The influence of physical organic chemistry on studies of organometallic complexes

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Biography: Akio Yamamoto was born in Tokyo in 1930. He was graduated from Waseda University getting the bachelor's degree in 1954 and moved to Tokyo Institute of Technology to get a doctor's degree in 1959. He was a postdoctoral fellow with Professor Melvin Calvin at the University of California, Berkeley, as a Fulbright fellow in 1960 to 1962 and then with Professor G. Wilke at Max Planck Institute for Coal Research at Mülheim in 1962 to 1963. He was Full Professor of the Research Laboratory of Resources Utilization at Tokyo Institute of Technology since 1971 and became Director in 1988. He moved to Waseda University in 1990 as a Professor. He has been the recipient of the Chemical Society of Japan Award, The Society of Polymer Science Award, and the Violet Ribbon Award by the Japanese government, and served as Science Advisor for the Ministry of Education, Science, and Culture and as the President of the Chemical Society of Japan in 1995-1996.

The first organotransition metal complex, $[PtCl_3(C_2H_4)]K \cdot H_2O$ was prepared serendipitously in 1825 and was reported in Latin (1). However, unequivocal characterization of its structure was made much later, to reveal its remarkable structure with the ethylene molecule coordinated perpendicular to the $PtCl_3$ molecular plane, by means of X-ray and neutron diffraction crystallographic studies. The bonding mode was elucidated on the basis of molecular orbital theory by Dewar, Chatt, and Duncanson in the early 1950's (2). This example illustrates how the development of the chemistry of organotransition metal complexes has been helped by physico-chemical methods and molecular orbital theory. The rapid surge of organotransition metal chemistry in the 1950's, which was sometimes dubbed as the Renaissance of inorganic chemistry, coincided with the advent and spreading use of modern physico-chemical means such as IR and NMR spectroscopies as well as X-ray crystallography from the very beginning of the growth of organotransition metal chemistry. It is fascinating to read how Wilkinson and Woodward were led to the proposal of the sandwich structure for ferrocene with full utilization of the physico-chemical means available at the time (3). Discovery and structure elucidation of bis(benzene)chromium and metal-carbene complexes by E. O. Fischer provide us with other examples of the happy initial period of development in organotransition metal chemistry aided by physico-chemical methods and molecular orbital theory.

An important contribution of NMR spectroscopy to organotransition metal chemistry is the establishment of the concept of the non-rigid dynamic properties of organotransition metal complexes in solution (4). Soon after the structure of bis(cyclopentadienyl)iron was established as having the two cyclopentadienyl rings bound with the central iron atom in a parallel manner, Wilkinson and coworkers found other cyclopentadienyl complexes of transition elements in which a central metal atom is bonded with a cyclopentadienyl moiety through a sigma bond whereas NMR spectroscopy at room temperature indicated the presence of only one type of CH in the cyclopentadienyl ring. This discovery was the first example of fluxional behavior of organotransition metal complexes (5). Further intriguing development was made in the elucidation of the stereochemical isomerization of $Fe(CO)_5$ between a trigonal bipyramid configuration and a square pyramidal form. The so-called Berry mechanism to account for the pseudorotation of the penta-coordinated complexes brought us an essential concept regarding the stereochemical transformations of penta-coordinate transition metal complexes (4).

The concept of fluxionality based on the behavior of the simplest transition metal complexes spread to other complexes having more complicated structures. Based on the information of the behavior of organotransition metal complexes we are now in a situation to specifically control synthetic routes to complicated organic compounds utilizing the NMR information, for example, of the behavior of π-allylic complexes.

Discovery of the Ziegler-Natta polymerization (6) attracted the worldwide recognition by industrial chemists of the importance of organotransition metal complexes. Although the clarification of the nature of the active site in the Ziegler type catalyst has been hindered by the complex and heterogeneous nature of the catalyst systems, the original proposal of Cossee (7) to describe the active site of the Ziegler catalyst system essentially as an alkyltitanium compex coordinated with an olefin gave a good account of the basic properties of the Ziegler type catalysts. However, because of the scarcity of isolable alkyltransition metal complexes the proposal had remained as a hypothesis until recently. It is surprising to recall now that in 1950's even a theory to account for the instability and unavailability of alkyltransition metal complexes was proposed (8). Fortunately this theory did not have a universal utility and we now have quite a variety of alkyltransition metal complexes isolated which are suitable for fundamental studies regarding the elementary steps in the catalytic processes.

During the initial period of studies on the mechanism of stereospecific polymerization, Natta's school (9) as well as Miyazawa (10) and Ikeda (11) in Japan studied the opening mode of propylene and ethylene with Ziegler type catalysts by using isotope-labelled monomers, an approach often used in physical organic chemistry. They succeeded in establishing the *cis* opening mode of the double bonds in the monomers in the olefin polymerization. The results are consistent with the coordination of the olefins in a side-on manner (π-type coordination) with the transition metal active center having the alkyl chain bound to the metal with a σ-bond.

A development in a field gives an impact to a field nearby. The concept of side-on coordination of an olefin with the active metal center led to further development of a concept of steric control of olefin coordination, studied by using optically active ligands and later to successful commercialization of asymmetric catalysis (12). The development of the concept of asymmetric olefin hydrogenation was also based on various basic works, notably the work of Wilkinson on olefin hydrogenation with rhodium and ruthenium catalysts, where every possible approach available in physical organic chemistry was employed (13).
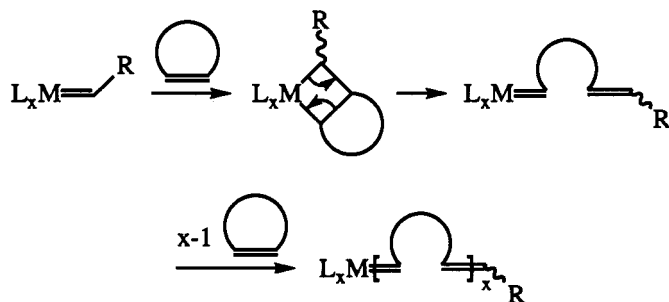
The concept of controlling the coordination and insertion mode of an olefin into a transition metal alkyl active center coordinated with a chiral ligand(s) gave a feedback to stereospecific synthesis of polyolefins by employing metallocene catalyst systems having a C_2 symmetry around the active center (14). The metallocene systems where two specifically substituted cyclopentadienyl rings are fixed by a bridge in a way such as shown in Scheme 1 allow fine tuning of the active center, thus controlling the olefin coordination and the subsequent insertions.
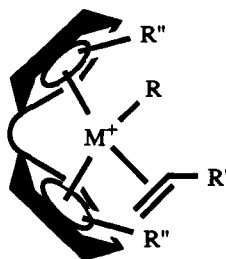
Scheme 1. The concept of active species in metallocene-catalyzed polymerization where a transition metal alkyl coordinated with an olefin plays a crucial role.

The other development worth mentioning here is the ring-opening metathesis polymerization (ROMP) of cyclic olefins, where a polymer growth from a transition metal active center bearing an alkylidene ligand takes place on interaction with an incoming olefin to form a four-membered ring complex (metallacyclobutane) that rearranges with double bond migration to give a metallacarbene complex with a growing polymer end (Scheme 2) (15).

It is interesting to note that the original discovery of this type of polymerization was made by Natta in the early 1960's in a study of polymerization of cyclic olefins (16), and mechanistic studies using labeled compounds established that a double bond rearrangement is involved in the reaction (17). At the same time a heterogeneous catalyst system such as alumina impregnated with molybdenum or tungsten carbonyls was found to convert propylene into a mixture of ethylene and 2-butene in a process called the olefin metathesis or olefin disproportionation. The mechanism of the olefin metathesis process as well as the ring opening polymerization of cyclic olefins attracted much attention (18). After a heated controversy on the mechanism

Scheme 2. The concept of ring-opening metathesis polymerization involving the coordination of an olefin to a metallacarbene complex forming a metallacyclobutane that rearranges to a carbene complex with a growing polymer chain.

of olefin metathesis by researchers utilizing various approaches used in physical organic chemistry and molecular orbital concepts, it was finally established that the olefin metathesis takes a course involving carbene and metallacyclobutane intermediates (19) and a mechanism involving a quasi-cyclobutane intermediate was refuted. Further development of the application of the cleavage of metallacyclobutanes involving rearrangement of double bonds led to evolution of the concept of ring closing metathesis (20). On the other hand, the concept of formation of an alkylidene-metal hydride complex by abstraction of an α-hydrogen from the alkyl group attached to metal through an agostic interaction led to a proposal of an intermediate having an alkylidene-metal entity that may exert an important influence on the course of olefin polymerization in Ziegler type catalysis (21).

So evolved the chemistry of organotransition metal complexes aided with the development of physicochemical means and the progress of molecular orbital theories. The development has been accelerated by mutual interaction with nearby fields such as polymer chemistry and organic synthesis and cross fertilization resulted.

Those people who were involved in the early development of organotransition metal chemistry were truly fortunate to witness the rapid growth of organotransition metal chemistry, the discovery of unexpected phenomena, and the synthesis of novel complexes; naturally experiencing myriad difficulties in their going through untrodden paths in their pioneering work. Various discoveries made on serendipitous findings were reported one after another.

The following personal account may be of interest for the non-Japanese physical organic chemist readers who are not familiar with the basic concepts in homogeneous catalysis using organometallic compounds. When I joined the organotransition metal chemistry myself, the first period of gold-rush was over, but still I could fully enjoy the sensation that even a young and unexperienced youth as I was might be given a chance of finding something big as long as I have kept working in the field of organotransition metal chemistry (22).
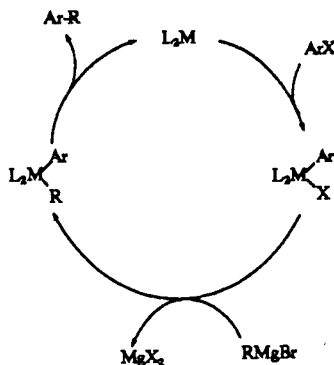
As I have written in a review article on the development of organometallic chemistry in Japan (23), Japan was a latecomer in the development of science and technology. When Japan opened her ports to foreign countries after her seclusion for more than two centuries, the industrial revolution was already over, leaving behind oriental countries including Japan in an underdeveloped state. When exposed to the advanced science and technologies developed in western countries, Japanese were startled by the enormous difference between the western level of science and technology and that of Japan. It was a long and hard catch-up process for Japanese to reach the level of western science and technology in the fields where the basic progress had been already made. However, as far as organometallic chemistry was concerned the difference was not so huge to let us despair.

The fertile field of organotransition metal chemistry had been opened when I started my work in Japan after returning from Germany, where I had the privilege of working in Wilke's group. The pioneering work of G. Wilke (24), who elegantly showed that isolated and well-characterized pure complexes such as naked nickel complexes, as he often used to describe, having only hydrocarbon ligands, can serve as excellent catalysts for transformation of dienes and α-olefins. The discovery removed the myth attached to catalysis, which was somehow believed to need the mysterious action of a metal surface. In my work started later in Japan I was surprised by an accidental finding of the formation of thermally stable alkyl complexes of nickel, cobalt and iron that are active in butadiene oligomerization when we were seeking isolation of low valent

complexes of these metals coordinated with ligands such as 2,2′-bipyridine from catalytic systems to oligomerize butadiene. The characterization of the isolated complexes took time to confirm the attachment of the ethyl groups with these transition metals, since we were hindered by the unavailability of NMR spectrophotometers and automatic X-ray diffractometers at that time and had to resort mostly to chemical means to identify the isolated complexes (Japan was still poor in the early 1960's after the end of the devastating World War II). After the successful isolation of the alkylnickel complexes various transition metal alkyls and hydrides having supporting ligands such as nitrogen bases and tertiary phosphines could be prepared.

With the increase in the number of isolated organotransition metal complexes and clarification of the behavior of these complexes the basic concepts concerning the elementary processes relevant to catalysis gradually evolved. The following are the most important elementary processes related to transition metal-catalyzed organic syntheses, particularly those involving the late transition metal complexes: (i) oxidative addition and reductive elimination, (ii) insertion of unsaturated compounds such as olefins and carbon monoxide into transition metal-to-carbon bonds and the reverse deinsertion processes, and (iii) external attack of nucleophiles on the coordinated ligands such as olefin, π-allyl ligand, and carbon monoxide. The elucidation of the fundamental processes led to gradual clarification of elementary steps in metal-catalyzed homogeneous systems that are usually composed of multistep catalytic cycles.

Let us take an example of alkyl-aryl coupling processes catalyzed by palladium complexes that have been used quite extensively in organic synthesis (25) along with other palladium-catalyzed synthetic methods, developed by Heck, Tsuji, and Trost (26). The basic catalytic cycle of the palladium-catalyzed cross-coupling process between aryl halides and organometallic compounds of main-group elements can be expressed by Scheme 3.

Ar-R L_2M ArX

$L_2M \begin{smallmatrix} Ar \\ R \end{smallmatrix}$ $L_2M \begin{smallmatrix} Ar \\ X \end{smallmatrix}$

MgX_2 RMgBr

Scheme 3. The mechanism of metal-catalyzed cross-coupling reaction between aryl halide and alkylmagnesium bromide.

The catalytic cycle can be represented by combination of the following elementary processes: (i) oxidative addition of aryl halide to a Pd(0) complex to give an arylpalladium halide complex, (ii) transmetallation of an alkyl group from an alkylmagnesium bromide to palladium to give an intermediate having both alkyl and aryl ligands, and (iii) reductive elimination to liberate the cross-coupling product of the alkyl and aryl groups with regeneration of a palladium(0) species that carries further the catalytic cycle. The essential process apparently looks simple but a detailed study revealed that the catalytic cycle in fact involves further complications involving stereoisomerism of the square planar *trans* and *cis* palladium complexes (27). Although I would not go into detail here about the complexity of the results, in-depth mechanistic studies regarding the elementary processes employing kinetic as well as isotopic techniques revealed unexpected behavior of simple dialkylpalladium complexes having tertiary phosphine ligands as supporting ligands (22, 28). The kinetic study on the thermolysis of dialkylpalladium complexes having two tertiary phosphines varied depending on the stereochemistry of the complexes. We found that the *trans*-dimethylpalladium complex must first be isomerized to the *cis* complex to undergo the reductive elimination to produce the coupling product. Also for the reductive elimination of Me-Me from *cis*-PdMe$_2$L$_2$ to proceed, partial dissociation of a tertiary phosphine from the square planar complex was required. The results suggested the involvement of a T-shaped dialkylpalladium intermediate to cause the reductive elimination (Scheme 4).

As a synthetic experimental chemist I could not confidently propose the involvement of a T-shaped dialkylpalladium intermediate as a necessary step in the reductive elimination from a dialkylpalladium complex having two tertiary phosphine ligands. The support was provided by theoretical studies of Tatsumi and
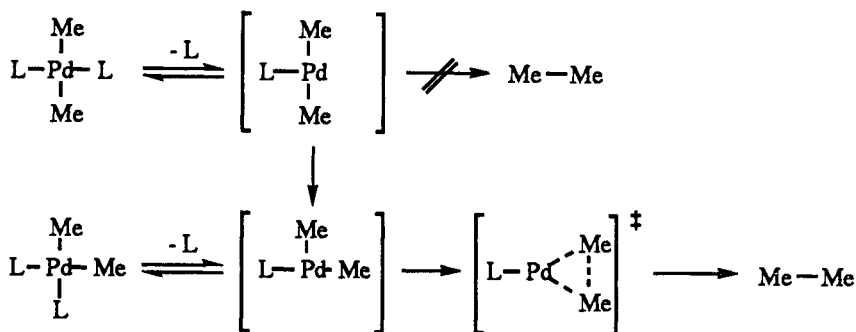
Scheme 4. The courses of reductive elimination of ethane from *cis-* and *trans-*PdMe$_2$L$_2$ (L = tertiary phosphine) through T-shaped *cis-* and *trans-*PdMe$_2$L intermediates.

Hoffmann (29), which were extended further to account for the courses of reductive elimination from pentacoordinated dialkylnickel complexes involving square planar and trigonal bipyramidal intermediates (30).

The assumption of the T-shaped intermediates in the reaction courses of dialkylpalladium complexes was also applicable to account for the product distributions in insertion of CO into diethyl- and dimethylpalladium complexes having two tertiary phosphine ligands of *trans* and *cis* configurations (31). Our further attempt to clarify the reaction course of the alkylpalladium complexes with carbon monoxide led to finding of a novel double carbonylation process to convert aryl and allylic halides into α-keto acid derivatives (32, 33).

Now about the prospect of the possible development of chemistry in the 21st century. From the above brief account of the development of organotransition metal chemistry and homogeneous catalysis, it is evident that the recent progress was helped enormously by the concepts and methodologies developed in physical organic chemistry. This is no wonder since organometallic chemistry is a discipline in, or close to, organic chemistry.

In every field you can find pessimistic people. Even in organometallic chemistry, which is a newcomer in the vast field of organic chemistry, some people say that organometallic chemistry is now matured and you may not find exciting things happen in the future. It is my firm belief that we still have tremendous opportunities in the field of organometallic chemistry.

It is amusing to read the reminiscence of Walter Hieber, the great pioneer of metal carbonyls. When he got iron pentacarbonyl in 1927 from Mittasch of BASF he was emphatically warned of the great danger inherent in the use of highly toxic carbonyl complexes. Mittasch coupled his warning with the comment that in this field one could expect only a great deal of trouble and results of little scientific value (34)! It is not necessary to tell you that the subsequent growth of organometallic chemistry, partly based on information of metal carbonyl chemistry, has been fantastic and has had a far reaching impact on basic science as well as on laboratory and industrial applications. In organometallic chemistry, where we deal with such a variety of metals in an enormous number of combinations with organic ligands, one does not have to be afraid of a dearth of research topics.

As a synthetic organometallic chemist I am not in a situation to venture the prophecy of the future of the discipline of physical organic chemistry in the 21st Century. But I do hope that physical organic chemistry keeps providing us with useful tools for clarifying mechanisms of reactions and giving us the in-depth knowledge concerning what is happening at the molecular level.

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