Electronic Supplementary Information

Homolytic H_2 cleavage by a mercury-bridged Ni(I) pincer complex [{(^{tBu}PNP)Ni}$_2${μ-Hg}]

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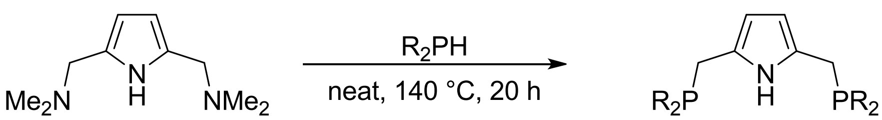
1. Experimental details

1.1 General considerations

All synthetic and spectroscopic manipulations were carried out under an atmosphere of purified nitrogen, either in a Schlenk apparatus or in a glovebox. Solvents were dried and deoxygenated either by distillation under a nitrogen atmosphere from sodium benzophenone ketyl (THF, pentane, hexane) or by an MBraun GmbH solvent purification system (all other solvents). NMR data were recorded on a Bruker DPX 200, Bruker DRX 400, a Bruker Avance III 400, Bruker Avance II 300 or a Bruker Avance III 600 MHz spectrometer at ambient temperature unless stated otherwise. The residual solvent signal was used as a chemical shift reference (δ_H = 7.16 for benzene, 7.26 for chloroform, 3.58 for α-H of THF) for the ^{1}H NMR spectra and the solvent signal (δ_C = 128.06 ppm for benzene, 77.17 for chloroform, 67.21 for α-C of THF) for the ^{13}C NMR spectra. Elemental analyses were performed by combustion and gas chromatographic analysis with an elementar varioMICRO or elementar varioMICRO CUBE instrument. All chemicals were purchased from Acros or Aldrich and were used without further purification. NiX_2(dme) (X = Cl, Br),[1] 2,5-Bis((alkyl-phosphino)methyl)-1H-pyrrole[2] and R_2PH (R = *i*Pr, *t*Bu)[3] were synthesized according to literature procedures. H_2 (5.0, 99.999 Vol. %), D_2 (2.8, 99.8 Vol. %) and N_2O (2.5, 99.5 Vol. %) gas, were purchased from Westfalen AG and used as received.

1.2 Synthesis of 2,5-Bis((alkyl-phosphino)methyl)-1H-pyrrole (1a and 1b)



1a R = *i*Pr
1b R = *t*Bu

In a typical experiment[4] 2,5-bis((alkyl-phosphino)methyl)-1H-pyrrole (1 equiv.) and R_2PCl (R = *i*Pr, *t*Bu) (2.05 equiv.) were mixed and heated under N_2 at 140 °C for 20 h. After that time all volatiles were removed under dynamic vacuum at 60 °C for at least 2 h.

1.2.1 2,5-Bis((di-*iso*-propyl-phosphino)methyl)-1H-pyrrole (1a)

Pyrrole **1a** was obtained as a yellow-brown oil in 90% yield.

^{1}H NMR (200 MHz, C_6D_6, ambient temperature): δ =) 8.14 (br s, 1H, NH), 5.97 (d, J_{HH} = 2.8 Hz, 2H, CH-Pyr), 2.58 (s, 4H, CH_2), 1.57 (dsep, J_{HH} = 7.1 Hz, J_{HP} = 2.3 Hz, $CH(CH_3)_2$), 0.99 (dd, J_{HH} = 7.2 Hz, J_{HP} = 2.4 Hz, 6H, $CH(CH_3)_2$), 0.93 (d, J_{HH} = 7.1 Hz, 6H, $CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, ambient temperature): δ = 127.6 (d, J_{CP} = 9.6 Hz, C2/5), 107.0 (d, J_{CP} = 4.8 Hz, C3/4), 23.8 (d, J_{CP} = 15.3 Hz, $CH(CH_3)_2$), 21.8 (d, J_{CP} = 20.1 Hz, CH_2), 19.9 (d, J_{CP} = 14.5 Hz, $CH(CH_3)_2$), 19.1 (d, J_{CP} = 10.8 Hz, $CH(CH_3)_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 1.00 ppm. **Elemental analysis:** Anal. Calcd for $C_{18}H_{35}NP_2$: C, 66.03, H, 10.77, N, 4.28 Found: C, 66.21, H, 10.86, N, 4.66. The **E.I. mass** spectrum (70 eV) showed a molecular ion at *m*/*z* = 327 amu with the following isotopic cluster distribution for: $C_{18}H_{35}NP_2$ (calcd %, observd %): 327.2 (100, 100), 328.2 (20, 21), 329.2 (2, 2).

1.2.2 2,5-Bis((di-*tert*-butyl-phosphino)methyl)-1H-pyrrole (1b)

Pyrrole **1b** was obtained in 85% yield as a viscous brown oil, which solidified after several days at ambient temperature. Crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at −24°C.

^{1}H NMR (200 MHz, C_6D_6, ambient temperature): δ = 8.57 (br. s, 1H, N<u>H</u>), 6.06 (d, J_{HH} = 2.5 Hz, 2H, C<u>H</u>-Pyr), 2.72 (s, 4H, C<u>H</u>$_2$), 1.04 (d, J_{HP} = 10.6 Hz, C(C<u>H</u>$_3$)$_3$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, ambient temperature): δ = 128.9 (d, J_{CP} = 12.9 Hz, <u>C</u>2/5), 106.9 (d, J_{CP} = 5.7 Hz, <u>C</u>3/4), 31.4 (d, J_{CP} = 22.9 Hz, <u>C</u>(CH$_3$)$_3$), 29.7 (d, J_{CP} = 12.9 Hz, C(<u>C</u>H$_3$)$_3$), 20.7 (d, J_{CP} = 23.5 Hz, <u>C</u>H$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 23.00 ppm. **Elemental analysis:** Anal. Calcd for $C_{22}H_{43}NP_2$: C, 68.90, H, 11.30, N, 3.65 Found: C, 68.44, H, 11.11, N, 4.27. The **E.I. mass** spectrum (70 eV) showed a molecular ion at m/z = 383 amu with the following isotopic cluster distribution for: $C_{22}H_{43}NP_2$ (calcd %, observd %): 383.3(100, 100), 384.3 (25, 24), 382.3 (6, 3).

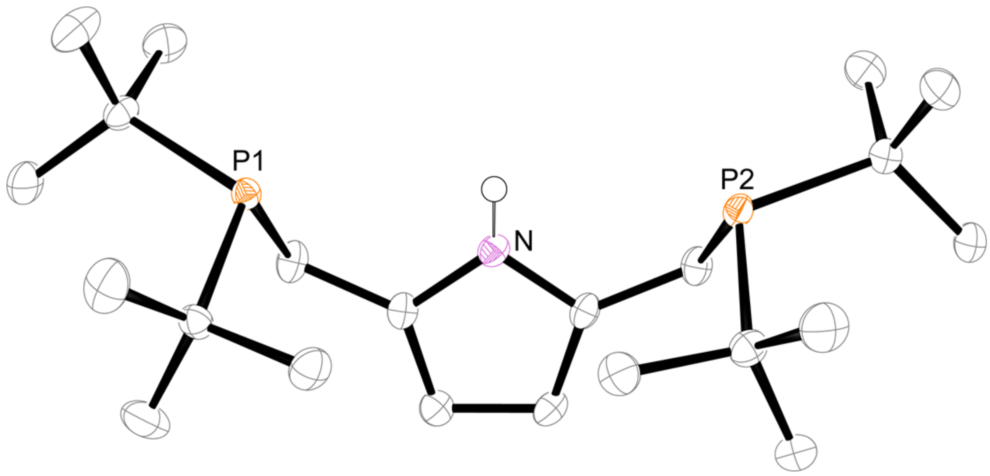
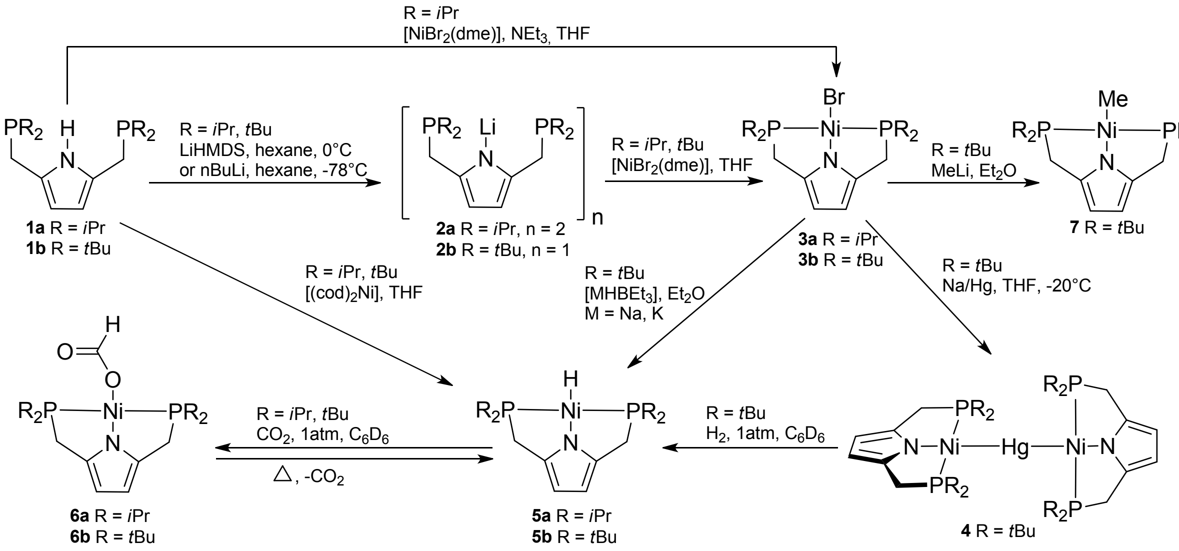


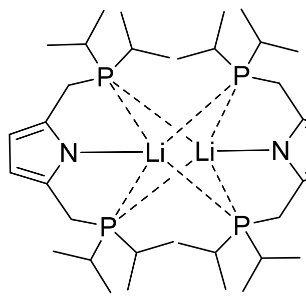
Figure S1. Displacement ellipsoid plot (50% probability) of **1b**. Hydrogen atoms, except NH, are omitted for clarity. Only one of the two independent molecules in the asymmetric unit is shown. Both molecules display approximate mirror symmetry, and a least-squares fit of both molecules (one inverted) gives a r.m.s. deviation of 0.10 .



Scheme S1. Complex synthesis and labeling scheme

1.3 Synthesis of lithium salts [(^{R}PNP)Li]$_x$

1.3.1 Synthesis of [(^{iPr}PNP)Li]$_2$ (2a)



To a solution of **1a** (1000 mg, 3.06 mmol) in 30 mL of pentane was added 2.1 mL (3.2 mmol, 1.6 M) *n*BuLi at −78 °C. After 30 min a beige suspension was obtained, which was warmed to room temperature giving a clear orange solution. After stirring overnight the pentane was removed under dynamic vacuum and the solid residue was washed with a minimal amount of pentane. After recrystallization from hexane −24 °C pale yellow crystals were obtained, which were suitable for X-ray analysis. Yield: 296 mg (0.89 mmol, 30%).

^{1}H NMR (400 MHz, C_6D_6, ambient temperature): δ = 6.25 (s, 4H, C<u>H</u>-Pyr), 3.21 (s, 8H, C<u>H</u>$_2$), 1.75 – 1.63 (m, 8H, C<u>H</u>(CH$_3$)$_2$), 1.07 (app. q. (dvt) CH(C<u>H</u>$_3$)$_2$), 0.98 (app. q. (dvt) CH(C<u>H</u>$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, ambient temperature): δ = 135.9 (s, <u>C</u>2/5), 108.6 (s, <u>C</u>3/4), 25.7 (s, <u>C</u>H$_2$), 22.6 (s, <u>C</u>H(CH$_3$)$_2$), 19.8 (s, CH(<u>C</u>H$_3$)$_2$), 19.4 (s, CH(<u>C</u>H$_3$)$_2$) ppm. **^{31}P{^{1}H} NMR** (162MHz, C_6D_6, ambient temperature): δ = 0.00 (sep, J_{PLi} = 24.7 Hz) ppm. **Elemental analysis:** Anal. Calcd for $C_{36}H_{68}N_2P_4Li$: C, 64.85, H, 10.28, N, 4.20 Found: C, 64.41, H, 10.26, N, 4.28.

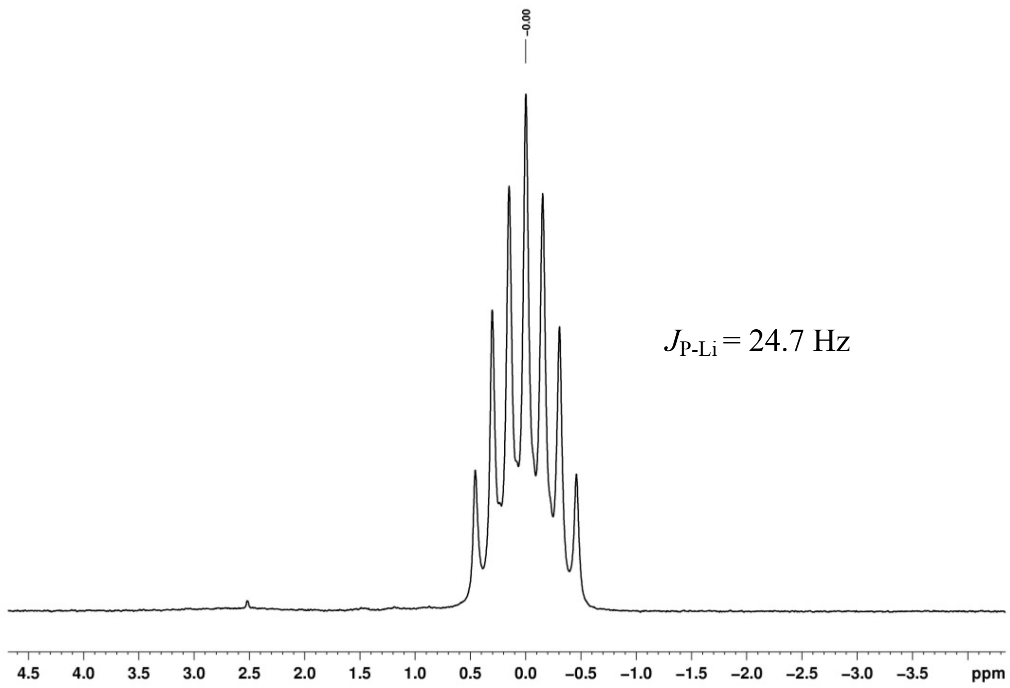


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **1a** recorded in C_6D_6 at ambient temperature.

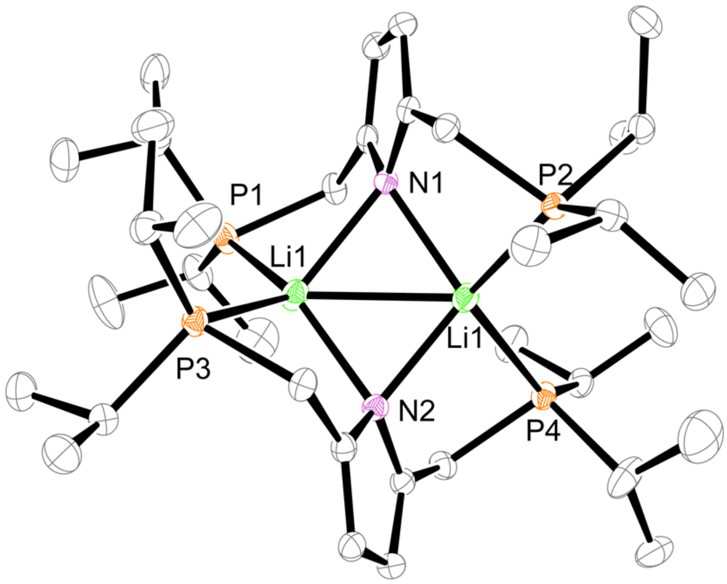
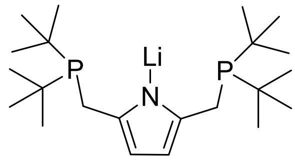


Figure S3. Displacement ellipsoid plot (50% probability) of [(^{iPr}PNP)Li]$_2$ (**2a**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Li1-N1 2.063(3), Li1-N2 2.064(3), Li1-P1 2.540(3), Li1-P3 2.548(3), Li2-N2 2.056(3), Li2-N1 2.114(3), Li2-P2 2.544(3), Li2-P4 2.501(3), Li1···Li2 2.484(4), N1-Li1-N2 106.98(12), N1-Li2-N2 105.34(12).

1.3.2 Synthesis of [(^{tBu}PNP)Li]$_2$ (2b)

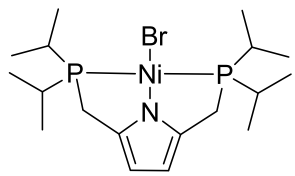


Pyrrole **1b** (4.0 g, 10.43 mmol) was dissolved in hexane (50 mL) and cooled to 0 °C and $LiN(SiMe_3)_2$ (1.8 g; 10.76 mmol) in hexane (20 mL) was added at this temperature with stirring. The mixture was allowed to warm to room temperature and stirred overnight. The pale-brown suspension was filtered and the collected solid was washed with hexane (20 mL). Lithium salt **2b** was obtained as an off-white powder. Yield: 3.1 g (7.96 mmol, 76%). Lithium salt **2b** was found to be significantly less soluble than **2a**, which suggested the formation of higher aggregates. Therefore, a small amount of THF had to be added to the C_6D_6 suspension of **2b**, before NMR spectra could be recorded.

^{1}H NMR (300 MHz, C_6D_6 + a few drops of THF, ambient temperature): δ = 6.04 (s, 2H, C<u>H</u>-Pyr), 3.04 (s, 4H, C<u>H</u>$_2$), 1.09 (d, J_{PH} = 10.2 Hz, 18H, CH_3) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6 + a few drops of THF, ambient temperature): δ = 134.4 (d, J_{CP} = 8.1 Hz, <u>C</u>2/5), 105.1 (s, <u>C</u>3/4), 31.3 (d, J_{CP} = 20.5 Hz, <u>C</u>(CH$_3$)$_3$), 30.2 (d, J_{CP} = 11.1 Hz, C(<u>C</u>H$_3$)$_3$), 25.1 (d, J_{CP} = 15.7 Hz, <u>C</u>H$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6 + a few drops of THF, ambient temperature): δ = 21.6 (s) ppm. **Elemental analysis:** Anal. Calcd for $C_{22}H_{42}NP_2Li$: C, 67.85, H, 10.87, N, 3.60 Found: C, 67.14, H, 11.02, N, 3.56.

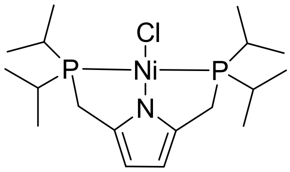
1.4 Synthesis of nickel bromide complexes [(^{R}PNP)NiBr]

1.4.1 Synthesis of [(^{iPr}PNP)NiBr] (3a)



To a suspension of [NiBr$_2$(dme)] (469 mg, 1.53 mmol) in 20 mL of THF was added **1a** (500 mg, 1.53 mmol) dissolved THF (5 mL) with stirring. The mixture turned dark red immediately; NEt_3 (0.42 mL; 3.06 mmol) was added and the mixture stirred at ambient temperature overnight. The volatiles were removed under dynamic vacuum, and the remaining residue was extracted with Et_2O (4 x 10 mL) and filtered. The solvent was removed under dynamic vacuum, leaving red crystalline material. Yield: 280 mg (0.61 mmol, 40%).

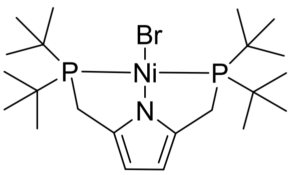
^{1}H NMR (400 MHz, C_6D_6, ambient temperature): δ = 6.31 (s, 2H, C<u>H</u>-Pyr), 2.50 (vt, J_{HP} = 4.4 Hz, 4H, C<u>H</u>$_2$), 2.03 – 1.90 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 1.39 (app. q. (dvt), 6H, CH(C<u>H</u>$_3$)$_2$), 0.98 (app. q. (dvt), 6H, CH(C<u>H</u>$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, ambient temperature): δ = 137.9 (vt, J_{CP} = 7.4 Hz, <u>C</u>2/5), 105.9 (vt, J_{CP} = 5.4 Hz, <u>C</u>3/4), 24.1 (vt, J_{CP} = 11.0 Hz, <u>C</u>H(CH$_3$)$_2$), 22.5 (vt, J_{CP} = 10.4 Hz, <u>C</u>H$_2$), 18.7 (vt, J_{CP} = 2.0 Hz, CH(<u>C</u>H$_3$)$_2$), 17.7 (s, CH(<u>C</u>H$_3$)$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 62.6 (s) ppm. **Elemental analysis:** Anal. Calcd for $C_{18}H_{34}NP_2NiBr$: C, 46.49, H, 7.37, N, 3.01 Found: C, 46.55, H, 7.37, N, 3.15. The **E.I. mass spectrum** (70 eV) showed a molecular ion at *m/z* = 465 amu with the following isotopic cluster distribution for: $C_{18}H_{34}NP_2NiBr$ (calcd %, observd %): 465.1 (100, 100), 463.1 (74, 79), 467.1 (32, 30), 466.1 (21, 20), 464.1 (15, 17), 468.1 (6, 7), 469.1 (5, 5).



The corresponding **[(^{iPr}PNP)NiCl]** was synthesized following the same procedure using **1a** (185 mg, 0.57 mmol) and [$NiCl_2$(dme)] (124 mg, 0.57 mmol). Yield: 162 mg (0.39 mmol, 68%) of a red-brown solid.

^{1}H NMR (300 MHz, C_6D_6, ambient temperature): δ = 6.27 (s, 2H, C<u>H</u>-Pyr), 2.49 (vt, J_{HP} = 4.4 Hz, 4H, C<u>H</u>$_2$), 2.01 – 1.84 (m, 4H, C<u>H</u>(CH_3)$_2$), 1.40 (app. q. (dvt), 6H, CH(C<u>H</u>$_3$)$_2$), 1.01 (app. q. (dvt), 6H, CH(C<u>H</u>$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, ambient temperature): δ = 137.9 (vt, J_{CP} = 7.5 Hz, <u>C</u>2/5), 105.9 (vt, J_{CP} = 5.3 Hz, <u>C</u>3/4), 23.7(vt, J_{CP} = 10.7 Hz, <u>C</u>H(CH_3)$_2$), 22.0 (vt, J_{CP} = 10.5 Hz, <u>C</u>H$_2$), 18.6 (vt, J_{CP} = 1.9 Hz, CH(<u>C</u>H$_3$)$_2$), 17.6 (s, CH(<u>C</u>H$_3$)$_2$) ppm. **^{31}P{^{1}H} NMR** (121MHz, C_6D_6, ambient temperature): δ = 60.1 (s) ppm.

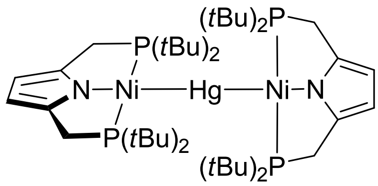
1.4.2 Synthesis of [(^{tBu}PNP)NiBr] (3b)



To a suspension of [$NiBr_2$(dme)] (234 mg, 0.77 mmol) in THF (10 mL) was added a solution of **2b** (300 mg, 0.77 mmol) dissolved in THF (10 mL) at ambient temperature. The mixture turned red and was stirred at room temperature overnight. The THF was removed under dynamic vacuum and the residue was extracted with Et_2O (4 x 5 mL) and filtered. After removal of the solvent the product **3b** was obtained as a red solid. Yield: 208 mg (0.40 mmol, 52%). Crystals suitable for X-ray diffraction were grown from a concentrated Et_2O solution at −24 °C as dark-red tetrahedrons.

^{1}H NMR (200 MHz, C_6D_6, ambient temperature): δ = 6.15 (s, 2H, C<u>H</u>-Pyr), 2.70 (vt, J_{HP} = 4.3 Hz, 4H, C<u>H</u>$_2$), 1.40 (vt, J_{HP} = 6.7 Hz, C(C<u>H</u>$_3$)$_3$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, ambient temperature): δ = 138.1 (br. s, <u>C</u>2/5), 105.0 (vt, J_{CP} = 5.0 Hz, <u>C</u>3/4), 35.4 (vt, J_{CP} = 6.9 Hz, <u>C</u>(CH_3)$_3$), 29.5 (vt, J_{CP} = 2.3 Hz, C(<u>C</u>H$_3$)$_3$), 23.7 (vt, J_{CP} = 9.5 Hz, <u>C</u>H$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 67.1 (s) ppm. **Elemental analysis:** Anal. Calcd for $C_{22}H_{42}NP_2NiBr$: C, 50.71, H, 8.12, N, 2.69 Found: C, 50.91, H, 8.21, N, 2.85. The **E.I. mass spectrum** (70 eV) showed a molecular ion at *m/z* = 521 amu with the following isotopic cluster distribution for: $C_{22}H_{42}NP_2NiBr$ (calcd %, observd %): 521.2 (100, 100), 519.2 (74, 84), 523.1 (32, 32), 522.1 (26, 25), 520.1 (18, 16), 524.1 (9, 15), 525.1 (4, 6).

1.5 Synthesis of [{(^{tBu}PNP)Ni}$_2$(μ-Hg)] (4)



A solution of **3b** (240 mg, 0.462 mmol) in 10 mL of THF was added to a suspension of sodium amalgam (0.5% Na, 56 mg, 2.44 mmol) in 10 mL of THF at −20°C. The mixture turned dark brown-red and turbid; it was stirred at room temperature for 3h. The supernatant was decanted and filtered over celite. The solvent was removed under dynamic vacuum and the blackish residue was washed with pentane (2 x 2 mL). Yield: 219 mg (0.202 mmol, 87% per Ni). Very dark brown-red plates were obtained from a concentrated THF solution at -35 °C or by slow evaporation of benzene at room temperature. The complex proved to be stable in C_6D_6 solution at least for 4 days at 80 °C.

^{1}H NMR (600 MHz, C_6D_6, ambient temperature): δ 6.39 (s, 2H, C<u>H</u>-Pyr), 2.89 (vt, J_{HP} = 3.6 Hz, 4H, C<u>H</u>$_2$), 1.31 (vt, J_{HP} = 6.3 Hz, 18H, C(C<u>H</u>$_3$)$_3$ ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, ambient temperature): δ = 134.4 (vt, J_{CP} = 5.5 Hz, <u>C</u>2/5), 104.5 (vt, J_{CP} = 2.6 Hz, <u>C</u>3/4), 34.4 (vt, J_{CP} = 5.0 Hz, <u>C</u>(CH$_3$)$_3$), 30.6 (s, C(<u>C</u>H$_3$)$_3$), 26.7 (vt, J_{CP} = 10.5 Hz, <u>C</u>H$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 76.6 (s, strong Hg-satellites J_{PHg} = 333 Hz) ppm. **Elemental analysis:** Anal. Calcd. for $C_{44}H_{84}N_2P_4Ni_2Hg$: C, 48.80, H, 7.82, N, 2.59 Found: C, 48.29, H, 7.41, N, 2.49.

When **4** was treated with LiBr in in C_6D_6 at 80 °C only a very small amount of nickel bromide **3b** (< 1%) was formed.

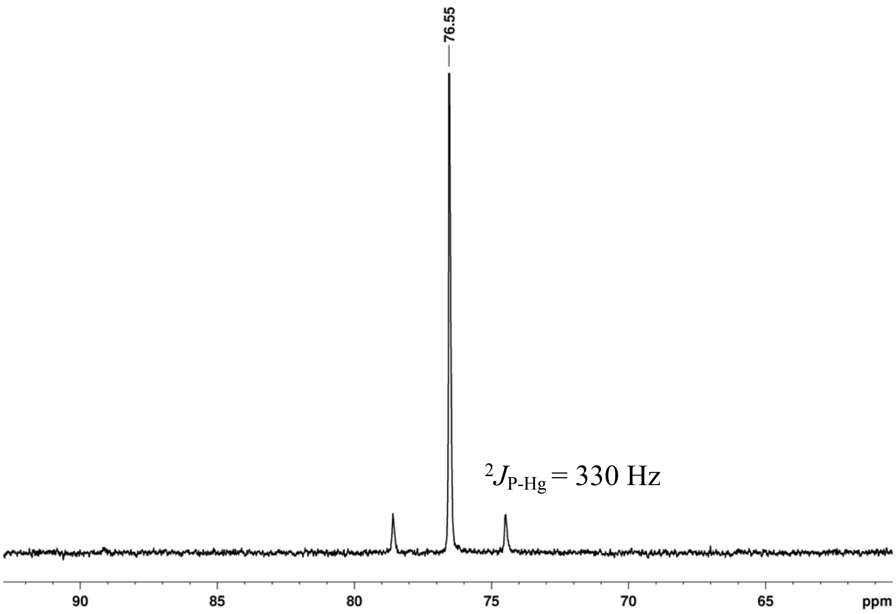
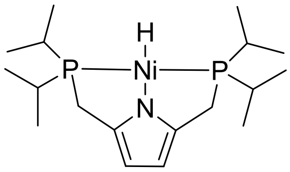


Figure S4. ^{31}P{^{1}H} NMR spectrum of **4** with ^{199}Hg satellites.

1.5 Synthesis of nickel hydride [(^{R}PNP)NiH]

1.5.1 Synthesis of [(^{iPr}PNP)NiH] (5a)



To a solution of [(cod)$_2$Ni] (437 mg, 1.59 mmol) in THF (15 mL) was added a solution of **1a** (521 mg, 1.59 mmol) in 15 mL of THF. The mixture turned dark brown and was stirred at room temperature overnight. The solvent was removed under dynamic vacuum and the sticky residue was extracted with pentane, reduced to minimum volume and cooled to −25 °C. After 12 h brown crystalline material was obtained. Yield: 340 mg (0.88 mmol, 55%).

^{1}H NMR (400 MHz, C_6D_6, ambient temperature): δ = 6.53 (s, 2H, C<u>H</u>-Pyr), 2.89 (vt, J_{HP} = 4.3 Hz, 4H, C<u>H</u>$_2$), 1.82 – 1.70 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 1.12 (app. q. (dvt), J_{HH} = J_{HP} = 7.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 0.94 (app .q. (dvt), J_{HH} = J_{HP} = 7.0 Hz, CH(C<u>H</u>$_3$)$_2$), −17.59 (t, J_{HP} = 59 Hz, 1H, Ni-<u>H</u>) ppm. **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, ambient temperature): δ = 135.9 (vt, J_{CP} = 7.6 Hz, <u>C</u>2/5), 104.8 (vt, J_{CP} = 5.2 Hz, <u>C</u>3/4), 25.3 (vt, J_{CP} = 10.0 Hz, <u>C</u>H$_2$), 24.7 (vt, J_{CP} = 11.8 Hz, <u>C</u>H(CH$_3$)$_2$), 19.5 (vt, J_{CP} = 2.8 Hz, CH(<u>C</u>H$_3$)$_2$), 18.4 (s, CH(<u>C</u>H$_3$)$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 77.8 (s) ppm. **Elemental analysis:** Anal. Calcd for $C_{18}H_{34}NP_2NiBr$: C, 55.99, H, 9.14, N, 3.63 Found: C, 56.58 H, 9.30, N, 3.61. **IR** (ATR): 1868 cm^{-1} (w), Ni-H. The **E.I. mass spectrum** (70 eV) showed a molecular ion at *m*/*z* = 385 amu with the following isotopic cluster distribution for: $C_{18}H_{35}NP_2Ni$ (calcd %, observd %): 385.2 (100, 100), 387.2 (39, 38), 386.2 (20, 24), 388.2 (9, 10), 389.2 (5, 6).

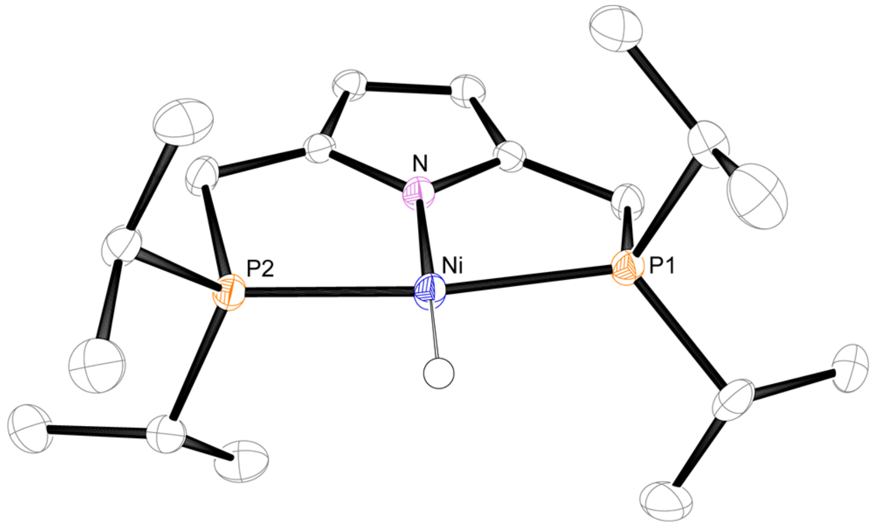
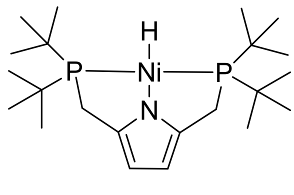


Figure S5. Displacement ellipsoid plot (50% probability) of [(^{iPr}PNP)NiH] (**5a**). Hydrogen atoms, except Ni-H, are omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N 1.8691(15), Ni-P1 2.1466(6), Ni-P2 2.1535(6), Ni-H 1.44(2), N-Ni-H 178.9(1), P1-Ni-P2 170.40(2), N-Ni-P1 85.24(5), N-Ni-P2 85.24(5), P1-Ni-H 94.45(96), P2-Ni-H 95.03(96).

1.5.2 Synthesis of [(^{tBu}PNP)NiH] (5b)



Method A: A BÜCHI TINYCLAVE reactor was charged with **1b** (300 mg, 0.78 mmol) and [(cod)$_2$Ni] (214.2 mg, 0.78 mmol) in 3 mL of C_6H_6. The reactor was then pressurized with H_2 (5 bar) and the reaction mixture was heated at 80 °C for 5 h. After that time the mixture was stirred at room temperature for 12 h. Full and clean conversion of **5b** was verified by $^{31}P\{^1H\}$ NMR spectroscopy. The solvent was removed under dynamic vacuum. Pentane (2 mL) was added to the residue and the solvent was then removed under dynamic vacuum to remove free COD and to give a brown sticky solid, which was recrystallized from hexane at −30 °C to give red-brown crystals. Yield: 144 mg (0.33 mmol, 42%).

Method B: Complex **3b** (100 mg, 0.193 mmol) was dissolved in Et_2O (5 mL) and $NaHBEt_3$ (0.193 mL, 1M in THF) was added at room temperature. The mixture turned red-brown and was stirred overnight. Volatiles were removed under dynamic vacuum and the residue was washed with $(Me_3Si)_2O$ and extracted with Et_2O (2 mL). The extracts were filtered over Celite and dried under dynamic vacuum. The residue was suspended in hexane and a minimum quantity of Et_2O was added until the solid fully dissolved. The solution was filtered and then stored at −25 °C overnight to yield a dark-red amorphous material. While nickel hydride **5b** was formed by this procedure, the product was always contaminated by some boron-containing species as indicated by ^{11}B NMR spectroscopy ($^{11}B\{^1H\}$ NMR (ambient temperature, C_6D_6): δ 1.94 (v. br.), −12.1 ($NaHBEt_3$), −16.4 ppm). Unfortunately, these B-containing species could not be efficiently removed by crystallization.

Method C: A J. YOUNG NMR tube was charged with complex **4** (18 mg, 0.017 mmol) and C_6D_6 (1 mL). The N_2 atmosphere was replaced by H_2 (1 atm) and the mixture was heated at 60 °C for 2 h. A color change from deep red-brown to red was observed and Hg precipitated as a grey powder. The conversion to the nickel hydride **5b** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. However, it should be mentioned that in some cases when using a BUCHI TINYCLAVE reactor for this reaction (5 bar of H_2, grade 5.0), we also observed the formation of small amounts of **3b** (by EI-MS spectrometry and $^{31}P\{^1H\}$ NMR spectroscopy (δ 67.1 ppm)) and a minor quantities of a second species that was characterized as the nickel hydroxide complex [(^{tBu}PNP)NiOH)] on the basis of EI-MS spectrometry and $^{31}P\{^1H\}$ NMR spectroscopy (δ 61.5 ppm). We attribute the formation of these complexes to small contaminations of **4** with NaBr, which was not completely removed during workup, and to minute levels of adventitious H_2O contamination. However, as shown by the reactivity studies on [{(^{tBu}PNP)Ni}$_2$(μ-Hg)] (**4**) (see chapter 1.5) these side reactions are very slow in the absence of H_2 suggesting that H_2 is required to trigger the formation of these products.

Crystals suitable for X-ray diffraction were obtained from a concentrated hexane solution of **6b** at −25°C overnight.

^{1}H NMR (600 MHz, C_6D_6, ambient temperature): δ 6.50 (s, 2H, C<u>H</u>-Pyr), 3.02 (vt, J_{HP} = 3.9 Hz, 4H, C<u>H</u>$_2$), 1.20 (vt, J_{HP} = 6.6 Hz, 18H, C<u>H</u>$_3$), −17.65 (t, J_{HP} = 55.7 Hz, 1H, Ni-<u>H</u>) ppm. **^{13}C{^{1}H} NMR** (150 MHz, C_6D_6, ambient temperature): δ = 137.1 (vt, J_{CP} = 7.7 Hz, <u>C</u>2/5), 104.3 (vt, J_{CP} = 4.9 Hz, <u>C</u>3/4), 33.5 (vt, J_{CP} = 8.3 Hz, C(CH$_3$)$_3$), 29.5 (vt, J_{CP} = 3.3 Hz, C(CH$_3$)$_3$), 25.7 (vt, J_{CP} = 8.8 Hz, CH$_2$) ppm. **^{31}P{^{1}H} NMR** (242 MHz, C_6D_6, ambient temperature): δ = 98.9 (s) ppm. **Elemental analysis:** Anal. Calcd for. $C_{22}H_{43}NP_2Ni$: C, 59.75, H, 9.80, N, 3.17. Found: C, 58.99, H, 9.81, N, 3.57. The **E.I. mass spectrum** (70 eV) showed a molecular ion at m/z = 441 amu with the following isotopic cluster distribution for: $C_{22}H_{43}NP_2Ni$ (calcd %, observd %): 441.2 (100, 100), 443.2 (38.6, 37.1), 442.2 (24.3, 29.6), 444.2 (11.0, 11.2), 445.2 (6.8, 6.4), 447.2 (1.5, 1.5), 446.2 (1.3, 1.6). **IR** (ATR): 1832 cm^{-1} (s), Ni-H.

Nickel hydride **5b** exhibited no reactivity towards D_2 (5 bar) or C_2H_4 (1atm) at ambient temperature or when heated to 80 °C. However, when **5b** was exposed to CO_2 (5 bar, 80 °C, 2h) an equilibrium between **5b** and the corresponding formate complex [^{tBu}PNPNi(OCOH)] (**6b**) (IR (ATR): 1630 cm^{-1} (s), CO) was observed. The ratio of **5b** : **6b** was *ca.* 1.8 : 1 as judged by ^{31}P{^{1}H} NMR spectroscopy. Nevertheless, CO_2 readily deinserted when this mixture was heated.

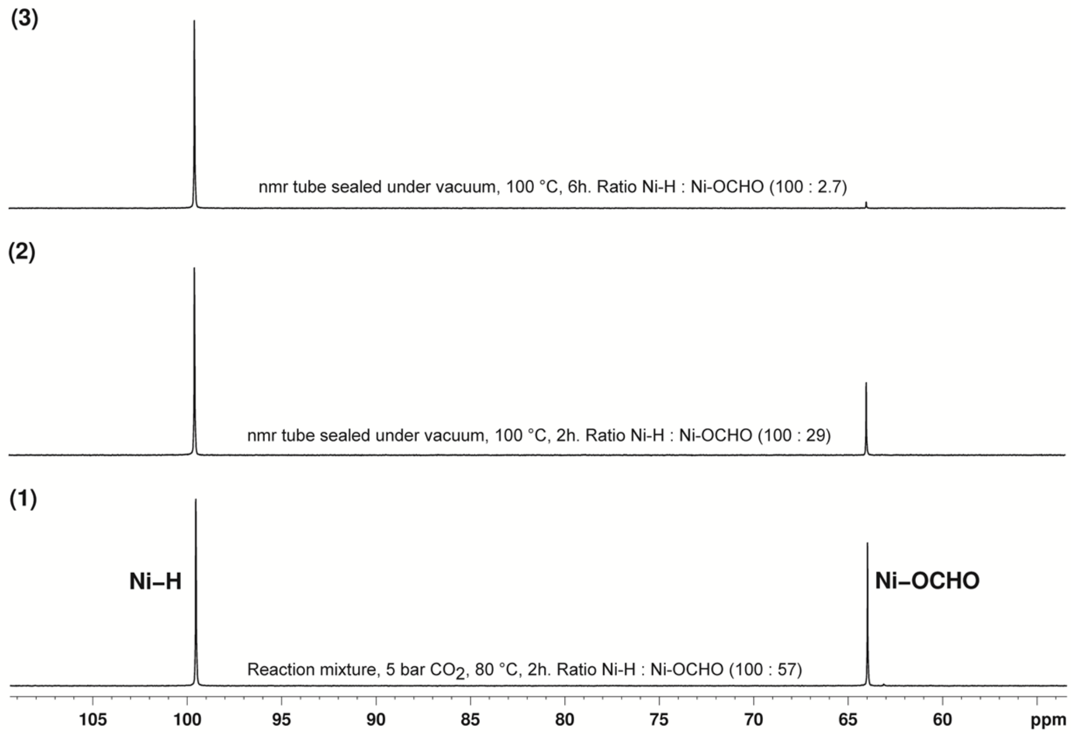
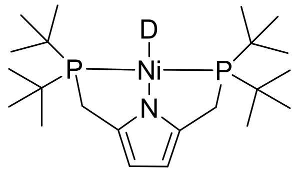


Figure S7: ^{31}P{^{1}H} NMR spectra of the reaction mixture **5b** and **6b**.

In contrast, nickel hydride **5b** proved to be stable in the presence of H_2O in C_6D_6 at 80 °C and no reaction to [(^{tBu}PNP)NiOH)] was observed. Furthermore, by adding an excess amount of LiBr to a sample of **5b** in C_6D_6 only minimal conversion (<1%) to nickel bromide **3b** was observed after heating this mixture at 80 °C for 4.5 hours.



The corresponding nickel-deuteride [(^{tBu}PNP)NiD] (d_1-**5b**) was synthesised following *method C* in a BÜCHI TINYCLAVE reactor in C_6D_6 solution with D_2 gas (5 bar, grade 2.8).

^{1}H NMR (300 MHz, C_6D_6, ambient temperature): δ 6.50 (s, 2H, CH-Pyr), 3.02 (vt, J_{HP} = 4.0 Hz, 4H, CH_2), 1.19 (vt, J_{HP} = 6.5 Hz, 18H, CH_3) ppm. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, ambient temperature): δ = 137.1 (vt, J_{CP} = 7.4 Hz, C2/5), 104.3 (vt, J_{CP} = 5.1 Hz, C3/4), 33.5 (vt, J_{CP} = 8.1 Hz, $C(CH_3)_3$), 29.5 (vt, J_{CP} = 3.2 Hz, $C(CH_3)_3$), 25.7 (vt, J_{CP} = 9.0 Hz CH_2) ppm. **^{31}P{^{1}H} NMR** (242 MHz, C_6D_6, ambient temperature): δ = 99.6 (t, J_{PD} = 8.5 Hz) ppm. The **E.I. mass spectrum** (70 eV) showed a molecular ion at *m*/*z* = 442 amu with the following isotopic cluster distribution for: $C_{22}H_4DNP_2Ni$ (calcd %, observd %): 442.2 (100, 100), 444.2 (39, 39), 443.2 (24, 39), 445.2 (9, 9), 446.2 (5, 7). **IR** (ATR): 1321 cm^{-1} (s), Ni-D.

As observed for the preparation of nickel hydride **5b** from complex **4** with H_2 a small amount of nickel hydroxide [(^{tBu}PNP)NiOH)] was detected in the reaction mixture by ^{31}P{H} NMR spectroscopy, but no deuterium label was incorporated, strengthening the argument that adventitious H_2O contamination is responsible for [(^{tBu}PNP)NiOH)] formation.

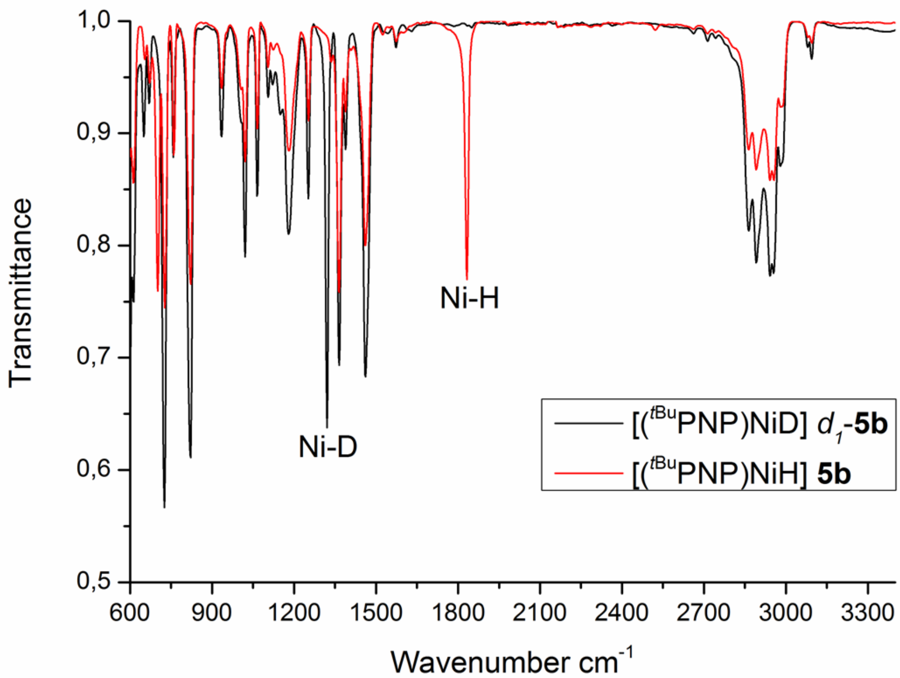
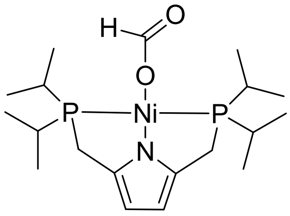


Figure S7: IR spectra of **5b** and d_1-**5b**.

1.6 Synthesis of nickel formate [(^{iPr}PNP)NiOC(O)H] (6a)



A solution of [^{iPr}PNPNiH] (**5a**) (142 mg, 0.37 mmol) in benzene-d$_6$ (3 mL) was exposed to CO_2 (2.5 bar, grade 5.0). The mixture was stirred at room temperature overnight. During this time the colour changed from brown to red. Full conversion to **6a** was monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. Formate complex **6a** was recrystallised from hexane forming red needles, which were suitable for X-ray diffraction. Yield: 86 mg (0.20 mmol, 54%)

^{1}H NMR (400 MHz, C_6D_6, ambient temperature): δ = 7.81 (t, J_{HH} = 3.5 Hz, 1H, OC<u>H</u>O), 6.25 (s, 2H, C<u>H</u>-Pyr), 2.44 (vt, J_{HP} = 4.5 Hz, 4H, CH2), 1.92 – 1.74 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 1.36 (app. q. (dvt), 6H, CH(C<u>H</u>$_3$)$_2$), 1.03 (app. q. (dvt), CH(C<u>H</u>$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, ambient temperature): δ = 167.2 (s, O<u>C</u>OH), 137.9 (vt, J_{CP} = 7.2 Hz, <u>C</u>2/5), 106.1 (vt, J_{CP} = 5.1 Hz, <u>C</u>3/4), 24.0 (vt, J_{CP} = 9.9 Hz, CH$_2$), 21.0 (vt, J_{CP} = 11.3 Hz, <u>C</u>H(CH$_3$)$_2$), 18.3 (vt, J_{CP} = 2.3 Hz, CH(<u>C</u>H$_3$)$_2$), 17.6 (s, CH(<u>C</u>H$_3$)$_2$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 57.0 (s) ppm. **Elemental Analysis:** Anal. Calcd for $C_{19}H_{35}NO_2P_2Ni$: C, 53.05, H, 8.20, N, 3.26 Found: C, 53.62 H, 8.23, N, 3.43. **IR** (ATR): 1623 cm^{-1} (vs), CO.

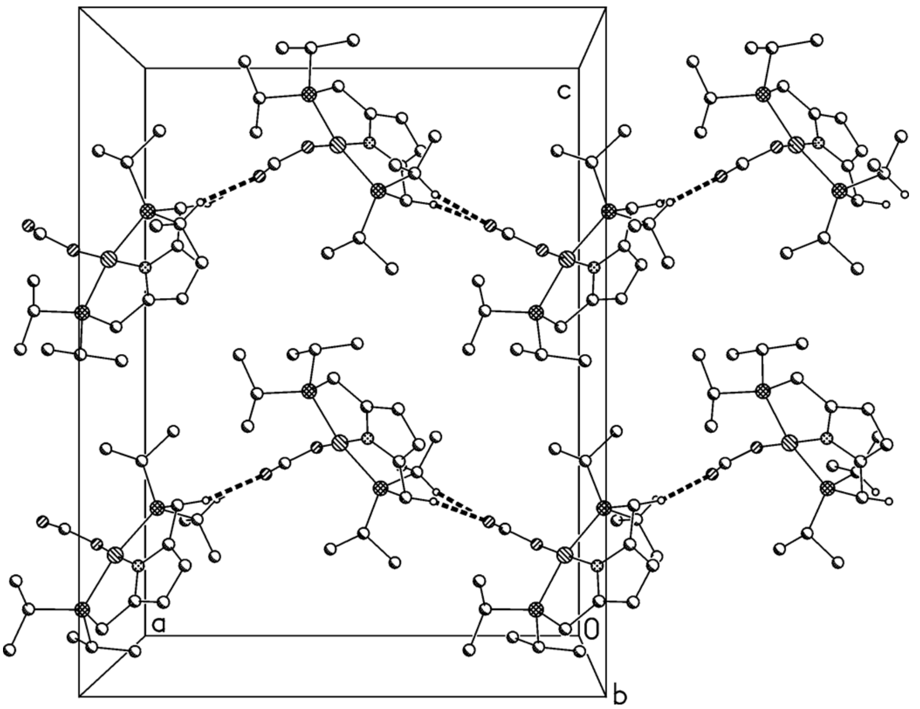
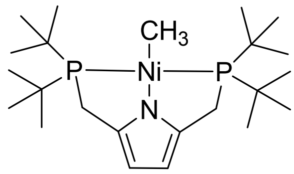


Figure S8: Packing diagram of compound 6a, showing the formation of hydrogen-bonded chains via the interactions H12B□O2 2.59 and H13□O2 2.43 Å (dotted bonds).

1.7 Synthesis of the nickel methyl complex [(^{tBu}PNP)NiMe] (7)



To a solution of **3b** (100 mg, 0.193 mmol) in Et_2O (10 mL) was added a suspension of CH_3Li (4.5 mg, 0.193 mmol) in Et_2O (5 mL) at room temperature. The mixture was stirred overnight and filtered through celite to give a brown-green solution. Removal of the solvent under dynamic vacuum gave a brown-green solid. Yield: 68 mg (0.149 mmol, 77%). Crystals suitable for X-ray analysis were grown from a concentrated Et_2O / pentane solution overnight at −25°C.
^{1}H NMR (200 MHz, C_6D_6, ambient temperature): δ 6.40 (s, 2H, C<u>H</u>-Pyr), 2.91 (vt, J_{HP} = 4.0 Hz, 4H, C<u>H</u>$_2$), 1.23 (vt, J_{HP} = 6.3 Hz, 18H, C(C<u>H</u>$_3$)$_3$, −0.25 (t, J_{HP} = 7.8 Hz, 3H, Ni-C<u>H</u>$_3$) ppm. **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, ambient temperature): δ = 135.8 (vt, J_{CP} = 6.5 Hz, <u>C</u>2/5), 103.8 (vt, J_{CP} = 5.1 Hz, <u>C</u>3/4), 34.7 (vt, J_{CP} = 6.5 Hz, <u>C</u>(CH$_3$)$_3$), 29.6 (s, C(<u>C</u>H$_3$)$_3$), 25.9 (vt, J_{CP} = 9.7 Hz, <u>C</u>H$_2$), −27.2 (t, J_{CP} = 24.5 Hz, Ni-C<u>H</u>$_3$) ppm. **^{31}P{^{1}H} NMR** (81MHz, C_6D_6, ambient temperature): δ = 68.9 (s) ppm. **Elemetal analysis:** Anal. Calcd for $C_{23}H_{45}NP_2Ni$: C, 60.55, H, 9.94, N, 3.07 Found: C, 59.95, H, 9.81, N, 3.28. The **E.I. mass spectrum** (70 eV) showed a molecular ion at *m/z* = 455 amu with the following isotopic cluster distribution for: $C_{23}H_{45}NP_2Ni$ (calcd %, observd %): 455.2 (100, 100), 457.2 (39, 36), 456.2 (26, 26), 458.2 (10, 11), 459.2 (5, 6).

Remarkably, complex **7** showed no reaction with CO, CO_2, H_2 or C_2H_4 in C_6D_6 at ambient conditions or elevated temperatures. Reaction with H_2O at 80 °C for 1 h in a mixture of C_6D_6 with a few drops THF resulted in slow degradation of **7** to free ligand **1b** (~16%). However, no further reaction was observed after 5 d at ambient temperature. The lack of reactivity may be attributed to the severe steric demand of the *t*Bu-groups, effectively blocking the axial positions in complex **6**. In contrast, the less sterically crowded and more flexible phenyl-substituted derivative [(^{Ph}PNP)NiMe] was reported to slowly insert CO into the Ni-Me bond at 50 °C.[5]

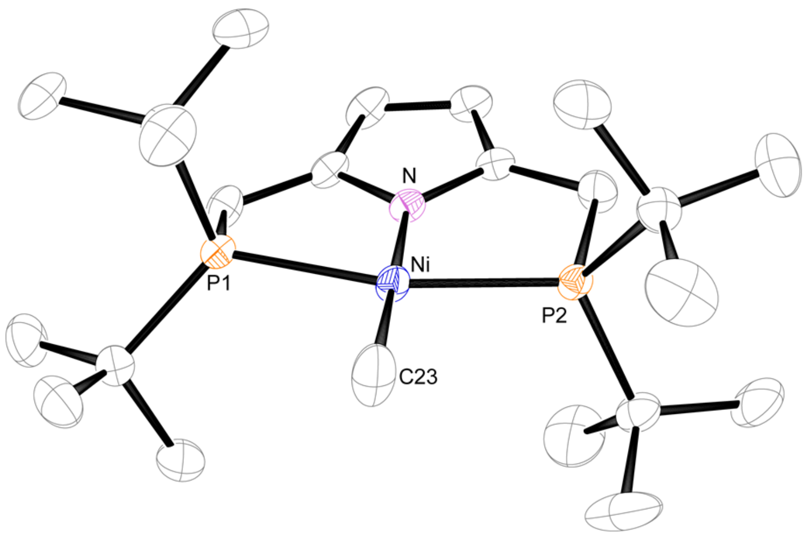


Figure S9. Displacement ellipsoid plot (50% probability) of [(^{tBu}PNP)NiMe] (**7**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N 1.8951(16), Ni-C23 1.957(2), Ni-P1 2.2027(6), Ni-P2 2.2142(6), N-Ni-C23 179.29(9), P1-Ni-P2 166.89(2), N-Ni-P1 84.14(5), N-Ni-P2 83.87(5), P1-Ni-C23 96.50(7), P2-Ni-C23 95.53(7).

2. Crystallographic data

X-ray diffraction studies. Data were recorded at 100(2) K on Oxford Diffraction diffractometers using monochromated Mo Kα or mirror-focussed Cu Kα radiation (see Table S1). Absorption corrections were applied on the basis of multi-scans. The structures were refined anisotropically on F^2 using the SHELXL-97 program.[6, 7] NiH and NH hydrogens and the formate hydrogen of 6a were refined freely; other hydrogen atoms were included as rigid methyl groups allowed to rotate but not tip, or using a riding model starting from calculated positions. The Ni-H bond lengths are consistent with the average value of 1.46 Å in the Cambridge Database (excluding obviously erroneous values). The absolute configuration was confirmed where applicable by the Flack parameter; however, all the structures that crystallize in chiral space groups do so by chance. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-1037224-1037231 in the same order as in Tables S1. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Special features and exceptions: Structures **1b** and **4**·C_6H_6 display a pseudo *B*-centring. For the latter, the solvent molecules are well-ordered. For **2a**, one isopropyl group is disordered over two positions; a system of similarity restraints was employed to improve refinement stability, but the dimensions of disordered groups should be interpreted with caution. Crystals of **6a** shatter at 100 K, presumably because of a phase transition; the data were therefore recorded at 130 K. Data for **7** were recorded at 183 K. Compound pairs **5a**/**6a** and **5b**/**7** are effectively isotypic, despite slight chemical differences. Compound **3b** is not isotypic to the latter pair despite the closely similar cells, as can be seen from inspection of the nickel *x* coordinates, which are approximately ½ for **5b** but ¾ for **3b** and **7**; no transformation in $P2_12_12_1$ can interconvert these values.

Table S1. Crystallographic data

Compound	**1b**	**2a** (dimer)	**3b**	**4·(C$_6$H$_6$)**	**5a**	**5b**	**6a**	**7**
CCDC-Number	1037224	1037225	1037226	1037227	1037228	1037229	1037230	1037231
Chemical formula	$C_{22}H_{43}NP_2$	$C_{36}H_{68}Li_2N_2P_4$	$C_{22}H_{42}BrNNiP_2$	$C_{50}H_{90}HgN_2Ni_2P_4$	$C_{18}H_{35}NNiP_2$	$C_{22}H_{43}NNiP_2$	$C_{19}H_{35}NNiO_2P_2$	$C_{23}H_{45}NNiP_2$
Formula Mass	383.51	666.68	521.13	1161.13	386.12	442.22	430.13	456.25
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
a/Å	13.7199(5)	24.1538(5)	11.4257(2)	13.9339(5)	13.2113(6)	11.0422(2)	15.7937(4)	11.4225(4)
b/Å	12.3613(5)	13.7672(3)	14.4710(3)	16.4179(5)	14.5597(8)	14.7303(2)	13.5622(3)	14.6398(5)
c/Å	28.1443(10)	12.0771(3)	15.0601(3)	24.9947(8)	21.1415(12)	14.7768(2)	20.6530(5)	14.9390(5)
α/°	90.00	90.00	90.00	108.376(3)	90.00	90.00	90.00	90.00
β/°	96.935(4)	90.00	90.00	96.539(3)	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	97.870(3)	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	4738.2(3)	4016.00(16)	2490.06(8)	5299.7(3)	4066.6(4)	2403.53(6)	4423.79(18)	2498.15(15)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	130(2)	183(2)
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$Pbca$	$P2_12_12_1$	$Pbca$	$P2_12_12_1$
No. of formula units per unit cell, Z	8	4	4	4	8	4	8	4
Radiation type	Mo Kα	Mo Kα	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Mo Kα
Absorption coefficient, μ/mm^{-1}	0.189	0.213	4.257	3.747	1.109	0.947	2.718	0.913
No. of reflections measured	115355	103142	52074	294221	60953	209772	42437	23103
No. of independent reflections	14008	11890	5154	31636	6061	7458	4648	3827
R_{int}	0.0854	0.0475	0.0535	0.0919	0.0887	0.0481	0.0444	0.0287
Final R_1 values ($I > 2\sigma(I)$)	0.0562	0.0355	0.0241	0.0403	0.0415	0.0204	0.0257	0.0210
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1126	0.0784	0.0593	0.0672	0.0783	0.0463	0.0644	0.0488
Final R_1 values (all data)	0.0977	0.0448	0.0252	0.0710	0.0732	0.0237	0.0301	0.0237
Final $wR(F^2)$ values (all data)	0.1289	0.0821	0.0599	0.0760	0.0887	0.0474	0.0667	0.0499
Goodness of fit on F^2	1.024	1.062	1.034	1.033	1.041	1.056	1.040	1.066
Flack parameter	-	-0.01(5)	-0.011(14)	-	-	-0.010(6)	-	0.012(10)

3. Computational details

All calculations were carried out with the employed Gaussian 09[8] and the long-range dispersion-corrected Grimme's functional (B97D).[9] For comparison we also used the BP86 functional as incorporated in Gaussian 09.[8] No symmetry restrictions were imposed (C_1). C, H, N and P were represented by an all-electron 6-311G(d,p) basis set, whereas a Stuttgart-Dresden ESP as implemented in Gaussian 09 was used for Hg. The nature of the extrema (minima) was established with oder analytical frequency calculations. The zero point vibration energy (ZPE) and entropic contributions were estimated within the harmonic potential approximation. The Gibbs free energy, ΔG, was calculated for T= 298.15 K and 1 atm. Geometrical parameters were reported within an accuracy of 10^{-3} Å and 10^{-1} degrees.

Table S2. Energies of the optimized structures

Compound	spin-state	DFT functional	E(0 K)^a [Ha]	H(298 K)^b [Ha]	G(298 K)^b [Ha]
[{(^{tBu}PNP)Ni}$_2$(μ-Hg)]	S = 0	B97D	-6372.222699	-6372.153434	-6372.315561
		BP86	-6372.433654	-6372.360699	-6372.534456
[{(^{tBu}PNP)Ni}$_2$(μ-Hg)]	S = 1	B97D	-6372.191450	-6372.120485	-6372.291074
		BP86	-6372.405781	-6372.332062	-6372.510757

^{a}DFT energy incl. ZPE. ^{b}standard conditions: T = 298.15 K and p = 1 atm.

Table S3. Comparison between experimental and computed structures for [{(^{tBu}PNP)Ni}$_2$(μ-Hg)] (**4**)

Bond distances (Å) and angles (°)	X-ray data	S=0 (B97D)	S=0 (BP86)	S=1 (B97D)	S=1 (BP86)
Ni-N	1.922(3) / 1.921(3)	1.925 / 1.929	1.913 / 1.918	1.934 / 1.923	1.918 / 1.915
Ni-P	2.2191(9), 2.2230(9) / 2.2248(9), 2.2174(8)	2.204, 2.202 / 2.192, 2.187	2.242, 2.240 / 2.230, 2.237	2.249, 2.212 / 2.207, 2.215	2.287, 2.290 / 2.253, 2.226
Ni-Hg	2.6488(4) / 2.6491(4)	2.629 / 2.644	2.673 / 2.699	2.781 / 2.749	2.863 / 2.867
Ni-Hg-Ni	178.699(13)	174.0	174.8	174.6	173.7

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