Polymerization Catalysts

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Molybdenum(III) Compounds as Catalysts for 2-Methylpropene Polymerization**

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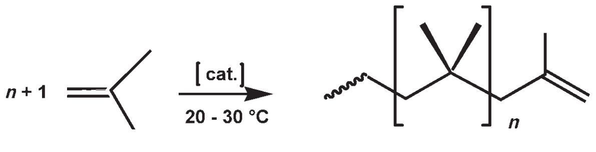
Dedicated to Süd-Chemie on the occasion of its 150th anniversary

Commercial polyisobutenes [Eq. (1)] can be classified into three groups based on their molecular weights, characteristic properties, and varied applications.[1] The high-molecular-weight ($M_n = 300\ \mathrm{kg\,mol^{-1}}$) polyisobutenes are rubber-like and thus have applications in the rubber goods industry and are used for insulation purposes. Mid-range polyisobutenes with molecular weights ranging from $M_n = 40$–$120\ \mathrm{kg\,mol^{-1}}$ are used in glues, sealants, and as chewing-gum base. The low-molecular-weight polyisobutenes have weights from $M_n = 0.5$–$5\ \mathrm{kg\,mol^{-1}}$ and are colorless, honeylike viscous liquids. The so-called highly reactive polyisobutenes belong to this class of polymers; they have more than 60% terminal (*exo*) C=C bonds (usually 70–80%) and are of significant commercial interest. After functionalization, these olefins are applied as lubricants or oil additives.[2,3]



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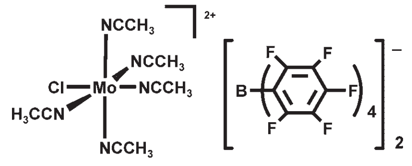
It has been known for many years that polymerization of 2-methylpropene ("isobutene") can be achieved by means of cationic initators like Brønsted or Lewis acids. Typical catalysts are $AlCl_3$, BCl_3, or BF_3 in combination with water or alcohols as co-initiator. Solvents like methyl chloride, dichloromethane, and *n*-hexane can be used in a temperature range of −20 °C to −80 °C, depending on the desired molecular weight of the polymeric product. Polymerization under these conditions is fast and exothermic, but it is expensive to maintain the reaction temperatures. Each year, several 100000 t of highly reactive polyisobutene are produced industrially using these methods.

Recently, a new type of catalyst has been described, consisting of solvent-ligated Mn^{II} complexes with bulky, non-coordinating counterions. These compounds are applicable for the polymerization of 2-methylpropene.[4–7] The great advantage of these systems is that polymerization takes place at room temperature or above.[4–7] We have now found that certain molybdenum(III) compounds significantly surpass the Mn^{II} complexes in activity and have other important advantages that are desirable for the preparation of highly reactive polyisobutenes. Herein, these Mo^{III} complexes and their applications in polymerization catalysis are described.

The complexes **1**–**3** are obtained in three steps starting by reaction of $Mo_2(O_2CCH_3)_4$ with a fourfold stoichiometric excess of HCl and KCl. The product $K_4[Mo_2Cl_8]\cdot 2H_2O$ is



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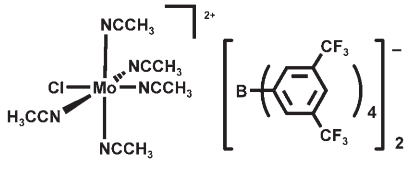

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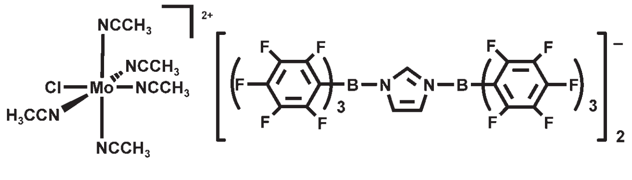

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transformed to $[Mo_2Cl_4(NCCH_3)_4]$ with $AgBF_4$.[8] The reaction of $[Mo_2Cl_4(NCCH_3)_4]$ and $[Ag(NCCH_3)_4][B(C_6F_5)_4]$ yields $[Mo(NCCH_3)_5Cl][B(C_6F_5)_4]_2$ (**1**) in approximately 75% yield. The derivatives **2** and **3** are prepared in a similar fashion in yields above 80%. Compounds **1**–**3** are stable at room temperature and can be handled in ambient conditions for brief periods of time. When heated, compound **1** (the most stable of the complexes under examination) begins to decompose at 173 °C. Compounds **2** and **3** decompose at 62 °C and 113 °C, respectively. According to the TGA-MS data (TGA = thermogravimetric analysis), the first decomposition step is associated with the loss of the acetonitrile ligands. At a temperature of roughly 200 °C, anion fragmentation begins. The CN stretching vibrations detected in the IR spectra are shifted to higher energy in comparison to free acetonitrile. This effect is due to the σ donation of electron density from the lone pairs of the nitrogen atoms, which have some antibonding character. The EPR spectra confirm the paramagnetic character of compounds **1**–**3**. An X-ray structure determination was carried out on compound **1**. Despite severe disordering of the anion, the analysis revealed that the dication (Figure 1) adopts a distorted octahedral structure, which has three acetonitrile ligands in the equatorial plane and one acetonitrile ligand *trans* to the chlorine atom. Unfortunately, the heavy disorder of the anions prohibits a detailed discussion of the cation structure. Very few related compounds have been characterized by X-ray crystallography, among them a Cr^{III} derivative.[9]

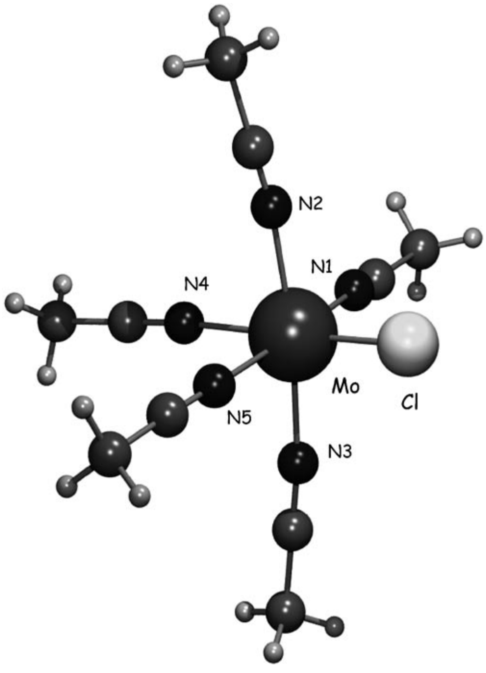

Figure 1. Ball-and-stick drawing of the dicationic part ($[Mo(NCCH_3)_5Cl]^{2+}$) of the solid-state structure of compound **1**.

Table 1: Polymerization of 2-methylpropene with catalysts **1**–**3**.[a]

Complex	c_{cat} [10^{-4} mol L^{-1}]	Conv [%]	M_n [g mol^{-1}]	PDI[c]
1	0.5	90	1300	3.2
2	0.5	94	1400	3.1
3	0.5	96	1000	2.7
Mn complex **4**[b]	0.5	76	2800	2.3

[a] Solvent CH_2Cl_2; initial isobutene concentration $[IB]_0 = 1.78$ mol L^{-1}; $T = 30$ °C; $t = 10$ h; [b] $[Mn(NCCH_3)_6][N_2C_3H_3\{B(C_6F_5)_3\}_2]_2$; $t = 16$ h.[4] [c] Polydispersity index.

With respect to the (industrially) desired polymer products, compounds **1**–**3** perform as well in 2-methylpropene polymerization as the best previously described Mn catalyst $[Mn(NCCH_3)_6][N_2C_3H_3\{B(C_6F_5)_3\}_2]_2$ (**4**; Table 1). However, the analysis of the products at shorter reaction times revealed that the Mo catalysts, particularly compound **3**, reach impressive conversions after a reaction time of just 30 min, whereas for the Mn compounds at least 10 h were needed for a reasonable polymer yield (Figure 2). This noteworthy improvement in activity might be ascribed, at least in part, to the higher Lewis acidity of the cation.[7e] From an industrial point of view, CH_2Cl_2 is not a desirable solvent, and so CH_2Cl_2/*n*-hexane and CH_2Cl_2/toluene mixtures have been employed as reaction media. Table 2 shows the catalyst performance in 1:1 CH_2Cl_2/*n*-hexane mixtures. Increasing the amount of *n*-hexane in the mixture leads to a decrease of conversion. With pure *n*-hexane, the reaction is no longer observed.

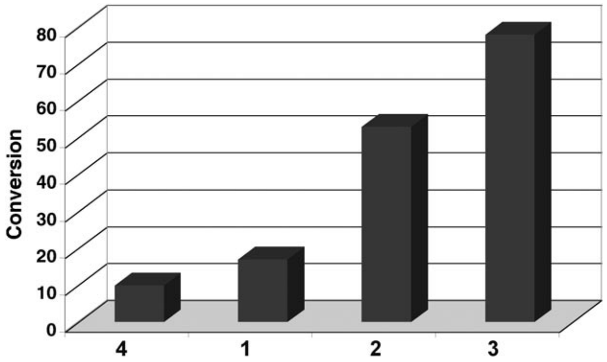

Figure 2. 2-Methylpropene conversion with compounds **1**–**3** or Mn complex **4** as the catalyst in CH_2Cl_2 at room temperature with a catalyst concentration of 0.5×10^{-4} mol L^{-1} after a reaction time of 30 min.

Table 2: Polymerization of 2-methylpropene in a CH_2Cl_2/*n*-hexane (1:1) with catalysts **1**–**3**.[a]

Complex	Conversion [%]	M_n [g mol^{-1}]	PDI	*exo* End groups [%]
1	84	800	2.13	65
2	31	1600	2.38	84
3	82	600	1.83	62

[a] $[IB]_0 = 1.78$ mol L^{-1}; $c_{cat} = 0.5 \times 10^{-4}$ mol L^{-1}; $T = 30$ °C; $t = 2$ h.

The same negative effect is not seen, however, in toluene. Particularly in the case of compound **3**, the performance in pure toluene is satisfying. Conversions of 67% ($M_n = 600$ g mol^{-1}, PDI = 1.5, *exo* end group content = 90%) are reached at room temperature within only two hours with a catalyst concentration of $0.5\times10^{-4}\,\mathrm{mol\,L^{-1}}$. When reducing the catalyst concentration to $0.125\times10^{-4}\,\mathrm{mol\,L^{-1}}$, the conversion under the same reaction conditions drops to 54 %, but M_n, PDI, and *exo* group content remain in the same order of magnitude. Furthermore, replacement of the acetonitrile ligands by benzonitrile proves to be advantageous in several respects. Apart from good solubility, nearly complete conversion is achieved within just 15 min with a catalyst concentration of $0.5\times10^{-4}\,\mathrm{mol\,L^{-1}}$, and an M_n value of $1300\,\mathrm{g\,mol^{-1}}$ is obtained.

To summarize, complexes of the type $[\mathrm{MoCl(NCCH_3)_5}][\mathrm{A}]_2$, with “A” being a noncoordinating counterion, prove to be extremely active catalysts for the preparation of highly reactive polyisobutenes at room temperature. The $\mathrm{Mo^{III}}$ catalysts share all relevant advantages of the previously described $\mathrm{Mn^{II}}$ catalysts in comparison to the current industrial catalyst systems. Furthermore, the compounds described herein achieve higher reaction velocity than the Mn systems even at much lower catalyst concentrations and can be used in nonchlorinated solvents such as toluene.

Experimental Section

1: $[\mathrm{Mo_2(NCCH_3)_4Cl_4}]$ (45.0 mg, 0.009 mmol) was added to a solution of $[\mathrm{Ag(NCCH_3)_4}][\mathrm{B(C_6F_5)_4}]$ (344.0 mg, 0.36 mmol) in dry $\mathrm{CH_3CN}$ (10.0 mL) under argon, and the mixture was stirred at room temperature for 12 h in darkness. The solution was filtered, and the precipitate that had formed (AgCl) was removed. The filtrate was concentrated to 1.0 mL under vacuum (oil pump) and cooled to −35 °C. Compound **1** (0.35 g, 75 % yield) was obtained as a dark green crystalline solid. IR (KBr): $\tilde{\nu} = 2288, 2321\,\mathrm{cm^{-1}}$ (ν_{CN}). Elemental analysis calcd (%) for $\mathrm{C_{58}H_{15}MoB_2ClF_{40}N_5}$ (1694.751): C 41.10, H 0.89, N 4.13; found: C 41.06, H 0.84, N 4.32.

X-ray structure determination on compound **1**: Data collection was aborted after collecting a few images. The solution based on these data revealed a severe disorder of the dication and nonresolvable, disordered solvent molecules. $2[(\mathrm{C_{24}BF_{20}})^-]$, $[(\mathrm{C_{10}H_{15}ClMoN_5})^{2+}]\cdot n(\mathrm{CH_2Cl_2})$, green fragment ($0.15\times0.48\times0.64\,\mathrm{mm^3}$), monoclinic, space group $P2_1/c$ (No. 14), $a = 13.1364(1)$, $b = 35.2848(5)$, $c = 16.7086(3)$ Å, $\beta = 109.7620(15)°$, $V = 7288.6(2)\,\mathrm{Å^3}$, $Z = 4$. Preliminary examination and data collection were carried out on a κ-CCD device (Nonius Mach3) with an Oxford Cryosystems cooling system at the window of a rotating anode (Nonius FR591) with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å). Data collection was performed at 123 K. Full-matrix least-squares refinements were aborted at $R1 = 0.0690$ [6814 intensities, $I_o > 2\sigma(I_o)$], $wR2 = 0.2117$ [8313 intensities, all data].

Polymerization of isobutene: For higher screening efficiency, the homopolymerization of isobutene was performed in pressure tubes in a drybox. A maximum of eight tubes were prepared at the same time. Each tube was filled with dried dichloromethane (20 mL, water content ca. 1.7 ppm) at −25 °C, and the catalyst ($0.5\times10^{-4}\,\mathrm{mol\,L^{-1}}$) was added. A magnetic stirring bar was added to each tube. Various amounts of isobutene, which had been condensed into a separate steel tube, were added. The pressure tubes were sealed and quickly removed from the drybox. The polymerization was performed in a thermostatically controlled water bath equipped with a magnetic stirrer at the desired temperature (e.g. 30 °C). The polymerization was quenched with methanol (5 mL), and 2,2′-methylene-bis(4-methyl-6-di-*tert*-butyl)phenol (0.2 g) was added to prevent oxidation. The solvents were removed under oil-pump vacuum, and the remaining polymer was dried under vacuum at 40 °C until the weight remained constant.

Gel permeation chromatography (GPC) measurements were performed with an Agilent Technologies series 1100 GPC system with a Lichrogel PS 40 column and UV detector. Chloroform was used as solvent. End-group analysis was performed by ^{1}H and ^{13}C NMR spectroscopy (see ref. [6]). The spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.13 MHz (^{1}H) or 125.23 MHz (^{13}C). $\mathrm{CDCl_3}$ was used as solvent, lock, and internal standard ($\delta(^1\mathrm{H}) = 7.26$ pm, $\delta(^{13}\mathrm{C}) = 77.00$ pm).

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