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Industrial Metal Alkyls and Their Use in Polyolefin Catalysts

Dennis B. Malpass

Serenity Consulting, Magnolia, TX, USA

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 to 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.

Most industrial polyethylene (PE) is obtained through use of transition metal catalysts (about 75–80% of the total; the balance is produced via free radical initiators). Essentially 100% of industrial polypropylene (PP) is produced with transition metal catalysts. Transition metals are integral to Ziegler–Natta (ZN), "Phillips," and single-site catalysts (SSC).

Though Phillips (chromium) catalysts do not require metal alkyls, metal alkyls are essential to the performance of industrial ZN catalysts and most SSC. (SSC that do not require cocatalysts have been reported [3], but only recently have been used industrially.) This handbook deals primarily with discussions of characteristics and performance of transition metal polymerization catalysts. However, this chapter will stress practical aspects of metal alkyls, particularly those used with industrial polyolefin catalysts. We will answer questions such as:

- What are the distinguishing properties of metal alkyls?
- Which are the commercially important metal alkyls?

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Handbook of Transition Metal Polymerization Catalysts, Second Edition. Edited by Ray Hoff.

- Which companies are the major manufacturers of 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 for metal alkyls will be briefly summarized, but 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. (Lithium alkyls are metal alkyls also produced in large quantities. However, because lithium alkyls are used primarily in anionic polymerization of dienes, they will not be discussed here.) Other organometallics are employed in the production of polyolefins but in much smaller quantities. These include organometallic compounds containing zinc and boron and a range of metallocenes. First-generation supported chromium catalysts (so-called 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 SSC 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 carbon and the metal. Hence, some non-metallocene SSC 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. Key functions are illustrated in simplified equations below.

- Metal alkyls in catalyst synthesis:
  - Reduction of the transition metal “precatalyst,” exemplified as follows with titanium tetrachloride and ethylaluminum sesquichloride (EASC[1]):

$$\begin{aligned}2TiCl_4 + 2(C_2H_5)_3Al_2Cl_3 &\rightarrow 2TiCl_3\downarrow + 4C_2H_5AlCl_2\\ &\quad + C_2H_4 + C_2H_6\end{aligned} \tag{1.1}$$

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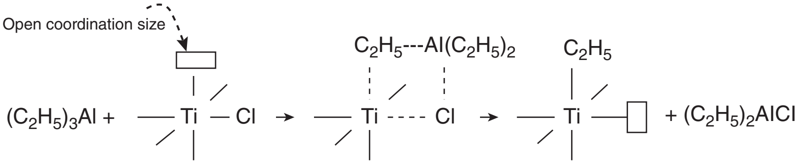
[1] $Et_3Al_2Cl_3$.

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

$$R_2Mg + 2HCl \rightarrow MgCl_2 \downarrow + 2RH \uparrow \tag{1.2}$$

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



(1.3)

Aluminum alkyls also serve the purpose of scavenging catalyst poisons (water, O_2, etc.). Poisons enter as ppm contaminants in materials commonly used in polyolefin processes such as monomer, comonomer, solvents, and chain transfer agents (CTA). Reaction of the aluminum alkyl with contaminants generates alkylaluminum derivatives that are less damaging to catalyst performance. For example, water reacts with TEAL to produce small amounts of ethylaluminoxane (EAO) as in Eq 1.4

$$2(C_2H_5)_3Al + H_2O \rightarrow (C_2H_5)_2Al - O - Al(C_2H_5)_2 + 2C_2H_6 \uparrow \tag{1.4}$$

Typically, aluminum alkyls are used in large excess in ZN catalyst systems. For example, Al/Ti ratios of 20–30 are common in industrial PE processes. Hence, there is ample TEAL to fulfill the roles discussed previously. Aluminum alkyls are also 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 too toxic (e.g., beryllium) 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 CTA.

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 alkyls" is meant to include any compound that contains a direct carbon–aluminum *σ*-bond and encompasses R_3Al, R_2AlCl, $R_3Al_2Cl_3$ (the so-called sesquichlorides), $RAlCl_2$, R_2AlOR', and R_2AlH. Among commercially important aluminum alkyls, R is typically a C_1 to C_4 alkyl, but compounds where R is an ethyl group (C_2H_5) are most important. Methylaluminoxanes (MAOs) are also aluminum alkyls and have become important in recent years as cocatalysts for SSC. However, MAOs exhibit significantly different properties than conventional aluminum alkyls and will be discussed separately.

Aluminum alkyls have been produced commercially since 1959 using technology originally licensed by Nobel laureate Karl Ziegler. Ziegler's revolutionary "direct process" was discovered in the early 1950s, not long after his extraordinary discoveries in olefin polymerization. Ziegler's direct process has become the most important method for industrial production of aluminum alkyls. Large-scale production of a trialkylaluminum compound via Ziegler chemistry was pioneered by Texas Alkyls, Inc., then a joint venture of Hercules and Stauffer Chemical, but now part of AkzoNobel, with production of triisobutylaluminum (TIBAL) in November of 1959. Ziegler's direct process, in effect, involves reaction of aluminum metal, olefin, and hydrogen to produce trialkylaluminum compounds. (This is necessarily an oversimplification of the direct process. Please see Refs. [4, 9–12] for more details.) Key reactions involved in Ziegler's direct process for TEAL are shown in the following equations:

$$\text{Hydrogenation: } 2(C_2H_5)_3Al + Al + 3/2H_2 \rightarrow 3(C_2H_5)_2AlH \tag{1.5}$$

$$\text{Addition: } 3C_2H_4 + 3(C_2H_5)_2AlH \rightarrow 3(C_2H_5)_3Al \tag{1.6}$$

Adding these equations gives the overall reaction for the direct process shown as follows:

$$\text{Overall reaction: } 3C_2H_4 + Al + 3/2H_2 \rightarrow (C_2H_5)_3Al \tag{1.7}$$

However, the aforementioned reaction does not take place in the absence of "preformed" TEAL.

Up until the early 1990s, large quantities of TEAL were also produced industrially by the so-called exchange process (also developed by Ziegler's group), which employed the reaction of TIBAL with ethylene:

$$(isoC_4H_9)_3Al + 3C_2H_4 \rightarrow (C_2H_5)_3Al + 3isoC_4H_8 \tag{1.8}$$

Isobutylene may be recycled. TEAL from the exchange process always contained small amounts of residual TIBAL, as well as somewhat larger amounts of tri-*n*-butylaluminum (TNBAL).

Both the direct and exchange processes may be run in either batch or continuous mode. Economics favor the continuous direct process. The direct product is also purer. The exchange process is no longer used for TEAL, but is still used for specialty products such as “isoprenylaluminum” (IPRA) (from reaction of TIBAL or diisobutylaluminum hydride (DIBAL-H) with isoprene [17]).

The Ziegler direct process technology is vastly superior to historical methods for synthesis of trialkylaluminum compounds. Ziegler’s technology has become the global standard for production of trialkylaluminum compounds and is used at several locations in North America, Europe, and Asia to manufacture many millions of pounds annually. Excellent conversions and yields are obtained with relatively little waste, because all raw materials are incorporated into the product. Aluminum alkyls are pyrophoric and violently reactive with water [4, 6, 12]. Considering these properties, it is remarkable that thousands of metric tons of aluminum alkyls are produced each year and have been supplied to the polyolefins industry worldwide for more than 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 physical and chemical properties of industrial aluminum alkyls are summarized as follows:

- *Appearance*: Commercially important aluminum alkyls are typically clear, colorless liquids at ambient temperatures and are miscible in all proportions with aliphatic hydrocarbons (HC). Large quantities of aluminum alkyls are supplied as solutions in HC, because solutions are *perceived* to be safer. Except for “isoprenylaluminum” (a low-volume specialty product used in manufacture of PE), common commercially available aluminum alkyls exhibit low viscosities
- *Reactivity with air and water*: Most ignite spontaneously when exposed to air and react explosively with water. (Please see the appendix for a discussion of pyrophoricity of metal alkyls.)
- *Purity*: Purity of aluminum alkyls used in manufacture of polyolefins varies. For example, TEAL, as supplied to the polyolefins industry, is typically about 95% pure owing to the presence of relatively large amounts of TNBAL. However, purities of trimethylaluminum (TMAL) and diethylaluminum chloride (DEAC) are quite high (~99%).

R_3Al compounds commonly contain small amounts of other trialkylaluminum compounds (R'_3Al, $R' \neq R$). 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 typically low (<0.5% by wt). An exception is TEAL where, as previously noted, TNBAL content (from the aforementioned reaction) is typically ~5%.

Table 1.1 Commercially available aluminum alkyls.

Product	Acronym	Formula	CAS number	Theoretical wt% Al
Trimethylaluminum	TMAL	$(CH_3)_3Al$	75-24-1	37.4
Dimethylaluminum chloride	DMAC	$(CH_3)_2AlCl$	118-58-3	29.2
Methylaluminum sesquichloride	MASC	$(CH_3)_3Al_2Cl_3$	12542-85-7	26.3
Triethylaluminum	TEAL	$(C_2H_5)_3Al$	97-93-8	23.6
Diethylaluminum chloride	DEAC	$(C_2H_5)_2AlCl$	96-10-6	22.4
Diethylaluminum iodide	DEAI	$(C_2H_5)_2AlI$	2040-00-8	12.7
Ethylaluminum sesquichloride	EASC	$(C_2H_5)_3Al_2Cl_3$	12075-68-2	21.8
Ethylaluminum dichloride	EADC	$C_2H_5AlCl_2$	563-43-9	21.3
Isobutylaluminum dichloride	MONIBAC[a]	$i\text{-}C_4H_9AlCl_2$	1888-87-5	17.4
Tri-*n*-butylaluminum	TNBAL	$(C_4H_9)_3Al$	1116-70-7	13.6
Triisobutylaluminum	TIBAL	$(i\text{-}C_4H_9)_3Al$	100-99-2	13.6
Diisobutylaluminum hydride	DIBAL-H	$(i\text{-}C_4H_9)_2AlH$	1191-15-7	19.0
Tri-*n*-hexylaluminum	TNHAL	$(C_6H_{13})_3Al$	1116-73-0	9.6
Tri-*n*-octylaluminum	TNOAL	$(C_8H_{17})_3Al$	1070-00-4	7.4
Di-*n*-octylaluminum iodide	DNOAI	$(C_8H_{17})_2AlI$	7585-14-0	7.1
"Isoprenylaluminum"	IPRA	na	70024-64-5	na
Diethylaluminum ethoxide	DEAL-E	$(C_2H_5)_2AlOC_2H_5$	1586-92-1	20.7
Ethylpropoxyaluminum chloride	EPAC	$(C_2H_5)(C_3H_7O)AlCl$		17.9
Diisobutylaluminum butylated oxytoluene	DIBAL-BOT	$(i\text{-}C_4H_9)_2AlO[C_6H_2(CH_3)(t\text{-}C_4H_9)_2]$	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."

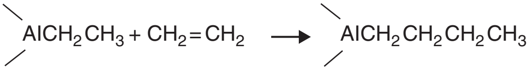


Figure 1.1 Insertion of ethylene into an ethyl-aluminum bond to form an n-butylaluminum group.

Total assays are not routinely conducted on commercially available aluminum alkyls. Since most impurities are also organometallics, the typical total organometallic assay of commercially available metal alkyls will be ≥98.5%. 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 C_6–C_8 aliphatic HC) used to wash reactors and process lines. For a few products (TEAL and DEAC, to name a couple), assays will approach 100% because the product is routinely purified by distillation.

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

a) *Hydride content*: Most commercially important R_3Al compounds contain small amounts of R_2AlH (R = ethyl or higher; TMAL does not typically contain hydride). Hydride content is expressed as AlH_3 by tacit convention among major suppliers and ranges from about 0.02% (wt) in TEAL to about 0.5% in TIBAL. In the vast majority of ZN catalyst systems, hydride content and the presence of small amounts of other trialkylaluminum compounds (R'_3Al, discussed earlier in this section) are not damaging to performance. However, for certain PP catalysts that employ alkoxysilanes as external donors, hydride can cause a reduction in isotactic content and lowered catalyst activity [18]. 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 [19].
b) *Compatibility with organic solvents*: Aluminum alkyls are compatible with commonly available HC solvents such as heptane and toluene. However, aluminum alkyls are highly reactive with many of the other typical organic solvents. Indeed, reaction with certain halogenated HC (e.g., CCl_4 and $CHCl_3$) may be explosive after a quiescent period [20]. Organic compounds with labile 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 react exothermically to form coordination complexes.

c) *Reactivity with CO_2 and CO*: R_3Al are reactive with CO_2 [21]. In fact, reaction of TMAL with CO_2 has been used to produce MAO cocatalysts for SSC [22–24]. The R_3Al/CO_2 reaction is easily controlled and has been used to passivate aluminum alkyl waste streams [25]. However, R_3Al are unreactive with CO at moderate temperatures and pressures. Aluminum alkyls containing halogen or oxygen (DEAC, diethylaluminum ethoxide (DEAL-E), etc.) are not reactive with CO_2.

d) *Distillation*: Lower molecular weight aluminum alkyls (TMAL up to TIBAL) are distillable. TNBAL may also be distilled but requires wiped film evaporators and reduced pressure. Higher homologues (C_6 or higher) are not distillable in industrial process equipment and are usually purified by filtration.

e) *Association*: 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 bonding [26] (also called "electron-deficient" bonding [27]) 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 *T*, rapid alkyl exchange occurs and methyls are indistinguishable by NMR.

Halogenated and oxygenated aluminum alkyls are even more strongly associated, most often as dimers. Ligands containing heteroatoms 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).

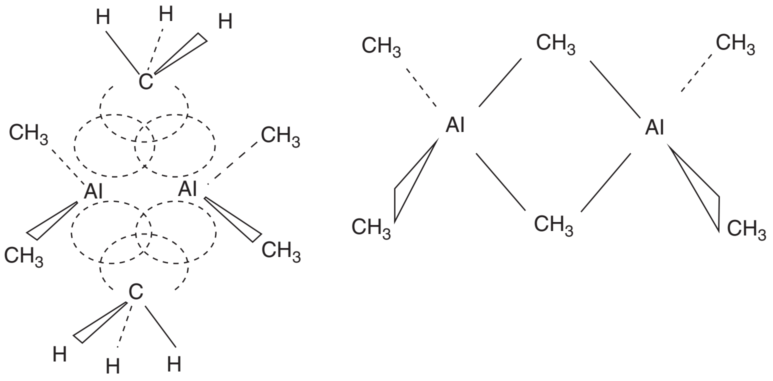


Figure 1.2 Schematic representations of electron-deficient bonding in TMAL dimer. Figure on left depicts partial overlap of sp^3 orbitals from bridging methyl groups with lobes of tetracoordinate sp^3 aluminums. Figure on right shows more common way of depicting electron-deficient bonding in metal alkyls. *Source:* Adapted from Malpass and Band [28].

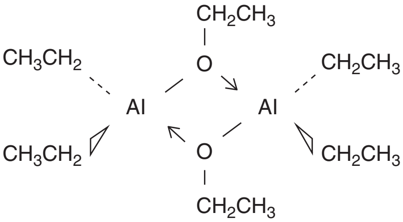


Figure 1.3 Dimer structure of diethylaluminum ethoxide.

Table 1.2 Thermal decomposition data of selected aluminum alkyl compounds.

Product	Acronym	*T*°C-onset[a]	% decomposed (3 h at 180°C)
Triethylaluminum	TEAL	120	64
Tri-*n*-butylaluminum	TNBAL	100	87
Triisobutylaluminum	TIBAL	50	92
Tri-*n*-octylaluminum	TNOAL	60	90
Diethylaluminum chloride	DEAC	174	2
Diisobutylaluminum chloride	DNBAC	165	4
Diethylaluminum ethoxide	DEAL-E	192	0

Source: Adapted from Sakharovskaya et al. [29].

a) Estimated temperature at which decomposition is first observed in inert atmosphere.

f) *Storage stability*: 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 alkyls manufacturing site formerly known as Texas Alkyls, Inc. (now AkzoNobel), 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 acquired a faint amber tint after 10 years. Within analytical variance, aluminum and chloride contents and the hydrolysis gas composition were essentially unchanged.

g) *Thermal stability*: Aluminum alkyls demonstrate moderate to excellent thermal stability, depending on ligands. Thermal stability is especially important for aluminum alkyls used in solution processes for PE since these often operate at >190°C. Table 1.2 provides thermal stability data on selected aluminum alkyls. Lower R_3Al 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*

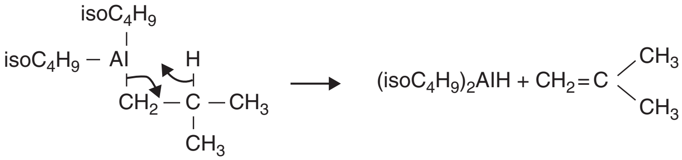


Figure 1.4 Decomposition of triisobutylaluminum.

> *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* [30]. *If confined, an explosion could result.*

Thermal decomposition of aluminum alkyls typically occurs by β-hydride elimination, exemplified in the following with TIBAL (Figure 1.4).

Aluminum alkyls that contain ligands with halogen or oxygen are more stable thermally than the analogous R_3Al compounds. Thus, while TEAL begins to decompose at ~120°C, DEAC is stable up to 174°C and DEAL-E up to 192°C.

1.4 Manufacturers of Aluminum Alkyls

Today, major manufacturers of aluminum alkyls are as follows:

- AkzoNobel (formerly Texas Alkyls, Inc.)
- Albemarle (formerly Ethyl Corp.)
- Chemtura (formerly Crompton, Witco, and Schering)
- Gulbrandsen

These companies supply aluminum alkyls globally and also produce a variety of other organometallics, including metal alkyls of boron, magnesium, and zinc. AkzoNobel and Albemarle have their principal aluminum alkyl manufacturing facilities in the United States. Chemtura's main site is in Germany. Gulbrandsen started up a world-scale site in 2005 near Vadodara, India, where the company manufactures TEAL and a complementary range of other aluminum alkyls. It also produces diethylzinc (DEZ).

AkzoNobel, Albemarle, and Chemtura have joint ventures and satellite plants in other parts of the world. Some have manufacturing facilities; others have only repackaging and solvent blending capabilities. AkzoNobel started up a major manufacturing site for metal alkyls in 1996 in Rotterdam, the Netherlands.

A few regional suppliers, such as Tosoh Finechem Corporation and Nippon Aluminum Alkyls in Japan, also manufacture aluminum alkyls but have lower capacities and a narrower product range. A joint venture between Albemarle and SABIC (announced in 2009 and started up in 2013 called Saudi Organometallic Chemicals Company [31]) has a capacity of about 6000 tons/year of TEAL.

Sasol [32] announced construction of a plant in 2010 to manufacture TEAL (6000 tons/year capacity) in Brunsbüttel, Germany. It did not disclose capacities for metal alkyls other than TEAL. Its plant started up in 2012.

Petronad Asia (a subsidiary of Kimyagaran Emrooz, an Iranian chemical company) was scheduled to begin production of TEAL in Mahshar in 2013. No capacity figures were provided, nor was it disclosed whether other aluminum alkyls would be manufactured in Mahshar.

Sigma-Aldrich is a US company headquartered in St. Louis, MO, and is an excellent supplier of small to medium quantities of organometallic compounds. It provides a wide range of air- and moisture-sensitive organometallic compounds in a variety of innovative packaging. The Sure/Seal package is especially attractive to academia because it permits convenient and safe extraction via syringe techniques of small quantities of these highly reactive materials for laboratory use. However, Aldrich has limited large-scale production capabilities. More information may be obtained at www.sigma-aldrich.com (see especially Technical Bulletin AL-134).

1.5 Pricing and Selection Criteria for Aluminum Alkyls

In the early history of industrial ZN catalysts, 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. Throughout the 1980s, TEAL grew in importance and eventually became the largest-volume aluminum alkyl used by manufacturers of polyolefins. Today, many millions of pounds of TEAL are sold annually into the global polyolefins industry. Though DEAC and EASC have been displaced by TEAL in the polyolefins industry, they continue to be produced in large quantities (thousands of tons per year).

As usual in commercial operations, cost is the key factor in selecting an aluminum alkyl. However, prices vary by region and because of other considerations (such as volume discounts). Depending upon product and geographical market, prices for *major* aluminum alkyls currently range from about \$2 to about \$8/lb, Prices are higher for “specialty” products such as TMAL, DEAI, DEZ, and IPRA. Specialty products often require costly multistep processes or expensive raw materials, for example, elemental iodine.

Though the price of DEAC is today slightly lower than that of TEAL, it is not typically used with supported catalysts because it does not match the performance of TEAL. For example, DEAC may cause lower catalyst activity or reduced stereoregularity in polypropylene. It will also leave low levels of chloride-containing residues in the polymer that can corrode equipment or degrade the polymer.

TIBAL is a commercially available R_3Al that performs as well as TEAL with many ZN catalysts. Historically, TIBAL was *less* expensive than TEAL on a $/lb basis. Even though TEAL was more expensive than TIBAL in years past, TEAL was preferred over TIBAL. Why? The reason is that if other factors are equal, polyolefin manufacturers buy on the basis of *contained* aluminum. On a molar basis, TEAL contains about 70% more aluminum than TIBAL. Consequently, even if TIBAL were comparable with TEAL on a $/lb basis, it could actually cost *more* than TEAL based on aluminum content.

The TEAL–TIBAL pricing dichotomy can be illustrated as follows: Assume that a world-scale linear low-density polyethylene (LLDPE) manufacturing facility uses 200 000 lb/year of TEAL and that TIBAL and TEAL perform equally (at the same Al/Ti) in the process. Assume further that the price of TEAL is $4/lb and TIBAL costs $3/lb. This amounts to an annual TEAL cost of $800 000. The amount of contained aluminum in 200 000 lb of TEAL (typical Al content of 23.2%) is 46 400 lb. However, the amount of TIBAL (typical Al content of 13.6%) needed to obtain 46 400 lb of aluminum is about 341 000 lb for an annual cost of $1 023 000. Hence in this illustration, the annual cost advantage of TEAL relative to TIBAL amounts to $223 000, even though TIBAL costs less on a $/lb basis. For this illustration, TIBAL would have to be priced at $2.34/lb for costs to be equivalent. Though this illustration was based on hypothetical prices, similar calculations should be made in today’s market to ensure that the most cost-effective aluminum alkyl is being selected.

As suggested previously, 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 LLDPE process was shown to produce LLDPE with lower extractables and improved film tear strength [33]. Another example is that the use of IPRA as cocatalyst can result in ultrahigh molecular weight PE with broader molecular weight distribution (MWD) [17, 34]. (IPRA is a complex composition [35] 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 superseding the increased cost of cocatalyst.

1.6 Methylaluminoxanes

1.6.1 Conventional Methylaluminoxane

Conventional MAO is produced by partial hydrolysis of TMAL in toluene. Reaction must be closely controlled. 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. Unfortunately, even with these precautions, explosions and serious injuries have been reported during preparations. In most cases, polyolefin producers leave synthesis of MAO to aluminum alkyl manufacturers. By doing so, they obviate handling the highly pyrophoric TMAL and struggling to control its reaction with water. Moreover, polyolefin producers avoid having to deal with the untoward properties of MAO solutions, such as poor storage stability at ambient temperatures. A simplified overall reaction is given in Eq 1.9:

$$x\left(\mathrm{CH_3}\right)_3\mathrm{Al} + x\mathrm{H_2O} \rightarrow\sim \left(\mathrm{CH_3AlO}\right)_x \sim + 2x\mathrm{CH_4}\uparrow \tag{1.9}$$

Yields are usually low (<60%). The toluene-soluble product is called MAO or, less commonly, polymethylaluminoxane (PMAO). MAO has been offered commercially since the late 1980s. Recently, improved industrial processes with much higher yields have been developed [36].

MAO was reported to be an excellent cocatalyst for metallocene SSC by Kaminsky, Sinn, and coworkers [37] in the late 1970s. Though MAO has been the subject of intense study since then, its composition remains poorly understood. Key properties of commercially available MAO are summarized as follows:

- 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 HC, but has excellent solubility in aromatic HC. 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.

  If one assumes the following:
  - Commercially available MAO contains only MAO and “free TMAL.”
  - Commercially available MAO contains 43.5% Al.
  - Theoretical Al content in MAO is 46.5%.
  - TMAL contains 37.4% Al.

With these assumptions, the composition of commercially available MAO may be calculated to be about 74% MAO and 26% TMAL. This is in reasonable agreement with the “free TMAL” content found by various analytical methods in commercially available MAO.

- Differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) studies have shown MAO to be thermally stable at least up to about 220°C [30]. 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" [38–40].
- Gas chromatographic (GC) analysis of hydrolysis gas from MAO typically shows ≥99% methane. The balance is mostly ethane.
- Proton NMR analysis suggests that the CH_3/Al in MAO is about 1.4 [41]. Upon hydrolysis, measurement of the moles of methane generated per Al atom will always show higher than theory. The observed methane/Al is 1.6–1.8. Elevated methane to Al is attributable to "free TMAL" commonly present in MAO.
- MAO is not distillable. However, if MAO is subjected to vacuum distillation conditions, some of the so-called free TMAL will distill [22, 41].
- Storage stability of MAO solutions is poor [22–24, 41]. 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. Stability of commercially available MAO solutions has been improved recently by using optimized processes and by producing MAO solutions at lower concentrations [36].
- Published data on MAO isolated from toluene have shown a wide range of molecular weights (MWs) (300–3000 amu,[2] 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 [41]. Beard reported "corrected" cryoscopic MWs of ~850, suggesting x in Eq 1.9 to be ~15.

Perhaps the most important drawback of MAO is its cost, which is substantially higher than conventional aluminum alkyls. Despite its high cost and untoward properties, MAO remains the most widely used cocatalyst for SSC.

1.6.2 Modified Methylaluminoxanes

Modified methylaluminoxanes (MMAOs[3]) have been offered commercially since the early 1990s. MMAO [42] is a generic term encompassing all products wherein some of the methyl groups are replaced by other alkyl groups, usually

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[2] Atomic mass units, also known as Daltons (Da).

[3] Generic term used by AN for modified methylaluminoxanes; various types designated by suffix.

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 [42]. 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 in Eqs 1.10–1.12:

$$2R'_3Al + H_2O \rightarrow R'_2AlOAlR'_2 + 2R'H \tag{1.10}$$

$$(CH_3)_3Al + R'_2AlOAlR'_2 \rightarrow (CH_3)_3Al - O - (AlR'_2)_2 \tag{1.11}$$

$$(CH_3)_3Al - O - (AlR'_2)_2 + H_2O \rightarrow \sim(RAlO)\sim + RH \tag{1.12}$$

(where R is 65–95% methyl and the balance R′).

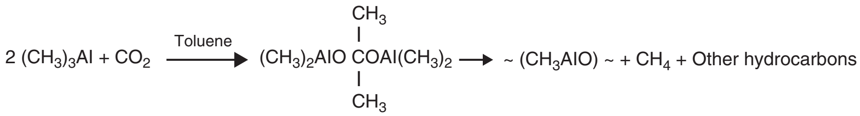
There are several versions of MMAO (differentiated by a suffix, e.g., “MMAO-3A”), each with different composition and properties (see Table 1.4). MMAO-7 is produced by a nonhydrolytic method (described in the succeeding text). MMAO-12 contains ~95% methyl groups and is the MMAO that most closely approximates MAO.

Relative to conventional MAO, MMAOs exhibit much improved storage stability, and some are highly soluble in aliphatic HC. (Manufacturers of PE prefer to avoid toluene because of toxicity concerns, especially if resins are destined for food contact.) Most importantly, because yields are higher, MMAO formulations are typically 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, MMAO should be considered niche cocatalysts for SSC.

1.6.3 Nonhydrolytic Methylaluminoxanes

A nonhydrolytic method has been reported [22–24] for production of MAOs suitable as cocatalysts for SSC. 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 CO_2 with TMAL to form an intermediate. Subsequent pyrolysis produces PMAO-IP. The detailed chemistry is complex and involves evolution of methane and other HC, including products resulting from Friedel–Crafts reactions with toluene. A simplified equation is shown as follows (Eq 1.13):



$$2\,(CH_3)_3Al + CO_2 \xrightarrow{\text{Toluene}} (CH_3)_2AlO\,\overset{CH_3}{\underset{CH_3}{C}}OAl(CH_3)_2 \longrightarrow \sim(CH_3AlO)\sim + CH_4 + \text{Other hydrocarbons}$$

(1.13)

Reactant proportions are chosen such that the O/Al in PMAO-IP is ~0.8 [23], as it is in conventional MAO [41]. PMAO-IP contains much lower "free TMAL" than hydrolytic MAO, which may explain the higher activity with selected SSC. It appears to be especially effective in solution processes for PE. However, performance of PMAO-IP does not extend across the entire range of SSC, and it cannot be considered a "drop-in" replacement for conventional MAO.

1.6.4 Other Alkylaluminoxanes

Other alkylaluminoxanes are also available, more easily produced, and less costly than MAO. EAO (see Eq 1.4) and isobutylaluminoxane (IBAO) have been used industrially since 1970 in catalyst systems for polymerization and copolymerizations of epichlorohydrin to produce elastomers [43]. However, EAO and IBAO perform poorly as cocatalysts for SSC. Preparation and properties of alkylaluminoxanes have been extensively reviewed [40, 44, 45].

Alkylaluminoxanes have been shown to exist as highly associated oligomeric, cage, or cluster structures [46, 47]. Barron et al. prepared *t*-butylaluminoxane (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 coworkers proposed a nonameric cluster structure for MAO wherein aluminum is exclusively tetracoordinate [48]. IBAO, a commercially available alkylaluminoxane isomeric with TBAO, has been shown to have a cryoscopic MW of ~950 [49], in agreement with nonameric association.

1.6.5 Why Are MAOs So Costly?

All commercially available MAOs employ TMAL as the starting material. Because TMAL must be manufactured by less efficient processes [30], 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

Table 1.3 Commercially available alkylaluminoxane compounds.

Product	Acronym	Approximate formula	Wt% Al[a]
Methylaluminoxane	MAO	$-((CH_3)AlO)_x-$	46.5
Polymethylaluminoxane-improved performance	PMAO-IP	$-((CH_3)AlO)_x-$	46.5
Modified methylaluminoxane, type 3A	MMAO-3A	$-((CH_3)_{0.7}(i\text{-}C_4H_9)_{0.3}AlO)_x-$	38.2
Modified methylaluminoxane, type 7	MMAO-7	$-((CH_3)_{0.86}(n\text{-}C_8H_{17})_{0.14}AlO)_x-$	37.6
Modified methylaluminoxane, type 12	MMAO-12	$-((CH_3)_{0.95}(n\text{-}C_8H_{17})_{0.05}AlO)_x-$	42.9
Isobutylaluminoxane, type 65	IBAO-65	$-(i\text{-}C_4H_9)AlO_x-$	27.0
Bis(diisobutylaluminum)oxide	DIBAL-O	$(i\text{-}C_4H_9)_2AlOAl(i\text{-}C_4H_9)_2$	18.1

DIBAL-O, available only in hydrocarbon solution, O/Al ~0.50; IBAO-65, available only in hydrocarbon solution, O/Al ~0.65; MAO, also called PMAO, available only in toluene solution; MMAO-3A, available in heptane; MMAO-7, produced via nonhydrolytic process, available in Isopar E™; MMAO-12, available only in toluene; PMAO-IP; product by nonhydrolytic process, available only in toluene solution.

Notes: (i) 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. (ii) ™Isopar E is a trade name of Exxon Mobil Corporation for an aromatics-free hydrocarbon liquid mixture, boiling range 114–140°C. (iii) DIBAL-O is also known as tetraisobutyldialuminoxane (TIBAO). (iv) All products listed are not available from a single supplier.

remain very expensive relative to conventional aluminum alkyls. Commercially available alkylaluminoxanes are listed in Table 1.3.

1.6.6 Pricing and Selection Criteria of Methylaluminoxanes

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 either \$/wt of contained Al, \$/wt of the calculated amount of contained MAO, or \$/wt of solution. The following calculations 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 lb 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

$$5000\ \text{lb} \times 0.133 \times \$150/\text{lb of contained Al} = \$99750$$

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 follows:

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

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

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

If suppliers Y and Z were to price their MAO to be comparable with supplier X, their base prices would have to be $70/lb (instead of $100) of MAO and $20/lb (instead of $35) of MAO solution, respectively.

Ultimately, performance of the MAO in the specific customer application is the most important criterion for selection. A low price is of little value if performance is poor. Since polyolefin manufacturers use different SSC 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.

1.7 Magnesium Alkyls

1.7.1 Properties of Magnesium Alkyls

Impetus for using magnesium alkyls in ZN catalyst synthesis was provided by the discovery that magnesium salts, especially $MgCl_2$ [50], are excellent supports for ZN catalysts. "Magnesium alkyls" may be considered to encompass both Grignard reagents (organomagnesium halides, "RMgX") and dialkylmagnesium compounds (R_2Mg). The two are linked by the so-called "Schlenk" equilibrium (Eq 1.14):

$$2RMgX \leftrightarrows R_2Mg + MgX_2 \tag{1.14}$$

Grignard reagents are produced by reaction of an alkyl halide with magnesium metal in an ether, usually diethyl ether or tetrahydrofuran (THF). 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

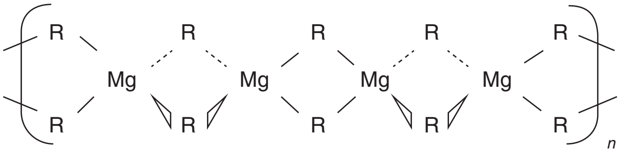


Figure 1.5 Dialkylmagnesium oligomer structure.

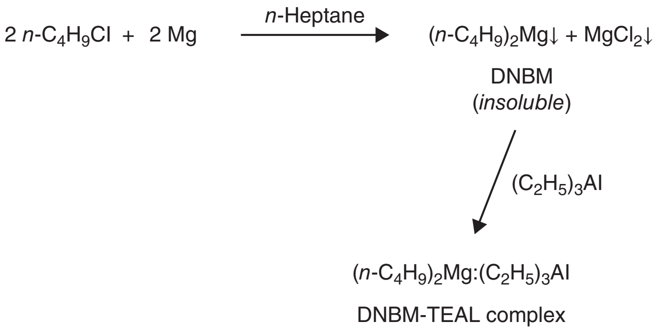
excellent reviews are available [10, 11]. A survey of processes for commercially available dialkylmagnesium compounds is also available [51].

Dialkylmagnesium compounds have been shown to be highly associated 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 [26], mentioned previously in the discussion of TMAL association. Because *n* is very large for simple R_2Mg ($R = CH_3$ to n-C_4H_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 in the laboratories of Texas Alkyls, Inc., later to become AkzoNobel. 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) [51]. Such reactions are exemplified in Eq 1.15 with TEAL:



$$2\ n\text{-}C_4H_9Cl + 2\ Mg \xrightarrow{n\text{-Heptane}} \underset{\substack{\text{DNBM}\\ (\textit{insoluble})}}{(n\text{-}C_4H_9)_2Mg\downarrow} + MgCl_2\downarrow \xrightarrow{(C_2H_5)_3Al} \underset{\substack{\text{DNBM-TEAL complex}\\ (\textit{soluble; Mg/Al}\sim 6\text{–}9)}}{(n\text{-}C_4H_9)_2Mg{:}(C_2H_5)_3Al} \quad (1.15)$$

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 processes [52] 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®)
- *n*-Butyl(*sec*-butyl)magnesium (also called “dibutylmagnesium” (DBM))

BEM was discovered in 1978 at Texas Alkyls [53] (now AkzoNobel) and has since become the largest-volume dialkylmagnesium compound. Since the early 1980s, BEM has been used worldwide in the production of catalysts for manufacture of PE. Simplistically, BEM may be viewed as a 1:1 complex between diethylmagnesium (DEM) and DNBM. However, it is important to remember that alkyl groups are rapidly exchanged by way of electron-deficient bonding mentioned previously (see also discussion of methyl group exchange in TMAL in Section 1.3.e). Like all lower R_2Mg compounds (where $R = C_1$ to *n*-C_4), DEM and DNBM are independently insoluble in HC. However, BEM is highly soluble in HC, though solutions are highly viscous.

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 pyrophoric solids.

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 1.15, *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 information on process chemistry).

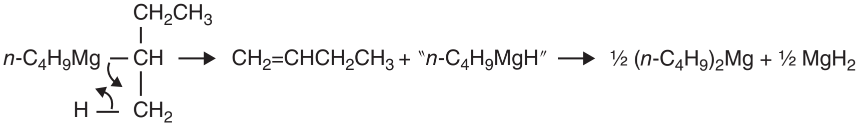
Though the nomenclature of RMgR′ might suggest near equal amounts of R and R′, that is true only for BEM. Yield of HC-soluble BEM is maximized when the ratio of *n*-butyl to ethyl is ~1.0 [53]. However, the ratio of *n*-butyl to *n*-octyl in BOM is 2.5–3.0, and the *n*-butyl to *sec*-butyl ratio in DBM 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 soluble in HC, but the solutions are very viscous. Consequently, a viscosity reducing agent must be added. A small quantity of TEAL (1–2 molar %, 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 1.15.

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 ~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 (daltons). As mentioned previously, BEM solutions are highly viscous. Even at relatively low concentrations (~15% by weight), solution viscosities are $>10^3$ 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 MgH_2 as in Eq 1.16:

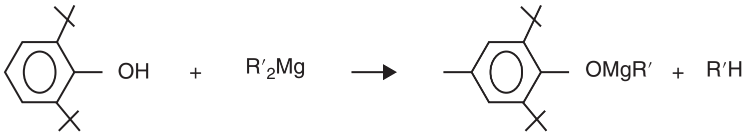


$$n\text{-}C_4H_9Mg-\underset{\substack{|\\ H-CH_2}}{\overset{\substack{CH_2CH_3\\ |}}{CH}} \longrightarrow CH_2{=}CHCH_2CH_3 + \text{“}n\text{-}C_4H_9MgH\text{”} \longrightarrow \tfrac{1}{2}\,(n\text{-}C_4H_9)_2Mg + \tfrac{1}{2}\,MgH_2 \quad (1.16)$$

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.

1.7.2 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[4]), with standard BEM, as in Eq 1.17:



(1.17)

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[4] Aka 2,6-di-*t*-butyl-4-methylphenol.

BHT is added in ~0.5 and 1.0% amounts (molar, relative to Mg), These formulations, known as BEM-2436 (BEM to which has been added 0.5 mol% BHT) and BEM-4436 (BEM to which has been added 1.0 mol% BHT), respectively, are used to produce catalysts primarily for the 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 1.17. 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 [54], its viscosity-lowering effect is slight compared with 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:

$$\begin{aligned} &R_2'Mg + n\text{-}C_4H_9OH \rightarrow R'MgO - n - C_4H_9 + R'H\uparrow \\ &(\textit{where } R' \textit{ is} \sim 50\%\ \textit{ethyl and} \ \sim 50\%\ \textit{n-butyl}) \end{aligned} \tag{1.18}$$

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 1.18, 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 the 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.

1.7.3 Pricing and Selection Criteria for RMgR′

Commercially available dialkylmagnesium compounds used in 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, 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-*n*-butylmagnesium[c]	$(n\text{-}C_4H_9)_2\,Mg$	17.8	1191-47-5
n-Butyl(ethyl)magnesium[d]	$n\text{-}C_4H_9MgC_2H_5$	22.0	62202-86-2
n-Butyl(ethyl)magnesium *n*-Butoxide[e]	$n\text{-}C_4H_9(C_2H_5)Mg_2(O\text{-}n\text{-}C_4H_9)_2$	17.3	
n-Butyl(*n*-octyl)magnesium[f]	$(n\text{-}C_4H_9)_{1.5}Mg(n\text{-}C_8H_{17})_{0.5}$	14.8	94279-45-5
n-Butyl(*sec*-butyl)magnesium[g]	$n\text{-}C_4H_9Mg\text{-}sec\text{-}C_4H_9$	17.9	39881-32-8

a) Theoretical.
b) Chemical Abstracts Service Registry No.
c) DNBM, available only as a complex with triethylaluminum, Mg/Al, in the complex from 6 to 9.
d) BEM, 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.
e) BEM-B, considered a commercial in 2003, now a developmental product.
f) BOM. The *n*-butyl to octyl ratio is typically 2.5–3.0, theoretical Mg percent calculated for *n*-butyl/*n*-octyl ratio = 3.
g) DBM. The *n*-butyl/*sec*-butyl ratio is typically 1.3–1.5. Note: The products may not all be available from a single supplier.

For illustration, assume that separate customers use 100 000 lb/year of the three major RMgR′ products with the following prices:

- Customer A uses BEM @$25/lb supplied as a solution typically containing 3.31% Mg.
- Customer B uses BOM @$20/lb supplied as a solution typically containing 2.93% Mg.
- Customer C uses DBM @$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/lb × 100 000 lb × (0.0331/0.220) = ~$376 000
- Customer B’s annual cost for BOM = $20/lb × 100 000 lb × (0.0293/0.146) = ~$401 000
- Customer C’s annual cost for DBM = $30/lb × 100 000 lb × (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 aforementioned prices but converting from \$/lb of RMgR′ to \$/lb of contained magnesium, the adjusted prices are:

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

1.8 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.

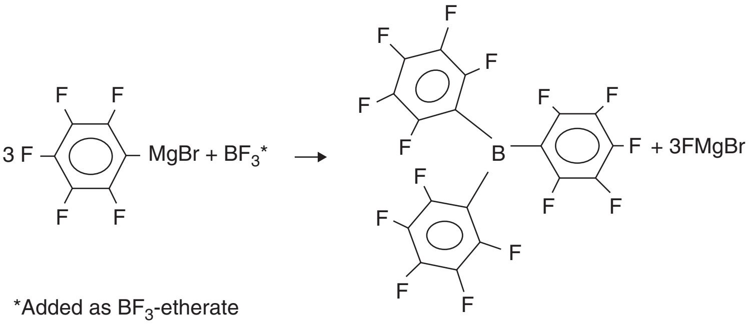
Like TEAL, TEB is a clear, colorless liquid that ignites upon contact with air. Unlike TEAL, TEB is monomeric and unreactive with water. TEB burns with a green flame. Though TEB decomposes slowly (to R_2BH and RBH_2 and

Table 1.5 Commercially available organoboron compounds.

Acronym or abbreviation	Formula	Formula weight	CAS no.[a]	Boiling point (°C at mm Hg)	Stability
TEB	$(C_2H_5)_3B$	97.99	97-94-9	95 at 760	Good
TNBB	$(n\text{-}C_4H_9)_3B$	182.15	122-56-5	170 at 222	Good
DEB-M	$(C_2H_5)_2OCH_3$	99.96	7397-46-8	88–89 at 760	Good
DEB-IP	$(C_2H_5)_2OCH(CH_3)_2$	128.02	74953-03-0	115–117 at 760	Good
FAB	$(C_6F_5)_3B$	512.0	1109-15-5		Good
LTB	$Li^+ (C_6F_5)_4B$	685.9			Poor
TTB	$Ph_3C^+(C_6F_5)_4B$-		922.1		Poor
NTB	$PhNH(CH_3)_2{}^+(C_6F_5)B^-$	801.1	118612-00-3		Poor

DEB-IP, diethylboron isopropoxide (not used in polyolefin technologies); DEB-M, diethylboron methoxide (not used in polyolefin technologies); FAB, mp = 126°C cocatalyst for SSC; LTB, used as cocatalyst for SSC; NTB, used as cocatalyst for SSC; SSC, single-site catalysts; TEB, used in 3rd-generation Phillips catalysts; TNBB, not used in polyolefin technologies; TTB, used as cocatalyst for SSC.

a) Chemical Abstracts Service Registry Numbers.



*Added as BF_3-etherate

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

ethylene) above ~100°C, DSC tests have shown that TEB does not undergo *hazardous* exothermic decomposition at least up to ~200°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 [55]. 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 MWD by increasing the low molecular fractions of PE. This suggests that TEB somehow facilitates chain transfer for supported chromium catalysts. (More recently, TEB has become important in asymmetric synthesis for statin production.)

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" [56] 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) MAOs. Though a variety of fluorinated boranes and borates have been synthesized and used as cocatalysts for SSC [57], the most widely available (beyond FAB) are the products of Eqs 1.19–1.21:

$$\begin{gathered}\left(C_6F_5\right)_3B + C_6F_5Li \rightarrow Li^+\left(C_6F_5\right)_4B^- \\ \textit{lithium tetrakis}\left(\textit{pentafluorophenyl}\right)\textit{borate}\left(\textit{LTB}\right)\end{gathered} \tag{1.19}$$

$$\begin{gathered}Li^+\left(C_6F_5\right)_4B^- + Ph_3CCl \rightarrow Ph_3C^+\left(C_6F_5\right)_4B^- + LiCl \\ \textit{trityl tetrakis}\left(\textit{pentafluorophenyl}\right)\textit{borate}\left(\textit{TTB}\right)\end{gathered} \tag{1.20}$$

$$\begin{gathered}Li^+\left(C_6F_5\right)_4B^- + PhNH\left(CH_3\right)_2^{\ +}Cl^- \rightarrow PhNH\left(CH_3\right)_2^{\ +}\left(C_6F_5\right)4B^- + LiCl \\ N,N-\textit{dimethylanilium tetrakis}\left(\textit{pentafluorophenyl}\right)\textit{borate}\left(\textit{NTB}\right)\end{gathered} \tag{1.21}$$

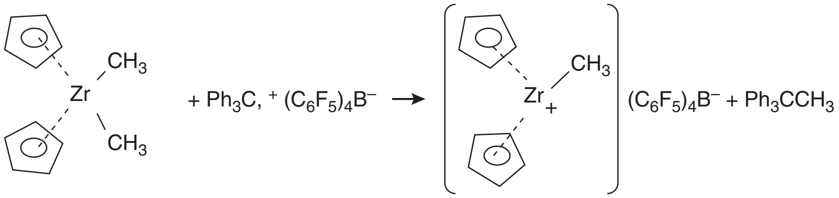


Figure 1.7 Activation of a metallocene by TTB.

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 1.19–1.21 exhibit poor thermal stability and are not storage stable [57].

FAB, lithium tetrakis(pentafluorophenyl)borate (LTB), trityl tetrakis (pentafluorophenyl)borate (TTB), and *N*,*N*-dimethylanilinium tetrakis (pentafluorophenyl)borate (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.

1.9 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 [58]. DEZ is the only organozinc compound with a significant role in polyolefins. DEZ (Chemical Abstracts Service (CAS) registry # 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 1848–1850 [59–61].

DEZ is a monomeric, linear molecule that exists as a clear, colorless liquid at ambient *T*. DEZ is distillable (bp ~ 117°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 *T*, 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 that 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 CTA in ZN catalyst systems in the past [62, 63]. Today, chain transfer in ZN catalyst systems is achieved chiefly by hydrogenolysis. However, significant quantities of DEZ are still employed in the polyolefins 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 "turnaround." 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, which are 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 [36, 64]. 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 CTA.

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INFUSE® is a registered trademark of Dow.

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