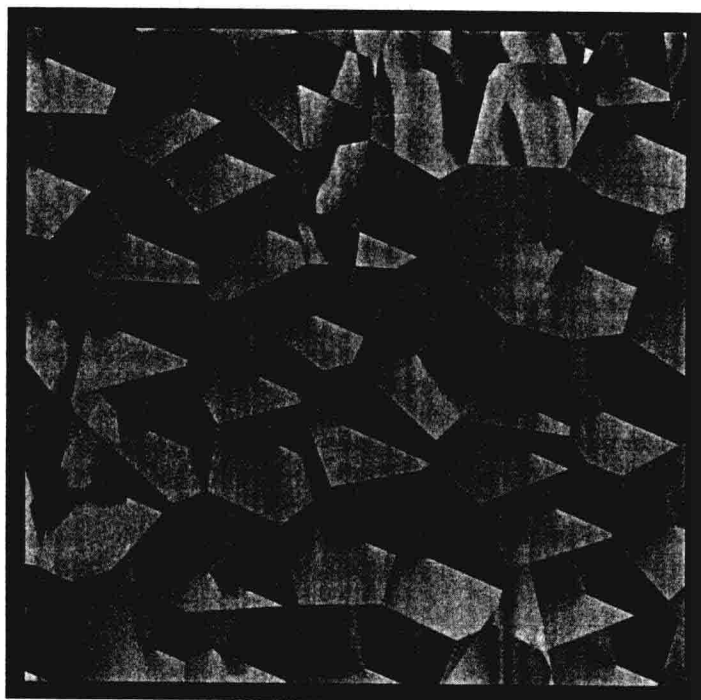


METALLOCENE-CATALYZED POLYMERS

*Materials, Properties,
Processing & Markets*



George M. Benedikt
Brian L. Goodall



Society of Plastics Engineers



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FOREWORD

INTRODUCTORY REMARKS

This book represents a collection of papers describing advances made in the area of metallocene catalysts for olefin polymerization over the last 3-4 years. There are contributions from most of the major industrial companies active in the field as well as from a number of academic groups. In this introductory chapter we attempt to "set the scene" for the technical papers which comprise the text by giving a brief overview of the "Metallocene Revolution", putting metallocenes into a historical perspective in the development of olefin polymerization catalysts and finally we attempt to assist the interested readers in finding their way to the various contributions of particular interest to them.

The origins of Ziegler catalysis and Ziegler-Natta catalysts can be traced back to the mid-1950's. First, there was Karl Ziegler's discovery that zirconium and titanium salts, in combination with aluminum alkyl co-catalysts, are able to polymerize ethylene to high molecular weight, linear polyethylene at low pressures followed less than a year later by Giulio Natta's finding that propylene can be polymerized to form crystalline, isotactic polypropylene using certain crystalline modifications of titanium trichloride. These landmark inventions resulted in the commercialization of the world's biggest thermoplastics (HDPE, LLDPE and polypropylene) and in Ziegler and Natta sharing the Nobel Prize for chemistry.

While the vast majority of the world's capacity for both polyethylene and polypropylene is still based on heterogeneous titanium catalysts directly derived from those first systems, the phrase "Metallocene Revolution" has become a ubiquitous expression within the polyolefins industry over the last decade.

THE HISTORICAL ORIGINS OF METALLOCENE CATALYSTS

The phrase "Metallocene Revolution" was coined to explain the enormous changes brought about to polyolefin preparation and design as a result of the discovery and development of the metallocene catalysts. Initially the excitement in metallocenes was limited to their ability to homopolymerize ethylene at unprecedented rates, but over the last several years it has become overly clear that metallocene catalysts (by virtue of their well-characterized, homogeneous nature) offer the ability for rational design and tailoring of the catalysts. Even after more than 40 years of study and development of the commercial heterogeneous catalysts this is simply not possible with the titanium chloride catalysts due to their ill-defined, heterogeneous nature. Indeed the difference between the two classes of catalysts is perhaps best explained by another ubiquitous phrase used to define metallocene systems - they are "single-site catalysts" whereas the heterogeneous systems, by their very nature comprise a multiplicity of active sites with differing activity, selectivity, hydrogen (molecular weight regulator) response, etc. The ability to rationally design the metallocenes results in unprecedented control over polymer microstructure (isotactic, syndiotactic, atactic, stereo-block), unprecedented control over molecular weight and polydispersity as well as some additional flexibility in terms of co-polymerizing

"difficult to polymerize monomers" such as certain cyclic olefins (e.g., cyclopentene and norbornenes).

The origins of metallocene catalysts can also be traced back to the 1950's when Natta and Breslow (of Hercules, Inc.) both discovered that titanocene dichloride in combination with aluminum alkyls could homopolymerize ethylene. In 1973 Breslow found that the addition of water resulted in increased activity. In the later 1970's attention turned from titanocenes to zirconocenes due to the work of Professors Sinn and Kaminsky at the University of Hamburg (patents to BASF and Hoechst). During this period Sinn and Kaminsky reported that methaluminoxane (the product of the controlled addition of water to trimethylaluminum) was a unique cocatalyst with regard to its ability in the activation of zirconocene dichloride. During this period (and subsequently) much effort was expended in finding the most effective route to generate methaluminoxane (for example by reacting trimethylaluminum with the water of crystallization of aluminum sulfate octadecahydrate), defining its catalytic role(s) and elucidating its composition and structure. The resulting catalyst systems showed unprecedented reaction rates in the polymerization of ethylene.

THE METALLOCENE "REVOLUTION"

The use of zirconocene dichloride in the polymerization of propylene inevitably gave rise to atactic polypropylene of low molecular weight. Breakthroughs were reported in 1984 when John Ewen of Exxon (using titanocenes) and Walter Kaminsky (using zirconocenes) showed that the use of chiral ansa-metallocenes (first prepared by Hans Brintzinger of the University of Konstanz and reported in 1982) resulted in control of the stereostructure of the polypropylene produced. Ewen described blocky, partially isotactic PP using titanium while Kaminsky reported the first ever example of highly isotactic polypropylene using a homogeneous catalyst (with zirconium). In retrospect, the history of metallocene development until this point (1955-1984) was probably evolution rather than revolution. However, the reports of Ewen and Kaminsky opened the floodgates in terms of research expenditure in the area and the true metallocene revolution was started.

Other key metallocene catalyst contributions over the last decade include the use of a titanocene catalyst to generate highly syndiotactic polystyrene (Ishihara of Idemitsu Kosan) in 1985, highly syndiotactic polypropylene (Ewen and Razavi of Fina) in 1988, the first "single component" zirconocene catalysts (Hlatky and Turner of Exxon, Jordan of the University of Iowa) in 1988/9 (using fluorinated phenylboron counter-anions), "Constrained Geometry" catalysts (Bercaw of CalTech, Stevens of Dow) in 1990, sophisticated ansa-zirconocene catalysts representing the first metallocenes capable of generating commercially viable (high MW and very highly stereospecific) isotactic polypropylene (Spaleck of Hoechst) in 1993 and "oscillating" metallocene catalysts (no bridge between the two cyclopentadiene rings) which generate elastomeric, stereoblock polypropylene (Waymouth of Stanford, Moore of Amoco) in 1995.

COMMERCIAL APPLICATIONS OF METALLOCENE CATALYSTS

Up to the present time there are fewer commercial milestones in the metallocene development story than catalyst/technology milestones but this will surely change over the next decade as metallocenes gradually replace more conventional heterogeneous titanium catalysts. Indeed, at present, the volume of commercial polyolefins generated using metallocenes totals only a few percent (less than 10%) of

total polyolefin production capacity. Considering the huge investments that have been made in metallocene research and development, it is safe to conclude that this situation will change, but it is likely that some of the first products will be specialty polyolefins that cannot be manufactured with proven, existing catalysts. Commercial milestones to date include Dow and Idemitsu beginning joint development of syndiotactic polystyrene (1989), Exxon announcing the first commercial metallocene-made resin ("Plastomer" in 1991), Dow announcing plans for commercial LLDPE production with "Constrained Geometry" catalysts (1995) and Hoechst and Mitsui test marketing "Topas", a copolymer of ethylene and norbornene (1996).

AN OVERVIEW OF THIS BOOK'S CONTENTS

This book includes a collection of papers presented at the recent meetings Polyolefins IX and X, as well as Antec '96 and '97. The authors belong mostly but not exclusively to industry, specifically to some of the major players in the metallocene based polymer technology like Dow Chemical (with its INSITE™ process), Exxon Chemical, DuPont-Dow Elastomers, Phillips Petroleum, Montell Polyolefins, Fina Oil and Chemical Company, and Union Carbide Co. Academia, as well as other industrial companies, either already participating or contemplating to play a role in this field are also represented.

Based on the subjects treated, the papers can naturally be grouped into the four selected areas:

- *Materials*, dealing with the more recent advances in catalyst and polymer production technology,
- *Properties*, presenting various areas where metallocene based polymers differentiate themselves from their Ziegler-Natta cousins,
- *Processing*, concentrating on the effect of the different metallocene polymer molecular structures and properties on their processability, and lastly,
- *Markets*, encompassing both some general views of the directions where this technology is heading in the years ahead, as well as some specific attempts to replace other existing, well established, commodity polymers such as PVC.

It would probably be unfair to direct the reader to only a few of the almost 50 papers included. They have all been selected for inclusion here since each contributes to the grand picture, through theoretical or practical studies, small scale or large-scale applications, inventions or innovations. What is important to mention are the major issues, the solution of which will dictate the economics of the successful technology in the targeted market application.

In the *Materials* section the cost of the catalyst at various production scales is an important issue. The cost itself (in \$/lb) is misleading though, if one neglects the productivity of the catalyst and this could vary widely depending on the ligand/metal and process selection in order to obtain a tailored composition. The engineer's desire to develop a "drop-in" system into the existing commercial installations is on one hand a natural drive, but on the other it is bound to require some more or less extensive modifications of the existing production lines. Due to the variety of target polymer compositions (and where applicable microtacticity and sequence distribution), from polyethylene to polypropylene and polycyclic olefins with their copolymers, as well as from elastomers to thermoplastics, not one single process is expected to dominate: solution, slurry, liquid bulk, gas phase,

combined liquid-gas phase. Low pressure as well as high pressure and high temperature "drop-in" processes are described. In a few instances, some compositions are only accessible via metallocene based chemistry, such as syndiotactic polystyrene or syndiotactic polypropylene. The production systems have to be selected and optimized for these compositions. The use of a mixed metallocene catalyst targeted at obtaining a bimodal molecular weight distribution for improved processability is also discussed.

In the *Properties* section the effect of: the metallocene polymers' narrower molecular weight distributions with low molecular weight extractables, together with their controlled content of long chain branching, as well as their ultralow densities, on the morphology, crystallization kinetics, melt rheology and relaxation is discussed. Thermal stability with and without antioxidants, the toughening of clear polypropylene by a metallocene poly(ethylene-co-butene or octene) plastomer, frictional behavior, adhesion (including self-adhesion) and paintability are also important property issues presented. A special mention needs to be made to the development of reactive silane grafted elastomeric metallocene polymers allowing for the use of a secondary moisture cure in foam and wire and cable applications, optimized via modeling of the corresponding architecture.

In the *Processing* section the practical issues of metallocene polymer injection molding, film extrusion, glass fiber reinforcement, fiber spinning, blending and alloying are presented comparatively, when appropriate, with the conventional Ziegler-Natta analogs.

In the *Markets* section the various homo and copolymers available via metallocene chemistry, and which cover elastomers as well as plastomers are discussed in terms of their present and future in specific applications. Food packaging films, electrical insulation applications, impact modifiers in blends, molded goods for automotive, medical and other durables, as well as foams and adhesives are just the first commercial target markets. Obviously, attempts to overtake PVC markets, especially in medical applications, are to be expected and, indeed, there is research directed at replacing this commodity material if the price and performance could be improved.

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Economic Factors for the Production of Metallocene and Perfluorinated Boron Cocatalysts

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ABSTRACT

Metallocene production costs are evaluated for a wide range of molecules currently under development for polyolefin catalyst systems, including bridged and unbridged ligands prepared from cyclopentadienes, indenenes, and fluorenes. Production costs are evaluated on a life cycle basis and on a functional basis. Lifecycle costs are useful for budgeting and planning, and functional costs are useful for comparisons between competing alternatives. Examples from Boulder Scientific's production experience are given for each category of metallocenes and for perfluorinated boron cocatalysts.

INTRODUCTION

Metallocenes were developed in the 1950's, beginning with the discovery of ferrocene⁴ followed shortly thereafter by the synthesis of titanocene dichloride and zirconocene dichloride.⁹ By 1960, hundreds of metallocene molecules had been synthesized and characterized. Extensive reviews^{3,9} described the state of the art at that time. Interest in metallocenes continued to grow gradually during the past 30 years until their recent application to polyolefin catalysis.

Within the past 3 years, commercial interest in metallocene production for catalyst applications has increased dramatically. While some of the more common metallocenes (ferrocene and zirconocene, for example) have been commercially available in large quantities for a number of years, most of the metallocenes and cocatalysts currently under development for polyolefin production were either unknown or produced only for laboratory research. The sudden surge in demand for kilogram and megagram quantities of complex metallocene molecules has exerted pressure to get into production rapidly and drive costs down as soon as possible.

The Boulder Scientific Company, located in Mead, Colorado, has been producing metallocenes commercially for over 15 years. Recent interest in substituted cyclopentadienyl metallocenes, indenyl metallocenes, silyl-bridged metallocenes, and boron-based cocatalysts has spawned extensive laboratory development and commercial-scale production at the Mead facility. In response to the rapidly changing polyolefin market, Boulder Scientific now offers over 30 metallocene products, many of which are produced in kilogram to 100-kilogram quantities.

Boulder Scientific has scaled approximately 20 metallocene production processes from 10 grams to batch sizes as large as 100 kg. As these production processes have matured, many lessons have been learned and trends in production costs have been identified. This paper summarizes production economics for a variety of metallocenes and boron cocatalysts, so that polyolefin producers may have a

guide to the relative cost of candidate catalyst molecules. Just as new drug molecules are screened for effectiveness and production costs, new metallocene molecules can be evaluated on a similar basis. The costs in this paper represent production costs of bulk metallocenes and boron cocatalysts but do not include the costs of producing the finished supported catalyst.

COST METHODOLOGY

Metallocene production costs can be evaluated on a product life-cycle basis and on a functional basis. Product life-cycle evaluation is chronologically oriented and includes development, initial scale-up (or pilot plant), early commercial production, and mature commercial production. Production costs are (in general) inversely related to quantity. It is not uncommon to experience a 4 to 10-fold reduction in cost from early kilogram-scale production to mature commercial production. Functional evaluation is dependent on the molecular structure and synthetic building blocks and can be conducted at any point in the product life cycle. Factors such as raw-material cost, air and moisture sensitivity, number of synthetic steps, purification requirements (in process and final), and yield are all factored into a

functional cost analysis. Table 1 summarizes various cost contributions and whether they contribute to a functional analysis, life-cycle analysis, or both.

Table 1. Functional and Life-Cycle Cost Contributions

Economic Factor	Functional	Life Cycle
Raw materials	1	3
Labor	3	1
Number of steps	1	3
Air or moisture sensitivity	1	3
Yield	1	3
Production scale	2	1
Purification requirements	1	2
Final delivery form	2	2

Key: 1-significant impact; 2-moderate impact; 3-minimal impact

The two cost approaches in Table 1 serve different purposes. Functional analysis provides relative cost between two or more alternatives, but life-cycle cost analysis provides actual production costs for budgets, planning, or accounting.

Functional analysis is very useful early in the development cycle, particularly for comparing between competing alternatives. If, for example, 5 metallocenes were under evaluation for use in polyolefin production, a functional cost analysis could rank the products by production

cost. Functional cost analysis is also useful in comparing competing metallocenes under development by different polyolefin producers. Although the catalytic activity (which is not always available in the public domain) is required for a complete analysis, the relative metallocene cost can be easily determined using a functional cost analysis. Life-cycle cost analysis is more useful once a production commitment has been made, and ultimate cost projections are required for long-term planning. Since the cost of the metallocene is often a significant portion of the overall catalyst cost, economic viability of polyolefin production may depend on the ultimate price of the bulk metallocene.

PRODUCT LIFE-CYCLE COST ANALYSIS

Detailed cost models for multi-step metallocene production can be extremely complex and time consuming. At Boulder Scientific, cost projections follow these four steps.

1. **Development cost.** A substantial effort is invested to develop a "plant-ready" process on the laboratory bench top. Typically, a process is "ready" for the pilot plant when a large-scale (12 L glassware at Boulder Scientific) process runs successfully and repeatably on the bench. The development cost associated with this phase varies widely, depending on the number of steps and the starting point for development. Syntheses reported in the literature are sometimes difficult to reproduce and scale up. Costs are usually directly proportional to the number of chemist hours required (raw materials are rarely a significant contribution to development cost at the bench scale). Development times at Boulder Scientific range from one week (40 chemist hours) to six weeks (240 chemist hours) per synthetic step. An average of 100 chemist hours per synthetic step is useful for planning purposes, but should be replaced by actual hours or hours from a comparable process if these data are available.

The cost of a chemist-hour should include direct costs, as well as R&D overhead (analytical support, raw material purchasing, and any other administrative support). General supplies and chemicals can be accounted for by adding a weekly "use charge" to cover the cost of one chemist working for one week. Depending on the nature of the process and on the definition of R&D overhead, use charges between \$500.00 and \$2000.00 per week may be appropriate. Using the average values of 100 chemist-hours per step, \$1000.00 per week use fee, and a \$100.00/hr fully burdened labor rate, the development cost for a four-step process would be \$50,000.00 and would require 10 weeks. Any special equipment or unusually expensive raw materials should be added to this estimate.

2. **Pilot-plant scale.** Once a process is developed at the bench scale, production begins in the pilot plant. A pilot plant may consist of 25, 50, and 75-L glasslined reactors, or may involve conventional reactors in sizes from a few liters up to 1000 L. The size of the pilot plant is generally dependent on the size of the company's full-scale manufacturing operations. Costs in the pilot-plant phase are highly influenced by labor costs, since the number of labor hours per kg of material produced is quite large compared to full-scale manufacturing. It is not unusual to require as many or more hours of labor for a batch in the pilot plant as in the full-scale manufacturing plant, but the quantity produced is a fraction of full-scale production. For these reasons, product pricing is often very flat in the 3 to 10 kg range. Pilot-plant costs include set-up, raw material usage, production labor, support labor (R&D chemists, analytical chemists, and QA/QC), and waste treatment or disposal. At Boulder Scientific, these costs are modeled on a simple spreadsheet program with sections for each cost category. Production labor is a function of elapsed time and number of workers required for each step. For example, a multi-step process might require 110 hours of continuous clock time and an average of 1.25 workers, resulting a total of 137.5 production hours. In general, it is difficult to accomplish more than one synthetic step per day in the pilot plant, and 2(24-hour) days is a better general estimate. For complex processes, one full week (120 hours) is not unusual for each synthetic step. Raw material costs may be as low as 1/10 the labor cost or as

high as the pilot-plant labor costs. The impact of raw material cost is discussed in more detail in other sections.

3. Early full-scale manufacturing. In a traditional product development cycle, substantial study at the laboratory and pilot-plant level provides ample design detail for full-scale manufacturing. In the rapidly changing metallocenes field, however, projects are frequently rushed from laboratory to pilot scale to full scale manufacturing. Consequently, the first few production batches serve to debug the process and work out final scale-up details. Production campaigns at full scale are usually short, because metallocene demand for polyolefins has not yet reached maximum levels. Production costs in this phase are noticeably reduced because of economy of scale. Raw material costs are relatively constant (on a per kg of metallocene basis), but labor per kg produced declines substantially. Actual costs from this phase form the first reliable basis for projecting long-term manufacturing cost. Batch turnaround time is a good indicator of labor costs, and batch yields can be combined with turnaround time to produce a reliable production cost. Raw material to labor cost ratios vary from 3 to 1 down to 0.25 to 1, depending on the process.
4. Mature full-scale manufacturing. Within the next 3 years, as polyolefin technology matures and penetrates the market, several metallocenes and cocatalysts will enter this phase. This phase is marked by relatively large volumes, stable demand, and regular delivery schedules. For competitive reasons, cost pressure continues to be exerted on suppliers and the delivered price continues to fall until a plateau is reached. The level of the plateau is determined by raw material costs, scale of manufacturing, production technology, and labor cost. Production costs may include capital recovery for new equipment installed to meet the ongoing demand for metallocene products.

FUNCTIONAL COST ANALYSIS

Functional cost analysis provides insight into the relative cost of molecules based on their structure, properties, and synthesis. It can be useful for comparing different competing molecules, or different processes for producing the same molecule. The following factors go into a functional cost analysis.

1. Raw material cost, weighted at each step for yield
2. Overall yield (the mass yield is more useful than a molar yield)
3. Number of synthetic steps
4. Number of purification steps (distillation, recrystallization, etc.)
5. Special handling requirements (e.g. air or moisture sensitivity)

At Boulder Scientific, spreadsheet programs calculate raw material requirements for each step based on stoichiometry, reaction yield, and purification losses. In indene-based ligands, for example, it is not uncommon to require 5 to 10 of indene for every kg of finished metallocene. The raw material cost, in total dollars per kg of finished metallocene, can then be readily calculated. The spreadsheets also reveal the most costly raw materials, which might suggest alternate routes, substitute raw materials, or more competitive sources to reduce costs. Finally, the raw material cost per kg of finished metallocene may be a useful screening tool between competing molecules or synthetic routes.

Yields can be compared on a molar basis or a mass basis. Molar yields (those typically reported in the literature) can be converted to mass yields using the appropriate molecular weights. For example, a metallation reaction might proceed in 47% molar yield, but the increase in molecular weight might pro-

duce a mass yield of nearly 100% (1 kg of metallocene per kg of ligand). Multi-step processes typically have low overall molar yields because of yield compounding. A 90% molar yield over 5 steps produces an overall yield of 59%; an 80% molar yield over 5 steps produces a 33% overall yield. Even when converted to mass yields, these low overall yields result in substantial losses in raw material conversion. When calculating raw material costs, mass yields are required, but when comparing processes or products, molar yields are a better indicator of overall effectiveness.

EXAMPLES OF SPECIFIC COMPOUNDS

Examples from several different classes of metallocenes provide different insights into production costs and issues. In order to span the wide range of metallocenes under consideration today, the following molecules have been included: Brintzingers catalyst (an ethylene-bridged indenyl zirconocene), a substituted cyclopentadienyl zirconocene, a mono-cyclopentadienyl catalyst (a silyl bridged molecule), and a perfluorinated boron cocatalyst molecule.

BIS(INDENYL)ZIRCONIUM DICHLORIDE AND RELATED DERIVATIVES

In the early 1980's Brintzingers and coworkers synthesized racemic ethylene-bridged bis(indenyl)zirconium dichloride, $\text{Et(Ind)}_2\text{ZrCl}_2$, and evaluated its properties as a polymerization catalyst.^{7,8} Since then, Brintzinger's catalyst and various derivatives have been evaluated by companies worldwide for activity and performance. Commercial preparation of the metallocene (or its substituted forms) can be divided into 4 parts:

1. Preparation and purification of the starting indene (substituted or not).
2. Bridging the indene molecule to form the bis-indenyl ethane ligand.
3. Reacting the ligand with zirconium tetrachloride to form the metallocene.
4. Isolating and purifying the racemic isomer of the metallocene.

Step 1 can require a simple distillation or drying (commercial indene is typically 90% pure and contains some water), or can be more involved if a functional group must be attached to the indene molecule. Step 2 is usually conducted using ethylene dibromide, and the resulting bis-indenyl ethane can be isolated as a solid. There are a variety of reaction schemes for step 3, and the crude material may be isolated as a solid or passed as a solution to step 4. The finished metallocene is/is not sensitive to air and moisture and must be handled accordingly.

At Boulder Scientific, one indenyl process required low-temperature operations for steps 2 and 3. The overall yield, from indene to finished metallocene varied from 10% to 25%, which made the resulting metallocene quite expensive. The process was run at the 10-kg scale, and the production costs were in excess of \$10,000 per kg. Clearly, this process was not economically viable in practice, even though paper analysis suggested that the cost should be substantially lower. An improved process with better yields and costs is currently under development for production of this metallocene.

SUBSTITUTED BIS(CYCLOPENTADIENYL)ZIRCONIUM DICHLORIDES

The preparation of bis(cyclopentadienyl)zirconium dichloride (zirconocene dichloride) was developed in the 1950's, and applications of zirconocene and titanocene to polymerization occurred in 1957.^{2,5} In addition to the unsubstituted forms of titanocene and zirconocene dichloride, many substituted cyclopentadienyl (Cp) metallocenes of zirconium and titanium are actively under development as polyolefin catalysts. Typically, these molecules consist of alkyl-substituted

cyclopentadienes reacted with zirconium tetrachloride to form the corresponding metallocene. The degree of substitution ranges from mono-substituted to penta-substituted cyclopentadiene. The production process for these metallocenes can be broadly described as follows:

1. Prepare substituted, purified cyclopentadiene
2. React cyclopentadiene with zirconium tetrachloride to form the metallocene
3. Isolate and purify the correct isomer of the metallocene.

Step 1, of course, can be the most difficult, since it may involve multiple chemical steps and purifications.

Synthetic chemists have developed numerous methods of preparing substituted cyclopentadienes. Boulder Scientific developed a proprietary 4-step process for producing a di-substituted cyclopentadiene, and scaled the process from laboratory to approximately 20-kg scale. Production cost data as a function of scale are given in Table 2.

This process was not highly sensitive to raw material cost (at the 20 kg scale, raw materials were approximately 20% of the total cost) and demonstrated excellent cost decreases with increasing scale and production experience. Unlike the Brintzingers process, yields in the plant continued to improve with time and experience. The overall economics were highly dependent on the production of a key intermediate (a substituted cyclopentadiene). Labor costs (in U.S. dollars) during development are plotted in Figure 1.

Table 2. Production Costs for Substituted Cp Metallocene.

Run#	Scale	Cost, \$/kg	Relative Cost
1	2 kg	9,356	1.00
2	5 kg	6,973	0.75
3	10 kg	3,623	0.39
4	20 kg	1,469	0.16

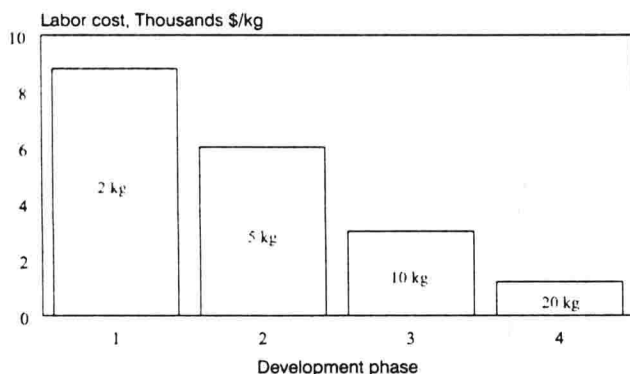


Figure 1. Labor Costs During Development of a Substituted Cyclopentadienyl Zirconocene.

CONSTRAINED-GEOMETRY SILYL-BRIDGED MOLECULES

In addition to "traditional" metallocene catalysts, constrained-geometry (CG) mono-cyclopentadienyl catalysts have been developed by Dow Plastics.⁶ These titanium-based catalysts can provide unique polyolefin properties, and follow a generic synthetic route similar to the previous examples. In the first step, a multi-step process is required to prepare purified ligand. In the second step, the ligand is attached to the metal (titanium, in this case). In the third step, the finished molecule is separated and purified.

Evaluating all metallocenes on a similar basis (ligand prep, metallocene prep, and final purification) facilitates cost comparisons for different processes and molecules. For example, consider the hypothetical comparison between 3 metallocenes in Table 3.

Table 3. Hypothetical Metallocene Comparison

Type	RM Index	Ligand Steps	Purifications	Ligand Yield	Metallocene Yield	Overall Yield
Substituted-bridged indenyl	1.0	3	2	40%	45%	18%
Substituted cyclopentadienyl	0.8	4	1	50%	45%	22.5%
Silyl-bridged CG	0.6	3	3	60%	35%	21%

The relative raw-material cost for each metallocene in Table 3 is the quotient of the RM Index (actual raw material cost per unit excluding yield) and the overall yield. Carrying out this multiplication provides the following rankings for raw material cost:

Silyl-bridged CG	2.85
Cp-based	3.56
Indenyl	5.56

After accounting for raw material costs, labor costs can be incorporated by evaluating the number of steps and number of purifications. In this example, assume that all steps require equal amounts of labor. If the labor cost per step is 1/2 the raw material cost of the indenyl metallocene, then the overall relative costs can be obtained as follows:

$$\text{Labor cost per step} = (0.5)(5.56) = 2.78$$

$$\text{Total labor cost} = (\text{number of steps})(2.78)$$

Table 4. Relative Cost Contributions for Hypothetical Metallocenes

Type	R.M.	Labor	Total
Silyl-bridged CG	2.85	16.68	19.53
Cp-based	3.56	13.90	17.46
Indenyl	5.56	13.90	19.46

The relative cost contributions are given in the Table 4. In Table 4, the compound with the lowest unit raw material cost wound up having the highest overall cost because of the labor contribution. This is not unusual for metallocene production at the 10 to 100 kg production scale. Labor costs become less significant as production increases in capacity, as illustrated in the final example.

TRIS(PENTAFLUOROPHENYL) BORON COCATALYST

All metallocene catalysts require cocatalysts for activation. Historically, organo-aluminum compounds, and specifically, methylalumoxanes, MAO, have filled this role. Some catalysts, however, have been activated by perfluorinated phenyl boron compounds, such as