



Design of catalytic processes based on studies of elementary processes

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Abstract

In the first part of the review, the personal reminiscences of the development period of organometallic chemistry are described referring to the unexpected discoveries of late transition metal alkyls through the effort of finding an active species involved in catalysis. The isolation and examination of the behavior of these transition metal complexes led to findings of elementary processes important in catalysis. In the second part of the account, applications of the newly found elementary processes to organic syntheses are described, with emphasis on the recent development of environmentally benign catalytic processes utilizing the concept of the C–O bond cleavage in carboxylic acid derivatives combined with other elementary processes. The recently developed catalytic processes include conversion of carboxylic anhydrides and acids into aldehydes, ketones, perfluoroketones, benzylation of olefins, and conversion of allylic formates into unsaturated carboxylic acids.

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1. Introduction

On the occasion of the 40th Anniversary of the Journal of Organometallic Chemistry I would like to congratulate the publisher, the editors, and researchers who have contributed to the development of organometallic chemistry. I have had a fortunate experience of witnessing the rapid burst of the new field over the 40 years. In the early 1960s almost everything we were studying was new and the frontiers were wide open before us, although we had uncertainties and anxieties in deciding the directions to go. As an old fellow who experienced the excitement of the burgeoning period, I feel the responsibility of leaving some part of my experiences on the record for the future generations hoping to convey them the excitement of being involved with organometallic chemistry in the early period.

Since I have already written a few review articles recalling the progress of organometallic chemistry in Japan [1,2] and my personal reminiscences on some of my past work [3–5], I would like to add some other aspects here avoiding undue overlap with my previous accounts.

2. Situations of organometallic chemistry in the early 1960s

The organometallic chemistry in the early 1960s was in a taking off stage preceding the period when the progress picked up the momentum and reached a steady growth rate. The discoveries of ferrocene and Ziegler type catalysts that took place in the early ninety fifties clearly marked the tremendous impact of organometallic chemistry on the future development of chemistry. The launching of the Journal of Organometallic Chemistry marked an epoch of the birth of the new field.

Quite fortunately I had the experience of staying in Max Planck Institute for Coal Research as a Humboldt

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postdoctoral fellow in the period of 1962–1963 for 9 months, when Professor K. Ziegler was the director of the Institute and Professor G. Wilke was then a group leader.

It was an exciting time. After the discoveries of the Ziegler catalyst [6] in the Institute and the tremendous development afterwards driven by Natta's group [7,8], Wilke and his coworkers [9] were producing fascinating fundamental discoveries with a huge potential for future applications. Before the advent of their work the catalysis was regarded as operated by some mysterious phenomena occurring on the solid surface. Wilke established that catalytic processes could be explained in principles of chemistry by demonstrating that the chemistry of isolated organotransition metal complexes can be treated as in organic chemistry. He and his group demonstrated that the effect of ligand and transition metals in active catalysts could account for various aspects of catalytic processes. As a young and green fellow who just entered the field I was strongly influenced by his elegant way of research and was fascinated by the clear cut explanations offered by them, examining the properties of the newly isolated catalytically active transition metal complexes.

In the 1950s and in 1960s Japan was in the takeoff period in economy as well as in science and technology. Polymer science and technology looked rosy in prospect. Ziegler–Natta type mixed catalysts were attracting the attention of the both industrial and academic sectors. However, clarifying the mechanism of the mixed catalysts composed of transition metal compounds and organoaluminum compounds was a tough subject baffling attempts of various researchers. Based on my experiences I gained in the Wilke group, I felt that the mechanism of olefin polymerization with Ziegler–Natta type catalysts could be explained by examining the behavior of model complexes of transition metals having suitable ligands controlling the catalytic activity of metal centers.

2.1. Isolation of late transition metal alkyls and their catalytic activities

It was at the time that Cossee proposed a simple and clear-cut mechanism for explaining the transition metal-initiated polymerization processes by assuming the transition metal alkyl as the catalyst center generated in a mixture of a titanium chloride and an alkylaluminum compound. He proposed further that an olefin coordinates to the titanium alkyl and is inserted into the metal–alkyl bond to initiate the olefin polymerization and the subsequent propagation processes that lead to polymers [10].

The mechanism accommodated the previous knowledge of organotransition metal chemistry involving the formation of transition metal alkyls and olefin coordi-

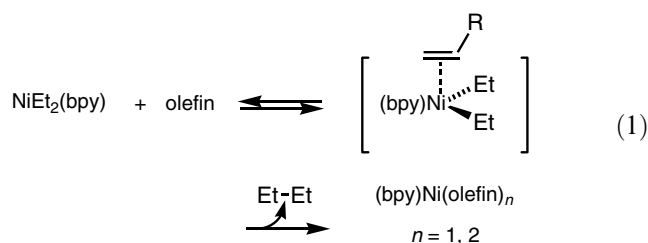
nation through the metal– π bond. A problem of the hypothesis was the lack of information about the behavior of transition metal alkyls due to their instability. Only limited examples of transition metal alkyls were known at the time and the concept of activation of transition metal alkyls by the olefin coordination was not established [11]. Shortly before the time when the paper by Cossee came to my attention, Professor Yasuzo Uchida of Tokyo University approached me after I gave a lecture on the isolation and properties of three-coordinated nickel(0) complexes, bonded with norbornene and dicyclopentadiene, which I could isolate in Wilke's group. He proposed me a joint work to attempt isolation of an active species in the butadiene oligomerization catalysts they were working. His group was examining the butadiene oligomerization with mixed catalyst systems containing nickel, cobalt and iron acetylacetonates with triethylaluminum in the presence of ligands such as tertiary phosphines and 2,2'-bipyridine. Having attended my talk on the isolation of unstable π complexes, Uchida thought that the experiences I gained in the Wilke group might be useful in isolating low-valent transition metal complexes from their catalyst systems.

The joint work we started turned out to be an extremely lucky venture. We succeeded in isolation of $\text{NiEt}_2(\text{bpy})$ (**1**), a square planar nickel diethyl complex having the bipyridine ligand, quite unexpectedly, in the almost first attempt of our experiment treating nickel acetylacetonate with diethylaluminum monoethoxide in the presence of bipyridine [12]. It took some time to convince us of the identity of the isolated complex mostly on the basis of chemical means but it turned out to be one of the then rare transition metal alkyl complexes.

In a similar experiment we could isolate $\text{FeEt}_2(\text{bpy})_2$ (**2**), an octahedral iron diethyl complex coordinated with two bipyridine ligands from the mixture of iron acetylacetonate, diethylaluminum monoethoxide, and bipyridine [13].

2.2. Importance of elementary processes

The isolation of the nickeldiethyl and iron diethyl complexes coordinated with the bipyridine ligand(s) provided us with the opportunities of examining the feasibility of the Cossee mechanism. Treatment of the diethylnickel complex (**1**) with olefins such as acrylonitrile yielded olefin-coordinated diethylnickel complexes having the bipyridine ligand at low temperatures. Bringing the complexes to room temperature caused coupling of the two ethyl groups releasing butane with liberation of nickel(0) complexes coordinated with various olefins. The result provided an indirect support for the validity of the concept of activation of a metal–alkyl bond by π coordination of an olefin [14].



We did not realize at the time, but this was one of the very early examples of demonstration of the reductive elimination as an important elementary process in organotransition metal chemistry. The concepts of elementary processes including oxidative addition, reductive elimination, olefin and CO insertion and deinsertion, and nucleophilic attack on the olefin or CO coordinated with the metal, were gradually being recognized among organometallic chemists [15].

In the period of the 1960s when the early issues of the Journal of the Organometallic Chemistry were launched the examples of thermally stable transition metal alkyls were quite limited and the concept of reductive elimination was not presented in a clear form. It was the time when G. Wilkinson was working on the mechanisms of olefin hydrogenation and hydroformylation and proposed clear-cut mechanisms for these processes on the basis of elementary processes. At that time he also proposed that the most important route to cause the decomposition of transition metal alkyls is through the β -hydrogen abstraction by a transition metal to generate a transition metal hydride and an olefin. He did not place importance then on the other route leading to decomposition through the reductive elimination.

2.3. Study of olefin polymerization mechanisms with transition metal alkyls and hydrides

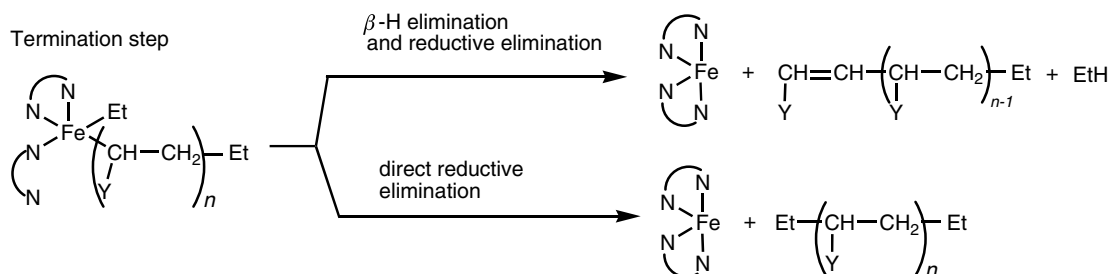
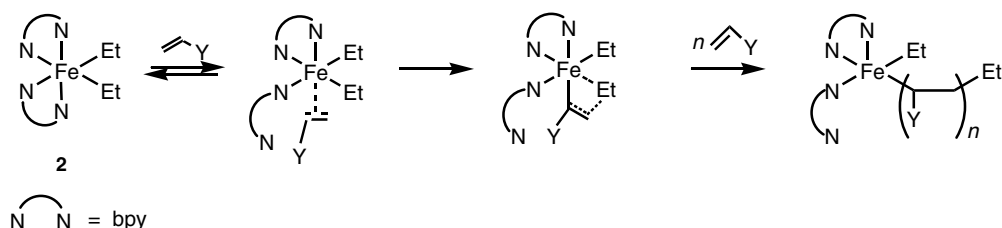
Treatment of the iron diethyl complex **2** with vinyl monomers led to their polymerization without the aid of alkylaluminum compounds, providing an example of coordination polymerization. Although our system involving late transition metal alkyls differed from the early transition metal alkyls, for which Cossee proposed his hypothesis, I was convinced that proper control of the ligands would somehow fill the gaps between the early and late transition metal alkyls.

The polymerization mechanism of olefins initiated by the iron diethyl complex (**2**) as shown in Scheme 1 accounted for essential features of the olefin polymerization.

We worked on the olefin polymerization with transition metal alkyls and hydrides for about 10 years and thought that we had a relatively clear picture of the olefin polymerization mechanism. There were very few research groups following the similar line and our work did not attract much attention.

However, after we left the project of olefin polymerization using isolated transition metal alkyls, the pronounced enhancement of the olefin polymerization activity of metallocene-type early transition metal complexes was realized by Kaminsky by using MAO (methylaluminoxane). The work was further developed to stereospecific polymerization of propylene and other monomers by Brintzinger and others to attract a wide interest among the industrial and academic researchers [16]. On the other hand, Brookhart and Gibson [17] made an epoch-making breakthrough in the olefin

Initiation and propagation steps



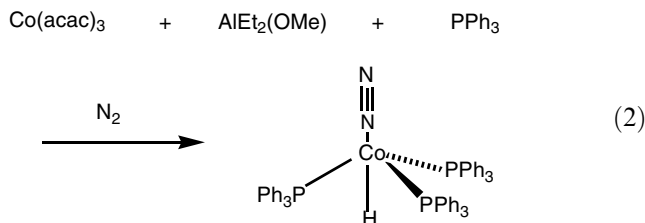
Scheme 1. Mechanisms of olefin polymerization by iron ethyl complex having the bipyridine ligands.

polymerization employing diimine-coordinated late transition metal complexes in combination with MAO. They found that late transition metals of iron, cobalt, nickel and palladium having diimine ligands substituted with bulky groups are capable of acting as excellent olefin polymerization catalysts.

In the both Brintzinger–Kaminsky systems and Brookhart–Gibson systems the steric effects of the ligands were revealed to have pronounced influence in controlling the coordination of the monomer and the chain-propagation processes. Another important factor revealed was creation of an active cationic transition metal center on interaction of the transition metal complexes with the MAO in controlling the catalyst activity. Since we were concerned ourselves in simplified systems coordinated with simple ligands such as bipyridine without examining the steric effect of the ligands extensively, we failed in developing more active catalyst systems. Another factor we overlooked was the role of cationic transition metal complexes in controlling the catalyst activities, although we found later the pronounced effect of creating a cationic center in relation to the enhancement of various catalyst activities [18,19].

In retrospect we may have abandoned the issue of olefin polymerization with transition metal alkyls somewhat prematurely [20]. However, I do not have much regret in what we did, since we have been able to enjoy the other aspects of chemistry of organometallic complexes related to organic synthesis, thanks to the wide frontiers left unexplored yet in the arena of organotransition metal chemistry.

It was around the time that we isolated a nitrogen-coordinated cobalt complex serendipitously [21] when we were working to isolate a cobalt complex that may show a catalytic activity for butadiene oligomerization. We were fortunate at the time that we were poor and could not use argon as a blanket gas, as it was the usual practice at the much richer Max Planck Institute for Coal Research. In fact, the nitrogen we used reacted with the cobalt complex having triphenylphosphine ligands to give one of the very first N₂-coordinated complexes (Eq. (2)). If we were using argon gas only, we would not have come across with the discovery of nitrogen binding with cobalt.



We were excited on the finding since we had never dreamed of encountering such an unsuspected discovery ourselves. I found later that this complex was

nicknamed as “Pearl Harbor Complex” implying the surprise attack associated with the name of Admiral Yamamoto who directed the attack. The name is not so agreeable for a Japanese, but I can understand the shock it gave to people who were working closely in similar systems using argon, since we were most surprised ourselves by the unexpected finding.

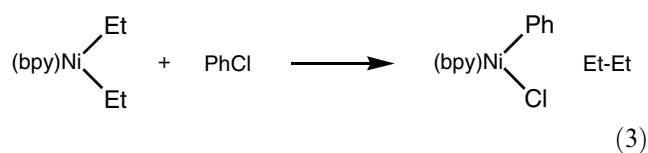
Once the first example of the isolation of an N₂-coordinated complex is made, the ensuing examples came in succession to make the N₂-coordination a common place. At that time we entertained ourselves with the possible prospect of discovering a catalytic system for nitrogen fixation. The issue, however, turned out to be a pretty tough one and we retreated from the field after we found some examples of nitrogen fixation with early as well as late transition metals [22]. Thus we returned to the familiar arena of organotransition metal chemistry that always provided us with intriguing and unexpected findings.

3. Design of catalytic processes based on studies of elementary processes

3.1. Design of catalytic processes involving carbon–halogen bond cleavage

Since we encountered the first transition metal alkyl complexes we were concerned for some time with attempts of isolation of new alkyls and hydrides of transition metals including Cr, Mn, Fe, Co, Ni, Ru, Rh, and Cu and studied their chemical behaviors in detail. Every organotransition metal complex differed from each other and exhibited interesting particular behavior. However, if one is too much concerned with pursuit of a project without paying attention on the neighboring area, one may miss the good opportunities of finding applications. As I have already described in the special issue commemorating the 40th anniversary of the discovery of cross-coupling process [2] we missed a chance of finding quite interesting and general method for accomplishing the transition metal-catalyzed C–C coupling processes.

After our successful isolation of the nickeldiethyl complex **1**, we were involved with its characterization in relation to propylene dimerization [23]. We treated it with chlorobenzene and observed the formation of a new phenylnickel chloride complex with release of butane by coupling of the two ethyl groups,



This was an interesting observation showing the effect of interaction of chlorobenzene to cause reductive elimination of the two ethyl groups with concomitant oxidative addition of chlorobenzene. We did not realize the applicability of the reaction at the time. Keen observers with application mind did not overlook the potential of application of the reaction to organic synthesis. Tamao and Kumada [24] in Japan and Corriu [25] in France came to the idea of applying the reaction to realize the catalytic cross coupling process of aryl halide and alkyl Grignard agents by a mechanism as shown in Scheme 2.

The mechanism of the catalytic cross-coupling process can be accounted for by combination of simple elementary processes involving oxidative addition of aryl halide with a zero valent metal complex, transmetalation of the halide ligand with added metal alkyl compound, and reductive elimination of the aryl and alkyl groups [26]. Crucial idea here to devise the catalytic cycle was incorporation of the transmetalation process in the catalytic cycle.

Once a novel reaction involving organometallic compounds such as Eq. (3) is found, it provides with opportunities of getting incorporated into a catalytic cycle in combination with other known elementary processes as exemplified in Scheme 2. The experience of having missed the chance of discovering the important catalytic process gave me a lesson to be more attentive to application of the elementary processes to organic synthesis.

Once a successful incorporation of the elementary process in a catalytic cycle is achieved, many other researchers join the game attempting to modify the catalytic cycle for expanding the applicability of the process or for enhancing the catalytic turnover. The discovery of the nickel-catalyzed cross coupling process marked the epoch of directing attention of synthesis-minded people

to organometallic chemistry. The discovery of the nickel-based catalytic cross coupling process was followed by finding of more convenient and versatile processes using palladium complexes in combination with various organometallic agents including Sn, B, Al, Zn, Li, Si, and Zr. Some types of organometallic compounds such as organoboron compounds are getting more popularity among synthetic organic chemists because of their less toxicity and convenience of handling.

We ourselves have extended the applicability of the cross coupling process by using bifunctional substrates such as dichloroarenes to prepare polyarenes by polycondensation process [27].

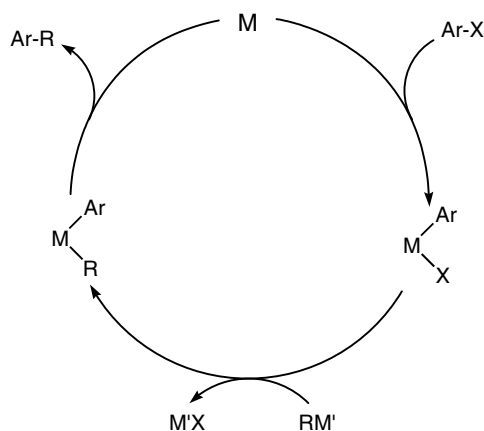
It was around the same time that Mizoroki and Heck developed a palladium-catalyzed process of substituting an olefin with aryl groups [28]. The process also involves the oxidative addition of aryl halide to a Pd(0) complex to give arylpalladium halide, where an olefin is inserted into the aryl–Pd bond to be followed by β -hydrogen elimination releasing the aryl-substituted olefin.

Another important means indispensable now in organic synthesis is discovery of palladium-catalyzed allylation of nucleophiles developed by Tsuji and Trost [29].

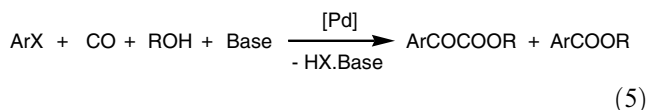
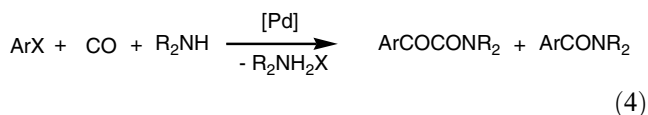
This was the period when these palladium-catalyzed processes were being developed in a rapid succession and marked the rapid growth of OMCOS (Organometallic Chemistry directed toward Organic Synthesis).

We also developed another type of palladium-catalyzed process involving the concept of aryl-halide cleavage on interaction with a Pd(0) catalyst. The process of double carbonylation of aryl halides to give α -keto acid derivatives [30] was developed through our fundamental studies on the mechanisms of reductive elimination of dialkylpalladium complexes [31] and of the CO insertion processes into Pd–alkyl bond [32]. The idea to develop the catalytic double carbonylation process came to us through our studies on the courses of CO insertion into Pd–alkyl bond. In our attempts to clarify the mechanisms of CO insertion into the Pd–alkyl bonds and the ensuing isomerization we assumed the intermediate formation of acylpalladium species. Expecting the generation of an amide we treated the acylpalladium species with CO and a secondary amine to be surprised by finding the formation of an α -keto amide in addition to the expected amide.

Upon finding the formation of α -keto amide we did not miss the chance of applying the finding to development of a catalytic process this time. By combining the known process of oxidative addition of aryl halide with the Pd(0) species giving arylpalladium halide with the newly discovered process to produce α -keto amide, we could develop a novel process of catalytic double carbonylation of aryl halides to prepare α -keto amides and esters [33].



Scheme 2. Mechanism of transition metal-catalyzed cross coupling of aryl halide with alkylmetal compound.

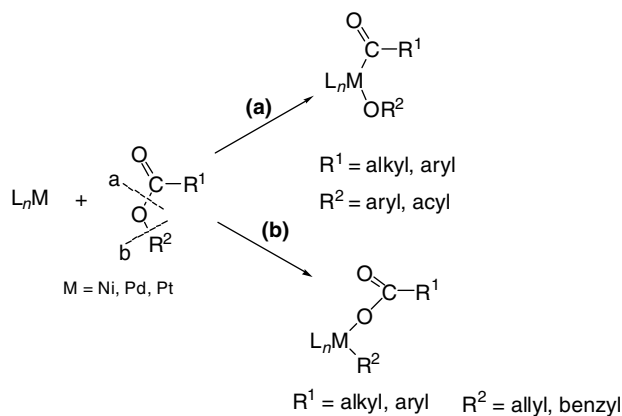


3.2. Toward development of environmentally benign synthetic processes

Although the palladium-catalyzed C–C coupling processes utilizing the oxidative addition of aryl or vinyl halides have been widely utilized, a disadvantage is involved in the process that the organic halides have to be prepared first, and later the halide used has to be removed as metal halides or as salts of hydrogen halide with the aid of a base producing waste salts.

For making these transition metal-catalyzed processes more atom efficient and environmentally benign we started examination of the cleavage of the C–O bonds in oxygen-containing organic compounds on interaction with low valent transition metal complexes [34,35]. We found first that Ni(0) complexes interact with various organic compounds causing cleavage of the C–O bonds [36]. Scheme 3 shows examples of cleavage of the C–O bonds in carboxylic esters and carboxylic anhydrides on interaction with low valent transition metal complexes.

During my tenure at Tokyo Institute of Technology before the preset retirement age of 60, we could not make this process catalytic. Fortunately, I was invited by Waseda University and could continue the research there and develop some new processes to make the C–O bond cleavage processes catalytically useful by

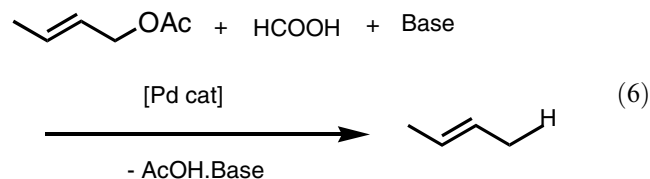


Scheme 3. Two types of C–O bond cleavage in the reactions of carboxylic esters and anhydrides with low valent transition metal complexes.

combining them with other fundamental processes. In the following section I would like to describe such catalytic processes based on the concept of the C–O bond cleavage applied to catalytic processes [37].

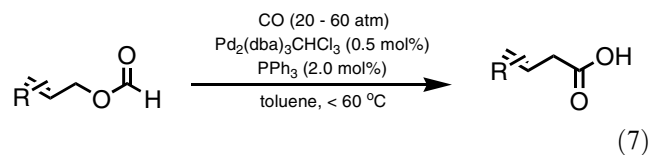
3.2.1. Application of the C–O bond cleavage in allylic carboxylates to organic synthesis

The C–O bond in allylic carboxylates or carbonates can be cleaved readily on interaction with electron-rich nickel(0) and palladium(0) complexes. Tsuji and Trost developed catalytic processes of allylation of nucleophiles utilizing the C–O bond cleavage process combining it with nucleophilic attack on the η^3 -allylpalladium intermediate involved. Another type of application using the allyl carboxylate is palladium-catalyzed reductive conversion of allylic carboxylate into olefins in the presence of a formic acid and a base [38].

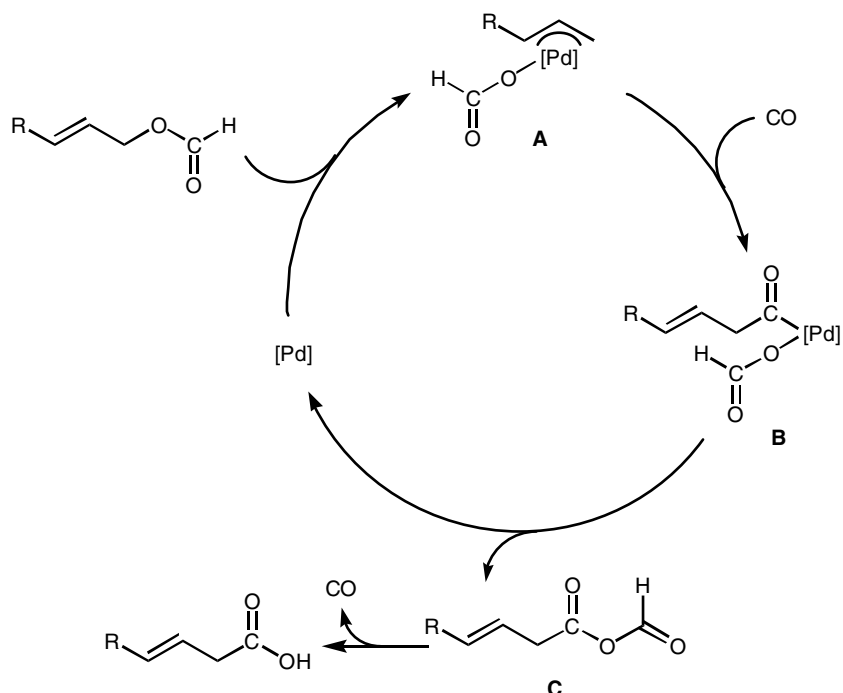


Mechanistic studies on the catalytic conversion of the allylic carboxylates into olefins indicated that the reaction proceeds through oxidative addition of the allyl carboxylate with a Pd(0) species to give a η^3 -allylpalladium carboxylate and the subsequent exchange of the carboxylate ligand with the formate anion giving a η^3 -allylpalladium formate. The decarboxylation of the formate ligand yielding an allylpalladium hydride followed by reductive elimination produces the olefin as we established on the basis of the behavior of model complexes [39].

We found further that introduction of carbon monoxide into the system containing allylic formates unexpectedly led to formation of unsaturated carboxylic acids [40].

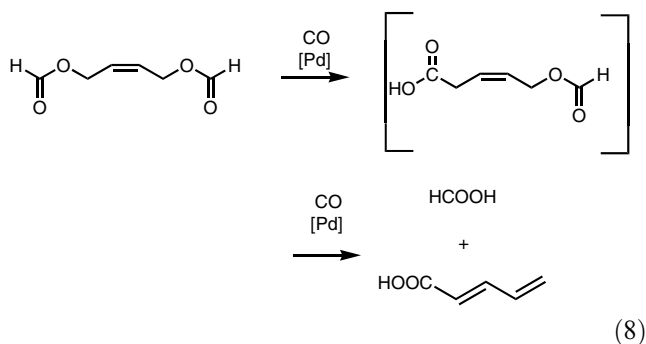


Scheme 4 accounts for the mechanism of conversion of an allylic formate into an unsaturated carboxylic acid. It is comprised of the elementary processes, (a) cleavage of the allylic C–O bond to give η^3 -allylpalladium species A, (b) CO insertion into the η^3 -allyl–Pd bond to give acylpalladium formate species B, (d) reductive elimination of a mixed anhydride C, and (e) the subsequent spontaneous decarbonylation to afford β,γ -unsaturated acid.



Scheme 4. Mechanism of Pd-catalyzed conversion of allylic formates into unsaturated carboxylic acids.

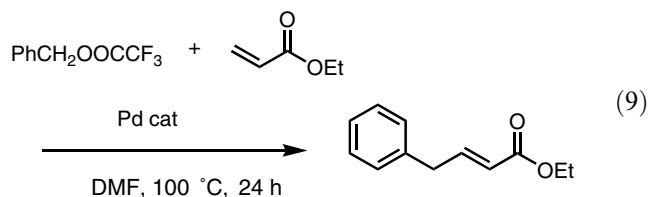
When the reaction as shown in Eq. (7) is applied to a diformate of bifunctional diol, but-2-ene-1,4-diol, the diformate was found to be converted into penta-2,4-dienoic acid with liberation of formic acid,



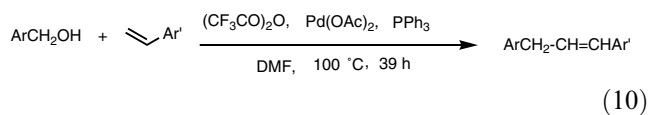
The process is considered to proceed through a two-step mechanism to give the dienoic acid. In the first step, the carbonylative conversion of the substrate leads to an intermediate carboxylic acid having the formate group. The second C–O bond cleavage of the allylic–formate bond followed by the β -H elimination affords the dienoic acid [40b].

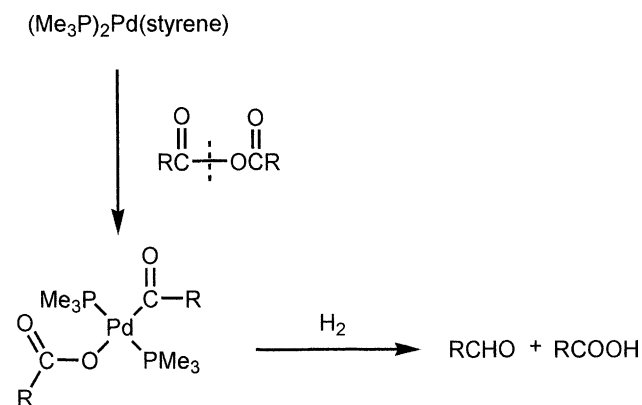
As will be described later, the carboxylic acids obtained in these processes can be converted into aldehydes and ketones by combination with other palladium-catalyzed processes.

Benzylic carboxylates have properties somewhat similar to allylic carboxylates and undergo the benzyl–O bond cleavage upon interaction with Pd(0) complexes to give benzylpalladium carboxylates [41]. We found recently that the palladium-promoted C–O bond cleavage in benzyl trifluoroacetate can be used for performing the Mizoroki–Heck type benzylation of olefins [42]. The process is considered to proceed through olefin insertion into the benzylpalladium species followed by β -H elimination to afford benzylation of olefins catalytically,



For performing the benzylation of olefins, prior synthesis of benzyl trifluoroacetate as in Eq. (9) is not necessary. The in situ formation of an ester from the benzylic alcohol and trifluoroacetic anhydride can be accommodated in the catalytic process to realize the benzylation of an olefin by using benzylic alcohol directly in the presence of trifluoroacetic anhydride as shown in,



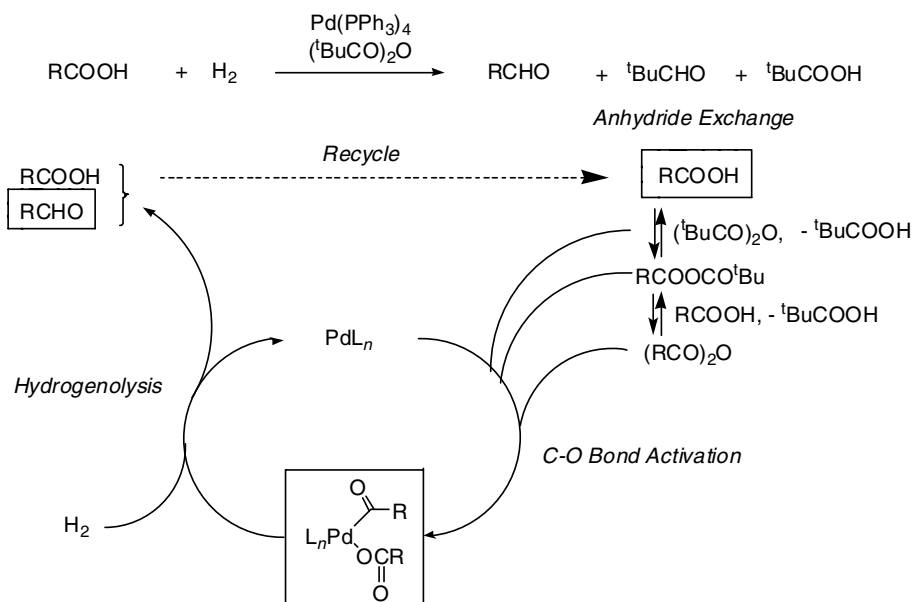
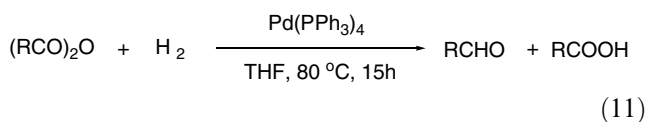


Scheme 5. Cleavage of C–O bond in carboxylic anhydride on interaction with Pd(0) complex.

3.2.2. Application of the cleavage of acyl–O bonds in carboxylic esters and anhydrides to organic synthesis

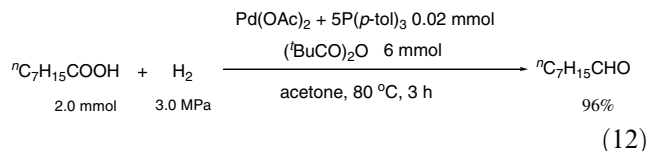
As shown in type (a) in Scheme 3, the C–O bond in carboxylic anhydrides and carboxylic esters can be cleaved on interaction with a Pd(0) complex to give an acylpalladium carboxylate or acylpalladium aryloxide complex. We found that the acylpalladium carboxylate reacts further with hydrogen to release an aldehyde and a carboxylic acid (Scheme 5) [43].

Based on the finding we could develop a new type of catalytic process to convert carboxylic anhydrides into aldehydes and carboxylic acids,



Scheme 6. Mechanism of catalytic hydrogenation of carboxylic acid into aldehyde in the presence of pivalic anhydride added as the external agent.

We could later make the process catalytic for conversion of carboxylic acids directly into aldehydes without using the carboxylic anhydrides by combining the process of Eq. (11) with use of an additive such as pivalic anhydride [44],

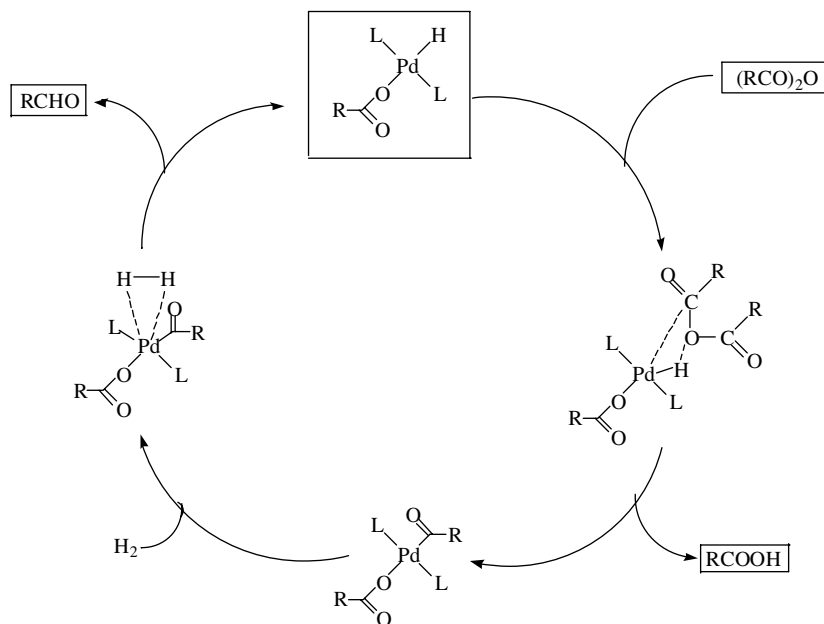


Scheme 6 illustrates the concept of the mechanism of the direct conversion of carboxylic acid into aldehyde in the presence of pivalic anhydride.

Unlike the work on coordination polymerization with the iron diethyl complex, the work soon attracted attention. Following our work Gooßen developed a similar catalytic system producing aldehydes with somewhat different experimental conditions [45].

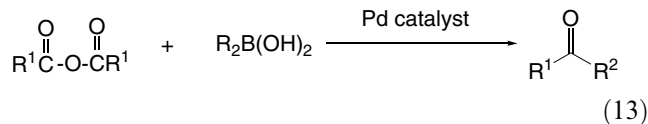
We have further studied the mechanism of the catalytic conversion of carboxylic anhydride with DFT calculation and proposed a novel type of a mechanism involving the cleavage process where carboxylic anhydride interacts with a hydridopalladium carboxylate as shown in Scheme 7 [46].

Among various palladium-catalyzed cross-coupling processes the Suzuki–Miyaura coupling using aryl or alkenyl halide in combination with arylboronic acids has been widely utilized recently in organic synthesis [47]. The mechanism of the Suzuki–Miyaura process involves the oxidative addition of aryl or alkenyl halide to a Pd(0) complex combined with transmetalation using arylboronic acid, followed by reductive elimination of the aryl (or alkenyl) group with the aryl group. We

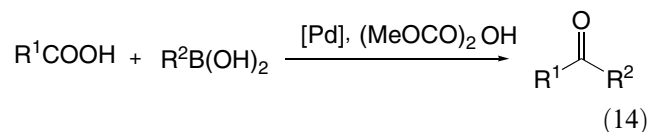


Scheme 7. Mechanism of catalytic hydrogenation of carboxylic anhydride through involvement of hydridopalladium carboxylate species.

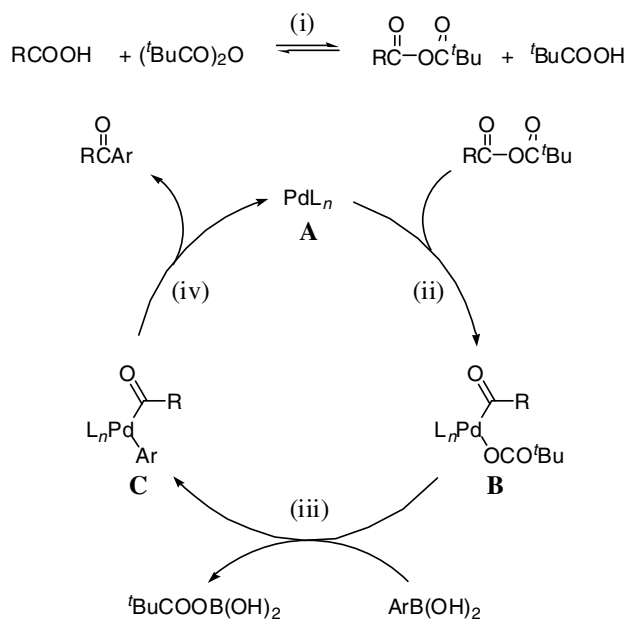
found that the cleavage of the C–O bond in carboxylic anhydride producing an acylpalladium intermediate can be combined with a similar concept of transmetalation with arylboronic acid to produce acyl(aryl)palladium intermediate that reductively eliminates a ketone. Thus we could develop a new catalytic process converting carboxylic anhydrides into ketones [48],



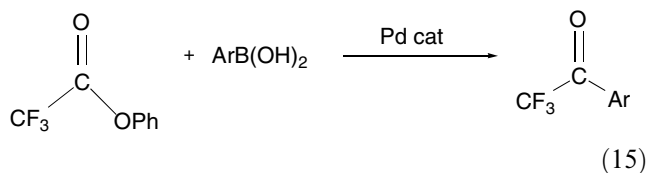
By application of the similar concept shown in Scheme 6, we combined the exchange process of an added activator such as dimethyl dicarbonate with a carboxylic acid to develop a new method for synthesis of ketones directly from carboxylic acids and arylboronic acid as shown in Eq. (13) and in Scheme 8 [49,50].

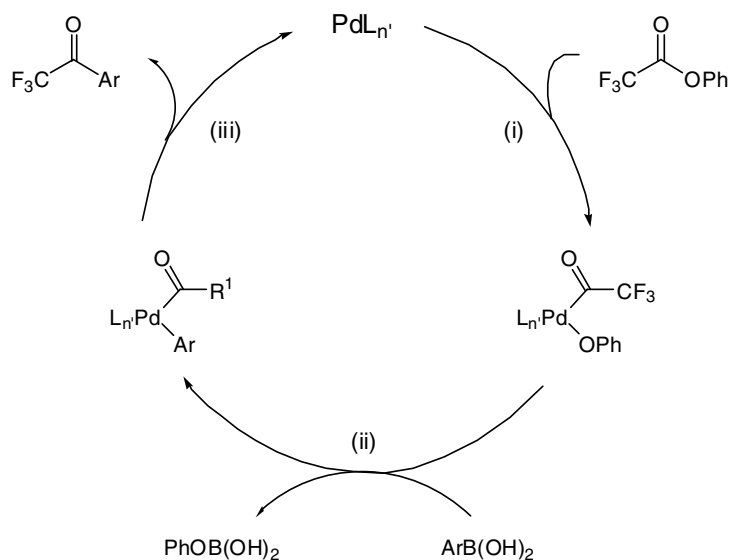


Cleavage of the C–O bond takes place not only with carboxylic anhydride but also with carboxylic esters, particularly with electron-poor esters such as those of fluorinated carboxylic acids [41]. By combining the C–O bond cleavage of perfluorinated carboxylic esters with Pd(0) complexes, we could develop a new process to catalytically produce perfluoroalkyl aryl ketones,



Scheme 8. Catalytic cycle for ketone synthesis from carboxylic acid and organoboronic acid catalyzed by a palladium species in the presence of pivalic anhydride.





Scheme 9. Mechanism of aryl trifluoromethyl ketone synthesis from phenyl trifluoroacetate and arylboronic acid.

The mechanism of the trifluoromethyl aryl ketone synthesis from phenyl trifluoroacetate and arylboronic acid is presented in Scheme 9.

Gooßen also developed similar processes of ketone synthesis based on the concept of the C–O bond cleavage [51].

4. Conclusions

The palladium-catalyzed synthetic applications shown above illustrate just several attempts of applying the C–O bond cleavage processes to organic synthesis. Further examples combining the C–O bond cleavage with other known elementary processes will undoubtedly follow. Palladium complexes offered excellent chances for designing new catalytic processes since many of the reaction patterns have been reasonably well established. However, unexpected behaviors of other types of organotransition metal complexes possessing capabilities of synthetic applications are being found and will be undoubtedly found in the future.

It was gratifying for me that I was involved with organotransition metal chemistry for half a century from the early stage of its development. It offered me the constant challenge and pleasures. Working in this exciting field I have never felt boring, since I have come across on many pleasant surprises. True that I missed some chances of applications but at the same time I was offered with other types of unexpected findings. Through my experiences of failures I learned the ways to apply the fundamental knowledge to organic synthesis for developing some useful catalytic processes.

Since organotransition metal chemistry is so rich in the variety of transition elements and each complex can be modified by coordination of various ligands to meet the specific requirement for applications, you do not have to feel the death of research topics in the foreseeable future. It still offers ample chances for the future generations.

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