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Solvent-Ligated Copper(II) Complexes for the Homopolymerization of 2-Methylpropene

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Dedicated to Professor Dr. Dr. h.c. mult. W. A. Herrmann on the occasion of his 60th birthday

Abstract: Copper(II) complexes with weakly coordinating counter anions can be utilized as highly efficient catalysts for the synthesis of poly(2-methylpropene) ("polyisobutene") with a high content of terminal double bonds. These copper(II) compounds are significantly more active than the manganese(II) complexes described previously, can be applied in chlorine-free solvents such as toluene, are easily accessible, and can be handled at room temperature and in laboratory atmospheres for brief periods, but they are sensitive to excess water, thereby losing their catalytic activity. Replacing the acetonitrile ligands by benzonitrile ligands improves the solubility and catalytic activity in nonpolar and nonchlorinated solvents. However, the benzonitrile copper(II) compounds have lower thermal stability than their acetonitrile congeners.

Keywords: methylpropene · copper · homogeneous catalysis · polymerization

Introduction

Polyisobutenes (PIBs) have numerous industrial applications: for example, as a chewing gum base and as rubbers, sealants, lubricants, and oil additives.

Lubricating oils and additives for lubricants, gasoline, and diesel fuel are by far the largest end-use markets for PIB. This segment represents 75–80 % of the PIB market. All of the PIB consumed in these mineral oil applications, however, is low molecular weight PIB (LM-PIB). The largest product category in the lubricating oil additive sector is dispersants/detergents. Almost all dispersant products are based on PIB polymers, their succinic anhydrides (PIBSAs) and succinimides (PIBSIs), and other chemical derivatives. Dispersants made from PIB and its derivatives in engine oils used for passenger cars and heavy-duty trucks protect the engine in many ways: for suspension of oil contaminants (by-products of combustion and debris from wear); to reduce friction and hence increase fuel economy; to protect from corrosion; and to emulsify water accumulating in the oil phase.

When used as a gasoline and diesel additive, these products act as detergents and keep injection systems clean. In addition to their application as intermediates for lubricating oil and fuel additives, PIBs can be used as stand-alone lubricants or predominantly as components of formulated lubricant packages. Lubricating oils usually consist of base oils, additives, and diluents, with PIBs added as a thickening agent as well as to increase lubricity, to control deposits, to reduce exhaust smoke, to control exhaust system blocking, and to enhance anti-scuffing protection.

More fuel-efficient operation of cars and trucks is made possible by using these products. Oil change intervals are

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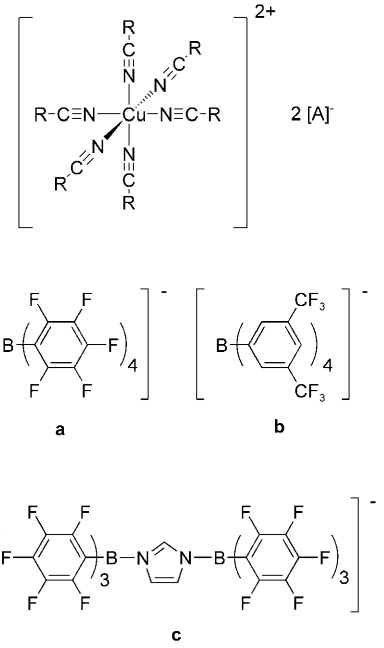
longer and thus both the consumption of engine oil and the repair cycles of engines are reduced. In addition, with the increasing need to reduce exhaust gases (NO_x) and fine dust particles in the diesel fumes as well as to use a greater proportion of biofuels, highly efficient additives with even better performance become more essential. Whereas LM-PIB-based materials are already being considered the most suitable products for these applications in general, highly reactive PIB (HR-PIB) is expected to gain a greater market share at the expense of conventional LM-PIB worldwide. Market prognoses clearly indicate that the production of PIB and PIB derivatives will increase in the coming years and higher quality products based on HR-PIB will be needed. The highly reactive polyisobutenes have low molecular weights (0.3–3 $\mathrm{kg\,mol^{-1}}$). This group of PIBs usually contains over 60% of terminal (*exo*) C=C double bonds.[1–3] So far the majority of LM-PIB is produced by the conventional cationic polymerization process using a large excess of $AlCl_3$ as catalyst, which leads to huge amounts of chlorine containing solid waste as well as thousands of tons of chlorine containing wastewater. On the other hand, the low-temperature HR-PIB process (at −20°C) requires cooling, with considerable energy consumption.

Manganese(II) complexes, namely $[\mathrm{Mn(NCCH_3)_6}][\mathrm{B(C_6F_5)_4}]_2$, $[\mathrm{Mn(NCCH_3)_6}][(\mathrm{C_6F_5})_3\mathrm{B{-}C_3H_3N_2{-}B(C_6F_5)_3}]_2$, and $[\mathrm{Mn(NCCH_3)_6}][\mathrm{B\{C_6H_3}(m\text{-}\mathrm{CF_3})_2\}_4]_2$, have recently been applied successfully as catalysts for the homopolymerization of 2-methylpropene.[4,5] However, we have found that use of manganese(II) complexes in the homopolymerization of isobutene is not an isolated case of a transition metal(II) complex being active as a catalyst in 2-methylpropene polymerization. Our group has synthesized new catalytic copper(II) complexes which can provide catalysts with a significantly better performance and make it possible to use more environmentally benign nonchlorinated solvents. The more active copper(II) catalysts, allowing elimination of chlorinated solvents and the possibility of room-temperature polymerizations, seem in principle to be very promising alternatives for industrial applications. In this paper, which follows a preliminary communication,[6] we describe a detailed study of these catalysts.

Results and Discussion

Synthesis and characterization: The general formula of the copper(II) complexes synthesized is $[\mathrm{Cu(NC{-}R)_6}][\mathrm{A}]_2$, with R = Me (**1**), benzyl (Bn) (**2**), or Et (**3**)

The three different weakly coordinating anions $[\mathrm{A}]^-$ (**a**–**c**) in compounds **1**–**3** are as shown. Due to the insolubility of the compounds with anion **c** in all the solvents applied, only compounds **2a**,**b** and **3a**,**b** were fully characterized and examined in this study.



Anions **a** and **b** were prepared according to Scheme 1; anion **c** was synthesized by literature procedures[7] and then transferred to the respective silver salt as in the case of the anions **a** and **b.**

$$\mathrm{R'Br} + n\mathrm{BuLi} \xrightarrow{1)} \mathrm{R'Li} \xrightarrow{2)} \mathrm{Li[B(R')_4]} \xrightarrow{3)} \mathrm{K[B(R')_4]} \xrightarrow{4)} \mathrm{Ag[B(R')_4]}$$

Scheme 1. Preparation of anions **a** and **b.** 1) Et_2O at −78°C, 30 min; 2) BCl_3, Et_2O at −78°C, 30 min; 3) saturated KCl solution in water at RT, 2 h; 4) $AgNO_3$, CH_3CN/Et_2O at RT in darkness, 1 h; R′ = pentafluorobenzene bromide or 3,5-bis(trifluoromethyl)bromobenzene.

Compounds **1a**–**c** were synthesized by reaction of water-free copper(II) chloride with the silver salts of the corresponding anions in acetonitrile (anion exchange). Compounds **2a** and **3a, 2b** and **3b** were synthesized according to Equation (1), with R = Bn (**2**) and R = Et (**3**).

$$2\,[\mathrm{Ag(NCCH_3)}_n][\mathrm{A}] + \mathrm{CuCl_2} + 6\,\mathrm{NCR} \xrightarrow[\mathrm{RT}]{\mathrm{CH_2Cl_2}} [\mathrm{Cu(NCR)_6}][\mathrm{A}]_2 + 2\,\mathrm{AgCl} \qquad (1)$$

Complexes **1**–**3** were stored at −35°C under an argon atmosphere to prevent decomposition and oxidation over long storage periods. When exposed to air at room temperature (25°C), there was no detectable decomposition (elemental analysis) after 30 min for **1** and **3**. However, **2** was less stable than the other two compounds (decomposition was not detected for only about 5 min in the laboratory atmosphere) and more sensitive to trace amounts of water in the solvent or moist air (laboratory atmosphere), which may due to weaker coordination of the benzonitrile ligands to the metal center.

Spectroscopic analysis: Compounds **1a–c**, **2a**,**b**, and **3a**,**b** are paramagnetic as their BF_4^- congeners and were characterized by IR spectroscopy, EPR spectroscopy, thermogravimetry, and elemental analysis. The infrared (IR) spectra of the complexes, recorded in a KBr matrix, exhibited two sharp $\tilde{\nu}$(CN) absorptions of medium intensity (assigned to the fundamental $\tilde{\nu}_2$(CN) stretching mode and a combination mode $(\tilde{\nu}_3+\tilde{\nu}_4)$)[8] at 2317 and 2340 cm^{-1} (**1a**), 2303 and 2332 cm^{-1} (**1b**), and 2284 and 2313 cm^{-1} (**1c**). The higher energy of both observed vibrations in comparison to those of free acetonitrile ($\tilde{\nu}$(CN) = 2253 and 2293 cm^{-1}) is caused by σ donation of electron density from the lone pair of the nitrogen, which has some *anti* bonding character.[8,9] Furthermore, a third, weaker absorption can be found for complexes **1a–c** at 2279, 2271, and 2263 cm^{-1} respectively. This three-peak absorption pattern had also been observed for the complex $(Cr(NCCH_3)_6((tfpb(_2$[8] (tfpb=tetrakis(3,5-bis[trifluoromethyl]phenyl)borate). This absorption has been assigned to the presence of two slightly more weakly coordinating "axial" CH_3CN ligands (relative to the four other, "equatorial", CH_3CN molecules). This is consistent in principle with a hexacoordinated metal center as found, for example, by X-ray crystal analysis of compound **1a**.[6]

Similar shifts of absorption bands are observed for the complexes **2a** and **2b**; the two sharp $\tilde{\nu}$(CN) peaks occurring at 2287, 2255 cm^{-1} (**2a**) and 2285, 2254 cm^{-1} (**2b**) have a higher energy level than the free benzonitrile ($\tilde{\nu}$(CN) = 2178, 2219 cm^{-1}). For complexes **3a** and **3b**, the two sharp $\tilde{\nu}$(CN) peaks are shifted to 2319, 2287 cm^{-1} and 2313, 2279 cm^{-1} respectively, as compared to the higher energy levels for free propionitrile ($\tilde{\nu}$(CN) = 2243, 2298 cm^{-1}). No other related peaks are observed for complexes **2a**,**b** and **3a**,**b**, however; either the absorption band signals might be too weak for observation or the difference between "axial" and "equatorial" ligands is less pronounced (see below).

The EPR spectra of the copper complexes $[Cu(NC{-}R)_6][A]_2$, **1–3**, are typical of copper(II) systems ($3d^9$, $S = 1/2$) in the distorted octahedral coordination (tetragonal elongation) expected because of the so-called Jahn–Teller effect. The copper(II) compounds can be described by an axially symmetric spin Hamiltonian in accordance with the symmetry of the molecule (see the crystal structure). The ^{63,65}Cu hyperfine splitting (quartet of lines) due to the interaction of the unpaired electron with the nuclear spins of ^{63}Cu and ^{65}Cu ($I = 3/2$, natural abundance ≈69 and 31 % respectively, isotopic splitting not resolved) is resolved only for the parallel part of the EPR spectra of frozen solutions. The g values (see Table 1) and hyperfine coupling constants $A_{\parallel}(^{63,65}Cu)$ are identical within experimental error for all counter anions, but they vary for the three different nitrile ligands. The spectral parameters, in particular the extraordinarily large g anisotropy, reflect the strong tetragonal distortion (elongation) of the pseudo-octahedral coordination environment. This tetragonal distortion is more pronounced for complex **1** (acetonitrile), indicating that this complex is even more distorted than the benzonitrile (**2**) and propionitrile (**3**) systems. The clear relationship $g_{\parallel} \gg g_{\perp} > 2.0$ indicates a $d(x^2-y^2)$ ground state for the unpaired electron.[10–12]

Table 1. EPR parameters[a] of the copper complexes $[Cu(NCR)_6][A]_2$, **1a–3c**, obtained by simulation of the spectra using an axially symmetric spin Hamiltonian (second-order perturbation theory).

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}$ (^{63,65}Cu) [$\times10^{-4}$ cm^{-1}]
1a–c	2.405	2.085	2.192	146
2a,**b**	2.384	2.082	2.183	150
3a,**b**	2.365	2.088	2.180	149

[a] Experimental errors: $g = \pm 0.002$, $A = \pm 3\times10^{-4}$ cm^{-1}; $g_{av} = (2g_{\parallel} + g_{\perp})/3$

Thermogravimetric analysis: Complexes **1a–c**, **2a**,**b**, and **3a**,**b** were subjected to thermogravimetric analysis with increasing temperatures from room temperature to 800 °C at 10 °C min^{-1} (Figures 1 and 2). In general, they start to decompose above 100 °C, and at 800 °C only approximately 10–15 % of their original weight remains.

The first onset of decomposition of **1a** occurs at 167 °C, associated with a mass loss of around 14 %; this corresponds to the loss of all six acetonitrile ligands, which comprise 14.7 % of the total mass of **1a**. The second and final decom-

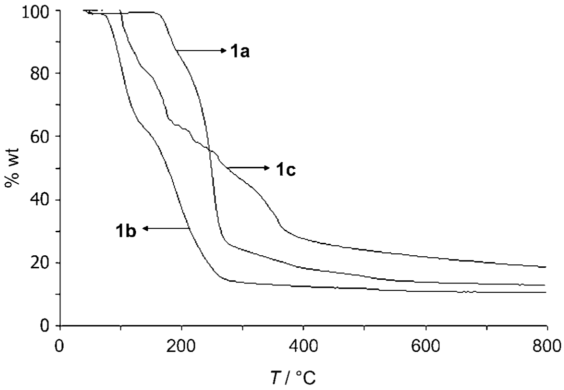


Figure 1. TG curves of complexes **1a**, **1b**, and **1c**, heated at 10 °C min^{-1}.

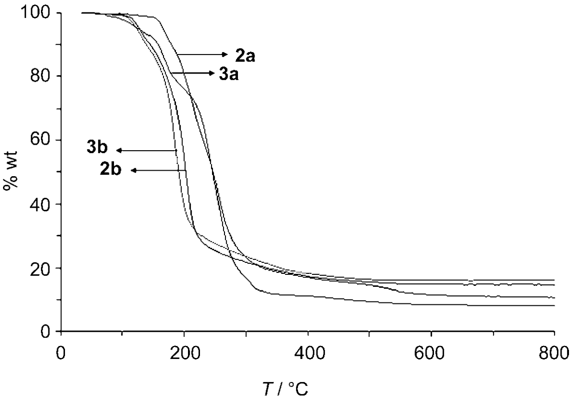


Figure 2. TG curves of complexes **2a**, **2b**, **3a**, and **3b**, heated at 10 °C min^{-1}.

position step starts at 235 °C and corresponds to a loss of about 65 % of the original mass. Since K[B(C_6F_5)] shows a mass loss of 50 % starting at approximately the same temperature, it can be argued that this decomposition step accounts for anion fragmentation. Among **1a–c**, **1b** exhibits the lowest thermal stability. The first decomposition step occurs at 89 °C and accounts for a mass loss of approximately 38 %, in accord with the loss of all acetonitrile ligands (12 %) and additional anion fragmentation. Complex **1c** shows the most complicated decomposition pattern among the three, probably due to its much more sophisticated counter anion. Its first decomposition step (18 %) can also be assigned to the loss of all acetonitriles (9.8 %) and additional anion decomposition. More detailed information is listed in Table 2.

Table 2. TG analysis of complexes **1a–c**.

Complex	1st T_{onset} [°C]	Wt. loss [%]	2nd T_{onset} [°C]	Wt. loss [%]	3rd T_{onset} [°C]	Wt. loss [%]	4th T_{onset} [°C]	Wt. loss [%]	5th T_{onset} [°C]	Wt. loss [%]	Total loss [%]
1a	167.8	13.9	235.3	65.2	–	–	–	–	–	–	87.2
1b	88.9	37.8	165.2	48.1	–	–	–	–	–	–	90.1
1c	106.6	18.4	161.4	17.5	179.1	7.4	257.2	9.1	344.8	14.8	83.5

The degradation patterns of **2a**,**b** and **3a**,**b** are similar to those of **1a** and **1b**, except that **3a** and **3b** are less stable than their benzonitrile congeners. However, the curves of **2a**,**b** and **3a**,**b** do not display very pronounced decomposition steps. More detailed information is listed in Table 3.

Table 3. TG analysis of complexes **2a**, **2b**, **3a**, and **3b**.

Complex	1st T_{onset} [°C]	Wt. loss [%]	2nd T_{onset} [°C]	Wt. loss [%]	3rd T_{onset} [°C]	Wt. loss [%]	4th T_{onset} [°C]	Wt. loss [%]	Total loss[%]
2a	160.9	12.5	196.9	35.5	246.0	34.4	383.5	5.0	85.5
2b	114.1	14.0	187.4	56.3	235.5	11.7	–	–	85.8
3a	148.8	19.5	226.3	65.3	–	–	–	–	92.0
3b	112.9	12.8	175.0	55.3	268.6	12.4	–	–	85.0

Polymerization of 2-methylpropene with Cu^{II}-based catalysts

Comparison of [Cu($NCCH_3$)$_6$]$^{2+}$ and [Mn($NCCH_3$)$_6$]$^{2+}$ complexes: To elaborate on the performance of copper(II) complexes in the polymerization of 2-methylpropene, comparison with the manganese(II) complexes[4,5] is necessary. In general, significant enhancement by copper(II) complexes of the rate of 2-methylpropene polymerization is associated with better polydispersity index (PDI) values and lower molecular weights. The most active catalyst is **1b**, which can achieve 2-methylpropene conversion of up to 78 % within 30 min (Table 4, entry 2). The low conversion obtained with **1c** is most probably owed to its very low solubility in all the solvents applied. The performance of the complexes **1a–c** and their Mn congeners is compared in detail in Table 4.

Table 4. Influence of the central metal atom on 2-methylpropene polymerization in dichloromethane with [IB] = 1.76 mol L^{-1}, T = 30 °C.

Complex	Time [h]	C_{cat} [10^{-4} mol L^{-1}]	Conversion [%]	M_n [g mol^{-1}]	PDI
1a	0.5	1.0	40	1700	1.4
1b	0.5	1.0	78	1400	1.4
1c	0.5	6.0	3	2000	1.4
a[a]	16	2.5	6.8	7843	1.7
b[a]	9	2.5	16.9	9023	1.7
c[a]	16	2.5	17.5	6133	1.7

[a] Complexes **a–c** are the manganese congeners of complexes **1a–c**. Data from ref. [4]

Performance in nonchlorinated solvents: Dichloromethane/hexane solvent mixtures were used in 2-methylpropene polymerization with **1a–c** as catalysts. With **1a** excellent conversions (≈80 %) can still be obtained when the proportion of *n*-hexane reaches 80 vol % in the mixture; but with **1b** as the catalyst, the conversion is already down to 35 % when only 20 vol % of *n*-hexane is used (Figure 3).

In dichloromethane/toluene solvent mixtures, **1a** performs even better (Figure 4): it is able to work in pure toluene and the 2-methylpropene conversion obtained (≈90 %) is higher than in dichloromethane; moreover, the *exo* terminal double bonds ratio is excellent (≈85 %) and the PDI is 1.9, which is impossible in the case of conventional Lewis acid catalysts.[11] The application of nonchlorinated solvents at room temperature has a signifi-

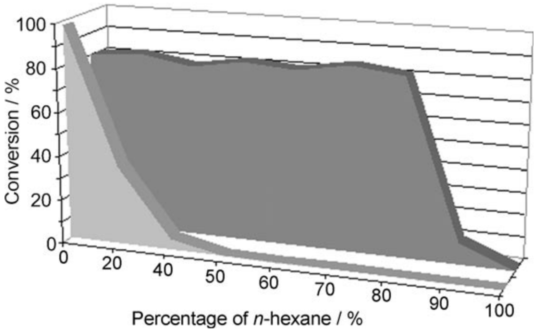


Figure 3. Performance of compounds **1a** (dark gray) and **1b** (pale gray) in a dichloromethane/*n*-hexane solvent. Water content 4 ppm; 2-methylpropene 1.76 mol L^{-1}; T = 30 °C; polymerization time 28 h; c_{cat} = 0.0001 mol L^{-1}.

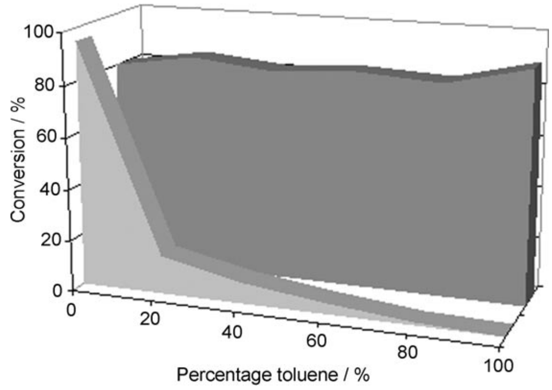


Figure 4. Performance of compounds **1a** (dark gray) and **1b** (pale gray) in a dichloromethane/toluene solvent. Water content 4 ppm; 2-methylpropene 1.76 molL^{-1}; T=30 °C; polymerization time 28 h; c_{cat}=0.0001 molL^{-1}.

Table 5. Influence of polymerization time and catalyst concentrations on conversion and terminal carbon double bond content with complex **2a**.

Time [h]	C_{cat} [10^{-4} molL^{-1}]	Conversion [%]	M_n [gmol^{-1}]	PDI [M_w/M_n]	*Exo* C=C content [%]
0.25	0.5	73	600	1.3	76
0.5	0.5	80	600	1.4	52
1	0.5	81	600	1.5	47
1	0.25	78	500	1.4	69
1	0.0625	37	900	1.5	82

$c_{isobutene}$=1.78 molL^{-1}; solvent toluene; T=30 °C; for *exo*-double bond calculations, see the Experimental Section and ref. [5a,c].

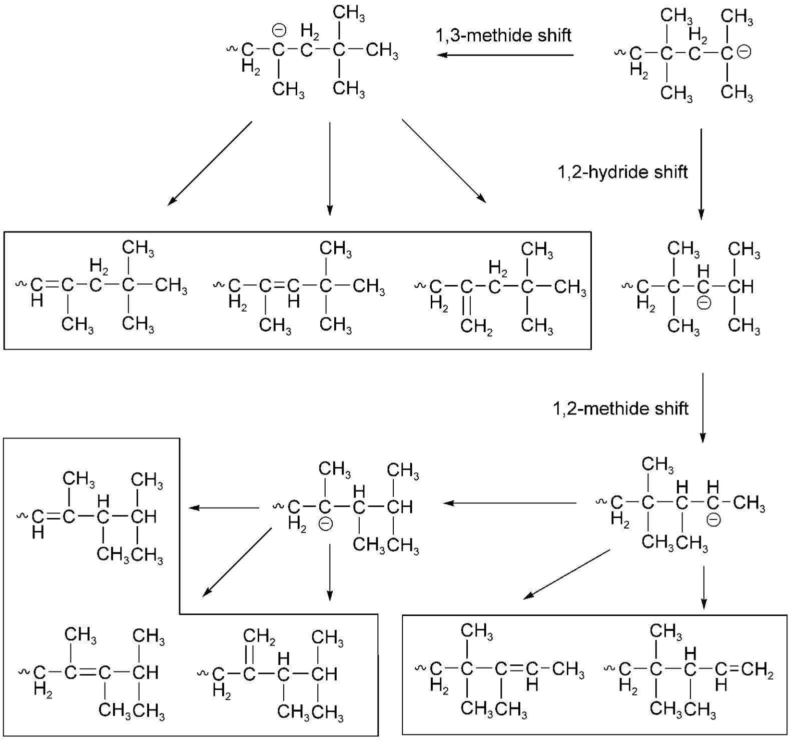
cant advantage over the manganese(II) systems as a more environmentally friendly process results.

Performance of benzonitrile-ligated complexes: In the search for better catalyst performance, acetonitrile was replaced by benzonitrile and propionitrile. The new complexes (**2a,b**–**3a,b**) were also tested for the homopolymerization of 2-methylpropene. It was observed that **2b**, **3a**, and **3b** did not produce any polymerization of 2-methylpropene in toluene at room temperature. Although 0.5×10^{-4} molL^{-1} of each complex and 1.78 molL^{-1} of 2-methylpropene were used, the three complexes did not display any catalytic activity even after 20 h of reaction.

However, with 0.5×10^{-4} molL^{-1} of **2a**, a conversion of 80% and a PDI of 1.4 could be obtained within 30 min (Table 5, entry 2), which is superior to even the best results obtained previously from **1b** in dichloromethane (Table 4, entry 2). This result might be ascribed to the better solubility of this complex in toluene and the lower coordinating ability of benzonitrile ligands than those of its acetonitrile congeners.

Additionally, as shown in Table 5, with **2a** the polymerization conversion reached 73% within 15 min, with a reasonably high ratio of *exo* terminal double bonds (≈76%). The significant reduction in the ratio of *exo* terminal double bonds when the reaction time increases (Table 5, entries 1–3) might be attributed to a double bond isomerization (Scheme 2) catalyzed by **2a**. Interestingly, the pace of the isomerization increases faster than that of the catalytic polymerization. This observation was confirmed when the ratio of terminal *exo* double bonds increased as the concentration of the catalyst **2a** decreased (Table 5, entries 3–5).

Influence of water: When the water content of the solvent is halved from ≈7 to 3.5 ppm, the reaction conversion is not influenced significantly for **1b** (the most active among the compounds examined) under the given conditions (dichloromethane, 30 °C). However, the average molecular weight increases from 1400 to 3800 gmol^{-1} and the PDI rises from 1.4 to 1.8, with the same catalyst concentration. As its content is increased the effect of water on the conversions becomes more pronounced, and when it is present in more than a 10-fold excess with respect to the catalyst a significant negative effect on the conversions can be observed. As the water



Scheme 2. Double bond isomerization of polyisobutene according to Puskas et al.[14]

concentration rises higher the conversion diminishes further until finally the polymerization process ceases completely.

A similar observation was made for **1a** (Figure 5). The effect on the conversion is minimal until a 10-fold excess of water is present. The conversion decreases drastically to 30 % when a 100-fold excess of water is added. This observation implies—as in the case of manganese(II) catalysts[4]—that the copper(II) complexes can tolerate quite large amounts of water, up to 10-fold excesses in comparison to the amount of catalyst applied. For the manganese(II) compounds it was found that two water molecules replace two *trans*-acetonitrile ligands if a large excess of water (≥10-fold) is present; this new complex is catalytically inactive.[4] It can be assumed that a similar reaction takes place in the case of copper(II) catalysts.

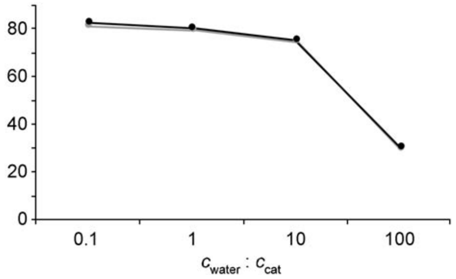


Figure 5. Effects of water on the conversion of isobutene to poly(isobutene) (catalyst **1a**; solvent CH_2Cl_2; $c_{2\text{-methylbutene}}$ 1.76 mol L^{-1}; $T = 30\,°C$; reaction time 2 h; $c_{cat} = 1.0 \times 10^{-4}$ mol L^{-1}).

Conclusion

$[Cu^{II}(NCR)_6]^{2+}$ ions (R = Me, Bn, Et), associated with weakly coordinating anions, are more active as catalysts than the manganese(II) congeners for synthesis of highly reactive polyisobutenes at room temperature. The best results can be obtained with **1a** and **1b**, both of which can work in pure toluene; the isobutene conversions obtained are between 73 % to 92 %, and the *exo* terminal double bond ratios are excellent (≈76–85 %). With benzonitrile ligands, **1b** can even reduce the reaction time from 28 h (needed for Mn complexes) to 15 min. This is very advantageous compared to the manganese(II) system applied previously. Only very recently have we found that certain molybdenum(III) complexes show a comparably high activity and solubility in nonpolar solvents.[13] Further work on immobilization of the most active catalysts, searching for more reactive metals, and tailoring weakly coordinating anions for better solubility and thermal stability is currently under way in our laboratories, together with mechanistic studies.

Experimental Section

Synthesis and characterization: All preparations and manipulations were carried out under an argon atmosphere using standard Schlenk techniques and all the solvents were dried by standard procedures. Unless otherwise stated, all the chemicals were used as received from Aldrich. IR was recorded by using a Perkin–Elmer FT-IR spectrometer using KBr pellets as matrix. EPR spectra were recorded by means of a JEOL JES-RE2X at X-band frequency ($\nu \approx 9.05$ GHz, microwave power 2 mW, modulation frequency 100 kHz). Elemental analyses were carried out at the Mikroanalytisches Labor of TU München. Thermogravimetric analysis (TGA) studies were performed by using a Mettler TA 3000 system at a heating rate of 10 K min^{-1} under a static air atmosphere.

General procedure for the synthesis of 1a, 1b, and 1c: *endo*-$CuCl_2$ (0.13–1.3 mmol) was added to a dry solution of the silver salt (0.22–2.14 mmol) in acetonitrile (20 mL). The resulting mixture was stirred for 2 h in darkness. After filtration the solvent was removed under high vacuum, affording the crude product, which was redissolved in dry dichloromethane (10 mL). The small amount of precipitate was removed by filtration and the solvent was removed under high vacuum to afford the desired product as a green solid.

*$[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ (**1a**)*: Preparation as described above, with $CuCl_2$ (175.0 mg, 1.3 mmol), $[Ag(NCCH_3)_4][B(C_6F_5)_4]$ (1.94 g, 2.14 mmol). Yield: 1.37 g (80 %); selected IR (KBr): $\tilde{\nu}$CN = 2279, 2317 cm^{-1}; elemental analysis calcd (%) for $C_{60}H_{18}CuB_2F_{40}N_6$ (1667.974): C 43.41, H 1.08, N 5.02; found: C 42.98, H 1.22, N 5.09.

*$[Cu(NCCH_3)_6][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ (**1b**)*: Preparation as described above, with $CuCl_2$ (115.0 mg, 0.85 mmol), $[Ag(NCCH_3)_2][B\{C_6H_3(m\text{-}CF_3)_2\}_4]$ (2.21 g, 2.14 mmol). Yield: 1.32 g (79 %); selected IR (KBr): $\tilde{\nu}$CN = 2303, 2332 cm^{-1}; elemental analysis calcd (%) for $C_{76}H_{42}CuB_2F_{48}N_6$ (2036.326): C 44.83, H 2.08, N 4.13; found: C 44.63, H 2.13, N 4.01.

*$[Cu(NCCH_3)_6][(C_6F_5)_3B\text{–}C_3H_3N_2\text{–}B(C_6F_5)_3]_2$ (**1c**)*: Preparation as described above, with $CuCl_2$ (17.8 mg, 0.13 mmol), $[Ag(NCCH_3)_2][(C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3]$ (0.30 g, 0.22 mmol). Yield: 0.23 g (85 %); selected IR (KBr): $\tilde{\nu}$CN = 2284, 2313 cm^{-1}; elemental analysis calcd (%) for $C_{90}H_{24}CuB_4F_{60}N_{10}$ (2491.982): C 43.38, H 0.97, N 5.62; found: C 43.35, H 1.26, N 6.11.

General procedure for the synthesis of 2a,b and 3a,b: *endo*-$CuCl_2$ (0.13–1.3 mmol) was added to a dry solution of the silver salt (0.22–2.14 mmol) in dichloromethane (10 mL). Then dry benzonitrile or dry propionitrile (30 equiv relative to the calculated amount of $CuCl_2$) was added. The resulting mixture was stirred for 8 h in darkness. After filtration the volatile component was removed under high vacuum, affording the product as a green solid.

*$[Cu(NCC_6H_5)_6][B(C_6F_5)_4]_2$ (**2a**)*: Preparation as described above, with $CuCl_2$ (17.8 mg, 0.132 mmol), $[Ag(NCCH_3)_4][B(C_6F_5)_4]$ (200 mg, 0.22 mmol), benzonitrile (0.22 mL, 3.3 mmol). Yield: 167 mg (75 %); selected IR (KBr): $\tilde{\nu}$(CN) = 2287, 2255 cm^{-1}; elemental analysis calcd (%) for $CuC_{90}H_{30}N_6B_2F_{40}$ (2040.37): C 52.9, H 1.48, N 4.12; found C 51.80, H 1.58, N 4.28.

*$[Cu(NCC_6H_5)_6][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ (**2b**)*: Preparation as described above, with $CuCl_2$ (15.7 mg, 0.116 mmol), $[Ag(NCCH_3)_2][B\{C_6H_3(m\text{-}CF_3)_2\}_4]$ (200 mg, 0.19 mmol), benzonitrile (0.19 mL, 2.9 mmol). Yield: 171 mg (73 %); selected IR (KBr): $\tilde{\nu}$(CN) = 2285, 2254 cm^{-1}; elemental analysis calcd (%) for $CuC_{106}H_{55}N_6B_2F_{48}$ (2408.722): C 52.85, H 2.26, N 3.49; found C 51.63, H 2.71, N 4.02.

*$[Cu(NCC_2H_5)_6][B(C_6F_5)_4]_2$ (**3a**)*: Preparation as described above, with- $CuCl_2$ (17.8 mg, 0.132 mmol), $[Ag(NCCH_3)_4][B(C_6F_5)_4]$ (200 mg, 0.22 mmol), propionitrile (0.24 mL, 3.3 mmol). Yield: 180 mg (82 %); selected IR (KBr): $\tilde{\nu}$(CN) = 2319, 2287 cm^{-1}; elemental analysis calcd (%) for $CuC_{66}H_{30}N_6B_2F_{40}$ (1752.13): C 45.24, H 1.72, N 4.29; found C 44.10, H 2.02, N 5.00.

*$[Cu(NCC_2H_5)_6][B\{C_6H_3(m\text{-}CF_3)_2\}_4]_2$ (**3b**)*: CuCL$_2$ (15.7 mg, 0.116 mmol), $[Ag(NCCH_3)_2][B\{C_6H_3(m\text{-}CF_3)_2\}_4]$ (200 mg, 0.19 mmol), propionitrile (0.21 mL, 2.9 mmol); Yield 193 mg (84 %). Selected IR (KBr) $\tilde{\nu}$(CN), 2313, 2279 cm^{-1}; elemental analysis calcd (%) for $CuC_{82}H_{54}N_6B_2F_{48}$ (2120.482) C 46.44, H 2.57, N 3.96; found C 45.70, H 2.60, N 4.36.

Polymerization reactions

Polymerization of 2-methylpropene: For higher screening efficiency, 2-methylpropene was homopolymerized in pressure tubes using a dry box. A maximum of 12 tubes were prepared at the same time. Each tube was filled with dry dichloromethane (20 mL) at −40 °C and the catalyst was added ($c_{cat} = 0.5\times10^{-4}$ mol L^{-1}). Various amounts of 2-methylpropene, which had been condensed into a separate tube previously, were added. The pressure tubes were sealed and removed quickly from the dry box. The polymerization was performed in a water bath mounted on a magnetic stirring plate; a temperature accuracy of ±0.1 °C could be obtained.

The polymerization was stopped with methanol (5 mL) and 2,2′-methylenebis(4-methyl-6-di-*tert*-butyl)phenol (0.2 g) was added to prevent oxidation. The solvents were removed in an oil-pump vacuum and the remaining polymer was dried to constant weight in high vacuum at 30 °C. The polymeric products were stored under an inert gas atmosphere. All polymerization experiments were performed with a control experiment, with dichloromethane (20 mL), complex **2a** (0.5×10^{-4} mol L^{-1}), isobutene (2 g), reaction time 2 h, reaction temperature 30 °C.

Exo *double bond determination*: *Exo* double bonds were calculated by using ^{1}H and ^{13}C NMR spectroscopy as described previously.[5a,c] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.13 MHz for ^{1}H and at 125.23 MHz for ^{13}C. $CDCl_3$ was used as solvent, lock, and internal standard ($\delta(^1H) = 7.26$ ppm, $\delta(^{13}C) = 77.00$ ppm) for the standard measurements.

The end group structure and the ratio of internal to terminal end group double bonds in the polyisobutene products were studied by ^{1}H NMR spectroscopy. As outlined previously, proton abstraction from the tertiary cation of the growing polyisobutene chain normally leads to *exo* or *endo* double bonds as end groups. By transfer reactions (isomerization) a variety of internal unsaturated bonds can be formed as well.[14,15] NMR signals were assigned on the basis of 1D and 2D NMR methods and confirmed the data given by Puskas et al.[14] and Stadermann et al.[16]

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