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# Homo- and heterometallic carboxylate cage complexes as precatalysts for olefin polymerization—Activity enhancement through “inert metals”

Paul-Gerhard Lassahn,<sup>a</sup> Vasile Lozan,<sup>a</sup> Grigore A. Timco,<sup>b</sup> Paul Christian,<sup>b</sup>  
Christoph Janiak,<sup>a,\*</sup> and Richard E.P. Winpenny<sup>b</sup>

<sup>a</sup> Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany

<sup>b</sup> Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

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## Abstract

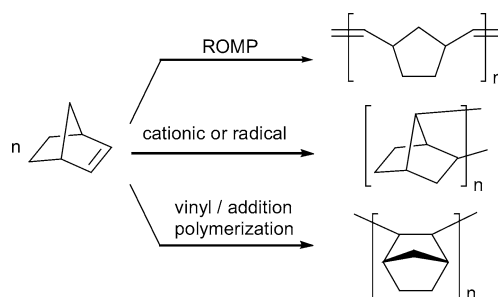
The polymerization behavior of novel polynuclear cage complexes as precatalysts in the vinyl or addition polymerization of norbornene has been investigated and correlated with the results of the known mononuclear precatalyst  $M(\text{acac})_x$  ( $M = \text{Ni}^{\text{II}}, \text{Co}^{\text{III}}, \text{Cr}^{\text{III}}, \text{and Fe}^{\text{III}}$ , acac = acetylacetonate,  $x = 2$  or 3) and mixtures thereof. The cage complexes can be activated with the Lewis acids methylalumoxane (MAO) as well as with tris(pentafluorophenyl)borane,  $\text{B}(\text{C}_6\text{F}_5)_3$ , in combination with or without triethylaluminum ( $\text{AlEt}_3$ ). It is shown that nickel is the most active metal in the polymerization of norbornene with heterometallic precatalysts. The homo- and heterometallic nickel cage compounds reveal a maximum activity *per nickel* in the presence of “inert metal” atoms—an effect which is not seen when  $\text{Ni}(\text{acac})_2$  is only physically mixed with other metal-acac salts. The inert metal effect may be advantageously applicable to other valuable catalysts when used as heterometallic polynuclear compounds.

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**Keywords:** Polymerization; Norbornene; Nickel; Tris(pentafluorophenyl)borane; Methylalumoxane; Cluster

## 1. Introduction

Heterometallic compounds may offer significant advantages as catalysts. The presence of one metal may influence the reactivity of another, or cooperative binding of different components of a catalyzed reaction may bring the substrates into close proximity. Most previous work on heterometallic homogeneous catalysts has concentrated on low-valent metal clusters [1]. We have begun an investigation into the use of small heterometallic carboxylate cages in catalysis. Metal carboxylate cages are already known to act as catalysts for the oxidation of alkenes [2,3]. Initial results reported here show that some simple cages also show promising reactivity for olefin polymerization, e.g., for the homopolymerization of norbornene. The homopolymerization of norbornene can be accomplished by three different routes with each route leading to its own polymer type with different structure and properties (Scheme 1).



Scheme 1.

Polymers produced via ring-opening metathesis polymerization (ROMP) still contain double bonds in the polymer backbone and can be obtained by a number of transition metals in high oxidation state [4–6]. Only few reports describe the formation of low-molar-mass oligomeric materials with 2,7-connectivity of the monomer from the cationic or radical homopolymerization of norbornene [7]. Finally, the vinyl or addition polymerization of norbornene yields saturated 2,3-inserted rotationally constrained polymers in which the bicyclic structural unit remains intact and only the double

\* Corresponding author.

E-mail addresses: janiak@uni-freiburg.de (C. Janiak), richard.winpenny@man.ac.uk (R.E.P. Winpenny).

bond of the  $\pi$ -component was opened. Catalysts containing the metals titanium [8,9], zirconium [10–14], chromium [15], and currently the late transition metals cobalt [16–18], nickel [19–34], and palladium [32,35–50] are described in the literature for the vinyl/addition polymerization of norbornene [51–58]. With regard to multinuclear catalysts only a few examples of homodinuclear  $\text{Ni}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Cr}^{\text{III}}$  complexes [15,18,22,24,59] were previously investigated for norbornene polymerization [51].

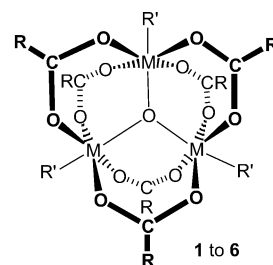
The late-transition-metal complexes are commonly activated with methylalumoxane (MAO) [20–23,37,51], except for the cationic palladium complexes  $[\text{Pd}(\text{NCR})_4]^{2+}2\text{A}^-$  (NCR weakly bound nitrile ligand; A = “non”-coordinating counterion) [38–48]. Another cocatalytic system for the activation of metal complexes is the organo-Lewis acid tris(pentafluorophenyl)borane,  $\text{B}(\text{C}_6\text{F}_5)_3$ , with or without triethylaluminum ( $\text{AlEt}_3$ ). This cocatalytic system is known from the activation process of early transition-metal group 4 metallocene catalysts in olefin polymerization [60–68] and was recently also applied to the activation of late-transition-metal complexes for the (co)polymerization of cyclopentene [69], ethene [70], norbornene, and norbornene derivatives [19,34,35,52–58].

In this work three families of structurally characterized cages have been studied as precatalysts for the vinyl polymerization of norbornene using MAO as cocatalyst: a series of  $\{\text{M}_3\text{O}\}$  and  $\{\text{M}_2\text{NiO}\}$  oxo-centered triangles **1–6** ( $\text{M} = \text{Cr}^{\text{III}}$  or  $\text{Fe}^{\text{III}}$ ) [71–74], a series of homometallic  $\{\text{Ni}_2\}$  and  $\{\text{Ni}_4\}$  cages **7–10** [75], and a series of  $\{\text{Cr}_7\text{M}(\mu\text{-F})_8\}$  wheels **11–16** ( $\text{M} = \text{Cr}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ) [75–77] (Scheme 2). In addition the cages have mostly the pivalate anion ( $^-\text{O}_2\text{C}^t\text{Bu}$ ) as bridging ligands between the metal atoms. Different terminal ligands ( $\text{H}_2\text{O}$ ,  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $^t\text{BuCO}_2\text{H}$ , nitrogen bases) can conclude the metal coordination sphere.

## 2. Experimental

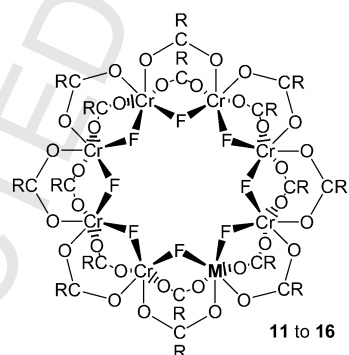
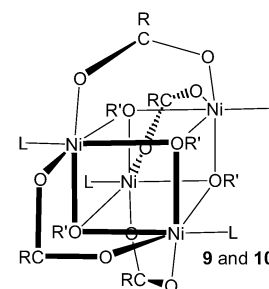
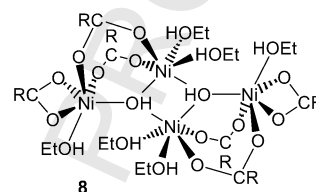
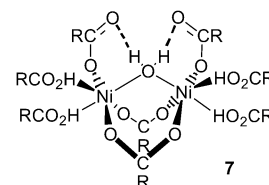
### 2.1. General procedures

All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk, or drybox techniques. IR spectra (KBr pellet) were measured on a Bruker Optik IFS 25. Gel-permeation chromatography (GPC) analyses were performed on a PL-GPC 220 (columns PL gel 10  $\mu\text{m}$  MIXED-B) with polymer solutions in 1,2,4-trichlorobenzene (concentration of 2–3 mg/mL). The GPC was measured at 140 °C with an injection volume of 200  $\mu\text{L}$  and with a flow rate of 1 mL/min. The  $^1\text{H}$  NMR spectra of the poly(norbornene)s (50–60 mg PNB/0.5 mL of *o*-1,4-dichlorobenzene- $d_4$ ) were recorded on a Bruker Avance 500 operating at 500 MHz ( $^1\text{H}$  NMR) and 333 K (60 °C). Chemical shifts were referenced against the solvent signal from the residual proton resonances (*o*- $\text{C}_6\text{D}_4\text{Cl}_2$  7.21 and 6.95 ppm).



- 1**  $[\text{Cr}_3\text{O}(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})_3]\text{ClO}_4$  57  
**2**  $[\text{Cr}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3]\text{O}_2\text{C}^t\text{Bu}$  58  
**3**  $[\text{Cr}_2\text{NiO}(\text{O}_2\text{C}^t\text{Bu})_6(\text{pip})_3]$  59  
**4**  $[\text{Fe}_3\text{O}(\text{O}_2\text{C}^t\text{Bu})_6(\text{H}_2\text{O})_3]\text{O}_2\text{C}^t\text{Bu}$  60  
**5**  $[\text{Fe}_2\text{NiO}(\text{O}_2\text{C}^t\text{Bu})_6(\text{pip})_3]$  61  
**6**  $[\text{Fe}_2\text{NiO}(\text{O}_2\text{C}^t\text{Bu})_6(\text{mor})_3]$  62  
 pip = piperidine, mor = morpholine; 63  
 Ni atoms are disordered over  $\text{M}_3$  64

- 7**  $[\text{Ni}_2(\text{H}_2\text{O})(\text{O}_2\text{C}^t\text{Bu})_4(\text{HO}_2\text{C}^t\text{Bu})_4]$  66  
**8**  $[\text{Ni}_4(\text{OH})_2(\text{O}_2\text{C}^t\text{Bu})_6(\text{EtOH})_6]$  67  
**9**  $[\text{Ni}_4(\text{OCH}_3)_4(\text{O}_2\text{C}^t\text{Bu})_4(\text{MeOH})_4]$  68  
 $\text{R}' = \text{CH}_3$ ,  $\text{L} = \text{MeOH}$  69  
**10**  $[\text{Ni}_4(\text{O}_2\text{C}^t\text{Bu})_4(\text{OMq})_4]$  70  
 $\text{R}' = (\text{O})\text{Mq}$ ,  $\text{L} = \text{N}(\text{Mq})$  71  
 HOMq = 6-hydroxy-2-methylquinoline 72



- (Cat) $[\text{Cr}_7\text{MF}_8(\text{O}_2\text{C}^t\text{Bu})_{16}]$  83  
**11** no cation,  $\text{M} = \text{Cr}^{\text{III}}$  84  
**12** Cat =  $\text{Me}_2\text{NH}_2^+$ ,  $\text{M} = \text{Ni}^{\text{II}}$  85  
**13** Cat =  $\text{Et}_2\text{NH}_2^+$ ,  $\text{M} = \text{Ni}^{\text{II}}$  86  
**14** Cat =  $\text{Et}_2\text{NH}_2^+$ ,  $\text{M} = \text{Co}^{\text{II}}$  87  
**15** Cat =  $\text{Et}_2\text{NH}_2^+$ ,  $\text{M} = \text{Mn}^{\text{II}}$  88  
**16** Cat =  $^n\text{Bu}_2\text{NH}_2^+$ ,  $\text{M} = \text{Fe}^{\text{II}}$  89  
 M atoms are disordered over  $\text{Cr}_7\text{M}$  90

Scheme 2.

### 2.2. Materials

Methylalumoxane (10% solution in toluene, Witco), tris(pentafluorophenyl)borane (Aldrich), and triethylaluminum (1 mol/L solution in hexane, Merck-Schuchardt) were used as received. Toluene was dried over sodium metal, distilled, and stored under nitrogen. Methylene chloride was dried over  $\text{CaH}_2$  and distilled under argon prior to use. Norbornene (bicyclo[2.2.1]hept-2-ene, Aldrich) was purified by distillation and used as a solution in toluene. The precatalysts **1–6** [71–74], **7–10** [75], and **11–16** [75–77] were synthesized by published literature procedures.

### 2.3. Polymerization procedures

#### 2.3.1. General

The precatalysts were applied as a fine suspension via ultrasonication (for precatalysts **1**) or as solutions (for precatalysts **2 to 16**) in methylene chloride. Polymerizations were

1 conducted at room temperature in a water bath to ensure  
2 a constant temperature during the reaction. Polymerization  
3 runs were carried out at least three times to ensure repro-  
4 ducibility. The IR spectra of the poly(norbornene)s obtained  
5 with the catalysts **1** to **16** showed the absence of double  
6 bond at 1620 to 1680 cm<sup>-1</sup>. This ensured the vinyl/addition  
7 polymerization instead of a ring-opening metathesis poly-  
8 merization. The conversion was calculated by gravimetric  
9 analysis of the polymer.

### 11 2.3.2. General procedure for the homopolymerization of 12 norbornene with MAO as cocatalyst

13 A Schlenk flask was charged with the norbornene solu-  
14 tion and the MAO solution was added. After 1 min the solu-  
15 tion or suspension of the precatalyst was added via syringe  
16 and the mixture was stirred with a magnetic stirrer. The poly-  
17 merization was stopped through the addition of 30 mL of a  
18 10/1 methanol/concd HCl mixture. The precipitated poly-  
19 mer was filtered, washed with methanol, and dried in vacuo  
20 for 5 h. To rule out an affect of activation time the solution  
21 or suspension of the precatalyst was reacted with MAO for  
22 10 min. The polymerization was started by the addition of  
23 norbornene and stopped by the described procedure.

### 25 2.3.3. General procedure for the homopolymerization of 26 norbornene with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> as cocatalysts

27 A Schlenk flask was charged with the norbornene solu-  
28 tion. The solution or suspension of the precatalyst followed  
29 by the separate cocatalyst components [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and AlEt<sub>3</sub>]  
30 was quickly added via syringe and the mixture was stirred  
31 with a magnetic stirrer. The polymerization was stopped  
32 through the addition of 40 mL of a 10/1 methanol/concd  
33 HCl mixture. The precipitated polymer was filtered, washed  
34 with methanol, and dried in vacuo for 5 h.

35 From studies of a number of metal complexes which did  
36 not show any polymerization activity with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>,  
37 we conclude that the combination of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> alone  
38 is not polymerization active.

## 40 3. Results and discussion

41 The polymerization results are summarized in Table 1.  
42 The activity of the homometallic, Ni-free triangles (**1**, **2**, **4**)  
43 is much less (by a factor of 10<sup>2</sup>–10<sup>3</sup>) than the heterometallic  
44 {M<sub>2</sub>Ni} triangles (**3**, **5**, **6**). The latter have similar activi-  
45 ties of around 10<sup>7</sup> g<sub>polymer</sub> mol<sub>metal</sub><sup>-1</sup> h<sup>-1</sup>. They are already  
46 10-fold more active *per metal* than Ni(acac)<sub>2</sub>/MAO under  
47 equivalent conditions. Also the Cr<sub>3</sub> cages are 5 to 10 times  
48 more active *per metal* than mononuclear Cr(acac)<sub>3</sub>/MAO  
49 under equivalent conditions (see Table 1).

50 Nickel(II) is clearly vital for a high polymerization ac-  
51 tivity; unfortunately the oxo-centered {Ni<sub>3</sub>} triangle is not  
52 known. The four homometallic {Ni<sub>2</sub>} and {Ni<sub>4</sub>} cages  
53 **7–10** show similar high activities of around 1.5 × 10<sup>7</sup>

54 g<sub>polymer</sub> mol<sub>metal</sub><sup>-1</sup> h<sup>-1</sup> (Table 1). On a per metal basis this ac-  
55 tivity matches those of the heterometallic {M<sub>2</sub>Ni} triangles  
56 **3**, **5**, and **6**, yet, the activity of the {Ni<sub>2</sub>} and {Ni<sub>4</sub>} cages *per*  
57 *nickel* is lower than in the {M<sub>2</sub>Ni} mixed-metal systems.

58 The final group of complexes examined have the general  
59 formula (Cat)[Cr<sub>7</sub>M(μ-F)<sub>8</sub>(μ-O<sub>2</sub>C<sup>t</sup>Bu)<sub>16</sub>] (M = Cr<sup>III</sup>, Ni<sup>II</sup>,  
60 Co<sup>II</sup>, Mn<sup>II</sup>, Fe<sup>II</sup>) (**11–16**) and the common structure of an  
61 octanuclear wheel. A secondary ammonium cation is found  
62 within the cavity of the wheels in **12–16** [75–77].

63 The activity of **11–16** (Table 1) shows the same trend  
64 observed for the heterometallic trinuclear cages **1–6**. With  
65 no nickel present (**11**, **14**, **15**, and **16**) the activity of the  
66 {Cr<sub>7</sub>M(μ-F)<sub>8</sub>} wheels is mediocre around 10<sup>5</sup> g<sub>polymer</sub> ×  
67 mol<sub>metal</sub><sup>-1</sup> h<sup>-1</sup> or less. Incorporation of Ni<sup>II</sup> as {Cr<sub>7</sub>Ni(μ-F)<sub>8</sub>}  
68 in **12** and **13** increases the activity of the wheels by almost  
69 two orders of magnitude. A comparison of the activities of  
70 **1–16** shows an approximately equivalent activity per metal  
71 of 10<sup>7</sup> g<sub>polymer</sub> mol<sub>metal</sub><sup>-1</sup> h<sup>-1</sup> when at least one Ni<sup>II</sup> is present,  
72 regardless of whether the cage contains four Ni centers, or  
73 seven Cr and only one Ni. Yet the activity per nickel is  
74 highest in the {Cr<sub>7</sub>Ni(μ-F)<sub>8</sub>} wheels **12** and **13** with 10<sup>8</sup>  
75 g<sub>polymer</sub> mol<sub>nickel</sub><sup>-1</sup> h<sup>-1</sup>. Also the homometallic Cr<sub>8</sub> wheel **11**  
76 has a higher activity than Cr(acac)<sub>3</sub>.

77 The activity of the Ni-containing catalysts is graphically  
78 depicted in Fig. 1. The activity of the cages depends on the  
79 presence of Ni<sup>II</sup>, but, unexpectedly, the activity per nickel is  
80 higher in the heterometallic than in the homometallic cages.  
81 This activity trend is difficult to explain, but suggests that  
82 the clusters must retain some portion of their structure in  
83 solution; complete decomposition would lead to similar ac-  
84 tivities per nickel rather than per metal. Electrospray MS of  
85 solutions of **12** to **16** suggests that the structures are largely  
86 retained in solution, albeit under different conditions than  
87 those used in the catalytic studies.

88 To rule out an effect of activation time the precatalysts  
89 were reacted with MAO for 10 min before the addition of  
90 monomer (column PA in Table 1 and “with preactivation”  
91 in Fig. 1). A comparison reveals some effect but not as pro-  
92 nounced as to invalidate the above trends. Also the “appar-  
93 ent activity” is usually defined as to include the activation  
94 process. In many catalytic processes the active species is not  
95 fully known. So, if a precatalyst is more slowly activated or  
96 does not fully reach the active species in some sort of equi-  
97 librium then this precatalyst will be considered less active.  
98 Furthermore, a 10-min preactivation time may already in-  
99 clude some decay for highly active species. The nature of  
100 the active species will be the subject of future work.

101 The high activity of the heterometallic nickel complexes  
102 may be reasoned as a “metal dilution” effect. A decrease  
103 in metal concentration with respect to monomer, that is,  
104 an increase in the monomer/metal ratio was shown to lead  
105 to an increase in activity [37]. The same molar amount of  
106 10.6 × 10<sup>-3</sup> mmol metal in a total volume of 10 mL was  
107 used in the typical polymerization experiments. Depending  
108 on the nickel fraction in the cages this translates into 10.6 ×  
109 10<sup>-3</sup> mmol of Ni in complexes **7–10** and in Ni(acac)<sub>2</sub> while  
110  
111  
112

Table 1  
Norbornene (NB) polymerization activities of complexes **1** to **16** and MAO as cocatalyst<sup>a</sup>

Complex	Metal core	Time [min]	Polymer yield [%] <sup>b</sup>		Activity			
			NPA <sup>c</sup>	PA <sup>c</sup>	[g <sub>polymer</sub> /mol <sub>metal</sub> h]		[g <sub>polymer</sub> /mol <sub>Ni</sub> h]	
					NPA <sup>c</sup>	PA <sup>c</sup>	NPA <sup>c</sup>	PA <sup>c</sup>
<b>1</b> <sup>d</sup>	Cr <sub>3</sub>	10	30.4	–	1.7 × 10 <sup>5</sup>	–	–	–
<b>2</b>	Cr <sub>3</sub>	60	53.1	–	5.0 × 10 <sup>4</sup>	–	–	–
<b>3</b>	Cr <sub>2</sub> Ni	1/6	45.6	41.9	1.5 × 10 <sup>7</sup>	1.4 × 10 <sup>7</sup>	4.8 × 10 <sup>7</sup>	4.3 × 10 <sup>7</sup>
<b>4</b>	Fe <sub>3</sub>	60	6.8	–	6.4 × 10 <sup>3</sup>	–	–	–
<b>5</b>	Fe <sub>2</sub> Ni	1/6	60.6	20.3	2.1 × 10 <sup>7</sup>	6.9 × 10 <sup>6</sup>	6.5 × 10 <sup>7</sup>	2.1 × 10 <sup>7</sup>
<b>6</b>	Fe <sub>2</sub> Ni	1/6	28.6	24.8	9.7 × 10 <sup>6</sup>	8.4 × 10 <sup>6</sup>	2.9 × 10 <sup>7</sup>	2.5 × 10 <sup>7</sup>
<b>7</b>	Ni <sub>2</sub>	1/6	39.3	58.2	1.3 × 10 <sup>7</sup>	2.0 × 10 <sup>7</sup>	1.3 × 10 <sup>7</sup>	2.0 × 10 <sup>7</sup>
<b>8</b>	Ni <sub>4</sub>	1/6	45.2	54.4	1.5 × 10 <sup>7</sup>	1.9 × 10 <sup>7</sup>	1.5 × 10 <sup>7</sup>	1.9 × 10 <sup>7</sup>
<b>9</b>	Ni <sub>4</sub>	1/6	49.6	62.7	1.7 × 10 <sup>7</sup>	2.1 × 10 <sup>7</sup>	1.7 × 10 <sup>7</sup>	2.1 × 10 <sup>7</sup>
<b>10</b>	Ni <sub>4</sub>	1/6	46.4	–	1.6 × 10 <sup>7</sup>	–	1.6 × 10 <sup>7</sup>	–
<b>11</b>	Cr <sub>8</sub>	10	46.4	–	2.6 × 10 <sup>5</sup>	–	–	–
<b>12</b>	Cr <sub>7</sub> Ni	1/6	44.2	25.7	1.5 × 10 <sup>7</sup>	8.7 × 10 <sup>6</sup>	1.2 × 10 <sup>8</sup>	7.0 × 10 <sup>7</sup>
<b>13</b>	Cr <sub>7</sub> Ni	1/6	36.7	28.2	1.2 × 10 <sup>7</sup>	9.6 × 10 <sup>6</sup>	9.8 × 10 <sup>7</sup>	2.9 × 10 <sup>7</sup>
<b>14</b>	Cr <sub>7</sub> Co	10	19.4	–	1.1 × 10 <sup>5</sup>	–	–	–
<b>15</b>	Cr <sub>7</sub> Mn	60	29.7	–	2.8 × 10 <sup>4</sup>	–	–	–
<b>16</b>	Cr <sub>7</sub> Fe	10	26.0	–	1.5 × 10 <sup>5</sup>	–	–	–
<b>1–16</b> <sup>e</sup>		60	0	–	0	–	0	–
Ni(acac) <sub>2</sub>	10.6 × 10 <sup>-3</sup> mmol	1	62.9	–	3.6 × 10 <sup>6</sup>	–	3.6 × 10 <sup>6</sup>	–
Ni(acac) <sub>2</sub> <sup>f</sup>	1.325 × 10 <sup>-3</sup> mmol	1	48.3	–	2.2 × 10 <sup>7</sup>	–	2.2 × 10 <sup>7</sup>	–
Co(acac) <sub>3</sub>		60	0.4	–	3.5 × 10 <sup>2</sup>	–	–	–
Cr(acac) <sub>3</sub>		60	11.0	–	1.0 × 10 <sup>4</sup>	–	–	–
Fe(acac) <sub>3</sub>		60	6.8	–	6.4 × 10 <sup>3</sup>	–	–	–
Ni(acac) <sub>2</sub> /Co(acac) <sub>3</sub>	1/7 <sup>g</sup>	5	3.4	–	3.9 × 10 <sup>4</sup>	–	3.1 × 10 <sup>5</sup>	–
Ni(acac) <sub>2</sub> /Cr(acac) <sub>3</sub>	1/7 <sup>g</sup>	1	12.5	–	7.1 × 10 <sup>5</sup>	–	5.7 × 10 <sup>6</sup>	–
Ni(acac) <sub>2</sub> /Fe(acac) <sub>3</sub>	1/7 <sup>g</sup>	1	49.6	–	2.8 × 10 <sup>6</sup>	–	2.2 × 10 <sup>7</sup>	–

<sup>a</sup> General conditions: 10.6 × 10<sup>-3</sup> mmol metal<sub>complex</sub> (solution in 4.0 mL CH<sub>2</sub>Cl<sub>2</sub>), 1.06 mmol Al<sub>MAO</sub> (solution in toluene, metal/Al = 1/100), 1.00 g (10.6 mmol) NB (solution in toluene, metal/NB = 1/1000), total volume 10.0 mL, room temperature, start of the polymerization see under c, termination by the addition of a methanol/concd HCl solution.

<sup>b</sup> Yield = *m*(polymer)/1.00 g(NB) × 100%, corresponds to conversion.

<sup>c</sup> NPA, no preactivation, polymerization start by addition of metal complex solution; PA, with preactivation, metal complex and MAO were stirred for 10 min, start of the polymerization by the addition of NB; no entry means that the experiment has not been carried out.

<sup>d</sup> Fine suspension of the catalyst in CH<sub>2</sub>Cl<sub>2</sub> through ultrasonication.

<sup>e</sup> No MAO cocatalyst.

<sup>f</sup> 1.325 × 10<sup>-3</sup> mmol Nickel<sub>complex</sub> (solution in 4.0 mL CH<sub>2</sub>Cl<sub>2</sub>).

<sup>g</sup> 10.6 × 10<sup>-3</sup> mmol metal<sub>complex</sub> including 1.325 × 10<sup>-3</sup> mmol Nickel<sub>complex</sub> (solution in 4.0 mL CH<sub>2</sub>Cl<sub>2</sub>).

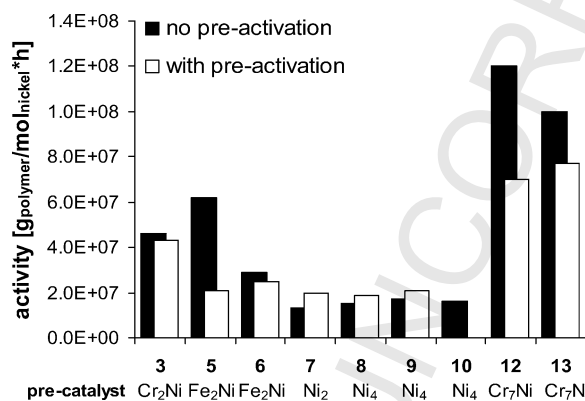


Fig. 1. Polymerization activities per nickel of nickel-containing pre-catalysts with and without activation time. Detailed conditions are given in Table 1.

the least for any of the nickel-containing complexes was supplied in the {Cr<sub>7</sub>Ni(μ-F)<sub>8</sub>} wheels **12** and **13** with 1.325 ×

10<sup>-3</sup> mmol of Ni. To test for this dilution effect we have run the polymerization experiments also with a Ni(acac)<sub>2</sub> amount of 1.325 × 10<sup>-3</sup> mmol. The activity does indeed increase from 3.6 × 10<sup>6</sup> g<sub>polymer</sub> mol<sub>Ni</sub><sup>-1</sup> h<sup>-1</sup> for 10.6 × 10<sup>-3</sup> mmol of Ni(acac)<sub>2</sub> to 2.2 × 10<sup>7</sup> g<sub>polymer</sub> mol<sub>Ni</sub><sup>-1</sup> h<sup>-1</sup> for 1.325 × 10<sup>-3</sup> mmol of Ni(acac)<sub>2</sub> (see Fig. 2).

Furthermore, it could be argued that a complicated combination of metals in one compound is not needed since the heterometallic complex will disintegrate upon activation with MAO and a simple physical mixture of metal salts may have had the same effect. This hypothesis was tested with the precatalysts M(acac)<sub>x</sub> with M = Ni<sup>II</sup>, Co<sup>III</sup>, Cr<sup>III</sup>, and Fe<sup>III</sup>, *x* = 2 and 3, respectively, and acac = acetylacetonate. The results are graphically depicted in Fig. 2. As expected Ni(acac)<sub>2</sub> is up to 10<sup>5</sup>-fold more active than the corresponding Co<sup>III</sup>-, Cr<sup>III</sup>-, and Fe<sup>III</sup>-acac precatalysts. Mixtures of Ni(acac)<sub>2</sub> with Co<sup>III</sup>-, Cr<sup>III</sup>-, and Fe<sup>III</sup>-acac in a 1/7 Ni-to-metal ratio are less active on a per nickel basis for Co

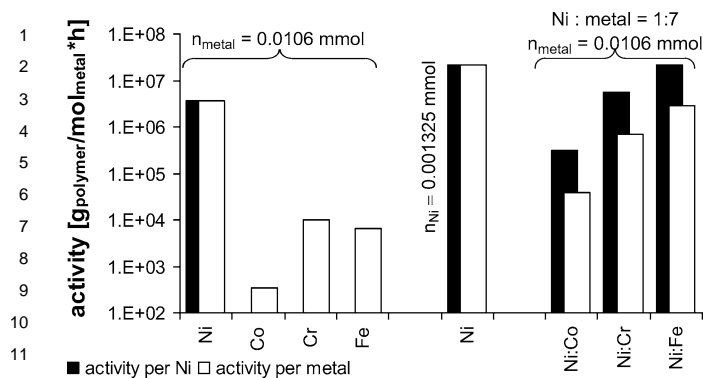


Fig. 2. Polymerization activities of the pre-catalysts  $M(\text{acac})_x$  with  $M = \text{Ni(II)}, \text{Co(III)}, \text{Cr(III)}, \text{Fe(III)}$ ,  $x = 2$  (Ni) or 3 (Co, Cr, Fe), acac = acetylacetonate and mixtures of  $\text{Ni}(\text{acac})_2$  and  $M(\text{acac})_3$  ( $M = \text{Co}, \text{Cr}, \text{Fe}$ ) using a molar ratio of 1/7. The pre-catalysts were activated with the cocatalyst MAO and the polymerization activities were calculated per metal as well as per nickel. Detailed conditions are given in Table 1.

Table 2

Polymer characteristics of selected polymer samples from gel-permeation chromatography (detailed conditions are given in Table 1)

Catalyst	Metal core	$M_n$ [g mol <sup>-1</sup> ]	$M_w$ [g mol <sup>-1</sup> ]	$Q = M_w/M_n$
3/MAO	Cr <sub>2</sub> Ni	$2.1 \times 10^5$	$6.2 \times 10^5$	2.9
5/MAO	Fe <sub>2</sub> Ni	$1.3 \times 10^5$	$4.2 \times 10^5$	3.1
7/MAO	Ni <sub>2</sub>	$2.6 \times 10^5$	$6.6 \times 10^5$	2.5
8/MAO	Ni <sub>4</sub>	$2.1 \times 10^5$	$6.7 \times 10^5$	3.1
9/MAO	Ni <sub>4</sub>	$2.5 \times 10^5$	$7.5 \times 10^5$	3.0

and Cr than  $\text{Ni}(\text{acac})_2$  alone at a molar amount of  $1.325 \times 10^{-3}$  mmol. Only the mixture of  $\text{Ni}(\text{acac})_2$  and  $\text{Fe}(\text{acac})_3$  was found not to be deactivating in comparison to the same molar amount of  $\text{Ni}(\text{acac})_2$  alone (see Fig. 2). In particular a mixture of  $\text{Ni}(\text{acac})_2$  and  $\text{Cr}(\text{acac})_3$  with the corresponding molar ratio of Ni/Cr = 1/7 as in the  $\{\text{Cr}_7\text{Ni}(\mu\text{-F})_8\}$  wheels **12** and **13** was found 20 times less active than the latter. Thus, the admixture of  $\text{Cr}(\text{acac})_3$  to  $\text{Ni}(\text{acac})_2$  can be viewed as deactivating.

The activity-enhancing effect of the “inert metals” requires their close proximity to the active centers within a single compound. This supports the notion that the heterometallic complexes **1–16** remain at least in part intact upon activation with MAO. As a mode of action of the inert metal centers we suggest that the hard metal Cr<sup>III</sup> may exert an electron-withdrawing effect on the adjacent active nickel centers. Furthermore, the oxophilic Cr<sup>III</sup> after partial ligand abstraction through MAO may function as a scavenger toward impurities in the near vicinity of the active nickel center. Also, having the active nickel center embedded in a heterometallic complex creates a protective and stabilizing matrix akin of the peptide hull in metalloenzymes.

Selected polymer samples were investigated by gel-permeation chromatography and displayed monomodal molar mass distribution curves with  $M_w/M_n$  around 3, somewhat broadened when compared to a theoretical Schulz-Flory-type distribution of 2 for an ideally behaved polymerization

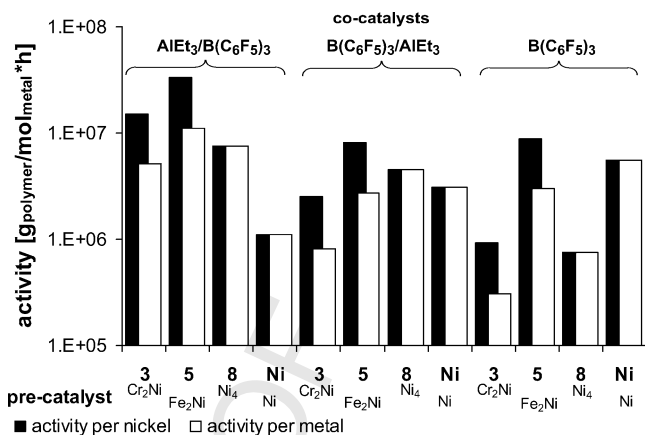


Fig. 3. Activities of the pre-catalysts **3**, **5**, **8**, and  $\text{Ni}(\text{acetylacetonate})_2$  with  $\text{B}(\text{C}_6\text{F}_5)_3/\text{AlEt}_3$  or  $\text{B}(\text{C}_6\text{F}_5)_3$  alone as cocatalyst in the polymerization of norbornene. The polymerization activities were calculated per metal as well as per nickel. Detailed conditions are given in Table 3.

with a chain-termination reaction (see Table 2). A dispersity of 3 can be explained with a homogeneous catalyst species and its very high activity which gives rise to a viscous reaction mixture within a few seconds.

In order to gain additional information about the activation process the activator was changed from MAO to the better defined cocatalyst  $\text{B}(\text{C}_6\text{F}_5)_3$  with or without triethylaluminum ( $\text{AlEt}_3$ ). The pre-catalysts **3** ( $\text{Cr}_2\text{Ni}$ ), **5** ( $\text{Fe}_2\text{Ni}$ ), and **8** ( $\text{Ni}_4$ ) were tested in the vinyl/addition polymerization of norbornene using different kinds of addition sequences for the cocatalytic system and the results are summarized in Table 3 and Fig. 3. For comparison the polymerization data of  $\text{Ni}(\text{acac})_2$  are included.

The hetero- and homometallic complexes **3**, **5**, and **8** can be transformed into highly active catalysts for the vinyl or addition polymerization of norbornene in combination with appropriate borane-containing cocatalysts and the activities cover a range of  $7.5 \times 10^5$  (**8**/ $\text{B}(\text{C}_6\text{F}_5)_3$ ) to  $3.3 \times 10^7$   $\text{g}_{\text{polymer}}/\text{mol}_{\text{Ni}} \text{ h}$  (**5**/ $\text{AlEt}_3/\text{B}(\text{C}_6\text{F}_5)_3$ ) when calculating the polymerization activities per nickel. With the exception of an activation with the Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  alone the polymerization activities of the pre-catalysts **3**, **5**, and **8** are in the range or even higher than that of the reference compound  $\text{Ni}(\text{acac})_2$ . It is interesting to note that the addition sequence of the cocatalytic compounds  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{AlEt}_3$  influences the polymerization activity.

The higher activities are obtained using the addition sequence “pre-catalyst  $\rightarrow \text{AlEt}_3 \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$ ” instead of “pre-catalyst  $\rightarrow \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{AlEt}_3$ .” The equimolar combination of  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{AlEt}_3$  leads to a facile aryl/alkyl group exchange and results in the formation of  $\text{Al}(\text{C}_6\text{F}_5)_3$  as the main product [78,79]. Accordingly,  $\text{B}(\text{C}_6\text{F}_5)_3$  with an equivalent of  $\text{AlEt}_3$  undergoes an analogous ligand exchange reaction and the <sup>19</sup>F NMR spectrum showed the expected signals of  $\text{Al}(\text{C}_6\text{F}_5)_3$  at  $-122.3$  ppm (*o*-F),  $-152.2$  ppm (*p*-F), and  $-161.7$  ppm (*m*-F). Also, the <sup>19</sup>F NMR spectrum revealed the formation of heteroleptic and possibly

Table 3

Polymerization of norbornene (NB) with complexes **3**, **5**, and **8** and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>–(AlEt<sub>3</sub>) as cocatalyst<sup>a</sup>

Catalyst <sup>a</sup> /sequence of addition/	Metal core	Time [min]	Polymer yield [%] <sup>b</sup>	Activity	
				[g <sub>polymer</sub> /mol <sub>metal</sub> h]	[g <sub>polymer</sub> /mol <sub>Ni</sub> h]
<b>3</b> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Cr <sub>2</sub> Ni	1/6	15.0	5.1 × 10 <sup>6</sup>	1.5 × 10 <sup>7</sup>
<b>5</b> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Fe <sub>2</sub> Ni	1/6	32.6	1.1 × 10 <sup>7</sup>	3.3 × 10 <sup>7</sup>
<b>8</b> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni <sub>4</sub>	1/6	22.2	7.6 × 10 <sup>6</sup>	7.6 × 10 <sup>6</sup>
Ni(acac) <sub>2</sub> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni	1	18.8	1.1 × 10 <sup>6</sup>	1.1 × 10 <sup>6</sup>
<b>3</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Cr <sub>2</sub> Ni	1	14.6	8.2 × 10 <sup>5</sup>	2.5 × 10 <sup>6</sup>
<b>5</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Fe <sub>2</sub> Ni	1	47.5	2.7 × 10 <sup>6</sup>	8.1 × 10 <sup>6</sup>
<b>8</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Ni <sub>4</sub>	1	78.7	4.5 × 10 <sup>6</sup>	4.5 × 10 <sup>6</sup>
Ni(acac) <sub>2</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Ni	1	54.8	3.1 × 10 <sup>6</sup>	3.1 × 10 <sup>6</sup>
<b>3</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Cr <sub>2</sub> Ni	5	27.5	3.1 × 10 <sup>5</sup>	9.3 × 10 <sup>5</sup>
<b>5</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Fe <sub>2</sub> Ni	1	52.1	3.0 × 10 <sup>6</sup>	8.9 × 10 <sup>6</sup>
<b>8</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni <sub>4</sub>	1	13.3	7.5 × 10 <sup>5</sup>	7.5 × 10 <sup>5</sup>
Ni(acac) <sub>2</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni	1	97.4	5.5 × 10 <sup>6</sup>	5.5 × 10 <sup>6</sup>
<b>3</b> , <b>5</b> , <b>8</b> , Ni(acac) <sub>2</sub> /AlEt <sub>3</sub>		60	0	0	0

<sup>a</sup> General conditions: 0.03 mmol metal<sub>complex</sub> (solution in 10.0 mL CH<sub>2</sub>Cl<sub>2</sub>), 0.27 mmol B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (solution in 14 mL toluene, metal/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> = 1/9), 0.3 mmol AlEt<sub>3</sub> (solution in 0.3 mL hexane, metal/Al = 1/10), 2.834 g (30.1 mmol) NB (solution in toluene, metal/NB = 1/1000), total volume 40.0 mL, room temperature.

<sup>b</sup> Yield =  $m(\text{polymer})/2.834 \text{ g}(\text{NB}) \times 100\%$ , corresponds to conversion.

Table 4

Polymer characteristics of selected polymer samples from gel-permeation chromatography (detailed conditions are given in Table 3)

Catalyst	Metal core	$M_n$ [g mol <sup>-1</sup> ]	$M_w$ [g mol <sup>-1</sup> ]	$Q = M_w/M_n$
<b>3</b> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Cr <sub>2</sub> Ni		Not soluble	
<b>5</b> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Fe <sub>2</sub> Ni	1.4 × 10 <sup>5</sup>	3.0 × 10 <sup>5</sup>	2.2
<b>8</b> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni <sub>4</sub>	2.3 × 10 <sup>5</sup>	4.8 × 10 <sup>5</sup>	2.1
Ni(acac) <sub>2</sub> /AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni	2.3 × 10 <sup>5</sup>	4.2 × 10 <sup>5</sup>	1.8
<b>3</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Cr <sub>2</sub> Ni	2.7 × 10 <sup>5</sup>	7.9 × 10 <sup>5</sup>	2.9
<b>5</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Fe <sub>2</sub> Ni	1.3 × 10 <sup>5</sup>	2.5 × 10 <sup>5</sup>	1.9
<b>8</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Ni <sub>4</sub>	1.4 × 10 <sup>5</sup>	4.8 × 10 <sup>5</sup>	3.5
Ni(acac) <sub>2</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	Ni	8.2 × 10 <sup>4</sup>	2.6 × 10 <sup>5</sup>	3.2
<b>3</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Cr <sub>2</sub> Ni	6.2 × 10 <sup>5</sup>	1.4 × 10 <sup>6</sup>	2.2
<b>5</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Fe <sub>2</sub> Ni	3.5 × 10 <sup>5</sup>	9.3 × 10 <sup>5</sup>	2.6
<b>8</b> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni <sub>4</sub>	5.1 × 10 <sup>5</sup>	1.0 × 10 <sup>6</sup>	2.0
Ni(acac) <sub>2</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ni	5.1 × 10 <sup>5</sup>	1.2 × 10 <sup>6</sup>	2.3

dimeric aluminum species of the type [AlEt<sub>3-x</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>x</sub>]<sub>2</sub> ( $x = 1-2$ ) as side products [32,80]. When AlEt<sub>3</sub> is added first such ligand-exchange reaction can take place rapidly upon the subsequent addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to the catalyst mixture. Thus, the metal complexes will then be activated with the stronger Lewis acid Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. When B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is added first to the metal complex precatalyst the boron atom will coordinate to the donor atom of a ligand to increase its coordination number to four [35]. Such a coordination completes the coordination sphere of the small boron atom and slows the C<sub>6</sub>F<sub>5</sub>/Et-ligand exchange with the subsequently added AlEt<sub>3</sub> [80]. When AlEt<sub>3</sub> is added first it will also coordinate to ligand donor atoms. However, the larger aluminum atom has a more open coordination sphere with coordination number six being possible as well. The slow C<sub>6</sub>F<sub>5</sub>/Et-ligand exchange in the sequence precatalyst → B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> → AlEt<sub>3</sub> gives rise to a number of cocatalytic species of the type AlEt<sub>3-x</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>x</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3-x</sub>Et<sub>x</sub>. This may be the reason for the slight increase in polymer dispersity when compared to polymers from the sequence

precatalyst → AlEt<sub>3</sub> → B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone as a cocatalyst (Table 4).

Beside MAO and the cocatalytic system B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>, the borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone can be used as an effective activator for the new hetero- and homometallic precatalysts. In contrast to MAO, whose exact composition and structure is still not entirely clear, the well-defined nature of the cocatalysts B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> makes possible an investigation of the activation process and a determination of the active species [13,35,64,80–84].

Connections between catalyst type and poly(norbornene) microstructure have been attempted through the use of NMR spectroscopy [21,34]. Arndt and Gosmann reported the different <sup>13</sup>C CPMAS NMR spectra of poly(norbornene)s made with Ni(acac)<sub>2</sub>/MAO (type I), *rac*-[Me<sub>2</sub>Si(Ind)<sub>2</sub>]ZrCl<sub>2</sub>/MAO (type II) and Pd(acac)<sub>2</sub>/MAO (type III) [21]. Goodall and co-workers presented <sup>1</sup>H and <sup>13</sup>C NMR spectra of poly(norbornene)s obtained with [(η<sup>3</sup>-crotyl)Ni(cyclo-octa-1,5-diene)]PF<sub>6</sub> (no cocatalyst) (type PNB1) and with Ni(2,2,6,6-tetramethyl-3,5-heptanedionate)<sub>2</sub> or [Ni(Ph)(Ph<sub>2</sub>

Table 5

Polymer characteristics of selected polymer samples from  $^1\text{H}$  NMR spectroscopy at 60 °C in *o*-dichlorobenzene-d<sub>4</sub>

Polymer type	Complex	
	<b>3</b> (Cr <sub>2</sub> Ni)	<b>8</b> (Ni <sub>4</sub> )
Activator		
MAO	PNB1	PNB1
AlEt <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Not soluble	PNB1
B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /AlEt <sub>3</sub>	PNB2	PNB2
B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	PNB2	PNB2

The designation of the polymer types was adopted from the work of Goodall and co-workers [34].

PCH=C(O)Ph)]<sub>2</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> (type PNB2) [34]. Type I and PNB1 spectra were identical. The different types of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for poly(norbornene) can only be explained by differences in the polymer architectures (tacticity), but broad and unresolved signals in the spectra made it difficult to assign the exact stereochemistry of the polymers. Still, similar NMR spectra of the norbornene homopolymer could suggest related active species and Goodall and co-workers correlated the PNB2-type spectra with an activation of the metal complex through a C<sub>6</sub>F<sub>5</sub> transfer from B to Ni.

Results of the  $^1\text{H}$  NMR investigations of the poly(norbornene)s from **3** (Cr<sub>2</sub>Ni) and **8** (Ni<sub>4</sub>) in combination with different cocatalytic systems are summarized in Table 5. All  $^1\text{H}$  NMR spectra of the investigated poly(norbornene)s showed broad signals in the range of  $\delta = 2.6\text{--}0.9$  ppm and corresponded in each case to the spectra of the two different polymer types (PNB1 or PNB2) pictured in the paper of Goodall and co-workers [34].

Activation of the precatalysts **3** and **8** with MAO led to the polymer type PNB1 which was correlated with a cationic nickel complex as polymerization active species. The  $^1\text{H}$  NMR features of PNB1 were also obtained when activating complex **8** with AlEt<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> using the addition sequence precatalyst  $\rightarrow$  AlEt<sub>3</sub>  $\rightarrow$  B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. On the other hand, activation of the precatalysts **3** and **8** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone or with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and AlEt<sub>3</sub> (sequence precatalyst  $\rightarrow$  B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>  $\rightarrow$  AlEt<sub>3</sub>) led to the polymer-type PNB2, thereby implying a different active species. Thus, the primary addition of an aluminum activator (MAO, AlEt<sub>3</sub>) led to a norbornene homopolymer of type PNB1 whereas primary activation with the borane B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (even when followed by AlEt<sub>3</sub>) resulted in the formation of a PNB2-type polymer. Investigations directed to the activation process of the precatalysts and correlations of the polymer types to the catalyst/cocatalyst system will be part of future work.

#### 4. Conclusions

Polynuclear cage complexes represent a new class of precatalysts for the vinyl/addition polymerization of norbornene. These precatalysts can be activated with the Lewis acids methylalumoxane or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and a combination

of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/triethylaluminum. The novel polynuclear cage complexes clearly show a higher polymerization activity than mononuclear complexes. It is shown that nickel is the most active metal in the polymerization of norbornene with heterometallic precatalysts. The homo- and heterometallic nickel cage compounds reveal a maximum activity per nickel in the presence of inert metal atoms—an effect which is not seen when a nickel salt like Ni(acac)<sub>2</sub> is only physically mixed with other metal-acac salts.

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