

*Supporting Information*

**A low-coordinate nickel(II) hydride complex and its reactivity**

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## Experimental Section

**General Considerations:** All experiments were carried out in a dry argon atmosphere using an MBraun glovebox and/or standard Schlenk techniques. Solvents were purified employing a MBraun Solvent Purification System SPS. Deuterated solvents were purified using the appropriate techniques. All organic reagents were purified by conventional methods.  $^1\text{H}$  NMR spectra were recorded on a *Bruker* AV 400 NMR spectrometer (400.13 MHz). Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to  $\text{SiMe}_4$ . Mass spectrometry data were collected with a Varian MAT311A/AMD Spectrometer at 70eV. EPR spectra were recorded at the X-band spectrometer ERS 300 (ZWG/Magnettech Berlin/Adlershof, Germany) equipped with a fused quartz Dewar for measurements at liquid nitrogen temperature. The g-factors were calculated with respect to a  $\text{Cr}^{3+}/\text{MgO}$  reference ( $g = 1.9796$ ). Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR-8400S spectrometer. Microanalyses were performed on a *Leco* CHNS-932 elemental analyser. Magnetic measurements were performed with an *Alfa* magnetic susceptibility balance at r.t. Solution magnetic susceptibilities were determined by the Evans method.<sup>1</sup> Both  $\text{LNi}(\mu\text{-Br})_2\text{Li}(\text{thf})_2$  ( $\text{L} = (\text{HC}(\text{CMeNC}_6\text{H}_3(i\text{-Pr})_2)_2)$ ) and  $(\text{LNi})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_5\text{Me})$  were synthesized according to slightly modified literature procedures.<sup>2</sup>

### Synthesis:

**$[\text{LNi}(\mu\text{-H})]_2$ , 1.** A colourless solution of  $\text{KBEt}_3\text{H}$  (0.29 g, 2.09 mmol, 1.1 eq.) in diethylether (5 mL) was added dropwise to a stirred dark purple solution of  $\text{LNi}(\mu\text{-Br})_2\text{Li}(\text{thf})_2$  (1.50 g, 1.90 mmol) in diethylether (20 mL). After stirring the resulting green-brown solution for 10 minutes all volatiles were removed in vacuo. The green-brown residue was extracted twice with hexane (10 mL). After concentration in vacuo, the deep green solution was kept at  $-30\text{ }^\circ\text{C}$  for 2 days, affording dark green crystals of **1** (0.32 g, 36 %) which were isolated by filtration (Found: C, 73.01; H, 8.75; N, 5.77. Calc. for  $\text{C}_{58}\text{H}_{84}\text{N}_4\text{Ni}_2$ : C, 72.97; H, 8.87; N,

5.87%);  $\mu_{\text{eff}} = 3.05$  B.M.;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3057w, 2961vs, 2925vs, 2867vs, 1924w, 1861w, 1798w, 1582w, 1522vs, 1463vs, 1437vs, 1383vs, 1474vs, 1342w, 1314vs, 1284w, 1256s, 1191w, 1174s, 1101s, 1056w, 1036w, 1019s, 933s, 855w, 796vs, 763s, 752s, 719w, 707w, 641w, 629w, 527w, 454w.

**LNi(4-dimethylaminopyridine), 2.** Method A: A clear solution of 4-dimethylaminopyridine (26 mg, 0.21 mmol, 2 eq.) in diethylether (5 mL) was added dropwise to a stirred dark green solution of **1** (100 mg, 0.10 mmol) in diethylether (10 mL). After 1 hour the colour of the mixture had changed to orange-red, and all volatiles were removed in vacuo. The resulting orange residue was dissolved in 5 mL of hexane. Cooling the solution to  $-30$  °C for 3 days afforded orange-red crystals of **2** (63 mg, 50 %) which were isolated by filtration.

Method B: A clear solution of 4-dimethylaminopyridine (47 mg, 0.38 mmol, 2 eq.) in diethylether (5 mL) was added to a stirred dark red solution of  $(\text{LNi})_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_6\text{H}_5\text{Me})$  (200 mg, 0.19 mmol) in diethylether (5 mL). The reaction mixture immediately changed colour to orange-red and all volatiles were removed in vacuo. The resulting orange residue was dissolved in 5 mL of hexane. Cooling the solution to  $-30$  °C for 3 days afforded orange-red crystals of **2** (65 %) which were isolated by filtration (Found: C, 72.24; H, 8.59; N, 9.36. Calc. for  $\text{C}_{36}\text{H}_{51}\text{N}_4\text{Ni}$ : C, 72.17; H, 8.48; N, 9.28%);  $\mu_{\text{eff}} = 2.03$  B.M. ( $\text{C}_6\text{D}_6$ , 25 °C); EPR (toluene, 77K)  $g = 2.078, 2.141, 2.340$ ;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3054w, 2958vs, 2923s, 2864s, 1906w, 1855w, 1781w, 1622vs, 1531vs, 1461vs, 1434vs, 1412vs, 1387vs, 1358w, 1320vs, 1265w, 1253w, 1225s, 1177s, 1101s, 1057w, 1019s, 950w, 934w, 815w, 801s, 793s, 760s, 737s, 718w, 526w;  $\delta_{\text{H}}(400.13 \text{ MHz}, \text{C}_6\text{H}_6)$  ;  $m/z$  (EI) 597.3464 ( $\text{M}^+$ ,  $\text{C}_{36}\text{H}_{51}\text{N}_4\text{Ni}$  requires 597.3467).

**LNiNCEt, 3. 3** was prepared in close analogy to the procedure applied for the synthesis of **2**. Yellow crystals (73 %). (Found: C, 71.38; H, 8.78; N, 7.66. Calc. for  $\text{C}_{32}\text{H}_{46}\text{N}_3\text{Ni}$ : C, 72.32; H, 8.72; N, 7.91%);  $\mu_{\text{eff}} = 1.94$  B.M. ( $\text{C}_6\text{D}_6$ , 25 °C); EPR (toluene, 77 K)  $g = 2.039, 2.143,$

2.344;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3056w, 2959vs, 2933s, 2865s, 2239vs, 1911w, 1854w, 1793w, 1536s, 1518s, 1460vs, 1436vs, 1409vs, 1380s, 1366s, 1358s, 1320vs, 1257s, 1228s, 1177s, 1099s, 1071s, 1057s, 1023w, 934w, 857w, 792vs, 762s, 756vs, 744s, 717w, 630w, 444w;  $\delta_{\text{H}}(400.13 \text{ MHz}, \text{C}_6\text{H}_6)$  ;  $m/z$  (EI) 530.3044 ( $\text{M}^+$ ,  $\text{C}_{32}\text{H}_{46}\text{N}_3\text{Ni}$  requires 530.3045)

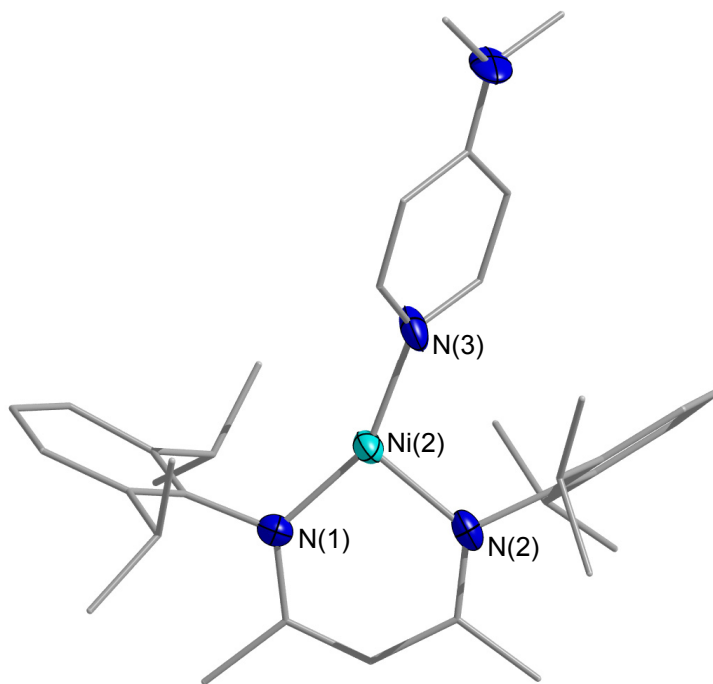
### Procedure for Hydrogen Detection

Any hydrogen produced was detected chemically: The complex  $[\text{IrCl}(\text{PPh}_3)_3]$ , **II**, is known to react irreversibly with molecular hydrogen via oxidative addition and to form the simple dihydride adduct  $[\text{Ir}(\text{H})_2\text{Cl}(\text{PPh}_3)_3]$ , **III**, which can be clearly identified via characteristic signals for the metal-bound hydrogen-atoms in the  $^1\text{H}$  NMR spectrum.<sup>3</sup> Example for a procedure: A solution of propionitrile (1.2 mg, 0.02 mmol) in benzene (1 ml) was added to a solution of **1** (21 mg, 0.02 mmol) in benzene (2 ml) in a test tube sealed with a septum. The evolving gas was passed into an orange solution of **II** (10 mg, 0.01 mmol) in 0.6 ml  $\text{C}_6\text{D}_6$  via cannula. The formation of **III** can be verified by its hydride signals in the  $^1\text{H}$  NMR spectrum at -10.66 ppm and -20.48 ppm.

### Crystallographic data

**Crystal structure determinations:** Suitable crystals of **1**, **2** and **3** were obtained via slow evaporation of the solvent from saturated diethylether solutions at  $-30$  °C. The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer. The data of **1**, **2** and **3** were collected on a Stoe IPDS 2T diffractometer using  $\text{MoK}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ . In all cases, the structures were solved by direct methods (SHELXS-97)<sup>4</sup> and refined versus F2 (SHELXL-97)<sup>5</sup> with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model.

**Crystal data for LNi(4-dimethylaminopyridine), 2:**  $C_{36}H_{51}N_4Ni$ ,  $M = 598.52$ , monoclinic,  $a = 8.6270(5)$ ,  $b = 22.8973(13)$ ,  $c = 16.9475(10)$  Å,  $\beta = 91.210(5)^\circ$ ;  $V = 3347.0(3)$  Å<sup>3</sup>,  $T = 100(2)$  K, space group  $P 2_1$ ,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.609$  mm<sup>-1</sup>, 26845 reflections measured, 11309 unique ( $R_{\text{int}} = 0.1074$ ),  $R_1 = 0.0921$ ,  $wR_2 = 0.2655$  (all data).



**Fig. 1** Crystal structure of LNi(4DMAP) **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)-N(1) 1.878(9), Ni(1)-N(2) 1.925(8), Ni(1)-N(3) 1.954(9); N(1)-Ni(1)-N(2) 96.0(4), N(1)-Ni(1)-N(3) 153.4(4), N(2)-Ni(1)-N(3) 110.6(3).

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