

1 Commercially Available Metal Alkyls and Their Use in Polyolefin Catalysts

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1.1 INTRODUCTION

Organometallics are defined as compounds that contain a *direct* carbon–metal bond. Such compounds may be regarded as the interface between organic and inorganic chemistry. There are two basic types of organometallics: metallocenes and metal alkyls. Metallocenes contain a carbon–metal *pi* (π) bond and most often involve transition metals from groups 3–11 of the periodic table and aromatic ligands such as cyclopentadienyl (“Cp”) or indenyl.^{1,2} Metal alkyls are defined as organometallic compounds containing a carbon-to-metal *sigma* (σ) bond.

Metal alkyls are essential to the performance of industrial Ziegler–Natta (ZN) catalysts and most single-site catalysts (SSCs that do not require cocatalysts were recently reported³ but are not yet in industrial use). This chapter will stress practical aspects of metal alkyls, particularly those used with transition metal polyolefin catalysts. We will answer questions such as:

- What are the distinguishing properties of metal alkyls?
- Which are the commercially important metal alkyls?
- How do metal alkyls function in polyolefin catalyst systems?
- What are the impurities in commercial metal alkyls and how do these impurities influence catalyst performance?
- What selection criteria are used for metal alkyls in polyolefin catalyst systems?

Key synthetic chemistries will be mentioned but are not discussed in depth. Detailed reviews of production, properties, and applications of metal alkyls are available elsewhere.⁴⁻¹²

In manufacture of polyolefins, the most important metal alkyls are those of aluminum and magnesium. Other organometallics are employed in production of polyolefins but in much smaller quantities. These include organometallic compounds containing boron and zinc and a range of metallocenes. First-generation supported chromium catalysts (“Phillips catalysts”) do not require metal alkyls.¹³ However, performance of some chromium catalysts developed in the 1970s–1980s is improved by metal alkyls.^{13,14} Metallocenes will not be discussed in detail in this chapter but will be addressed in the context of SSCs in subsequent chapters.

Note that the definition of organometallics excludes compositions such as metal alkoxides, metal carboxylates, and chelated metal complexes involving nitrogen and phosphorus, since there is an intervening heteroatom between the carbon and the metal. Hence, many nonmetallocene SSCs based on late transition metals^{15,16} are not technically organometallic compounds, though active centers are believed to contain direct metal–carbon σ bonds.

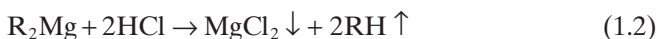
1.2 METAL ALKYLs IN ZIEGLER–NATTA CATALYSTS

Aluminum alkyls and magnesium alkyls fulfill several roles in ZN polymerization catalyst systems. The two most important are as raw materials for catalyst synthesis and as cocatalysts (sometimes called “activators”) for the transition metal catalyst. These key functions are illustrated in simplified equations below.

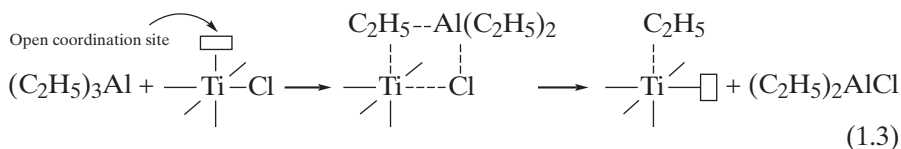
- *Metal alkyls in catalyst synthesis:* Reduction of the transition metal “precatalyst,” exemplified below with titanium tetrachloride and ethylaluminum sesquichloride (EASC):



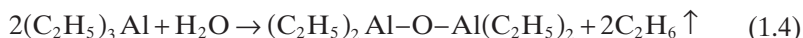
Production of a support, as shown in Eq. 1.2 with a dialkylmagnesium compound and anhydrous HCl:



- *Metal alkyls as cocatalysts:* Alkylation of the reduced transition metal compound to produce active centers for polymerization, illustrated below with triethylaluminum (TEAL) and TiCl_3 :



Aluminum alkyls also serve the purpose of scavenging catalyst poisons (water, O₂, etc.). Poisons enter as parts-per-million (ppm) contaminants in materials commonly used in polyolefin processes such as monomer, comonomer, solvents, and chain transfer agents. Reaction of the aluminum alkyl with contaminants generates alkylaluminum derivatives that are not as damaging to catalyst performance. For example, water reacts with TEAL to produce small amounts of ethylaluminumoxane:



Typically, aluminum alkyls are used in large excess in ZN catalyst systems. Aluminum-titanium ratios of 20–40 are common in industrial polyethylene processes. Hence, there is ample TEAL to fulfill the roles discussed above. Aluminum alkyls also are involved in chain transfer, but this is a minor function. (Hydrogen is used most often for chain transfer/termination reactions with modern ZN catalysts.)

Aluminum alkyls are preferred as cocatalysts because other metal alkyls are either too expensive or perform poorly. When tried as cocatalysts, magnesium alkyls may completely deactivate ZN catalysts. The reason for this is unknown, but it may stem from overreduction of the transition metal or blockage of active centers caused by strong coordination of magnesium alkyl. Use of zinc alkyls often lowers catalyst activity and reduces polymer molecular weight by acting as a chain transfer agent.

The vast majority of modern ZN catalysts employ aluminum alkyls as cocatalysts, while magnesium alkyls are used solely as raw materials for the production of catalysts.

1.3 ALUMINUM ALKYLs

The term “aluminum alkyl” is meant to include any compound that contains an alkylaluminum grouping and encompasses R₃Al, R₂AlCl, R₃Al₂Cl₃ (the so-called sesquichlorides), RAlCl₂, R₂AlOR', and R₂AlH. Among commercially available aluminum alkyls, R is typically a C₁–C₄ alkyl. Methylaluminumoxanes are also aluminum alkyls and have become important in recent years as cocatalysts for SSCs. However, methylaluminumoxanes exhibit significantly different properties than conventional aluminum alkyls and will be discussed separately (see Section 1.5).

Aluminum alkyls have been produced commercially since 1959 using technology originally licensed by Nobel laureate Karl Ziegler.⁹ Aluminum alkyls are pyrophoric and violently reactive with water.^{4,6,12} Considering these properties, it is remarkable that millions of pounds of aluminum alkyls are produced each year and have been supplied to the polyolefin industry worldwide for half a century with relatively few safety incidents.

Principal aluminum alkyls available in the merchant market (and their common acronyms) are provided in Table 1.1. Typical properties of commercially available aluminum alkyls are summarized below:

- Most ignite spontaneously when exposed to air and are explosively reactive with water. (Please see the appendix for a discussion of pyrophoricity of metal alkyls.)
- Aluminum alkyls are typically clear, colorless liquids at ambient temperature and are miscible in all proportions with aliphatic hydrocarbons (HCs). Large quantities of aluminum alkyls are supplied as solutions in HCs, because solutions are *perceived* to be safer.
- R₃Al compounds (R = ethyl or higher) contain small amounts of R₂AlH. Hydride content is expressed as AlH₃ by tacit convention among major suppliers and typically ranges from about 0.02% (wt) in TEAL to about 0.5% in triisobutylaluminum (TIBAL).

R₃Al compounds also commonly contain small amounts of other trialkylaluminum compounds (R'₃Al). This is usually a consequence of the purity of starting materials or of side reactions during manufacture, such as addition of an ethylaluminum moiety in TEAL across ethylene to produce an *n*-butylaluminum group (Figure 1.1).

R'₃Al contents are low, often <0.5% (by wt). An exception is TEAL where *n*-butylaluminum content (from the reaction above, expressed as tri-*n*-butylaluminum) is typically ~5%.

In the vast majority of ZN catalyst systems, hydride content and the presence of small amounts of other trialkylaluminum compounds (R'₃Al) are not damaging to performance. However, for certain polypropylene (PP) catalysts that employ alkoxy silanes as external donors, hydride can cause a reduction in isotactic content and lowered catalyst activity.⁵¹ Additional tests with TEAL containing up to 16% R'₃Al with a modern supported PP catalyst showed no loss of isotacticity and no loss of activity.⁵¹

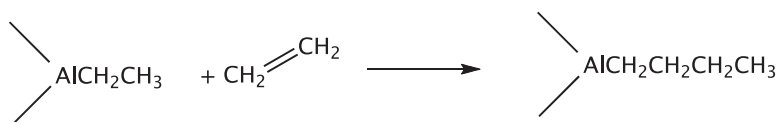


Figure 1.1 Insertion of ethylene into an ethyl group–aluminum bond to form butylaluminum.

TABLE 1.1 Principal Commercially Available Aluminum Alkyls

Product	Acronym	Formula	CAS Number	Theoretical wt % Al
Trimethylaluminum	TMAL	(CH ₃) ₃ Al	75-24-1	37.4
Dimethylaluminum chloride	DMAC	(CH ₃) ₂ AlCl	118-58-3	29.2
Methylaluminum sesquichloride	MASC	(CH ₃) ₂ Al ₂ Cl ₃	12542-85-7	26.3
Triethylaluminum	TEAL	(C ₂ H ₅) ₃ Al	97-93-8	23.6
Diethylaluminum chloride	DEAC	(C ₂ H ₅) ₂ AlCl	96-10-6	22.4
Diethylaluminum iodide	DEAI	(C ₂ H ₅) ₂ AlI	2040-00-8	12.7
Ethylaluminum sesquichloride	EASC	(C ₂ H ₅) ₃ Al ₂ Cl ₃	12075-68-2	21.8
Ethylaluminum dichloride	EADC	C ₂ H ₅ AlCl ₂	563-43-9	21.3
Isobutylaluminum dichloride	MONIBAC ^a	<i>i</i> -C ₄ H ₉ AlCl ₂	1888-87-5	17.4
Tri- <i>n</i> -butylaluminum	TNBAL	(C ₄ H ₉) ₃ Al	1116-70-7	13.6
Triisobutylaluminum	TIBAL	(<i>i</i> -C ₄ H ₉) ₃ Al	100-99-2	13.6
Diisobutylaluminum hydride	DIBAL-H	(<i>i</i> -C ₄ H ₉) ₂ AlH	1191-15-7	19.0
Tri- <i>n</i> -hexylaluminum	TNHAL	(C ₆ H ₁₃) ₃ Al	1116-73-0	9.6
Tri- <i>n</i> -octylaluminum	TNOAL	(C ₈ H ₁₇) ₃ Al	1070-00-4	7.4
Di- <i>n</i> -octylaluminum iodide	DNOAI	(C ₈ H ₁₇) ₂ AlI	7585-14-0	7.1
"isoprenylaluminum"	IPRA	Not available	70024-64-5	Not available
Diethylaluminum ethoxide	DEAL-E	(C ₂ H ₅) ₂ AlOC ₂ H ₅	1586-92-1	20.7
Ethylpropoxyaluminum chloride	EPAC	(C ₂ H ₅)(C ₃ H ₇ O)AlCl		17.9
Diisobutylaluminum butylated oxytoluene	DIBAL-BOT	(<i>i</i> -C ₄ H ₉) ₂ AlO[C ₆ H ₄ (CH ₃)(<i>t</i> -C ₄ H ₉) ₂]	56252-56-3	7.5

Note: IPRA: Also called ISOPRENYL. Complex composition produced by reaction of isoprene (2-methyl-1,3-butadiene) with TIBAL or DIBAL-H. DIBAL-BOT: Also called diisobutylaluminum 2,6-di-*t*-butyl-4-methylphenoxide; produced by equimolar reaction of TIBAL with BHT. MONIBAC: Acronym from "monoisobutylaluminum dichloride."

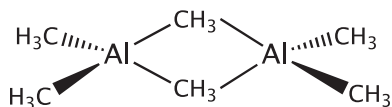


Figure 1.2 Trimethylaluminum dimer.

Aluminum alkyls also contain ppm amounts of aluminoxanes and alkoxides resulting from reaction with water (see Eq. 1.4 and oxygen, respectively). Water and oxygen enter as contaminants (typically <5 ppm) in process materials, for example, nitrogen, ethylene, and hydrogen. Aluminoxanes and alkoxides are usually undetectable (below 500 ppm) and, at these levels, cause no problems in polyolefin catalyst systems.

Total assays are not routinely conducted on commercially available aluminum alkyls. Since impurities mentioned above are also organometallics, total organometallic content of commercially available metal alkyls will typically exceed 99%. The balance is mostly process oils (a purified white mineral oil is used as lubricant and in agitator seals) and small amounts of solvents (mostly C₆–C₈ aliphatic HC) used to wash reactors and process lines.

- Aluminum alkyls are highly reactive with many of the common organic solvents. Indeed, reaction with halogenated hydrocarbons (CCl₄, CHCl₃, etc.) may be explosive after a quiescent period.¹⁷ Organic compounds with acidic protons, such as alcohols and carboxylic acids, may be violently reactive with aluminum alkyls. Carbonyl compounds, such as ketones, aldehydes, and esters, react with aluminum alkyls. Ethers and tertiary amines form exothermic coordination complexes.
- R₃Al are reactive with CO₂.¹⁸ In fact, reaction of trimethylaluminum (TMAL) with CO₂ has been used to produce methylaluminumoxane cocatalysts for SSCs^{19–21} (see Section 1.5.3). The R₃Al/CO₂ reaction is easily controlled and has been used to passivate aluminum alkyl waste streams.²² However, R₃Al are unreactive with CO. Aluminum alkyls containing halogen or oxygen (DEAC, DEAL-E, etc.) are not reactive with CO₂.
- Lower molecular weight aluminum alkyls (C₁, C₂, and isoC₄) are distillable under vacuum. However, higher homologs (*n*-C₄ to *n*-C₈) are not distillable in industrial process equipment and are purified by filtration.
- Most trialkylaluminum compounds are associated as dimers, except when steric bulk of alkyl groups (*t*-butyl, isobutyl, etc.) prevents association. For example, TMAL associates via three center–two electron bonding²⁴ (also called “electron-deficient” bonding²⁵) as depicted in Figure 1.2.
- At low temperature, proton nuclear magnetic resonance (NMR) spectra of TMAL show separate signals for terminal and bridging methyls. However, at room temperature, rapid alkyl exchange occurs and methyls are indistinguishable by NMR.

- Halogenated and oxygenated aluminum alkyls are even more strongly associated, most often as dimers. Heteroatom-containing ligands assume bridging positions. This may be exemplified by DEAL-E, which is dimeric with dative bonds between oxygen and an adjacent aluminum (Figure 1.3).
- In general, aluminum alkyls are stable indefinitely if stored properly (under dry inert gas and away from heat). Storage stability of aluminum alkyls may be illustrated anecdotally. At the aluminum alkyl manufacturing site formerly known as Texas Alkyls (now Akzo Nobel), a small carbon steel cylinder of DEAC was returned after having been stored unopened for 10 years in a customer's laboratory. The product was sampled and analyzed. The DEAC was still clear (free of particulates), though it had a faint amber tint after 10 years. Within analytical variance, aluminum and chloride contents and the hydrolysis gas composition were essentially unchanged.
- Aluminum alkyls demonstrate moderate to excellent thermal stability, depending on ligands. Thermal stability is especially important for aluminum alkyls used in solution processes for polyethylene since these often operate at $>190^{\circ}\text{C}$. Table 1.2 provides thermal stability data on selected aluminum alkyls. Lower R_3Al 's decompose slowly at elevated temperatures, but thermal stability diminishes as chain length or branching increases. While quality may be lowered, violent decomposition does not occur. *An exception is TMAL, which undergoes potentially hazardous self-accelerating decomposition above 120°C . Decomposition of TMAL is highly exothermic and is accompanied by generation of large amounts of methane.²³ If confined, an explosion could result.* Thermal decomposition of aluminum alkyls typically occurs by β -hydride elimination, exemplified in Figure 1.4 with TIBAL. Aluminum alkyls that contain ligands with halogen or oxygen are more stable thermally than the analogous R_3Al compounds. While TEAL begins to decompose at $\sim 120^{\circ}\text{C}$, DEAC is stable up to 174°C and DEAL-E up to 192°C .

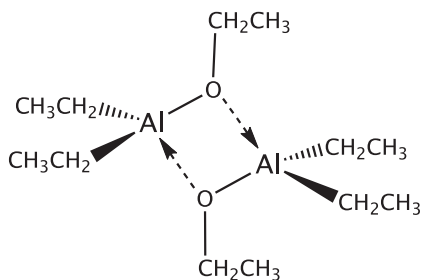


Figure 1.3 Dimer structure of diethylaluminum ethoxide.

TABLE 1.2 Thermal Decomposition Data of Selected Aluminum Alkyl Compounds

Product	Decomposition Temperature (°C) ^a	% Decomposed (3h at 180°C)
Triethylaluminum	120	64
Tri- <i>n</i> -butylaluminum	100	87
Triisobutylaluminum	50	92
Tri- <i>n</i> -octylaluminum	60	90
Diethylaluminum chloride	174	2
Diisobutylaluminum chloride	165	4
Diethylaluminum ethoxide	192	0

^aEstimated temperature at which decomposition is first observed in inert atmosphere.

Source: Data from G. Sakharovskaya, N. Korneev, N. Smirnov, and N. Popov, *J. Gen. Chem. USSR*, 44, 560 (1974).

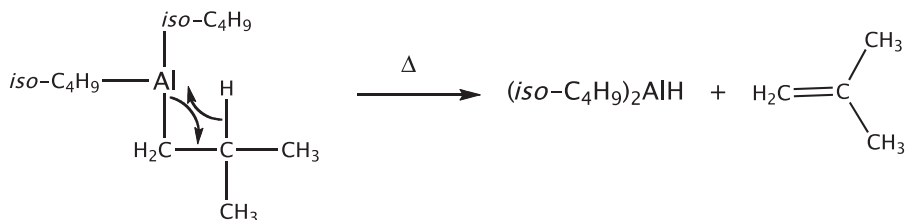


Figure 1.4 Decomposition of triisobutylaluminum.

1.4 PRICING AND SELECTION CRITERIA FOR ALUMINUM ALKYLs

In the early history of ZN catalysts, chlorinated aluminum alkyls such as DEAC and EASC were the most important and functioned as both reducing agents and cocatalysts. They were readily available and relatively inexpensive and performed well with first-generation ZN catalysts. However, as supported ZN catalysts began to emerge in the 1970s, TEAL supplanted EASC and DEAC because TEAL performed better. TEAL remains today the largest volume aluminum alkyl. Many millions of pounds are sold each year to the global polyolefin industry.

As usual, cost is a primary consideration in selecting an aluminum alkyl. Commercial prices for aluminum alkyls are currently between about \$5 and \$10 per pound but can be higher for “specialty” products such as TMAL, DEAI, and isoprenylaluminum (IPRA). The latter products require either multistep processes and/or expensive raw materials, for example, elemental iodine. Detailed current pricing for aluminum alkyls may be obtained from major commercial suppliers listed below:

- Akzo Nobel (formerly Texas Alkyls)
- Albemarle (formerly Ethyl Corp.)
- Chemtura (formerly Crompton, Witco, and Schering)

Though DEAC and EASC remain less costly than TEAL, they are not typically used with supported catalysts because they perform poorly. For example, they may cause lower catalyst activity or reduced stereoregularity in polypropylene. They also leave chloride-containing residues in the polymer that can corrode equipment or degrade the polymer.

TIBAL is a commercially available R_3Al that performs comparably to TEAL with many ZN catalysts and is slightly lower in price (per pound) than TEAL. So, why is TIBAL not the number one selling aluminum alkyl? The reason is that, if other factors are equal, polyolefin manufacturers buy on the basis of *contained* aluminum. Since TEAL contains about 70% more aluminum than TIBAL on a molar basis, TIBAL actually costs *more* than TEAL based on aluminum content. This can be illustrated as follows: Assume that a world-scale LLDPE manufacturing facility uses 200,000 pounds per year of TEAL as cocatalyst and that TIBAL and TEAL perform equally (at the same Al/Ti) in the process. Assume further that the price of each is \$10/pound. This amounts to an annual TEAL cost of $\$2.00 \times 10^6$. The amount of contained aluminum in 200,000 pounds of TEAL (typical Al content of 23.2%) is 46,400 pounds. However, the amount of TIBAL (typical Al content of 13.6%) needed to obtain 46,400 pounds of aluminum is about 341,000 pounds or an annual cost of $\$3.41 \times 10^6$. Hence in this illustration, the annual cost advantage of TEAL relative to TIBAL amounts to $\$1.4 \times 10^6$.

As mentioned above, selection of cocatalyst is often dictated by cost. In some cases, however, advantages of an alternative cocatalyst transcend the cost factor. This could be because the alternative cocatalyst provides better process performance (higher catalyst activity, improved kinetic profile, etc.) or enhanced polymer properties. For example, use of TMAL as cocatalyst in place of TEAL in a gas-phase linear low-density polyethylene (LLDPE) process provides product with lower extractables and improved film tear strength.²⁶ Use of IPRA as cocatalyst can result in ultrahigh molecular weight polyethylene (PE) with broader molecular weight distribution (MWD).^{27,28} (IPRA is a complex composition²⁹ produced by reaction of TIBAL or DIBAL-H with 2-methyl-1,3-butadiene, also known as isoprene.) Enhanced properties can translate into superior polymer performance and such resins command higher prices, thereby overcoming the increased cost of cocatalyst.

1.5 METHYLALUMINOXANES

1.5.1 Conventional Methylaluminoxane

Conventional methylaluminoxane is produced by partial hydrolysis of TMAL in toluene. Reaction must be closely controlled. Unfortunately, explosions and

serious injuries have been reported during preparations of methylaluminoxane. Water must be introduced at low temperature and in forms that moderate the potentially violent reaction. Water has been introduced as hydrated salts, ice shavings, or atomized spray. Even with these precautions, explosive reactions have occurred. In most cases, polyolefin producers leave synthesis of methylaluminoxane to aluminum alkyl manufacturers to obviate handling the highly pyrophoric TMAL and attempting to control its reaction with water. A simplified overall reaction is given as



Yields are low (usually <60%). The toluene-soluble product is called methylaluminoxane (MAO) or, less commonly, polymethylaluminoxane (PMAO). MAO has been offered commercially since the late 1980s. Recently, improved commercial processes with much higher yields have been developed.⁶¹

Though MAO was reported to be an excellent cocatalyst for metallocene SSC by Kaminsky, Sinn, and co-workers⁵² in the late 1970s and has been the subject of intense study since then, its precise composition remains poorly understood. Typical properties of commercially available MAO are summarized below:

- As isolated from toluene solution, neat MAO is an amorphous, friable white solid containing 43–44% Al (theory 46.5%). It is virtually insoluble in aliphatic hydrocarbons but has excellent solubility in aromatic hydrocarbons. MAO is supplied commercially as a toluene solution containing ~13% Al, which corresponds to ~28% concentration of MAO. Like most commercially available aluminum alkyls, it is pyrophoric and explosively reactive with water.
- Differential scanning and accelerating rate calorimetry (DSC, ARC) studies have shown MAO to be thermally stable at least up to about 220 °C.²³ MAO decomposes exothermically without melting above ~220 °C.
- Commercially available MAO contains residual TMAL (15–30%), called “free TMAL” or “active aluminum.” Both reductions and increases in SSC activity have been said to occur because of free TMAL.^{30–32}
- Gas chromatographic (GC) analysis of hydrolysis gas from MAO typically shows >99% methane. The balance is mostly ethane.
- Proton NMR analysis suggests that the CH₃/Al in MAO is about 1.4.³³ Measurement of the volume of methane generated upon hydrolysis will always show higher CH₃/Al (typically 1.6–1.8) because of free TMAL.
- MAO is not distillable. However, if MAO is subjected to vacuum distillation conditions, some of the so-called free TMAL will distill.^{19,33}
- Storage stability of MAO solutions is poor.^{19–21,33} Freshly prepared MAO solutions form gels within a few days when stored at ambient temperatures (>20 °C). Lower storage temperatures (0–5 °C) delay gel formation.

Consequently, MAO manufacturers store and transport molecular weights (MAO) solutions in refrigerated containers.

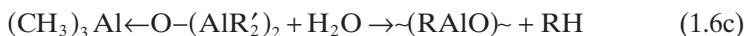
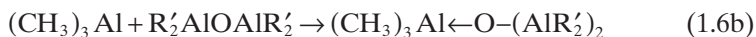
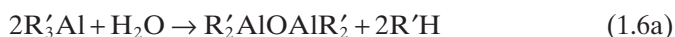
- Published data on MAO isolated from toluene have shown a wide range of molecular weights (MWs) (300–3000 amu, primarily using cryoscopic methods). Possible reasons for the irreproducibility were proposed by Beard et al., who showed that cryoscopic MW measurements of commercially available MAO are influenced by several variables, such as process oils, residual solvent (toluene), and TMAL content.³³ Beard reported “corrected” cryoscopic MWs of about 850, suggesting x in Eq. 1.5 to be about 15.

Perhaps the most important drawback of MAO is its cost (see Section 1.5.5), which is substantially higher than conventional aluminum alkyls (10–20 times). Despite its high cost and untoward features, MAO remains the most widely used cocatalyst for SSC.

1.5.2 Modified Methylaluminoxanes

Modified methylaluminoxanes (MMAOs) have been offered commercially since the early 1990s. MMAO³⁴ is a generic term encompassing all products wherein some of the methyl groups are replaced by other alkyl groups, usually isobutyl or *n*-octyl. All MMAOs contain >65% methyl groups and, as such, remain predominantly MAO.

Most MMAOs are prepared by reaction with water, as previously shown for MAO. However, the process for MMAOs permits the more controllable reaction of R_3Al with water *before* the TMAL/water reaction is attempted.³⁴ It is suggested that a coordination complex forms between TMAL and preformed alkylaluminoxane, resulting in a more moderate reaction of TMAL with water. This sequence of reactions is depicted as



where R is 65–95% methyl and the balance R'.

There are several versions of MMAOs (differentiated by a suffix, e.g., MMAO-3A), each with different composition and properties (See Table 1.3.). One (MMAO-7) is produced by a nonhydrolytic method (described below). Another (MMAO-12) contains ~95% methyl groups and is the MMAO that most closely approximates MAO.

Relative to conventional MAO, MMAOs exhibit much improved storage stability and some are highly soluble in aliphatic hydrocarbons. (Manufacturers of PE prefer to avoid toluene because of toxicity concerns, especially if

TABLE 1.3 Commercially Available Alkylaluminoxane Compounds

Product	Acronym	Approximate Formula	wt % Al ^o	Comment
Methylaluminoxane	MAO	$-((\text{CH}_3)\text{AlO})_x^-$	46.5	Also called PMAO, available only in toluene solution
Polymethylaluminoxane improved performance	PMAO-IP	$-((\text{CH}_3)\text{AlO})_x^-$	46.5	Product by nonhydrolytic process, available only in toluene solution
Modified methylaluminoxane, type 3A	MMAO-3A	$-((\text{CH}_3)_{0.7}(i\text{-C}_4\text{H}_9)_{0.3})\text{AlO})_x^-$	38.2	Available in heptane
Modified methylaluminoxane type 7	MMAO-7	$-((\text{CH}_3)_{0.68}(n\text{-C}_8\text{H}_{17})_{0.32})\text{AlO})_x^-$	37.6	Produced via nonhydrolytic process, available in Isopar E TM
Modified methylaluminoxane, type 12	MMAO-12	$-((\text{CH}_3)_{0.65}(n\text{-C}_8\text{H}_{17})_{0.35})\text{AlO})_x^-$	42.9	Available only in toluene
Isobutylaluminoxane, type 65	IBAO-65	$-((i\text{-C}_4\text{H}_9)\text{AlO})_x^-$	27.0	Available only in hydrocarbon solution, O/Al -0.65
Bis(diisobutylaluminum)oxide	DIBAL-O	$(i\text{-C}_4\text{H}_9)_2\text{AlOAl}(i\text{-C}_4\text{H}_9)_2$	18.1	Available only in hydrocarbon solution, O/Al -0.50

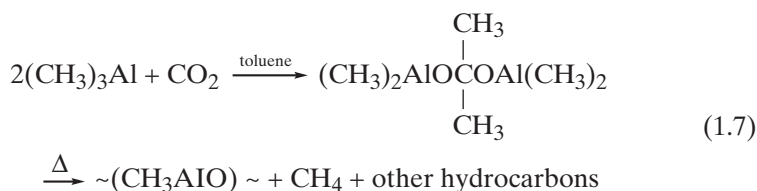
Notes: (1) Chemical Abstracts Service registry numbers, reading down: 120144-90-3, 206451-90-3, 146905-79-5, 206451-54-9, 206-54-9, 220326-29-4, 998-00-5. (2) Isopar ETM is a trade name of Exxon Mobil Corporation for an aromatics-free hydrocarbon liquid mixture, boiling range 114-140°C. (3) DIBAL-O is also known as tetraisobutylaluminoxane (TIBAO).

resins are destined for food contact.) Most importantly, because yields are higher, MMAO formulations are less costly than MAO. However, since MMAOs contain other types of alkylaluminoxanes, they do not duplicate performance of standard MAO in many SSC systems. Consequently, MMAOs should be considered niche cocatalysts for SSCs.

1.5.3 Nonhydrolytic Methylaluminoxanes

A nonhydrolytic method has been reported^{19–21} for production of MAOs suitable as cocatalysts for SSCs. This alternative synthesis avoids altogether the hazardous reaction of TMAL with water and affords essentially quantitative recovery of aluminum values. Because the product provides higher activity in a standard ethylene polymerization test using *rac*-ethylenebis(indenyl)zirconium dichloride, it was dubbed PMAO-IP (from polymethylaluminoxane-improved performance).

Though many precursors may be used, the simplest method involves reaction of CO₂ with TMAL to form an intermediate. Subsequent pyrolysis produces PMAO-IP. The detailed chemistry is complex and involves evolution of methane and other hydrocarbons, including products resulting from Friedel–Crafts reactions with toluene. A simplified equation is



Reactant proportions are chosen such that the O/Al in PMAO-IP is ~0.8,²⁰ as it is in conventional MAO.³³ PMAO-IP contains much lower free TMAL than hydrolytic MAO, which may explain the higher activity with selected SSCs. It appears to be especially effective in solution processes for polyethylene. However, performance of PMAO-IP does not extend across the entire range of SSCs and it cannot be considered a “drop-in” replacement for conventional MAO.

1.5.4 Other Alkylaluminoxanes

Other alkylaluminoxanes are also available, more easily produced and less costly than MAO. Ethylaluminoxane (EAO; see Eq. 1.4) and isobutylaluminoxane (IBAO) have been used industrially since 1970 in catalyst systems for polymerization and copolymerization of epichlorohydrin to produce elastomers.³⁵ However, EAO and IBAO perform poorly as cocatalysts for SSCs. Preparation and properties of alkylaluminoxanes have been extensively reviewed.^{32,36,37}

Alkylaluminumoxanes have been shown to exist as highly associated oligomeric, cage, or cluster structures.^{38,39} Barron et al., prepared *t*-butylaluminumoxane (TBAO) by equimolar direct hydrolysis of tri-*t*-butylaluminum at -78°C followed by thermolysis. TBAO was found to be primarily hexameric and nonameric, though some higher aggregates were also observed. Barron and co-workers proposed a nonameric cluster structure for MAO wherein aluminum is exclusively tetracoordinate.⁴⁰ IBAO, a commercially available alkylaluminumoxane isomeric with TBAO, has been shown to have a cryoscopic MW of approximately 950,⁴¹ in agreement with nonameric association.

1.5.5 Why Are MAOs So Costly?

All commercially available MAOs employ TMAL as the starting material. Because TMAL must be manufactured by less efficient processes,²³ it is much more expensive than other R_3Al compounds. This, coupled with low yields of MAO from typical processes for hydrolysis of TMAL, translates to very high costs for MAOs. Additionally, MAOs must be used in huge excess in many SSC systems, further increasing the cost. (Ratios of Al to transition metal >100 are common.) Even though nonhydrolytic MAO and the various MMAOs are obtained in higher yields than MAO, they are also derived from TMAL and remain very expensive relative to conventional aluminum alkyls. Commercially available alkylaluminumoxanes are listed in Table 1.3.

1.5.6 Pricing and Selection Criteria of MAOs

Unlike conventional aluminum alkyls, MAOs are supplied only in solution. When MAO became widely available in the early 1990s, pricing methods for solutions of MAO were not consistent. Suppliers used different pricing based upon \$/wt of contained Al, \$/wt of the calculated amount of contained MAO, or \$/wt of solution. Calculations below demonstrate a method of converting prices to a common basis so that direct comparisons may be made.

Assume that three suppliers provide the following pricing for 5000 pounds of a toluene solution of MAO containing 13.3% Al (the typical concentration of commercially available MAO):

- Supplier X: \$150/lb of contained Al
- Supplier Y: \$100/lb of contained MAO
- Supplier Z: \$35/lb of MAO solution

Pricing by supplier X uses the amount of aluminum supplied to the customer as determined by an accurate analytical method. Hence, the cost of MAO from supplier X would be

$$5000\text{ lb} \times 0.133 \times \$150/\text{lb of contained Al} = \$99,750$$

Supplier Y would calculate that the solution containing 13.3% Al corresponds to a 28.6% solution of MAO using the theoretical amount of aluminum in “pure” MAO (46.5%). The cost of MAO from supplier Y would then be calculated as

$$5000\text{lb} \times (0.133/0.465) \times \$100/\text{lb of contained MAO} = \$143,011$$

The cost of MAO from supplier Z is calculated straightforwardly using the total weight of solution:

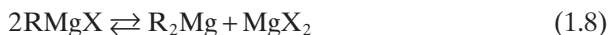
$$5000\text{lb} \times \$35/\text{lb of MAO solution} = \$175,000$$

Ultimately, performance of the MAO in the specific customer application is the most important criteria for selection. A low price is of little value if performance is poor. Since polyolefin manufacturers use different SSCs and processes, each must select the MAO that provides acceptable performance at the most attractive price. This is usually determined through laboratory and pilot plant evaluations.

1.6 MAGNESIUM ALKYLs

1.6.1 Properties of Magnesium Alkyls

Impetus for using magnesium alkyls in ZN catalyst synthesis was provided by the discovery that magnesium salts, especially MgCl_2 ,⁴² are excellent supports for ZN catalysts. Magnesium alkyls encompass both Grignard reagents (organomagnesium halides, RMgX) and dialkylmagnesium compounds (R_2Mg). The two are linked by the so-called Schlenk equilibrium:



Grignard reagents are produced by reaction of an alkyl halide with magnesium metal in an ether, usually diethyl ether or tetrahydrofuran. Detailed discussions of the Schlenk equilibrium and preparation and properties of Grignard reagents and R_2Mg compounds are beyond the scope of this text, but excellent reviews are available.^{43,44} A survey of processes for commercially available dialkylmagnesium compounds is also available.⁴⁶

Dialkylmagnesium compounds have been shown to be highly associated in linear structures wherein magnesium atoms are tetracoordinate as depicted in Figure 1.5.

The α -carbon atom in each R bridges adjacent magnesium atoms *via* three center–two electron bonding,²⁴ mentioned previously in the discussion of TMAL association. Because n is very large for simple R_2Mg ($\text{R} = \text{CH}_3$ to

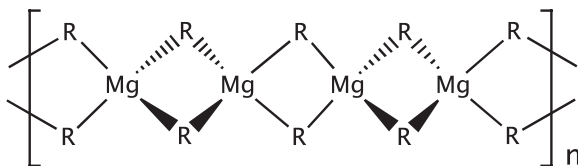
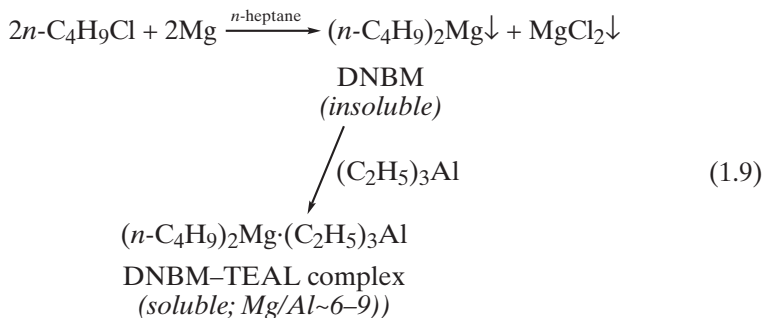


Figure 1.5 Dialkylmagnesium oligomer structure.

$n\text{-C}_4\text{H}_9$), such compounds are essentially polymeric. Hence, high molecular weight (rather than ionic character) accounts for the poor HC solubility of R_2Mg .

Since excessive amounts of ethers lower activity of polymerization catalysts, Grignard reagents were not preferred for industrial ZN catalyst preparations that began to emerge in the 1970s. However, most of the R_2Mg known in the early 1970s were insoluble in HC and were poorly suited to industrial production.

In the mid-1970s, an interim product was developed. It took advantage of the HC solubility of complexes of R_2Mg compounds. Addition of R_3Al to the reaction product of n -butyl chloride with magnesium in heptane affords an ether-free, HC-soluble complex of di- n -butylmagnesium (DNBM).⁴⁵ Such reactions are exemplified in Eq. 1.9 with TEAL:



Though the complex is shown as if it were discrete, rapid alkyl exchange occurs and alkyls are “scrambled” in the DNBM-TEAL complex.

Discovery of several HC-soluble “unsymmetrical” dialkylmagnesium compounds (RMgR') allowed more facile processes⁴⁶ and products that contained much lower amounts of R_3Al . Currently, the following RMgR' are offered commercially:

- n -butyl(ethyl)magnesium (BEM),
- n -butyl(n -octyl)magnesium (BOM or BOMAG[®]), and
- n -butyl(sec -butyl)magnesium (also called dibutylmagnesium, or DBM).

RMgR' are supplied only as HC solutions, usually 10–20% in *n*-heptane. (They cannot be supplied as the neat products because of the difficulties of handling infusible solids that are pyrophoric.)

BEM and BOM are manufactured by similar processes (reaction of alkyl chlorides with magnesium powder in HC). However, DBM must be produced by a different process. Although production of DBM begins with reaction of *n*-butyl chloride/Mg as in Eq. 1.9, *sec*-butyllithium is used to introduce the *sec*-butyl groups needed to render the composition HC soluble (Because *sec*-butyl chloride does not react with magnesium in the absence of donor solvents, *sec*-butyllithium must be used to introduce *sec*-butyl groups; see reference 46 for details on process chemistry.)

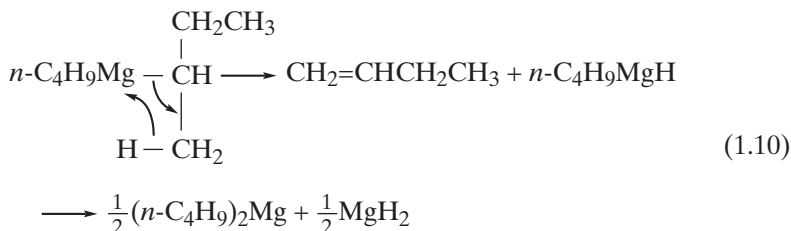
Though the nomenclature of RMgR' might suggest near-equal amounts of R and R', that is true only for BEM. Yield of HC-soluble BEM is maximized when the ratio of *n*-butyl to ethyl is ~1.0.⁴⁷ However, the ratio of *n*-butyl to *n*-octyl in BOM is 2.5–3.0 and the *n*-butyl to *sec*-butyl ratio in DBM is typically 1.3–1.5. The reason for this is economic. For BOM and DBM, the cost of *n*-butyl chloride is significantly lower than *n*-octyl chloride and *sec*-butyllithium, respectively.

BEM and BOM are inherently HC soluble, but the solutions are very viscous. Consequently, a viscosity-reducing agent must be added. A small quantity of TEAL (1–2 mol %, relative to Mg) is most commonly used for this purpose. TEAL forms nascent coordination complexes with the RMgR', thereby lowering the molecular weight of the magnesium alkyl and solution viscosity is reduced by two orders of magnitude. (The amount of TEAL required for viscosity reduction of BEM or BOM is much smaller than that required for solubilization of DNBM depicted in Eq. 1.9.)

DBM solutions are free flowing and do not require viscosity reducers. DBM differs from BEM and BOM in another way. At low temperatures (below ~5°C), a white precipitate may form in DBM solutions. To prevent this, a small quantity of *n*-octyl chloride was introduced (beginning in the mid-1980s) with *n*-butyl chloride. This generates *n*-octylmagnesium groupings that function as “antifreeze” in commercially available DBM. The overall proportions of *n*-butyl to *sec*-butyl to *n*-octyl in DBM are approximately 55:41:4.

As isolated from solution, BEM is an amorphous white solid that slowly decomposes without melting above about 140°C. The molecular weight of BEM has been determined (cryoscopically in cyclohexane) to be about 2700 amu. As mentioned above, BEM solutions are highly viscous. Even at relatively low concentrations (~15% by weight), solution viscosities are >10³ mPa·s in the absence of a viscosity-reducing agent.

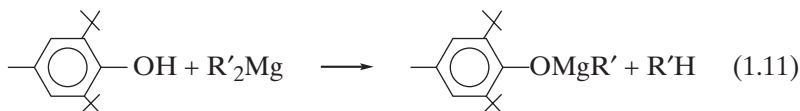
Magnesium alkyls are stable indefinitely if stored properly (under dry inert gas and away from heat). BEM is thermally stable up to about 140°C. However, DBM undergoes extensive decomposition at elevated temperatures. This occurs because *sec*-butyl groups in DBM readily undergo β -hydride elimination to produce butene-1 and MgH₂ as in



Also, butene-2 may be formed by β -hydride elimination from the methylene of the *sec*-butyl group. In both cases, the intermediate alkylmagnesium hydride is unstable and decomposes further to R_2Mg and magnesium hydride. The overall effect of subjecting DBM solutions to high temperatures is loss of soluble magnesium and appearance of a precipitate.

1.6.2 Modified BEM Compositions

Modified versions of BEM are produced by reaction of small amounts of 2,6-di-*t*-butyl-4-methylphenol, also known as butylated hydroxytoluene (BHT), with standard BEM, as in



BHT is added in approximately 0.5 and 1.0% amounts (molar, relative to Mg). These formulations, known as BEM-2436 and BEM-4436, respectively, are used to produce catalysts primarily for production of LLDPE. Because BHT is added in such small quantities, BEM-2436 and BEM-4436 are compositionally very close to standard BEM. Specifically, BEM-2436 and BEM-4436 contain 99.0 and 98.0 wt % BEM, respectively, and the balance is the product of Eq. 1.11. BHT is regenerated by hydrolysis when the resin is exposed to moist air. Because BHT functions as an antioxidant for polyolefins, BHT residues cause no problem for the polymer.

Though BHT was added initially as a viscosity-reducing agent,⁴⁸ its viscosity-lowering effect is slight compared to that of TEAL. However, small quantities of BHT improved the performance of BEM in selected catalyst systems and BEM-2436 and BEM-4436 became commercial products.

Another derivative of BEM that has been offered commercially is the product known as *n*-butyl(ethyl)magnesium *n*-butoxide (BEM-B), produced by the reaction of one equivalent of *n*-butyl alcohol with BEM:



where R' is ~50% ethyl and ~50% *n*-butyl.

Unlike BEM-2436 and BEM-4436, BEM-B is compositionally very distinct from standard BEM. Because *n*-butyl alcohol is typically used in slight excess (~3%), there is no remaining “free BEM” after reaction. While HC solutions of standard BEM are viscous, BEM-B solutions are mobile and do not require viscosity reducers.

The ethyl group in BEM may be slightly more reactive than the *n*-butyl. In the reaction to produce BEM-B illustrated in Eq. 1.12, the ethyl/*n*-butyl proportion in the BEM starting material is typically about 49/51. In the resultant BEM-B, the proportion of ethyl/*n*-butyl is ~47/53. Some of this apparent disparity may be due to the difficulty of removing by-product *n*-butane (relative to ethane) from the solution of BEM-B, thereby inflating the amount of *n*-butane observed in the GC analysis of the hydrolysis gas.

1.6.3 Pricing and Selection Criteria for RMgR'

Commercially available dialkylmagnesium compounds used in the production of polyolefin catalysts are listed in Table 1.4. BEM (including BEM-2436 and BEM-4436) is the most important and hundreds of metric tons are supplied annually, primarily to producers of LLDPE worldwide.

Since there are only minor differences in reactivity of alkyl groups in RMgR', selection hinges largely on cost. However, as in the discussion of TEAL and TIBAL pricing (see Section 1.4), it is important to consider the cost of *contained* magnesium rather than the cost per pound of RMgR'.

TABLE 1.4 Commercially Available Magnesium Alkyl Compounds

Product	Formula	wt % Mg ^a	CAS No. ^b
Di- <i>n</i> -butylmagnesium ^c	(<i>n</i> -C ₄ H ₉) ₂ Mg	17.8	1191-47-5
<i>n</i> -Butyl(ethyl)magnesium ^d	<i>n</i> -C ₄ H ₉ MgC ₂ H ₅	22.0	62202-86-2
<i>n</i> -Butyl(ethyl)magnesium <i>n</i> -butoxide ^e	<i>n</i> -C ₄ H ₉ (C ₂ H ₅)Mg ₂ (O- <i>n</i> -C ₄ H ₉) ₂	17.3	
<i>n</i> -Butyl(<i>n</i> -octyl)magnesium ^f	(<i>n</i> -C ₄ H ₉) _{1.5} Mg(<i>n</i> -C ₈ H ₁₇) _{0.5}	14.8	94279-45-5
<i>n</i> -Butyl(<i>sec</i> -butyl)magnesium ^g	<i>n</i> -C ₄ H ₉ Mg- <i>sec</i> -C ₄ H ₉	17.9	39881-32-8

^aTheoretical.

^bChemical Abstracts Service registry no.

^cDNBM, available only as a complex with triethylaluminum, Mg/Al in the complex from 6 to 9.

^dBEM, also available as modified versions called BEM-2436 and BEM 4436, obtained by adding 0.5 and 1.0 mol % BHT (2,6-di-*t*-butyl-4-methylphenol) to the standard.

^eBEM-B, considered a commercial in 2003, now a developmental product.

^fBOM. The *n*-butyl-to-octyl ratio is typically 2.5–3.0, theoretical Mg percent calculated for *n*-butyl/*n*-octyl ratio = 3.

^gDBM. The *n*-butyl/*sec*-butyl ratio is typically 1.3–1.5.

For illustration, assume that separate customers use 100,000 pounds per year of the three major RMgR' products with the following prices:

- Customer A uses BEM at \$25/lb supplied as a solution typically containing 3.31% Mg.
- Customer B uses BOM at \$20/lb supplied as a solution typically containing 2.93% Mg.
- Customer C uses DBM at \$30/lb supplied as a solution typically containing 2.64% Mg.

Using the theoretical amount of magnesium (see Table 1.4) in each product, the annual cost of each RMgR' may be calculated as follows:

- Customer A's annual cost for BEM = $\$25/\text{lb} \times 100,000 \text{ lb} \times (0.0331/0.220)$
= ~\$376,000.
- Customer B's annual cost for BOM = $\$20/\text{lb} \times 100,000 \text{ lb} \times (0.0293/0.146)$
= ~\$401,000.
- Customer C's annual cost for DBM = $\$30/\text{lb} \times 100,000 \text{ lb} \times (0.0264/0.176)$
= ~\$450,000.

Even though the BEM price is intermediate on the basis of \$/lb of RMgR', its total cost is lowest because it contains higher magnesium content than BOM and DBM. Using the prices above but converting from dollars per pound of RMgR' to dollars per pound of contained magnesium, the adjusted prices are:

- BEM: \$114/lb of magnesium.
- BOM: \$137/lb of magnesium.
- DBM: \$170/lb of magnesium.

1.7 ORGANOBORON COMPOUNDS

Though produced in substantially smaller quantities than aluminum and magnesium alkyls, two types of organoboron compounds are used in industrial polyolefin catalyst systems. Both are σ -bonded organometallics. Triethylborane (TEB) and arylboranes (including the closely related arylborates) are the most important, though used in different ways. TEB is used in third-generation silica-supported chromium ("Phillips") catalysts.¹³ Arylboranes and arylborates are used as cocatalysts for SSC. Principal commercially available organoboron compounds are listed in Table 1.5, though not all are used in polyolefin catalyst systems.

Like TEAL, TEB is a clear, colorless liquid that ignites upon contact with air. Unlike TEAL, TEB is monomeric and unreactive with water. TEB burns

TABLE 1.5 Commercially Available Organoboron Compounds

Name	Formula	Formula Weight	CAS No. ^a	Boiling Point (°C at mm Hg)	Stability	Remark
Triethylborane	(C ₂ H ₅) ₃ B	97.99	97-94-9	95 at 760	Excellent	Used in third-generation Phillips catalysts
Tri- <i>n</i> -butylborane	(n-C ₄ H ₉) ₃ B	182.15	122-56-5	170 at 222	Excellent	Not used in polyolefin technologies
Diethylborane methoxide	(C ₂ H ₅) ₂ OCH ₃	99.96	7397-46-8	88-89 at 760	Excellent	Not used in polyolefin technologies
Diethylborane isopropoxide	(C ₂ H ₅) ₂ OCH(CH ₃) ₂	128.02	74953-03-0	115-117 at 760	Excellent	Not used in polyolefin technologies
Tris(pentafluorophenyl)borane	(C ₆ F ₅) ₃ B	512.0	1109-15-5		Good	Melting point 126–131 °C
Lithium tetrakis(pentafluorophenyl) borate	Li ⁺ (C ₆ F ₅) ₄ B ⁻	685.9			Poor	Used as cocatalyst for SSC ^b
Trityl tetrakis(pentafluorophenyl) borate	Ph ₃ C ⁺ (C ₆ F ₅) ₄ B ⁻	922.1			Poor	Used as cocatalyst for SSC
<i>N,N</i> -Dimethylanilinium tetrakis(pentafluorophenyl) borate	PhNH(CH ₃) ₂ ⁺ (C ₆ F ₅) ₄ B ⁻	801.1	118612-00-3		Poor	Used as cocatalyst for SSC

^aChemical Abstracts Services registry numbers.

^bSSC = single site catalysts.

with a green flame. Though TEB decomposes slowly (to R_2BH and RBH_2 and ethylene) above $\sim 100^\circ C$, DSC tests have shown that TEB does not undergo *hazardous* exothermic decomposition at least up to $\sim 200^\circ C$. When stored properly (under nitrogen and away from heat), TEB is indefinitely storage stable.

TEB may be manufactured by reaction of TEAL with borate esters or by direct hydroboration of ethylene.⁴⁹ TEB has been commercially available since the 1960s but only became important as an adjuvant for Phillips catalysts in the mid-1980s.¹³ TEB broadens molecular weight distribution by increasing the low-molecular-weight fractions of polyethylene. This suggests that TEB somehow facilitates chain transfer for supported chromium catalysts.

Arylboranes are conveniently prepared by reaction of the corresponding Grignard reagent with BF_3 /etherate as shown in Figure 1.6 for tris (pentafluorophenyl)borane (“FAB”). FAB may be used to produce “ate complexes”⁵⁰ that are even stronger Lewis acids. FAB and ate complexes have been offered commercially since the mid-1990s and are used as cocatalysts for SSC in place of (or in combination with) methylaluminumoxanes. Though a variety of fluorinated boranes and borates have been synthesized and used as cocatalysts for SSC,^{51b} the most widely available (beyond FAB) are the products of Eqs 1.13–1.15:

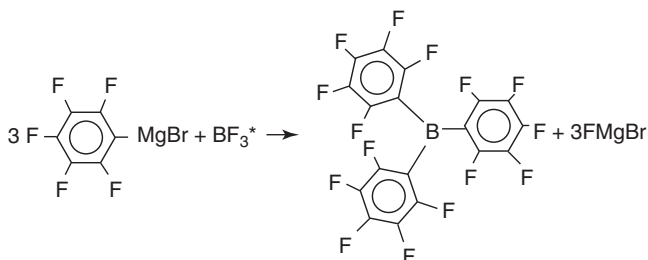
Lithium tetrakis(pentafluorophenyl)borate (LTB):



Trityl tetrakis(pentafluorophenyl)borate (TTB):



N,N-Dimethylanilium tetrakis(pentafluorophenyl)borate (NTB):



*Added as BF_3 -etherate

Figure 1.6 Synthesis of tris(pentafluorophenyl)borane (FAB).

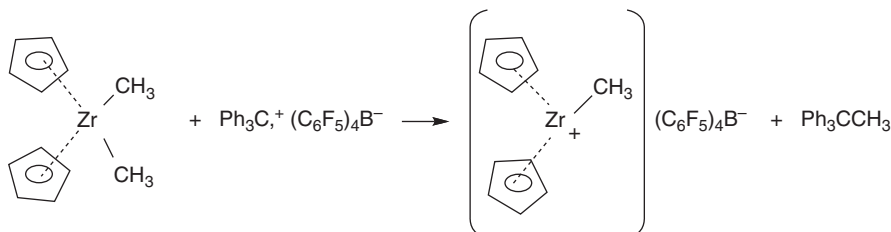


Figure 1.7 Activation of metallocene by tritylterakis(pentafluorophenyl)borate (TTB).

Arylboranes are typically white crystalline solids, essentially insoluble in aliphatic HC and sparingly soluble in aromatic solvents. They are virtually unreactive with air and water. The borates from Eqs 1.13–1.15 exhibit poor thermal stability and are not storage stable.⁵²

FAB, LTB, TTB, and NTB are strongly Lewis acidic and are capable of abstracting a ligand from metallocenes to generate cations (thought to be active centers for polymerization by SSC) as illustrated in Figure 1.7 with TTB and dimethylzirconocene. Further, the anionic counterions are weakly coordinated to the cationic SSC. (Weak coordination by the anion is thought to be essential for the cationic SSC to polymerize olefins.) The main advantage of arylboranes and borates is that they can be used in stoichiometric amounts, unlike aluminoxanes, which must be used in huge excess.

1.8 ORGANOZINC COMPOUNDS

Organozinc compounds were used widely in organic synthesis until displaced early in the twentieth century by the more versatile, more reactive Grignard reagent.⁵³ Diethylzinc (DEZ) is the only organozinc compound with a significant role in polyolefins. DEZ [Chemical Abstract Service (CAS) registry number 557-20-0] is among the earliest organometallic compounds synthesized. Sir Edward Frankland, an English chemist and pioneer in organometallic chemistry, synthesized DEZ from zinc metal and ethyl iodide in the mid-nineteenth century.^{54–56}

DEZ is a monomeric, linear molecule which exists as a clear colorless liquid at ambient T. DEZ is distillable (boiling point $\sim 117^\circ\text{C}$) and highly soluble in HC. It is pyrophoric and reacts vigorously with water, though reaction is not as difficult to control as R_3Al reactions with water. DEZ is unreactive with CO_2 .

Purity of commercially available DEZ is quite high. GC analysis of hydrolysis gas typically shows 99.8% ethane and observed zinc content is 52.7% (theory 52.9%).

Though stable when stored under an inert atmosphere at ambient temperature, DEZ is not stable at high temperatures. *Caution!* DEZ decomposes violently above 120°C . DEZ is also light sensitive, apparently undergoing homolytic scission of the C–Zn bond, ultimately leading to zinc metal, which causes turbidity. Since commercially available DEZ is supplied and stored

only in steel containers, light sensitivity is usually not a concern. DEZ has been produced commercially since the 1960s. It has been used as a chain transfer agent (CTA) in Ziegler–Natta catalyst systems in the past.^{57,58} Today, chain transfer in ZN catalyst systems is achieved chiefly by hydrogenolysis. However, significant quantities of DEZ are still employed in the polyolefin industry.

DEZ is used as a scavenger of poisons from process equipment for production of PE by supported chromium (Phillips) catalysts. Chromium catalysts are notorious for the difficulty of initiating polymerization after a “turn-around.” When process equipment is taken out of service for maintenance, the interior of reactors may be exposed to ambient air. This introduces oxygen and water, severe poisons for chromium catalysts. Even after inert gas (nitrogen) is reintroduced after maintenance activities are completed, trace amounts of poisons remain in the equipment and on interior surfaces. Exposure of process equipment to DEZ removes these poisons. When reactors are started up again, polymerization initiates more readily.

A unique industrial application of DEZ was recently disclosed.^{59,60} DEZ is being used in production of Dow’s INFUSE[®] block copolymers of ethylene and octene-1. A mixed SSC system involving hafnium and zirconium is used. The mechanism is called “chain shuttling.” It is believed to occur by transfer of polymeric chains between transition metals through the intermediacy of DEZ. This is consistent with the propensity of DEZ to function as a chain transfer agent.

ABBREVIATIONS

ARC	Accelerating rate calorimetry
BEM	<i>n</i> -Butylethylmagnesium
BEM-2436	BEM to which has been added 0.5 mol % BHT
BEM-4436	BEM to which has been added 1.0 mol % BHT
BEM-B	<i>n</i> -Butylethylmagnesium <i>n</i> -butoxide
BHT	Butylated hydroxy toluene (also called 2,6-di- <i>t</i> -butyl-4-methylphenol)
BOM	<i>n</i> -butyl- <i>n</i> -octylmagnesium
BOMAG	<i>n</i> -butyl- <i>n</i> -octylmagnesium
CAS	Chemical Abstract Services
Cp	Cyclopentadienyl (C ₅ H ₅) group; often a ligand in metallocenes or SSCs
DBM	Dibutylmagnesium
DEAC	Diethylaluminum chloride
DEAL-E	Diethylaluminum ethoxide
DEB-M	Diethylboron methoxide
DEB-IP	Diethylboron isopropoxide
DEZ	Diethylzinc

DIBAL-H	Diisobutylaluminum hydride
DNBM	Di- <i>n</i> -butylmagnesium
DSC	Differential scanning calorimetry
EAO	Ethylaluminumoxane
EASC	Ethylaluminum sesquichloride; Et ₃ Al ₂ Cl ₃
FAB	Tris(pentafluorophenyl)borane
GC	Gas chromatographic
HC	Hydrocarbon
IBAO	Isobutylaluminumoxane
IPRA	Isoprenylaluminum; reaction product of TIBAL or DIBAL-H with isoprene
ISOPRENYL	See IPRA
LLDPE	Linear low-density polyethylene
LTB	Lithium tetrakis(pentafluorophenyl)borate
MAO	Methylaluminumoxane
MMAO	Generic term used for modified methylaluminumoxanes; various types designated by suffix
MW	Molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance
NPL	Nonpyrophoric limit
NTB	<i>N,N</i> -Dimethylanilium tetrakis(pentafluorophenyl)borate
PE	Polyethylene
PMAO	Polymethylaluminumoxane
PMAO-IP	Polymethylaluminumoxane, improved performance
PP	Polypropylene
SSC	Single site catalyst
TBAO	<i>t</i> -Butylaluminumoxane
TEAL	Triethylaluminum
TEB	Triethylborane
THF	Tetrahydrofuran
TIBAL	Triisobutylaluminum
TMAL	Trimethylaluminum
TTB	Trityl tetrakis(pentafluorophenyl)borate
ZN	Ziegler–Natta catalysts

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