Diastereoselective Synthesis of Bulky, Strongly Nucleophilic and Configurationally Stable *P*-Stereogenic Tricyclic Phosphine

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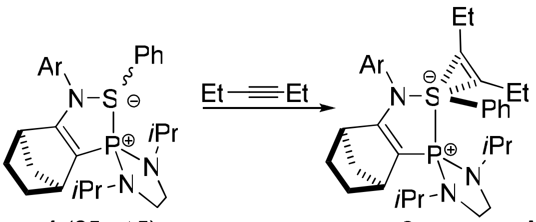
1-General

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. The product **1** was synthesized as previously reported (S1). ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were recorded on Avance 300 spectrometers. ^{1}H, ^{29}Si and ^{13}C NMR chemical shifts are reported in ppm relative to CH_4Si as internal standard. ^{31}P NMR downfield chemical are expressed in ppm relative to 85% H_3PO_4. ^{1}H correlation spectra were obtained using standard procedures. Infrared spectra were obtained as KBr pellets with a Varian 640-IR FT IR spectrophotometer. Optical rotations were recorded on a Perkin–Elmer-241 polarimeter (10 cm cell, 589 nm). Analytical high performance liquid chromatography (HPLC) was performed on an Alliance Waters (Waters 996 diode array detector) instrument using a chiral column Daicel Chiralpack AD-H (0.46 cm x 25 cm). The data of the structures for the compounds **2a**, **3b**, **3c** and **7a** were collected on a Bruker-AXS APEX II diffractometer at a temperature of 193(2) K with graphite-monochromated MoKα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. Semi-empirical absorption corrections were employed. (S2). The structures were solved by direct methods, using SHELXS-97 (S3) and refined using the least–squares method on F^2(S4). All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model.

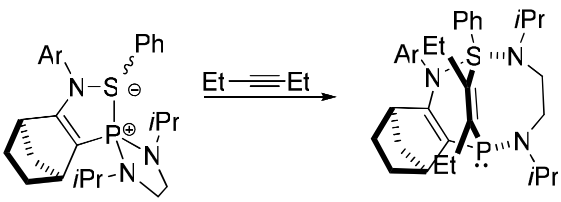
2-Experimental procedures and characterisation data



1 (85 15) **2a** Ar = 2 6-iPr$_2$-C$_6$H$_3$

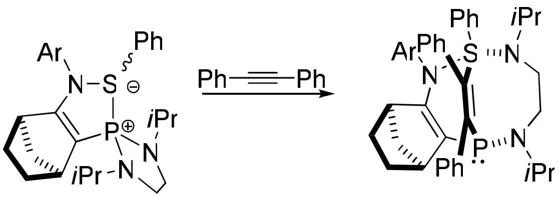
2a. At RT, under argon, to a solution of **1** (400.4 mg, 0.734 mmol) in THF (2 mL) diethylacethylene (1.6 mL, 20 equiv) was added. The solution was stirred for 10 hours ($^{31}P\{^{1}H\}$ NMR: 84%, **2a**; 7%, **1**; 9%, **3a**). Then, all the volatiles were removed under vacuum and the pale yellow residue was purificated by crystallization from diethyl ether afforded a colorless crystals that were filtered off, washed with pentane (2 x 1 mL) and vacuum-dried (263.8 mg, 55.5%). Mp: 192-193°C. ^{1}H NMR (300.18 MHz, THF-D$_8$, -40ºC): $\delta = 0.30$ (st, $J_{HH} = 7.6$ Hz, 3H, CH_{3SiCEt}), 0.42 (d, $J_{HH} = 6.4$ Hz, 3H, CH_{3PNiPr}), 0.51

(d, J_{HH} = 6.7 Hz, 3H, CH_{3PNiPr}), 0.85 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.86 (overlapped with the methyl signal, 1H, ½ $CH_{2bridge}$), 0.98 (st, J_{HH} = 5.9 Hz, 6H, 2 x CH_{3PNiPr}), 1.06-1.17 (m, 12H, CH_{3Et}, 3 x CH_{3iPr}), 1.18 (m, 1H, ½ $CH_{2bridge}$), 1.33 (m, 1H, ½ $CH_{2CbridgeheadCP}$), 1.48 (m, 1H, PNCH), 1.61 (m, 3H, ½ $CH_{2CbridgeheadCP}$, $CH_{2CbridgeheadCN}$), 1.68 (m, 2H, CH_{2SiCEt}), 2.23 (brs, 1H, $PCCH_{bridgehead}$), 2.58, 2.26 (2 x m, 2H, CH_{2Et}), 2.78 (m, 2H, $PNCH_2$), 2.91 (brs, 1H, $NCCH_{bridgehead}$), 2.95, 3.09 (2 x m, 2H, $PNCH_2$), 3.27 (m, 2H, PNCH, CH_{iPr}), 3.74 (sep, J_{HH} = 6.7 Hz, 1H, CH_{iPr}), 6.92-7.55 ppm (8H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, THF-D_8, -40ºC): δ = 10.41 (s, CH_{3SiCEt}), 12.29 (d, J_{PC} = 2.4 Hz, CH_{3PCEt}), 16.44 (d, J_{PC} = 3.2 Hz, CH_{3PNiPr}), 19.92 (d, J_{PC} = 5.7 Hz, CH_{3PNiPr}), 20.18 (d, J_{PC} = 9.7 Hz, CH_{2PCEt}), 20.55 (s, CH_{3PNiPr}), 20.67 (d, J_{PC} = 2.8 Hz, CH_{3PNiPr}), 21.91 (s, CH_{2SiCEt}), 21.65, 21.70, 21.91, 23.12 (4 x s, 4C, CH_{3iPr}), 24.81 (s, $\mathit{C}H_{2CbridgeheadCP}$), 25.25 (s, CH_{iPr}), 25.62 (s, $\mathit{C}H_{2CbridgeheadCN}$), 25.79 (s, CH_{iPr}), 41.03 (d, J_{PC} = 7.1 Hz, $PNCH_2$), 43.62 (d, J_{PC} = 5.1 Hz, $PC\mathit{CH}_{bridgehead}$), 43.91 (s, CH_{2Norb}), 44.02 (d, J_{PC} = 3.1 Hz, $NC\mathit{CH}_{bridgehead}$), 44.76 (d, J_{PC} = 8.5 Hz, $PNCH_2$), 45.49 (d, J_{PC} = 18.6 Hz, PNCH), 46.80 (d, J_{PC} = 29.3 Hz, PNCH), 118.77 (d, J_{PC} = 31.9 Hz, P*C*=CN), 122.02, 122.13, 124.90, 127.09 (s, 4C, CH_{Ar}), 125.72 (s, 2C, CH_{Ar}), 133.06 (s, 2C, CH_{Ar}), 134.26 (d, J_{PC} = 20.5 Hz, SiC_{ipso}), 138.37 (s, NC_{ipso}), 146.01, 145.32 (2 x s, 2C, NC_{orto}), 154.12 (d, J_{PC} = 41.1 Hz, Si*C*=C), 159.45 ppm (d, J_{PC} = 22.2 Hz, SiC=*C*), 162.50 ppm (d, J_{PC} = 31.6 Hz, PC=*C*N). $^{29}Si\{^1H\}$ NMR (59.63 MHz, THF-D_8, 25ºC): δ = -99.3 ppm (d, J_{PSi} = 29.9 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, THF-D_8, -40ºC): δ = 70.7 ppm (s).



1 (85 15) **3a** Ar = 2 6-iPr_2-C_6H_3

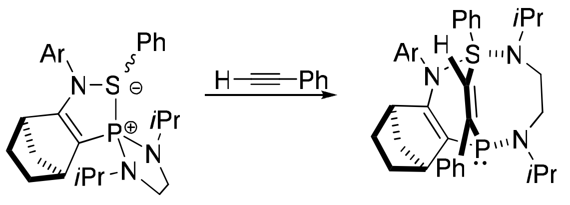
Phosphine 3a. At 30ºC, under argon, to a solution of **1** (500.1 mg, 0.9162 mmol) in THF (3 mL) diethylacethylene (0.600 mL, 6 equiv) was added. The solution was stirred for 96 hours. Then, all the volatiles were removed under vacuum and the white residue was washed with pentane (2 x 3 mL) and vacuum-dried (526.9 mg, 88.8%). Mp: 193-194°C. ^1H NMR (300.18 MHz, C_6D_6, 25ºC): δ = 0.52 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.78 (st, J_{HH} = 7.4 Hz, 3H, CH_{3SiCEt}), 1.09 (m, 1H, ½ $CH_{2bridge}$), 1.15 (d, J_{HH} = 6.7 Hz, 6H, CH_{3PNiPr}, CH_{3iPr}), 1.17 (J_{HH} = 6.6 Hz, 3H, CH_{3PNiPr}), 1.27 (J_{HH} = 6.3 Hz, 3H, $CH_{3SiNiPr}$), 1.31 (J_{HH} = 6.6 Hz, 6H, 2 x CH_{3iPr}), 1.32 (st, J_{HH} = 7.4 Hz, 3H, CH_{3PCEt}), 1.37 (J_{HH} = 6.7 Hz, 3H, $CH_{3\,SiNiPr}$), 1.15-1.40 (overlapped with the methyl signals, 2H, $CH_{2CbridgeheadCP}$), 1.49, 2.13 (2 x m, 2H, CH_{2SiCEt}), 1.77 (m, 2H, $CH_{2CbridgeheadCN}$), 1.97 (brd, J_{HH} = 8.0 Hz, 1H, ½ $CH_{2bridge}$), 2.48, 2.79 (2 x m, 2H, CH_{2PCEt}), 2.87 (br., 1H, $PCCH_{bridgehead}$), 3.04 (m, 1H, ½ $PNCH_2$), 3.18 (br., J_{HH} = 8.0 Hz, 1H, $NCCH_{bridgehead}$), 3.36 (m, 2H, CH_{iPr}, ½ $PNCH_2$), 3.45 (m, 2H, $SiNCH_2$), 3.73 (m, 2H, PNCH, CH_{iPr}) 3.88 (sep, J_{HH} = 6.4 Hz, 1H, SiNCH), 5.40-7.40 ppm (m, 8H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 25ºC): δ = 12.31 (s, CH_{3SiCEt}), 12.38 (d, J_{PC} = 6.5 Hz, CH_{3PCEt}), 20.45 (s, $CH_{3SiNiPr}$), 21.45 (d, J_{PC} = 6.4 Hz, CH_{3PNiPr}), 21.91 (s, CH_{3iPr}), 22.56 (d, J_{PC} = 5.4 Hz, CH_{3PNiPr}), 22.58 (s, CH_{3iPr}), 23.51 (s, CH_{3iPr}), 24.25 (s, $CH_{3SiNiPr}$), 25.55 (d, J_{PC} = 2.5 Hz, $\mathit{C}H_{2bridgeheadCP}$), 25.65 (d, J_{PC} = 1.7 Hz, CH_{2SiCEt}), 25.89 (s, CH_{iPr}), 26.44 (s, CH_{3iPr}), 26.51 (s, CH_{iPr}), 27.14 (s, $\mathit{C}H_{2bridgeheadCN}$), 28.80 (d, J_{PC} = 58.4 Hz, CH_{2PCEt}), 43.92 (d, J_{PC} = 3.3 Hz, s, CH_{2Norb}), 44.23 (d, J_{PC} = 2.2 Hz, $SiNCH_2$), 45.52 (d, J_{PC} = 1.8 Hz, $PC\mathit{CH}_{bridgehead}$), 46.80 (s, SiNCH), 46.96 (d, J_{PC} = 41.8 Hz, $NC\mathit{CH}_{bridgehead}$), 48.12 (d, J_{PC} = 11.3 Hz, $PNCH_2$), 56.63 (d, J_{PC} = 46.0 Hz, PNCH), 111.56 (d, J_{PC} = 9.0 Hz, P*C*=CN), 123.31, 123.51, 126.42 128.09 (4 x s, 4C, CH_{Ar}), 125.91 (br.-d, 2C, CH_{Ar}), 135.39 (br.-s, 2C, CH_{Ar}), 133.44 (s, 1C, C_{Ar}), 139.29 (s, C_{Ar}), 146.55 (s, C_{Ar}), 148.29 (s, C_{Ar}), 138.32 (d, J_{PC} = 4.1 Hz, Si*C*=CP), 154.32 (d, J_{PC} = 5.2 Hz, N*C*=CP), 155.40 ppm (d, J_{PC} = 26.3 Hz, SiC=*C*P). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 25ºC): δ = -25.4 ppm (d, J_{PSi} = 3.2 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25ºC): δ = 42.9 ppm (s).



1 (85 15) **3a** Ar = 2 6-iPr_2-C_6H_3

Phosphine 3b. At RT, under argon, to a solution of **1** (939.1 mg, 1.72 mmol) in THF (15 mL) diphenylacethylene (307.3 mg, 1.72 mmol) was added. The solution was stirred for 3 hours, and then the solution was concentrated. At -30ºC afforded yellow crystals that were filtered off, washed with diethyl ether (2 x 1 mL) and vacuum-dried (1020.8 mg, 83.3%). Mp: 182-183°C. ^1H NMR (300.18 MHz, C_6D_6, 25ºC): δ = 0.32 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.91 (d, J_{HH} = 6.1 Hz, 3H, CH_{3PNiPr}), 0.96 (d, J_{HH} = 6.1 Hz, 3H, CH_{3PNiPr}), 1.54 (d-pseudo-t, J_{HH} = 6.7, 1.8 Hz, 1H, ½ $CH_{2bridge}$), 1.31 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.39 (m, 2H, $CH_{2CbridgeheadCP}$), 1.45 (d, J_{HH} = 7.0 Hz, 3H, CH_{3iPr}), 1.24 (d, J_{HH} = 6.5 Hz, 6H, 2 x $CH_{3SiNiPr}$), 1.54 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.88 (m, 2H, $CH_{2CbridgeheadCN}$), 2.10 (br.-d, 1H, ½ $CH_{2bridge}$), 2.92 (br.-s, 1H, $PCCH_{bridgehead}$), 3.19 (m, 3H, $NCCH_{bridgehead}$, PNCH, ½ $PNCH_2$), 3.50 (dd, J_{HH} = 13.5, 6.5 Hz, 1H, ½ $PNCH_2$), 3.68 (m, 2H, CH_{iPr}, ½

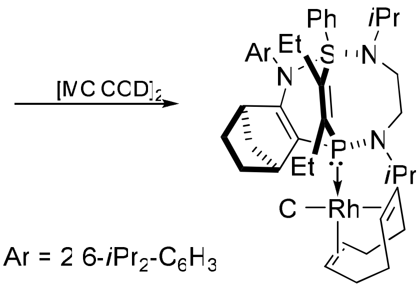
$SiNCH_2$), 3.97 (m, 2H, CH_{iPr}, ½ $SiNCH_2$), 4.24 (sep, J_{HH} = 6.5 Hz, 1H, SiNCH,), 6.44-7.38 ppm (m, 18H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 25ºC): δ = 22.39 (d, J_{PC} = 5.3 Hz, CH_{3PNiPr}), 22.71 (s, $CH_{3SiNiPr}$), 23.11 (d, J_{PC} = 7.3 Hz, CH_{3PNiPr}), 23.30 (s, CH_{3iPr}), 23.76 (s, CH_{3iPr}), 24.71 (s, CH_{3iPr}), 25.24 (s, $CH_{3SiNiPr}$), 26.61 (d, J_{PC} = 2.9 Hz, $\mathit{C}H_{2CbridgeheadCP}$), 27.08 (s, CH_{iPr}), 27.67 (s, CH_{3iPr}), 28.09 (br.-s, $\mathit{C}H_{2CbridgeheadCN}$), 28.13 (s, CH_{iPr}), 45.79 (m, $SiNCH_2$, s, CH_{2Norb}), 47.12 (d, J_{PC} = 1.0 Hz, $PC\mathit{CH}_{bridgehead}$), 47.61 (d, J_{PC} = 41.0 Hz, $NC\mathit{CH}_{bridgehead}$), 48.27 (s, SiNCH), 50.08 (d, J_{PC} = 11.1 Hz, $PNCH_2$), 57.19 (d, J_{PC} = 42.5 Hz, PNCH), 114.72 (d, J_{PC} = 15.7 Hz, P*C*=CN), 124.23, 124.30, 124.48, 126.36, 127.06, 128.09, 128.29, 129.32, 131.23, 131.36, 131.61, 136.35 (12 x s, 18C, CH_{Ar}), 132.70 (s, 1C, C_{Ar}), 140.39 (s, 1C, C_{Ar}), 143.19 (d, J_{PC} = 1.0 Hz, 1C, C_{Ar}), 143.56 (s, 1C, C_{Ar}), 145.75 (d, J_{PC} = 35.7 Hz, Si*C*=CP), 147.06 (s, 1C, C_{Ar}), 148.84 (s, 1C, C_{Ar}), 155.46 (d, J_{PC} = 4.3 Hz, N*C*=CP), 156.79 ppm (d, J_{PC} = 34.2 Hz, SiC=*C*P). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 25ºC): δ = -29.2 ppm (d, J_{PSi} = 2.1 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25ºC): δ = 46.6 ppm (s).



1 (85 15) **3a** Ar = 2 6-iPr_2-C_6H_3

Phosphine 3c. At RT, under argon, to a solution of **1** (150.9 mg, 0.276 mmol) in THF (2 mL) phenylacethylene (60.7 µL, 0.553 mmol) was added. The solution was stirred for 10 hours. Then, all the volatiles were removed under vacuum. the crystallization of the residue in diethyl ether afforded a yellow crystals. The solid was filtered off, washed with diethyl ether (2 x 1 mL) and vacuum-dried (139.3 mg, 32.1%). Mp: 173-174°C. ^1H NMR (300.18 MHz, $CDCl_3$, 25ºC): δ = 0.61 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 0.72 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.91 (d, J_{HH} = 6.4 Hz, 3H, $CH_{3SiNiPr}$), 0.92 (d, J_{HH} = 6.6 Hz, 3H, CH_{3PNiPr}), 0.94 (d, J_{HH} = 6.6 Hz, 3H, CH_{3PNiPr}), 0.98, 1.32 (2 x m, 2H, $CH_{2CbridgeheadCP}$), 1.05 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.07, 1.71 (2 x m, 2H, $CH_{2bridge}$), 1.14 (d, J_{HH} = 6.7 Hz, 3H, $CH_{3SiNiPr}$), 1.25 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.43, 1.67 (2 x m, 2H, $CH_{2CbridgeheadCN}$), 2.70 (br.-s, 1H, $PCCH_{bridgehead}$), 2.97 (m, 2H, $NCCH_{bridgehead}$, CH_{iPr}), 3.10 (m, 2H, $PNCH_2$), 3.34 (m, 3H, PNCH, $SiNCH_2$), 3.48 (sept, J_{HH} = 6.8 Hz, 1H, SiNCH), 3.60 (sept, J_{HH} = 6.8 Hz, 1H, CH_{iPr}), 6.19 (d, J_{PH} = 10.9, 1H, SiCH=CP), 6.66 (br.-d, J_{HH} = 8.1 Hz, 2H, H_{Ar}), 6.94 (pseudo-t, J_{HH} = 7.4 Hz, 2H, H_{Ar}), 7.02-7.27 (7H, H_{Ar}), 7.45 ppm (br.-d, J_{HH} = 8.1 Hz, 2H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 21.29 (s, $CH_{3SiNiPr}$), 23.50 (d, J_{PC} = 5.8 Hz, CH_{3PNiPr}), 23.93 (s, CH_{3iPr}), 24.30 (d, J_{PC} = 5.8 Hz, CH_{3PNiPr}), 25.19 (s, $CH_{3SiNiPr}$), 25.32 (s, CH_{3iPr}), 25.60 (s, CH_{3iPr}), 26.95 (d, J_{PC} = 1.7 Hz, $\mathit{C}H_{2CbridgeheadCP}$), 27.26 (s, CH_{3iPr}), 27.94 (s, CH_{iPr}), 28.17 (s, CH_{iPr}), 28.90 (s, $\mathit{C}H_{2CbridgeheadCN}$), 45.22 (d, J_{PC} = 2.2 Hz, $SiNCH_2$), 45.83 (d, J_{PC} = 3.9 Hz, s, CH_{2Norb}), 47.28 (d, J_{PC} = 2.0 Hz, PC$\mathit{CH}_{bridgehead}$), 48.08 (s, SiNCH), 49.43 (d, J_{PC} = 45.4 Hz, NC$\mathit{CH}_{bridgehead}$), 50.38 (d, J_{PC} = 11.2 Hz, $PNCH_2$), 57.86 (d, J_{PC} = 43.5 Hz, PNCH), 111.09 (d, J_{PC} = 6.2 Hz, P*C*=CN), 125.07, 127.56, 127.77, 128.10, 128.21, 128.26, 128.67, 136.87 (8 x s, 13C, CH_{Ar}), 135.00 (d, J_{PC} = 2.0, Hz, Si*C*H=CP), 136.41, 140.59, 148.27, 150.40 (4 x s, 4C, C_{Ar}), 148.68 (d, J_{PC} = 29.1 Hz, PCAr_{orto}), 158.13 (d, J_{PC} = 6.8 Hz, N*C*=CP), 160.47 ppm (d, J_{PC} = 29.1 Hz, SiCH=*C*P). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25°C): δ = -32.5 ppm (d, J_{PSi} = 1.7 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25°C): δ = 41.7 ppm.

3a

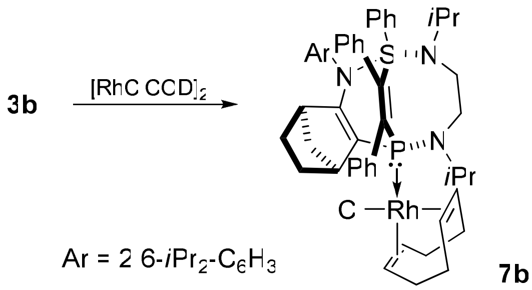


Ar = 2 6-*i*Pr_2-C_6H_3

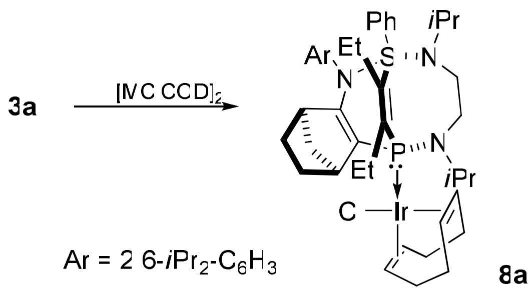
7a

[(3a)Rh(cod)Cl] (7a). At RT, under argon, to a solution of $[Rh(cod)Cl]_2$ (19.4 mg, 0.039 mmol) in CH_2Cl_2 (2 mL) **3a** (51.0 mg, 0.079 mmol) was added. The solution was stirred for 15 min and then the solvent was vacuum-evaporated. The orange solid was washed with pentane (1 x 1 mL) and vacuum-dried (60.6 mg, 86.1%). Crystals suitable for X-ray analysis were obtained by crystallization from diethylether. The related compounds **7-8** were prepared similarly. Yield: **7b**, 83.2%; **8a**, 88.4%; **8b**, 88.1%.

7a: ^1H NMR (300.18 MHz, $CDCl_3$, 25°C): δ = 0.27 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.70 (pseudo-t, J_{HH} = 7.3 Hz, 3H, CH_{3SiCEt}), 1.02 (d, J_{HH} = 6.6 Hz, 3H, $CH_{3SiNiPr}$), 1.11 (pseudo-t, J_{HH} = 6.6 Hz, 6H, 2 x CH_{3PNiPr}), 1.19 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.31 (br.-d, J_{HH} = 6.2 Hz, 6H, $CH_{3SiNiPr}$, CH_{3iPr}), 1.51 (pseudo-t, J_{HH} = 7.4 Hz, 3H, CH_{3PCEt}), 1.08-1.36 (overlapped with the methyl signals, 4H, ½ $CH_{2bridge}$, $CH_{2CbridgeheadCP}$, ½ CH_{2cod}), 1.43 (m, 1H, ½ CH_{2SiCEt}), 1.75 (m, 3H, ½ $CH_{2CbridgeheadCN}$, ½ CH_{2cod}, ½ CH_{2cod}), 1.96 (br.-s, 1H, ½ $CH_{2bridge}$), 2.10 (m, 1H, ½ CH_{2cod}), 2.28 (m, 3H, ½ CH_{2SiCEt}, ½ CH_{2cod}, ½ $CH_{2CbridgeheadCN}$), 2.52 (m, 1H, ½ CH_{2cod}), 2.68 (m, 1H, ½ CH_{2cod}), 2.75 (m, 2H, $PCCH_{bridgehead}$, ½ CH_{2cod}), 3.14 (m, 2H, CH_{2PCEt}), 3.31-3.58 (m, 7H, PNCH, CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 3.71 (m, 2H, CH_{iPr}, SiNCH), 4.24 (m, 2H, 2 x CH_{cod}), 5.25 (m, 2H, 2 x CH_{cod}), 5.70-8.10 ppm (m, 8H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 12.18 (s, 3H, CH_{3SiCEt}), 15.80 (d, J_{PC} = 3.0 Hz, 3H, CH_{3PCEt}), 22.14 (s, $CH_{3SiNiPr}$), 23.57 (s, CH_{3iPr}), 24.05 (d, J_{PC} = 7.9 Hz, CH_{3PNiPr}), 24.16 (s, CH_{3iPr}), 24.38 (s, CH_{3iPr}), 24.92 (s, CH_{3iPr}), 25.16 (s, CH_{3PNiPr}), 26.57 (s, $\mathit{C}H_{2CbridgeheadCP}$), 26.51 (s, $CH_{3SiNiPr}$), 26.62 (s, CH_{iPr}), 27.17 (d, J_{PC} = 9.6 Hz, CH_{2SiCEt}), 27.79 (s, CH_{iPr}), 29.94 (br.-s, CH_{2cod}), 30.92 (s, $\mathit{C}H_{2CbridgeheadCN}$), 31.04 (br.-s, 2C, 2 x CH_{2cod}), 33.42 (d, J_{PC} = 39.7 Hz, CH_{2PCEt}), 34.53 (br.-s, CH_{2cod}), 43.99 (s, $SiNCH_2$), 46.51 (d, J_{PC} = 7.7 Hz, $PC\mathit{CH}_{bridgehead}$), 47.00 (d, J_{PC} = 3.7 Hz, s, CH_{2Norb}), 47.57 (s, SiNCH), 48.02 (d, J_{PC} = 20.9 Hz, $NC\mathit{CH}_{bridgehead}$), 49.79 (d, J_{PC} = 7.0 Hz, $PNCH_2$), 50.16 (d, J_{PC} = 43.1 Hz, PNCH), 68.61 (d, J_{RhC} = 14.2 Hz, CH_{cod}), 72.89 (d, J_{RhC} = 13.5 Hz, CH_{cod}), 97.60 (m, 2C, 2 x CH_{cod}), 103.49 (d, J_{PC} = 50.4 Hz, P*C*=CN), 124.15 (s, 1C, CH_{Ar}), 124.96 (s, 1C, CH_{Ar}), 126.63 (brs, 2C, CH_{Ar}), 127.35 (s, 1C, CH_{Ar}), 129.08 (s, 1C, CH_{Ar}), 132.72 (s, 1C, C_{Ar}), 136.92 (brs, 2C, CH_{Ar}), 140.33 (s, 1C, C_{Ar}), 144.23 (d, J_{PC} = 3.3, Si*C*=CP), 146.65 (s, 1C, C_{Ar}), 149.95 (s, 1C, C_{Ar}), 152.81 (d, J_{PC} = 17.5, SiC=*C*P), 162.79 (d, J_{PC} = 3.1 Hz, N*C*=CP). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -23.9 ppm (d, J_{PSi} = 6.7 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 75.0 ppm (d, J_{RhP} = 156.6 Hz).

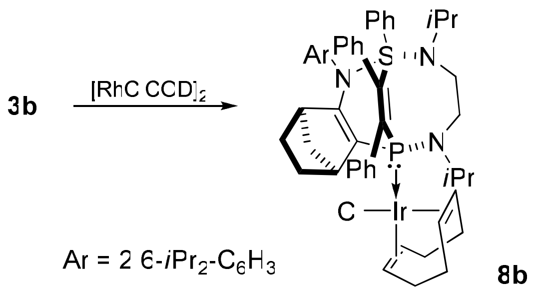


[(3b)Rh(cod)Cl] (7b). ^1H NMR (300.18 MHz, C_6D_6, 25ºC): δ = 0.57 (d, J_{HH} = 6.5 Hz, 3H, CH_{3iPr}), 1.05 (d, J_{HH} = 6.1 Hz, 3H, CH_{3PNiPr}), 1.12 (d, J_{HH} = 6.1 Hz, 3H, CH_{3PNiPr}), 1.24 (st, J_{HH} = 6.0 Hz, 6H, 2 x $CH_{3SiNiPr}$), 1.31 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.72 (d, J_{HH} = 6.5 Hz, 3H, CH_{3iPr}), 1.77 (d, J_{HH} = 6.4 Hz, 3H, CH_{3iPr}), 1.10-1.55 (overlapped with the methyl signals, 4H, ½ $CH_{2bridge}$, $CH_{2CbridgeheadCP}$, ½ CH_{2cod}), 1.80-2.30 (m, 7H, ½ $CH_{2bridge}$, 3 x CH_{2cod}), 2.52 (m, 1H, ½ CH_{2cod}), 3.01 (brs, 1H, $PCCH_{bridgehead}$), 3.19 (m, 2H, ½ $CH_{2CbridgeheadCN}$, PNCH), 3.45 (m, 2H, $NCCH_{bridgehead}$, ½ $PNCH_2$), 3.58-3.99 (m, 6H, CH_{iPr}, SiNCH, ½ $PNCH_2$, $SiNCH_2$, ½ $CH_{2CbridgeheadCN}$), 4.29 (m, 1H, CH_{cod}), 4.74 (sep, J_{HH} = 6.5 Hz, 1H, CH_{iPr}), 5.34 (m, 1H, CH_{cod}), 5.51 (m, 1H, CH_{cod}), 6.30-7.41 ppm (m, 18H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 25ºC): δ = 21.83 (s, CH_{3iPr}), 23.52, 23.97, 24.30, 24.81, 24.92, 25.08 (6 x s, 6C, 2 x $CH_{3SiNiPr}$, 2 x CH_{3iPr}, 2 x CH_{3PNiPr}), 25.50 (s, $\mathit{C}H_{2CbridgeheadCP}$), 27.01 (s, CH_{iPr}), 27.70 (br.-s, CH_{2cod}), 28.10 (s, CH_{iPr}), 28.18 (s, CH_{3iPr}), 29.21 (s, $\mathit{C}H_{2CbridgeheadCN}$), 29.78 (d, J_{PC} = 2.7 Hz, CH_{2cod}), 32.02 (d, J_{PC} = 2.5 Hz, CH_{2cod}), 34.54 (d, J_{PC} = 2.8 Hz, CH_{2cod}), 45.09 (s, $SiNCH_2$), 47.16 (d, J_{PC} = 7.6 Hz, PC$\mathit{CH}_{bridgehead}$), 47.67 (d, J_{PC} = 3.8 Hz, s, CH_{2Norb}), 48.09 (s, SiNCH), 48.94 (d, J_{PC} = 23.4 Hz, NC$\mathit{CH}_{bridgehead}$), 50.10 (d, J_{PC} = 13.5 Hz, PNCH), 50.51 (d, J_{PC} = 6.5 Hz, $PNCH_2$), 68.24 (d, J_{RhC} = 13.8 Hz, CH_{cod}), 68.64 (d, J_{RhC} = 13.1 Hz, CH_{cod}), 96.22 (dd, J_{RhC} = 16.6 Hz, J_{PC} = 7.4 Hz, CH_{cod}), 97.18 (dd, J_{RhC} = 12.4 Hz, J_{PC} = 9.2 Hz, CH_{cod}), 104.47 (d, J_{PC} = 50.4 Hz, P*C*=CN), 124.51, 124.69, 125.75, 126.28, 126.34, 126.48, 126.59, 127.29, 128.99, 129.55, 131.46, 131.59, 137.87 (13 x s, 18C, CH_{Ar}), 131.54 (s, 1C, C_{Ar}), 141.43 (s, 1C, C_{Ar}), 144.20 (d, J_{PC} = 10.9 Hz, 1C, C_{Ar}), 145.11 (d, J_{PC} = 6.4 Hz, 1C, C_{Ar}), 145.51 (d, J_{PC} = 25.3 Hz, Si*C*=CP), 146.68 (s, 1C, C_{Ar}), 150.28 (s, 1C, C_{Ar}), 154.45 (d, J_{PC} = 23.0 Hz, SiC=*C*P), 161.69 (d, J_{PC} = 4.7 Hz, N*C*=CP). $^{29}Si\{^1H\}$ NMR (59.63 MHz, C_6D_6, 25ºC): δ = -28.0 ppm (d, J_{PSi} = 4.7 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 25ºC): δ = 66.4 ppm (d, J_{RhP} = 154.3 Hz).



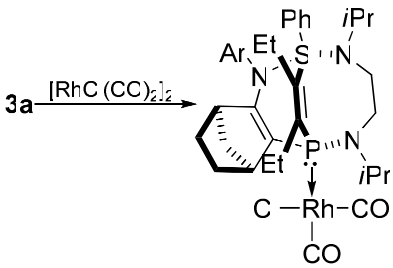
[(3a)Ir(cod)Cl] (8a). ^1H NMR (300.18 MHz, $CDCl_3$, 25ºC): δ = 0.26 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 0.70 (pseudo-t, J_{HH} = 7.4 Hz, 3H, CH_{3SiCEt}), 1.18 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.05 (J_{HH} = 6.7 Hz), 1.14 (J_{HH} = 6.4 Hz), 1.15 (J_{HH} = 6.3 Hz), 1.24 (J_{HH} = 6.4 Hz), 1.31 (J_{HH} = 6.5 Hz), 1.32 (J_{HH} = 6.0 Hz) (6 x d, 18H, 2 x CH_{3iPr}, 2 x $CH_{3SiNiPr}$, 2 x, CH_{3PNiPr}), 1.42 (pseudo-t, J_{HH} = 7.4 Hz, 3H, CH_{3SiCEt}), 1.10-1.38 (overlapped with the methyl signals, 5H, ½ $CH_{2bridge}$, $CH_{2CbridgeheadCP}$, ½ CH_{2cod1}, ½ CH_{2cod}), 1.46 (overlapped with the methyl signal, 1H, ½ CH_{2SiCEt}), 1.81 (m, J_{HH} = 10.1, 4.2 Hz, 1H, ½ $CH_{2CbridgeheadCN}$), 1.87-2.03 (m, 3H, ½ $CH_{2bridge}$, ½ CH_{2cod}, ½ CH_{2cod}), 2.15 (m, 2H, ½ CH_{2cod}, ½ CH_{2cod}), 2.34 (m, 1H, ½ CH_{2SiCEt}), 2.48 (m, 2H, ½ CH_{2cod}, ½ CH_{2cod}), 2.72 (brs, 1H, $PCCH_{bridgehead}$), 3.01 (m, 2H, CH_{2PCEt}), 3.16-3.45 (m, 7H, ½ $CH_{2CbridgeheadCN}$, CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 3.60-3.85 (m, 4H, CH_{iPr}, SiNCH, PNCH, CH_{cod}) 3.92 (sq, J_{HH} = 5.9 Hz, 1H, CH_{cod}), 4.81 (m, 2H, 2 x CH_{cod}), 6.70-8.30 ppm (m, 8H, H_{Ar}).

$^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25°C): δ = 13.04 (d, J_{PC} = 1.3 Hz, CH_{3SiCEt}), 16.86 (d, J_{PC} = 3.2 Hz, CH_{3PCEt}), 23.44 (s, CH_{3iPr}), 24.72, 25.32, 26.16, 26.36 (4 x s, 4C, 2 x $CH_{3SiNiPr}$, 2 x CH_{3iPr}), 25.44 (st, 2C, J_{PC} = 3.6 Hz, 2 x CH_{3PNiPr}), 25.67 (br.-s, $\mathit{C}H_{2CbridgeheadCP}$), 27.82 (d, J_{PC} = 3.6 Hz, CH_{2cod}), 27.85 (s, 2C, CH_{iPr}, CH_{3iPr}), 28.36 (d, J_{PC} = 11.3 Hz, CH_{2SiCEt}), 29.11 (s, CH_{iPr}), 31.84 (s, $\mathit{C}H_{2CbridgeheadCN}$), 32.83 (pseudo-t, J_{PC} = 3.0 Hz, 2C, 2 x CH_{2cod}), 34.66 (d, J_{PC} = 36.7 Hz, CH_{2PCEt}), 36.51 (d, J_{PC} = 4.2 Hz, CH_{2cod}), 45.12 (br.-s, $SiNCH_2$), 47.65 (d, J_{PC} = 8.3 Hz, $PC\mathit{CH}_{bridgehead}$), 48.25 (d, J_{PC} = 4.0 Hz, s, CH_{2Norb}), 48.81 (s, SiNCH), 47.66 (d, J_{PC} = 18.3 Hz, $NC\mathit{CH}_{bridgehead}$), 50.90 (d, J_{PC} = 5.6 Hz, $PNCH_2$), 51.08 (d, J_{PC} = 12.5 Hz, PNCH), 52.14 (br.-s, CH_{cod}), 57.28 (br.-s, CH_{cod}), 86.27 (d, J_{PC} = 3.0 Hz, CH_{cod}), 86.49 (d, J_{PC} = 7.2 Hz, CH_{cod}), 105.32 (d, J_{PC} = 58.7 Hz, P*C*=CN), 125.43 (s, 1C, CH_{Ar}), 126.19 (s, 1C, CH_{Ar}), 127.88 (br.-s, 2C, CH_{Ar}), 128.59 (s, 1C, CH_{Ar}), 130.34 (s, 1C, CH_{Ar}), 133.88 (s, 1C, C_{Ar}), 138.11 (s, 2C, 2 x CH_{Ar}), 141.41 (s, 1C, C_{Ar}), 146.65 (d, J_{PC} = 5.8 Hz, Si*C*=CP), 147.88 (s, 1C, C_{Ar}), 151.10 (s, 1C, C_{Ar}), 155.52 (d, J_{PC} = 28.4 Hz, SiC=*C*P), 164.59 ppm (d, J_{PC} = 2.0 Hz, N*C*=CP). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25°C): δ = -22.7 ppm (d, J_{PSi} = 7.1 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25°C): δ = 71.5 ppm (s).



[(3b)Ir(cod)Cl] (8b). ^1H NMR (300.18 MHz, $CDCl_3$, 25°C): δ = 0.46 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.15-1.49 (m, 21H, CH_{3iPr}, 2 x CH_{3iPr}, 2 x $CH_{3SiNiPr}$, 2 x CH_{3PNiPr}), 1.10-1.38 (overlapped with the methyl signals, 4H, ½ $CH_{2bridge}$, $CH_{2CbridgeheadCP}$, ½ CH_{2cod}), 1.65-2.04 (m, 6H, ½ $CH_{2CbridgeheadCN}$, ½ $CH_{2bridge}$, 2 x CH_{2cod}), 2.22 (m, 2H, CH_{2cod}), 2.31 (m, 1H, ½ CH_{2cod}), 2.80 (br.-s, 1H, $PCCH_{bridgehead}$), 3.07 (m, 1H, ½ $CH_{2CbridgeheadCN}$), 3.25 (br.-s, 1H, $NCCH_{bridgehead}$), 3.30-3.74 (m, 8H, CH_{iPr}, SiNCH, PNCH, CH_{cod}, $PNCH_2$, $SiNCH_2$), 3.91 (m, 1H, CH_{cod}), 4.21 (sep, J_{HH} = 6.5 Hz, 1H, CH_{iPr}), 4.32 (m, 1H, CH_{cod}), 4.79 (m, 1H, CH_{cod}), 6.28-7.55 ppm (m, 18H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25°C): δ = 21.60 (s, CH_{3iPr}), 23.03, 24.13, 24.23, 24.30, 24.94, 25.32 (6 x s, 6C, 2 x $CH_{3SiNiPr}$, 2 x CH_{3iPr}, 2 x CH_{3PNiPr}), 25.06 (s, $\mathit{C}H_{2CbridgeheadCP}$), 27.56 (br.-s, CH_{2cod}), 26.86 (s, CH_{iPr}), 27.69 (s, CH_{iPr}), 27.80 (s, CH_{3iPr}), 29.24 (s, $\mathit{C}H_{2CbridgeheadCN}$), 29.94 (d, J_{PC} = 2.8

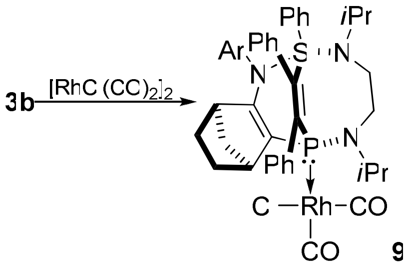
Hz, CH_{2cod}), 32.41 (d, J_{PC} = 2.1 Hz, CH_{2cod}), 35.34 (d, J_{PC} = 3.7 Hz, CH_{2cod}), 44.65 (s, $SiNCH_2$), 46.79 (d, J_{PC} = 7.9 Hz, $PC\mathit{CH}_{bridgehead}$), 47.59 (d, J_{PC} = 3.8 Hz, s, CH_{2Norb}), 47.78 (s, SiNCH), 48.12 (d, J_{PC} = 21.0 Hz, $NC\mathit{CH}_{bridgehead}$), 49.55 (d, J_{PC} = 11.9 Hz, PNCH), 50.48 (d, J_{PC} = 5.1 Hz, $PNCH_2$), 50.84 (s, CH_{cod}), 52.02 (s, CH_{cod}), 83.36 (d, J_{PC} = 18.8 Hz, CH_{cod}), 86.67 (d, J_{PC} = 14.3 Hz, CH_{cod}), 104.22 (d, J_{PC} = 60.4 Hz, P*C*=CN), 124.11, 124.34, 125.21, 125.74, 126.02, 126.37, 127.55, 128.60, 128.70, 130.70, 137.47 (11 x s, 18C, CH_{Ar}), 131.08 (s, 1C, C_{Ar}), 140.91 (s, 1C, C_{Ar}), 144.07 (d, J_{PC} = 12.1 Hz, 1C, C_{Ar}), 145.06 (d, J_{PC} = 24.3 Hz, Si*C*=CP), 146.63 (s, 1C, C_{Ar}), 147.07 (d, J_{PC} = 7.4 Hz, 1C, C_{Ar}), 149.72 (s, 1C, C_{Ar}), 155.52 (d, J_{PC} = 30.9 Hz, SiC=*C*P), 162.39 (d, J_{PC} = 3.1 Hz, N*C*=CP). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25°C): δ = -27.7 ppm (d, J_{PSi} = 5.6 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25°C): δ = 59.5 ppm (s).



9a

[(3a)Rh(CO)$_2$Cl] (9a). At RT, under argon, to a solution of $[Rh(CO)_2Cl]_2$ (29.9 mg, 0.077 mmol) in CH_2Cl_2 (2 mL) **3a** (99.7 mg, 0.154 mmol) was added. The solution was stirred for 15 min. Then, all the volatiles were removed with a stream of CO. The light yellow solid was washed with pentane (1 x 1 mL) and dried with a stream of CO. (121.2 mg, 93.5%). The rhodium analogue **9a** was prepared similarly (yield: 91.2%).

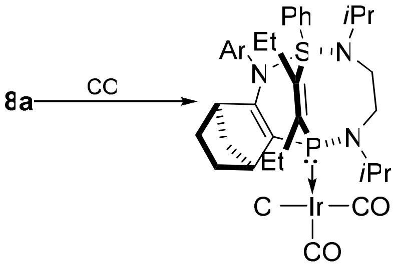
9a: ^1H NMR (300.18 MHz, $CDCl_3$, 25°C): δ = 0.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.71 (pseudo-t, J_{HH} = 7.4 Hz, 3H, CH_{3SiCEt}), 1.03 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.19 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.23 (d, J_{HH} = 6.4 Hz, 3H, CH_{3PNiPr}), 1.27 (d, J_{HH} = 6.5 Hz, 6H, CH_{3PNiPr}, $CH_{3SiNiPr}$), 1.32 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.36 (d, J_{HH} = 6.2 Hz, 3H, $CH_{3SiNiPr}$), 1.41 (pseudo-t, J_{HH} = 7.3 Hz, 3H, CH_{3CPEt}), 1.2-1.3 (overlapped with the methyl signals, 2H, ½ $CH_{2bridge}$, ½ $CH_{2CbridgeheadCP}$), 1.40-1.52 (overlapped with the methyl signal, 2H, ½ $CH_{2CbridgeheadCP}$ ½ CH_{2SiCEt}), 1.83 (m, J_{HH} = 10.6, 3.6 Hz, 1H, ½ $CH_{2CbridgeheadCN}$), 1.96 (br.-d, J_{HH} = 8.4 Hz, 1H, ½ $CH_{2bridge}$), 2.37 (m, 1H, ½ CH_{2SiCEt}), 2.74 (br.-s, 1H, $PCCH_{bridgehead}$), 2.96 (m, 3H, CH_{2PCEt}, ½ $CH_{2CbridgeheadCN}$), 3.13-3.52 (m, 7H, 2 x CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 3.78 (sep, J_{HH} = 6.4 Hz, 1H, SiNCH), 4.21 (m, 1H, PNCH), 5.60-8.30 ppm (m, 8H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 11.25 (s, CH_{3SiCEt}), 15.68 (d, J_{PC} = 2.2 Hz, CH_{3PCEt}), 22.34 (s, $CH_{3SiNiPr}$), 23.18 (s, 2C, CH_{3iPr}, $CH_{3SiNiPr}$), 23.60 (s, CH_{3iPr}), 23.79 (s, CH_{3PNiPr}), 24.76 (s, $\mathit{C}H_{2CbridgeheadCP}$), 24.99 (s, CH_{3iPr}), 25.17 (s, CH_{3PNiPr}), 26.77 (s, CH_{iPr}), 26.96 (s, CH_{3iPr}), 27.205 (d, J_{PC} = 12.4 Hz, CH_{2SiCEt}), 27.76 (s, CH_{iPr}), 29.92 (s, $\mathit{C}H_{2CbridgeheadCN}$), 32.26 (d, J_{PC} = 35.1 Hz, CH_{2PCEt}), 43.91 (s, $SiNCH_2$), 46.70 (d, J_{PC} = 4.6 Hz, s, CH_{2Norb}), 46.75 (d, J_{PC} = 8.3 Hz, $PC\mathit{CH}_{bridgehead}$), 47.97 (s, SiNCH), 48.47 (d, J_{PC} = 24.8 Hz, $NC\mathit{CH}_{bridgehead}$), 48.53 (d, J_{PC} = 4.2 Hz, $PNCH_2$), 52.52 (d, J_{PC} = 14.2 Hz, PNCH), 101.77 (d, J_{PC} = 57.9 Hz, P*C*=CN), 124.44 (s, 1C, CH_{Ar}), 124.89 (s, 1C, CH_{Ar}), 126.92 (br.-s, 2C, CH_{Ar}), 127.73 (s, 1C, CH_{Ar}), 129.47 (s, 1C, CH_{Ar}), 131.78 (s, 1C, C_{Ar}), 136.67 (br.-s, 2C, 2 x CH_{Ar}), 139.47 (s, 1C, C_{Ar}), 146.59 (s, 1C, C_{Ar}), 146.85 (d, J_{PC} = 6.3 Hz, Si*C*=CP), 149.43 (s, 1C, C_{Ar}), 150.96 (d, J_{PC} = 25.9 Hz, SiC=*C*P), 165.12 (br.-s, N*C*=CP), 182.42 (dd, J_{PC} = 137.4 Hz, J_{RhC} = 57.9 Hz, CO), 182.42 ppm (dd, J_{PC} = 13.4 Hz, J_{RhC} = 71.7 Hz, CO). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -24.1 ppm (d, J_{PSi} = 7.6 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 79.5 ppm (brd, J_{RhP} = 141.8 Hz). IR (KBr pellets, cm^{-1}): ν(CO) 2076.5, 1993.6.



9b

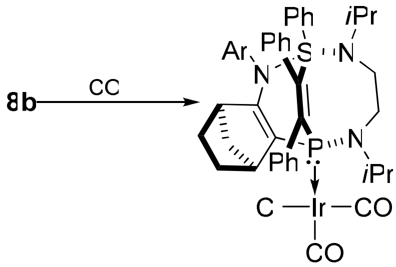
[(3b)Rh(CO)$_2$Cl] (9b). ^1H NMR (300.18 MHz, $CDCl_3$, 25ºC): δ = 0.44 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.20 (d, J_{HH} = 6.1 Hz, 3H, CH_{3iPr}), 1.28 (pseudo-t, J_{HH} = 6.8 Hz, 6H, CH_{3iPr}, CH_{3iPr}), 1.37 (J_{HH} = 6.7 Hz, 3H, $CH_{3SiNiPr}$), 1.40 (d, J_{HH} = 6.8 Hz, 3H, CH_{3PNiPr}), 1.46 (pseudo-t, J_{HH} = 6.3 Hz, 6H, CH_{3PNiPr}, $CH_{3SiNiPr}$), 1.2-1.5 (overlapped with the methyl signals, 3H, ½ $CH_{2bridge}$, $CH_{2CbridgeheadCP}$), 1.85 (br.- pseudo-t, J_{HH} = 10.5 Hz, 1H, ½ $CH_{2CbridgeheadCN}$), 2.01 (br.-d, J_{HH} = 8.4 Hz, 1H, ½ $CH_{2bridge}$), 2.73 (m, 1H, ½ $CH_{2CbridgeheadCN}$), 2.85 (br.-s, 1H, $PCCH_{bridgehead}$), 3.38-3.75 (m, 8H, SiNCH, 2 x CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 4.33 (m, 1H, PNCH), 6.20-7.45 ppm (m, 18H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 21.43 (s, CH_{3iPr}), 23.67 (s, $CH_{3SiNiPr}$), 23.88 (s, 2C, CH_{3iPr}, CH_{3PNiPr}), 24.00 (s, CH_{3PNiPr}), 24.90 (s, CH_{3iPr}), 25.04 (s, CH_{3iPr}), 25.36 (s, $\mathit{C}H_{2CbridgeheadCP}$), 27.07 (s, CH_{iPr}), 27.67 (s, $CH_{3SiNiPr}$), 27.89 (s, CH_{iPr}), 29.36 (s, $\mathit{C}H_{2CbridgeheadCN}$), 44.46 (s, $SiNCH_2$), 47.27 (s, CH_{2Norb}), 47.30 (d, J_{PC} = 12.8 Hz, $PC\mathit{CH}_{bridgehead}$), 47.99 (s, SiNCH), 48.22 (d, J_{PC} = 22.1 Hz, $NC\mathit{CH}_{bridgehead}$), 48.88 (d, J_{PC}

= 4.0 Hz, $PNCH_2$), 53.17 (d, J_{PC} = 14.7 Hz, PNCH), 103.44 (d, J_{PC} = 59.3 Hz, P*C*=CN), 124.49, 124.81, 125.00, 125.83, 126.53, 126.76, 127.00, 128.01, 128.15, 130.76, 131.71, 137.21 (12 x s, 18C, CH_{Ar}), 130.65 (s, 1C, C_{Ar}), 140.03 (s, 1C, C_{Ar}), 144.04 (s, 1C, C_{Ar}), 144.35 (s, 1C, C_{Ar}), 146.67 (s, 1C, C_{Ar}), 149.16 (s, 1C, C_{Ar}), 149.41 (d, J_{PC} = 8.7 Hz, Si*C*=CP), 153.45 (d, J_{PC} = 27.0 Hz, SiC=*C*P), 164.58 (d, J_{PC} = 3.3 Hz, N*C*=CP), 173.4 (br, CO), 182.0 ppm (br, CO). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -27.3 ppm (d, J_{PSi} = 6.0 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 73.0 ppm (very broad). IR (KBr pellets, cm^{-1}): ν(CO) 2079.6, 1992.1.



10a

[(3a)Ir(CO)$_2$Cl] (10a). At RT, under argon, a dichloromethane solution (2 mL) of [(**3b**)Ir(cod)Cl] **8a** (84.6 mg, 0.086 mmol) was placed under 1 atm of CO. Then, all the volatiles were removed with a stream of CO. The light yellow solid was washed with pentane (4 x 1 mL) and vacuum-dried. (68.6 mg, 85.6%). The iridium analogue **10a** was prepared similarly (yield: 86.9%). ^1H NMR (300.18 MHz, $CDCl_3$, 25ºC): δ = 0.23 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 0.71 (pseudo-t, J_{HH} = 7.3 Hz, 3H, CH_{3SiCEt}), 1.05 (d, J_{HH} = 6.5 Hz, 3H, CH_{3iPr}), 1.19 (J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.21-1.34 (m, 14H, ½ $CH_{2bridge}$, ½ $CH_{2CbridgeheadCP}$, 2 x CH_{3PNiPr}, $CH_{3SiNiPr}$, CH_{3iPr}), 1.34-1.44 (m, 8H, CH_{3iPr}, CH_{3PCEt}, ½ $CH_{2CbridgeheadCP}$, ½ CH_{2SiCEt}), 1.81 (br.- pseudo-t, J_{HH} = 10.8, 1H, ½ $CH_{2CbridgeheadCN}$), 1.97 (br.-d, J_{HH} = 7.7 Hz, 1H, ½ $CH_{2bridge}$), 2.38 (m, 1H, ½ CH_{2SiCEt}), 2.73 (br.-s, 1H, $PCCH_{bridgehead}$), 2.92 (m, 3H, CH_{2PCEt}, ½ $CH_{2CbridgeheadCN}$), 3.10-3.62 (m, 7H, 2 x CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 3.79 (sep, J_{HH} = 6.3 Hz, 1H, SiNCH), 4.37 (m, 1H, PNCH), 5.60-8.20 ppm (m, 8H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 11.01 (s, CH_{3SiCEt}), 15.69 (br.-s, CH_{3PCEt}), 22.39 (s, $CH_{3SiNiPr}$), 23.15 (s, CH_{3iPr}), 23.49 (d, J_{PC} = 6.4 Hz, CH_{3PNiPr}), 23.64, 23.73, 25.01, 25.14 (4 x s, $CH_{3SiNiPr}$, CH_{3iPr}, CH_{3iPr}, CH_{3PNiPr}), 24.30 (s, *C*$H_{2CbridgeheadCP}$), 26.80 (s, CH_{iPr}), 27.06 (s, CH_{3iPr}), 27.29 (d, J_{PC} = 13.5 Hz, CH_{2SiCEt}), 27.75 (s, CH_{iPr}), 30.03 (s, *C*$H_{2CbridgeheadCN}$), 32.01 (d, J_{PC} = 32.2 Hz, CH_{2PCEt}), 43.82 (s, $SiNCH_2$), 46.70 (d, J_{PC} = 8.2 Hz, PC*CH*$_{bridgehead}$), 46.84 (d, J_{PC} = 3.7 Hz, CH_{2Norb}), 47.99 (s, SiNCH), 48.43 (d, J_{PC} = 18.9 Hz, NC*CH*$_{bridgehead}$), 48.43 (d, J_{PC} = 1.8 Hz, $PNCH_2$), 52.16 (d, J_{PC} = 11.5 Hz, PNCH), 101.95 (d, J_{PC} = 66.8 Hz, P*C*=CN), 124.48 (s, 1C, CH_{Ar}), 124.96 (s, 1C, CH_{Ar}), 126.98 (br.-s, 2C, CH_{Ar}), 127.78 (s, 1C, CH_{Ar}), 129.53 (s, 1C, CH_{Ar}), 131.63 (s, 1C, C_{Ar}), 136.64 (br.-s, 2C, 2 x CH_{Ar}), 139.32 (s, 1C, C_{Ar}), 146.56 (s, 1C, C_{Ar}), 148.54 (d, J_{PC} = 8.9 Hz, Si*C*=CP), 149.41 (s, 1C, C_{Ar}), 151.59 (d, J_{PC} = 36.0 Hz, SiC=*C*P), 166.31 (br.-s, N*C*=CP), 169.7 (br, CO), 176.7 ppm (br, CO). $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -24.0 ppm (d, J_{PSi} = 8.4 Hz). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 76.4 ppm (s). IR (KBr pellets, cm^{-1}): ν(CO) 2058.6, 1978.3.



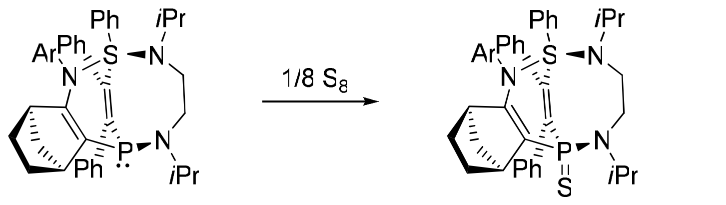
10b

[(3b)Ir(CO)$_2$Cl] (10b). ^{1}H NMR (300.18 MHz, $CDCl_3$, 25ºC): δ = 0.45 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.10 (br.-d, J_{HH} = 5.4 Hz, 3H, $CH_{3SiNiPr}$), 1.21 (pseudo-t, J_{HH} = 6.7 Hz, 6H, CH_{3iPr}, $CH_{3SiNiPr}$), 1.36 (br.-s, 3H, CH_{3PNiPr}), 1.41 (d, J_{HH} = 6.4 Hz, 3H, CH_{3PNiPr}), 1.47 (br.-d, J_{HH} = 6.3 Hz, 3H, CH_{3iPr}), 1.58 (d, J_{HH} = 6.6 Hz, 3H, CH_{3iPr}), 1.18 (overlapped with the methyl signals, 1H, ½ $CH_{2bridge}$), 1.30-1.42 (overlapped with the methyl signals, 2H, $CH_{2CbridgeheadCP}$), 1.79 (m, 1H, ½ $CH_{2CbridgeheadCN}$), 1.99 (br.-d, J_{HH} = 8.3 Hz, 1H, ½ $CH_{2bridge}$), 2.86 (brs, 1H, $PCCH_{bridgehead}$), 2.92 (m, 1H, ½ $CH_{2CbridgeheadCN}$), 3.40-3.60 (m, 6H, CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 3.67 (sep, J_{HH} = 6.5 Hz, 1H, SiNCH), 3.88 (m, 1H, CH_{iPr}), 4.49 (m, 1H, PNCH), 6.20-7.50 ppm (m, 18H, H_{Ar}). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 21.17 (s, $CH_{3SiNiPr}$), 22.02 (s, $CH_{3SiNiPr}$), 23.76 (s, 3C, CH_{3iPr}, 2 x CH_{3PNiPr}), 24.65 (s, CH_{3iPr}), 24.90 (s, CH_{3iPr}), 25.65 (s, *C*$H_{2CbridgeheadCP}$), 26.98 (s, CH_{iPr}), 27.89 (s, 2C, CH_{iPr}, CH_{3iPr}), 30.10 (s, *C*$H_{2CbridgeheadCN}$), 44.39 (s, $SiNCH_2$), 47.20 (s, CH_{2Norb}), 47.37 (d, J_{PC} = 7.8 Hz, PC*CH*$_{bridgehead}$), 47.87 (s, SiNCH), 48.36 (d, J_{PC} = 13.4 Hz, NC*CH*$_{bridgehead}$), 48.75 (br.-s, $PNCH_2$), 52.69 (d, J_{PC} = 12.3 Hz, PNCH), 106.44 (d, J_{PC} = 47.3 Hz, P*C*=CN), 124.55, 124.78, 125.17, 125.96, 126.59, 126.82, 127.14, 128.11, 128.20, 130.59, 131.79, 137.17 (12 x s, 18C, CH_{Ar}), 130.64 (s, 1C, C_{Ar}), 139.91 (s, 1C, C_{Ar}), 143.78 (s, 1C, C_{Ar}), 144.30 (s, 1C, C_{Ar}), 147.58 (s, 1C, C_{Ar}), 149.31 (s, 1C, C_{Ar}), 149.63 (d, J_{PC} = 7.8 Hz, Si*C*=CP), 154.88 (d, J_{PC} = 24.7 Hz, SiC=*C*P), 166.11 (d, J_{PC} = 3.2 Hz, N*C*=CP), 170.0 (br, CO), 178.0 ppm (br, CO). $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -27.0 ppm (d, J_{PSi} = 7.9 Hz). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 70.9 ppm (br.-s). IR (KBr pellets, cm^{-1}): ν(CO) 2063.9, 1977.2.

3-Determination of enantiopurity (*ee %*) of chiral phosphines

The starting material for the synthesis of chiral phosphines ***R,S,R$_P$,S$_{Si}$*-3a,b**, the phosphonium sila-ylide with a enantiomerically pure norbornene fragment (***R,S,R$_{Si}$*-1** and ***R,S,S$_{Si}$*-1**) was prepared by the previous reported method[S1] The chiral (*R,S*)-norbornanon was obtained by the oxidation of commercially available (*R,S*)-(+)-*endo*-2-norborneol.[5]

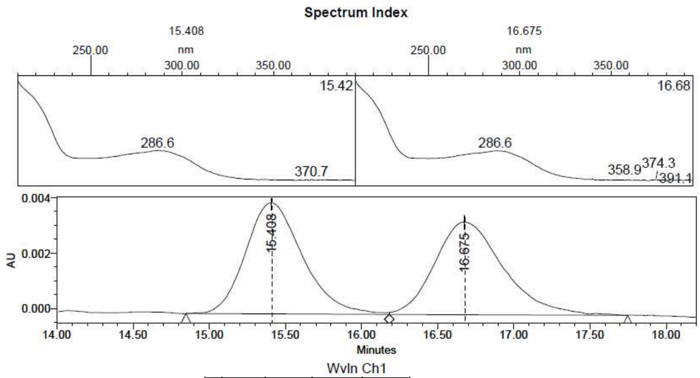
***R,S,R$_P$,S$_{Si}$*-3a.** *Ee* = 99%, $[\alpha]_{D,22°C}$ = +15.2 (*c* = 1.105, CH_2Cl_2). The enantiomeric ratio was determined by HPLC analysis of the **3a- thioxide**, obtained by reaction of the **3a** with S_8, using a Chiralpack AD-H (99.5/0.5 heptane/2-propanol, 0.25 mL/min); major isomer t_r = 15.6 min and minor isomer t_r = 17.0 min.



***R,S,R$_P$,S$_{Si}$*-3a-thioxide.** At RT, to a solution of ***R,S,R$_P$,S$_{Si}$*-3a** (20.5 mg, 0.0316 mmol) in CH_2Cl_2 (1 mL) S_8 (2.0 mg, 2 equiv) was added. The solution was stirred for 10 min. Purification by flash chromatography on alumina with pentane/CH_2Cl_2 (1:1) as eluent gave ***R,S,R$_P$,S$_{Si}$*-3a-thioxide** (20.2 mg, 93.9%) as a white solid. Mp: 173-174°C. ^{1}H NMR (300.18 MHz, $CDCl_3$, 25°C): δ = 0.24 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.70 (pseudo-t, J_{HH} = 7.3 Hz, 3H, CH_{3SiCEt}), 1.05 (d, J_{HH} = 6.6 Hz, 6H, CH_{3PNiPr}, CH_{3iPr}), 1.14 (d, J_{HH} = 6.6 Hz, 3H, CH_{3PNiPr}), 1.23 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.27 (d, J_{HH} = 6.8 Hz, 3H, $CH_{3SiNiPr}$), 1.28 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.30 (pseudo-t, J_{HH} = 7.3 Hz, 3H, CH_{3PCEt}), 1.17 (m, 1H, ½ $CH_{2CbridgeheadCP}$), 1.23 (overlapped with the methyl signals, 1H, ½ $CH_{2bridge}$), 1.36 (d, J_{HH} = 6.3 Hz, 3H, $CH_{3SiNiPr}$), 1.43 (m, 2H, ½ $CH_{2CbridgeheadCP}$, ½ CH_{2SiCEt}), 1.86 (m, J_{HH} = 11.4, 3.9 Hz, 1H, ½ $CH_{2CbridgeheadCN}$), 1.93 (dst, J_{HH} = 8.4, 1.3 Hz, 1H, ½ $CH_{2bridge}$), 2.25 (m, 2H, ½ CH_{2SiCEt}, ½ $CH_{2CbridgeheadCN}$), 2.51 (m, 1H, ½ CH_{2PCEt}), 2.74 (br.-s, 1H, $PCCH_{bridgehead}$), 3.00-3.50 (m, 8H, ½ CH_{2PCEt}, 2 X CH_{iPr}, $NCCH_{bridgehead}$, $PNCH_2$, $SiNCH_2$), 3.78 (sep, J_{HH} = 6.5 Hz, 1H, SiNCH), 4.83 (m, 1H, PNCH), 6.04 (br.-s, 1H, H_{Ar}), 6.81 (br.-s, 1H, H_{Ar}), 7.05 (dd, J_{HH} = 7.6, 1.7 Hz, 1H, H_{Ar}), 7.19-7.37 (m, 4H, H_{Ar}), 7.79 ppm (brs, 1H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25°C): δ = 12.17 (d, J_{PC} = 1.7 Hz, d, J_{PC} = 2.2 Hz, CH_{3SiCEt}), 16.31 (s, CH_{3PCEt}), 22.17 (s,

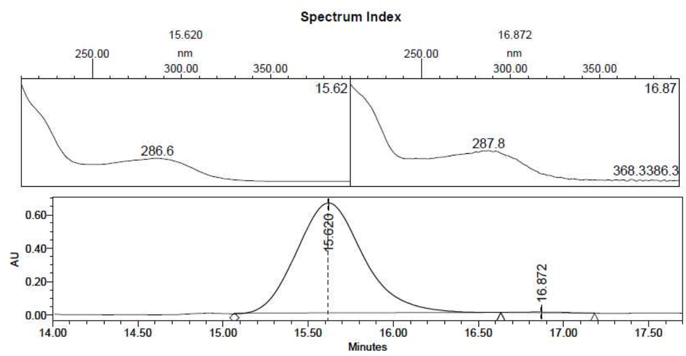
$CH_{3SiNiPr}$), 22.40 (d, J_{PC} = 2.7 Hz, CH_{3PNiPr}), 22.77 (d, J_{PC} = 1.7 Hz, CH_{3PNiPr}), 23.26 (s, CH_{3iPr}), 24.87 (s, CH_{3iPr}), 23.30 (s, CH_{3iPr}), 24.97 (s, $CH_{3SiNiPr}$), 24.97 (d, J_{PC} = 18.8 Hz, CH_{2SiCEt}), 27.07 (s, CH_{iPr}), 27.09 (d, J_{PC} = 1.8 Hz, $\mathit{C}H_{2CbridgeheadCP}$), 27.31 (s, CH_{3iPr}), 27.59 (d, J_{PC} = 19.2 Hz, CH_{2PCEt}), 27.60 (s, CH_{iPr}), 29.48 (s, $\mathit{C}H_{2CbridgeheadCN}$), 43.77 (s, $SiNCH_2$), 44.52 (d, J_{PC} = 7.1 Hz, PNCH), 46. 73 (d, J_{PC} = 5.9 Hz, CH_{2Norb}), 47.57 (d, J_{PC} = 3.0 Hz, $PNCH_2$), 47.66 (d, J_{PC} = 10.5 Hz, $NC\mathit{CH}_{bridgehead}$), 48.26 (s, SiNCH), 48.54 (d, J_{PC} = 11.7 Hz, $PC\mathit{CH}_{bridgehead}$), 106.40 (d, J_{PC} = 107.5 Hz, P*C*=CN), 124.55 (s, 1C, CH_{Ar}), 124.64 (s, 1C, CH_{Ar}), 127.13 (br.-s, 2C, CH_{Ar}), 127.78 (s, 1C, CH_{Ar}), 129.59 (s, 1C, CH_{Ar}), 132.44 (s, 1C, C_{Ar}), 135.96 (br.-s, 1C, CH_{Ar}), 136.60 (br.-s, 1C, CH_{Ar}), 139.05 (s, 1C, C_{Ar}), 142.15 (d, J_{PC} = 19.1, Si*C*=CP), 146.85 (s, 1C, C_{Ar}), 149.37 (s, 1C, C_{Ar}), 153.54 (d, J_{PC} = 82.4, SiC=*C*P), 161.89 ppm (d, J_{PC} = 5.3, N*C*=CP). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -22.5 ppm (d, J_{PSi} = 8.8 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 56.4 ppm (s).

HPLC data for racemic 3a-thioxide



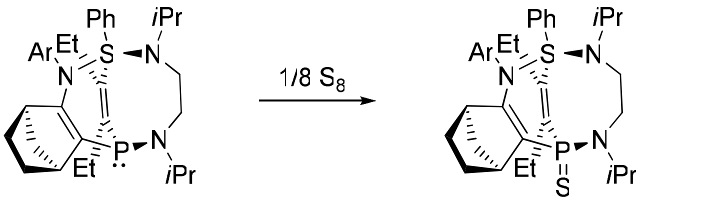
	Name	RT	Area	% Area
1		15.408	104874	50.03
2		16.675	104751	49.97

HPLC data for *R,S,R_P,S_Si*-3a-thioxide



	Name	RT	Area	% Area
1		15.620	17888055	99.50
2		16.872	90515	0.50

***R,S,R$_P$,S$_{Si}$*-3b.** *Ee* = 99%, $[\alpha]_{D,22°C}$ = +6.7 (*c* = 1.61, CH_2Cl_2). The enantiomeric ratio was determined by HPLC analysis of the **3b-thioxide**, obtained by reaction of **3b** with S_8, using a Chiralpack AD-H (99.5/0.5 heptane/2-propanol, 0.30 mL/min); minor isomer t_r = 9.2 min and major isomer t_r = 13.3 min.

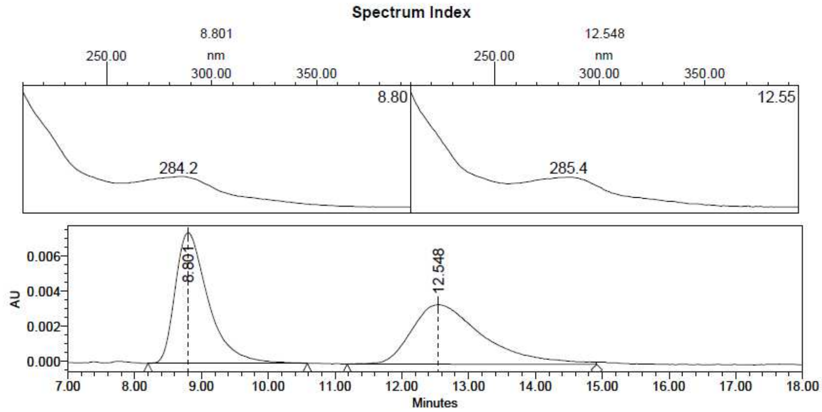


***R,S,R$_F$,S$_{Si}$*-3b** Ar = 2 6-*i*Pr$_2$-C$_6$H$_3$ ***R,S,R$_F$,S$_{Si}$*-3b-thioxide**

***R,S,R$_P$,S$_{Si}$*-3b- thioxide.** At RT, to a solution of ***R,S,R$_P$,S$_{Si}$* -3b** (32 9 mg, 0.045 mmol) in CH_2Cl_2 (1 mL) S_8 (2.9 mg, 2 equiv) was added. The solution was stirred for 10 min. Purification by flash chromatography on alumina with 1:1 pentane-CH_2Cl_2 as eluent gave ***R,S,R$_P$,S$_{Si}$*3b-thioxide** (36.0 mg, 96.1%) as white solids. Mp: 171-172°C. ^{1}H NMR (300.18 MHz, $CDCl_3$, 25°C): δ = 0.06 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 0.98 (d, J_{HH} = 6.5 Hz, 3H, CH_{3PNiPr}), 1.09 (d, J_{HH} = 6.8 Hz, 3H, CH_{3PNiPr}), 1.155 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.28 (d, J_{HH} = 6.6 Hz, 3H, $CH_{3SiNiPr}$), 1.32 (d, J_{HH} = 6.8 Hz, 3H, CH_{3iPr}), 1.13 (overlapped with the methyl signals, 1H, ½ $CH_{2CbridgeheadCP}$), 1.21 (overlapped with the methyl signals, 1H, ½ $CH_{2bridge}$), 1.405 (d, J_{HH} = 6.2 Hz, 3H, $CH_{3SiNiPr}$), 1.41 (d, J_{HH} = 6.7 Hz, 3H, CH_{3iPr}), 1.35 (m, 1H, ½ $CH_{2CbridgeheadCP}$,), 1.78 (m, J_{HH} = 11.0, 3.9 Hz, 1H, ½ $CH_{2CbridgeheadCN}$), 1.96 (d- pseudo-t, J_{HH} = 8.3, 1.3 Hz, 1H, ½ $CH_{2bridge}$), 2.13 (m, 1H, ½ $CH_{2CbridgeheadCN}$), 2.70 (br.-s, 1H, $PCCH_{bridgehead}$), 3.20-3.42 (m, CH_{iPr}, $NCCH_{bridgehead}$, ¼ $PNCH_2$), 3.44-3.79 (m, 4H, CH_{iPr}, ½ $PNCH_2$, $SiNCH_2$), 3.89 (sep, J_{HH} = 6.4 Hz, 1H, SiNCH), 4.22 (m, 1H, PNCH), 6.13-7.33 ppm (18H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25°C): δ = 22.72 (m, 3CH_3, $CH_{3SiNiPr}$, 2 x CH_{3PNiPr}), 23.36 (s, CH_{3iPr}), 24.13 (s, CH_{3iPr}), 24.85 (s, CH_{3iPr}), 24.92 (s, $CH_{3SiNiPr}$), 27.18 (d, J_{PC} = 2.0 Hz, $CH_{2CbridgeheadCP}$), 27.25 (s, CH_{iPr}), 27.61 (s, CH_{3iPr}), 28.19 (s, CH_{iPr}), 29.11 (s, $CH_{2CbridgeheadCN}$), 44.68 (s, $SiNCH_2$), 45.25 (d, J_{PC} = 6.5 Hz, PNCH), 47.28 (d, J_{PC} = 5.7 Hz, CH_{2Norb}), 47.465 (d, J_{PC} = 10.4 Hz, $NC\mathit{CH}_{bridgehead}$), 47.82 (d, J_{PC} = 2.9 Hz, $PNCH_2$), 48.47 (s, SiNCH), 48.88 (d, J_{PC} = 11.6 Hz, $PC\mathit{CH}_{bridgehead}$), 108.86 (d, J_{PC} = 104.8 Hz, P*C*=CN), 124.41 (s, 1C, CH_{Ar}), 124.58 (s, 1C, CH_{Ar}), 124.61 (s, 1C, CH_{Ar}), 125.61 (d, 1C, J_{PC} = 2.1, CH_{Ar}), 126.25 (s, 1C, CH_{Ar}), 126.28 (d, 1C, J_{PC} = 2.5, CH_{Ar}), 126.36 (s, 2C, CH_{Ar}), 126.46 (d, 1C, J_{PC} = 1.3 Hz, CH_{Ar}), 126.60 (s, 1C, CH_{Ar}), 127.55 (s, 1C, CH_{Ar}), 127.71 (s, 1C, CH_{Ar}), 128.25 (d, 1C, J_{PC} = 1.4

Hz, CH_{Ar}), 128.83 (s, 1C, CH_{Ar}), 129.24 (d, 1C, J_{PC} = 4.2 Hz, CH_{Ar}), 130.82 (s, 1C, C_{Ar}), 133.78 (d, 1C, J_{PC} = 2.5 Hz, CH_{Ar}), 136.33 (s, 2C, CH_{Ar}), 139.39 (d, J_{PC} = 13.4 Hz, SiC(*C*)=C(C)P), 139.44 (s, 1C, C_{Ar}), 142.61 (d, J_{PC} = 20.8 Hz, SiC(C)=C(*C*)P), 146.15 (d, J_{PC} = 22.0 Hz, SiC=CP), 146.53 (s, 1C, C_{Ar}), 148.85 (s, 1C, C_{Ar}), 155.24 (d, J_{PC} = 81.6 Hz, SiC=*C*P), 161.35 ppm (d, J_{PC} = 4.4 Hz, N*C*=CP). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$, 25ºC): δ = -24.5 ppm (d, J_{PSi} = 7.1 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 25ºC): δ = 53.7 ppm (s).

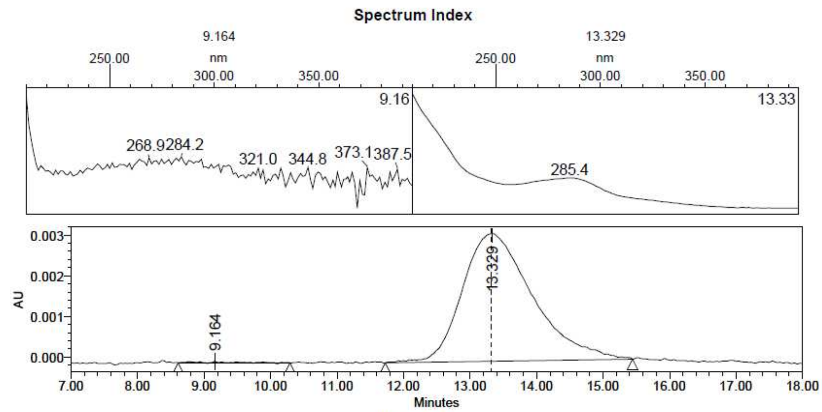
HPLC data for racemic 3b-thioxide



Wvln Ch1

	Name	RT	Area	% Area
1		8.801	256725	50.42
2		12.548	252476	49.58

HPLC data for enantioenriched 3b-thioxide

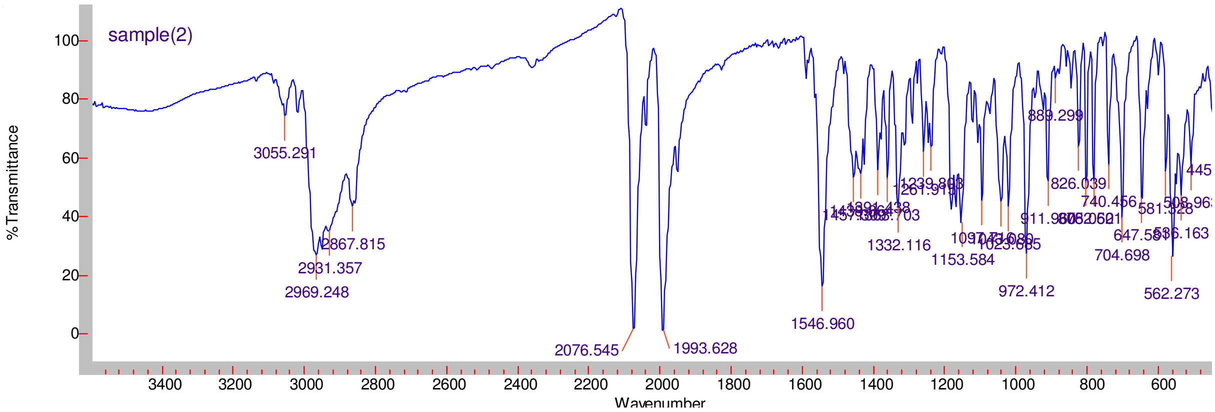


Wvln Ch1

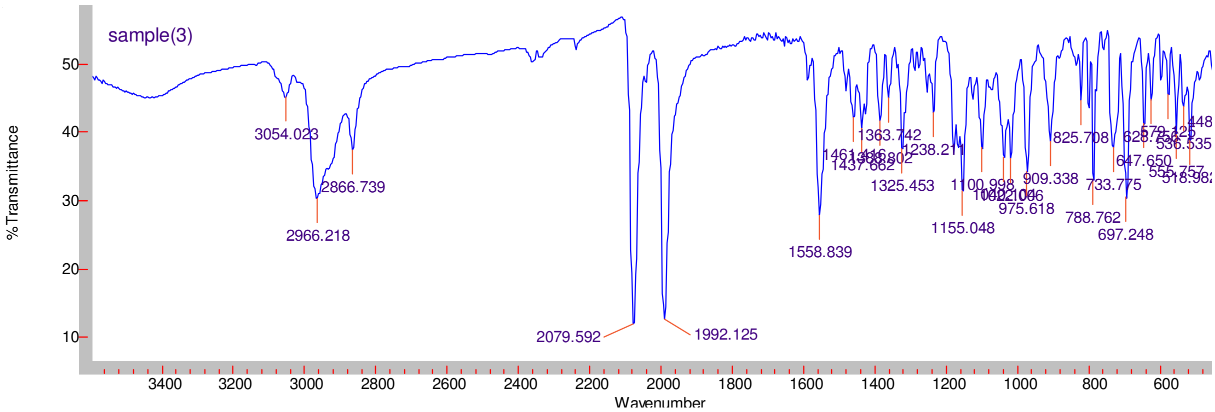
	Name	RT	Area	% Area
1		13.329	230004	99.60

4 - IR spectres of phosphine Rhodium- and Iridium-carbonyl complexes

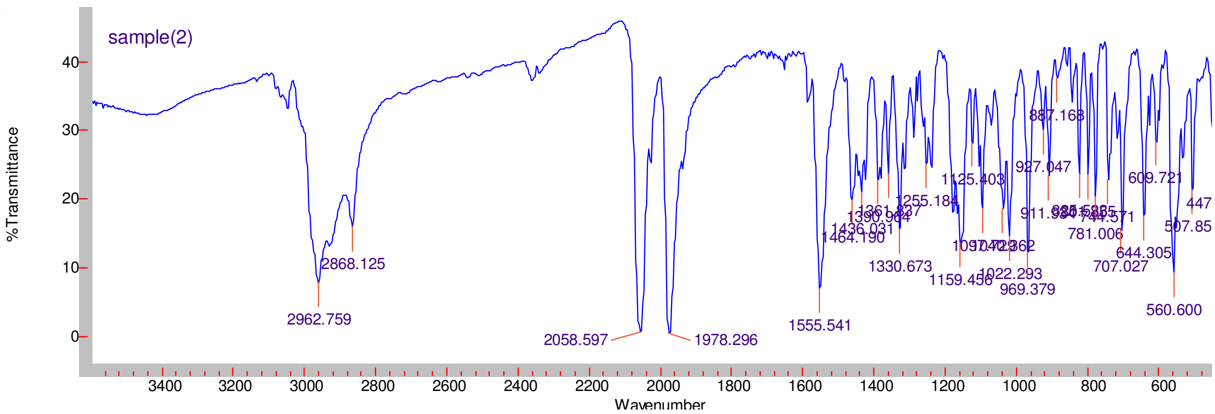
IR spectra for 9a in KBr



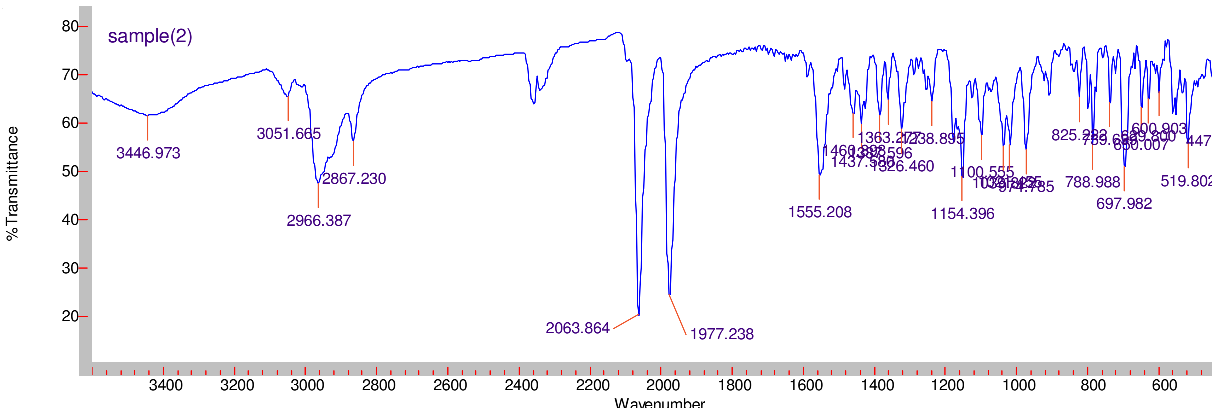
IR spectra for 9b in KBr



IR spectra for 10a in KBr

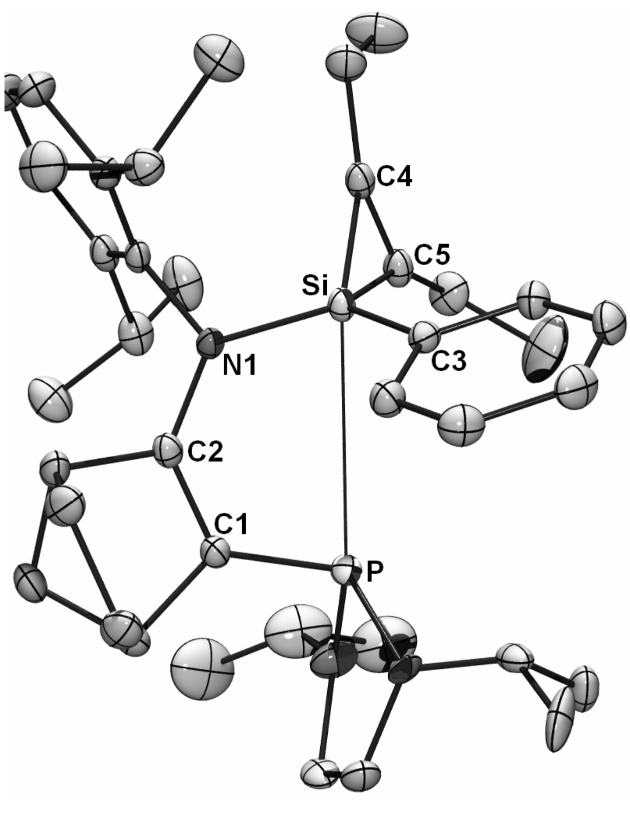


IR spectra for 10b in KBr

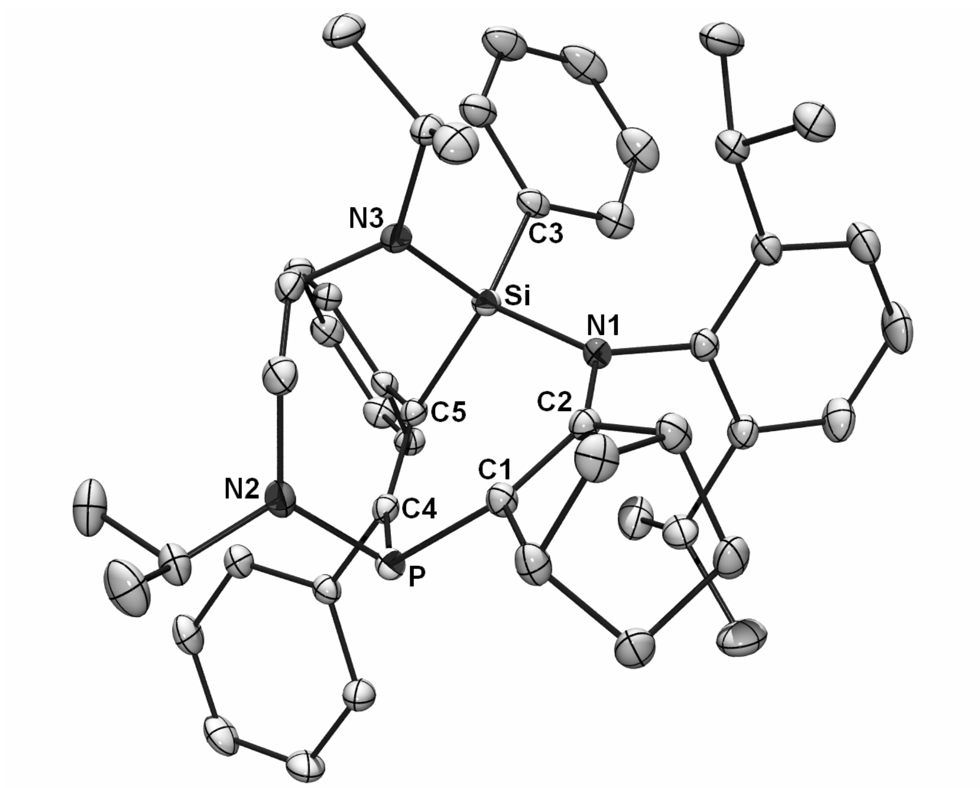


5-X-Ray analysis

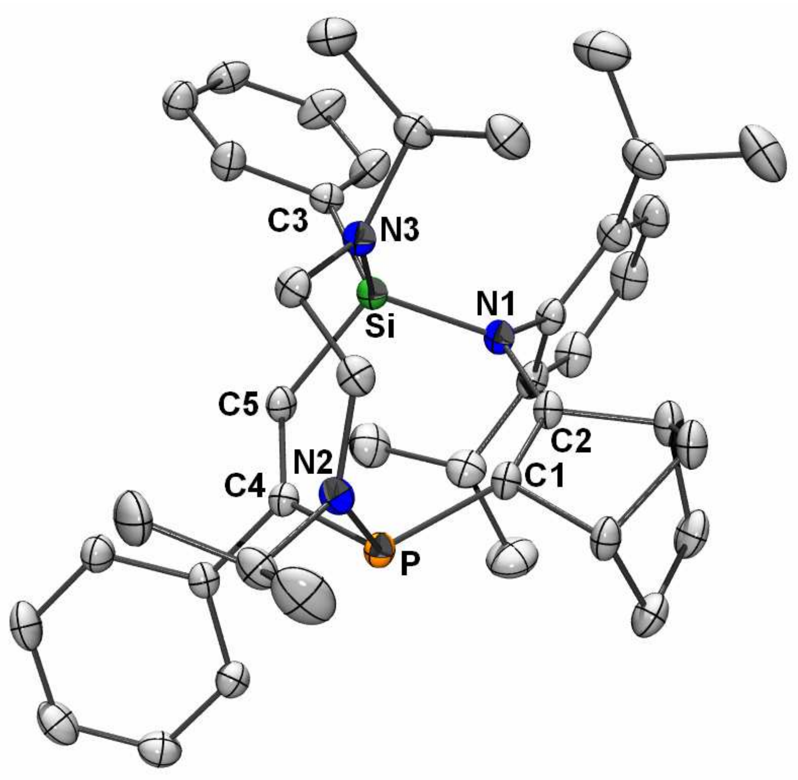
2a: $C_{39}H_{58}N_3PSi$, *M*=627.94, Triclinic, space group $P\bar{1}$, a=10.2808(2)Å, b=11.0503(2)Å, c=17.9965(4)Å, α=84.5520(10), β=89.2500(10)°, γ=67.9810(10)°, *V*=1886.26(7) Å^3, *Z*=2, crystal size 0.60 x 0.32 x 0.10 mm^3, 18499 reflections collected (7564 independent, R_{int}=0.0275), 494 parameters, *R*1 [I>2σ(I)]= 0.0459, *wR*2 [all data]= 0.1236, largest diff. peak and hole: 0.319 and -0.313 e.Å^{-3}.



3b: $C_{51}H_{66}N_3OPSi$, *M*=796.13, Triclinic, space group $P\bar{1}$, a=11.7590(3)Å, b=12.4590(2)Å, c=18.4860(3)Å, α=72.4900(10), β=85.6140(10)°, γ=62.5760(10)°, *V*=2286.38(8) Å^3, *Z*=2, crystal size 0.60 x 0.40 x 0.40 mm^3, 17311 reflections collected (9223 independent, R_{int}=0.0255), 568 parameters, *R*1 [I>2σ(I)]= 0.0541, *wR*2 [all data]= 0.1540, largest diff. peak and hole: 0.617 and -0.521 e.Å^{-3}.

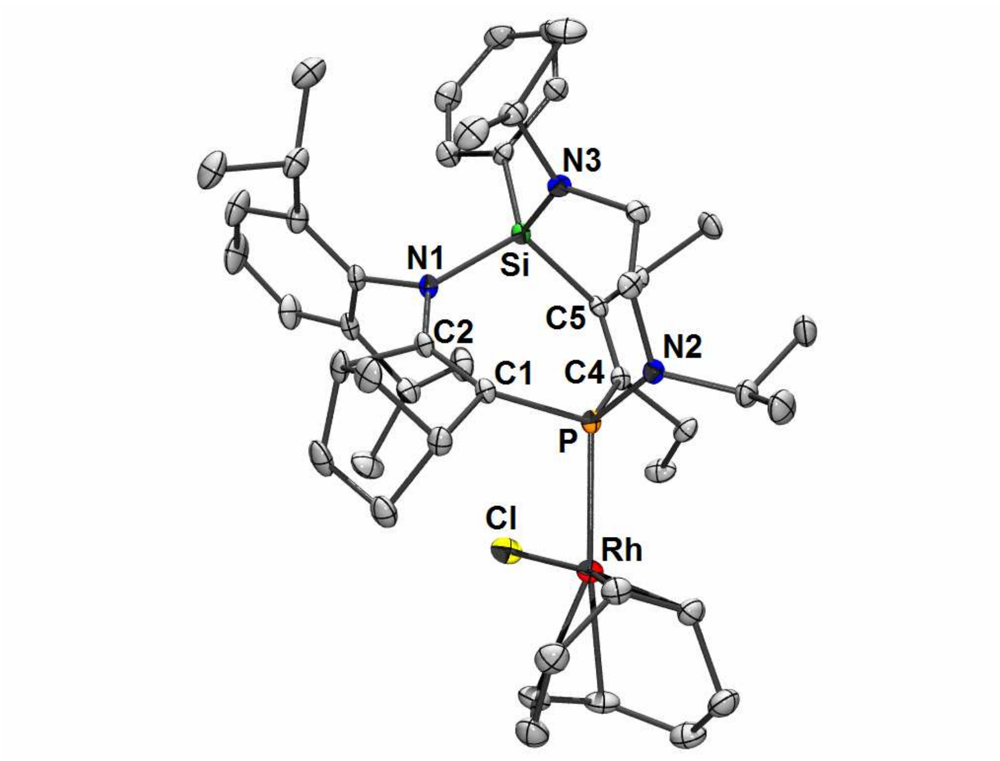


3c: $C_{41}H_{54}N_3PSi$, *M*=647.93, Monoclinic, space group *P* 2_1/n, a=11.2805(8)Å, b=10.0135(7)Å, c=33.283(2)Å, β=93.313(2)°, α=γ=90°, *V*=3753.2(5) Å^3, *Z*=4, crystal size 0.15 x 0.15 x 0.10 mm^3, 37287 reflections collected (7844 independent, R_{int}=0.0927), 423 parameters, *R*1 [I>2σ(I)]= 0.0556, *wR*2 [all data]= 0.1328, largest diff. peak and hole: 0.232 and -0.286 e.Å^{-3}.



Thermal ellipsoids represent 30 % probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] : P-N3 1.700(2), P-C2 1.798(2), P-C4 1.865(2), Si-N2 1.709(2), Si-N1 1.766(2), Si-C5 1.850(3), Si-C3 1.886(2), N1-C1 1.409(3), C1-C2 1.356(3), C4-C5 1.344(3), N3-P-C2 101.83(10), N3-P-C4 106.13(10), C2-P-C4 107.99(11), P-C1-C2 140.20(19), P-C4-C5 127.26(18), C2-C1-N1 130.7(2), C1-N1-Si 118.23(15), C4-C5-Si 128.31(19), N2-Si-N1 112.19(10), N2-Si-C5 108.09(10), N1-Si-C5 109.10(10).

7a: $C_{47}H_{70}ClN_3PRhSi$, CH_2Cl_2, M=959.41, triclinic, space group $P\ \bar{1}$, a=10.2915(2)Å, b=14.4688(2)Å, c=17.2543(3)Å, β=108.789(1)°, β=100.115(1)°,γ=92.699(1)°, V=2379.69(7)Å^3, Z=2, crystal size 0.18 x 0.14 x 0.06 mm^3, 34326 reflections collected (12555 independent, R_{int}=0.0564), 524 parameters, $R1$ [I>2σ(I)]=0.0451, $wR2$ [all data]=1067, largest diff. peak and hole: 0.765 and -0.521 e.Å^{-3}.



Thermal ellipsoids represent 30 % probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] : P-Rh 2.3830(7), P-C1 1.798(3), P-C4 1.856(3), P-N2 1.705(2), C4-C5 1.350(3), Si-C5 1.891(3), C1-C2 1.362(4), C2-N1 1.396(3), N1-Si 1.766(2), Si-C3 1.892(3), Si-N3 1.720(2), N2-P-Rh 117.67(8), C1-P-Rh 105.39(8), C4-P-Rh 112.90(8), N2-P-C1 103.10(11), N2-P-C4 105.86(10), C1-P-C4 111.55(12), P-C4-C5 126.07(19), C4-C5-Si 126.39(19), P-C1-C2 136.5(2), C1-C2-N1 131.8(2), C2-N1-Si 118.02(16), N3-Si-N1 112.35(11), N3-Si-C5 108.88(10), N1-Si1-C5 109.35(10), N3-Si-C3 107.20(11), N1-Si-C3 109.35(11), C5-Si-C3 109.66(11).

S1 Gau, D.; Kato, T.; Saffon-Merceron, N.; Cossío, F. P.; Baceiredo, A. *J. Am. Chem. Soc.* **2009**, *131*, 8762.

S2 SADABS, Program for data correction, Bruker–AXS.

S3 M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.

S4 SHELXL−97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, **1997**.Gau, D.; Kato, T.; Saffon-Merceron, N.; Cossío, F. P.; Baceiredo, A. *J. Am. Chem. Soc*. **2009**, *131*, 8762–8763.
S5 J. M. Lim, Y. Do, J. Kim, Eur. *J. Inorg. Chem*. **2006**, 711-717.