Supporting Information

Functional nickel complexes of N-heterocyclic carbene ligands in pre-organized and supported thin film materials


The synthesis of complexes [NiCl₂(C₁₂MIM)₂] (1) and [NiCl₂(C₁₂C₁₂IM)₂] (2)

General Methods. All air- and moisture-sensitive experiments were carried out under nitrogen using standard Schlenk techniques or in an MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. 1-dodecyl-3-methylimidazolium chloride, ammonium hexafluorophosphate and bis(triphenylphosphine)nickel(II) dichloride were purchased from Merck, Acros and Aldrich, and used as received. 1,3-Didodecylimidazolium chloride was prepared according to the literatures.¹ ¹H NMR spectra were recorded on JEOL 400 MHz and 270 MHz instruments operating at respective frequencies of 399.782 MHz and 269.714 MHz.
with a probe temperature of 23 °C. $^{13}$C NMR spectra were recorded on JEOL 400 MHz and 270 MHz instruments operating at respective frequencies of 100.525 MHz and 67.82 MHz with a probe temperature of 23 °C. Chemical shifts were reported relative to the peak for SiMe$_4$ using 1H (residual) chemical shifts of the solvent as a secondary standard and are reported in ppm. Elemental analysis results were obtained from the Analytical Laboratories at the Friedrich-Alexander-University Erlangen-Nürnberg (Erlangen, Germany).

**Preparation of [C$_{12}$MIM][PF$_6$], [C$_{12}$C$_{12}$IM][PF$_6$].** In a typical reaction, a solution of NH$_4$PF$_6$ (1.1 g, 6.64 mmol) in acetonitrile (5 mL) was added to a solution of 1-dodecyl-3-methylimidazolium chloride (0.635 g, 2.21 mmol) in acetonitrile (5 mL). The mixture was stirred for 2 h, followed by removal of the solvent. CH$_2$Cl$_2$ (10 mL) was then added to the mixture, and the resulting precipitate was removed by filtration. The solution was evaporated to dryness to give 1-dodecyl-3-methylimidazolium hexafluorophosphate. Yield: 0.841 g, (96 %).

[C$_{12}$MIM][PF$_6$] $^1$H NMR (400 MHz, CDCl$_3$): δ 8.47 (s, 1H, imidazole C(2)H), 7.28 (s, 1H, imidazole C=CH), 7.24 (s, 1H, imidazole CH=CH), 4.11 (t, $J = 7.5$ Hz, 2H, NCH$_2$), 3.89 (s, 3H, NC$_3$H$_3$), 1.84 (quintet, $J = 6.8$ Hz, 4H, NCH$_2$CH$_2$), 1.19 (m, 36H, (CH$_2$)$_n$), 0.86 (t, $J = 6.8$ Hz, 3H, CH$_3$). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$): δ 136.03, 123.70, 122.06, 50.26, 36.30, 31.97, 29.98, 29.67, 29.58, 29.42, 29.40, 28.99, 26.27, 22.74, 14.16. Anal. Calcd for C$_{16}$H$_{31}$N$_2$PF$_6$: C, 48.48; H, 7.88; N, 7.07. Found: C, 48.88; H, 8.03; N, 6.82.

[C$_{12}$C$_{12}$IM][PF$_6$] $^1$H NMR (270 MHz, DMSO-$d_6$): δ 9.15 (s, 1H, imidazole C(2)H), 7.75 (d, $J = 1.2$ Hz, 2H, imidazole CH=CH), 4.11 (t, $J = 7.0$ Hz, 4H, NCH$_2$), 1.74 (quintet, $J = 6.8$ Hz, 4H, NCH$_2$CH$_2$), 1.19 (m, 36H, (CH$_2$)$_n$), 0.81 (t, $J = 6.5$ Hz, 3H, CH$_3$). $^{13}$C $^1$H NMR (67.5 MHz, DMSO-$d_6$): δ 136.46, 123.00, 49.38, 31.84, 29.74, 29.58, 29.56, 29.46, 29.40, 29.26, 28.85, 25.96, 22.63, 14.46, 14.44. Anal. Calcd for C$_{27}$H$_{53}$N$_2$PF$_6$: C, 58.89; H, 9.70; N, 5.09. Found: C, 59.18; H, 10.08; N, 5.08.

**Preparation of [NiCl$_2$(C$_{12}$MIM)$_2$] (1) and [NiCl$_2$(C$_{12}$C$_{12}$IM)$_2$] (2).** In a typical reaction, a solution of potassium tert-butoxide (108.4 mg, 1.2 mmol) in THF was added to a suspension of [C$_{12}$MIM][PF$_6$] (396.4 mg, 1 mmol) in 5 mL THF and stirred for 2 h. THF was removed in vacuum to yield a yellow-orange solid. The resulting material was dissolved in 15 mL of hexane and filtered through a small amount of celite. The filtrate was concentrated and dried in vacuum
to yield a light yellow powder and then redissolved in 3 mL THF, and slowly added to a solution of \([\text{NiCl}_2(\text{PPh}_3)_2]\) (235.6 mg, 0.36 mmol) in 5 mL THF. After 1h of stirring at room temperature, THF was removed in vacuum to yield a brown solid, which was washed with hexane to remove PPh\(_3\) and excess carbene. The resulting material was dried in vacuo to yield a yellow brown product. Yield: 183.8 mg (81\%).

\[\text{NiCl}_2(\text{C}_{12}\text{MIM})_2\] (1) \(^1\)H NMR (270 MHz, C\(_6\)D\(_6\)): \(\delta\) 6.00 (s, 2 H, \(\text{CH} = \text{CH}\)), 5.85 (s, 2 H, \(\text{CH} = \text{CH}\)), 4.83 (t, \(J = 7.0\) Hz, 4 H, NCH\(_2\)H\(_2\)), 4.20 (s, 6 H, CH\(_3\)), 2.33 (m, 4 H, NCH\(_2\)CH\(_2\)), 1.44-1.17 (m, 36 H, (CH\(_2\))\(_n\)), 0.83 (t, \(J = 8.0\) Hz, CH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (100 MHz, C\(_6\)D\(_6\)): \(\delta\) 170.10, 120.93, 119.84, 50.60, 36.93, 32.07, 31.65, 31.44, 29.89, 29.77, 29.67, 29.56, 27.32, 22.84, 22.74, 14.09, 14.04. Anal. Calcd for C\(_{32}\)H\(_{60}\)N\(_4\)NiCl\(_2\): C, 60.96; H, 9.59; N, 8.89. Found: C, 61.53; H, 9.53; N, 8.63.

\[\text{NiCl}_2(\text{C}_{12}\text{C}_{12}\text{IM})_2\] (2) \(^1\)H NMR (270 MHz, C\(_6\)D\(_6\)): \(\delta\) 6.10 (s, 4 H, \(\text{CH} = \text{CH}\)), 4.96 (t, \(J = 7.4\) Hz, 8 H, NCH\(_2\)), 2.32 (quintet, \(J = 7.2\) Hz, 8 H, NCH\(_2\)CH\(_2\)), 1.52-1.28 (m, 72 H, (CH\(_2\))\(_n\)), 0.87 (t, \(J = 6.5\) Hz, CH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (67.5 MHz, C\(_6\)D\(_6\)): \(\delta\) 169.98, 119.69, 50.69, 32.08, 31.40, 29.97, 29.94, 29.91, 29.81, 29.59, 27.42, 22.85, 14.09. Anal. Calcd for C\(_{54}\)H\(_{104}\)N\(_4\)NiCl\(_2\): C, 69.07; H, 11.16; N, 5.97. Found: C, 69.11; H, 10.95; N, 5.99.

References


$^1$H NMR (400 MHz) for [C$_{12}$MIM][PF$_6$] in CDCl$_3$

$^{13}$C NMR (100 MHz) for [C$_{12}$MIM][PF$_6$] in CDCl$_3$
$^{1}H$ NMR (270 MHz) for $[C_{12}C_{12}IM][PF_{6}]$ in DMSO-d$_{6}$

$^{13}C$ NMR (67.5 MHz) $[C_{12}C_{12}IM][PF_{6}]$ in DMSO-d$_{6}$
$^1$H NMR (270 MHz) for $[\text{NiCl}_2(\text{C}_{12}\text{MIM})_2]$ (1) in C$_6$D$_6$

$^{13}$C NMR (100 MHz) for $[\text{NiCl}_2(\text{C}_{12}\text{MIM})_2]$ (1) in C$_6$D$_6$
$^{1}H$ NMR (270 MHz) for [NiCl$_2$(C$_{12}$C$_{12}$IM)$_2$] (2) in C$_6$D$_6$.

$^{13}$C NMR (67.5 MHz) for [NiCl$_2$(C$_{12}$C$_{12}$IM)$_2$] (2) in C$_6$D$_6$. 
Procedure and preparation of the Diffuse Reflectance Infrared Spectroscopy (DRIFTS). The ILC-SILP materials were grinded with dehydrated potassium bromide KBr (5wt.% of ILC-SILP) in a mortar for one minute and the then placed into the reactor. During the experiments the reactor was maintained under a flow of 4 mL min\(^{-1}\) of nitrogen, at a pressure of 10 mbar. The experimental procedure is schematically depicted in the top panel of Figure S2. The ILC-SILP material is first dried in-situ for 20 min at 349 K. The first measurement cycle then starts with another 20 min at 301 K, the powder was then heated to 349 K at a rate of 0.52 K min\(^{-1}\), maintained at 349 K for 10 min, and cooled again to 301 K at 0.52 K min\(^{-1}\). Diffuse reflectance spectra were acquired during the ramps in time-resolved mode at a rate of one spectrum K\(^{-1}\), with a resolution of 2 cm\(^{-1}\). This measurement cycle was performed three times. All DRIFTS experiments were performed in a High Temperature Reaction Chamber (Harrick HVC-DRP-4) with a volume capacity of 4 ml. The reactor was mounted in a Praying Mantis™ (Harrick), installed in a Fourier transform infrared spectrometer (FTIR) (Bruker Vertex 80v). The FTIR has been modified in house to be able to evacuate the optical path during DRIFTS measurements. Synchronization of the heating cycles and infrared measurements is fully automated. The temperature is calibrated first on pure Silica100 mixed with KBr using a type K thermocouple. The thermocouple is not present during the experiments. The DRIFTS measurements were then performed with fully loaded silica100 on ILC-SILP materials 1 and 2.
Figure S1. DRIFT spectroscopy. The top frame shows the experimental procedure. After a 20 min drying period at 349 K, three measurement cycles are started, consisting in heating from 301 to 349 K at 0.52 K/min, waiting 10 min at 349 K and then cooling again to room temperature. The DRIFTS measurements are performed during the ramps only at the rate of one spectrum per K. The spectra are treated similarly to the IRAS spectra. The maximum of absorption in the CH\textsubscript{2} stretching region is shown as a function of the temperature for [NiCl\textsubscript{2}(C\textsubscript{12}MIM)\textsubscript{2}] \textbf{1} (middle pane) and [NiCl\textsubscript{2}(C\textsubscript{12}C\textsubscript{12}IM)\textsubscript{2}] \textbf{2} (bottom pane).
Preparation of ILC-SILP material with pore filling $\alpha=1$. The LC-SILP materials were prepared by dissolution of the ionic liquid [C$_{12}$C$_{12}$IM][BF$_4$] in water free tetrahydrofuran (<75 ppm H$_2$O) by stirring the mixture for 30 min under inert gas atmosphere. The desired amount of support material was added to this solution and the resulting suspension was stirred for another 30 min at room temperature. After slow evaporation of the solvent at 333 K, the SILP material was dried at 333 K under 4·10$^{-4}$ mbar vacuum over night.

Preparation of 10 wt.% Ni-NHC complexes in ionic liquid [C$_{12}$C$_{12}$IM][BF$_4$]. The ILC-SILP materials were prepared by dissolving the ionic liquid [C$_{12}$C$_{12}$IM][BF$_4$] and the Ni-carbene-complexes in dry benzene (<10 ppm H$_2$O) and stirring the mixture for 30 min under inert gas atmosphere. For screening the influence of these additives on liquid crystallinity, the solvent was removed at 333 K under vacuum and the samples were dried over night at 333 K under 4·10$^{-4}$ mbar vacuum.
Figure S2. a) DSC curves, second heating cycle, and b) POM images (tenfold magnification of microscope) at 338 K produced with a heating rate of 5 K min\(^{-1}\) of \(\text{[C}_{12}\text{C}_{12}\text{IM}]\text{[BF}_{4}]\) immobilized on porous silica-100 with a pore filling \(\alpha=1\).
Figure S3. DSC curves, second heating cycle, produced with a heating rate of 5 K min\(^{-1}\) and 10 wt.% of a) \([\text{NiCl}_2(\text{C}_{12}\text{MIM})_2]\) 1 and b) \([\text{NiCl}_2(\text{C}_{12}\text{C}_{12}\text{IM})_2]\) 2, in \([\text{C}_{12}\text{C}_{12}\text{IM}][\text{BF}_4]\).
**Figure S4.** POM images (tenfold magnification of microscope) produced with a heating rate of 5 K min$^{-1}$ and 10 wt.% of a) [NiCl$_2$(C$_{12}$MIM)$_2$] $\mathbf{1}$ at 333 K and b) [NiCl$_2$(C$_{12}$C$_{12}$IM)$_2$] $\mathbf{2}$ at 333 K, in [C$_{12}$C$_{12}$IM][BF$_4$].
Figure S5. POM images (tenfold magnification of microscope) produced with a heating rate of 5 K min$^{-1}$ and 10 wt.% of a) $[\text{NiCl}_2(\text{C}_{12}\text{MIM})_2]$ 1 at 333 K and b) $[\text{NiCl}_2(\text{C}_{12}\text{C}_{12}\text{IM})_2]$ 2 at 333 K, in $[\text{C}_{12}\text{C}_{12}\text{IM}][\text{BF}_4]$ immobilized on porous silica-100 with a pore filling $\alpha = 1.0$. 