

# Ethylene polymerization in supercritical carbon dioxide with binuclear nickel(II) catalysts

Damien Guironnet, Tobias Friedberger and Stefan Mecking\*

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A series of new, highly fluorinated neutral ( $\kappa^2$ -*N,O*) chelated Ni(II) binuclear complexes based on salicylaldimines bridged in *p*-position of the *N*-aryl group were prepared. The complexes are single-component catalyst precursors for ethylene polymerization in supercritical carbon dioxide and toluene. Solubility of the catalyst precursors in supercritical carbon dioxide is effected by a large number of up to 18 trifluoromethyl groups per molecule. Semicrystalline polyethylene with a low degree of branching is formed (*ca.* 10 branches/1000 carbon atoms). Polymer microstructures are independent of the nature of the bridging moiety, while stability of the catalysts appears to differ.

## Introduction

Polymerization of olefins catalyzed by complexes of  $d^8$  metals (late transition metals) has been investigated intensively recently.<sup>1</sup> In comparison to their early transition metal counterparts, they are much more tolerant towards functional groups in the substrates<sup>2a,b</sup> or reaction media.<sup>2c</sup> Thus, ethylene and 1-olefins can be copolymerized with electron-deficient polar vinyl monomers, such as *e.g.* acrylates<sup>3</sup> or even acrylonitrile,<sup>4</sup> and multiple insertion of acrylates affords low molecular weight polyacrylate *via* an insertion mechanism.<sup>5,6</sup> Polymerization of ethylene and 1-olefins can be carried out in oxygenated reaction media such as water<sup>7</sup> or dense carbon dioxide.<sup>8</sup>

Dense carbon dioxide, that is liquid or supercritical CO<sub>2</sub> (scCO<sub>2</sub>), possesses unique properties, such as the possibility of variation of its density and solvent properties over a wide range.<sup>9</sup> In polymerization processes and polymer processing, dense carbon dioxide can be useful as a solvent or suspension medium.<sup>9b,10</sup> It can be removed conveniently by variation of the pressure, resulting in a dry polymer powder. While free-radical polymerization in dense CO<sub>2</sub> has been studied most intensely,<sup>11</sup> various examples of coordination polymerization have been reported.<sup>12–14</sup> Ethylene polymerization has been studied in scCO<sub>2</sub> with cationic palladium diimine complexes<sup>8a–c</sup> as well as with neutral ( $\kappa^2$ -*N,O*) nickel complexes.<sup>8d,e</sup>

Current developments of late transition metal catalyzed olefin polymerization have resulted in a renewed<sup>15</sup> interest in neutral Ni(II) complexes.<sup>16</sup> This class of catalysts appears to be particularly suited for polar (protic) reaction media.<sup>7,17</sup> Substantial effort is devoted to the finding of catalysts with increased polymerization productivity. One approach studied are binuclear complexes, which often polymerize with higher activities than their mononuclear analogues.<sup>18</sup> The origin of this increased reactivity is ill-understood, cooperative effects have been suggested to operate in certain cases.<sup>18b</sup> Another aim of catalyst development is an appropriate solubility in the specific reaction media. In aqueous

emulsion systems this can be crucial for the control of nanoparticle size and structure.<sup>7d,e</sup> Concerning reactions in CO<sub>2</sub>, tailoring of the catalyst precursors to provide solubility in the reaction medium is required.

We now report binuclear salicylaldiminato Ni(II) methyl complexes soluble in dense CO<sub>2</sub> and their polymerization properties.

## Results and discussion

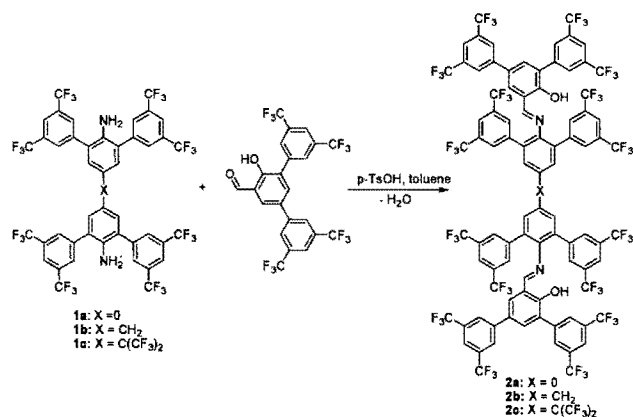
### Synthesis of ligands and complexes

Most commonly, solubility of organic compounds and of catalysts, in particular, in dense CO<sub>2</sub> is brought about by longer perfluoroalkyl groups, as exemplified by the commercially available tris[3-(perfluorooctyl)phenyl]phosphine. Introduction of such perfluoroalkyl moieties is associated with considerable synthetic effort and specific work up procedures. A convenient alternative can be the introduction of a sufficiently large number of trifluoromethyl groups. It is worth noting that such electron withdrawing groups will also modify the electrophilicity of the metal center and consequently catalytic properties (*vide infra*). The binuclear complexes reported here are based on 3 differently bridged salicylaldimine ligands, **3a** (benzidine bridge), **3b** (methylene bridge) and **3c** (hexafluoroisopropylidene bridge).

Dianilines **1a** (benzidine scaffold) and **1b** (methylene bridge) were prepared according to known procedures.<sup>18f</sup> **1c** (hexafluoroisopropylidene bridge) was obtained analogously by selective ortho-bromination of 4,4'-diamino diphenyl 1,1,1,3,3,3-hexafluoropropane, and subsequent Suzuki coupling with 3,5-bis(trifluoromethyl)phenyl boronic acid in good yield (overall yield: 63%). Condensation of the dianilines **1a–c** with 3,5-bis[3,5-bis(trifluoromethyl)phenyl] salicylaldehyde in toluene under Dean–Starck conditions afforded the novel salicylaldimines **2a–c** (Scheme 1). The crude products obtained upon solvent evaporation were washed with methanol. The identity and purity of the dianilines and di(salicylaldimines) were established by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, mass spectrometry and elemental analysis (see Experimental).

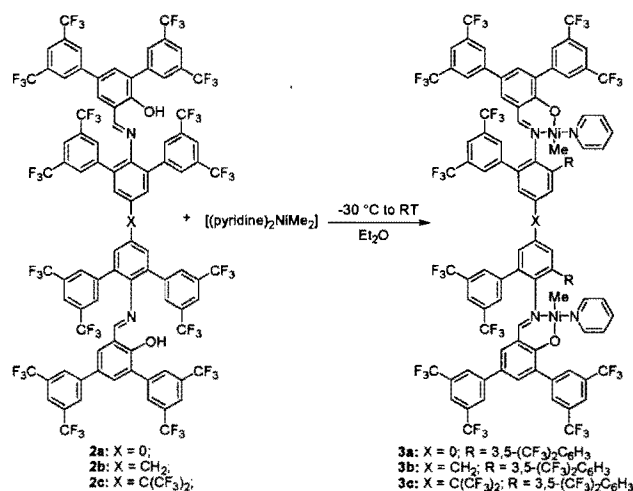
Reaction of the respective di(salicylaldimines) with 3 equivalents of [(pyridine)<sub>2</sub>Ni(CH<sub>3</sub>)<sub>2</sub>] in cold diethylether suspension

Chair of Chemical Materials Science, Dept. of Chemistry, University of Konstanz, 78464, Konstanz, Germany. E-mail: stefan.mecking@uni-konstanz.de; Fax: +49 7531 885152; Tel: +49 7531 885151



**Scheme 1** Preparation of binuclear salicylaldimine ligands.

was found to be a viable route for the preparation of complexes **3a–c** (Scheme 2). The relatively poor solubility of the ligand in diethylether slows down the reaction. Consumption of the starting material could be followed by a colour change (from yellow to dark red), and by the evolution of methane. Decomposed excess Ni(II) starting material was removed by filtration.



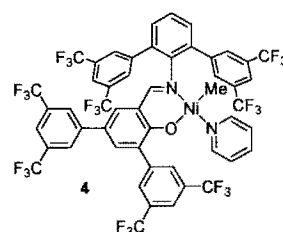
**Scheme 2** Preparation of ( $\kappa^2$ -*N,O*) salicylaldiminato nickel-methyl pyridine complexes.

All complexes are diamagnetic in solution as evidenced by sharp resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. This suggests a square planar coordination geometry of the nickel center, as reported

previously for other Ni(II)-Me salicylaldiminato complexes.<sup>16g,18f,19</sup> Most characteristic are the high field nickel methyl resonances around  $-1.0$  ppm in the  $^1\text{H}$  NMR and  $-8$  ppm in the  $^{13}\text{C}$  NMR spectra. This unique resonance confirms that both metal centers are magnetically identical in the binuclear structure, as expected.

### Catalytic ethylene polymerization with binuclear ( $\kappa^2$ -*N,O*) salicylaldiminato Ni(II) methyl pyridine complexes

Polymerization studies were performed in toluene as a reaction medium (Table 1). In this case monitoring of the polymerization *via* mass-flow meters, not possible with the set-up for polymerization in supercritical fluids, gives insights on catalyst stability. The mononuclear analogue **4<sup>8d</sup>** was studied as a catalyst precursor for comparison (entries 1-7 and 1-8).



The novel catalyst precursors are active for ethylene polymerization at  $50\text{ }^\circ\text{C}$  under 40 bar ethylene pressure in toluene. Independently of the bridge, activities observed were on the same order as for the mononuclear analogue ( $3 \times 10^4$  TO  $\text{h}^{-1}$  average in a 30 min experiment). At a polymerization temperature of  $70\text{ }^\circ\text{C}$ , higher polymerization rates were observed (Table 1). This is likely associated with an enhanced dissociation of the pyridine donor. At this temperature, the nature of the bridge does have a clear effect on catalyst stability. Complexes **3a,b** as well as **4** decomposed rapidly. By contrast, **3c** consumed ethylene steadily over the 30 min duration of the experiment.

The polymers obtained are semicrystalline ( $\chi \sim 50\%$ ) with a melt peak temperature in the range from  $105$  to  $122\text{ }^\circ\text{C}$ . A relatively low number of methyl branches was detected by  $^{13}\text{C}$  NMR spectroscopy (15 per 1000 carbon atoms) along with very few ethyl branches (2 per 1000 carbon atoms). Note that these branches result from 'chain walking',<sup>20</sup> commonly observed with late transition metal catalysts. In detail, the lowest branching and highest polymer molecular weight was observed for **3c**, which can be related to the electron-withdrawing character of the hexafluoropyridine bridge. An increased electrophilicity is

**Table 1** Polymerization in toluene<sup>a</sup>

Run	Complex	$T/^\circ\text{C}$	TOF <sup>c</sup> $10^3/\text{h}^{-1}$	$M_n^d$ $10^3/\text{g mol}^{-1}$	$M_w/M_n^d$	$T_m^e/^\circ\text{C}$	$\chi^f$ (%)	$N_{\text{Me}}/1000\text{C}^g$	$N_{\text{Et}}/1000\text{C}^g$
1-1	<b>3a</b>	50	18	23.0	2.4	115	50	14	< 1
1-2	<b>3a</b>	70	64	3.8	3.1	104	45	19	2
1-3	<b>3b</b>	50	20	25.1	2.8	119	51	11	< 1
1-4 <sup>h</sup>	<b>3b</b>	70	25	2.6	3.9 <sup>h</sup>	110	47	15	2
1-5	<b>3c</b>	50	29	38.9	2.6	122	54	9	< 1
1-6	<b>3c</b>	70	91	12.7	2.1	115	54	14	< 1
1-7 <sup>h</sup>	<b>4</b>	50	32	14.3	2.4	110	48	17	2
1-8 <sup>h</sup>	<b>4</b>	70	70	8.3	2.2	105	46	19	2

<sup>a</sup> Reaction conditions: 100 mL of toluene,  $p(\text{ethylene}) = 40$  bar,  $t = 30$  min,  $n(\text{Ni}) = 10\text{ }\mu\text{mol}$ . <sup>b</sup>  $n(\text{Ni}) = 5\text{ }\mu\text{mol}$ . <sup>c</sup> TOF in mol ( $\text{C}_2\text{H}_4$ ) mol ( $\text{Ni}$ )<sup>-1</sup> h<sup>-1</sup>.

<sup>d</sup> Determined by GPC. <sup>e</sup> Determined by DSC from second heat. <sup>f</sup> Determined by  $^{13}\text{C}$  NMR. <sup>h</sup> Bimodal distribution.

**Table 2** Polymerization in scCO<sub>2</sub><sup>a</sup>

Run	Cat.	<i>T</i> /°C	TOF <sup>e</sup> 10 <sup>3</sup> /h <sup>-1</sup>	<i>M<sub>n</sub></i> <sup>f</sup> 10 <sup>3</sup> /g mol <sup>-1</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>f</sup>	<i>T<sub>m</sub></i> <sup>g</sup> /°C	χ <sup>g</sup> (%)	<i>N<sub>mc</sub></i> /1000C <sup>h</sup>	<i>N<sub>lit</sub></i> /1000C <sup>h</sup>
2-1 <sup>b</sup>	<b>3a</b>	50	2.7	15.3	2.3	121	48	14	< 1
2-2 <sup>b</sup>	<b>3b</b>	50	4.3	29.2	2.5	119	47	n.d.	n.d.
2-3	<b>3b</b>	70	10.4	1.8	3.8	98	36	17	2
2-4 <sup>b</sup>	<b>3b<sup>c</sup></b>	70	15.1	12.0	2.1	99	36	17	2
2-5 <sup>b</sup>	<b>3c</b>	50	3.4	26.1	2.3	124	54	9	< 1
2-6	<b>3c</b>	70	8.9	2.3	4.6	105	43	14	1
2-7	<b>3c<sup>c</sup></b>	70	14.3	2.7	3.4	105	43	14	2
2-8	<b>4<sup>d</sup></b>	50	5.7	33.3	2.1	123	49	5	< 1
2-9	<b>4<sup>d</sup></b>	70	10.9	2.9	3.4	97	40	19	2

<sup>a</sup> Reaction conditions: *n*(Ni) = 10 μmol, *t* = 30 min, *m*(CO<sub>2</sub>) = 45.5 g, *m*(C<sub>2</sub>H<sub>4</sub>) = 6 g. <sup>b</sup> *m*(C<sub>2</sub>H<sub>4</sub>) = 2 g. <sup>c</sup> *n*(Ni) = 5 μmol. <sup>d</sup> *n*(Ni) = 2.5 μmol. <sup>e</sup> TOF in 10<sup>3</sup> mol (C<sub>2</sub>H<sub>4</sub>) mol (Ni)<sup>-1</sup> h<sup>-1</sup>. <sup>f</sup> Determined by GPC. <sup>g</sup> Determined by DSC from second heating. <sup>h</sup> Determined by <sup>13</sup>C NMR.

known to reduce the tendency for β-H elimination, a key step of both branch formation and chain transfer.<sup>16m</sup>

Polymerizations in scCO<sub>2</sub> were performed in a high pressure reactor equipped with sapphire windows, which enable a visual monitoring of the reaction. Catalyst precursors were found to dissolve at a moderate pressure in the supercritical fluid (50 °C, 35 MPa), to form a bright yellow-orange solution. After addition of ethylene, an immediate onset of turbidity was observed due to the precipitation of the polyethylene formed. Upon careful venting of the reactor after the desired polymerization time, the polymer was obtained directly as a dry powder. The binuclear complexes polymerized ethylene in scCO<sub>2</sub> with up to 10<sup>4</sup> TO h<sup>-1</sup> at 70 °C (Table 2). As previously observed for catalytic polymerization of ethylene in dense carbon dioxide with other salicylaldehyde complexes,<sup>8d</sup> productivities are significantly decreased by comparison to polymerization in organic hydrocarbon solvent. A possible explanation for these lower activities is an enclosure of the intact catalyst in the precipitated polymer, which will also be less swollen with solvent by comparison to toluene as a reaction medium. Polymers prepared at 50 °C possess similar molecular weights, degrees of branching, and melting properties as observed in toluene. However, the reduction of polymer molecular weight with increased reaction temperature is more pronounced in scCO<sub>2</sub> than the organic solvent. It can be speculated that a coordinating nature of CO<sub>2</sub> contributes to chain transfer *via* an associative mechanism.<sup>16b</sup>

## Summary and conclusion

Three novel highly fluorinated binuclear Ni(II) methyl pyridine complexes of di(salicylaldehydes) bridged in the *p*-position of the *N*-aryl moiety were prepared and characterized. These compounds were found to be single-component catalyst precursors for the polymerization of ethylene in supercritical carbon dioxide as a reaction medium. A polymerization temperature of 70 °C resulted in higher polymerization activities than at 50 °C, likely due to enhanced pyridine dissociation, however at the expense of polymer molecular weights, which was particularly pronounced in scCO<sub>2</sub> by comparison to an organic reaction medium. Semicrystalline polyethylene with a rather moderate degree of branching and moderate molecular weight is formed invariable of the catalyst structure. However, the bridging moiety does influence catalyst stability over time, as observed for polymerization in toluene.

## Experimental

### Materials and general considerations

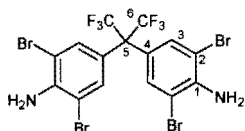
Unless noted otherwise, all manipulations of metal complexes were carried out under an inert atmosphere using standard glovebox or Schlenk techniques. All glassware was flame-dried under vacuum before use. Toluene and benzene were distilled from sodium, diethylether from sodium/benzophenone ketyl under argon. Ethylene (99.95%) and carbon dioxide (99.9995%) supplied by Praxair and Air Liquide, respectively, were used as received. All other solvents were commercial grade. 4,4'-diamino diphenyl 1,1,1,3,3,3-hexafluoropropane was purchased from Aldrich. [(pyridine)<sub>2</sub>Ni(CH<sub>3</sub>)<sub>2</sub>] was synthesized by a modified literature procedure<sup>21</sup> and stored at -30 °C in a glovebox. 3,5-bis[3,5-bis(trifluoromethyl)phenyl] salicylaldehyde,<sup>22</sup> 3,3',5,5'-tetrakis(3,5-bis(trifluoromethyl)-phenyl)-4,4'-diaminodiphenylmethane,<sup>18d</sup> 3,3',5,5'-tetrakis[3,5-bis(trifluoromethyl)phenyl]benzidine,<sup>18d</sup> and complex **4**<sup>22</sup> were prepared according to reported procedures.

NMR spectra were recorded on a Varian Unity INOVA 400 or on a Bruker Avance DRX 600 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to the solvent signal. NMR assignments were confirmed by <sup>1</sup>H, <sup>1</sup>H gCOSY, <sup>1</sup>H, <sup>13</sup>C gHSQC and <sup>1</sup>H, <sup>13</sup>C gHMBC experiments. Elemental analyses were performed up to 950 °C on an Elementar Vario EL. High-temperature NMR measurements of polyethylenes were performed in 1,1,2,2-tetrachloroethane-d<sub>2</sub> at 130 °C. Size exclusion chromatography (GPC) was carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min<sup>-1</sup> on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index-, viscosity—and light scattering—(15° and 90°) detectors. Data reported were determined *vs.* polyethylene standards. Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 at a heating rate of 10 K min<sup>-1</sup>. DSC data reported are from second heating cycles. Polymer crystallinity was calculated based on a melt enthalpy of 293 J g<sup>-1</sup> for 100% crystalline polyethylene.

### 3,3',5,5'-Tetrabromo 4,4'-diamino diphenyl 1,1,1,3,3,3-hexafluoropropane

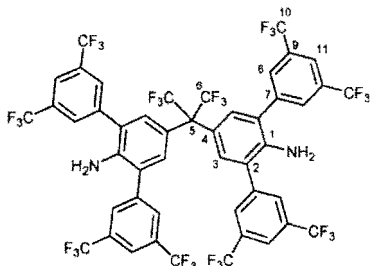
To a suspension of tetra-*n*-butylammonium tribromide (17.31 g, 36 mmol) and calcium carbonate (3.59 g, 36 mmol) in 70 mL of methanol was added a solution of 4,4'-diamino diphenyl 1,1,1,3,3,3-hexafluoropropane (3.00 g, 9 mmol) in 30 mL of

methanol, and the mixture was stirred at room temperature. The colour changed from an initial orange to light green. After 12 h, the solvent was removed *in vacuo*, and the residue was extracted with hot toluene on a frit. The extract was concentrated to dryness and washed twice each with water and methanol. The resulting crude product was recrystallized from toluene as brown large needles.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm); 7.36 (s, 2 H, 3H), 4.76 (s, 2 H,  $\text{NH}_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  (ppm); 143.10, 133.32 (C3), 123.97 (q,  $^1J_{\text{CF}} = 287$  Hz), 123.24, 108.13, 62.60 (septet,  $^2J_{\text{CF}} = 26.8$ , C5). Anal. calcd for  $\text{C}_{15}\text{H}_8\text{Br}_4\text{F}_6\text{N}_2$  ( $M = 649.24$  g  $\text{mol}^{-1}$ ): C 27.72, H 1.24, N 4.32. Found: C 28.74, H 1.44, N 4.17.



### 3,3',5,5'-Tetrakis(3,5-bis(trifluoromethyl)phenyl) 4,4'-diamino diphenyl 1,1,1,3,3,3-hexafluoropropane

To a mixture of 3,3',5,5'-tetrabromo 4,4'-diamino diphenyl 1,1,1,3,3,3-hexafluoropropane (0.86 mmol, 0.56 g), 5 equiv. of 3,5-bis(trifluoromethyl)phenyl boronic acid (4.28 mmol, 1.10 g), 2.5 mol%  $[\text{Pd}(\text{dba})_2]$  (0.02 mmol, 12 mg), and 5 mol% triphenyl phosphine (0.04 mmol, 11 mg) were added 20 mL of toluene, 5 mL of ethanol and 10 mL of a 2 M  $\text{Na}_2\text{CO}_3$  aqueous solution in a Schlenk flask under protective atmosphere. The suspension was heated with vigorous stirring to 90 °C for 24 h. The resulting biphasic mixture was stirred for 30 min under air (resulting in formation of palladium black) and poured into a separatory funnel, water and diethyl ether were added until all salts and organic material dissolved. The aqueous phase was extracted with additional 2  $\times$  25 mL of diethyl ether. The organic phases were combined, and filtrated through a plug of silica to remove Pd black. The solvents were removed under vacuum. The product was dissolved in hot hexane and recrystallised slowly out of this solution. Yield: 87%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm); 7.84 (s, 4 H, 11-H), 7.81 (s, 8 H, 8-H), 7.18 (s, 4 H, 3-H), 3.77 (s, 4 H,  $\text{NH}_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  (ppm): 141.66 (s, C7), 140.56 (s, C1), 132.75 (s, C3), 133.06 (q,  $^2J_{\text{CF}} = 33.7$ , C9), 129.76 (s, C8), 125.30 (s, C4), 123.40 (s, C2), 124.44 (q,  $^1J_{\text{CF}} = 287.5$ , C10) (q,  $^1J_{\text{CF}} = 273.3$ , C6), 122.38 (septet,  $^3J_{\text{CF}} = 3.5$ , C11), 63.82 (septet,  $^2J_{\text{CF}} = 26.0$ , C5). Anal. calcd for  $\text{C}_{47}\text{H}_{20}\text{F}_{30}\text{N}_2$  ( $M = 1182.63$  g  $\text{mol}^{-1}$ ): C 47.73, H 1.70, N 2.37. Found: C 48.31, H 2.31, N 2.32.



### General procedure for condensation of anilines with 3,5-bis(trifluoromethyl)phenyl salicylaldehyde.

In a flask equipped with a Dean–Stark condenser, the aniline, the aldehyde (1.1 equiv.) and a catalytic amount of *p*-toluenesulfonic

acid were dissolved in 100 mL of toluene. The mixture was degassed by several cycles of evacuating and back filling with inert atmosphere. The mixture was stirred at 80 °C, and the pressure was reduced until the solvent boiled. The mixture was kept at 80 °C for 12 h. The reaction mixture was concentrated, and to the brown viscous residue was added 20 mL of methanol to afford the precipitation of the desire product as a yellowish powder.

### $[\{(\text{2,6-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2\text{-4-yl-C}_6\text{H}_4)\text{-N=C(H)-(3,5-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2\text{-2-(OH)-C}_6\text{H}_4)\}_2)]$ (2a)

Yield: 56%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm): 12.85 (2 H, s), 8.21 (2 H, s), 8.07 (4 H, s), 8.03 (8 H, s), 7.94 (2 H, s), 7.92 (4 H, s), 7.90 (8 H, s), 7.87 (2 H, s), 7.70 (2 H, s), 7.28 (2 H, s). MALDI-TOF-MS:  $m/z$  2090.2 ( $[\text{M} + \text{H}]^+$ ) Anal. calcd for  $\text{C}_{90}\text{H}_{36}\text{F}_{48}\text{N}_2\text{O}_2$  ( $M = 2089.2$  g  $\text{mol}^{-1}$ ): C 51.74, H 1.74, F 43.65, N 1.34. Found: C 50.58, H 2.34, F 43.68, N 1.74.

### $[\text{CH}_2\{(\text{2,6-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2\text{-4-yl-C}_6\text{H}_4)\text{-N=C(H)-(3,5-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2\text{-2-(OH)-C}_6\text{H}_4)\}_2)]$ (2b)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm): 12.72 (br. s, 2 H) 8.13 (s, 2 H), 7.98 (s, 4 H), 7.87 (s, 10 H), 7.81 (s, 10 H), 7.59 (d,  $^4J_{\text{HH}} = 2.3$ , 2 H), 7.45 (s, 4 H), 7.12 (d,  $^4J_{\text{HH}} = 2.3$ , 2 H), 4.32 (s, 2 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  (ppm): 169.54, 158.70, 143.88, 141.44, 140.60, 139.43, 138.37, 133.63, 132.93, 132.84 (q,  $^2J_{\text{CF}} = 33$ ), 132.43 (q,  $^2J_{\text{CF}} = 33$ ), 131.87, 131.47 (q,  $^2J_{\text{CF}} = 33$ ), 131.45, 130.40, 130.12, 130.09, 129.68, 128.69, 126.90, 123.56 (q,  $^1J_{\text{CF}} = 273$ ), 123.40 (q,  $^1J_{\text{CF}} = 273$ ), 123.22 (q,  $^1J_{\text{CF}} = 273$ ), 121.85, 121.58, 118.85, 40.85. MALDI-TOF-MS:  $m/z$  2104.2 ( $[\text{M} + \text{H}]^+$ ) Anal. calcd for  $\text{C}_{91}\text{H}_{38}\text{F}_{48}\text{N}_2\text{O}_2$  ( $M = 2103.2$  g  $\text{mol}^{-1}$ ): C 51.97, H 1.82, F 43.36, N 1.33. Found: C 50.97, H 1.82, F 43.40, N 1.32.

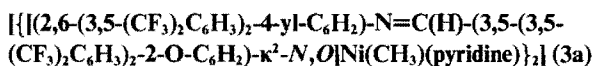
### $[\text{C}(\text{CF}_3)_2\{(\text{2,6-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2\text{-4-yl-C}_6\text{H}_4)\text{-N=C(H)-(3,5-(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_2\text{-2-(OH)-C}_6\text{H}_4)\}_2)]$ (2c)

Yield: 75%.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  (ppm): 12.52 (s, 2 H), 8.16 (s, 2 H), 8.05 (s, 4 H), 7.89 (s, 16 H), 7.87 (br. s, 2 H, OH), 7.71 (s, 4 H), 7.70 (d,  $^4J_{\text{HH}} = 2.1$ , 2 H), 7.24 (d,  $^4J_{\text{HH}} = 2.1$ , 2 H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  (ppm): 170.46, 159.01, 146.87, 141.76, 140.25, 138.89, 134.37, 133.28, 133.25, 132.73 (q,  $^2J_{\text{CF}} = 33$ ), 132.68 (q,  $^2J_{\text{CF}} = 33$ ), 132.27, 132.04 (q,  $^2J_{\text{CF}} = 33$ ), 131.98, 130.74, 130.61, 130.14, 128.85, 127.37, 124.04 (q,  $^1J_{\text{CF}} = 273$ ), 123.91 (q,  $^1J_{\text{CF}} = 273$ ), 123.62 (q,  $^1J_{\text{CF}} = 273$ ), 122.59, 122.16, 121.74, 119.16. MALDI-TOF-MS:  $m/z$  2240.2 ( $[\text{M} + \text{H}]^+$ ) Anal. calcd for  $\text{C}_{93}\text{H}_{36}\text{F}_{54}\text{N}_2\text{O}_2$  ( $M = 2239.2$  g  $\text{mol}^{-1}$ ): C 49.88, H 1.62, F 45.82, N 1.25. Found: C 49.85, H 2.26, F 45.84, N 1.20

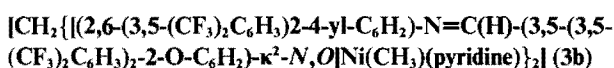
### General procedure for the synthesis of ( $\kappa^2$ -*N,O*)-salicylaldiminato nickel methyl pyridine complexes

5 mL of cold diethylether were added to a mixture of 3 equiv. of  $[(\text{pyridine})_2\text{NiMe}_2]$  and the respective difunctional salicylaldimine in a 25 mL Schlenk tube under stirring. A slow evolution of methane was observed within 15 to 30 min. The deep red mixture was stirred for another 120 min at 25 °C. The solvent was removed *in vacuo*. The residue was dissolved in a small amount of benzene and filtered through a syringe filter. The volatiles were removed by sublimation at –10 °C (crushed ice/sodium chloride) under

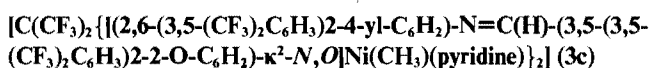
high vacuum ( $10^{-3}$  mbar) to yield quantitatively pure pyridine complexes.



Yield: 93%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  (ppm): 8.22 (s, 8 H), 7.90 (br. s, 4 H), 7.82 (s, 4 H), 7.72 (s, 6 H), 7.60 (s, 2 H), 7.57 (s, 4 H), 7.07 (s, 2 H), 6.95 (s, 4 H), 6.90 (s, 2 H), 6.72 (s, 2 H), 6.58 (br. s, 2 H), 6.15 (br. s, 4 H), -0.89 (s, 6 H). Anal. calcd for  $\text{C}_{102}\text{H}_{50}\text{F}_{48}\text{N}_4\text{Ni}_2\text{O}_2$  ( $M = 2392.82$  g mol $^{-1}$ ): C 51.20, H 2.12, N 2.34. Found: C 51.89, H 2.29, N 2.17.



Yield: 89%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  (ppm): 8.32 (s, 8 H), 8.08 (m, 4 H), 8.03 (s, 4 H), 7.87 (s, 4 H), 7.75 (s, 4 H), 7.69 (s, 4 H), 7.61 (s, 2 H), 7.57 (s, 2 H), 7.51 (m, 2 H), 7.44 (s, 4 H), 7.14 (s, 2 H), 6.92 (m, 4 H), 4.30 (s, 2 H), -1.07 (s, 6 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  (ppm): 168.83, 165.04, 150.97, 149.19, 142.77, 141.70, 141.40, 139.91, 137.49, 134.12, 133.68, 133.41, 132.24 (q,  $^1J_{\text{CF}} = 273$ ), 132.38 (q,  $^1J_{\text{CF}} = 273$ ), 131.97, 131.14, 131.13, 130.90 (q,  $^1J_{\text{CF}} = 273$ ), 129.58, 126.42, 126.40, 124.21, 124.14, 124.11 (q,  $^2J_{\text{CF}} = 33$ ), 124.09 (q,  $^2J_{\text{CF}} = 33$ ), 124.06 (q,  $^2J_{\text{CF}} = 33$ ), 122.05, 122.01, 121.01, 120.57, 120.25, 40.88, -7.37. Anal. calcd for  $\text{C}_{103}\text{H}_{52}\text{F}_{48}\text{N}_4\text{Ni}_2\text{O}_2$  ( $M = 2406.85$  g mol $^{-1}$ ): C 51.40, H 2.18, N 2.18. Found: C 51.86, H 2.26, N 2.12.



Yield: 77%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  (ppm): 8.26 (s, 8 H), 8.08 (dt,  $^3J_{\text{HH}} = 5.1$ , 4 H, *meta*-pyr), 8.06 (s, 4 H), 7.89 (s, 4 H), 7.78 (s, 4 H), 7.68 (s, 4 H), 7.65 (s, 4 H), 7.62 (s, 2 H), 7.60 (d,  $^4J_{\text{HH}} = 2.5$ , 2 H), 7.54 (t,  $^3J_{\text{HH}} = 7.7$ , 2 H), 7.18 (d,  $^4J_{\text{HH}} = 2.5$ , 2 H), 6.94 (t,  $^3J_{\text{HH}} = 7.7$ , 4 H, *ortho*-pyr), -1.12 (s, 6 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  (ppm): 168.54, 165.26, 151.63, 150.96, 142.66, 141.24, 140.68, 137.66, 134.59, 134.10, 133.39, 132.97, 132.55 (q,  $^2J_{\text{CF}} = 33$ ), 132.47 (q,  $^2J_{\text{CF}} = 33$ ), 132.39, 132.25, 131.04, 131.02, 130.96 (q,  $^2J_{\text{CF}} = 33$ ), 129.60, 129.58, 126.47, 126.44, 124.59, 124.25, 124.11 (q,  $^1J_{\text{CF}} = 273$ ), 124.04 (q,  $^1J_{\text{CF}} = 273$ ), 123.91 (q,  $^1J_{\text{CF}} = 273$ ), 122.70, 120.77, 120.69, 120.41, -7.68. Anal. calcd for  $\text{C}_{105}\text{H}_{50}\text{F}_{50}\text{N}_4\text{Ni}_2\text{O}_2$  ( $M = 2540.18$  g mol $^{-1}$ ): C 49.59, H 1.98, F 40.35, N 2.20. Found: C 49.74, H 2.02, F 40.32, N 2.11.

### Polymerizations in organic solvent

The polymerizations in organic solvent were carried out in a 250 mL stainless steel mechanically stirred (750 rpm) pressure reactor equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. A valve controlled by a pressure transducer allowed for applying and keeping up a constant ethylene pressure. The required flow of ethylene, corresponding to ethylene consumed by polymerization, was monitored by a mass flow meter and recorded digitally. Prior to a polymerization experiment, the reactor was heated under vacuum to the desired reaction temperature for 30–60 min, back-filled with argon, and charged with solvent. The catalyst precursor was weighed into a dry

syringe in the glovebox. In a slight argon stream, solvent from the reaction was pulled into the syringe several times, dissolving and transferring to the reactor the catalyst precursor. The reactor was closed and a constant ethylene pressure was applied. After the desired reaction time, the reactor was rapidly vented and cooled to room temperature. The reaction mixture was stirred with an excess volume of methanol. The polymer was isolated by filtration, washed several times with methanol, and dried *in vacuo* at 50 °C.

### Polymerizations in supercritical carbon dioxide (scCO<sub>2</sub>)

The polymerizations in scCO<sub>2</sub> were carried out in a high-pressure view cell (NWA GmbH, Lörrach, Germany). The stainless steel cell has a variable internal volume between 30 and 60 cm<sup>3</sup> tuneable by means of a piston operated by a hydraulic system. The piston material is a transparent sapphire which, together with a sapphire view window on the opposite side of the cell, allows for visually observing the contents of the cell. The cell contents can be agitated by means of a magnetically coupled stainless steel mechanical propeller stirrer. Heating is provided by means of two stainless steel cartridge heaters lodged in cavities of the metallic body of the cell. The temperature inside the cell is measured by a thermocouple, and the pressure is monitored with a Bourdon type manometer.

The gases were introduced *via* high pressure pumps (up to 60 MPa for carbon dioxide and up to 40 MPa for ethylene) which employ the corresponding cold condensed liquids as a reservoir. The rate of the ethylene addition was controlled by a two way HPLC valve, with an internal loop volume of 1 mL. The quantities of gases introduced were estimated by the change in piston position and the pressure. Prior to a polymerization experiment, the reactor was heated under a low pressure of carbon dioxide (6 MPa) to the desired reaction temperature for 30 to 60 min, and then flushed 3 times with carbon dioxide. The catalyst precursor was added as a compressed pellet *via* a modified syringe to the empty reactor. The reactor was closed and filled with carbon dioxide to the desired pressure (10 MPa). Under continuous stirring the pressure was increased (to 30 MPa) by decreasing the cell volume *via* the piston, and the ethylene was added at constant pressure. After the addition of the desired amount of monomer, polymerizations were carried out at a pressure of 65 MPa, adjusted by moving the piston forward. The reaction was stopped by increasing the volume of the cell and the reactor was carefully vented.

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