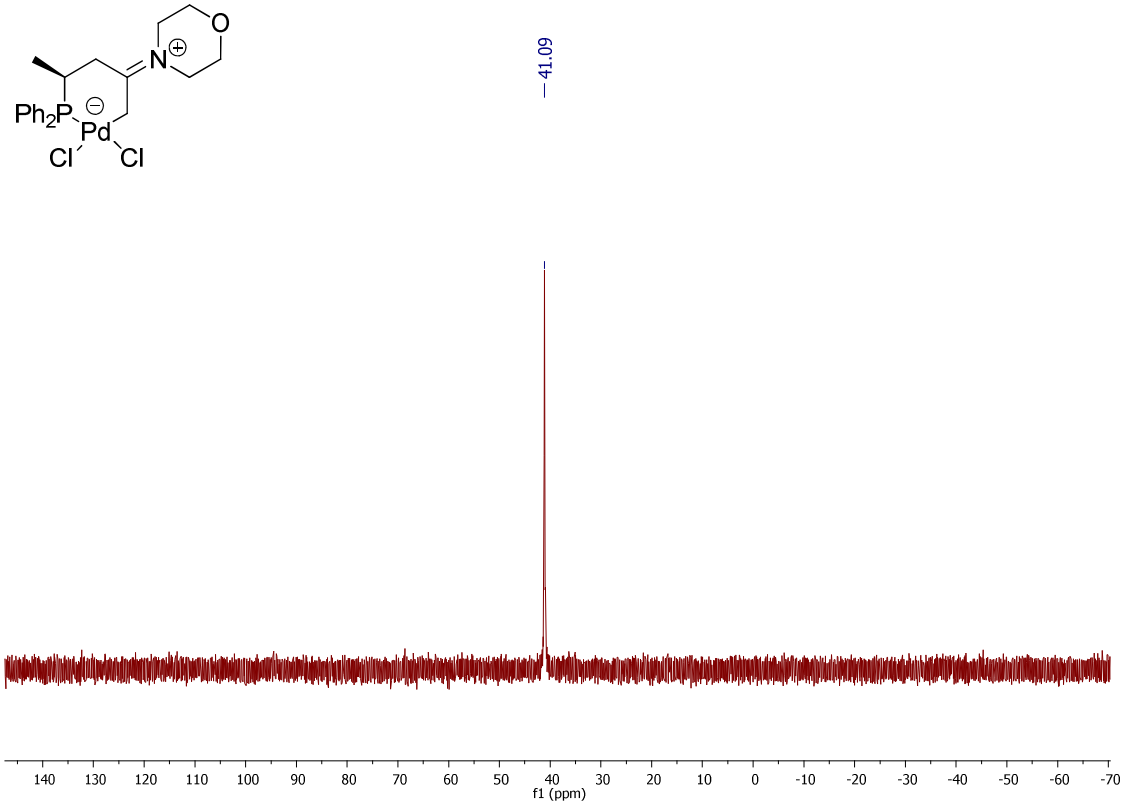

Figure S12 ^{31}P{^{1}H} NMR spectrum of **2c** recorded in DMSO-d6

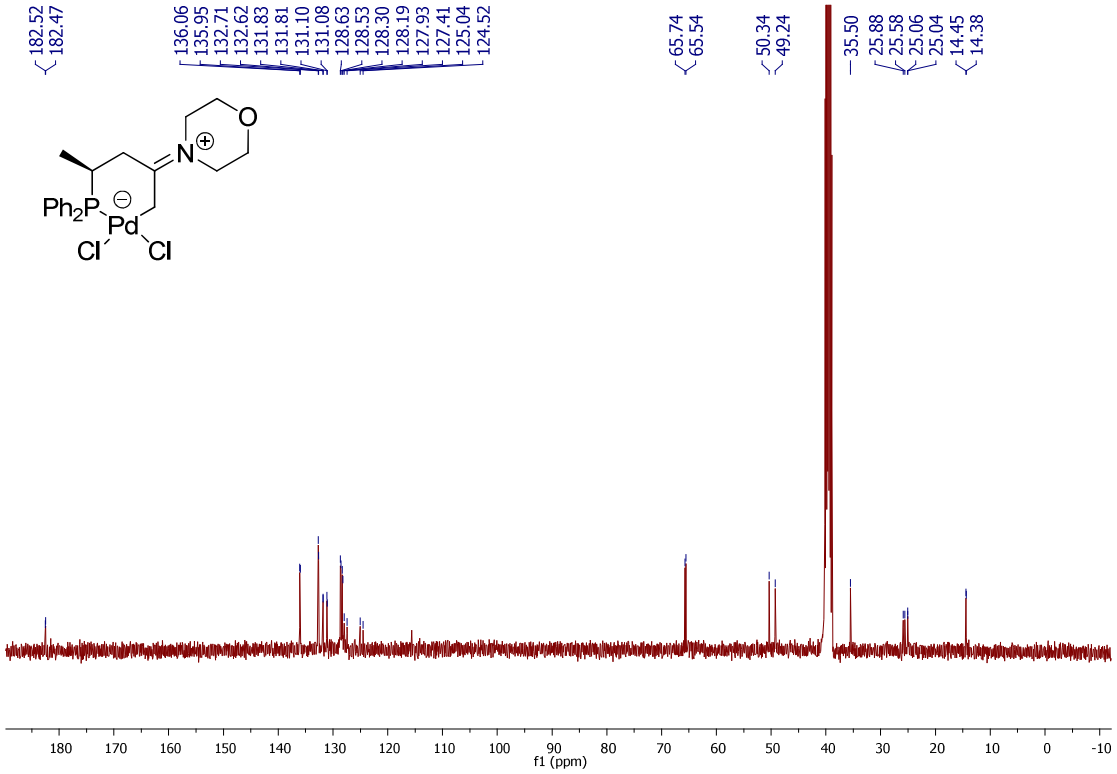

Figure S13 $^{13}C\{^{1}H\}$ NMR spectrum of **2c** recorded in DMSO-d6

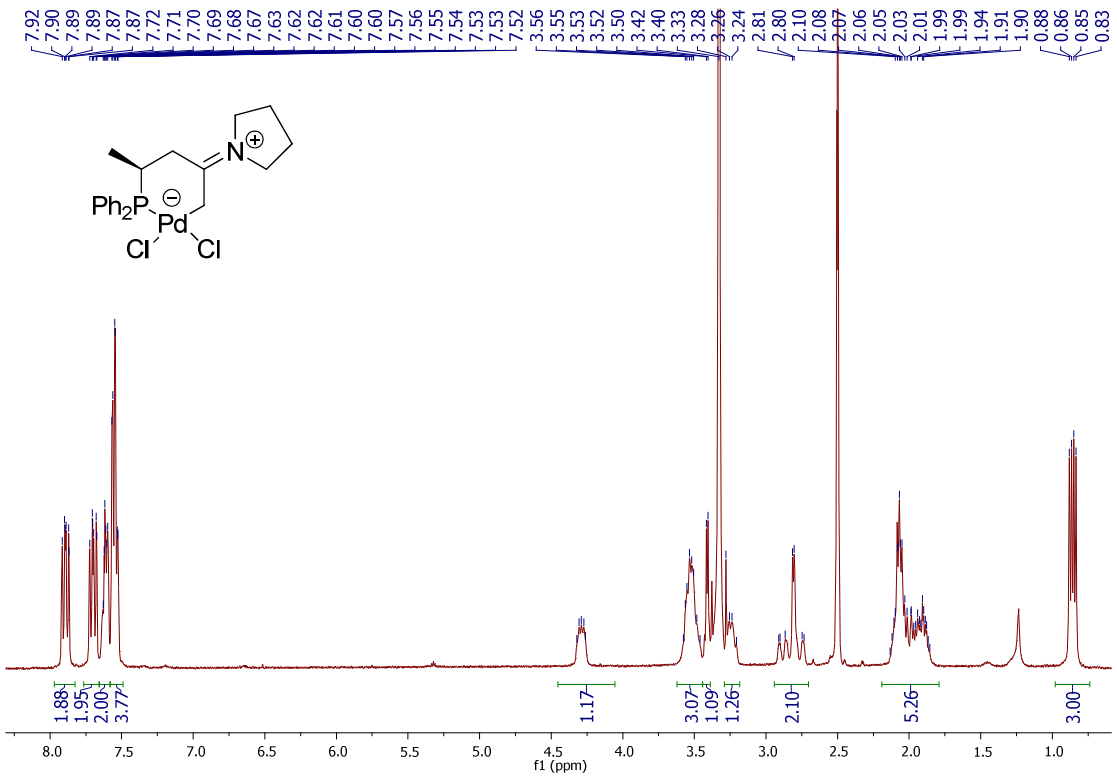

Figure S14 ^{1}H NMR spectrum of **2d** recorded in DMSO-d6

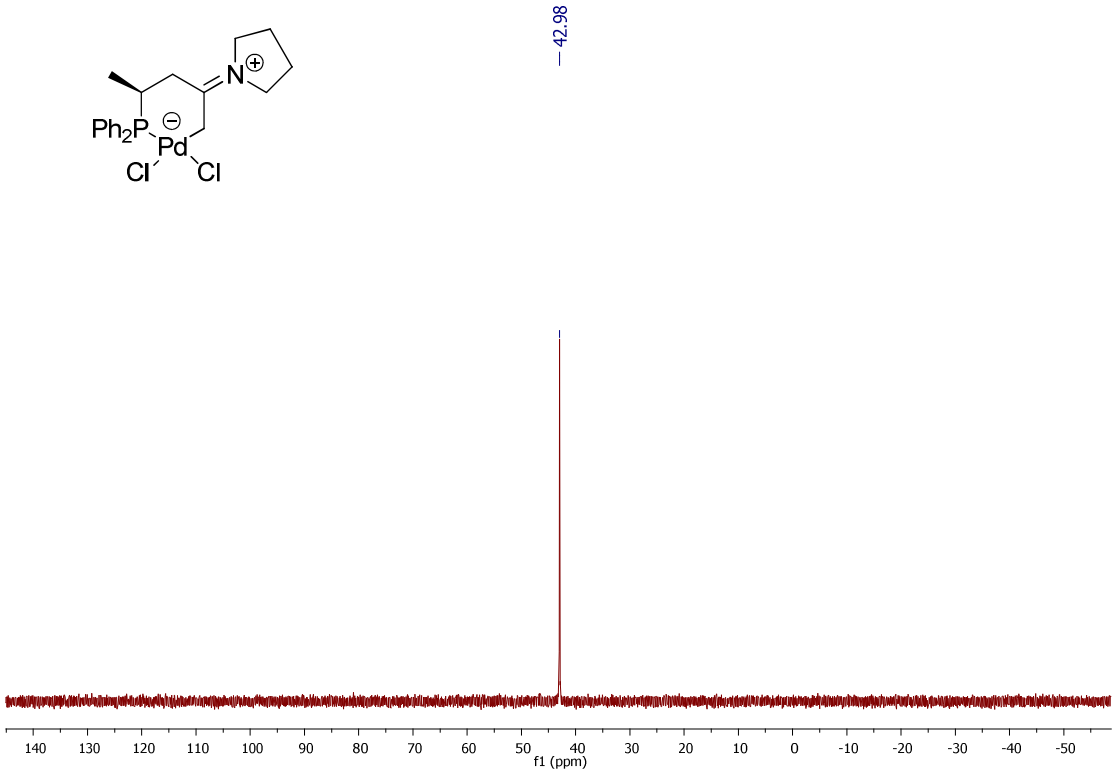

Figure S15 $^{31}P\{^{1}H\}$ NMR spectrum of **2d** recorded in DMSO-d6

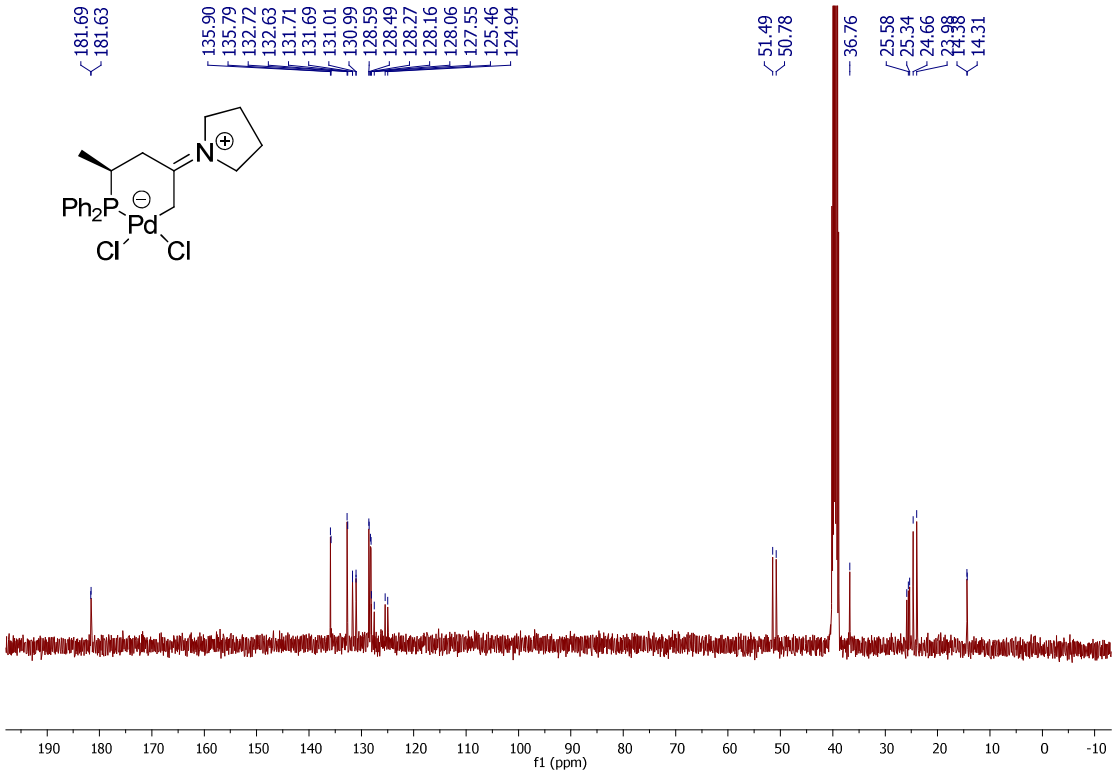

Figure S16 $^{13}C\{^{1}H\}$ NMR spectrum of **2d** recorded in DMSO-d6

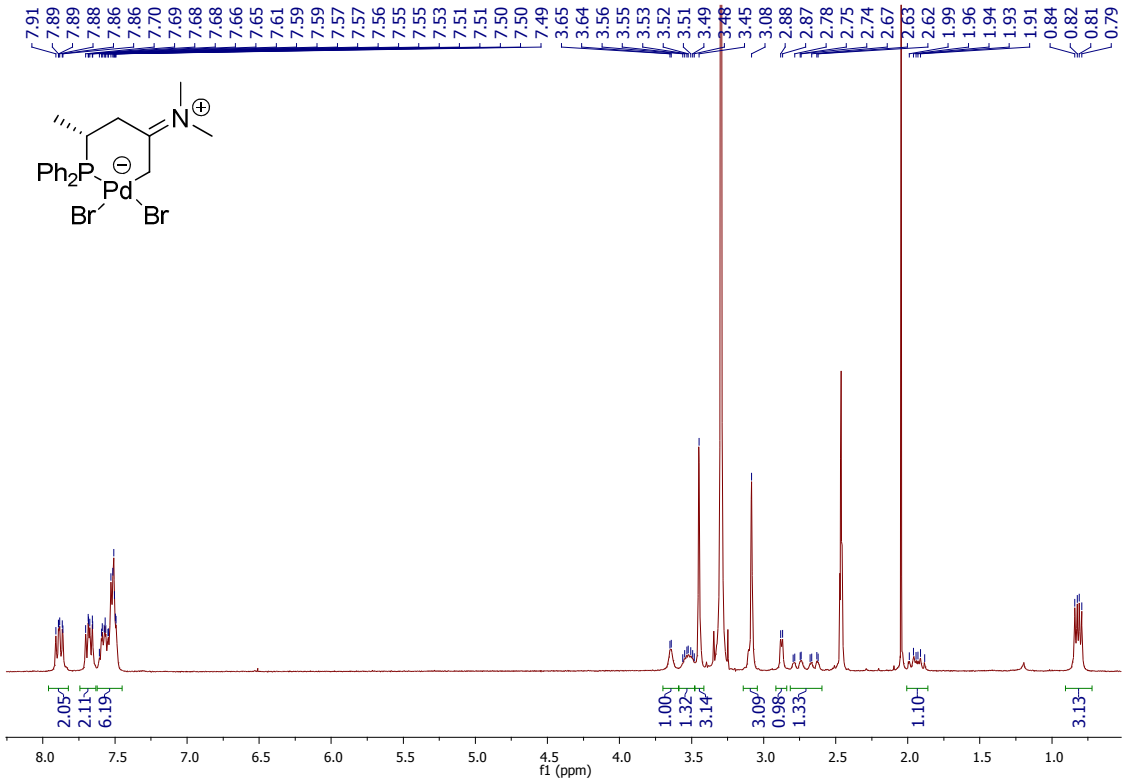

Figure S17 ^{1}H NMR spectrum of **3a** recorded in DMSO-d6

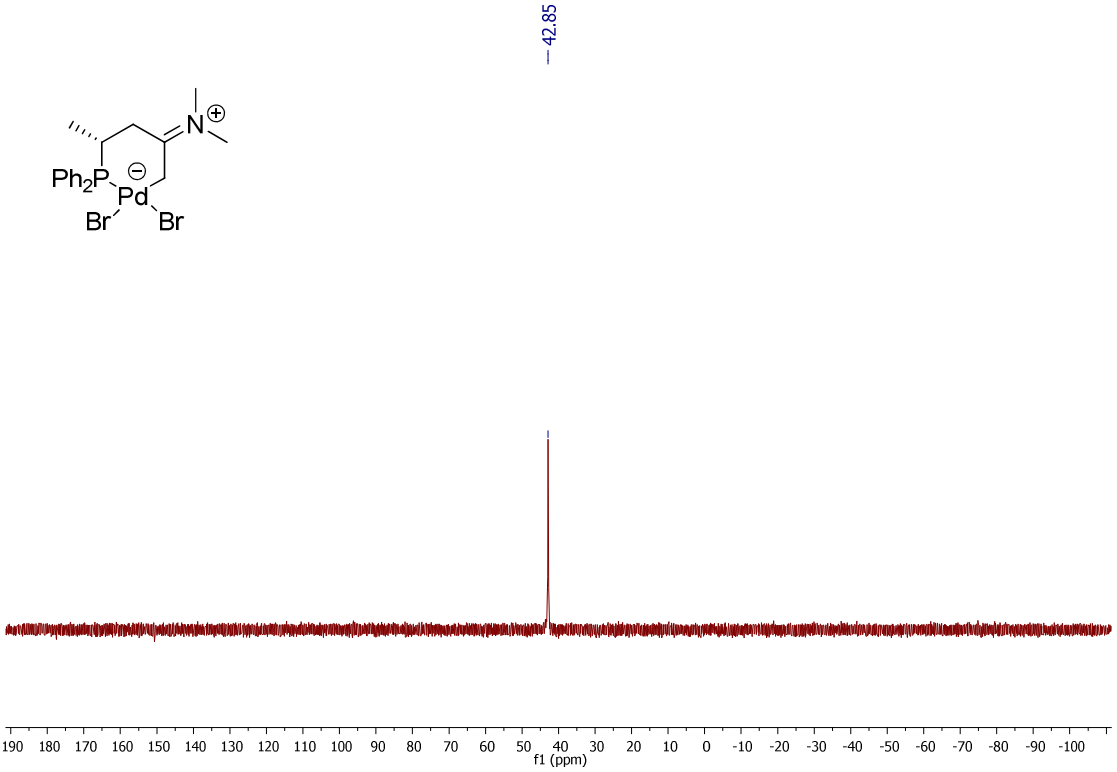

Figure S18 ^{31}P{^{1}H} NMR spectrum of **3a** recorded in DMSO-d6

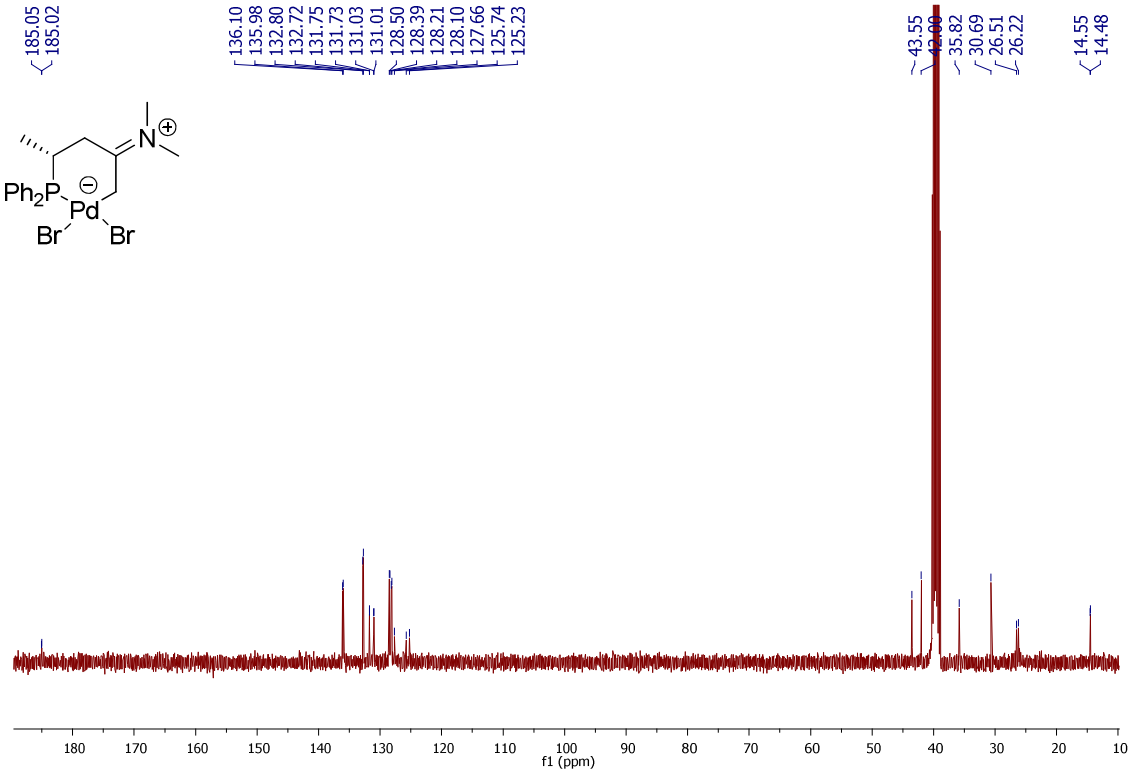

Figure S19 $^{13}C\{^{1}H\}$ NMR spectrum of **3a** recorded in DMSO-d6

X-ray crystallographic data

Computing details

Data collection: *CAD-4 EXPRESS* for 2a_ac, 2b;[5] *APEX3* v2017.3-0 for 2a_CHCl3.[6] Cell refinement: *CAD-4 EXPRESS* for 2a_ac, 2b;[5] *APEX3* v2017.3-0 for 2a_CHCl3.[6] Data reduction: *XCAD4* for 2a_ac, 2b;[7] *APEX3* v2017.3-0 for 2a_CHCl3.[6] Program(s) used to solve structure: *SHELXS2013* for 2a_ac;[8] *SIR92* for 2b;[9] SHELXT 2014/5 for 2a_CHCl3.[10] Program(s) used to refine structure: *SHELXL2016*/4 for 2a_ac, (2b);[11] *SHELXL2016*/6 for 2a_CHCl3.[10] Molecular graphics: *ORTEP-3 for Windows* for 2a_ac and 2b;[12] shelXle for 2a_CHCl3.[13] Software used to prepare material for publication: *WinGX* publication routines for 2a_ac and 2b;[12] *APEX3* v2017.3-0 for 2a_CHCl3.[6]

(2a_ac)

Table S1 Crystal data

$2(C_{19}H_{24}Cl_2NPPd)\cdot C_3H_6O$	D_x = 1.53 Mg m^{-3}
M_r = 1007.4	Mo $K\alpha$ radiation, λ = 0.71073 Å

Orthorhombic, $P22_12_1$	Cell parameters from 25 reflections
a = 8.848 (1) Å	θ = 9.4–16.7°
b = 14.919 (1) Å	μ = 1.17 mm^{-1}
c = 16.567 (1) Å	T = 298 K
V = 2186.9 (3) $Å^3$	Block, colourless
Z = 2	0.25 × 0.2 × 0.15 mm
F(000) = 1024	

Table S2 Data collection

Enraf Nonius MACH3 diffractometer	2675 reflections with $I > 2\sigma(I)$
Radiation source: Enraf Nonius FR590	R_{int} = 0.036
Graphite monochromator	θ_{max} = 25.6°, θ_{min} = 2.6°
non–profiled ω scans	h = -4→10
Absorption correction: ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta. Cryst. A24, 351 Number of ψ scan sets used was 4 Theta correction was applied. Averaged transmission function was used. Fourier smoothing - Window value 5	k = -7→18
T_{min} = 0.850, T_{max} = 0.987	l = -20→20
3312 measured reflections	3 standard reflections every 334 reflections
2965 independent reflections	intensity decay: none

Table S3 Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.047	$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 4.9132P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.097	$(\Delta/\sigma)_{max} < 0.001$
S = 1.13	$\Delta\rangle_{max}$ = 0.55 e $Å^{-3}$
2965 reflections	$\Delta\rangle_{min}$ = -0.64 e $Å^{-3}$
240 parameters	Absolute structure: Flack x determined using 521 quotients [(I+)-(I-)]/[(I+)+(I-)][14]
0 restraints	Absolute structure parameter: -0.11 (6)
0 constraints	

Table S4 Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

(2b)

Table S5 Crystal data

$C_{22}H_{28}Cl_2NPPd$	$F(000) = 1048$
$M_r = 514.72$	$D_x = 1.508$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 25 reflections
$a = 11.195$ (1) Å	$\theta = 6.7–15.0°$
$b = 14.223$ (2) Å	$\mu = 1.13$ mm^{-1}
$c = 14.237$ (3) Å	$T = 298$ K
$V = 2266.9$ (6) Å^3	Block, yellow
$Z = 4$	0.25 × 0.2 × 0.16 mm

Table S6 Data collection

Enraf Nonius MACH3 diffractometer	1243 reflections with $I > 2\sigma(I)$
Radiation source: Enraf Nonius FR590	$R_{int} = 0.011$
Graphite monochromator	$\theta_{max} = 25.5°$, $\theta_{min} = 2.7°$
non–profiled ω scans	$h = -4 \rightarrow 13$
Absorption correction: ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta. Cryst. A24, 351 Number of ψ scan sets used was 3 Theta correction was applied. Averaged transmission function was used. Fourier smoothing - Window value 5	$k = -6 \rightarrow 17$
$T_{min} = 0.844$, $T_{max} = 0.965$	$l = 0 \rightarrow 17$
2403 measured reflections	2 standard reflections every 126 reflections
2365 independent reflections	intensity decay: 2%

Table S7 Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 2.086P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.183$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.99$	$\Delta\rangle_{max} = 0.81$ e Å^{-3}
2365 reflections	$\Delta\rangle_{min} = -0.72$ e Å^{-3}
246 parameters	Extinction correction: *SHELXL2016*/4[11]
222 restraints	Extinction coefficient: 0.0001 (5)

0 constraints	Absolute structure: Classical Flack method preferred over Parsons because only 2 suitable Friedel pairs available.
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: -0.09 (16)
Secondary atom site location: structure-invariant direct methods	

Table S8 Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

(2a_CHCl3)

Table S9 Crystal data

$C_{19}H_{24}Cl_2NPPd \cdot CHCl_3$	$D_x = 1.615$ Mg m^{-3}
$M_r = 594.03$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 139 reflections
$a = 8.7588$ (3) Å	$\theta = 3.4–23.1°$
$b = 11.4719$ (4) Å	$\mu = 1.38$ mm^{-1}
$c = 24.3197$ (8) Å	$T = 296$ K
$V = 2443.65$ (14) Å^3	Rod, yellow
$Z = 4$	0.93 × 0.16 × 0.07 mm
$F(000) = 1192$	

Table S10 Data collection

Bruker D8 Venture diffractometer	4644 independent reflections
Radiation source: INCOATEC IμS 3.0, sealed tube microsource	4470 reflections with $I > 2\sigma(I)$
Multilayer mirror monochromator	$R_{int} = 0.050$
Detector resolution: 7.3910 pixels mm^{-1}	$\theta_{max} = 25.7°$, $\theta_{min} = 2.4°$
ϕ and ω scans	$h = -10 \rightarrow 10$
Absorption correction: numerical *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	$k = -14 \rightarrow 14$
$T_{min} = 0.62$, $T_{max} = 0.75$	$l = -29 \rightarrow 29$
88585 measured reflections	

Table S11 Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.023$	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 1.4048P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rangle_{max} = 0.51$ e Å^{-3}
4644 reflections	$\Delta\rangle_{min} = -0.46$ e Å^{-3}
257 parameters	Extinction correction: *SHELXL2016*/6 (Sheldrick 2016)
0 restraints	Extinction coefficient: 0.0005 (4)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack x determined using 1884 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.006 (10)

Table S12 Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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