Nickel N-heterocyclic carbene complexes in homogeneous catalysis

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Chapter 7

Nickel N-heterocyclic carbene complexes in the vinyl polymerization of norbornene[†]

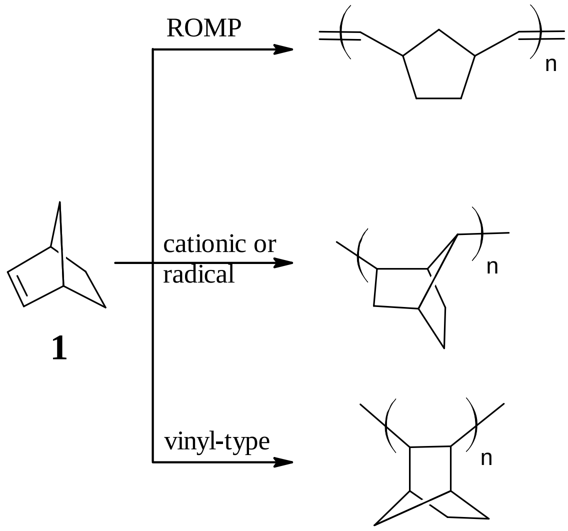
Abstract. *Three types of nickel(II) complexes with N-heterocyclic carbene (NHC) ligands, described in this thesis, have been used in the catalytic vinyl polymerization of norbornene under a range of conditions. Specifically, two nickel complexes bearing a chelating bis(NHC) ligand, two nickel complexes bearing two chelating anionic N-donor functionalized NHC ligands as well as one nickel(II) diiodide complex with two monodentate NHCs were tested. The solid-state structure of bis(1,3-dimethylimidazol-2-ylidene)diiodidonickel(II), as determined by X-ray crystallography, is presented. The highest activity of 2.6 × 10^7 g·(mol cat)$^{-1}$·h^{-1} was observed using the latter nickel complex as catalyst, activated by methylaluminoxane. The norbornene polymers thus obtained are of high molecular weight and narrow polydispersity.*

[†] Based on: J. Berding, M. Lutz, A. L. Spek, E. Bouwman, *in preparation*.

7.1 Introduction

In the last few decades, the polymerization of norbornene (bicyclo[2.2.1]hept-2-ene, **1**) has become a field of active research. Three types of (homo)polymer may be obtained from norbornene, following different mechanisms (Scheme 7.1).[1] The most studied is the ring-opening metathesis polymerization (ROMP), which gives polymers with unsaturated backbones and high solubility in a large range of solvents. ROMP is commonly catalyzed by complexes of molybdenum, tungsten, rhenium or ruthenium.[2] An organic radical or aluminum-initiated mechanism leads to the less well known and less understood cationic or radical polymerization, which usually results in low-molecular weight polymers with 2,7-connectivity.[3, 4] The third type of polymerization, which leads to opening of the π-component of the double bond, leaves the bicyclic unit intact. This is known in literature as addition or vinyl polymerization and this reaction was recently reviewed.[2] Vinyl-polymerized norbornene has some useful properties such as good mechanical strength, optical transparency and heat resistance.[5, 6] Several transition metal complexes have been described in the literature as active catalysts for the vinyl polymerization of norbornene. The most common metals in these catalysts are zirconium, titanium, chromium, and the late transition metals cobalt, nickel and palladium. Generally, these metals need to be activated with a cocatalyst, such as methylaluminoxane (MAO), or $B(C_6F_5)_3/AlEt_3$.[2]

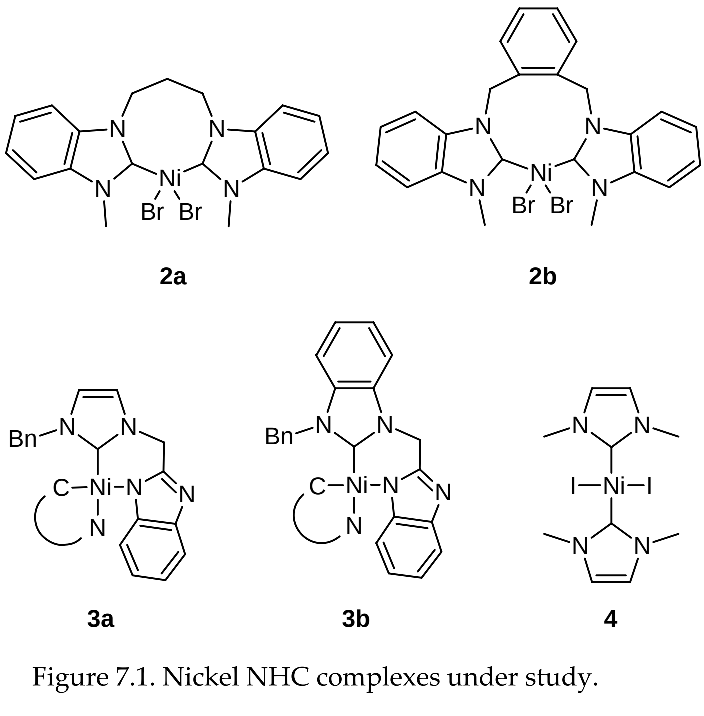
The use of nickel complexes in the vinyl polymerization of norbornene was first described in 1993; the catalysts were obtained by a reaction of the nickel allyl trifluoroacetate dimer with hexafluoro- or hexachloroacetone and did not need any cocatalyst to start the reaction.[7] Other nickel complexes used in this reaction have ligands based on acetylacetonates, carboxylic acids, salen,[8] or other chelating [N_2]-,[9-12] [N_4]-,[13] [N,O]-,[14, 15] [N,S]-,[16] and [P,N][17]-ligands. Furthermore, some bisphosphane-based ligands have been reported in the nickel catalyzed vinyl polymerization of norbornene.[18] To the best of our knowledge, the use of nickel N-heterocyclic carbene



Scheme 7.1 Three types of norbornene polymerization.

complexes in this reaction has only been reported twice. These are a complex with two picolyl-functionalized NHC ligands,[19] and a nickel compound bearing one bulky monodentate NHC and one η^3-coordinated benzyl moiety.[20]

N-Heterocyclic carbenes (NHCs) are increasingly used in homogeneous catalysis as stable, versatile spectator ligands. Some excellent reviews describe a large number of reactions in which these strong σ-donor ligands have been investigated.[21, 22] Because of their electron-donating properties they are often compared to the frequently used and intensively studied tertiary phosphane ligands, even though they have been assumed to have less π-back bonding properties,[23-26] and have a different shape. In some cases, replacing a phosphane ligand by a NHC ligand proved to be beneficial for the catalytic activity.[27] As described in Chapter 4, a number of nickel complexes bearing chelating benzimidazole-based bisNHC ligands has been synthesized.[28] As nickel complexes bearing chelating phosphanes are capable of polymerizing norbornene,[18, 29] it was decided to study the activity of the bisNHC complexes in this polymerization reaction. Given the successful use of N-donor ligands in the catalytic polymerization of norbornene, it was decided to investigate the catalytic properties of two nickel complexes with benzimidazolato-functionalized NHC ligands described in Chapter 6,[30] as well. Furthermore, in order to assess the effect of chelation of the ligand, one complex bearing two monodentate NHC ligands with small substituents (Chapter 3) is tested under the same conditions.



2a **2b**

3a **3b** **4**

Figure 7.1. Nickel NHC complexes under study.

7.2 Results and Discussion

7.2.1 Nickel complexes

Three types of nickel(II) complexes were tested in the vinylpolymerization of norbornene (depicted in Figure 7.1): nickel dihalide complexes with chelating bisNHC ligands (**2a**, **2b**), nickel complexes bearing two chelating N-donor functionalized NHCs (**3a**, **3b**) and a nickel(II) dihalide complex bearing two monodentate NHC ligands (**4**). The synthesis and characterization of these complexes are described in Chapters 3 – 5.

7.2.2 Description of the crystal structure of complex 4.

Although the compound has been reported previously in the literature,[25] and several other nickel(II) complexes of monodentate NHC ligands have been structurally characterized,[31] the crystal structure of complex **4** was so far not elucidated. Single crystals of **4** were obtained by slow evaporation of a concentrated solution of the compound in THF and the structure was determined using X-ray diffraction. The molecular structure is shown in Figure 7.2. In the crystal structure the molecule has an exact C_{2h} symmetry. The coordination geometry around the nickel(II) center is nearly perfectly square planar, with the coordination of two carbene carbons and two iodides in *trans* positions. Due to symmetry, the I1–Ni1–I1A and the C1–Ni1–C1A bonds are perfectly linear. The Ni–C and Ni–I bond distances are within the range reported for other nickel NHC complexes.[31] The imidazole rings are oriented nearly perpendicular to the coordination plane, with a N1–C1–Ni1–I1 torsion angle of 88.48(19)°.

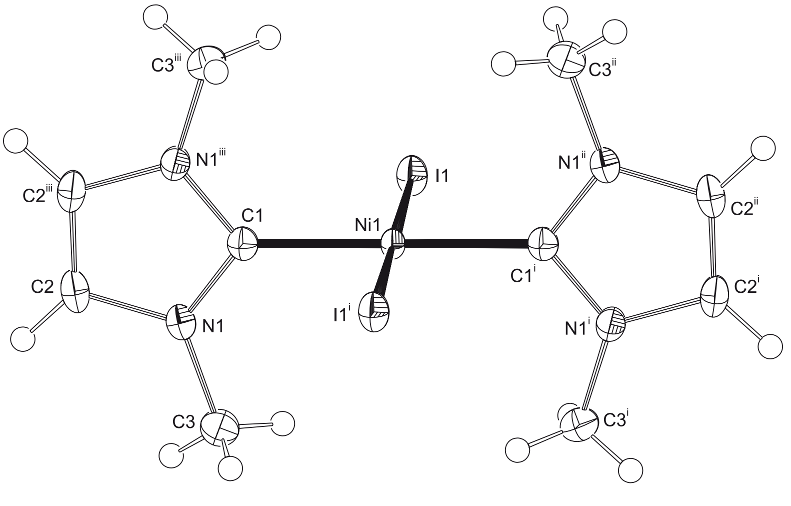


Figure 7.2. Molecular structure of **4** in the crystal showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ni1–C1 1.905(2), Ni1–I1 2.50729(17), C1–N1 1.349(2), C2–C2^{i} 1.342(2), C1–Ni1–I1 90.01(7), C1–Ni1–I1^{i} 89.99(7), N1–C1–N1^{iii} 104.5(2). Symmetry operations i: –x, y, –z; ii: –x, –y, –z; iii: x, –y, z.

7.2.3 Catalytic studies

Compounds **2** – **4** were tested for their catalytic activity in the vinyl polymerization of norbornene (**1**). The results of the most pertinent polymerization reactions using MAO as cocatalyst are summarized in Table 7.1. In this table the

Table 7.1. Overview of catalytic vinyl polymerization experiments using nickel NHC complexes.[a]

Entry	Cat	**1**/Ni (× 10^3)	Solv [b]	Temp (°C) [c]	Time (min)	Yield (%) [d]	Activity (×10^6 g·(mol cat)$^{-1}$·h^{-1})	M_w (× 10^5 g/mol)	PDI [e]
1 [f]	**2a**	3.3	DCM	RT	5	21	0.8	7.9	3.2
2	**2a**	3.3	DCM	RT	5	71	2.7	9.9	2.1
3 [g]	**2a**	3.3	DCM	RT	5	71	2.7	11.0	2.2
4	**2a**	6.7	DCM	RT	5	72	5.4	11.1	2.3
5	**2a**	3.3	DCE	RT	5	65	2.5	>14	
6	**2a**	3.3	DCE	40	5	68	2.6	>14	
7	**2a**	3.3	DCE	60	5	73	2.7	>14	
8	**2b**	3.3	DCM	RT	5	80	3.0	14.1	2.1
9	**2b**	6.7	DCM	RT	5	50	3.8	7.5	2.0
10	**2b**	10.0	DCM	RT	5	42	4.7	8.4	2.0
11	**2b**	3.3	DCM	0	5	65	2.5	4.0	2.3
12	**2b**	6.7	DCM	0	5	33	2.5	4.3	2.8
13	**3a**	3.3	DCE	RT	5	26	1.0	>14	
14	**3a**	6.7	DCE	RT	5	14	1.0	>14	
15	**3a**	3.3	DCE	60	5	22	0.8	>14	
16	**3a**	3.3	DCE	RT	10	40	0.8	n.d.	
17	**3b**	3.3	DCE	RT	5	10	0.4	>14	
18	**3b**	6.7	DCE	RT	5	5	0.4	n.d.	
19	**3b**	3.3	DCE	60	5	11	0.4	>14	
20	**3b**	3.3	DCE	60	15	22	0.3	n.d.	
21	**4**	3.3	DCM	RT	5	71	2.7	>14	
22	**4**	10.0	DCM	RT	5	41	4.6	>14	
23	**4**	3.3	DCE	RT	2	78	7.4	>14	
24	**4**	6.7	DCE	RT	2	77	14.6	n.d.	
25	**4**	3.3	DCE	60	1	85	16.0	>14	
26	**4**	1.0	DCE	RT	0.2	91	25.8	>14	
27 [h]	**4**	3.3	DCE	RT	3	76	4.8	>14	
28 [i]	**4**	1.0	DCE	RT	5	66	0.7	n.d.	
29 [i]	**4**	3.3	DCE	RT	5	45	1.7	n.d.	
30 [j]	**4**	3.3	DCM	RT	15	0	0		
31 [k]	-	-	DCM	RT	15	0	0		

[a] Unless otherwise noted, a 0.5 M solution of norbornene was used and a 500 : 1 MAO to nickel ratio; [b] solvent, DCM = dichloromethane; DCE = 1,2-dichloroethane; [c] RT = room temperature [d] Isolated yield; [e] Polydispersity index = M_w/M_n; [f] MAO/Ni = 100; [g] MAO/Ni = 1000; [h] 0.17 M norbornene solution; [i] 83 mM norbornene solution; [j] No MAO was added; [k] **1**/MAO = 8.

polymer yields and characteristics, and the catalytic activities of all five nickel complexes under various conditions are presented. Variations were made in the amount of cocatalyst, the catalyst loading, the solvent, the temperature, the norbornene concentration and the reaction time. The polymers were characterized by IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy and size exclusion chromatography (SEC). The IR spectra of the polymer products are consistent with the spectrum reported for vinyl-polymerized norbornene.[19] Peaks indicative of double bonds (1680 – 1620 cm^{-1}) are not observed, indicating that the product was not obtained *via* ROMP.[18] The ^{1}H and ^{13}C NMR spectra are very similar to those reported and also show no resonances assignable to double bonds.[11, 17] The SEC measurements of several samples indicated that high-molecular weight polymers with a narrow polydispersity are formed. Unfortunately, a large number of polynorbornene samples could not be analyzed by size exclusion chromatography; due to the high molecular weight these polymers could not be dissolved in the commonly used chlorobenzene or 1,3,5-trichlorobenzene, even after stirring at elevated temperatures for several days. It is estimated that the molecular weight of these polymers is at least $1.4 \cdot 10^6$ g/mol, the highest molecular weight found for a soluble polymer sample (entry 8). As expected,[32] the polymers are stable up to 390 °C under an argon atmosphere, as shown by TGA studies.

The influence of the Ni:MAO ratio on the efficiency of the reaction may be found from entries 1 to 3. An increase of the amount of MAO from 100 to 500 equivalents gives a large enhancement of polymer yield, whereas a further increase to 1000 equivalents does not improve the yield. The average molecular weight of the polymers appears to increase slightly with a larger amount of MAO. It was decided to use a Ni:MAO ratio of 1:500 in the other catalytic experiments. Although Ni to MAO ratios of 1:100 have been used,[18] often a much larger excess is applied, up to 1:9000.[15]

Initially, the catalytic runs were performed in dichloromethane. This solvent has been used by others for the polymerization of norbornene.[33, 34] However, due to its low boiling point, this solvent cannot be used to test the catalytic performance of the catalysts at elevated temperatures. Therefore, a number of catalytic runs were performed in 1,2-dichloroethane (DCE) as well.[35] The two solvents are of comparable polarity and the change in solvent is not expected to have a large influence on the reactivity of the catalyst. Indeed, a comparison of entries 2 and 5 shows that difference in reactivity of the catalyst in the two solvents is small.

Under standard conditions (MAO/Ni = 500, **1**/Ni = 3.3×10^3, 0.5 M norbornene, 5 min at room temperature, entries 2, 8, 13, 17 and 21) the five different catalysts may be compared. Under these conditions, the reactivity of the catalysts increases in the order **3b** < **3a** << **4** ≈ **2a** < **2b**.

The influence of the temperature on the activity of complex **2a** is rather limited. Entries 5 – 7 show only a small increase in the yield of the reaction when going from room temperature to 60 °C. This was also observed for complex **2b**, which shows a decrease in activity going from room temperature to 0 °C (entries 9 and 12, or 8 and 11). The influence on the molecular weight of the resulting polymer, however, is larger; M_w drops considerably when performing the catalytic reaction at lower temperatures. For catalysts **3a** and **3b** the influence of the temperature on the activity is also limited. The influence of the temperature on the activity of complex **4** appears to be larger, as at room temperature a yield of 78% is reached within two minutes, whereas at 60 °C a yield of 85% is obtained within one minute (entries 23 and 25).

The catalyst loading, expressed as the norbornene:nickel complex ratio, has a large influence on the activity of the catalyst. For instance, using complex **2a** or **4** the average activity more than doubles on using half the amount of catalyst under the same conditions (entries 2 and 4, or 23 and 24), although the effect is less pronounced in the less active catalysts **3a** and **3b**. Probably the reaction using the higher catalyst loading was actually deactivated before complete conversion was reached and the quenching was started, leading to an underestimation of the activity.

As catalysts **3a** and **3b** are not very active catalysts in the vinyl polymerization, compared to the other complexes, some experiments were performed to determine whether the reaction had stopped after the standard 5 minutes, or whether a longer reaction time would lead to a higher yield. Indeed, it is clear (entries 13 and 16, or 19 and 20) that the reaction is not finished after 5 minutes, although the resulting overall activity drops with longer reaction times.

In the initial test complex **4** showed good activity (Table 7.1, entry 21). It then was attempted to get an estimation of the initial rate of the reaction, by quenching the reaction after short reaction times (entries 23 – 26). The highest overall activity thus found is 2.6×10^7 g/(mol cat)·h, which was reached when a reaction of **4** with 1000 equivalents of norbornene at room temperature furnished 91% yield within 12 seconds. This may still be an underestimation of the real catalyst activity, as a thick slurry formed even before all of the catalyst solution had been added. Unfortunately, a shorter reaction time was experimentally unattainable.

In addition, it was attempted to perform the catalytic reaction in more diluted reaction mixtures (entries 27 – 29). This way, the polymerization of norbornene using complex **4** was slowed down, giving only 45% yield in 5 minutes in a solution that was six times diluted, compared to 78% yield in 2 minutes (entry 23). Control experiments (entries 30 and 31) show that complex **4** without MAO does not catalyze the polymerization reaction, nor does MAO alone, as was reported before.[19]

It is clear from the results shown in Table 7.1 that the activity of the catalyst is highly dependent on the type of complex used. For instance, complex **4** is very active, while complexes **3a** and **3b** are not. The differences in reactivity between **2a** and **2b** and the differences between **3a** and **3b** are not very large; however, more experiments are needed to draw a conclusion on the exact influence of the various substituents.

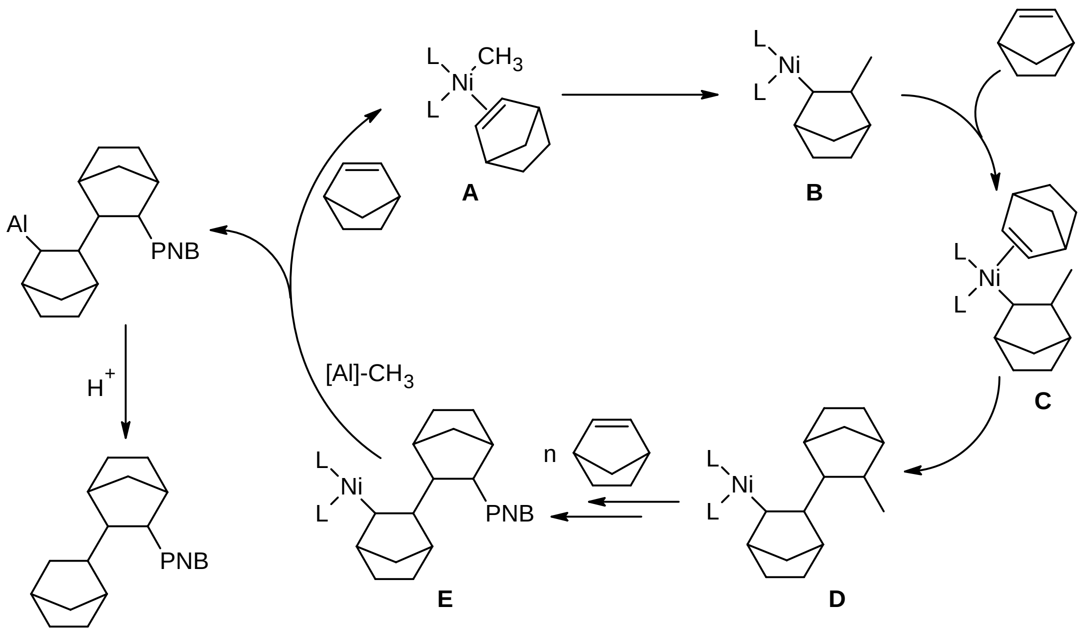
Nickel catalysts for the vinyl polymerization of norbornene have been reported to have activities in the wide range of 10^3 to 10^9 g/(mol cat)·h.[2] The highest activity reported so far of 1.68 × 10^9 g/(mol cat)·h was achieved with a nickel complex with two benzimidazole ligands.[9]

In the literature, two other types of nickel NHC complexes have been reported to be active the norbornene polymerization catalysts. Wang *et al.*[19] reported activities up to 2.6 × 10^7 g/(mol cat)·h using a cationic nickel complex bearing two picolyl functionalized NHCs (**1**/Ni = 68000, Al/Ni = 4500, 10 min. at 80 °C in chlorobenzene), with molecular weights up to 4.2 × 10^6 and polydispersity indices ranging from 1.3 to 3.5. More recently, Sujith *et al.*[20] reported neutral and cationic η^3-benzylnickel(II) complexes bearing one bulky imidazole-based carbene, which were found to be active norbornene polymerization catalyst, even without cocatalyst. The highest activity observed with this type of complex was 3.3 × 10^5 g/(mol cat)·h (**1**/Ni = 5000, 20 min. at 130 °C in toluene), with molecular weights up to 4.1 × 10^5 and polydispersity indices ranging from 2.4 to 3.3. Interestingly, analogous complexes with imidazoline-based carbene ligands were not active. Unfortunately, due to the different reaction conditions used, a comparison between these complexes and the complexes of the present study cannot be made.

7.2.4 Mechanistic considerations

The mechanism for the vinyl polymerization of norbornene has been proposed to comprise the steps depicted in Scheme 7.2.[11] A reaction between the catalyst precursor and MAO in the presence of norbornene yields a nickel compound with a methyl ligand and a coordinated norbornene (**A**). The norbornene then inserts into the Ni–CH_3 bond to give the coordinatively unsaturated species **B**. By repeating the coordination and insertion steps the polymer chain grows, until species **E** reacts with a methyl aluminium species resulting in chain transfer and regeneration of nickel species **A**. The aluminium species is hydrolyzed during work-up yielding the free polynorbornene polymer chain.

It is clear from a comparison of the molecular weights of the polymers and the ratio between norbornene and nickel catalyst that only few nickel centers are actually catalytically active. If, for instance (Table 7.1, entry 2), every nickel center that was introduced to the reaction mixture would react, the average polymer would consist of approximately 2360 norbornene monomers, which is equal to a molecular weight of about 2 × 10^5 g/mol. In the experiments, however, the average molecular weight is significantly higher (1 × 10^6 g/mol in this example). Apparently, once a nickel catalyst starts the polymerization reaction, the rate of propagation is considerably higher than the rate of elimination. The low polydispersity measured for a number of polymers indicates that the catalyst operates through a single site active species, in line with the proposed mechanism.[18]



Scheme 7.2. Proposed mechanism for the nickel catalyzed vinyl polymerization of norbornene. (L = carbene ligand; PNB = polynorbornene). Adapted from ref. 11.

The large difference in reactivity between the highly active catalysts **2a**, **2b** and **4**, and the less active **3a** and **3b** may arise from the fact that in the first case a halide anion must be replaced to activate the catalyst, while in the latter case this is a benzimidazolato group. This benzimidazolato moiety remains in the vicinity of the catalyst, which may hinder the chain growth. The small difference in activity between complexes **2a,b** and **4** may indicate that chelation is not of importance for this catalytic reaction. For the polymerization reaction to occur, the monodentate ligands in **4** must adopt *cis* positions, similar to the configuration of complexes **2a,b**.

7.3 Conclusion

Five nickel(II) N-heterocyclic carbene complexes, comprising the three types described in Chapters 3 – 5, have been tested for their catalytic activity in the MAO-activated vinyl polymerization of norbornene over a range of conditions. The small $Ni(NHC)_2I_2$ compound showed the highest activity of 2.6×10^7 g/(mol cat)·h. The poor solubility of most of the polymers thus obtained indicate that these are of high ($>1.4 \times 10^6$) molecular weight. The polymers that are soluble are of low polydispersity.

7.4 Experimental

General considerations. All experiments were performed under an atmosphere of dry argon, using standard Schlenk techniques. Dichloromethane and 1,2-dichloroethane were dried by distillation from calcium hydride and stored over molecular sieves under argon. Norbornene (bicyclo[2.2.1]hept-2-ene) was obtained from Aldrich and distilled under argon from sodium. Methylaluminoxane (MAO, 10 wt% solution in toluene) was obtained from Aldrich and used as received. Complexes **2a,b**,[28] **3a,b**,[30] and **4**,[36] were synthesized following the procedures described in Chapters 3 – 5 and were added from a 3.0 mM stock solution in dichloromethane or 1,2-dichloroethane.

NMR spectra were recorded on a Bruker DPX-300 at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR), in *o*-dichlorobenzene-d_4, referenced against TMS. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. The size-exclusion chromatography (SEC) measurements were carried out with a multiple detection system consisting of an interferometric RI detector (Optilab DSP, Wyatt Technology) in series with a multi-angle laser light scattering detector (Dawn DSP-F, Wyatt Technology). With this configuration absolute molecular weights are obtained on-line. The samples were measurxed on two Styragel columns (300 x 7.5 mm, Waters Associates) in chlorobenzene with a flow of 1 ml/min. The columns were kept at 40 °C. The concentration was 5 mg/ml; sample load was 100 μl. Molecular weights are calculated using dn/dc=0.062 ml/g, calculated from the response of the refractive index detector for injections with known concentration.

General procedure for the vinyl polymerization of norbornene. To a solution of norbornene in dichloromethane to 1,2-dichloroethane was added MAO (10 wt% in toluene). While stirring thoroughly with a magnetic stir bar, a solution of nickel complex in the same solvent was added. The total reaction volume was 20 mL in all cases. The reaction was kept at the required temperature by placing the reaction vessel in an oil bath. After the appropriate reaction period the reaction was quenched by the addition of 5 mL of a 10% HCl solution in ethanol. The reaction mixture was poured into 100 mL 10% HCl in ethanol and stirred for several hours. After filtration and washing with copious amounts of ethanol the colorless residue was dried under vacuum at 50 °C until no further weight loss occurred. IR (neat): 2946 (vs), 2866 (vs), 1474 (m), 1453 (s), 1294 (m), 1258 (w), 1148 (m), 1107 (m), 942 (w), 890 (m) cm^{-1}. ^{1}H NMR (300 MHz, *o*-dichlorobenzene-d_4, 300 K) δ 2.8 – 0.8 (m, with maxima at 2.28, 1.62, 1.39, 1.22, 1.12). ^{13}C NMR (75 MHz, *o*-dichlorobenzene-d_4, 300 K) δ 52 – 26 (broad signals, maxima at 52.0, 47.8, 38.3, 31.4).

X-ray crystal structure determination. $C_{10}H_{16}I_2N_4Ni$, Fw = 504.78, red block, 0.33 x 0.24 x 0.09 mm^3, monoclinic, C2/m (no. 12), a = 13.5582(4), b = 8.5892(2), c = 8.4350(3) Å, β = 128.126(2)°, V = 772.73(4) Å^3, Z = 2, D_x = 2.169 g/cm^3, μ = 5.24 mm^{-1}. 8666 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150(2) K. Intensities were integrated with EvalCCD[37] taking into account a large anisotropic mosaicity about the b-axis. An absorption correction based on multiple measured reflections was performed using the program SADABS[38] (correction range 0.16-0.63). 950 Reflections were unique (R_{int} = 0.032), of which 924 were observed [$I>2\sigma(I)$]. The structure was solved with automated Patterson methods using the program DIRDIF-99.[39] The structure was refined with SHELXL-97[40] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined freely with isotropic displacement parameters. 60 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0131 / 0.0317. R1/wR2 [all refl.]: 0.0141 / 0.0320. S = 1.141. Residual electron density between –0.63 and 0.43 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[41]

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