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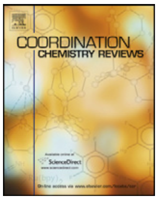

Review

Inorganic/organometallic catalysts and initiators involving weakly coordinating anions for isobutene polymerisation

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ABSTRACT

Polyisobutenes have numerous industrial applications, e.g. as rubbers, sealants, lubricants and oil additives. For the latter two applications, being the largest end-use markets, polyisobutenes are produced on a several 105 t scale per year. Polyisobutenes applied in mineral oil applications are of low molecular weight. They are industrially produced at temperatures below 0 °C, usually with very active but simple inorganic Lewis acid initiators. During the last decade, research groups developed and examined new types of mostly inorganic/organometallic initiators that work closer to ambient temperatures and provide polymer products of high quality, being at least on a par with the current large scale produced industrial products. An overview on the state of the art and new developments is given in this article.

1. Introduction

Isobutene (IB) is one of the best investigated monomers for cationic polymerisation [1]. Polyisobutenes (PIB) are chemically resistant and non-toxic. They have high dumping properties and are among the best-known carbon-based barrier for gases. Commercial PIBs are categorised according to the molecular weight. The applications of PIB cover a wide range, from sealants and roofing (high molecular weight PIB above of 300,000 g/mol) to adhesives, extenders, and chewing gum base (medium molecular weight PIB between 4000 and 120,000 g/mol) and finally to glues, lubricants and modifiers and oil additives (low molecular weight PIB between 500 and 5000 g/mol) [2]. Lubricating oils and additives for lubricants, gasoline and diesel fuel comprise by far the largest end-use

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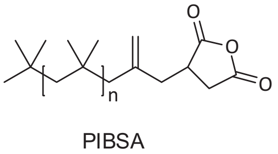


Scheme 1.1. PIB derivatives Glissopal® (PIBSA) and Kerocom® (PIBSI).

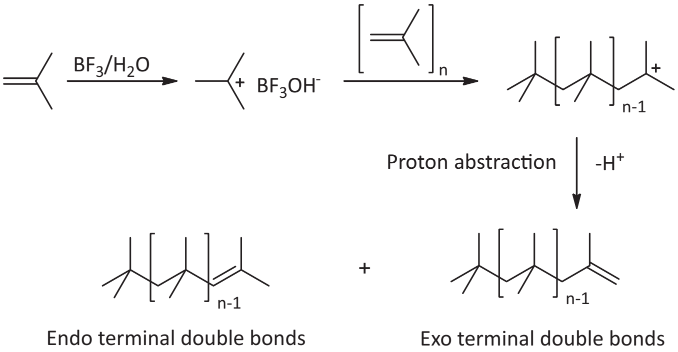
products for PIBs, representing between 75% and 80% of the market. All PIBs used for these applications are however low molecular weight PIBs (LM-PIB) and their derivatives, such as Glissopal® (PIBSA) and Kerocom® (PIBSI) (Scheme 1.1) from BASF SE.

The synthesis of PIB is mainly dominated by the use of Lewis acids as coinitiators and traces of alcohol or water as initiators [3,4], such as H_2O/BF_3 [5]. In a typical cationic polymerisation of IB, the proton adds to the monomer to produce a carbenium ion, which undergoes electrophilic attack of another monomer. The proton abstraction from the growing PIB chain – by transfer to monomer or solvent – results in two main types of terminal unsaturated end groups, which are *exo* double bonds (α-termination) and *endo* double bonds (β-termination) as shown in Scheme 1.2. Additionally, internal double bonds are found in PIB, arising probably from a 1,3-methide shift, concerted 1,2-hydride-1,2 methide shift and tail-to-tail addition of isobutylene [6].

Exo terminal double bonds are highly reactive and less thermodynamically stable, while the *endo* terminal and other internal double bonds are more stable and thermodynamically favoured. It is only to some extent valid for PIB that the molecular weights are controlled by the monomer/initiator ratio in a polymerisation. Because of pronounced chain transfer reactions, achievable molecular weights are highly governed by the reaction temperatures. Therefore, in order to control the polymerisation process and maintain the desired molecular weights of PIB the effect of temperature on the molecular weight can be expressed by the Arrhenius plots (M_n dependence on $1/T$) [5] and a narrow polydispersity index (PDI), cationic polymerisation of isobutene is typically carried out at costly cryogenic temperatures (−100 to −20 °C) and chlorinated solvents to minimise the unfavourable chain transfer reactions. It is therefore relatively environmentally taxing. In addition to IB homopolymers, there is also significant interest in copolymers with isoprene (IP), styrene and derivatives [7–11].

Nevertheless, the industrial processes (Scheme 1.3) based on this type of chemistry have enjoyed considerable longevity, e.g. with a plant first commissioned in 1938 by IG Farben for homopolymerisation of IB [12], and the technology of copolymerisation of IB and IP (butyl rubber) introduced in 1943 [13].

Traditional Lewis acid initiated polymerisation of IB has been the main or co-subject of several books and reviews varying in both length and scope [5,15–26]. With this review, recent developments during the last 15 years in this field are being covered with focus on non-traditional organometallic and transition metal catalysts/initiators (in most cases complex cations associated with weakly coordinating anions). It should be emphasized, however, that reaction mechanisms and mechanistic considerations are not in the focus of this review, particularly since some – in principal – important work has only been communicated in conference papers, which are difficult to access or not available any more. Due to the same reasons, whether the polymerisation is a catalytic process or a polymerisation process started by an initiator (the initiator is usually consumed and becomes part of the polymer chain, etc.) will not be discussed in detail for each system. This work mainly summarizes – and if necessary, comments on – recently published practical work in the specific field.



Scheme 1.2. The typical mechanism for isobutene polymerisation via protonation and the two main types of terminal unsaturated end groups formed [6].

2. Catalyst systems

2.1. Role of weakly coordinating anions

The importance of weakly coordinating anions (WCAs) in homogeneous catalysis can be explained by the fact that they support the creation of vacant coordination sites on metal centres. Since S.H. Strauss' article in *Chemical Reviews* [27], numerous new WCAs appeared. Many of them were initially published in the patent literature, demonstrating their potential for various industrial applications. During the last two decades, WCAs have been widely applied in the fields of metallocene-based olefin polymerisation, fundamental coordination chemistry, catalytic organic transformations, ionic liquids, etc. [28].

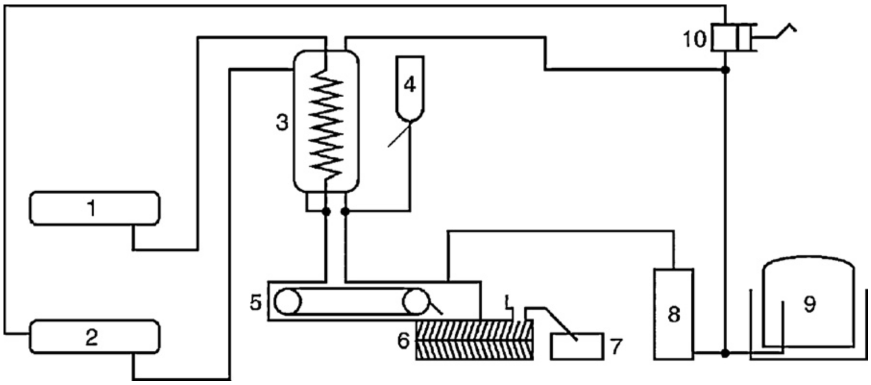
The most widely known applications of WCAs are group IV metallocene-based olefin polymerisation reactions [29]. The importance of WCAs in metal-catalysed polymerisations can be acknowledged from the activation process (Scheme 2.1), in which the hydride/alkyl abstraction of the precatalysts by the co-catalysts generates the active cationic catalysts. The co-catalysts, which become counteranions after the activation process, are the vital part of a catalytically active cation–anion pair and may significantly influence polymerisation characteristics and polymer properties. Scheme 2.1 [29] depicts the afore mentioned relationships between catalysts and co-catalysts in metal-catalysed olefin polymerisation systems.

Although the chemistry of the propagation and chain-transfer steps of carbocationic polymerisation is often complicated, it is generally agreed [5,15,21–26,30,31] that the rates of chain transfer are strongly affected by the nature of the counteranion (or other Lewis base) and can be minimised by the use of WCAs. Therefore, the cationic polymerisation can be carried out at higher temperatures. As a result, there has been increasing interest in synthesis and application of WCA-incorporated catalysts/initiators for homo- and copolymerisation of isobutenes during the last 15 years.

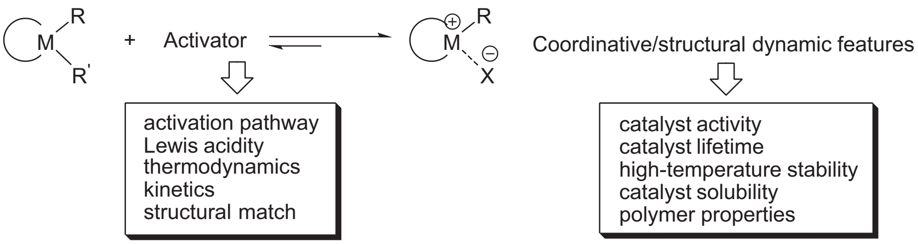
Indeed, the necessity and advantages of using WCAs is not only for protic initiators, but for nearly all types of catalysts/initiators that will be reviewed in this article. The effect and influence of various types of WCAs will be discussed in detail in the following sections.

2.2. Metallocene-based and related initiators

Group IV metallocene compounds are well known as homogeneous catalysts in Ziegler-type polymerisation of 1-alkenes [29,32,33]. The most active catalysts are the formally 14-electron, cationic complexes $[Cp'_2MR]^+$ (Cp′ = functionalised cyclopentadienyl; M = Ti, Zr, Hf; R = alkyl, H) [34–36]. Another family of compounds satisfying the apparent requirements for Ziegler–Natta



Scheme 1.3. Process for the manufacture of Oppanol B®: 1: liquid isobutene, 2: liquid ethylene, 3: cooler-mixer, 4: BF_3-ethylene reservoir, 5: continuous belt, 6: compacting rolls, 7: product, 8: CaO to purify ethylene recycle, 9: gasometer, and 10: compressor [14].



Scheme 2.1. Relationships between catalysts and co-catalysts in metal-catalysed olefin polymerisation [29].

catalysis are 10-electron, monocyclopentadienyl complexes of the type $[Cp'MR_2]^+$. These electronically less saturated and sterically less hindered complexes are expected to exhibit even higher reactivities than their metallocene counterparts.

2.2.1. 10-Electron monocyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)MMe_2][WCA]$ (M = Ti, Hf)

First reported in 1995 [37], Baird and co-workers showed that the reaction of Cp^*TiMe_3 [38] with highly electrophilic Lewis acid $B(C_6F_5)_3$ [39] results in the formation of methyl-bridged compound $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (Scheme 2.2, compound A), which readily dissociates the borate anion to form the 10-electron, cationic species $[Cp^*TiMe_2]^+$.

The latter is a very effective initiator for homopolymerisation of isobutene at temperatures around −40 °C, therefore somewhat higher than those normally used industrially. This method provides PIB with M_w up to 10^6 g/mol and PDIs of the range 1.9–3.2 (Table 2.1) [40]. While changing initiator concentration has little effect on the molecular weight distribution, lowering the polarity of the solvent results in narrow PDI values. The molecular weights are generally lower at lower temperatures and in more polar solvents. This is due to the fact that the formation of the ion pairs, as well as chain-transfer events takes place more easily in polar solvents, such as CH_2Cl_2 [5,15,21,23–25].

Table 2.1
Selected results of homopolymerisation of isobutene and copolymerisation of isobutene and isoprene with $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ as initiator[a].

Entry	Solvent	T (°C)	M_w (kg/mol)	PDI	Conv. (%)
1	CH_2Cl_2	−40	210	3.2	78
2	CH_2Cl_2	−60	740	2.7	68
3	CH_2Cl_2	−75	820	3.0	34
4	Toluene	−40	620	2.1	62
5	Toluene	−60	1,070	1.9	78
6	Toluene	−75	910	1.9	49

[a] Average of two runs, initiator conc.: 0.004 M. Data from Ref. [40].

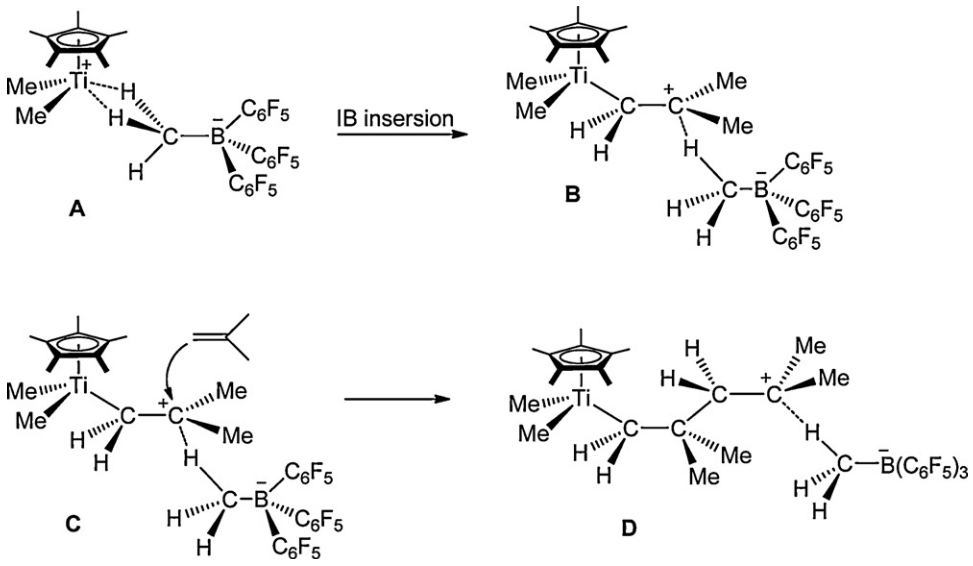
Table 2.2
Selected results of polymerisation of isobutene at −30 °C in toluene under reduced pressure (IB:Ti = 2800:1).

Entry	WCA	M_w (kg/mol)	PDI	Conv. (%)	Ref.
1	$[BMe(C_6F_5)_3]^-$	421	1.6	20	[43]
2	$[n\text{-}C_{18}H_{37}OB(C_6F_5)_3]^-$	429	1.6	26	[43]
3	$[n\text{-}C_{18}H_{37}SB(C_6F_5)_3]^-$	417	1.5	8	[43]
4[a]	$[B(C_6F_5)_4]^-$	434	1.9	100	[43]
5	$[AlMeC_6F_5)_3]^-$	298	1.75	7	[43]
6[b]	$[n\text{-}C_{17}H_{35}CO_2(B(C_6F_5)_3)_2]^-$	682	1.60	100	[44]
7[b]	$[n\text{-}C_{17}H_{35}CO_2B(C_6F_5)_3]^-$	–	–	0	[44]

[a] IB:Ti = 11160:1.
[b] DCM as solvent.

A number of observations, such as the inverse dependence of M_w on temperature, the polymer microstructures, the identities of the end groups of the polymers, and the fact that the system induces dimerisation of 1,1-diphenylethylene to 1,3,3-triphenyl-3-methylindan, strongly suggest a conventional carbocationic mechanism, as shown in Scheme 2.2 [17,40]. No clear evidence for a typical Ziegler–Natta process is available, as reported by Shaffer for the copolymerisation of ethylene and isobutene, using $(Cp^*)(N\text{-}c\text{-}C_{12}H_{23})(SiMe_2)TiMe_2$ as catalyst [41]. On the other hand, a possible protic mechanism was excluded by Baird and co-workers based on the fact that $[Cp^*TiMe_3]$ readily eliminates additional proton sources. The use of proton traps such as 2,6-di-*tert*-butylpyridine (DTBP) [42] was also inappropriate, since the supposedly nonnucleophilic base does indeed coordinate to the Ti centre, forming a π-complex (Scheme 2.3, compound E) [40].

Baird and co-workers also found that in association with WCAs of the type $([(n\text{-}C_{18}H_{37}E)B(C_6F_5)_3]^-$, E = O or S), the cationic species $[Cp^*TiMe_2]^+$ effects the polymerisation of isobutene to high molecular polymers with moderate to high conversions in the temperature range of −40 to −20 °C (Table 2.2, entries 2, 3) [43]. This system is comparable to the model system $[Cp^*TiMe_2][BMe(C_6F_5)_3]$. On the other hand, the $[Cp^*TiMe_2][B(C_6F_5)_4]$ and $[Cp^*TiMe_2][AlMe(C_6F_5)_3]$ systems are



Scheme 2.2. Initiation and propagation of IB polymerisation by Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ [37].

very different; the former provides PIB with unusually high rates and conversions, which is consistent with results with initiator systems using the [B(C$_6$F$_5$)$_4$]$^-$ anion [31]. The aluminium system, however, exhibits low activity, probably due to the stronger coordination abilities of the [AlMe(C$_6$F$_5$)$_3$]$^-$ anion.

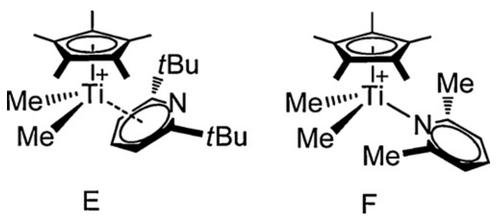
Subsequent investigations [44] further proved the effect of WCAs on homopolymerisation of isobutene; initiators incorporating the anion from the 1:2 adduct of n-C$_{17}$H$_{35}$CO$_2$H and B(C$_6$F$_5$)$_3$ lead to a much more effective initiator than those with the anion of the 1:1 adduct, which only lead to trace amounts of polymers (Table 2.2, entries 6, 7). For WCAs shown in Scheme 2.4, Arrhenius-type plots of log(M_n) vs. T^{-1} could be obtained for polymerisation in toluene [43], and the activation energies for the polymerisation were in the range −11 to −27 kJ/mol, comparable to most conventional isobutene polymerisation initiators.

The same initiator systems are also very active for copolymerisation of isobutene and IP [44,45]. With [BMe(C$_6$F$_5$)$_3$]$^-$ as counterion, conversions are higher in the more polar solvents (Table 2.3, entries 1, 6, 7). This is consistent with the behaviour in the homopolymerisation of isobutene. Except [n-C$_{18}$H$_{37}$SB(C$_6$F$_5$)$_3$]$^-$, complexes paired with other WCAs are also excellent initiators (Table 2.3, entries 3–5) in CH$_2$Cl$_2$, affording copolymers of isobutene and IP with quantitative conversions and in general higher molecular weights than in the case of [BMe(C$_6$F$_5$)$_3$]$^-$, demonstrating the weakly coordinating nature of the according anions. Interestingly, in contrast to the case of homopolymerisation of isobutene, copolymerisation of isobutene and IP in CH$_2$Cl$_2$ does not require a 1:2 adduct of n-C$_{17}$H$_{35}$CO$_2$H and B(C$_6$F$_5$)$_3$. High conversions could also be obtained with the anion [n-C$_{17}$H$_{35}$CO$_2$B(C$_6$F$_5$)$_3$]$^-$ resulting from the 1:1 adduct (Table 2.3, entry 5). The analogous hafnium system was also assessed. The results show that the Hf complexes are almost as efficient as their Ti counter parts (Table 2.3, entries 9–11). The same group also investigated the Ti(CH$_2$Ph)$_4$/B(C$_6$F$_5$)$_3$ system [46] and found that the cationic species [Ti(CH$_2$Ph)$_3$]$^+$ is also applicable for the homopolymerisation of isobutene, affording medium molecular PIB with high conversions at elevated temperatures (molecular weight = 20,800 g/mol, conversion = 90%, PDI = 1.8, CH$_2$Cl$_2$).

Table 2.3
Copolymerisation of isobutene and IP using [Cp*MMe$_2$][WCA] (M = Ti, Hf) as initiators[a].

Entry	WCA	Solvent	M_w (kg/mol)	PDI	Conv. (%)	Ref.
1	[BMe(C$_6$F$_5$)$_3$]$^-$	CH$_2$Cl$_2$	290	1.8	100	[45]
2	[n-C$_{18}$H$_{37}$SB(C$_6$F$_5$)$_3$]$^-$	CH$_2$Cl$_2$	380	1.9	27	[45]
3	[n-C$_8$F$_{17}$CH$_2$OB(C$_6$F$_5$)$_3$]$^-$	CH$_2$Cl$_2$	500	1.7	100	[45]
4[b]	[n-C$_{17}$H$_{35}$CO$_2$(B(C$_6$F$_5$)$_3$)$_2$]$^-$	CH$_2$Cl$_2$	495	2.7	100	[44]
5[c]	[n-C$_{17}$H$_{35}$CO$_2$B(C$_6$F$_5$)$_3$]$^-$	CH$_2$Cl$_2$	373	1.9	100	[44]
6	[BMe(C$_6$F$_5$)$_3$]$^-$	CF$_3$C$_6$H$_5$	220	1.6	90	[45]
7	[BMe(C$_6$F$_5$)$_3$]$^-$	Toluene	170	1.5	9	[45]
8	[n-C$_8$F$_{17}$CH$_2$OB(C$_6$F$_5$)$_3$]$^-$	Toluene	100	1.7	50	[45]
9[d]	[BMe(C$_6$F$_5$)$_3$]$^-$	CH$_2$Cl$_2$	160	3.5	100	[45]
10[d]	[n-C$_8$F$_{17}$OB(C$_6$F$_5$)$_3$]$^-$	CH$_2$Cl$_2$	290	2.3	86	[45]
11[d]	[n-C$_8$F$_{17}$OB(C$_6$F$_5$)$_3$]$^-$	CF$_3$C$_6$H$_5$	250	1.9	86	[45]

[a] 12 mL IB, 100 mg IP, 25 mg B(C$_6$F$_5$)$_3$ (0.048 mmol), 11 mg (0.048 mmol) Cp*TiMe$_3$, 0.048 mmol of alcohol or thiol, −30 °C.
[b] 6.9 mL IB, 120 mg IP.
[c] 8.13 mL IB, 115 mg IP.
[d] Hf was used instead of Ti.

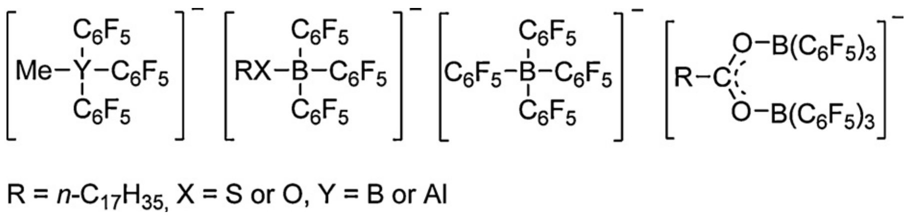


Scheme 2.3. Coordination of [Cp*TiMe$_2$]$^+$ with 2,6-di-*tert*-butylpyridine (DTBP) and 2,6-dimethylpyridine (DMP) [40].

2.2.2. 14-Electron cationic metallocene complexes [Cp'_2MR]$^+$

Soon after the discovery of Baird and co-workers [37], group IV metallocene-type compounds have become the focus of several other research groups in the field of cationic polymerisation of isobutene, especially for the groups of Bochmann [47–51] and Shaffer [41,42,52]. For example, zirconocene compounds of the type [Cp$^R_2$ZrMe$_2$][WCA] (Cp^R = Cp, C$_5$H$_4$SiMe$_3$, C$_5$Me$_5$; WCA = [BMe(C$_6$F$_5$)$_3$]$^-$, [B(C$_6$F$_5$)$_4$]$^-$), reported by Bochmann and co-workers are very good initiators for the polymerisation of isobutene at temperatures up to approximately −30 °C. It was found that the initiator efficiency is influenced by the following factors:

(a) Trace amounts of water. While the zirconocene alkyl species are highly active for polymerisation of isobutene (Table 2.4, entries



Scheme 2.4. Various WCAs associated with $[Cp^*TiMe_2]^+$ [37,40,43,44].

1, 2), their hydrolysis products show no activity at all (Table 2.4, entries 3, 4).

(b) Initiator concentration. Increasing the volume of isobutene leads to higher molecular weight polymers, particularly for homopolymerisation of isobutene (Table 2.4, entry 5).

(c) Counteranion effect. At higher temperatures, less coordinating anions, such as $[B(C_6F_5)_4]^-$ are more effective, affording significantly increased conversions and molecular weights comparable to $[BMe(C_6F_5)_3]^-$.

Another important feature of this initiator system is that the M_w of the copolymers are remarkably similar to those of the homopolymers. This is unusual for traditional Lewis acid initiators and both for the $[Cp_2Al][BMe(C_6F_5)_3]$ [53] and $[Zr(N(SiMe_3)_2)_3][BMe(C_6F_5)_3]$ [48] systems which will be mentioned latter in this chapter. The same phenomena, high M_w of the polymers and high conversions, were also observed for the zirconocene hydride complexes (see below).

It was subsequently discovered that cationic zirconocene hydride complexes derived from the reaction of $[Cp'_2ZrH(\mu\text{-}H)]_2$ ($Cp' = (C_5H_4SiMe_3)$) with $[CPh_3][B(C_6F_5)_4]$ are powerful initiators for the cationic polymerisation of isobutene and considerably more active than the corresponding dimethyl zirconocene Cp'_2ZrMe_2, particularly at higher temperatures [49]. The polymerisation rates and polymer yields are significantly higher than in the case of $[Cp_2ZrMe_2]$ under neat conditions (Table 2.4, entries 6, 8). Of particular importance is the high conversion in copolymerisation of isobutene and IP at −30 °C (Table 2.4, entry 9), whereas the $Cp_2ZrMe_2/[CPh_3][B(C_6F_5)_4]$ system produces only trace amounts of polymers under the same conditions. However, the molecular weight is much lower and the PDI value much broader (Table 2.4, entry 8), implying a different initiation mechanism than the zirconocene methyls. Indeed, detailed NMR studies and crystallographic evidence strongly suggest an initiation mechanism involving monomer insertion into a Zr–H bond (Scheme 2.5) [50].

Table 2.4
Selected results of homo- and copolymerisation of isobutene with zirconocene initiators and $B(C_6F_5)_3$ as co-initiator[a].

Entry	Initiator	T (°C)	M_w (kg/mol)	PDI	Conv. (%)	Ref.
1	$[Cp_2ZrMe_2]$	−78	144	3.9	21	[47]
2	$[Cp^*_2ZrMe_2]$	−70	1,285	2.7	60	[47]
3	$[Cp^*_2Zr(OH)_2]$	−70	2,500	4.0	2	[47]
4[b]	$[(Cp'_2ZrMe)_2(\mu\text{-}O)]$	−70	–	–	0	[47]
5[c]	$[Cp_2ZrMe_2]$	−78	2,500	3.8	10	[47]
6[d]	$[Cp_2ZrMe_2]$	−78	2,260	1.7	13	[47]
7[e]	$[Cp_2ZrMe_2]$	−78	137	3.6	22	[47]
8[c,f]	$[Cp'_2ZrH_2]_2$	−78	465	8.9	70	[49]
9[c,f]	$[Cp'_2ZrH_2]_2$	−30	142	2.7	42	[49]

[a] Conditions: 50 μmol of Cp_2ZrMe_2 in 1 mL CH_2Cl_2; 50 μmol of $B(C_6F_5)_3$ in 0.5 mL CH_2Cl_2; 10 mL IB; reaction time, 5 min.

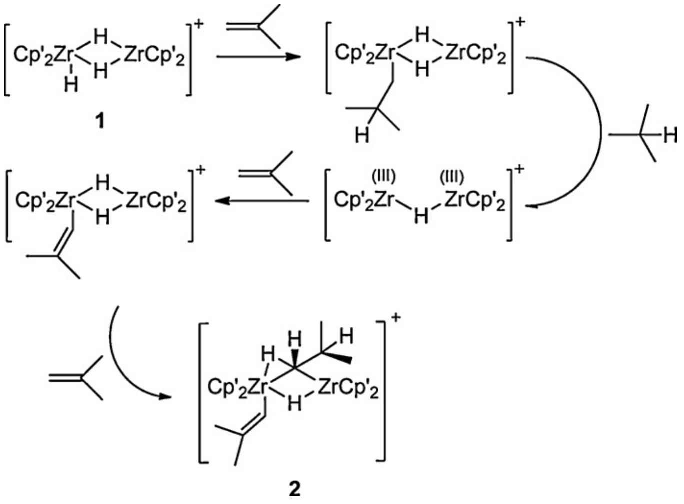
[b] $Cp' = C_5H_4SiMe_3$.

[c] 100 mL IB; reaction time, 30 min.

[d] 50 μmol of $[CPh_3][B(C_6F_5)_4]$.

[e] Copolymerisation of IB and IP; 0.15 mL IP.

[f] Premixed solutions of 50 μmol $[Cp'_2ZrH_2]_2$ and 100 μmol of $[Ph_3C][B(C_6F_5)_4]$ in 1 mL CH_2Cl_2.



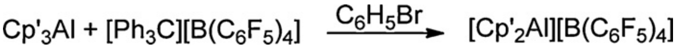
Scheme 2.5. Possible mechanism for the reaction of **1** with IB to give the proposed intermediate species **2** [50].

It is believed that these alkyl/hydride-bridged binuclear species clearly lead to initiation of polymerisation of isobutene, though it is still not conclusive whether these intermediates themselves are the initiating species.

Bochmann and co-workers also investigated the role of WCAs in more detail. It was reported that molecular weights of the polymers increased depending on the nucleophilicity of the WCA according to WCA = $[B(C_6F_5)_4] \approx [H_2N(B(C_6F_5)_3)_2] > [CN(B(C_6F_5)_3)_2]$. The hexahalocarborane anions $[CB_{11}H_6X_6]^-$ (X = Cl, Br, I) [54] are not compatible with the zirconocene hydride system, probably because of halide abstraction from the hydride. The addition of substoichiometric quantities of water to the reaction medium leads to a decrease in activity, with complete activity loss when $[H_2O] \approx [Zr]$. The molecular weight of the product polymers also decreases linearly with increasing $[H_2O]$, presumably due to a chain transfer mechanism. The zirconocene hydride system also provides much higher M_w than the classical Et_2AlCl/*tert*-butyl-Cl system under similar conditions, because of the much lower chain transfer inducing tendency of the applied WCAs compared to the chloroaluminate anions obtained in the other system.

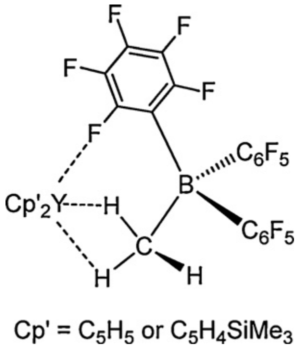
The same group also found that the easily synthesised non-metallocene cationic zirconium amide $[Zr(N(SiMe_3)_2)_3]^+$, paired with the WCA $[BMe(C_6F_5)_3]^-$, is active for polymerisation of IB and copolymerisation of isobutene and IP [48]. The polymerisation results are comparable to those obtained with $[ZrCp_2Me][B(C_6F_5)_3]$.

Shaffer et al. [42] extensively investigated group IV metallocene-like initiators $[Cp^*TiMe_3]$ and $[Cp^R_2MMe_2]$ (Cp^R = Cp, Cp* or $Me_2Si(THI)$, THI = tetrahydroindenyl; M = Zr or Hf) for homopolymerisation of isobutene and observed that the rate of polymerisations follows the order $[Cp^*TiMe_3] > [Cp^*_2ZrMe_2] \approx [(Me_2Si(THI)_2)ZrMe_2] > [Cp_2HfMe_2]$. Two initiation mechanisms were suggested: (a) metal cation addition to the olefin, and (b) initiation originating from protons generated by the reaction of



$$Cp'_3Al + [Ph_3C][B(C_6F_5)_4] \xrightarrow{C_6H_5Br} [Cp'_2Al][B(C_6F_5)_4]$$

Scheme 2.6. Synthesis of $[Cp'_2Al][B(C_6F_5)_4]$ through cyclopentadienide abstraction by the trityl cation [56].



Scheme 2.7. Yttrium compounds exist as tight ion pairs [58].

adventitious water with the metal cation. Yet, the application of proton traps for mechanistic studies in Shaffer's work has occasionally been considered as questionable, as mentioned in Baird's article [40] and in Section 2.2.1.

2.2.3. Group XIII and III metallocene compounds

The role of aluminium halides and alkyl aluminium halides as Lewis acids initiators in polymerisation of isobutene has been long known. Soon after the first isolation of strong Lewis acidic $[Cp^*_2Al]^+$ by Schnöckel and co-workers [55], Bochmann and co-workers explored the chemistry of aluminocenium cation for cationic polymerisation of isobutene. It was found that $[Cp_2Al]^+$, paired with $[BMe(C_6F_5)_3]$, is a highly active initiator for cationic polymerisation of isobutene, readily providing PIB of high molecular weight of 3×10^5 g/mol at −30 °C in 10 min, with narrow PDIs of ca. ~1.6; and copolymerisation of IB and IP to butyl rubber with $M_w = 7.8 \times 10^5$ g/mol and a PDI of 3.3 at −70 °C. However, the species rapidly decomposes in CH_2Cl_2 solution at temperatures above −20 °C. Shapiro and co-workers [56] attributed the poor thermal stability of the aluminocenium cation $[Cp_2Al]^+$ to the less steric hindered cyclopentadienyl ligand, compared to the bulkier Cp′ (C_5Me_4H) and Cp* (C_5Me_5). Whereas the bulkiest $[Cp^*_2Al]^+$ is the most thermally stable cation, the relative initiator activities follow the order: $[Cp_2Al]^+ \gg [Cp'_2Al]^+$ (Scheme 2.6) > $[Cp^*_2Al]^+$.

The striking effect of the size of the cyclopentadienyl ligand on the stability and activity of the aluminocenium cation was considered as strong evidence that the aluminocenium cation is indeed the initiator for the polymerisation of isobutene, in the sense that bulkier Cp rings hinder the access of isobutene molecule to the cationic aluminium centre. These observations are somewhat contrary to that of the analogous zirconocene system, in which the bulkier Cp rings lead to better results (Table 2.4, entries 1, 2). Therefore, the cationic initiation mechanism is generally accepted for the aluminocenium system [53,56,57], as opposed by the still unclear situation for the zirconocene system (see Section 2.2.2). In another report [57], Schnöckel and Krossing investigated the influence of WCAs for the aluminocenium system. As in other cases, the higher activity and thermal stability of the initiator $[Cp_2Al][Al(OC(CF_3)_3)_4]$ in comparison to $[Cp_2Al][BMe(C_6F_5)_3]$ are attributed to the less coordinating anion $[Al(OC(CF_3)_3)_4]^-$.

Bochmann and co-workers also described the synthesis of group III metallocene compounds $Cp'_2Y(\mu\text{-Me})B(C_6F_5)_3$ (Cp′ = C_5H_5, $C_5H_4SiMe_3$) and their application in cationic polymerisation of isobutene [58]. Different from their aluminium and zirconium analogues, NMR and crystallographic evidences prove the yttrium compounds exist as strong ion pairs (Scheme 2.7). The polymerisation tests showed that both polymer yields and molecular weight are comparable to those found for $[AlCp_2][BMe(C_6F_5)_3]$ and relatively higher than those reported for $Cp^*TiMe_3/B(C_6F_5)_3$.

2.3. Nitrile ligated metal complexes

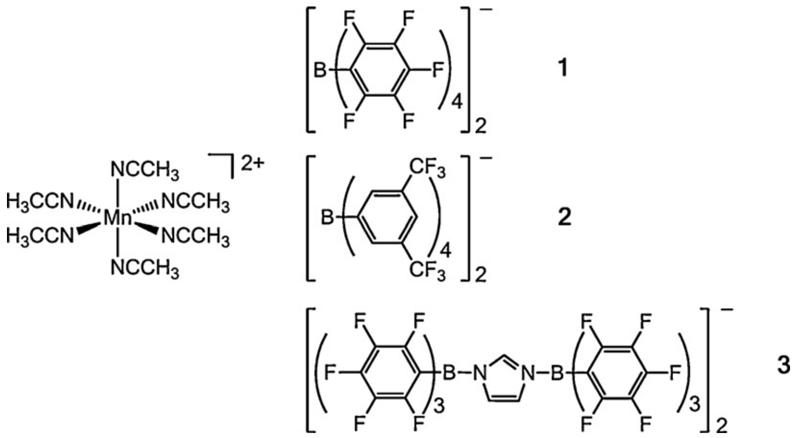
2.3.1. Cationic nitrile ligated complexes in olefin polymerisation

Transition metal nitrile complexes have been known for many years, and their reactivity, originating from the weak metal ligand bond, has made them attractive as reagents in a variety of reactions [59]. Shortly after the report on the synthesis of the dimolybdenum complex $[Mo_2(NCCH_3)_{10\text{-}n}][BF_4]_4$ by Cotton et al. in 1991 [60,61], McCann et al. tested such type of complexes, e.g. $[Mo_2(NCR)_6(\mu\text{-OOC-R})_2][A]_2$ (R = CH_3, $(H_3C)C{=}CH_2$; A = BF_4, CF_3SO_2, BF_3OH), for the polymerisation of norbornadiene and cyclopentadiene both homogeneously [62,63] and heterogeneously [64]. In 1998, Kühn and co-workers structurally characterised the compound $[Cr(NCCH_3)_4][BF_4]_2$ [65], which is a more active catalyst in the polymerisation of cyclopentadiene than a series of cationic dinuclear Mo_2 and Rh_2 nitrile complexes [66], affording polycyclopentene with a yield of 92% and molecular weight of 14,800 g/mol in 16 h at room temperature. Consequently, the group focused on the catalytic properties of mononuclear cationic transition metal nitrile complexes in the polymerisation of olefins [67]. It was found that the lower the ligand field stabilisation energies (LFSE) of M(II), the higher is the activity of the M-nitrile complex. It was also shown that a change of the counterion from the weakly coordinating BF_4 to the stronger coordinating BPh_4 leads to a drop in the catalytic activity.

2.3.2. Application in isobutene polymerisation

Soon after the finding that monometallic cationic all-nitrile ligated transition metal complexes can be used as catalysts for the polymerisation of cyclic olefins, such as norbornene, cyclopentene and cyclopentadiene, the research focused on the industrially more relevant polymerisation of isobutene (2-methylpropene). However, the complexes which were active in the polymerisation of cycloolefins were not active towards any other olefins. This was largely ascribed to the coordination of the anions BF_4 and BPh_4 to the metal centre and the resulting lack of Lewis acidity and free coordination sites, respectively. In 2003, Kühn, Nuyken and co-workers reported on the catalytic activity of $[Mn^{II}(NCCH_3)_6]^{2+}$ complexes **1**–**3**, bearing non-coordinating perfluorinated borate anions, such as $[B(C_6F_5)_4]^-$, $[B(C_6H_3(m\text{-}CF_3)_2)_4]^-$ or $[(C_6F_5)_3B\text{-}(C_3N_2)\text{-}B(C_6F_5)_3]^-$ (see Scheme 2.8) for isobutene polymerisation, giving highly reactive, honey-like viscous PIB [68,69].

The best results were obtained at temperatures between 20 and 60 °C, which is by far more convenient in comparison to the common syntheses with industrial initiators (see Section 1) which require temperatures far below 0 °C. Above 60 °C, the catalysts tend to decompose. Moreover, in all performed experiments, polyisobutene obtained with this type of catalysts exhibited rather low molecular weights (2530–4900 g/mol) and low PDIs, i.e. a narrow chain length distribution. The most active catalyst is the one bearing $[B(C_6F_5)_4]^-$ anions (Table 2.5). In all cases, the obtained polymers exhibited a high content of *exo* C=C double bonds (>70%). In general, the *exo* C=C content was increased when the catalyst concentration was decreased. The effect of the replacement of acetonitrile ligands by benzonitrile groups was also investigated [70]. It was shown that at concentrations of 2.8×10^{-5} mol%, the catalysts $[Mn(NCPh)_6][WCA]_2$ already give almost quantitative conversions of IB to PIB and molecular weights between 2500 and 3700 g/mol after 20 h at 30 °C in CH_2Cl_2 as solvent (see Table 2.5, entries 7–12). Higher concentrations led in some cases to a drastic decrease of the conversion and an increase of the molecular weight. The *exo* content of the C=C double bonds in the obtained polymers was between 64% and 70%. Kinetic studies revealed that in general,



Scheme 2.8. Overview of Mn(II)–acetonitrile complexes with different weakly coordinating anions as active catalysts for the polymerisation of isobutene [68].

the benzonitrile complexes exhibit a higher activity than the acetonitrile congeners. The Mn(II)–acetonitrile complexes (Table 2.5, entries 1–6) were active catalysts for copolymerisation of isobutene and isoprene. Here, the yield decreased with increasing isoprene content. As well, with increasing isoprene content the molecular weight of the copolymer decreased, pointing to a cationic polymerisation mechanism.

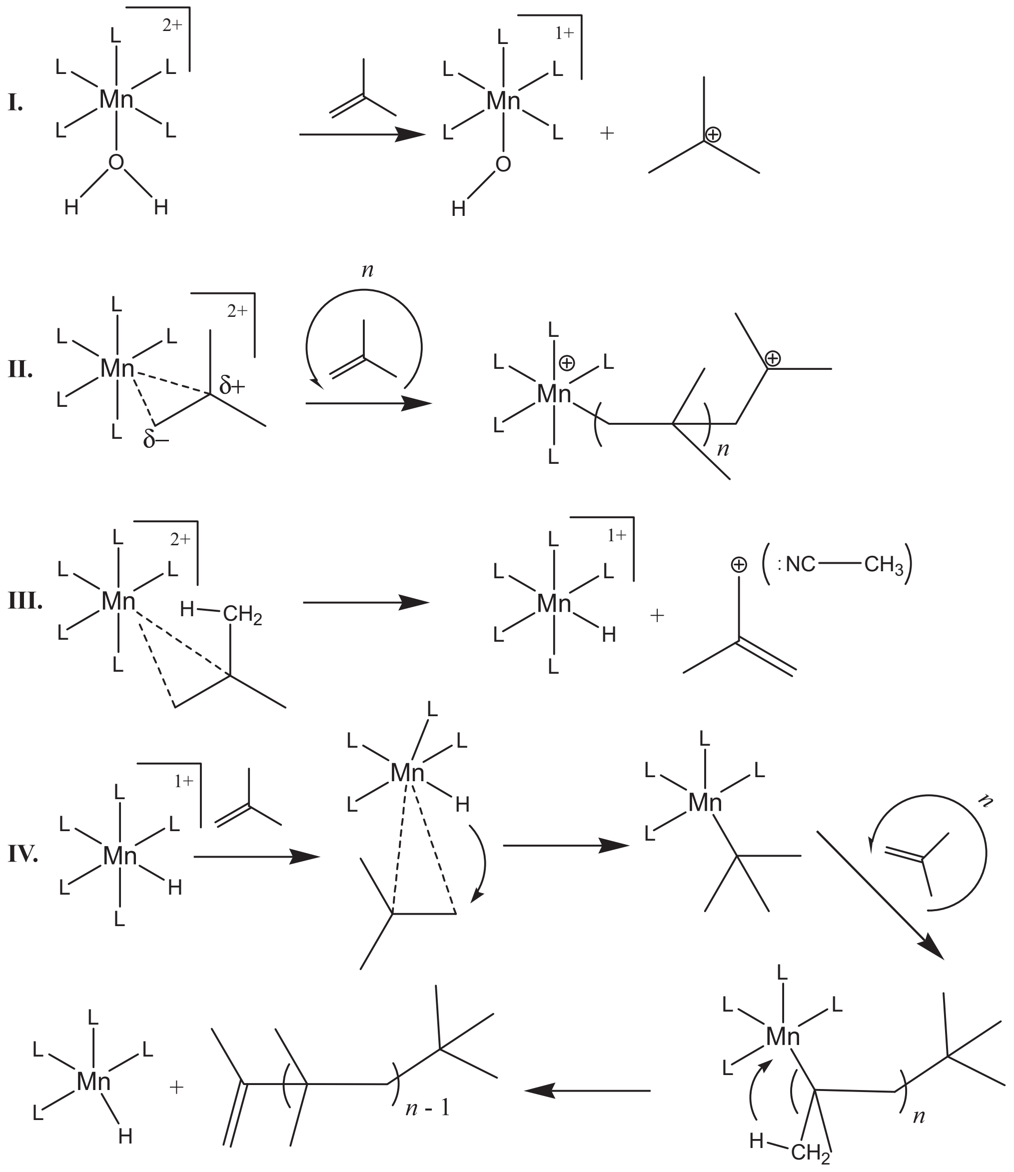
From a mechanistic point of view, few theoretical studies have been performed to date, and it is still not clearly understood how these catalysts are able to generate polymers. Yet, a number of hypotheses have been proposed and investigated. In 2006, Nuyken, Kühn and co-workers suggested that in the very first step, one nitrile ligand dissociates prior to coordination of isobutene according to Scheme 2.9II [14]. The π-complex might be converted to an π-complex, leading to a carbocation, which enables the chain propagation. The chain growth could occur either by (a) coordination of a second isobutene molecule and subsequent insertion into the M–C bond or (b) by a nucleophilic attack on another isobutene. Very recently, a quantum chemical study was undertaken by Kühn and co-worker to evaluate a number of hypotheses that have been proposed (Scheme 2.9) [71]. However, the originally proposed mechanistic steps by Nuyken, Kühn and co-workers as well as other possibilities shown in Scheme 2.9 were not feasible, at least not in the originally suggested form.

Among all the hypotheses shown in Scheme 2.9, the water effects (Scheme 2.9, I) have been partially investigated experimentally by Kühn, Nuyken and co-workers [69] prior to the quantum chemical calculations. The presence of water has a complicated effect on the isobutene polymerisation. On one hand, as predicted the molecular weights of the polymers decreased almost linearly with the increase of the [initiator]:[water] ratio. On the other hand, the negative effect of water on monomer conversions could only be observed when the ratio of [initiator]:[water] is higher than 10. Finally experiments in water-saturated dichloromethane did not yield any polymers. It is assumed that the catalyst is deactivated by water replacing two axial-coordinated acetonitrile ligands, yielding the complex $[Mn(H_2O)_2(NCMe)_4][WCA]_2$, which is proven to be inactive towards polymerisation of isobutene. The result is supported by ab initio calculations [71], showing that the protonation of isobutene monomer by either the bis

Table 2.5
Overview of the catalytic activities of $[M^{II}(NCR)_6]^{2+}$ and $[Mo^{III}Cl(NCR)_5]^{2+}$ complexes (M = Mn, Cu; R = CH_3, Ph) with different WCAs **1**–**3**.

Entry	Complex	WCA	Cat. conc. (10^{-4} mol%)	M_w (kg/mol)	Conv. (%)	PDI	Ref.
1[a]	$[Mn^{II}(NCCH_3)_6]^{2+}$	**1**	0.36	2.8	76	2.3	[68]
2[a]	$[Mn^{II}(NCCH_3)_6]^{2+}$	**1**	1.8	2.5	88	2.4	[68]
3[a]	$[Mn^{II}(NCCH_3)_6]^{2+}$	**2**	0.36	4.9	46	1.8	[68]
4[a]	$[Mn^{II}(NCCH_3)_6]^{2+}$	**2**	1.8	4.1	70	2.1	[68]
5[a]	$[Mn^{II}(NCCH_3)_6]^{2+}$	**3**	0.36	4.1	13	1.9	[68]
6[a]	$[Mn^{II}(NCCH_3)_6]^{2+}$	**3**	1.8	4.8	22	1.8	[68]
7[b]	$[Mn^{II}(NCPh)_6]^{2+}$	**1**	0.28	2.3	94	3.1	[70]
8[b]	$[Mn^{II}(NCPh)_6]^{2+}$	**1**	2.8	7.2	36	2.0	[70]
9[b]	$[Mn^{II}(NCPh)_6]^{2+}$	**2**	0.28	2.5	89	2.9	[70]
10[b]	$[Mn^{II}(NCPh)_6]^{2+}$	**2**	2.8	3.7	70	2.5	[70]
11[b]	$[Mn^{II}(NCPh)_6]^{2+}$	**3**	0.28	3.7	77	2.5	[70]
12[b]	$[Mn^{II}(NCPh)_6]^{2+}$	**3**	2.8	2.4	83	2.5	[70]
13[c]	$[Cu^{II}(NCCH_3)_6]^{2+}$	**1**	0.57	1.7	40	1.4	[72]
14[c]	$[Cu^{II}(NCCH_3)_6]^{2+}$	**1**	3.4	1.8	40	1.4	[72]
15[c]	$[Cu^{II}(NCCH_3)_6]^{2+}$	**2**	0.57	1.4	78	1.4	[72]
16[c]	$[Cu^{II}(NCCH_3)_6]^{2+}$	**2**	3.4	1.4	90	1.6	[72]
17[c]	$[Cu^{II}(NCCH_3)_6]^{2+}$	**3**	1.1	2.0	2	1.4	[72]
18[c]	$[Cu^{II}(NCCH_3)_6]^{2+}$	**3**	3.4	2.0	3	1.4	[72]
19[d]	$[Cu^{II}(NCPh)_6]^{2+}$	**1**	0.28	0.6	80	1.4	[73]
20[d]	$[Cu^{II}(NCPh)_6]^{2+}$	**1**	0.0035	0.9	37	1.5	[73]
21[e]	$[Mo^{III}Cl(NCCH_3)_5]^{2+}$	**1**	0.28	1.3	90	3.2	[74]
22[e]	$[Mo^{III}Cl(NCCH_3)_5]^{2+}$	**2**	0.28	1.4	94	3.1	[74]
23[e]	$[Mo^{III}Cl(NCCH_3)_5]^{2+}$	**3**	0.28	1.0	96	2.7	[74]

[a] CH_2Cl_2, 40 °C, 16 h.
[b] CH_2Cl_2, 30 °C, 20 h.
[c] CH_2Cl_2, 30 °C, 30 min, H_2O content: 7 ppm.
[d] Toluene, 30 °C for 30 min (entry 19) and 1 h (entry 20), respectively.
[e] CH_2Cl_2, 30 °C, 10 h.



Scheme 2.9. Summary of proposed mechanisms for the polymerisation of isobutene catalysed by Mn(II)–nitrile complexes [71].

axial-H_2O- coordinated Mn(II) species $[Mn(H_2O)_2(NCMe)_4]^{2+}$ or the mono H_2O-coordinated species $[Mn(H_2O)(NCMe)_5]^{2+}$ is highly unfavourable due to very high enthalpy change. Yet, due to the large size of the anions, it was not possible to consider them in the calculations, and the possibility remains that the WCAs play an important role in the stabilisation of some intermediates or products, which has not yet been accounted for.

Contrary to what has been observed for traditional cationic polymerisations, using the catalyst $[Mn(NCCH_3)_6][B(C_6F_5)_4]_2$ displayed a decrease in both the rate and the evolved molecular weight of the obtained polymers, and when water saturated dichloromethane was used as the reaction solution, no polymerisation was observed. The catalyst is deactivated when traces of water are present, yielding the complex $[Mn(NCCH_3)_4(H_2O)_2][WCA]_2$, which is inactive in the polymerisation of isobutene [69]. Therefore, the reason why water adversely affects the polymerisation could be that this deactivated catalyst species is formed.

Kühn, Nuyken and co-workers found that copper(II)–nitrile complexes of the type $[Cu(NCCH_3)_6][WCA]_2$ (WCA = $[B(C_6F_5)_4]^-$, $[B(C_6H_3(m\text{-}CF_3)_2)_4]^-$, $[(C_6F_5)_3B\text{-}(C_3N_2)\text{-}B(C_6F_5)_3]^-$) are more efficient than the manganese compounds; already after 30 min, the conversion of isobutene reaches 80–90% (Table 2.5, entries 13–18) [72]. However, in the case of Cu, the water content in the solvent and traces in the reaction flask and/or isobutene again play a crucial role for the activity of the catalyst. For instance, a rise of the water content in dichloromethane from 3.5 ppm to 7 ppm leads to a decrease of the average molecular weight from 4600 to 1400 g/mol. Only when the molar water:catalyst ratio is higher than 10:1, a negative effect on the catalytic activity was observed.

For an industrial application of these complexes, the use of chlorinated solvent is prohibited, due to economic and environmental factors (toxicity, disposal, etc.). In order to reduce the amount of dichloromethane in the catalysis, mixtures of toluene and *n*-hexane were tested as reaction media for isobutene polymerisation. Using 20 vol.% *n*-hexane, the conversion decreased to 35% with $[Cu(NCCH_3)_6][B(C_6H_3(m\text{-}CF_3)_2)_4]_2$, whereas the complex $[Cu(NCCH_3)_6][B(C_6F_5)_4]_2$ is more active in toluene than in dichloromethane, giving a yield of 90% HR-PIB with an average molecular weight of 2500 g/mol and a PDI of 1.9 after 30 min at 30 °C [72,73]. Analogous benzonitrile complexes are very active catalysts in toluene, giving HR-PIB with very low molecular weights (600–900 g/mol) and high *exo* C=C double bond contents (52–82%).

Table 2.6
Overview of the catalytic data of $[M(NCCH_3)_n]^{II}$ and $[Mo^{III}X(NCCH_3)_5]^{2+}$ (X = Cl, O) complexes with $[B(C_6F_5)_4]^-$ as counterion (except entries 4 and 5). Solvent: CH_2Cl_2, $T = 30\,^{\circ}C$.

Entry	Metal ion	t (h)	Cat. conc. (10^{-4} mol%)	M_w (kg/mol)	PDI	*Exo* C=C content (%)	Conv. (%)	Ref.
1	Cr^{II}	1	0.28	–	–	–	2	[76]
2	Mo^{III} **1** (X=Cl)	0.5	0.28	2.6	2.1	77	16	[74]
3	Mo^{III} **1** (X=Cl)	5	0.28	0.6	1.7	65	72	[74]
4	Mo^{III} **3** (X=Cl)	0.5	0.28	1.7	3.2	58	90	[74]
5	Mo^{III} **3** (X=Cl)	5	0.28	1.4	3.5	28	92	[74]
7	Mo^{III} **1** =O)	20	0.39	1.6	2.9	–	80	[75]
8	Mn^{II}	20	0.28	1.8	2.1	82	67	[68]
9	Fe^{II}	0.5	0.28	1.6	2.1	79	20	[76]
10	Fe^{II}	5	0.28	0.9	2.3	62	88	[76]
11	Co^{II}	10	0.28	1.6	1.7	–	20	[76]
12	Ni^{II}	5	0.28	1.4	1.7	–	17	[76]
13	Cu^{II}	0.5	0.28	1.7	1.4	85	40	[72]
14	Zn^{II}	0.5	0.28	5.3	1.9	71	24	[76]
15	Zn^{II}	5	0.28	0.9	1.9	58	88	[76]

Besides the nitrile complexes of manganese, copper and zinc, Kühn, Nuyken, Voit and co-workers also investigated the catalytic performance of molybdenum complexes in isobutene polymerisation. The octahedral complexes of the type $[Mo^{III}Cl(NCCH_3)_5][WCA]_2$ (WCA = anions **1**–**3**, see Scheme 2.8) were selected as the object of study; the only all-nitrile Mo-complex available to date, $[Mo_2(NCCH_3)_{10}][BF_4]_4$, is inactive in isobutene polymerisation. All examined Mo-complexes were active catalysts for the polymerisation of isobutene, reaching conversions of 90–96% after 10 h. The obtained PIB exhibit molecular weights between 1000 and 1400 g/mol and PDI of 2.7–3.2, and *exo* C=C double bond contents of 62–90% [74]. It was found that within the first 30 min of the reaction time, the Mo complexes reach up to 80% conversion of isobutene, and thus are much more active than the Mn complexes (Table 2.6, entry 1), giving rise to the higher Lewis acidity of Mo(III) vs. Mn(II). Whereas the conversion of isobutene decreased when a CH_2Cl_2/*n*-hexane 1:1 mixture was used as reaction medium, in the presence of neat *n*-hexane, no polymerisation occurred. However, in toluene, using $[Mo^{III}Cl(NCCH_3)_5][(C_6F_5)_3B\text{-}(C_3N_2)\text{-}B(C_6F_5)_3]_2$ as catalyst, the conversion reached 67%. A screening of the catalytic activities of 3rd row transition metal–acetonitrile complexes bearing the $[B(C_6F_5)_4]^-$ anion revealed that under identical reaction conditions (catalyst concentration, reaction temperature, solvent), the complex $[Mo^{III}Cl(NCCH_3)_5][(C_6F_5)_3B\text{-}(C_3N_2)\text{-}B(C_6F_5)_3]_2$ is the most efficient species, giving almost quantitative conversions already after 30 min (Table 2.6) [75]. Yet, the PDI is quite high and the content of *exo* C=C double bonds is rather low. Hence, the iron and zinc complexes give much more satisfying results. The Mo complexes with the WCAs **1** and **3** both give high conversions of isobutene, however, with increasing reaction times, the *exo* C=C content decreases.

In conclusion, an efficient catalyst of the polymerisation of isobutene must (a) be active at room temperature with a catalyst concentration of less than 10^{-5} mol% per 1 mol substrate, (b) be soluble in hydrocarbon solvents such as toluene or *n*-hexane, (c) exhibit conversions of >90% within 1 h, (d) yield polymers with M_W = 800–1800 g/mol, a PDI of 1.0–1.5 and an *exo* C=C content of >70%. Regarding all these factors, it can be concluded that the most efficient catalyst is the Cu–benzonitrile complex $[Cu^{II}(NCPh)_6][B(C_6F_5)_4]_2$.

Besides the application of weakly coordinating anions on the basis of perfluorinated borates, Kühn, Voit and co-workers also employed extremely bulky perfluoroalkoxy aluminates **4**–**6** [28,77] (see Scheme 2.10) in the synthesis of $[Zn(NCR)_6]^{2+}$ complexes (R = CH_3, Ph) for isobutene polymerisation [78]. The zinc complexes were synthesised from $ZnCl_2$ and the corresponding silver(I) aluminates in aceto- or benzonitrile [79,80].

The compound $[Zn(NCPh)_6][Al(OC(CF_3)_3)_4]_2$ was used as catalyst for the isobutene polymerisation. Treatment of a solution of isobutene in dichloromethane with the zinc catalyst ($c = 2.8 \times 10^{-5}$ mol%) at 30 °C led to a conversion of 87% after 1 h reaction time. The molecular weight and the PDI of the obtained polymer were determined to be 1500 g/mol and 2.7, respectively. The content of *exo* C=C double bonds was 72%.

The studies reviewed in this section show that cationic metal–nitrile complexes do not only allow the variation of the metal centre and the ligands, but also enable the free choice of the weakly coordinating anion. The anions – BF_4^- vs. $[B(C_6F_5)_4]^-$ or $[Al(OR)_4]^-$ – has a dramatic effect on the efficiency of the catalysts for the polymerisation of isobutene. Yet, the variations of the anion and the cation have a significant effect on various properties of the reaction including the rate of conversion, the generated molecular weight, the PDI and the fraction of terminal (*exo*) C=C end groups. However, the relationship is not straightforward and influence of other parameters, such as catalyst concentration and the solvent has to be considered.

2.3.3. Immobilisation of transition metal–nitrile complexes

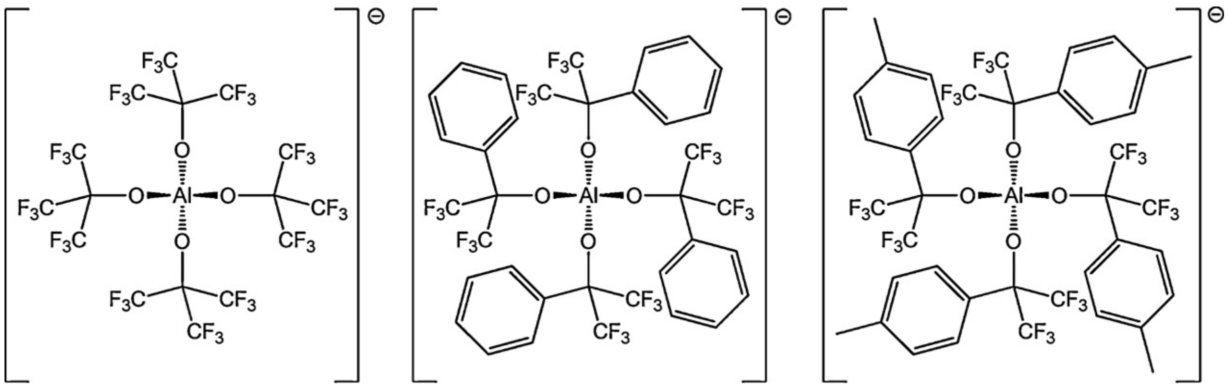
For the reason of a long-term industrial use of the catalysts presented in Section 2.2.2, the research on immobilisation of these solvent-ligated transition metal complexes had started in the groups of Kühn, Nuyken and Voit as soon as the first highly reactive complex was successfully synthesised and applied homogeneously. Generally speaking, two methods are possible: (i) the anchoring of the catalytically active cation either via direct binding of the metal centre or one (or more) anchored nitrile ligands, and (ii) the anchoring of the anion (Scheme 2.11).

Kühn and co-workers had shown that the complexes of the type $[M_2(NCCH_3)_{10}][BF_4]_4$ (M = Mo, Rh) [81–83] and $[M(NCCH_3)_n][BF_4]_2$ (M = Cr, Mn, Fe, Co, Ni, Zn; n = 4, 6) [84] could be successfully immobilised on the surface of MCM-41 via a terminal –Si–O–M bond.

The catalytic activities of the immobilised materials towards the polymerisation of cyclopentadiene, however, were significantly lower. This was attributed to the limited diffusion of substrate molecules through the channels of MCM-41 as well as to blocking of catalyst sites by growing polymer chains.

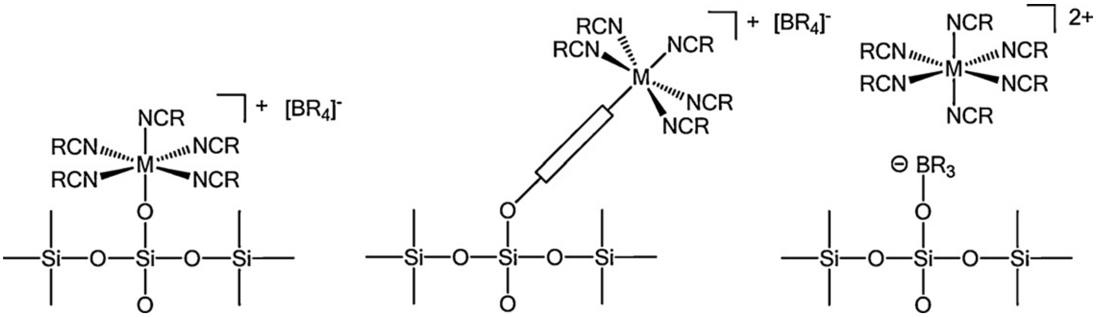
In 2004, Kühn and co-workers investigated the immobilisation of $[Mn(NCCH_3)_6][B(C_6F_5)_4]_2$ on MCM-41 via introduction of a pyrazolylpyridine-based anchor, which was previously grafted to Si–OH surfaces [85]. The same method was also used to graft $[Cu(NCCH_3)_6][B(C_6H_3(m\text{-}CF_3)_2)_4]_2$ to the surface of SBA-15 which was functionalised by a aminosilane [86].

Besides the immobilisation of metal–nitrile complexes via the cation, the immobilisation via the borate anion was reported as well. In this method, the nitrile-coordinated metal centre is generated *in situ* after the borate anion was anchored on the silica surface, as shown in Scheme 2.12 [87]. The cation is indirectly bound to the surface, since the Coulomb interaction with the anion prevents leaching. However, given the oxidation state +II of the metal centre,

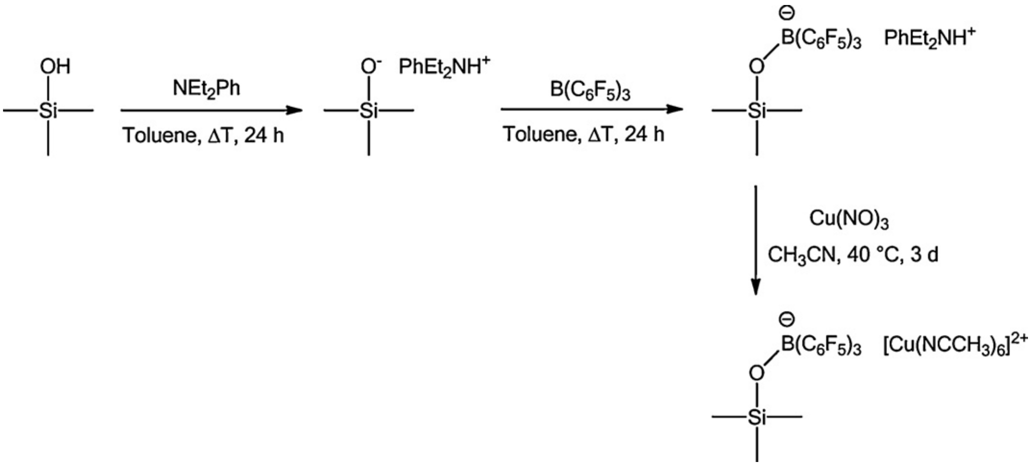


4 **5** **6**

Scheme 2.10. Weakly coordinating aluminates as counterions for cationic metal–nitrile catalysts for the polymerisation of isobutene [78].



Scheme 2.11. Schematic illustration of the possible methods of immobilisation of complexes of the type $[M(NCCH_3)_n][BF_4]_2$ on silica surfaces: direct binding of the metal centre (left), via anchored spacer ligands (middle) and via anion anchoring (right).



Scheme 2.12. Synthetic route to the immobilisation of $[M(NCCH_3)_n][BR_4]_2$ complexes via the borate anion [87].

two borate anions must be in proximity to be able to stabilise the cation, otherwise it will not bind to the anion tightly.

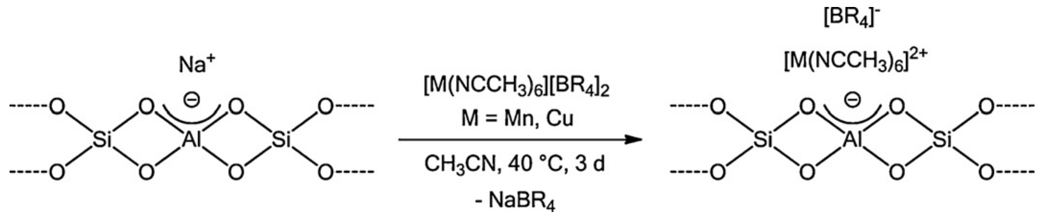
Ordered porous silica-aluminate materials were also successfully used as solid supports for the immobilisation of the complexes $[M(NCCH_3)_6][B(C_6F_5)_4]_2$ (M = Mn, Cu) (Scheme 2.13) [88–90].

A catalytic test of the polymerisation of isobutene, performed with the Mn-incorporated siliceous materials (dichloromethane, 30 °C, 28 h) gave polyisobutene in yields of 6–8%. Here, the limited access of the immobilised cation is the most presumable reason for the low conversion in comparison to the homogeneous catalysis.

Apart from immobilisation on siliceous materials, metal–nitrile complexes were also heterogenised on organic polymers. The complexes $[Cu(NCCH_3)_6][WCA]_2$ (WCA = $[B(C_6F_5)_4]$, $[B(C_6H_3(m\text{-}CF_3)_2)_4]$) were reacted with poly(4-vinyl)pyridine, leading to a substitution of one acetonitrile ligand by pyridine and thus binding the Cu complex to the polymer [91]. By this method, loadings of around 0.8–0.9 wt% Cu were found in the resulting materials.

2.4. Alkyl zinc based catalysts

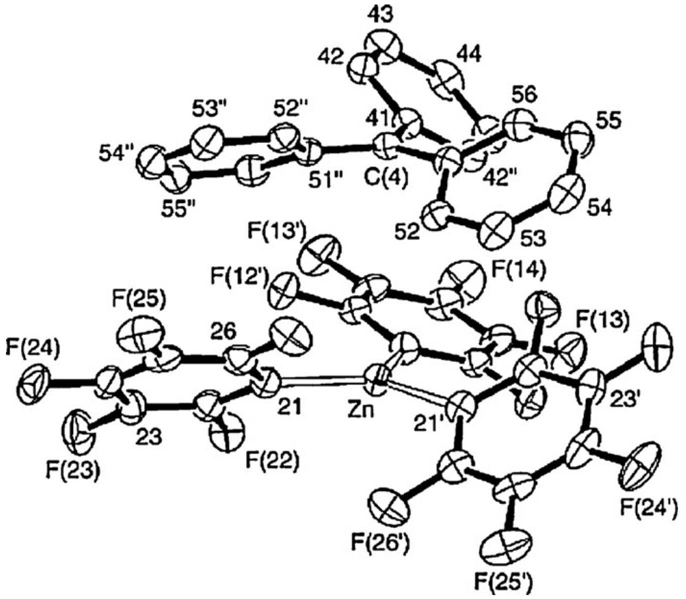
Zinc compounds have the advantage of being nontoxic and relatively cheap compared to metallocene/borate initiators. However, there had been no reports on the use of zinc compounds in isobutene homo- and co-polymerisations, until Bochmann and co-workers reported the arylzinc complexes as initiators for the



Scheme 2.13. Illustration of the heterogenisation of Cu and Mn–acetonitrile complexes via Coulomb interaction with anionic surfaces [88–90].

$$[\mathrm{Zn(C_6F_5)_2}] \quad + \quad \mathrm{RX} \quad \rightleftharpoons \quad \mathrm{R^+[ZnX(C_6F_5)_2]^-}$$

Scheme 2.14. Formation of carbocation and weakly coordinating zincate [92].



Scheme 2.15. Crystal structure of $[\mathrm{CPh_3}][\mathrm{Zn(C_6F_5)_3}]$ (ellipsoids are drawn at a 50% probability level). Selected bond lengths and angles: Zn–C(11) 2.030(6), Zn–C(21) 1.981(10), Zn–C(31) 2.056(11), C(21)–Zn–C(11) 120.7(5), C(11)–Zn–C(31) 118.5(5), C(21)–Zn–C(31) 120.7(2) [92].

copolymerisation of isobutene and IP with high molecular weight ($2–12 \times 10^5$ g/mol) and low PDI (1.7–2.0) [92]. Whereas anhydrous $\mathrm{ZnCl_2}$ is inactive in the presence of alkyl halides, such as ^{t}BuCl or MeCOCl at low temperatures (−35 to −78 °C), $[\mathrm{Zn(C_6F_5)_2}]$·toluene is highly active for copolymerisation of isobutene and IP under the same conditions. The proposed formation of carbocations and weakly coordinating zincate (Scheme 2.14) were proven by NMR investigations and X-ray crystallography (Scheme 2.15).

$[\mathrm{Zn(C_6F_5)_2}]$·toluene alone is also able to provide high-molecular-weight polyisobutene, presumably due to the reaction of the zinc based Lewis acids with adventitious traces of water. Replacement of MeCOCl by ^{t}BuCl resulted in much higher yields and molecular weight. Yet the system is sensitive to the isoprene concentration and to temperature. An increasing either of the parameters resulted in a general decrease in activity and polymer molecular weight.

When the aryl zinc compound $[\mathrm{Zn(C_6F_5)_2}]$·toluene is replaced by simpler and cheaper alkyl zinc chloride such as EtZnCl, the initiator system EtZnCl/^{t}BuCl gives medium molecular weight PIB containing up to 92% *exo* C=C double bond groups at room temperature within a relatively short period of time (ca. 30 min) (Table 2.7) [93].

A clear counteranion effect was observed. The more bulky and soluble anion $[\mathrm{Oct\text{-}ZnCl_2}]^-$ generated from the reaction of $\mathrm{PhCMe_2Cl}$ and Oct-ZnCl leads to PIB with higher M_w and higher yields. This is attributed to the more positive entropy of a more weakly coordinating anion with less restricted degrees of freedom [94], which is in accordance with previous investigations by Bochmann and co-workers on the effect of the bulkiness of perfluoroarylborate anions on the molecular weights [50].

In the proposed initiation mechanism (Scheme 2.16) [93], Bochmann and co-workers suggested that not only alkyl zinc chlorides, but also 'molecular' $\mathrm{ZnCl_2}$, which is formed *in situ* are responsible for initiation of the reaction. The argument, however, is not consistent with the distinct counteranion effect mentioned above, since '*if in situ generated* $\mathit{ZnCl_2}$ *had acted as the actual initiator, the polymer* M_w *would have been independent of the zinc source since in either case* $[\mathit{ZnCl_3}]^-$ *would have been the common counteranion*' [94].

To the best of the authors' knowledge, besides the nitrile ligated metal initiators examined in the groups of Kühn, Nuyken and Voit, this cationic process is the only system capable of generating medium molecular PIB at ambient temperatures. Another non-chemical advantage of the initiators of the type R-ZnCl is their low cost compared to fluoroarylborates/alkoxyaluminates based systems. This, combined with its ability to operate at ambient temperatures, make R-ZnCl interesting from an industrial point of view [95].

2.5. *Protic and lithium ion initiators*

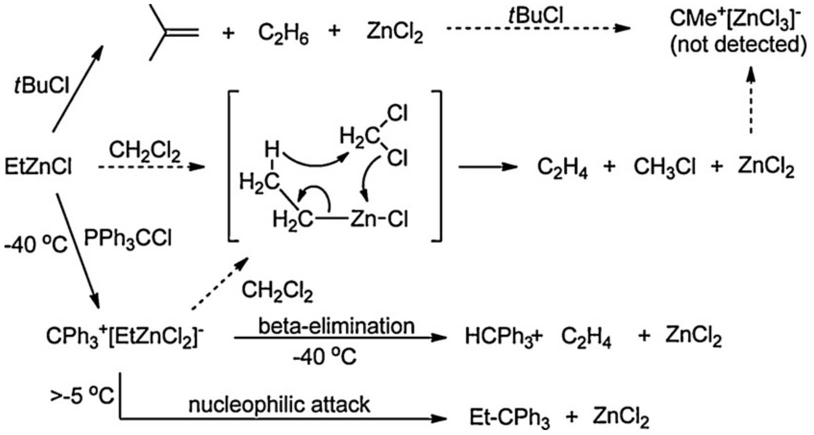
Although the roles of water and other kind of proton sources in conventional isobutene polymerisation systems as protic initiators and chain transfer agents have been deeply investigated and well understood, their effects in the recently developed WCA-involved metallocene and nitrile-ligated transition metal systems are complex and still under debate. Nevertheless, both *in situ* formed and well characterised WCA-partnered protons are widely acknowledged as very effective isobutene polymerisation initiators (Scheme 2.17).

For example, Shaffer et al. studied $[\mathrm{B(C_6F_5)_4}]^-$ partnered $\mathrm{Ph_3C^+}$ and $\mathrm{Et_3Si^+}$ cations as co-initiators for the polymerisation of isobutene in the presence of water or other proton sources (also see similar research on proton [31] and $\mathrm{Me_3Si^+}$ [96] from Kennedy and co-workers) (Table 2.8, entries 1–4) [42]. Through convincing and detailed NMR studies involving proton trap DTBP (as contrary to the debatable use of DTBP in the metallocene-based system), it was concluded that protons generated by the cations' reaction with adventitious water is the real initiation species. The very high reactivity of the protons are attributed to (a) proton acting as an inifer in the system: it regenerate continuously by chain transfer; and (b) the highly active proton is poorly stabilised by the $[\mathrm{B(C_6F_5)_4}]^-$ and cannot be consumed by it, as the counteranion is non-nucleophilic. In the same work, Shaffer et al. also described carbenium ion-initiated isobutene polymerisation, using lithium salt $\mathrm{Li[B(C_6F_5)_4]}$ as co-initiator (Table 2.8, entries 5–6). However, the results are relatively difficult to compare since the reaction conditions applied were quite different.

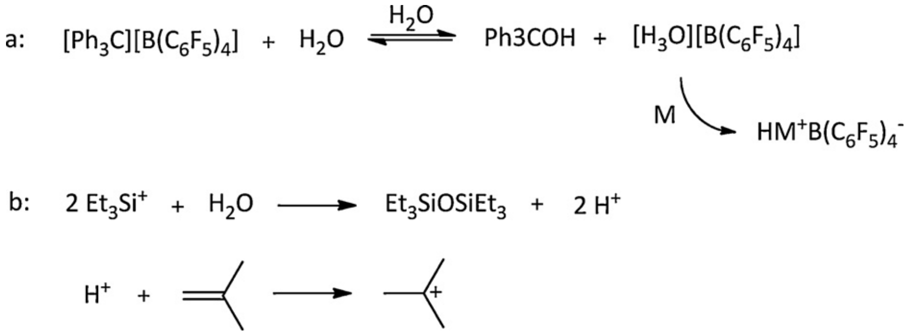
Table 2.7
Polymerisation of isobutene at 20 °C with EtZn/^{t}BuCl as initiator[a].

Entry	EtZnCl (10^{-3} mol/L)	^{t}BuCl (10^{-3} mol/L)	M_w (kg/mol)	PDI	Exo C=C (%)	Conv. (%)
1	2.1	1.6	51.1	1.9	92	6.8
2	4.3	3.2	45.0	1.6	85	21.7
3	6.4	4.8	33.8	2.0	85	30.6
4	19.3	14.5	29.0	2.0	60	95.0
5	38.7	29.0	25.3	2.5	60	98.0

[a] Data from Ref. [93].



Scheme 2.16. Proposed formation of $ZnCl_2$ and initiation mechanism by alkyl zinc based systems [93].



Scheme 2.17. *In situ* proton generation and their initiation of isobutene polymerisation [42].

The superior effect of WCAs was also observed with $[Al(OC(CF_3)_3)_4]^-$ [77], e.g. 5 mg of $[H(OEt_2)_2][Al(OC(CF_3)_3)_4]$ are sufficient to polymerise 12 g (20 mL) of isobutene at −60 °C in quantitative yield within 1 s [57,97].

Mechanistically, the chelating diboranes system developed by Piers et al. also belong to the category of protonic or carbenium ion initiated isobutene polymerisation. But from a practical point of view, chelating diboranes are rather independent from other systems and therefore, will be discussed separately in the following section.

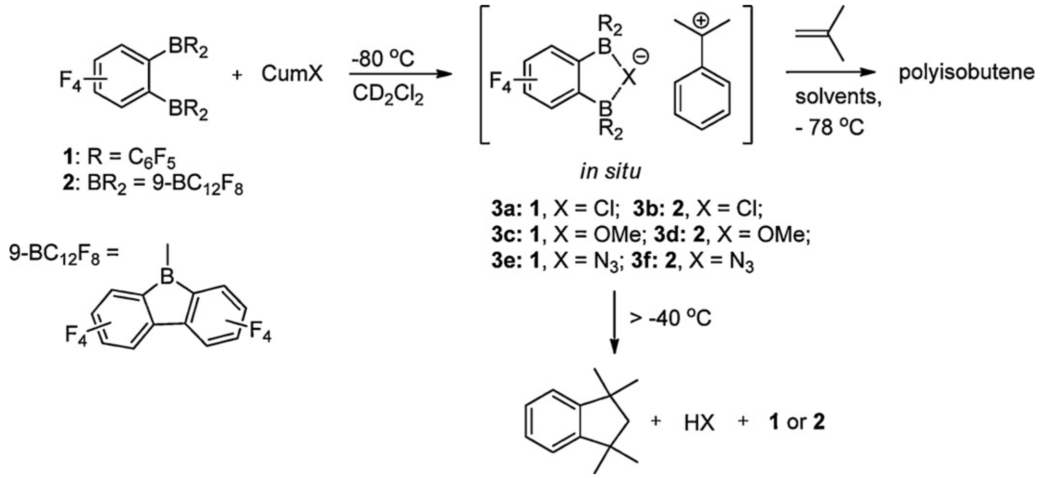
2.6. Chelating diboranes

Based on the discovery that certain chelating diboranes are active for olefin polymerisation [98–102], a chelating diborane system was developed and explored for the polymerisation of

Table 2.8
Selected results of isobutene polymerisation with protic and carbenium ion initiators involving $[B(C_6F_5)_4]^-$ as counteranion from Ref. [42].

Entry	Initiator	[ini.] × 10^3 (mol/L)	Solvent[a]	T (°C)	M_w (kg/mol)	PDI	Yield (%)
1[b]	Ph_3C^+	1.3	DCM	−20	28	2.3	56
2[c]	Ph_3C^+	1.3	DCM	−20	14	2.5	53
3	Et_3Si^+	9.4	MCH	−20	14	6.6	100
4	Et_3Si^+	2.77	MCH	−80	533	4.6	6
5[d]	Li^+	7.6	MCH	−80	198	3.8	100
6[e]	Li^+	2.5	DCM	−80	6,014	2.6	59

[a] MCH – methylcyclohexane.
[b] With $[H_2O] = 6.3 \times 10^{-3}$ mol/L.
[c] With $[H_2O] = 0.08 \times 10^{-3}$ mol/L and $[MeOH] = 1.2 \times 10^{-3}$ mol/L.
[d] With $[TBDCC] = 1.9 \times 10^{-3}$ mol/L, TBDCC – 1,3-bis(1-chloro-1-methylethyl)-5-*tert*-butylbenzene.
[e] With $[BzBr] = 2.5 \times 10^{-3}$ mol/L, BzBr – benzylbromide.

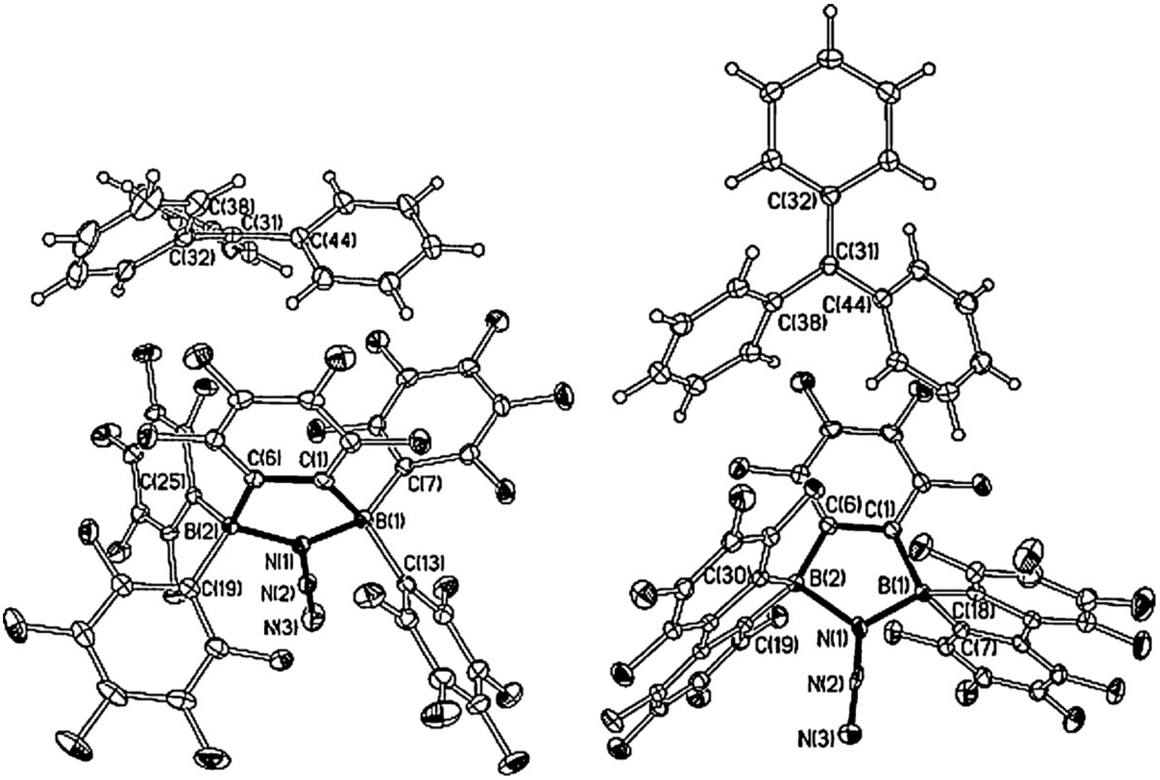


Scheme 2.18. Diboranes **1** and **2** act as effective co-initiators of isobutene, initiated by CumX [103,105].

isobutene [103–107]. As shown in Scheme 2.18, upon treatment of various cumyl compounds in CD_2Cl_2 at −80 °C, diboranes **1** and **2** formed an ion-pair **3**, being an effective initiator for IB polymerisation at −78 °C. The ion pair **3** was not stable at higher temperature, decomposing rapidly to yield indan, HX and diboranes **1** and **2** at temperatures higher than −40 °C. Nevertheless, the formation of ion pairs **3a**–**3f** was confirmed by comparing their NMR spectra with those of their trityl analogues **4a**–**4f** [105] (Scheme 2.19).

With background H_2O levels as low as 1–2 ppm [103], diboranes **1** and **2** are effective initiators for isobutene polymerisation even in non-polar media such as hexane (Table 2.9, entries 1–4). These polymerisations are characterised by quantitative conversions, relatively low M_w and broad PDI, being consistent with conventional protic initiation. Only when a 5–10 fold excess of 2,6-di-*tert*-butyl-4-methylpyridine (DtBMP) with respect to the diborane was added, the protic initiation could be effectively inhibited (Table 2.9, entry 5).

Controlled isobutene polymerisations initiated by CumCl and excess diborane **1** or **2** were possible with large excess of DtBMP in hexane solution (Table 2.9, entries 6–9), where M_w and yields correlate with the DtBMP concentration. Similar results were obtained with the more Lewis acidic diborane **2** (Table 2.9, entry 4, 8, 9), yet with lower M_w comparable to the analogous diborane compounds of formula **1** in each case. The differences of the obtained results by using diboranes **1** and **2** is probably due to at least one of the following reasons: (a) higher thermal stability of ion-pair **3b** leading to more efficient ionisation and thus initiation, (b) less shielded μ-Cl moieties, being more efficient in chain transfer and (c) combination of HCl (from decomposition of ion-pair **3b**) and diborane **2** reinitiating new chain growth [105].

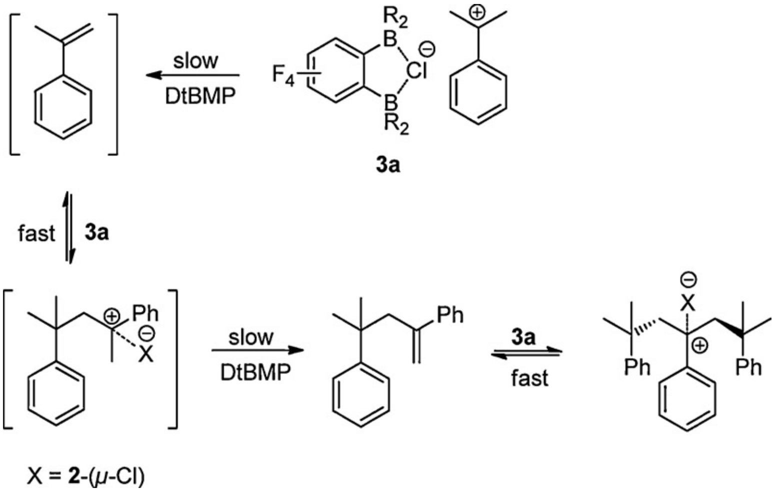


Scheme 2.19. Structures of the ion pairs **4e** and **4f**, at a 30% probability level and selected atomic labels [105].

Table 2.9
Selective results of polymerisation of IB using CumX initiators and diboranes **1** and **2**[a].

Entry	CumX	Diborane	DtBMP (mM)	M_w (kg/mol)	PDI	Conv. (%)	Ref.
1	–	**1**	0	172	2.6	100	[103]
2[b]	–	**1**	0	170	3.82	100	[107]
3[c]	–	**1**	0	37.0	2.27	100	[107]
4[b]	–	**2**	0	88.6	2.09	100	[107]
5	–	**1**	15.0	753	4.60	0.47	[103]
6	Cl	**1**	20.0	361	1.72	42	[103]
7	Cl	**1**	2.0	779	2.11	93	[103]
8	Cl	**2**	20.0	80	1.55	37	[105]
9	Cl	**2**	2.0	156	1.72	87	[105]
10	N_3	**1**	20.0	158	1.58	11	[105]
11[d]	N_3	**1**	20.0	275	1.50	17	[105]
12[e]	N_3	**1**	20.0	339	1.86	15	[105]
13	OMe	**1**	20.0	–	–	–	[105]
14[e]	OMe	**1**	20.0	75	1.52	3	[105]

[a] Stock solutions of DtBMP, diborane **1** or **2** (2.0 mM), and CumX (0.2 mM) in toluene were added into an IB solution (2.75 M) at −78 °C unless otherwise noted. Reactions were quenched with MeOH after 1 h.
[b] [diborane] = 0.2 mM.
[c] At −20 °C.
[d] Polymerisation in 60:40 (v/v) hexane/CH_2Cl_2 solution.
[e] Polymerisation in CH_2Cl_2 solution.



Scheme 2.20. Decomposition of **3a** in the presence of DtBMP [106].

Collins and co-workers pointed out in a separate investigation [106] that besides functioning as the inhibitor for protic initiation, DtBMP does react directly with carbocations bearing acidic α-protons, e.g. cumyl cation. However, it reacts with a significant lower rate than the propagation of α-methylstyrene proceeds (Scheme 2.20). The same study also proved that the common ion, e.g. protonated DtBMP has a profound influence on moderating the reactivity of cumyl cation partnered with μ-X diborane WCA.

Attempts were made to introduce further control into the reactions via the use of a variety of other ion-pair forming diborane systems with X = N_3 and OMe (Table 2.9, entries 10–14). However, both ion-pairs **3c** and **3e** gave lower conversions. It was found that polymerisations initiated by **3e** were characterised by considerable lower conversions in both polar and non-polar solvents (Table 2.9, entries 10–12). Detailed NMR investigations revealed that the low polymer yields were probably due to a competing Schmidt rearrangement [108], causing the degradation of $CumN_3$ to yield imine PhN═C(Me)$_2$. The unhindered imine generated *in situ* would terminate both initiating and propagating ion-pairs at rapid rates. Furthermore, partnered with diborane WCA, the common ion iminium PhNH═C(Me)$_2^+$ present in the system was anticipated to suppress the initiation rate, as been proven for protonated DtBMP [106]. In the case of **3c**, no polymer was formed in hexane (Table 2.9, entry 13) and only small quantities formed in CH_2Cl_2 (Table 2.9, entry 14). This was attributed to the instability of **3c**, with the decomposed byproduct MeOH being a very effective inhibitor for cationic polymerisation.

In conclusion, besides the Lewis acidity, the behaviour of diboranes as polymerisation co-initiators depends strongly on the nature of their interaction with the CumX species and the basicity of X, which appears to be strongly correlated with chain transfer [105]. In other words, the weakly coordinating nature of the chelating μ-X diborane anion is of great importance to the stability and effectiveness of the *in situ* formed initiator **3a**–**3f**. Chain transfer would be significantly suppressed with more shielded diborane **1** and less exposed μ-Cl (**3a**), e.g. a more weakly coordination, leading to PIBs with higher molecular weights and yields.

With diboranes **1** and **2** as co-initiators, it was also possible to polymerise IB in aqueous suspensions [109] featuring strong electrolytes, namely LiCl, 38 wt% sulphuric acid and 48 wt% HBF_4 (Table 2.10) [107].

The nature of the electrolytes has a significant influence on polymerisation yields, with HBF_4 being superior to LiCl and H_2SO_4 (Table 2.10, entries 1, 4, 9). As far as the molecular weight is concerned, no clear pattern of dependencies emerges from these data other than that of a temperature dependence. It should also be

Table 2.10
Selective results [107] of polymerisation of IB in aqueous suspension[a].

Entry	Initiator (mM)[b]	Electrolyte	Surfactant[c]	T (°C)	M_w (kg/mol)	PDI	Conv. (%)
1	**1** (0.322)	LiCl		−60	22.8	2.30	44
2	**1** (0.322)	LiCl	DTMB	−60	61.0	2.74	5
3	**1** (0.322)	LiCl	SDS	−60	31.8	2.37	32
4	**1** (0.625)	H_2SO_4		−60	28.3	2.05	29
5	**1** (0.625)	H_2SO_4	SDS	−60	37.2	2.69	18
6	**1** (0.625)	H_2SO_4	DTMB	−60	69.8	2.86	3
7	**1** (0.625)	H_2SO_4	DTMOTf	−60	41.3	2.32	18
8[d]	**1** (0.625)	$LiHSO_4$		−45	22.0	3.86	46
9	**1** (0.322)	HBF_4		−80	41.4	2.37	58
10	**1** (0.322)	HBF_4	SDS	−80	27.2	2.08	47
11	**1** (0.322)	HBF_4	$DTMBF_4$	−80	33.4	2.22	47
12	**2** (0.627)	LiCl		−60	91.9	2.27	40
13	**2** (0.625)	HBF_4		−80	49.4	2.15	58
14[e]	**2** (0.625)	HBF_4		−80	39.5	2.04	29

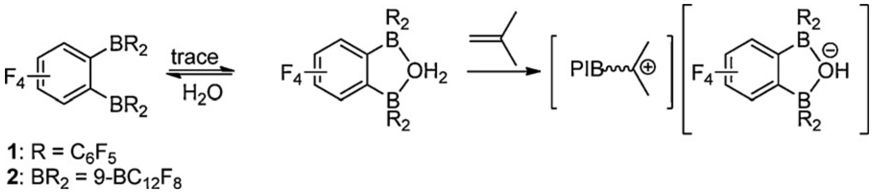
[a] The diborane initiator dissolved in 1.0 mL of toluene was added rapidly to a stirred (500 rpm) mixture of 18.0 mL of isobutene and 18.0 mL of aqueous electrolytes (LiCl:LiCl (23 wt%), NaCl (1.2 wt%), H_2O (75.8 wt%); H_2SO_4 (38 wt%); HBF_4 (7.0 M)) at the indicated temperatures unless otherwise noted.

[b] The concentration of diborane used is reported with respect to the total volume of the organic phase.

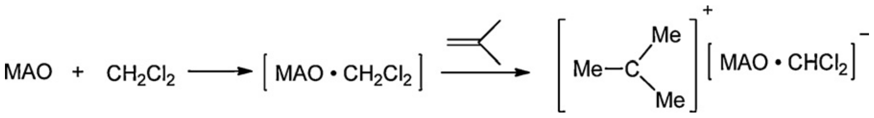
[c] Where used, 0.100 g of DTMB, SDS, DTMOTf, $DTMBF_4$ was added to the aqueous phase.

[d] A stock solution of diborane in toluene (1.0 mL) was added over 5 min to a suspension of 15.0 mL of isobutene and 15.0 mL of 5.0 M aqueous $LiHSO_4$ at −45 °C.

[e] A stock solution of diborane in toluene (1.0 mL) was added over 10 min to a suspension of 15.0 mL of isobutene and 15.0 mL of aqueous HBF_4.



Scheme 2.21. Proposed mechanism for isobutene polymerisation in aqueous suspensions [104,109].



Scheme 2.22. Polymerisation of IB initiated by MAO [113].

noted that the addition rates of co-initiators to these suspensions was a very significant variable influencing the results; higher yields of PIB were obtained by adding the co-initiator rapidly (Table 2.10, entries 13 and 14). In all cases, the use of surfactants led to a decrease in conversion (Table 2.10, entries 2, 3, 5–7, 10, 11). In the presence of DTMB, the yields were much lower (Table 2.10, entries 2 and 6). A possible explanation of the low conversions encountered in stabilised suspensions is the increased water concentration at the interface or inside monomer droplets during chain growth, with the diffusion of water increasing in the order BF_4 [110] ≪ $ROSO_3$ ~ HSO_4 [110] ~ CF_3SO_3 < Br ≪ Cl.

Concerning the polymerisation mechanism, detailed investigations suggest that both monodentate aqua complexes formed from diborane **1** and **2**, or even the kinetically stronger Lewis acids $B(C_6F_5)_3$ or $C_6F_4HB(C_6F_5)_2$, are not sufficiently acidic to initiate the polymerisation of isobutene. Instead, it was proposed that the μ-aqua complex formed from diborane and one molecule of water irreversibly protonates isobutene (Scheme 2.21).

2.7. Methyl aluminium oxide

Methylalumoxane (MAO) is widely used as a cocatalyst for the early transition metallocenes and other late transition organometallic catalysts in the polymerisation of α-olefins [111,112]. Methyl aluminium oxide (MAO) is active for the polymerisation of isobutene at ambient temperatures [113]. The mechanism believed to be operative involves generation of a *t*-butyl cation from isobutene, dichloromethane solvent and MAO (Scheme 2.22).

3. Conclusions and outlook

During the last 15 years, the field of cationic homo- and copolymerisation of isobutene has rapidly evolved. Though the cation parts of the initiator systems developed by Baird, Bochmann, Kühn, Collins/Piers are very different, nearly all systems share one similarity: incorporation of WCAs. To our opinion, the recognition that WCAs significantly reduce chain transfers in a cationic polymerisation process and hence enable the polymerisation of isobutene at much more controlled conditions (room temperature vs. low temperatures) is the key for all the developments. This is consistent with the fact that although for some systems it is not clear what exactly the initiating species is, it is generally accepted that the initiation mechanism for all the newly developed systems appears to be a conventional cationic process. From an industrial point of view, interesting systems might be Bochmann's zincate system and Kühn's nitrile ligated transition metal system, for they are able to produce high value-added low molecular PIB with high *exo* double bonds ratio at room temperature. However, their future application as potential industrial initiators/catalysts for the process still remains open, due to several not yet solved problems, e.g. high catalyst/initiator costs and recyclability in the case of the latter systems. Further work is certainly needed to fully understand the reaction mechanisms and to provide cheap and easily accessible initiator or catalyst systems to replace the currently applied technical processes to generate polyisobutene.

Acknowledgement

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