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# Organotransition-metal chemistry: past development and future outlook

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#### Abstract

The course of the development of organometallic chemistry is reviewed from the author's personal viewpoint. The impact of the discoveries of ferrocene and the Ziegler catalyst on the later development of organotransition-metal chemistry is discussed. Through evolution of fundamental concepts, such as the insertion of olefins and carbon monoxide into metal-carbon bonds, oxidative addition and reductive elimination, and attack of nucleophiles on coordinated ligands, together with reactivities of carbene and metallacyclic complexes, various important processes have been developed. The diversity of transition-metal complexes and their unique reactivities not found in usual organic compounds warrant further developments in the various forefronts related to organometallic chemistry with almost limitless possibilities in applications as well as in fundamental studies. © 2000 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

The latter half of the 20th century witnessed a tremendous development of organometallic chemistry. As one who personally experienced the rapid growth, I feel myself quite fortunate that I happened to be in this period and experienced the excitement myself. However, some younger pessimistic people these days seem to feel that the happy development period was closing towards the end of the century. I would not agree with this view. It often appears wiser and more intellectual to utter pessimistic views than optimistic ones, but history tells us that human imagination and endeavor have kept pushing back the horizon of knowledge, always discovering something new of great impact. Let me look back on the history of organometallic chemistry, from a personal point of view.

# 2. Impact of the discoveries of ferrocene and the Ziegler catalyst

Before the advent of ferrocene and the Ziegler catalyst, organometallic chemistry was treated in the realm of organic chemistry apart from the Werner-type coordination chemistry. Organometallic compounds of nontransition elements, such as lithium, magnesium and zinc, were applied as useful reagents in organic synthesis, but the chemistry of these organometallic compounds remained of somewhat a low profile, at least from the standpoint of outsiders. The quite novel structure of ferrocene [1], which was found serendipitously, aroused the interest of chemists, organic, inorganic, and physical chemists included, stimulated their imagination, and led to the exploration of the fertile field of organotransition-metal chemistry. A succession of exciting discoveries of a variety of new compounds spanning the whole width and depth of the periodic table ensued; the phenomenon was dubbed at the time as the renaissance of inorganic chemistry.

The pace of the development of organometallic chemistry initiated by the discovery of ferrocene was spurred by another unexpected discovery by Ziegler [2]. His discovery came out of his fundamental studies on

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the reactions of organolithium and aluminum compounds. Through his attempts to clarify the mysterious effect of nickel in the oligomerization of ethylene with triethylaluminum, his group examined the effects of transition-metal compounds in combination with aluminum compounds. His description of the scene of discovery, when they carried out the reaction of ethylene with triethylaluminum in the presence of zirconium acetylacetonate first, and later with titanium tetrachloride, and of his satisfaction to look at the surprised faces of visitors who were shown the new invention, was a fascinating story for me to read as a novice graduate student [3]. In the absence of the Angewandte Chemie International Edition in English, we had to read his papers in German, which took much time. It was the occasion when I thought that becoming a researcher in organometallic chemistry might be fun. His discovery was spectacular and had a far-reaching impact. But it had serendipitous luck and did not seem unreachable by an ordinary chemist if he was logical, observant, and imaginative. My later life has been involved in organometallic chemistry, spanning over 45 years; I never found the field of organometallic chemistry dull.

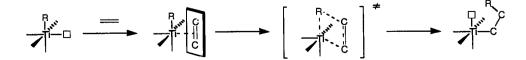
The discovery of the Ziegler catalyst was followed closely by the remarkable development by Natta [4]. The pace of further research developments into coordination polymerization by Natta's group was spectacular [5,6]. Besides the introduction of the concept of stereoregular polymerization, they have opened up new fields in ring-opening metathesis polymerization, diene polymerization, ring-opening polymerization of epoxides, and polymerization of acetylene. These discoveries produced in Natta's powerful group with many able co-workers, who later became the leading figures in the international community, were disclosed at a tremendous pace. Many of the Japanese polymer chemists at the time started to learn Italian just to understand what was being written in the papers published by Natta's group in Italian journals. The time before the advent of the Ziegler catalyst was when polymer chemistry had reached maturity after the rapid initial expansion period. However, the discoveries of Ziegler and Natta opened a new field of coordination polymerization to let us realize that we were at the start of the bursting development of polymer chemistry using transitionmetal complexes as catalysts.

Industry was alerted to the new era. At that time many Japanese companies sent their people to Mülheim and Milan for negotiation of the introduction of the license from Ziegler at the Max Planck Institute for Coal Research and from Montecatini in Milan with which Natta was closely associated. The production of polyethylene and polypropylene was realized after some initial troubles. In the commercialization of high-density polyethylene, for example, they had difficulties in finding a suitable use for the stiff polyethylene product. A savior of the predicament was the fad of the hulahoop, a toy plastic ring to whirl around the waist. It is amusing to see the old pictures of the time when everybody was crazy trying to whirl the plastic ring on the plaza and streets. But the fad helped to clear the enormous stock of high-density polyethylene produced in the initial period by petrochemical companies in Japan to set the fledgling Japanese petrochemical industry on track.

While the petrochemical industry in Japan was coping with the newly imported technology of producing the low-pressure high-density polyolefin process, chemists in universities were attracted to the coordination polymerization process and its mechanistic studies. How are the active species formed in the reaction of titanium halides with alkylaluminum compounds, what are the mechanisms of polymerization of a variety of monomers such as  $\alpha$ -olefins, dienes, and epoxides, and how is the stereoregulation controlled in polymerization of  $\alpha$ -olefins, particularly propylene? I remember the days when the halls for symposia and meetings concerning coordination polymerization in Japan were packed with people interested in the development of polymerization processes with Ziegler-type catalysts.

It was Cossee who first proposed a simplified mechanism to elucidate the formation of the active species in a mixed system composed of a titanium chloride and trialkylaluminum [7]. He proposed that the alkyltitanium complex is produced by alkylation of the titanium chlorides with alkylaluminum compounds. Side-on coordination of an olefin to a vacant site in the alkyltitanium species leads to activation of the alkyl-transitionmetal bond followed by insertion of the olefin into the transition-metal-carbon bond. Successive olefin insertion leads to a polymer (Scheme 1).

The proposal was simple and seemed quite attractive to me. This was the time when some mysterious function of the metal surface was still believed to be respon-



Scheme 1. Cossee's mechanism for the polymerization of ethylene.

sible for promoting the catalysis. It was Wilke who removed the myth and showed clearly that an isolated transition-metal complex can in fact catalyze homogeneous processes and that the catalysis can be interpreted in terms of fundamental processes amenable to the techniques of organic chemistry [8]. Wilke and his co-workers unequivocally established that the polymerization and oligomerization of  $\alpha$ -olefins and dienes can be catalyzed by isolated pure transition-metal complexes and the reaction course can be controlled by ligands added to the system.

The proposal by Cossee was later substantiated by the mechanistic studies concerning the olefin polymerization by single-site metallocene type complexes of early transition-metals having the alkyl group. However, because of the paucity of isolated transitionmetal alkyls in the 1960s and the lack of clear examples of polymerization of olefins initiated by the isolated transition-metal alkyls, it took some time for the Cossee mechanism to be generally accepted.

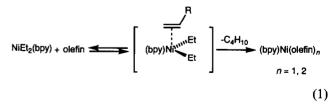
# 2.1. Evolution of concepts of fundamental elementary processes

On the other hand, the chemistry of low-valent transition-metal complexes attracted attention of various researchers. Low-valent late transition-metal complexes that gave particularly strong impacts were Vaska's complex,  $IrCl(CO)(PPh_3)_2$  [9], Wilkinson's complex RhCl(PPh\_3)\_3 and Pd(PPh\_3)\_4. Important organometallic terms such as oxidative addition and reductive elimination [10] were proposed in those days and have been accepted widely as important concepts since then.

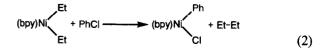
The concept of oxidative addition had a far-reaching impact on organic synthesis and catalysis. Since organic synthesis is a combination of operations of cleaving and connecting bonds, the oxidative addition process to a low-valent transition-metal complex provides a powerful means to generate a new reactive organotransition-metal complex susceptible to the ensuing reactions. The concept of reductive elimination processes also proved quite useful in designing organic synthesis using transition-metal catalysts because it is concerned with bond formation in the organic moiety.

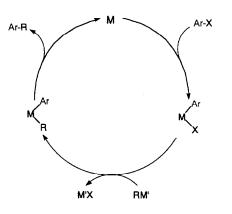
Various attempts were made to isolate transitionmetal alkyls, particularly in relation to the active species in Ziegler-type polymerization catalysts. Through many unsuccessful attempts and some limited successful results to prepare stable transition-metal alkyls, the reasons why some transition-metal complexes can exist and why some are not stable to be isolated were gradually revealed. However, the precise reasons for accounting for the instability of transition-metal alkyls remain to be established even today. When examples of isolated transition-metal alkyls were quite scarce [11], even a prediction was made that transition-metal alkyls are intrinsically unstable and they can be isolated in only special cases such as platinum alkyls [12]. Wilkinson reasoned that the common decomposition pathway for a transition-metal alkyl is the  $\beta$ -hydrogen elimination process and by blocking the route for the  $\beta$ -hydrogen elimination, one should be able to stabilize the transition-metal alkyls. His proposal was supported partly by the isolation of transition-metal complexes having the methyl and other alkyl ligands that are not amenable to  $\beta$ -elimination. However, there are other possible routes leading to decomposition of transition-metal alkyls, such as reductive elimination,  $\alpha$ and  $\gamma$ -elimination. Therefore, blocking the  $\beta$ -hydrogen elimination alone does not prevent a transition-metal alkyl from decomposition. Particularly, an important route is reductive elimination of diorganotransitionmetal complexes, since coupling of the two organic ligands by reductive elimination leads to new C-C bond formation. In the old days, when the number of isolated transition-metal alkyls was limited, synthesis of a stable transition-metal alkyl alone was worthwhile to draw attention. I was lucky in being able to isolate nickel, cobalt and iron alkyls coordinated by 2,2'bipyridine and to study their reactions [13]. In those days when organotransition-metal chemistry was not developed fully, one could come across important findings serendipitously and one could develop an interesting chemistry on the basis of the new findings, if one was prepared to catch the message of the finding.

After the first luck of being able to isolate  $NiEt_2(bpy)$  and  $FeEt_2(bpy)_2$ , we examined their reactivities. The diethyliron complexes were found to serve as the polymerization initiator of vinyl monomers, whereas the diethylnickel analogue on interaction with the electronegative olefins was found to undergo reductive elimination, causing coupling of the two ethyl groups (Eq. (1)) [14].



Further examination of the reactivities of the nickel diethyl complex with aryl halides led to the finding of a new type of reaction where both reductive elimination of the two alkyl ligands and oxidative addition of the aryl halide were involved (Eq. (2)) [15].





Scheme 2. Mechanism of transition-metal-catalyzed cross coupling of aryl and alkyl groups.

### 2.2. Application to organic syntheses

We did not recognize at the time that this finding could be coupled with the concept of alkyl transfer (transmetallation) to provide one of the very first examples of synthetic application to cross-coupling of the aryl and alkyl groups.

The application possibility was not overlooked by Kumada and Tamao at Kyoto [16] and Corriu and Masse in Montpellier [17]. They developed a nickel-catalyzed cross-coupling process of aryl halide with Grignard reagents (Eq. (3)) [18]. (3)

I did not feel chagrin at the time but it came later to me when I saw the tremendous expansion of the catalytic processes as quite an important synthetic methodology. The basic concept of the transition-metalcatalyzed cross-coupling processes can be represented by Scheme 2.

The catalytic cycle is composed of three elementary organometallic processes: (a) oxidative addition of an aryl halide to a low-valent transition-metal complex to give an aryltransition-metal species; (b) transmetallation to give an aryl-alkyltransition-metal species; and (c) reductive elimination to cause the coupling of the aryl and alkyl groups. A shortcoming of the cross-coupling with Grignard reagents is that the alkylmagnesium compounds used are so nucleophilic and they may attack the carbonyl-containing compounds such as a ketone. This disadvantage was overcome by Kosugi and Migita in Japan [19] and later by Stille in the USA [20] by using organotin compounds.

The utilization of the characteristics of organometallic compounds of non-transition-metal elements other than magnesium in combination with nickel and palladium led to the establishment of quite useful preparative methods. The other cross-coupling processes with usage of organoboron compounds (Suzuki coupling or Suzuki-Miyaura coupling) [21], organozinc [22], and aluminum compounds [23] (Negishi process), and organosilicon compounds (Hiyama-Hatanaka process) [24] have found wide customers among synthetic chemists interested in the synthesis of organic natural products and in fine chemicals.

When oxidative addition is coupled with the insertion of unsaturated compounds such as olefins, alkynes, and carbon monoxide, another type of transition-metal-catalyzed processes can be realized. Mizoroki [25] first found the palladium-catalyzed process of converting aryl halides and alkenes into arylated olefins and the process was later established as one of the most convenient processes to prepare unsaturated compounds by an important contribution by Heck [26]. The process is now simply called the Heck process without referring to the original contribution of the late Mizoroki.

Heck also developed a palladium-catalyzed carbonylation process to convert aryl and alkenyl halides into carbonyl compounds such as esters, amides, and carboxylic acids. The process comprises oxidative addition of aryl halides to give organopalladium complexes and CO insertion into the Pd–C bond. The process is finding ever-increasing uses in organic synthesis and is also called the Heck process.

Another useful process using transition-metal catalysts is called the Sonogashira process or the Hagihara– Sonogashira process [27] [28]. The palladium-catalyzed process employing copper co-catalysts provides a useful means for the preparation of compounds containing carbon-carbon triple bonds.

These are just a few examples of applications of the concepts of organotransition-metal chemistry to organic synthesis that came to my mind. One can find quite extensive use of transition-metal complexes as promoters and catalysts in organic synthesis [29,30]. It is noteworthy that most of these synthetic applications came out of the attempts of applying the basic principles in organotransition-metal chemistry to organic synthesis.

Synthetic organic chemists are usually reluctant to try less-well-proven reactions to their synthetic processes. Unless the utility of the process is established by the original contributors themselves, as done by Stille, or the new process should rapidly find applications by their fellow workers, the process may be slow to find the applications needed to receive proper recognition.

When we realized that we missed a big chance of finding a novel synthetic process applicable to crosscoupling processes during our studies of organonickel complexes with aryl halides, my coworker Takakazu Yamamoto, who had a background in polymer chemistry, applied the concept of oxidative addition, transmetallation, and reductive elimination to difunctional halides using magnesium [31]. The polyarenes produced by the nickel-catalyzed polycondensation process are active electrochemically, electrically conductive and light emitting and are finding uses in batteries and other electronic and optical devices [32-34].

#### 3. A look to the future

Organometallic chemistry is closely related to the neighboring fields, which include organic chemistry, polymer synthesis, materials science, and heterogeneous catalysis. Thus the results obtained in organometallic chemistry can have an impact on these neighboring fields. Those who are working in the neighboring fields can pick up the fruits developed in the fertile land of organometallic chemistry, if they have a sensitivity to what is happening in organometallic chemistry. As can be seen from the account of the past, developments in my specific field alone, simple combination of basic principles in organometallic chemistry, can lead to a variety of new developments. Furthermore, in-depth studies of some types of processes very specific to organometallic chemistry, such as  $\alpha$ -elimination to give alkylidene complexes, led to the development of new preparative and polymerization processes. An alkylidene complex interacts with an olefin to form a metallacycle and on rearrangement, another type of olefin and an alkylidene complex can be generated. Quite a variety of new polymerization processes and synthetic means such as ring-opening and ring-closing metathesis reactions have been developed and utilized conveniently in polymer synthesis and in organic synthesis [35-40].

# 3.1. Exploitation of specific properties of organometallic compounds of various metals

In the development so far achieved in organometallic chemistry and in its applications [41], the transitionmetals that have been utilized have been limited and are far from exhausted. Organometallic complexes of early transition-metals generally have found use in polymerization, whereas later transition-metal complexes, particularly those of palladium [42,43], ruthenium [44-46] and rhodium have found extensive uses in organic synthesis. The utility of the late transition-metal complexes in organic synthesis may arise partly from their tolerance to the presence of functional groups in the substrate because the late transition-metal alkyls are less nucleophilic towards the functional groups. This may partly be due to the ability of the late transitionmetal complexes to take high and low oxidation states in the process of oxidative addition and reductive elimination. The conversion between the high and low oxidation states is also involved in nucleophilic attack of the ligands such as allyl, olefin, and CO, coordinated to high oxidation state complexes, to produce low-valent transition-metal complexes in bond-forming processes.

Early transition-metal complexes, on the other hand, have been used as polymerization catalysts since the first discovery by Ziegler followed by recent developments of single-site metallocene-type catalysts [47]. Only a few late transition-metal alkyls had been known to show polymerization activity for electronegative monomers [48] until recently. The recent development in copolymerization of ethylene and carbon monoxide by a palladium-based catalyst [49-51] showed that late transition-metal alkyls are also capable of serving as polymerization catalysts. In fact, not only the copolymerization of CO and ethylene but also homopolymerization of ethylene and  $\alpha$ -olefins with Group 10 metal catalysts has been realized [52]. It was further found that iron and cobalt complexes having  $\alpha$ -diimine ligands are capable of initiating the polymerization of ethylene [53,54]. These developments indicate that there is no intrinsic difference in the abilities between the early and late transition-metal complexes in their reactions with unsaturated organic compounds. Thus, one can hope that by modifying the ligands appropriately, the reactivities of these organotransition-metal complexes can be modified within certain limits. The recent development also shows the ever-increasing utility of early transition-metal complexes in organic syntheses [55-58].

Besides organometallic compounds of d-elements, organometallic compounds of f-elements will be increasingly used in organic synthesis. An early example of the elimination of an alkyl group at the  $\beta$ -position by a metal was shown with an f-element, lutetium [59]. Polymerization activity of organolanthanoid complexes for methyl methacrylate and non-polar olefins provides another example of specific abilities of f-element complexes [60].

## 3.2. Prospect of further development in application of transition-metal complexes in organic synthesis

#### 3.2.1. Green chemistry

Many of the present industrial processes depend on technology where disposal problems are less severe. For the sustainable development of mankind, green chemistry is one of the most important issues. In order to save energy and resources for production of industrial materials, the previously developed less-efficient processes should be re-examined. Wherever possible, processes using stoichiometric amounts of reagents to produce unnecessary waste should be replaced by processes where only catalytic amounts of promoters are used. This is where chemistry is expected to play the most dominant role. Thus development of various efficient catalytic processes is increasingly demanded. For the production of organic compounds, new methodologies of accomplishing specific reactions should be developed.

In organic synthesis, the more useful means we have with transition-metal complexes of cleaving and connecting the bonds, under preferably mild conditions, the better chance we could expect in designing novel and desirable synthetic methodologies. The development achieved in organic synthesis with the utilization of transition-metal complexes is already tremendous. However, the methodologies so far developed have had limitations.

### 3.3. Development of halide-free processes

For example, many of the transition-metal-catalyzed organic syntheses such as cross-coupling and the Mizoroki-Heck processes are associated with the transition-metal-promoted cleavage of aryl halides or alkenyl halides in one of the elementary steps in the catalytic cycle. However, the halide has to be removed by a base with the production of a salt of hydrogen halide for synthesizing products that do not contain halide. Thus these processes are not environmentally favorable nor have high atom efficiency [61,62]. If one can cleave bonds other than the carbon-halogen bond, and if one does not need to remove the extra elements in the operation, the process will be more favorable from the viewpoint of atom efficiency and environmental aspect. The activation of C-H bonds by transition-metal complexes has attracted much attention [63,64]. The recent development of a catalytic utilization of the cleavage of the C-H bond promoted by ruthenium complexes [65] exemplifies one of the directions to be developed in the future. The further goal of the application of the concept of C-H bond activation by transition-metal complexes would be a realization of catalytic conversion of saturated hydrocarbons into useful compounds under mild conditions [66].

Cleavage of the C-C bonds in organic compounds, promoted by transition-metal complexes, is attracting increasing attention recently [67]. The examples reported previously of successful cleavage of C-C bonds in organic compounds promoted by transition-metal complexes have been achieved mostly with organic compounds having strained cyclic structures [68]. A new development can be seen in the application of the C-C bond cleavage to catalytic systems [69]. The recent work of Murakami and Ito shows the future possibility of the application of the transition-metal-promoted C-C bond cleavage in organic synthesis.

For accomplishing catalytic cleavage of C-C bonds in organic compounds, it is desirable to find general ways of performing the selective cleavage of a specific C-C bond in organic compounds. Although the chemistry of metal cluster complexes has been studied extensively, mostly from the preparative aspect of new clusters, it is felt that the chemistry has not given so strong an impact on the neighboring field. The studies even gave an impression that esthetics may have been the main factor driving the research, at least from the outsiders' viewpoint. Applications of metal cluster chemistry are now sought for materials science and in the preparation of new types of solid catalysts [70,71]. Among various attempts to achieve C-C bond cleavage, a recent development to cleave the C-C bond in ordinary aliphatic as well as aromatic compounds by trinuclear ruthenium complexes is noteworthy. Suzuki has shown that simple alkanes can be chopped up by the trinuclear complexes [72]. It is intriguing to see the future possibilities of this application.

In certain cases where catalytic processes have been studied, cooperation of different transition-metals has been shown to enhance the catalytic abilities of the processes dramatically [73]. It was also reported that conversion of dinitrogen into ammonia with dihydrogen was achieved by combination of two metal complexes [74]. Since the number of combinations of transition-metals in forming the heterometallic cluster complexes is almost limitless, future studies may lead to successful catalytic processes of cracking hydrocarbons and functionalizing organic compounds promoted by transition-metal complexes.

### 3.3.1. Cleavage of carbon-heteroatom bonds

In comparison to the abundant examples of carbon-halogen bond cleavage by low-valent transitionmetal complexes, examples of carbon-oxygen bond cleavage have attracted less attention except for palladium-promoted cleavage of allyl-oxygen bonds [75]. [76] Realization of the palladium-promoted C-O bond cleavage in carboxylic anhydrides and its application to catalytic hydrogenation as shown in the following process [77-79] demonstrates the potentiality of achieving atom-efficient, environmentally benign processes without producing undesired by-products (Eq. (4)).

$$RCOOH + H_2 \xrightarrow{[Pd], (iBuCO)_2O} RCHO(+ HOH)$$
(4)

The process was developed on the concept of C–O bond cleavage in carboxylic anhydrides by oxidative addition on interaction with Pd(0) complexes and the subsequent process of hydrogenolysis of the acyl-palladium bond to release aldehydes and carboxylic acids. Combination of the C–O bond cleavage process with exchange reactions of the liberated acid with the added carboxylic anhydride led to the development of a new catalytic process where no organic halides are used for direct production of aldehydes from carboxylic acids [80].

Obviously other processes to cleave the carbon-nitrogen, carbon-sulfur and related bonds are expected to be used to develop environmentally benign and less energy- and resource-consuming catalytic processes.

### 3.4. Heterogenization of homogeneous catalysts

One of the serious disadvantages of homogeneous catalytic systems, in comparison with heterogeneous ones, is the separation problem. Various biphasic systems comprising phase-transfer systems between aqueous and organic phases have been proposed [81]. Although many organometallic compounds are water sensitive, suitable processes can be constructed under special conditions so that biphasic system can be used. Further developments may be realized where catalytic processes can be performed conveniently in an aqueous phase.

Despite the obvious advantage of circumventing the separation problems, the methodologies to bind transition-metal complexes on the solid phase have not been developed sufficiently well to be accepted generally. Recent technical development in physical means such as STM and AFM to characterize the species on the catalyst surfaces is quite remarkable in enabling one to understand the phenomena taking place on the surfaces. The gap between the heterogeneous and homogeneous catalyses is narrowing. The forthcoming years will see more applications of the well-characterized heterogenized species used in catalytic systems suitable for industrial and laboratory processes.

# 3.5. Computational chemistry and organometallic chemistry

The recent progress in computers and computational chemistry is remarkable. Previously impossible problems, such as the establishment of molecular structures of complexes with large ligands, can now be solved with high speed and precision. The clarification of activation processes in reactions of organometallic complexes is still difficult, but further progress will result in the solving of these problems more easily. More cooperation between the experimental chemists and theoretical chemists will put our knowledge of reactions of organometallic compounds on a sounder basis. It will also bring more challenging problems for theoreticians as well as experimentalists.

Another important study to be achieved is to obtain fundamental data on metal-ligand bond strengths. Only on the basis of these data can one advance further discussions on the feasibility of preparation of specific organometallic compounds and the feasibility of particular reactions. The number of researchers involved in the study is still quite limited and promotion of the study is highly desirable.

#### 3.5.1. Asymmetric catalysts

Asymmetric catalytic processes have made remarkable progress recently. Asymmetric catalytic hydrogenation has been studied extensively and other catalytic processes including allylation of nucleophiles, hydroformylation, and alkyl-aryl cross-coupling processes have been developed fairly well. We shall see further development of other catalytic asymmetric syntheses for obvious importance of biologically active compounds [82,83].

### 4. Conclusions

Adolph von Baeyer, who received the Nobel Prize for his work in organic chemistry at the end of the 19th century is said to have remarked that he would not recommend younger people to work in organic chemistry since it has been fairly exhausted and there may not be a bright future in it. Hieber, who may be regarded as the father of metal carbonyl chemistry, reminisced that he was warned by Mitasch, who was working in chemistry using metal carbonyl compounds, that metal carbonyl chemistry is quite dangerous to work with and he saw no future in the possibility of development of chemistry using metal carbonyl compounds. We all know how remarkable progress has been made in organic chemistry and in metal carbonyl chemistry since then. It would be quite premature to state that organometallic chemistry has matured too much to be a topic for the future. The reasons I have presented will be enough, I hope, to convince the younger generations that there still remains much fun in working with organometallic chemistry.

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