

# Solvent-Ligated Manganese(II) Complexes for the Homopolymerization of Isobutene and the Copolymerization of Isobutene and Isoprene

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**Abstract:** Polyisobutenes with a high content of terminal olefinic groups can be synthesized by using manganese(II) initiators in homogeneous solution. These easily accessible complexes initiate the polymerization at room temperature and above, and afford highly reactive, gel-free polyisobutenes with high viscosities. Furthermore, the initia-

tors were successfully used for the copolymerization of isobutene with isoprene. The high activities of the Mn<sup>II</sup> initiators seem to be related to their

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weakly coordinating nitrile ligands, which are easily displaced by substrate molecules. Replacing the nitrile ligands by other more strongly coordinating ligands such as water reduces the initiator activity significantly. The Mn<sup>II</sup> initiators are surprisingly resistant to temperature.

## Introduction

First-row transition-metal complexes of the general formula  $[M(\text{NCCH}_3)_6](\text{A})_2$  ( $M^{\text{II}} = \text{Cr, Mn, Fe, Co, Ni, Cu, Zn}$ ;  $\text{A} =$  counterion) and some of their dimeric second- and third-row congeners of formula  $[M_2(\text{NCCH}_3)_{8-10}](\text{A})_2$  ( $M^{\text{II}} = \text{Mo, Tc, Re, Rh}$ ;  $\text{A} =$  counterion) have been known for several years and have found many interesting applications.<sup>[1,2]</sup> Among these is their use as initiators in the cationic polymerization of cyclopentadiene and methylcyclopentadiene in both homogeneous and heterogeneous phases.<sup>[3]</sup> In this case  $\text{BF}_4^-$  was used as counteranion and the Mn<sup>II</sup> complex was the most active initiator. However, the complexes mentioned above are not active in the polymerization of other

monomers, even at elevated temperatures.<sup>[3h,i]</sup> Replacement of the  $\text{BF}_4^-$  counterions, which coordinate to some of the monomeric metal units through one of their fluorine atoms,<sup>[1x]</sup> by more weakly coordinating ions leads to an extremely high activity in cyclopentadiene polymerization.<sup>[3o]</sup> We have recently shown that the use of these weakly coordinating ions also enables the polymerization and copolymerization of other monomers, one of which is isobutene.<sup>[4]</sup>

Polyisobutenes in general can be divided according to molecular weight into three large groups, which have different properties and uses. High-molecular-weight polyisobutenes with a molecular weight of at least  $120 \text{ kg mol}^{-1}$  are rubber-like polymers and are used, for example, in un-cross-linked rubber goods and as chewing gum base. They are generally produced with Lewis acid initiators and traces of water at temperatures significantly below  $-80^\circ\text{C}$ .<sup>[5]</sup>

Medium-molecular-weight polyisobutenes with molecular weights between 40 and  $120 \text{ kg mol}^{-1}$  are highly viscous liquids, mainly used as glues and sealing compounds.<sup>[5,6]</sup> Low-molecular polyisobutenes have molecular weights of  $0.3\text{--}3 \text{ kg mol}^{-1}$  and are viscous, honeylike liquids. They are available by means of Lewis acidic initiators, for example, aluminum alkyl chlorides or aluminum(III) chloride.<sup>[5,6]</sup> Usually, polyisobutenes prepared in this way contain less than 10% terminal double bonds (often described as  $\alpha$ -olefinic end groups, whereas internal double bonds are known as  $\beta$ -olefinic end groups) and have polydispersities between 2 and 5.

So-called highly reactive polyisobutenes differ from these conventional polyisobutenes. They contain a high percentage of terminal double bonds ( $>60\%$ ). These polymers are used in several applications, such as intermediates in the

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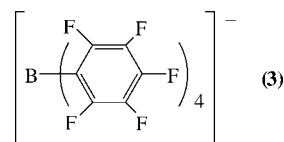
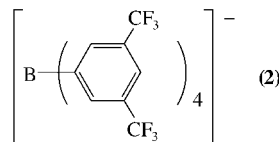
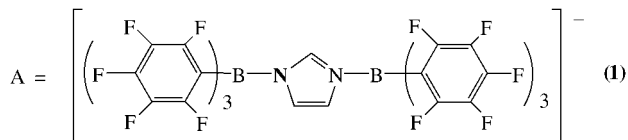
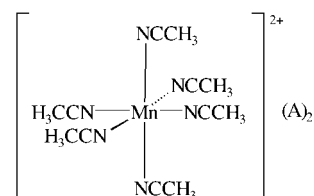
preparation of additives for lubricants and fuels.<sup>[7]</sup> In functionalization reactions the terminal double bonds play a very important role, and therefore a large number of terminal double bonds is an important quality criterion for these polyisobutenes. Adjustable molecular weights of 0.5–5 kg mol<sup>-1</sup> and molecular weight distributions are also of importance for the industrial application of highly reactive polyisobutenes. Several synthetic strategies towards the desired products have been described and patented. They focus mainly on the use of chloride-free, Lewis acid based initiators such as BF<sub>3</sub> for polymerization or aluminum(III) chloride as initiator with an additional step of dehydrochlorination of the thus-obtained chloride-terminated polyisobutenes.<sup>[8]</sup> In all cases the products can only be obtained in good yields and with a percentage of the desired terminal double bonds greater than 80% at reaction temperatures significantly below 0°C. However, performing the reaction at such low temperatures incurs considerable costs and greatly reduces the economy of the process.

Recently, we have published a new polymerization route that uses transition metal complexes as initiators for isobutene polymerization.<sup>[4]</sup> The great advantage of this route is that polymerization is performed at ambient temperature and gives polyisobutenes with molecular weights between 0.5 and 7 kg mol<sup>-1</sup>, mostly with a high content of terminal double bonds. The initiators can also be used for the copolymerization of isobutene and isoprene with incorporation of a high proportion of isoprene in the polymer.

## Results and Discussion

**Synthesis, spectroscopy, reactivity:** The complexes [Mn(NCCH<sub>3</sub>)<sub>6</sub>][N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (**1**), [Mn(NCCH<sub>3</sub>)<sub>6</sub>][B{C<sub>6</sub>H<sub>3</sub>(*m*-CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (**2**), and [Mn(NCCH<sub>3</sub>)<sub>6</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**3**) were synthesized from MnCl<sub>2</sub> and the silver salts AgA (A = [N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub>], [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [B{C<sub>6</sub>H<sub>3</sub>(*m*-CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>]) in acetonitrile. Related compounds with different (usually significantly more strongly coordinating) counterions have long been known.<sup>[1]</sup> Preparation strategies for the anions of **1–3** were established only much more recently.<sup>[9]</sup> The choice of Mn<sup>II</sup> salts for our studies was based on earlier results obtained with transition metal(II) nitrile cations with BF<sub>4</sub><sup>-</sup> counterions in cyclopentadiene polymerization. In this case, the Mn<sup>II</sup> complexes proved to be the most active initiators.<sup>[3b]</sup> This observation is also in accordance with what would be expected from studies on the exchange of acetonitrile ligands. Of all examined transition metal(II) cations, the Mn<sup>II</sup> complexes have the highest pseudo-first-order rate constants for acetonitrile exchange.<sup>[1y]</sup> Thus, acetonitrile exchange seems to play a decisive role in the initiation of polymerization reactions (see below).

The IR spectra of **1–3**, recorded in a KBr matrix, exhibit two sharp ν(CN) absorptions (assigned to the fundamental ν<sub>2</sub> CN stretching mode and a combination mode (ν<sub>3</sub>+ν<sub>4</sub>))<sup>[1x,y,10]</sup> of approximately equal, medium intensity at 2312 and 2286 (**1**), 2312 and 2284 (**2**), and 2316 and 2289 cm<sup>-1</sup> (**3**). These values are identical within the measurement error of the spectrometer and demonstrate clearly the negligible influ-



ence of the counterion. Free acetonitrile (ν(CN)=2293, 2253 cm<sup>-1</sup>) is absent in all measured spectra. The presence of only two CN vibrations is in accordance with expectations for an Mn<sup>II</sup> cation coordinated by six acetonitrile ligands in octahedral symmetry (O<sub>h</sub>). The higher energy of both observed vibrations in comparison with free acetonitrile is due to σ donation of electron density from the lone pair of the nitrogen atom, which has some antibonding character.<sup>[11]</sup>

Complexes **1–3** are paramagnetic, like their BF<sub>4</sub><sup>-</sup> congeners. The EPR spectra of **1–3** in liquid and frozen solutions are typical of octahedral high-spin manganese(II) systems (3d<sup>5</sup>) of the type MA<sub>6</sub> (Figure 1). The <sup>55</sup>Mn hyperfine splitting (sextet of lines) due to interaction of the unpaired electrons with the nuclear spin of <sup>55</sup>Mn (I=5/2, natural abundance ca. 100%) is mostly well resolved in liquid and in frozen solutions. The g values vary between 2.003±0.002 (**1**, **3**) and 2.005 (**2**). The <sup>55</sup>Mn hyperfine coupling constants are 93±2 (**2**), 94 (**1**), and 96 mT (**3**) (87, 88, and 90×10<sup>-4</sup> cm<sup>-1</sup>), respectively. However, the line widths depend on the solvent, counterion, and temperature. The most striking effects are observed in pure acetonitrile or toluene/acetonitrile in comparison with toluene or toluene/dichloromethane. The line broadening or additional anisotropy observed in liquid solution at room temperature when acetonitrile is present indicates ligand-exchange reactions (dynamic effects).

Compounds **1–3** are surprisingly temperature-stable. They decompose thermally under an argon atmosphere with the onset of decomposition at 271 (**1**), 249 (**2**), and 258°C (**3**). The thermogravimetry (TG) curve shows only one sharp step, equivalent to mass losses of about 85 (**1**), 92 (**2**), and 89% (**3**). It can be assumed that the **1–3** lose their CH<sub>3</sub>CN ligands in one step, and the remaining “naked” Mn atom reacts with the counterion to form dark residues which contain, according to elemental analyses, mainly Mn and F.

Complexes **1–3** are moderately stable to air and moisture and can be easily handled in the laboratory atmosphere. For storage over longer periods of time, the compounds are best kept under inert gas at low temperatures. Under such condi-

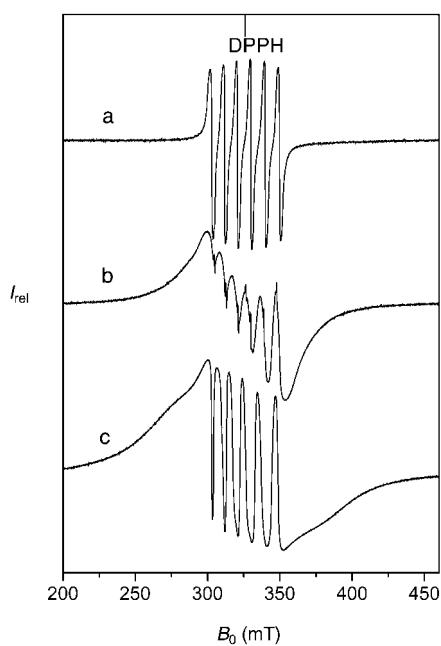


Figure 1. X-band EPR spectra of liquid ( $T=293$  K, a) and frozen solutions ( $T=140$  K; b, c) of **2** (c, in acetonitrile/toluene) and **3** (a, b; in toluene/dichloromethane).

tions, they remain active, even after several months. Reaction of **1–3** with an excess of water results in slow formation of  $[\text{Mn}(\text{H}_2\text{O})_2(\text{NCCH}_3)_4](\text{A})_2$ , in which the aqua ligands are *trans* to each other, so that the  $\text{Mn}^{\text{II}}$  center is coordinated in a square-planar fashion by four acetonitrile molecules, and the aqua ligands occupy the apexes of a (distorted) octahedron. This structure was exemplarily confirmed by X-ray diffraction on  $[\text{Mn}(\text{H}_2\text{O})_2(\text{NCCH}_3)_4][\text{N}_2\text{C}_3\text{H}_3\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]_2$  (**4**). This complex does not react further with an excess water of at room temperature, even when stirred for several days. According to our studies (see below), its formation is responsible for the loss of initiator activity in the presence of wet solvents.

Since we were unsuccessful in obtaining high-quality crystals of **1–3**,<sup>[4a]</sup> we crystallized the propionitrile analogue of **3** (**3a**). In both **3a** and **4**, no interaction between cation and anion is observed. Selected bond lengths and angles are summarized in Table 1, and ORTEP plots of the cations of compounds **3a** and **4** are shown in Figures 2 and 3.

### Homopolymerization of isobutene with $\text{Mn}^{\text{II}}$ -based initiators

**Kinetics:** In our initial polymerization experiments we varied the [monomer]:[initiator] ratio and obtained good results with an initiator concentration of  $2.5 \times 10^{-4} \text{ mol L}^{-1}$  and an isobutene concentration of  $1.38 \text{ mol L}^{-1}$ .<sup>[4]</sup>

For more detailed kinetic investigations, **1–3** were used as initiators for the homopolymerization of isobutene by the tube technique (see Experimental Section). For each experimental series twelve polymerization tubes with identical contents were prepared and kept at  $-40^\circ\text{C}$  to prevent polymerization during the preparation of all tubes due to the inactivity of the initiators at temperatures significantly below  $0^\circ\text{C}$ . The polymerization of all tubes was started at the same

Table 1. Selected interatomic distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **3a**- $\text{C}_3\text{H}_5\text{N}$ , **4**- $2\text{C}_4\text{H}_{10}\text{O}$ , and **7a**.

	<b>3a</b> - $\text{C}_3\text{H}_5\text{N}$ <sup>[a]</sup>	<b>4</b> - $2(\text{C}_4\text{H}_{10}\text{O})$ <sup>[b]</sup>	<b>7a</b>
M–N1	2.247(4)	2.235(2)	2.281(3)
M–N2	2.213(4)	2.242(2)	2.265(3)
M–N3/O1	2.214(4)	2.121(2)	2.279(3)
M–N4			2.298(3)
N1–M–N2	86.18(12)	88.79(6)	103.43(12)
N1–M–N3/O1	91.03(11)	91.88(7)	125.53(12)
N1–M–N4			98.77(12)
N1–M–N1 <sup>i</sup>	180	180	
N1–M–N2 <sup>i</sup>	93.82(12)	91.21(6)	
N1–M–N3/O1 <sup>i</sup>	88.97(11)	88.12(7)	
N2–M–N3/O1	87.52(12)	90.46(6)	107.29(12)
N2–M–N4			124.87(12)
N2–M–N2 <sup>i</sup>	180	180	
N2–M–N3/O1 <sup>i</sup>	92.48(12)	89.54(6)	
N3–M–N4			99.00(12)
N3/O1–M–N3/O1 <sup>i</sup>	180	180	

[a] Data given for molecule A (Mn1). The symmetry code for equivalent atoms (i) is:  $1-x, 1-y, -z$ . [b] The symmetry code for equivalent atoms (i) is:  $1-x, 1-y, 1-z$ .

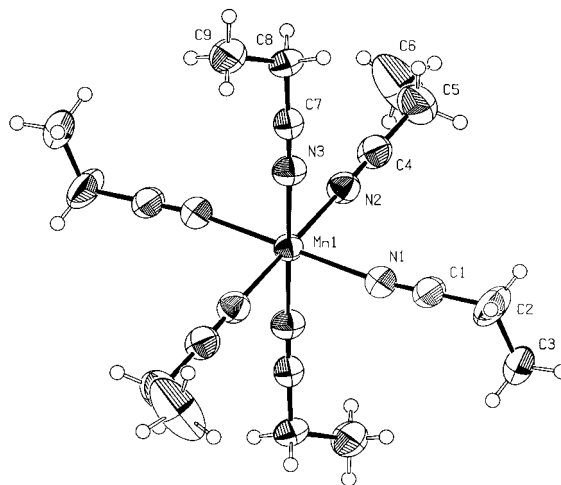


Figure 2. Structure of the dicationic part of compound **3a** in the solid state (ORTEP plot; thermal ellipsoids are drawn at the 50% probability level).

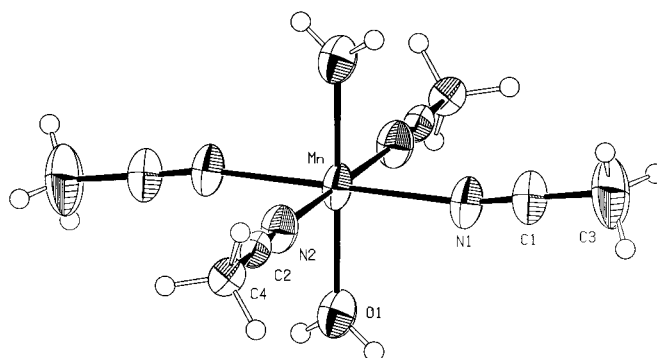


Figure 3. Structure of the dicationic part of compound **4** in the solid state (ORTEP plot; thermal ellipsoids are drawn at the 50% probability level).

time, and after the desired time period, a tube was removed and the polymerization was stopped. In contrast to common processes, which need lower temperatures, the polymerizations described here were carried out at  $30^\circ\text{C}$ . Figure 4

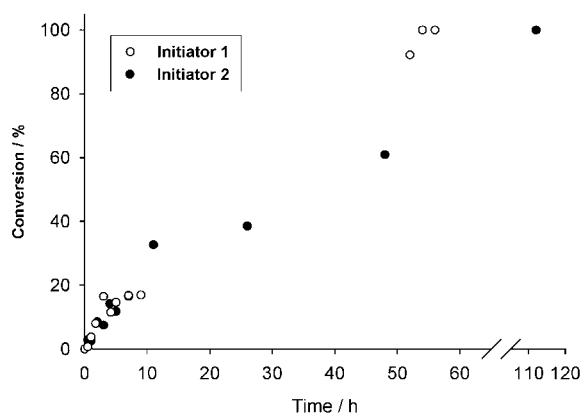


Figure 4. Time/conversion plot for the homopolymerization of isobutene (initiators **1** and **2**, solvent  $\text{CH}_2\text{Cl}_2$ ,  $[\text{Ini}] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{IB}] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{CH}_2\text{Cl}_2} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ , tube polymerization).

shows the time/conversion plot of the polymerization of isobutene with initiators **1** and **2**.

Polymerization with  $\text{Mn}^{\text{II}}$  initiators progresses very slowly. During the first 10 h, no difference in polymerization rates can be observed between initiators **1** and **2**. Nevertheless, complete conversion can be reached with initiator **1** after about 55 h. With initiator **2**, complete conversion can be reached after 110 h of polymerization time, which is slow compared to conventional cationic polymerisation of isobutene. The development of the conversion with increasing time at the initial state of the reaction can be well described by first-order kinetics with respect to monomer concentration.

The results presented in Figure 5, which depicts the change of molecular weight with conversion, show that the polymerization of isobutene initiated with **1** or **2** has no living character. Similar to a classical, nonliving cationic polymerization the molecular weights decrease with increasing conversion. The polydispersity index ( $\text{PDI} = M_w/M_n$ ) remains

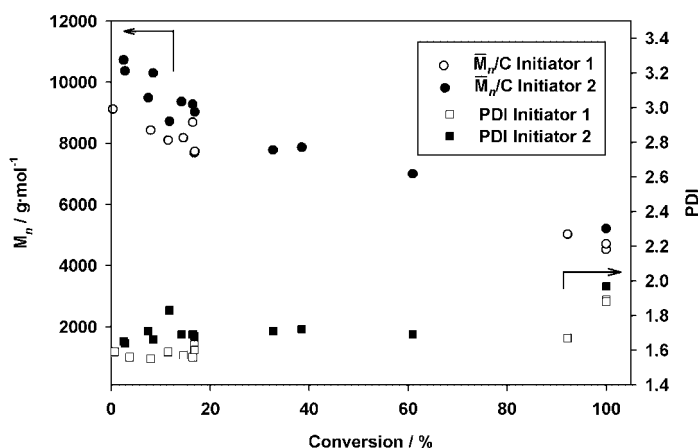


Figure 5. Homopolymerization of isobutene with initiators **1** and **2**; dependence of molecular weight and PDI on conversion (solvent  $\text{CH}_2\text{Cl}_2$ ,  $[\text{Ini}] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{IB}] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{DCM}} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ , tube polymerization).

constant at about 1.6–1.7 up to high conversions. The differences in PDI of polyisobutene initiated by **1** and **2** are small. However, these small differences indicate that the counterions play a certain role in these polymerizations.

In conclusion, polymerization of isobutene in dichloromethane with initiators **1** and **2** is slow but quantitative. Molecular weights between  $\bar{M}_n = 10.0$  (low conversion) and  $\bar{M}_n = 6.0 \text{ kg mol}^{-1}$  (high conversion) can be obtained. However, this polymerization does not show any living character.

**Solvent variation:** The polymerizations discussed so far were performed in dichloromethane. Owing to its aprotic and polar character it is an ideal solvent for the polymerization and for the initiator salts, which are highly soluble in this solvent. Hexane is commonly used in isobutene polymerization, owing to the solubility of polyisobutene. Therefore, it was of interest to use this solvent pure or as mixtures with dichloromethane.

As shown in Figure 6, conversion decreases rapidly with increasing amounts of hexane in the solvent mixtures. Above 60 vol% hexane, no polymerization can be observed.

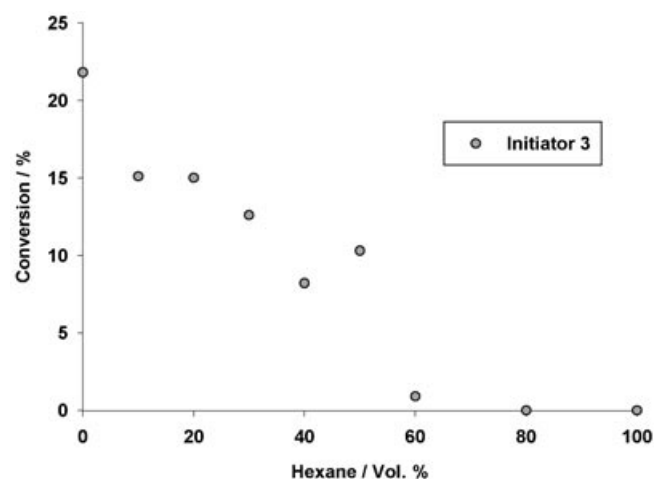


Figure 6. Homopolymerization of isobutene with initiator **3**; conversion as a function of hexane content in dichloromethane/hexane mixtures ( $[\text{Ini}] = 2.5 \cdot 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{IB}] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{DCM}} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization).

Since the initiator is a salt, its solubility decreases with increasing amount of hexane in the reaction mixture. Finally it precipitates completely and polymerization stops. Additionally, the active chain end is less stabilized in an apolar solvent than in a polar solvent. Therefore, the tendency for side reactions such as transfer increases with increasing amounts of hexane, and this leads to continuous reduction of the molecular weight (Figure 7).

The molecular weights decrease from  $6.5 \text{ kg mol}^{-1}$  (polymerization in dichloromethane, 0.0 vol% hexane) to about  $3.0 \text{ kg mol}^{-1}$  (60 vol% hexane). The PDI remains nearly constant, although the molecular weight is approximately halved.

Investigations with acetonitrile as second solvent showed a more strongly decreasing conversion with increasing aceto-

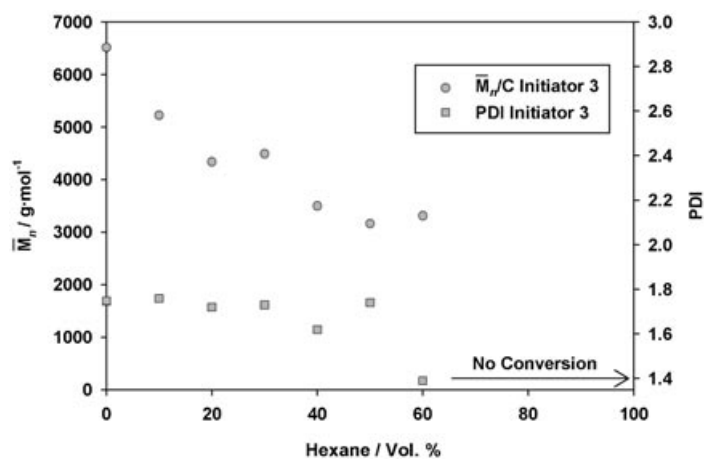


Figure 7. Homopolymerization of isobutene with initiator **3**; dependence of molecular weight and PDI on dichloromethane/hexane ratio ( $[Ini] = 2.5 \cdot 10^{-4} \text{ mol L}^{-1}$ ,  $[IB] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{CH}_2\text{Cl}_2} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization).

nitrile content in the solvent mixture. Since both acetonitrile and the substrate can coordinate to the cationic initiator, the presence of acetonitrile hinders initiation by competing for coordination sites. Accordingly, polar, noncoordinating solvents such as pure dichloromethane should be ideal reaction media.

**Influence of the water content:** Many of the initiating systems for isobutene polymerization described in the literature contain water as cationic species.<sup>[12]</sup> Examples of polymerization of isobutene above  $0^\circ\text{C}$  are very rare in the literature, probably due to extremely exothermic and fast reactions forming only oligomers within seconds under these conditions. Furthermore, it is known that polymerizations of isobutene with rigorously dried monomers and solvents are much slower than those under conventional conditions.<sup>[13]</sup> Therefore, the influence of water was examined. Dichloromethane saturated with water (0.134 mol water in 1 L  $\text{CH}_2\text{Cl}_2$ , determined by Karl Fischer titration) was mixed with dried dichloromethane (water content  $< 0.1 \text{ ppm}$ ) to obtain a well-defined amount of water in the polymerization mixture. The influence of water content on the conversion of isobutene is shown in Figure 8.

Up to a tenfold excess of water over initiator, the effect of water is not very significant; only a slight decrease in monomer conversion is observed. However, above this content of water the conversion decreases dramatically. Finally, experiments in water-saturated dichloromethane did not yield any polymers. One possible explanation for this deactivation of initiator is the step-by-step replacement of the two axial acetonitrile ligands by water. This intermediate water-containing complex was found to be rather stable (see above) but inactive for polymerization of isobutene.

To further characterize the influence of water on the polymerization system (isobutene in  $\text{CH}_2\text{Cl}_2$  with a controlled content of water, initiated by **3**), the attained molecular weights of the polymers were plotted against the  $[\text{water}]:[\text{initiator}]$  ratio (Figure 9). As predicted, the molecular

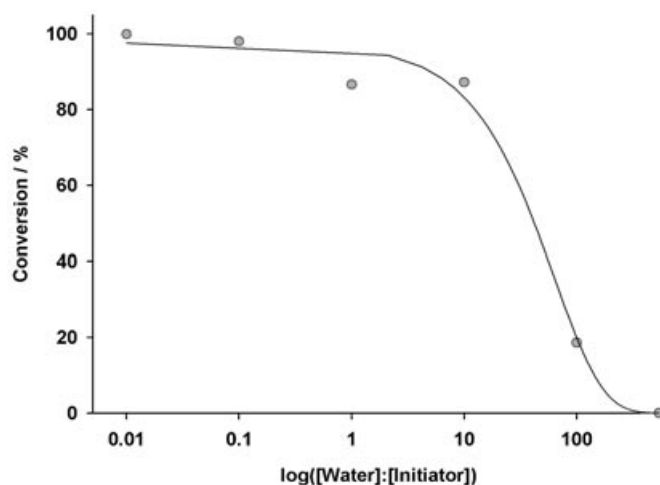


Figure 8. Homopolymerization of isobutene with initiator **3**, conversion as a function of  $\log([\text{water}]:[\text{initiator}])$  ( $[Ini] = 2.5 \cdot 10^{-4} \text{ mol L}^{-1}$ ,  $[IB] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{CH}_2\text{Cl}_2} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization).

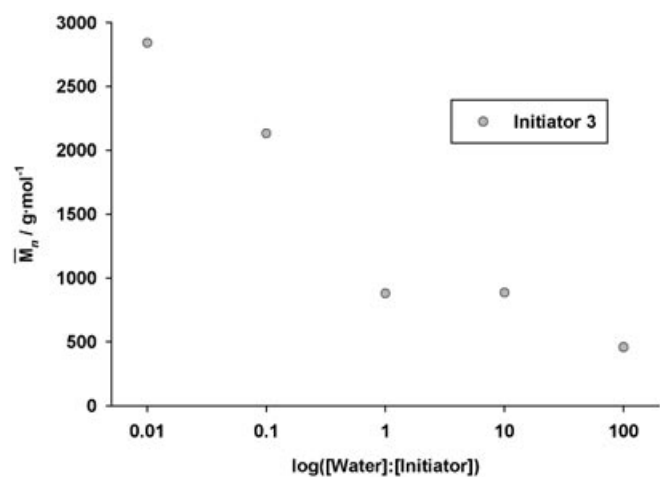


Figure 9. Homopolymerization of isobutene with initiator **3**; molecular weight as a function of  $\log([\text{water}]:[\text{initiator}])$  ( $[Ini] = 2.5 \cdot 10^{-4} \text{ mol L}^{-1}$ ,  $[IB] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{CH}_2\text{Cl}_2} = 20 \cdot 10^{-3} \text{ L}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization).

weight of polyisobutene decreases with increasing  $[\text{water}]:[\text{initiator}]$  ratio.

**Copolymerization of isobutene with isoprene:** With respect to technical applications, copolymerization of isobutene with isoprene is of significant interest. New transition-metal-based initiator systems containing  $\text{Zn}(\text{C}_6\text{F}_5)_2$  show activity at polymerization temperatures below  $-70^\circ\text{C}$ .<sup>[14]</sup> To the best of our knowledge no initiating system enabling the copolymerization of isobutene and isoprene at temperatures above  $0^\circ\text{C}$  has been described so far. Therefore, the effect of the initiators **1–3** on the copolymerization of isobutene with isoprene was studied in some detail (Figure 10).

Although the copolymerization of isobutene and isoprene is feasible with initiators **1–3**, the conversion decreases rapidly with increasing amount of isoprene in the monomer feed. However, for mixtures with less than 5% of isoprene, the decrease in conversion is moderate. These initiators

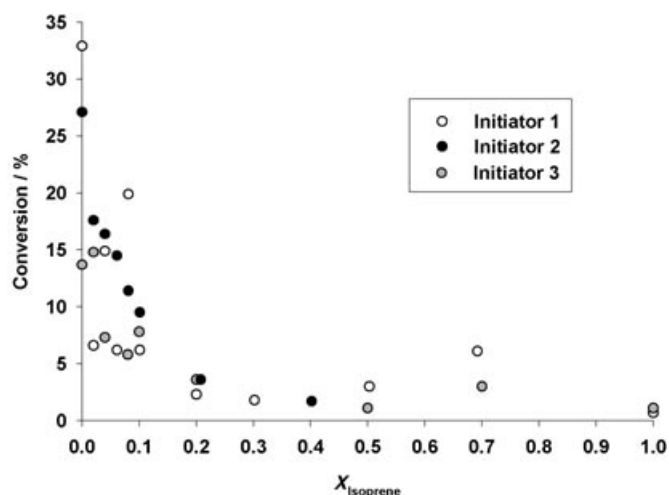


Figure 10. Copolymerization of isobutene/isoprene; conversion as a function of the isoprene content in the monomer feed (initiators 1–3,  $[Ini] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[IB] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{CH}_2\text{Cl}_2} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization,  $X_{\text{Isoprene}} = [\text{Isoprene}] / ([\text{Isoprene}] + [\text{Isobutene}])$ ).

were also used for the homopolymerization of isoprene, for which only initiators 1 and 3 show activity, whereas initiator 2 shows no activity. Nevertheless, it also enables copolymerization up to 40 mol% of isoprene in the monomer feed. The increasing isoprene content in the feed not only decreases the conversion but also the molecular weight of the copolymers (see Figure 11).

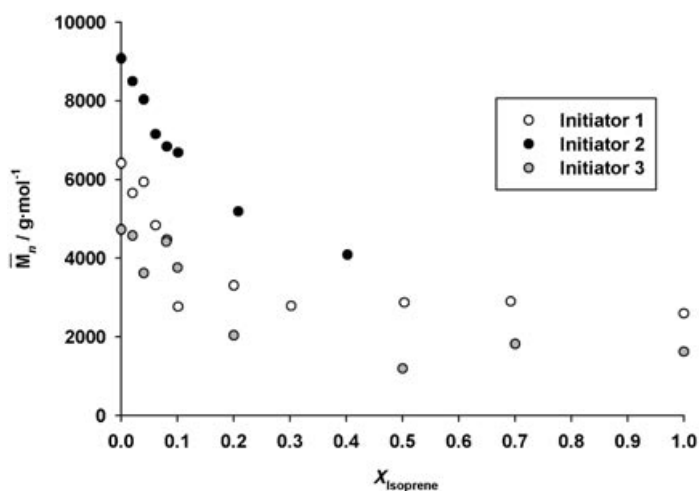


Figure 11. Copolymerization of isobutene/isoprene; molecular weight as a function of isoprene content in the monomer feed (initiators 1–3,  $[Ini] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[IB] = 1.38 \text{ mol L}^{-1}$ ,  $V_{\text{CH}_2\text{Cl}_2} = 20 \text{ mL}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization,  $X_{\text{Isoprene}} = [\text{Isoprene}] / ([\text{Isoprene}] + [\text{Isobutene}])$ ).

The decrease in molecular weight with increasing amount of isoprene in the feed is due to the well-known formation of a relatively stable allylic cation by addition of isoprene to the active chain end.  $^1\text{H}$  NMR analysis of the copolymers shows that incorporation of isoprene amounts to 60–70% for monomer ratios of isobutene:isoprene of less than than 0.16:0.04. Above this isoprene proportion, accurate NMR analysis is very unprecise due to overlapping signals of the components.

All homo- and copolymers are colorless, highly viscous liquids and are completely soluble, for example, in dichloromethane. No cross-linking takes place during the polymerization process, and even the homopolyisoprenes are thoroughly soluble. These isoprene containing homo- and copolymers can be stored under inert gas atmosphere for several days without changing the degree of unsaturation.

**Use of  $\text{Ag}^I$  cations:**  $\text{Ag}^I$  complexes were used as counterion-transfer agents in the synthesis of the  $\text{Mn}^{II}$  compounds (see above). Therefore, it was necessary to examine whether these  $\text{Ag}^I$  complexes show some initiator activity.

Since the  $\text{Ag}^I$  complexes 5–7 are completely inactive (see Table 2), one can exclude the possibility that traces of  $\text{Ag}^I$  complex may contribute to the initiator activity of the  $\text{Mn}^{II}$  complexes. With these results on hand, one can further exclude that the anions might be converted to Lewis acids, which would then initiate a conventional cationic polymerization of isobutene.

Table 2. Influence of the central metal atom on isobutene polymerization in dichloromethane (Fluka),  $[Ini] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[IB] = 1.38 \text{ mol L}^{-1}$ ,  $T = 30^\circ\text{C}$ ,  $t = 16 \text{ h}$ , tube polymerization.

Complex	Formula	Yield [%]	$M_n$ [ $\text{g mol}^{-1}$ ]	PDI
1	$[\text{Mn}(\text{NCCH}_3)_6]$	17.5	6133	1.74
2	$[\text{N}_2\text{C}_3\text{H}_3\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ $[\text{Mn}(\text{NCCH}_3)_6][\text{B}(\text{C}_6\text{H}_3(\text{m}-\text{CF}_3)_2)_4]$	16.9 (9 h)	9023	1.68
3	$[\text{Mn}(\text{NCCH}_3)_6][\text{B}(\text{C}_6\text{F}_5)_4]$	6.8	7843	1.65
5	$[\text{Ag}(\text{NCCH}_3)_4]$ $[\text{N}_2\text{C}_3\text{H}_3\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$	–	–	–
6	$[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{H}_3(\text{m}-\text{CF}_3)_2)_4]$	–	–	–
7	$[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$	–	–	–

As expected, the X-ray structure of the  $\text{Ag}^I$  complexes displays a tetrahedral coordination of the Ag atom by nitrile ligands and no interaction with the anion (see Table 1 and Figure 12). In this case it was also not possible to obtain a

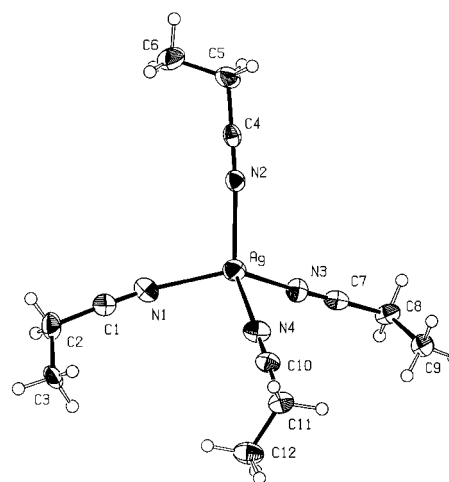


Figure 12. Structure of the cationic part of compound 7a in the solid state (ORTEP plot; the thermal ellipsoids are drawn at the 50% probability level).

good quality crystal for the acetonitrile complex, and therefore its propionitrile analogue was crystallized (**7a**).

**Polymer structure:** Polymerization of isobutene initiated by the Mn<sup>II</sup> complexes **1–3** yields polymers with a high content of olefinic end groups. They can be formed by proton transfer reaction<sup>[12]</sup> in the case of a cationic polymerization mechanism. Quantitative <sup>13</sup>C NMR spectroscopy in the presence of [Cr(acac)<sub>3</sub>] as relaxation agent allows the determination of the content of terminal ( $\alpha$ -olefinic) and internal ( $\beta$ -olefinic) end groups.<sup>[15]</sup>

In this method the integral of the signal of the terminal olefinic carbon atom ( $\delta=114.5$  ppm; Figure 13) is set to unity. The signal of the internal olefinic carbon ( $\delta=$

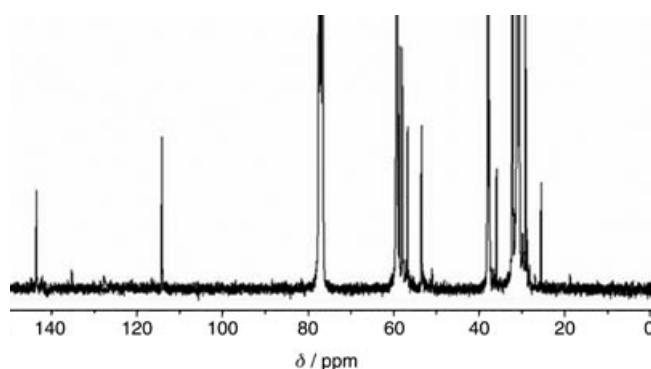


Figure 13. <sup>13</sup>C NMR spectra of liquid polyisobutene prepared at 30°C, molecular weight (NMR) about 1600 g mol<sup>-1</sup>, initiator **3**, NMR solvent CDCl<sub>3</sub> ( $\delta=77.0$  ppm), autoclave polymerization.

127.8 ppm) then has a value of 0.0138. The total contents of terminal and internal olefins can be calculated with the integral values of the methylene carbons and in comparison with the molecular weight of the polymer determined by size exclusion chromatography. On the basis of these data, one can calculate that more than 95% of the isobutene molecules are functionalized with terminal olefinic end groups, and only about 1% have internal olefinic groups. Given the error of the NMR experiments of about 5% (determined by calibration experiments), one can thus speak of fully olefinic terminated polyisobutenes.

No signal can be observed in the region of  $\delta=70$  ppm (quaternary carbon atom COH), that is, no OH termination takes place due to the absence of water in the reaction mixture. This fact allows a proton initiation mechanism caused by traces of water to be excluded. Furthermore, the lack of signals in the range of 0–18 ppm indicates that no branching due to methide shift reactions<sup>[12]</sup> took place.

However, long polymerization times at elevated temperatures lower the content of terminal olefin groups, and the above-mentioned branching can be observed. The amount of undesired products can be reduced by using lower polymerization temperatures. Higher [initiator]:[monomer] ratios also favor the formation of internal olefinic groups (see Table 3), most probably due to the incorporation of previously formed macromonomers via terminal olefinic end groups.

Table 3. Dependence of end-group content of polyisobutenes on the initiator:monomer ratio ([Ini]= $2.5 \times 10^{-4}$  mol L<sup>-1</sup>, solvent: dichloromethane).

Monomer: initiator (mol:mol)	Conversion [%]	T [°C]	M <sub>n</sub> [g mol <sup>-1</sup> ]	Terminal/internal olefin (%)
500 <sup>[a]</sup>	–	30	–	–
1000 <sup>[a]</sup>	56.1	30	1041	50/49
3000 <sup>[a]</sup>	100.0	30	1700	80/17
5000 <sup>[a]</sup>	100.0	30	2032	71/25
10000 <sup>[a]</sup>	100.0	30	2448	≥ 95/≤ 5
28000 <sup>[b]</sup>	95.1 (4 h)	30	1675	≥ 95/≤ 1
28500 <sup>[b]</sup>	21.7 (7 h)	10	3939	≥ 95/n.d. <sup>[c]</sup>
25000 <sup>[b]</sup>	5.29 (20 h)	0	6150	≥ 95/n.d.

[a] Tube polymerization. [b] Autoclave polymerization. [c] n.d.=not detected.

The terminal-olefin content can be increased by using higher monomer:initiator ratios. With [monomer]:[initiator] ≥ 10000, quantitative functionalization with terminal olefinic groups can be attained. This observation is in contrast to a “purely cationic” polymerization, in which normally no influence of the initiator concentration on the end-group content is detectable because of the thermodynamically driven equilibria. Since a higher [initiator]:[monomer] ratio also means a higher acetonitrile concentration in the polymerization solution, one can assume that the content of internal olefin increases with increasing amount of acetonitrile. The polyisobutenes initiated with **1–3** are honeylike, clear, viscous liquids. To the best of our knowledge, no polymerization reaction has been described so far in which low-molecular polyisobutenes with such a high content of olefinic groups and molecular weights could be obtained under similar conditions.

## Conclusion

Mn<sup>II</sup> cations, ligated by weakly coordinating nitrile ligands and associated with noncoordinating, extremely bulky counterions can be used as initiators for the polymerization of isobutene at room temperature and above to achieve highly reactive polyisobutenes with molecular weights between 0.5 and 13 kg mol<sup>-1</sup> and with a high content of terminal double bonds. The molecular weight and the content of terminal double bonds are dependent on the reaction conditions. Furthermore, the same initiators were effective for the copolymerization of isobutene with isoprene. Noncoordinating, polar solvents are optimal for the polymerization reaction, which seems to have a (mainly) cationic mechanism. The presence of excess water with respect to the initiator reduces and finally terminates the catalytic activity, due to partial replacement of the acetonitrile ligands by more strongly coordinating water molecules. The catalytic reaction seems to be initiated by the replacement of an acetonitrile ligand by a substrate (monomer) molecule. Accordingly, an excess of acetonitrile reduces the initiator activity dramatically. Once the active species is formed, cationic polymerization takes place that is probably terminated by proton transfer. There is some remaining doubt about the solely cationic

character of the polymerization, considering the high molecular weights of the polymer and the comparatively slow polymerization at the applied polymerization temperatures. The role of the nitrile ligands may include the possibility of acting additionally as a stabilizing agent for the active chain end. The structure of the polymers contains a high percentage of olefinic end groups, formed by kinetically driven transfer reactions. It can be assumed that subtle modifications of the initiators may significantly change their activity and that further improvements to the initiator systems are feasible. Examinations of cations containing other metals as well as more detailed mechanistic investigations are currently underway.

## Experimental Section

All preparations and manipulations were performed using standard Schlenk techniques under an oxygen- and water-free nitrogen atmosphere. Commercial-grade solvents were dried and deoxygenated by refluxing over appropriate drying agents under nitrogen atmosphere and distilled prior to use. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching (M. Barth). IR spectra were recorded on a Perkin-Elmer FTIR spectrometer by using KBr pellets as IR matrix. The EPR spectra were recorded with a JEOL JESRE2X at X-band frequency ( $\nu \approx 9.05$  GHz, microwave power 2 mW, modulation frequency 100 kHz). Thermogravimetric analysis (TGA) studies were performed using a Mettler TA 3000 system at a heating rate of  $5 \text{ K min}^{-1}$  under a static atmosphere of air.

**General purification procedures for reagents used for polymerization:** Dichloromethane used in autoclave polymerization was first distilled at a reflux ratio of 4:1. Then, it was refluxed over  $\text{CaH}_2$  for at least three days. Prior to each polymerization, it was freshly distilled under argon and kept over molecular sieves (water content of  $\text{CH}_2\text{Cl}_2 < 0.1$  ppm, determined by Karl Fischer titration).  $\text{CH}_2\text{Cl}_2$  used in tube polymerizations was purchased from Fluka (dry grade over molecular sieves, water content about 1.7 ppm, determined by Karl Fischer titration). *n*-Hexane was distilled over sodium metal wires.

Acetonitrile was refluxed for several hours over  $\text{CaH}_2$  and distilled freshly prior to use. Isobutene used in the autoclave polymerization was dried with two columns, one equipped with molecular sieves, the other filled with sodium/aluminum oxide. Isobutene used in tube polymerizations was dried with two columns, one filled with molecular sieves, and the other with potassium on activated charcoal. Isoprene was dried by distillation over sodium/aluminum oxide. Generally, all experimental precautions necessary for cationic polymerizations were applied.

**[Mn<sup>II</sup>(NCMe)<sub>6</sub>][(F<sub>5</sub>C<sub>6</sub>)<sub>3</sub>BC<sub>3</sub>H<sub>3</sub>N<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (1):**  $\text{MnCl}_2$  (74 mg, 0.44 mmol) was added to a solution of  $\text{Ag}[(\text{F}_5\text{C}_6)_3\text{BC}_3\text{H}_3\text{N}_2\text{B}(\text{C}_6\text{F}_5)_3]$  (0.95 g, 0.87 mmol) in dry MeCN (10 mL), and the mixture was stirred at room temperature for 12 h in darkness. The solution was filtered, and the colorless filtrate was concentrated under oil-pump vacuum to 3 mL and cooled to  $-35^\circ\text{C}$ . 0.89 g of **1** was obtained (81% yield). The product was stored at  $-35^\circ\text{C}$ . IR:  $\tilde{\nu} = 2312, 2286$  ( $\nu(\text{CN})$ )  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{B}_4\text{C}_{90}\text{F}_{60}\text{H}_{24}\text{MnN}_{10}$  (2483.3116): C 43.53, H 0.97, N 5.64; found: C 42.96, H 1.00, N 5.41.

**[Mn<sup>II</sup>(NCMe)<sub>6</sub>][B(C<sub>6</sub>H<sub>3</sub>(*m*-CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sub>2</sub> (2):**  $\text{MnCl}_2$  (89.0 mg, 0.5 mmol) was added to  $\text{Ag}[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$  (0.9 g, 1.1 mmol) dissolved in dry MeCN (20 mL). The mixture was stirred for 12 h at room temperature in the dark. The precipitate that formed was removed, and the remaining solution was reduced to 1.5 mL under oil-pump vacuum and kept at  $-35^\circ\text{C}$ . Over a few hours a solid formed (0.8 g, 77% yield). The product was stored at  $-35^\circ\text{C}$ . IR:  $\tilde{\nu} = 2315, 2288$  ( $\nu(\text{CN})$ )  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{B}_2\text{C}_{76}\text{F}_{48}\text{H}_{42}\text{MnN}_6$  (2027.6738): C 45.02, H 2.09, N 4.14; found: C 44.61, H 1.94, N 3.98.

**[Mn<sup>II</sup>(NCMe)<sub>6</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (3):**  $\text{MnCl}_2$  (120 mg, 0.95 mmol) was added to a dry solution of  $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$  (1.50 g, 1.91 mmol) in MeCN (15 mL), and the mixture was stirred at room temperature in the dark for 10 h.

The formed  $\text{AgCl}$  was filtered off leaving a pale pinkish filtrate. The filtrate was concentrated in vacuum to 5 mL and cooled to  $-35^\circ\text{C}$  and 1.22 g of solid was formed (73% yield). The product was stored at  $-35^\circ\text{C}$ . IR:  $\tilde{\nu} = 2312, 2284$  ( $\nu(\text{CN})$ )  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{B}_2\text{C}_{66}\text{F}_{40}\text{H}_{30}\text{MnN}_6$  (1743.485): C 45.47, H 1.73, N 4.15; found: C 44.99, H 1.72, N 4.13.

**X-ray crystallography:** Selected crystals were coated with perfluorinated ether, fixed in a capillary, transferred to the diffractometer, and cooled in a nitrogen stream (Oxford Cryosystems). Preliminary examination and data collection were carried out with a kappa-CCD device (Nonius MACH3) at the window of a rotating anode (Nonius FR591) with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).<sup>[16]</sup> Data were corrected for Lorentzian and polarization effects. Potential absorption effects and/or decay of the crystal were corrected during the scaling procedure.<sup>[17]</sup> All structures were solved by a combination of direct methods and difference Fourier syntheses. Full-matrix, least-squares refinements were carried out by minimization of  $\sum w(F_o^2 - F_c^2)^2$  with SHELXL-97 weighting scheme and stopped at  $\text{shift/err} > 0.001$ . Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.<sup>[18]</sup> All calculations were performed with the STRUX-V<sup>[19]</sup> system including the programs PLATON,<sup>[20]</sup> SIR92,<sup>[21]</sup> and SHELXL-97.<sup>[22]</sup>

**Crystal data, data collection, and refinement for 3a-C<sub>3</sub>H<sub>5</sub>N:**  $[(\text{C}_{18}\text{H}_{30}\text{MnN}_6)][(\text{C}_{24}\text{BF}_{20})_2\text{C}_3\text{H}_5\text{N}]$ ,  $M_r = 1798.60$ , colorless fragment ( $0.36 \times 0.51 \times 0.51$  mm), monoclinic,  $P2_1/a$  (no. 14),  $a = 17.9484(4)$   $b = 18.6777(5)$ ,  $c = 23.9134(6)$   $\text{\AA}$ ,  $\beta = 90.660(1)^\circ$ ,  $V = 8016.1(3)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.490$   $\text{g cm}^{-3}$ ,  $F_{000} = 3572$ ,  $\mu = 0.302$   $\text{mm}^{-1}$ . Data were collected at  $T = 153$  K in the range of  $2.31 < \theta < 25.35^\circ$ . A total of 23890 reflections were integrated. After merging ( $R_{\text{int}} = 0.044$ ), 10762 [5979 with  $I_o > 2\sigma(I_o)$ ] independent reflections remained, and all were used to refine 1094 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions (riding model). The refinements converged to  $R1 = 0.0487$  [ $I_o > 2\sigma(I_o)$ ],  $wR2 = 0.1145$  (all data), and  $\text{GOF} = 0.972$ . The final difference Fourier map showed no striking features ( $\Delta e_{\text{min/max}} = +0.24/-0.25$   $\text{e \AA}^{-3}$ ). Two solvent molecules could not be modeled properly. This problem was solved by using the PLATON Calc Squeeze procedure. The asymmetric unit cell contains two crystallographically independent Mn dications, both located around a center of inversion. At Mn2 a disorder of one methylene carbon atom over two positions (72:28) could be resolved.

**Crystal data, data collection, and refinement for 4-2C<sub>4</sub>H<sub>10</sub>O:**  $[(\text{C}_8\text{H}_{16}\text{MnN}_4\text{O}_2)][(\text{C}_{39}\text{H}_3\text{B}_2\text{F}_{30}\text{N}_2)]_2\text{C}_4\text{H}_{10}\text{O}$ ,  $M_r = 2585.54$ , colorless fragment ( $0.43 \times 0.51 \times 0.69$  mm), monoclinic,  $P2_1/n$  (no. 14),  $a = 14.9333(1)$   $b = 18.7111(1)$ ,  $c = 20.6918(1)$   $\text{\AA}$ ,  $\beta = 103.2510(2)^\circ$ ,  $V = 5627.74(6)$   $\text{\AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.526$   $\text{g cm}^{-3}$ ,  $F_{000} = 2558$ ,  $\mu = 0.268$   $\text{mm}^{-1}$ . Data were collected at  $T = 123$  K in the range of  $2.30 < \theta < 25.35^\circ$ . A total of 127052 reflections were integrated. After merging ( $R_{\text{int}} = 0.033$ ), 10297 [8871 with  $I_o > 2\sigma(I_o)$ ] independent reflections remained, and all were used to refine 784 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions (riding model). The hydrogen atoms of the water ligand were refined freely with restrained O–H distances. The refinements converged to  $R1 = 0.0338$  [ $I_o > 2\sigma(I_o)$ ],  $wR2 = 0.1010$  (all data), and  $\text{GOF} = 1.084$ . The final difference Fourier map showed no striking feature ( $\Delta e_{\text{min/max}} = +0.36/-0.26$   $\text{e \AA}^{-3}$ ). One solvent molecule could not be modeled properly. This problem was solved by using the PLATON Calc Squeeze procedure.

**Crystal data, data collection, and refinement for 7a:**  $[(\text{C}_{12}\text{H}_{20}\text{AgN}_4)][(\text{C}_{24}\text{BF}_{20})]$ ,  $M_r = 1007.24$ , colorless fragment ( $0.15 \times 0.23 \times 0.51$  mm), monoclinic,  $P2_1/c$  (no. 14),  $a = 11.1319(1)$   $b = 19.9011(2)$ ,  $c = 17.8334(1)$   $\text{\AA}$ ,  $\beta = 105.8975(3)^\circ$ ,  $V = 3799.66(6)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.761$   $\text{g cm}^{-3}$ ,  $F_{000} = 1984$ ,  $\mu = 0.663$   $\text{mm}^{-1}$ . Data were collected at  $T = 103$  K in the range of  $2.16 < \theta < 25.35^\circ$ . A total of 50981 reflections were integrated. After merging ( $R_{\text{int}} = 0.032$ ), 6951 [6415 with  $I_o > 2\sigma(I_o)$ ] independent reflections remained, and all were used to refine 639 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the final difference Fourier map were allowed to refine. The refinements converged to  $R1 = 0.0410$  [ $I_o > 2\sigma(I_o)$ ],  $wR2 = 0.0961$  (all data), and  $\text{GOF} = 1.360$ . The final difference Fourier map showed no striking features ( $\Delta e_{\text{min/max}} = +0.30/-0.41$   $\text{e \AA}^{-3}$ ).



CCDC-195403 (**3a**-C<sub>3</sub>H<sub>5</sub>N), CCDC-233993 (**4**-2C<sub>4</sub>H<sub>10</sub>O), and CCDC-233994 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### Polymerization reactions

**Autoclave polymerization of isobutene:** A polymerization autoclave (Büchi Eoclave 3500, equipped with 250 mL glass pressure tube, gas inlet, and septa) was dried and purged with argon. 185 mL of dry dichloromethane was added and tempered to the adjusted temperature. By using liquid nitrogen, the desired amount of isobutene was condensed into a separate metal pressure tube and weighed. Afterwards, the isobutene was defrosted and added to the solvent until saturation, reflected by a constant pressure of about 3 bar. Then the initiator, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), was injected with overpressure into the reaction mixture. The injecting system was washed with CH<sub>2</sub>Cl<sub>2</sub> (5 mL) (example:  $V(\text{CH}_2\text{Cl}_2)_{\text{tot}} = 200 \text{ mL}$ ,  $c_{\text{Initiator}} = 1.25 \cdot 10^{-4} \text{ mol L}^{-1}$ ). After a short induction period, which depends on the initiator used, the polymerization starts. Samples were taken during the whole polymerization process for monitoring progress by using metal syringes and septas of the autoclave. After the overpressure had been reduced to nearly atmospheric pressure, the reaction was quenched with methanol (50 mL). For stabilization against oxidation, 2,2'-methylene-bis(4-methyl-6-di-*tert*-butylphenol) (1 g) was added. The remaining reaction mixture was removed from the autoclave and the solvents were distilled off in vacuo. The remaining polymer was dried under fine vacuum until the weight remained constant.

**Tube polymerization of isobutene; copolymerization of isobutene/isoprene:** For higher screening efficiency, the homopolymerization of isobutene/copolymerization with isoprene was performed in pressure tubes in a dry box. A maximum of 12 tubes were prepared at the same time. Each tube was filled with dried dichloromethane (20 mL) at  $-40^\circ\text{C}$ , and the initiator added ( $c_{\text{Initiator}} = 2.5 \cdot 10^{-4} \text{ mol L}^{-1}$ ). A magnetic stirring bar was added to each tube. Various amounts of isobutene, which was previously condensed into a separate tube, and, in the case of copolymerization, freshly distilled isoprene were added. The pressure tubes were sealed and quickly removed from the dry box. The polymerization was performed by using a water quench equipped with a magnetic stirrer at the given temperature. The polymerization was stopped with methanol (5 mL) and 2,2'-methylene-bis(4-methyl-6-di-*tert*-butylphenol) (0.2 g) was added to prevent oxidation. The solvents were removed under oil-pump vacuum, and the remaining polymer dried under fine vacuum at  $30^\circ\text{C}$  until the weight remained constant. The polymeric products were stored under inert gas atmosphere. To prove reproducibility, in all experiments one standard polymerization was performed in the first tube, that is, dichloromethane (20 mL), initiator **3** ( $2.5 \cdot 10^{-4} \text{ mol L}^{-1}$ ), isobutene (1.5 g), reaction time 16 h, reaction temperature  $30^\circ\text{C}$ .

**NMR spectroscopic investigations of end groups:** Depending on the NMR method, different sample preparation techniques were applied. In general, the weighed amount of polymer was dissolved in CDCl<sub>3</sub> (0.5 mL) and relaxation agent [Cr(acac)<sub>3</sub>] was added when needed. The NMR spectrum was measured as quickly as possible. NMR parameters are listed in Table 4.

Table 4. Basic parameters applied in quantitative NMR investigations.

Technique	Frequency [MHz]	Scans relaxation time	Polymer [mg]	Relaxation agent [Cr(acac) <sub>3</sub> ] <sup>[a]</sup>
<sup>1</sup> H NMR	300.15	16/1 s	10	none
<sup>13</sup> C NMR	76.45	8000/0.5 s	150	17 mg mL <sup>-1</sup> CDCl <sub>3</sub>

[a] acac = 2,4-pentanedione.

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