Supplementary Information

A Readily Accessible PNP Pincer Ligand with a Pyrrole Backbone and its $Ni^{I/II}$ Chemistry

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General All manipulations were carried out under the exclusion of moisture by using standard schlenk and glove-box techniques. Argon 5.0, purchased from Messer Group GmbH, was used after drying over Granusic© phosphorus pentoxide (granulated). Solvents were dried according to literature procedures[1] and stored in glass ampules under an argon atmosphere. Et_2O and *n*-pentane were distilled from sodium/potassium alloy, benzene and *n*-hexane from potassium, CH_2Cl_2 and $CHCl_3$ from calcium hydride, and toluene from sodium. The same procedures were used to dry the deuterated solvents. Degassed solvents were obtained by three successive freeze–pump–thaw cycles. The ligand precursor was synthesized according to literature.[2] All other chemicals were used as received without further purification. NMR spectra were recorded on Bruker Avance III (600 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual proton solvent signals or carbon resonances.[3] H_3PO_4 (^{31}P) was used as an external standard. The following abbreviations were used: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad signal). High-resolution mass spectra were acquired on JEOL JMS-700 magnetic sector (FAB, EI) spectrometers at the mass spectrometry facility of the Institute of Organic Chemistry, the University of Heidelberg. Elemental analysis was carried out in the Microanalysis Laboratory of the Heidelberg Chemistry Department. GC-MS measurements were performed on a Trace GC Ultra instrument equipped with a BPX5 column.

X-ray Cristallographic Study Data collection: Bruker AXS Smart 1000 CCD (complex **3**) and Agilent Technologies Supernova-E CCD (complex **4**) diffractometers, Mo-K_α radiation, graphite monochromator (Bruker AXS instrument) or multilayer mirror optics (Agilent instrument), λ = 0.71073 Å. Lorentz, polarization and semi-empirical absorption correction[4-8]. Structure solution: direct methods with dual-space recycling[9] (complex **3**) or charge flip[10] (complex **4**). Refinement: full-matrix least squares methods based on F^2; all non-hydrogen atoms anisotropic, hydrogen atoms at calculated positions (refined riding).[11]

HPNP-Ph_2 (1): To 12.0 g (0.11 mol, 5.0 eq) KOtBu a solution of 8.2 g (47.3 mmol, 2.2 eq) $HPPh_2$ in 100 mL DMSO was added dropwise at room temperature. The resulting deep-red solution was stirred for 30 min and was then treated dropwise with a solution of 10.0 g (21.5 mmol, 1.0 eq) 2,5-bis[(trimethylammonio)methyl]pyrrole diiodide in 100 mL DMSO. The reaction mixture was stirred overnight, hydrolyzed by addition of degassed water and extracted with diethylether. The solvent was removed under reduced pressure to give a brown residue. The crude product was purified by column chromatography on silica gel (DCM/pentane (1:2) and NEt_3) to give a yellow oil. Yield: 3.5 g (7.6 mmol, 35%). ^1H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 3.26 (s, 4H, CH_2), 5.64 (d, J_{HH} = 2.7 Hz, 2H, Py-*H*), 7.28-7.34 (m, 20H, Ph-*H*), 7.56 (br, 1H, N*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 28.0 (d,

CH_2), 107.4 (d, Py-*C*H), 126.1 (d, Py-*C*), 128.4-128.5 (m, *m*Ph-*C*H), 128.7 (s, *p*Ph-*C*H), 132.7 (d, *o*Ph-*C*H), 138.2 (d, Ph-*C*). $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, rt) δ (ppm) −16.5 (s). HRMS (EI) *m/z* (%) calcd: 463.1619 found: 463.1635 (12.6) (M^+). Anal. Calcd for $C_{30}H_{27}NP_2$: C 77.74; H 5.87; N 3.02. Found: C 77.70 H 5.73 N 2.56.

[(PNP-Ph$_2$)NiCl] (2): To a solution of 250 mg (0.54 mmol, 1.0 eq) **1** in 20 mL THF was added 0.24 mL (1.1 eq) *n*-butyllithium (2.5 M in hexane) at −78 °C. The reaction mixture was stirred for 30 min and 154 mg (0.70 mmol, 1.3 eq) $NiCl_2$DME was added at −78 °C. The resulting suspension was warmed to room temperature and was stirred for 2 h. The mixture was filtered through a pad of Celite and the solvents of the filtrate were removed *in vacuo*. The resulting solid was washed with pentane to give a deep-red solid. Yield: 150 mg (0.27 mmol, 77%). ^1H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 3.59 (t, J_{PH} = 4.9 Hz, 4H, CH_2), 5.99 (s, 2H, Py-*H*), 7.41 (t, J_{HH} = 7.5 Hz, 8H, *m*Ph-C*H*), 7.47 (t, J_{HH} = 7.3 Hz, 4H, *p*Ph-C*H*), 7.86-7.90 (m, 8H, *o*Ph-C*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 31.7 (vt, *C*H_2), 105.8 (vt, Py-*C*H), 128.8 (vt, *m*Ph-*C*H), 130.4 (vt, Ph-*C*), 130.7 (s, *p*Ph-*C*H), 132.8 (vt, *o*Ph-*C*H), 138.2 (vt, Py-*C*). $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, rt) δ (ppm) 30.6 (s). HRMS (FAB) *m/z* (%) calcd: 555.0582 found: 555.0585 (22.1) (M^+). Anal. Calcd for $C_{30}H_{26}ClNNiP_2$: C 64.73; H 4.71; N 2.52. Found: C 64.82 H 4.93 N 2.22.

[(PNP-Ph$_2$)NiI] (3): To a solution of 50.0 mg (89.8 µmol, 1.0 eq) **2** in 10 mL acetone was added a solution of 37 mg (0.22 mmol, 2.5 eq) in 5 mL acetone. After stirring for 1 h the solvents were removed under reduced pressure and the crude product was dissolved in dichloromethane. The solution was filtered through a pad of Celite and the solvents were removed under reduced pressure to give a red solid. Yield: 57 mg (88.0 µmol, 98%). ^1H NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 3.67 (t, J_{PH} = 4.9 Hz, 4H, CH_2), 6.04 (s, 2H, Py-*H*), 7.39 (t, J_{HH} = 7.3 Hz, 8H, *m*Ph-C*H*), 7.45 (t, J_{HH} = 7.3 Hz, 4H, *p*Ph-C*H*), 7.80-7.84 (m, 8H, *o*Ph-C*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 34.1 (vt, *C*H_2), 105.3 (vt, Py-*C*H), 128.5 (vt, *m*Ph-*C*H), 130.7 (s, *p*Ph-*C*H), 130.9 (vt, Ph-*C*), 133.4 (vt, *o*Ph-*C*H), 137.2 (vt, Py-*C*). $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, rt) δ (ppm) 42.5 (s). HRMS (FAB) *m/z* (%) calcd: 646.9939 found: 646.9875 (25.9) (M^+). Anal. Calcd for $C_{30}H_{26}INNiP_2$: C 55.60; H 4.04; N 2.16. Found: C 55.85 H 4.26 N 1.79.

[(PNP-Ph$_2$)$_2$Ni$_2$] (4): 72.0 mg (0.155 mmol, 1.0 eq) **1** and 43.0 mg (0.155 mmol, 1.0 eq) were dissolved in 6 mL toluene. After stirring for 3 h the solvents were removed under reduced pressure. The residue was washed with pentane and toluene. The residue was dried *in vacuo* to give a green solid. Yield: 31.7 mg (30.4 µmol, 39%). $^1H\{^{31}P\}$ NMR (600.1 MHz, $CDCl_3$, rt): δ (ppm) 3.01 (d, J_{HH} = 16.2 Hz, 2H, CH_2), 3.22 (d, J_{HH} = 14.3 Hz, 2H, CH_2), 3.69 (d, J_{HH} = 14.3 Hz, 2H, CH_2), 3.94 (d, J_{HH}=16.2 Hz, 2H, CH_2), 6.53 (s, 4H, Py-C*H*), 6.72-7.01 (m, 32H, Ph-C*H*), 7.48-7.49 (m, 4H, Ph-C*H*), 7.94-7.96 (m, 4H, Ph-C*H*). ^{13}C NMR (150.9 MHz, $CDCl_3$, rt): δ (ppm) 31.1-31.7 (m, *C*H_2), 105.5 (s, Py-*C*H), 108.8 (vt, Py-*C*H), 127.4 (vt, Ph-*C*H), 128.0 (vt, Ph-*C*H), 128.1 (s, Ph-*C*H) 128.2 (vt, Ph-*C*H), 128.3 (vt, Ph-*C*H), 128.9 (s, Ph-*C*H), 129.2 (s, Ph-*C*H), 129.3 (s, Ph-*C*H), 131.7 (vt, Ph-*C*H), 132.0 (vt, Ph-*C*H), 132.7 (vt, Ph-*C*H), 133.4 (vt, Ph-*C*H), 133.6 (vt, Ph-*C*), 134.3 (vt, Py-*C*), 135.4 (s, Py-*C*), 136.1 (vt, Ph-*C*), 138.8-139.0 (m, Ph-*C*), 143.1-143.6 (m, Ph-*C*). $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, rt) δ (ppm) 14.4 (d, *J*=21.9 Hz), 25.2 (d,

J=21.9 Hz). HRMS (FAB) *m/z* (%) calcd: 1040.1788 found: 1040.1780 (41.8) (M^+). Anal. Calcd for $C_{60}H_{52}N_2Ni_2P_4$: C 69.14; H 5.03; N 2.69. Found: C 69.10; H 5.45; N 2.32.

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