Electronic Supplementary Information

Homolytic $\text{H}_2$ cleavage by a mercury-bridged Ni(I) pincer complex 
$\{[(\text{dBuPNP})\text{Ni}]_2\{μ-Hg}\}$

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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 ($\delta_H = 7.16$ for benzene, 7.26 for chloroform, 3.58 for $\alpha$-H of THF) for the $^1$H NMR spectra and the solvent signal ($\delta_C = 128.06$ ppm for benzene, 77.17 for chloroform, 67.21 for $\alpha$-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$_2$PH (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$_2$O (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)

\[
\text{Me}_2\text{N} \xrightarrow{\text{R}_2\text{PH}} \text{Me}_2\text{N} \quad \text{R}_2\text{P} \quad \text{R}_2\text{N} \\
\text{42^\circ C, 20 h}
\]

In a typical experiment$^4$ 2,5-bis((alkyl-phosphino)methyl)-1H-pyrrole (1 equiv.) and R$_2$PCl (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$_6$D$_6$, ambient temperature): $\delta$ = 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$_3$)$_2$), 0.93 (s, 6H, CH$_2$), 0.39 (d, $J_{HH} = 7.1$ Hz, 6H, CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$, ambient temperature): $\delta$ = 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$_6$D$_6$, ambient temperature): $\delta$ = 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: $\text{C}_{13}\text{H}_{35}\text{NP}_2$ (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 $-24^\circ\text{C}$.

$^1\text{H NMR}$ (200 MHz, $\text{C}_6\text{D}_6$, ambient temperature): $\delta = 8.57$ (br. s, 1H, NH), 6.06 (d, $J_{\text{HH}} = 2.5$ Hz, 2H, CH-Pyr), 2.72 (s, 4H, CH$_2$), 1.04 (d, $J_{\text{HP}} = 10.6$ Hz, C(CH$_3$)$_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $\text{C}_6\text{D}_6$, ambient temperature): $\delta = 128.9$ (d, $J_{\text{CP}} = 12.9$ Hz, C$_2$/5), 106.9 (d, $J_{\text{CP}} = 5.7$ Hz, C$_3$/4), 31.4 (d, $J_{\text{CP}} = 22.9$ Hz, C(CH$_3$)$_3$), 29.7 (d, $J_{\text{CP}} = 12.9$ Hz, C(CH$_3$)$_3$), 20.7 (d, $J_{\text{CP}} = 23.5$ Hz, CH$_2$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (81MHz, $\text{C}_6\text{D}_6$, ambient temperature): $\delta = 23.00$ ppm. **Elemental analysis:** Anal. Caled for $\text{C}_{22}\text{H}_{43}\text{NP}_2$: 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: $\text{C}_{22}\text{H}_{43}\text{NP}_2$ (calcd %, observd %): 383.3(100, 100), 384.3 (25, 24), 382.3 (6, 3).

![Figure S1](image-url)  
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 .
1.3 Synthesis of lithium salts [(RPNP)Li]_x

1.3.1 Synthesis of [(RPNP)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) nBuLi 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%).

^1H NMR (400 MHz, C_D6, ambient temperature): δ = 6.25 (s, 4H, CH-Pyr), 3.21 (s, 8H, CH3), 1.75 – 1.63 (m, 8H, CH(CH3)2), 1.07 (app. q. (dvt) CH(CH3)2), 0.98 (app. q. (dvt) CH(CH3)2) ppm. ^13C[^1H] NMR (100 MHz, C_D6, ambient temperature): δ = 135.9 (s, C2/5), 108.6 (s, C3/4), 25.7 (s, CH2), 22.6 (s, CH(CH3)2), 19.8 (s, CH(CH3)2), 19.4 (s, CH(CH3)2) ppm. ^31P[^1H] NMR (162MHz, C_D6, ambient temperature): δ = 0.00 (sep, J_P,Li = 24.7 Hz) ppm. Elemental analysis: Anal. Calcd for C_{2n}H_{6n}N_2P_4Li: C, 64.85, H, 10.28, N, 4.20 Found: C, 64.41, H, 10.26, N, 4.28.

Scheme S1. Complex synthesis and labeling scheme
Figure S2. $^{31}$P{¹H} NMR spectrum of 1a recorded in C$_6$D$_6$ at ambient temperature.

Figure S3. Displacement ellipsoid plot (50% probability) of [(²⁵⁴PNP)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 [(^tBuPNP)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$_6$D$_6$ suspension of 2b, before NMR spectra could be recorded.

$^1$H NMR (300 MHz, C$_6$D$_6$ + a few drops of THF, ambient temperature): $\delta$ = 6.04 (s, 2H, CH-Pyr), 3.04 (s, 4H, CH$_2$), 1.09 (d, $J_{PH}$ = 10.2 Hz, 18H, CH$_3$) ppm.

$^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$ + a few drops of THF, ambient temperature): $\delta$ = 134.4 (d, $J_{CP}$ = 8.1 Hz, C$_2$/5), 105.1 (s, C$_3$/4), 31.3 (d, $J_{CP}$ = 20.5 Hz, C(CH$_3$)$_3$), 30.2 (d, $J_{CP}$ = 11.1 Hz, C(CH$_3$)$_2$), 25.1 (d, $J_{CP}$ = 15.7 Hz, CH$_2$) ppm.

$^{31}$P{$^1$H} NMR (81MHz, C$_6$D$_6$ + a few drops of THF, ambient temperature): $\delta$ = 21.6 (s) ppm.

Elemental analysis: Anal. Calcd for C$_{22}$H$_{42}$NP$_2$L: 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 [(^RPNP)NiBr]

1.4.1 Synthesis of [(^iPrPNP)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$_2$O (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$_6$D$_6$, ambient temperature): $\delta$ = 6.31 (s, 2H, CH-Pyr), 2.50 (vt, $J_{HP}$ = 4.4 Hz, 4H, CH$_2$), 2.03 – 1.90 (m, 4H, CH(CH$_3$)$_2$), 1.39 (app. q. (dvt), 6H, CH(CH$_3$)$_2$), 0.98 (app. q. (dvt), 6H, CH(CH$_3$)$_2$) ppm.

$^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$, ambient temperature): $\delta$ = 137.9 (vt, $J_{CP}$ = 7.4 Hz, C$_2$/5), 105.9 (vt, $J_{CP}$ = 5.4 Hz, C$_3$/4), 24.1 (vt, $J_{CP}$ = 11.0 Hz, CH(CH$_3$)$_2$), 22.5 (vt, $J_{CP}$ = 10.4 Hz, CH$_2$), 18.7 (vt, $J_{CP}$ = 2.0 Hz, CH(CH$_3$)$_2$), 17.7 (s, CH(CH$_3$)$_2$) ppm. $^{31}$P{$^1$H} NMR (81MHz, C$_6$D$_6$, ambient temperature): $\delta$ = 62.6 (s) ppm. Elemental analysis: Anal. Calcd for C$_{18}$H$_{34}$NP$_2$NiBr: 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\(_2\)NiBr (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 \([^{(i}\text{Pr}PNP)\text{NiCl}]\) 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.

\(^1\text{H} \text{NMR} \) (300 MHz, C\(_6\)D\(_6\), ambient temperature): \( \delta = 6.27 \) (s, 2H, CH-Pyr), 2.49 (vt, \( J_{HP} = 4.4 \) Hz, 4H, CH\(_2\)), 2.01 – 1.84 (m, 4H, CH(CH\(_3\))\(_2\)), 1.40 (app. q. (dvt), 6H, CH(CH\(_3\))\(_2\)), 2.01 (app. q. (dvt), 6H, CH(CH\(_3\))\(_2\)) ppm. \(^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (75 MHz, C\(_6\)D\(_6\), ambient temperature): \( \delta = 137.9 \) (vt, \( J_{CP} = 7.5 \) Hz, C\(_2\)/5), 105.9 (vt, \( J_{CP} = 5.3 \) Hz, C\(_3\)/4), 137.9 (vt, \( J_{CP} = 10.7 \) Hz, CH(CH\(_3\))\(_2\)), 22.0 (vt, \( J_{CP} = 10.5 \) Hz, CH\(_2\)), 18.6 (vt, \( J_{CP} = 1.9 \) Hz, CH(CH\(_3\))\(_2\)), 17.6 (s, CH(CH\(_3\))\(_2\)) ppm. \(^{31}\text{P}\{^1\text{H}\} \text{NMR} \) (121MHz, C\(_6\)D\(_6\), ambient temperature): \( \delta = 60.1 \) (s) ppm.

1.4.2 Synthesis of \([^{(t}\text{Bu}PNP)\text{NiBr}]\) (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\(_2\)O (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\(_2\)O solution at −24 °C as dark-red tetrahedrons.

\(^1\text{H} \text{NMR} \) (200 MHz, C\(_6\)D\(_6\), ambient temperature): \( \delta = 6.15 \) (s, 2H, CH-Pyr), 2.70 (vt, \( J_{HP} = 4.3 \) Hz, 4H, CH\(_2\)), 1.40 (vt, \( J_{HP} = 6.7 \) Hz, CH(CH\(_3\))\(_2\)) ppm. \(^{13}\text{C}\{^1\text{H}\} \text{NMR} \) (75 MHz, C\(_6\)D\(_6\), ambient temperature): \( \delta = 138.1 \) (br. s, C\(_2\)/5), 105.0 (vt, \( J_{CP} = 5.3 \) Hz, C\(_3\)/4), 35.4 (vt, \( J_{CP} = 6.9 \) Hz, C(CH\(_3\))\(_2\)), 29.5 (vt, \( J_{CP} = 2.3 \) Hz, C(CH\(_3\))\(_2\)), 23.7 (vt, \( J_{CP} = 9.5 \) Hz, CH\(_2\)) ppm. \(^{31}\text{P}\{^1\text{H}\} \text{NMR} \) (81MHz, C\(_6\)D\(_6\), ambient temperature): \( \delta = 67.1 \) (s) ppm. **Elemental analysis:** Anal. Calcd for C\(_{22}\)H\(_{42}\)NP\(_2\)NiBr: 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\(_2\)NiBr (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 \([\{(\text{t-Bu} \text{PNP})\text{Ni}\}^2(\mu-\text{Hg})]\) (4)

A solution of \(3\text{b}\) (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 \(\text{C}_6\text{D}_6\) solution at least for 4 days at 80 °C.

\(^1\text{H}\) NMR (600 MHz, \(\text{C}_6\text{D}_6\), ambient temperature): \(\delta\) 6.39 (s, 2H, CH-Pyr), 2.89 (vt, \(J_{HP} = 3.6\) Hz, 4H, \(\text{CH}_2\)), 1.31 (vt, \(J_{HP} = 6.3\) Hz, 18H, \(\text{C(CH}_3)_3\)) ppm. \(^\text{13}\text{C}\{\text{^1}\text{H}\}\) NMR (75 MHz, \(\text{C}_6\text{D}_6\), ambient temperature): \(\delta\) = 134.4 (vt, \(J_{CP} = 5.5\) Hz, \(\text{C}_2\text{/5}\)), 104.5 (vt, \(J_{CP} = 2.6\) Hz, \(\text{C}_3\text{/4}\)), 34.4 (vt, \(J_{CP} = 5.0\) Hz, \(\text{C(CH}_3)_3\)), 30.6 (s, \(\text{C(CH}_3)_3\)), 26.7 (vt, \(J_{CP} = 10.5\) Hz, \(\text{CH}_2\)) ppm. \(^{31}\text{P}\{\text{^1}\text{H}\}\) NMR (81MHz, \(\text{C}_6\text{D}_6\), ambient temperature): \(\delta\) = 76.6 (s, strong Hg-satellites \(J_{\text{PHg}} = 333\) Hz) ppm. **Elemental analysis:** Anal. Calcd. for \(\text{C}_{44}\text{H}_{84}\text{N}_2\text{P}_4\text{Ni}_2\text{Hg}\): C, 48.80, H, 7.82, N, 2.59 Found: C, 48.29, H, 7.41, N, 2.49.

When \(4\) was treated with \(\text{LiBr}\) in in \(\text{C}_6\text{D}_6\) at 80 °C only a very small amount of nickel bromide \(3\text{b}\) (< 1%) was formed.

![Figure S4](https://example.com/FigureS4.png)

**Figure S4.** \(^{31}\text{P}\{\text{^1}\text{H}\}\) NMR spectrum of \(4\) with \(^{199}\text{Hg}\) satellites.
1.5 Synthesis of nickel hydride [(^8PNP)NiH]

1.5.1 Synthesis of [(^8PrPNP)NiH] (5a)

To a solution of [(cod)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%).

^1H NMR (400 MHz, C_6D_6, ambient temperature): δ = 6.53 (s, 2H, CH-Pyr), 2.89 (vt, J_{HiP} = 4.3 Hz, 4H, CH_2), 1.82 – 1.70 (m, 4H, CH(CH_3)_2), 1.12 (app. q. (dvt), J_{HiH} = J_{HiP} = 7.8 Hz, 6H, CH(CH_3)_2), 0.94 (app .q. (dvt), J_{HiH} = J_{HiP} = 7.0 Hz, CH(CH_3)_2), −17.59 (t, J_{HiP} = 59 Hz, 1H, Ni-H) ppm. ^31C[^1H] NMR (100 MHz, C_6D_6, ambient temperature): δ = 135.9 (vt, J_{Cr} = 7.6 Hz, C_2/5), 104.8 (vt, J_{Cr} = 5.2 Hz, C_3/4), 25.3 (vt, J_{Cr} = 10.0 Hz, CH_2), 24.7 (vt, J_{Cr} = 11.8 Hz, CH(CH_3)_2), 19.5 (vt, J_{Cr} = 2.8 Hz, CH(CH_3)_2), 18.4 (s, CH(CH_3)_2) ppm. ^31P[^1H] 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 [(^8PNP)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 [(tBuPNP)NiH](5b)

**Method A:** A BUCHI TINYCLAVE reactor was charged with 1b (300 mg, 0.78 mmol) and [(cod)2Ni] (214.2 mg, 0.78 mmol) in 3 mL of C6H6. The reactor was then pressurized with H2 (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 31P{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 Et2O (5 mL) and NaHBEt3 (0.193 mL, 1 M 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 (Me3Si)2O and extracted with Et2O (2 mL). The extracts were filtered over Celite and dried under dynamic vacuum. The residue was suspended in hexane and a minimum quantity of Et2O 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 11B NMR spectroscopy (11B{1H} NMR (ambient temperature, C6D6): δ 1.94 (v. br.), −12.1 (NaHBEt3), −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 C6D6 (1 mL). The N2 atmosphere was replaced by H2 (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 31P{1H} NMR spectroscopy. However, it should be mentioned that in some cases when using a BUCHI TINYCLAVE reactor for this reaction (5 bar of H2, grade 5.0), we also observed the formation of small amounts of 3b (by EI-MS spectrometry and 31P{1H} NMR spectroscopy (δ 67.1 ppm)) and a minor quantities of a second species that was characterized as the nickel hydroxide complex [(tBuPNP)NiOH] on the basis of EI-MS spectrometry and 31P{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 H2O contamination. However, as shown by the reactivity studies on [{(tBuPNP)Ni}2(μ-Hg)] (4) (see chapter 1.5) these side reactions are very slow in the absence of H2 suggesting that H2 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.

1H NMR (600 MHz, C6D6, ambient temperature): δ 6.50 (s, 2H, CH-Pyr), 3.02 (vt, JHP = 3.9 Hz, 4H, CH2), 1.20 (vt, JHP = 6.6 Hz, 18H, CH3), −17.65 (t, JHP = 55.7 Hz, 1H, Ni-H) ppm. 13C{1H} NMR (150 MHz, C6D6, ambient temperature): δ = 137.1 (vt, JCp = 7.7 Hz, C2/5), 104.3 (vt, JCp = 4.9 Hz, C3/4),
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. 

$^{31}P\{^1H\}$ NMR (242 MHz, C$_6$D$_6$, ambient temperature): $\delta = 98.9$ (s) ppm. **Elemental analysis:** Anal. Calcd for C$_{22}$H$_{43}$NP$_2$Ni: 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$_2$Ni (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$_2$H$_4$ (1 atm) at ambient temperature or when heated to 80 °C. However, when 5b was exposed to CO$_2$ (5 bar, 80 °C, 2 h) an equilibrium between 5b and the corresponding formate complex [(tBuPNPNi(OCOH)] (6b) (IR (ATR): 1630 cm$^{-1}$ (s), CO) was observed. The ratio of 5b : 6b was ca. 1.8 : 1 as judged by $^{31}P\{^1H\}$ NMR spectroscopy. Nevertheless, CO$_2$ readily desorbed when this mixture was heated.

![Figure S7: $^{31}P\{^1H\}$ NMR spectra of the reaction mixture 5b and 6b.](image)

In contrast, nickel hydride 5b proved to be stable in the presence of H$_2$O in C$_6$D$_6$ at 80 °C and no reaction to [(tBuPNPNiOH)] was observed. Furthermore, by adding an excess amount of LiBr to a sample of 5b in C$_6$D$_6$ 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 \([\{^{tBu}PNP\}NiD]\) \((d_{7}-5b)\) was synthesised following method C in a BÜCHI TINYCLAVE reactor in \(C_{6}D_{6}\) solution with \(D_{2}\) gas (5 bar, grade 2.8).

\(^1\text{H} \text{NMR}\) (300 MHz, \(C_{6}D_{6}\), ambient temperature): \(\delta\) 6.50 (s, 2H, CH-Pyr), 3.02 (vt, \(J_{HP} = 4.0\) Hz, 4H, CH\(_3\)), 1.19 (vt, \(J_{HP} = 6.5\) Hz, 18H, CH\(_3\)) ppm. \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (75 MHz, \(C_{6}D_{6}\), ambient temperature): \(\delta\) = 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 C\(_2H_2\)) ppm. \(^{31}\text{P}\{^1\text{H}\} \text{NMR}\) (242 MHz, \(C_{6}D_{6}\), ambient temperature): \(\delta\) = 99.6 (t, \(J_{PD} = 8.5\) Hz ) ppm. The \textbf{E.J. mass spectrum} (70 eV) showed a molecular ion at \(m/z = 442\) amu with the following isotopic cluster distribution for: \(C_{22}H_{44}D_{2}Ni\) (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 \(^{31}\text{P}\{^1\text{H}\}\) 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 \(d_{7}-5b\).](image-url)
1.6 Synthesis of nickel formate [(iPrPNP)NiOC(O)H] (6a)

A solution of [(iPrPNP)NiH] (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$_6$D$_6$, ambient temperature): δ = 7.81 (t, $J_{HH}$ = 3.5 Hz, 1H, OCHO), 6.25 (s, 2H, CH-Pyr), 2.44 (vt, $J_{HH}$ = 4.5 Hz, 4H, CH$_2$), 1.92 – 1.74 (m, 4H, CH(CH$_3$)$_2$), 1.36 (app. q. (dvt), 6H, CH(CH$_3$)$_2$), 1.03 (app. q. (dvt), CH(CH$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$, ambient temperature): δ = 167.2 (s, OCOH), 137.9 (vt, $J_{CP}$ = 7.2 Hz, C2/5), 106.1 (vt, $J_{CP}$ = 5.1 Hz, C3/4), 24.0 (vt, $J_{CP}$ = 9.9 Hz, CH$_2$), 21.0 (vt, $J_{CP}$ = 11.3 Hz, CH(CH$_3$)$_2$), 18.3 (vt, $J_{CP}$ = 2.3 Hz, CH(CH$_3$)$_2$), 17.6 (s, CH(CH$_3$)$_2$) ppm. $^{31}$P{$^1$H} NMR (81MHz, C$_6$D$_6$, ambient temperature): δ = 57.0 (s) ppm. Elemental Analysis: Anal. Calcd for C$_{19}$H$_{35}$NO$_2$P$_2$Ni: 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 [(d^6uPNP)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 solid. 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.

^1H NMR (200 MHz, C_6D_6, ambient temperature): δ 6.40 (s, 2H, CH-Pyr), 2.91 (vt, J_HP = 4.0 Hz, 4H, CH_2), 1.23 (vt, J_HP = 6.3 Hz, 18H, C(CH_3)_3), −0.25 (t, J_HP = 7.8 Hz, 3H, Ni-CH_3) ppm. ^31P{^1H} NMR (81MHz, C_6D_6, ambient temperature): δ = 68.9 (s) ppm.

The lack of reactivity may be attributed to the severe steric demand of the tBu-groups, effectively blocking the axial positions in complex 6. In contrast, the less sterically crowded and more flexible phenyl-substituted derivative [(PhPNP)NiMe] was reported to slowly insert CO into the Ni-Me bond at 50 °C.5

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 tBu-groups, effectively blocking the axial positions in complex 6. In contrast, the less sterically crowded and more flexible phenyl-substituted derivative [(PhPNP)NiMe] was reported to slowly insert CO into the Ni-Me bond at 50 °C.5
**Figure S9.** Displacement ellipsoid plot (50% probability) of [(tBuPNP)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·C₆H₆ 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 ¼ for 3b and 7; no transformation in $P2_12_12_1$ can interconvert these values.
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Table S1. Crystallographic data
3. Computational details

All calculations were carried out with the employed Gaussian 09\(^9\) and the long-range dispersion-corrected Grimme’s functional (B97D).\(^9\) For comparison we also used the BP86 functional as incorporated in Gaussian 09.\(^9\) 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, \(\Delta G\), 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

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<th>G(298 K)(^b) [Ha]</th>
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\(^a\)DFT energy incl. ZPE. \(^b\)standard conditions: \(T= 298.15\) K and \(p = 1\) atm.

**Table S3.** Comparison between experimental and computed structures for [(ttBuPNP)Ni\(_2\)(μ-Hg)] (4)

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4. References