

## Organometallic chemistry. Past, present, and future\*

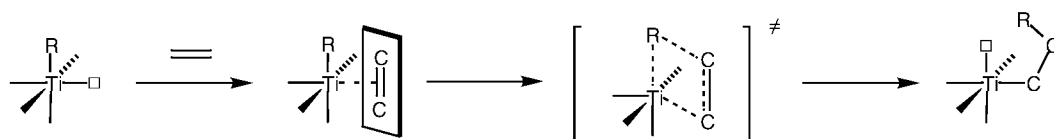
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*Abstract:* Development of organometallic chemistry in the past half century is reviewed from the author's personal viewpoint with focus on the establishment of fundamental concepts relevant to catalysis. Further development in the coming century is expected in view of the diversity of transition-metal complexes and their unique properties.

### IMPACT OF DISCOVERIES

Discoveries of ferrocene and Ziegler catalyst brought a new era to organometallic chemistry that had kept a rather low profile before their advent. The sandwich structure of ferrocene revealed after its serendipitous discovery was fascinating and aroused the interest of both theoretical and synthetic chemists. The  $\pi$  bonding theory was established encompassing the previously known Zeise's complex. The discovery of the Hoechst–Wacker process also served to direct the attention of many people to the potential applicability of palladium-catalyzed organic synthesis. Mechanistic studies of the process revealed the importance of the nucleophilic attack on the  $\pi$ -bonded olefin whose nature is modified by coordination to palladium. Another serendipitous discovery of Ziegler catalyst attracted the great interest of industrial people as well as academic chemists. The active species generated in the Ziegler-type catalyst by the reaction of titanium chlorides and organoaluminum compounds was proposed by Cossee to be a transition-metal alkyl that binds an olefin to initiate the coordination polymerization. The control of the mode of olefin coordination by the stereochemistry around the transition-metal alkyl was proposed as the key feature to produce stereoregular polymers (Scheme 1).



Scheme 1

However, the paucity of isolated transition-metal alkyls and poor understanding of the nature of the transition-metal alkyls hindered the immediate acceptance of the proposal. Quest for the isolable transition-metal alkyls and attempts to elucidate the reason for instability of the  $\sigma$ -bonded transition-metal alkyl complexes led to recognition of the role of the ligands to stabilize the transition-metal alkyls and in control of the behavior of these transition-metal complexes.

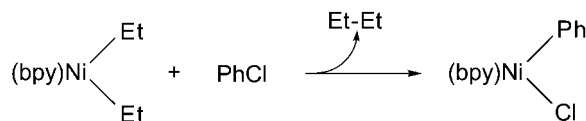
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## DEVELOPMENT OF FUNDAMENTAL CONCEPTS

In the 1960s, various unique properties of low-valent transition-metal complexes were revealed by pioneers in transition-metal chemistry, including Wilke, Wilkinson, and Vaska. Examination of the chemical properties of novel complexes that were synthesized often serendipitously gave birth to important concepts on the elementary processes taking place on transition-metal complexes. Fundamental concepts such as oxidative addition, reductive elimination, olefin and CO insertion into transition-metal alkyl bonds, together with the reverse of these processes such as  $\beta$ -hydrogen elimination and decarbonylation were established in this period. Also established were the concepts of nucleophilic attack on the molecule such as olefin, CO and allyl ligand coordinated to a transition-metal center. Detailed studies on the mode of attack and control of the stereochemistry successfully led to development of asymmetric synthesis. Design of ligands such as DIOP [(*R,R*)-2,3-0-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] and BINAP [(*R*)-2,2'-bis(diphenylphosphino)6,6'-dimethyl-1,1'-binaphthyl] led to achievement of catalytic asymmetric synthesis in high optical yields never realized before.

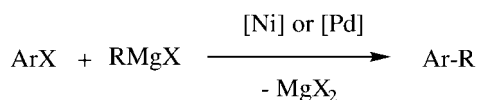
On the other hand, studies on the chemistry of transition-metal complexes led to discoveries of quite novel transition-metal complexes having multiple metal-to-carbon bonds (Fischer- and Schrock-type complexes). Further studies on the chemistry of these carbene and carbyne type complexes, as well as metallacycle compounds formed by their interaction with olefins, led to the development of the concept and application of olefin metathesis reactions. Application of the concept of ring opening olefin metathesis polymerization has provided the great potentiality of affording new types of polymers, whereas ring-closing olefin metathesis is finding a variety of applications in the synthesis of natural products.

Late transition-metal complexes have been found quite suitable as catalysts for organic synthesis, and many synthetic processes have been successfully developed in the past 30 years. The development was accelerated by mutual interaction between organometallic chemists and synthetic organic chemists who were eager to apply the concepts found in organometallic chemistry to new types of organic synthesis. As an example, let me describe a story concerning the development of transition metal-catalyzed cross-coupling processes. In the 1960s and 1970s, we were interested in isolation of transition-metal alkyls and their chemical properties. In a study related to propylene dimerization by a diethylnickel complex having bipyridine ligand the following reaction was found (Scheme 2), and we simply reported the result describing the chemistry without recognizing the application potentiality.



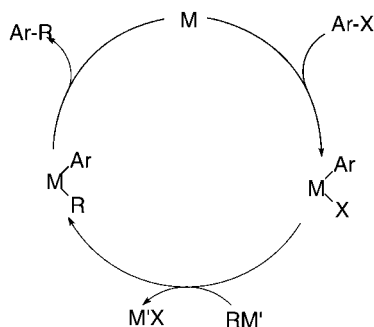
Scheme 2

Application-minded researchers did not overlook the importance of the finding where coupling of the two organic entities and cleavage of carbon-chloride bond are involved. By combining the concept of transmetalation with organometallic compounds such as Grignard reagents, versatile cross coupling processes have been developed by Tamao, Kumada, and Corriu (Scheme 3). The process was later expanded to synthesis employing alkyl-zinc, boron, aluminum, tin, silicon, and zirconium compounds. Many name reactions useful in organic synthesis have been developed.



Scheme 3

Scheme 4 shows the simplified mechanism of cross coupling of aryl halide with alkylmetal compounds where the concepts of oxidative addition, transmetalation, and reductive elimination are involved.



**Scheme 4**

Furthermore, by combination of the oxidative addition of aryl halide to a Pd(0) species with olefin insertion and the subsequent  $\beta$ -hydrogen elimination processes, palladium-catalyzed arylation of olefin was realized. Further application to catalytic carbonylation processes of organic halides was also developed by combining the oxidative addition with the CO insertion.

In contrast to the behavior of late transition-metal complexes that are susceptible to oxidative addition and reductive elimination, early transition-metal complexes had been regarded as more suitable for polymerization catalyst, being amenable to successive olefin insertion processes. Recent studies, however, revealed that late transition-metal complexes could be also transformed to act as polymerization initiators by employment of suitable ligands. More examples of early transition-metal complexes undergoing the oxidative addition and reductive elimination are being accumulated. Thus, the gap between the late and early transition-metal complexes is getting bridged in certain cases. Further design of suitable ligands may modify the properties of transition-metal complexes to fully exploit the potentials of these complexes.

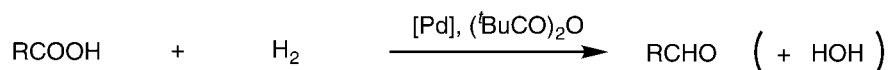
Other unexpected discoveries are the isolation and characterization of dinitrogen-coordinated complexes,  $\eta^2$ -H<sub>2</sub> complexes, and agostic interaction. Discoveries of these new complexes and development of concepts based on their behavior in the realm of organometallic chemistry has influenced and will keep influencing neighboring fields such as organic synthesis, polymer synthesis, heterogeneous catalysis, and materials science.

## PROSPECTS

Because the development of organotransition-metal chemistry coincided with rapid advancement in technical apparatuses such as IR, NMR, and X-ray as well as the fantastic progress of computer abilities, the study of structures and properties of organometallic complexes has been greatly facilitated. Enormous progress in theoretical chemistry enabled the ready determination of the ground-state structures of transition-metal complexes. Structures at transition state in certain reactions can now be clarified with reasonable certainties. Further progress is yet to come to completely change the study of chemistry of organotransition-metal complexes.

Although tremendous progress has been already made, the kinds of transition metals so far studied and utilized have still been limited. Further studies will reveal a greater variety of organotransition-metal complexes spanning the whole Periodic Table to reveal the unique nature of organometallic complexes of each transition metal. By combining the specific properties of the metal itself with particular ligands, further variety of transition-metal complexes will be prepared and their specific properties revealed.

The conventional industrial and laboratory processes in synthesis of organic compounds and polymer materials have been restricted because of the lack of proper available processes, and many of these processes are not environmentally benign nor atom efficient. With development of new methodologies based on the particular properties of organometallic compounds, further change in the approach of organic synthesis is expected to occur. New atom-efficient catalytic processes producing fewer by-products should replace synthetic methods using stoichiometric amounts or reagents with by-products to be discarded. As an example, we happened to find a new catalytic hydrogenation process of converting carboxylic acids directly to aldehydes on the basis of our fundamental studies on activation of C–O bond in carboxylic anhydrides.



Further studies will undoubtedly reveal many other new environmentally benign processes suitable for organic synthesis and for production of important materials of high applicability.

## REFERENCES

For references related to the work of historical significance, see: A. Yamamoto. *J. Organometal. Chem.* **600**, 1 (2000). For the other work of the author, see: A. Yamamoto. *J. Chem. Soc., Dalton Trans.* 1027 (1999) and references cited therein.