DALTON
PERSPECTIVE

Insertion chemistry into metal–carbon bonds

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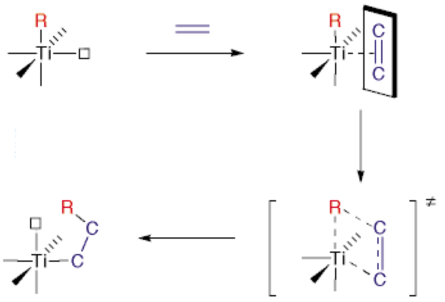
Transition metal alkyls (hydrocarbyls, including aryls) occupy a central position in organometallic chemistry. Particularly, their reactions with unsaturated compounds such as olefins and carbon monoxide are relevant to various important catalytic processes. The quest for the synthesis of various alkyltransition metal complexes and examination of their reactions with unsaturated compounds has led, often serendipitously, to findings of novel reactions. The present Perspective is an account of the personal inquiries of the author related to these transition metal alkyls and the results, including the polymerization of vinyl monomers and carbonylation of various substrates. Among various transition metal complexes studied, those of palladium were found most versatile, leading to findings of various novel catalytic processes.

Alkyl compounds of transition metals are now known for most of the transition metals in the Periodic Table.[1] They were a rarity, however, before the nineteen fifties, when I started my research work as a graduate student, except for platinum alkyls that were regarded as exceptions.[2] Only in the nineteen sixties some of the thermally stable transition metal methyl and ethyl complexes were isolated as stable complexes. As a young student I was fascinated at that time by the exciting discovery of the Ziegler catalyst[3,4] and by the subsequent development led by Natta in polymerization of various unsaturated compounds. I recall now the excitement filling the lecture halls in polymer chemistry divisions of the Chemical Society of Japan and of the Polymer Society, Japan, where people were heatedly discussing the mechanism of olefin polymerization by the mixed systems of titanium chlorides and alkylaluminium compounds.

Akio Yamamoto

Akio Yamamoto was born in Tokyo in 1930. He received his bachelor's degree from Waseda University and the doctor's degree from Tokyo Institute of Technology. He was promoted to Full professor of the Research Laboratory of Resources Utilization at Tokyo Institute of Technology in 1971 and has served as director since 1988. In 1990 he was invited by Waseda University and has worked as Research Professor since then. Recipient of the Chemical Society of Japan Award, Society of Polymer Science Award, and Violet Ribbon.

For me, however, it seemed to be extremely difficult to establish the nature of the active species in the Ziegler catalyst systems by examining the mixed catalyst systems themselves. It was Cossee[5] who first proposed a simple concept to elucidate the olefin polymerization mechanism by assuming the formation of titanium alkyls as the catalyst center generated by interaction of titanium chlorides with aluminium alkyls (Scheme 1). The initiation of polymerization was explained by subsequent π co-ordination of an olefin monomer with the titanium alkyl leading to insertion of the olefin into the metal alkyl bond followed by consecutive insertion of monomers, constituting the propagation steps in the olefin polymerization. However, verification of the mechanism was much delayed because of the paucity of transition metal alkyls suitable as models of the active site. It is now hard to imagine the difficulties involved in establishing the active site of the catalyst systems at that time if we view the situation from the standpoint where the synthesis and polymerization abilities of various single site polymerization catalysts having transition metal alkyls are established.[6]



Scheme 1 Cossee's mechanism for polymerization of ethylene.

Some mystery was still attached then to the catalysis by transition metals and their compounds. Many people did not believe that pure compounds could serve as the catalysts and some specific functions associated with the surface of transition metals or their compounds were believed to promote the catalysis. It was Wilke[7] who removed the myth by isolating pure low valent transition metal complexes that showed excellent catalytic activities for butadiene oligomerization and polymerization.

During my stay in his group at the Max Planck Institute for Coal Research in Mülheim, Germany in 1962 to 1963, I was very much influenced by the elegance of his work and by the power of the methodology of isolating low-valent transition metal complexes and examine the behavior of the complexes toward various unsaturated complexes. Some time after my return from Germany we initiated a joint work with Professor Uchida's group at Tokyo University attempting to isolate low valent, catalytically active transition metal compounds from mixed systems of nickel, cobalt and iron acetylacetonates and aluminium alkyls containing various ligands such as 2,2′-bipyridine (bpy) and tertiary phosphines (PR_3). The joint work quite unexpectedly led us to isolation of transition metal alkyls having the supporting bipyridine ligand(s) [eqns. (1)]. These alkyl complexes of late transition metals[8–10] proved to be the earliest examples of thermally stable, isolated transition metal alkyls except for platinum alkyls.

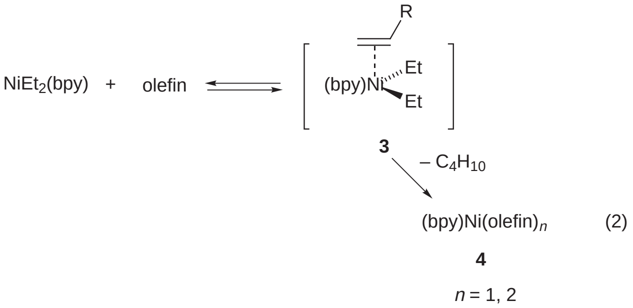
$$\mathrm{Ni(acac)_2 + AlEt_2(OEt) + bpy \longrightarrow \underset{\mathbf{1}}{NiEt_2(bpy)}}$$

$$\mathrm{Fe(acac)_3 + AlEt_2(OEt) + bpy \longrightarrow \underset{\mathbf{2}}{FeEt_2(bpy)_2}} \qquad (1)$$

$$\mathrm{Co(acac)_3 + AlEt_2(OEt) + bpy \longrightarrow CoEt(bpy)_2}$$

At that time NMR apparatus was not readily available in our group and characterization of the metal alkyls was made mostly on the basis of chemical reactions and elemental analyses. When we could convince ourselves that the nickel and iron complexes contain alkyl groups attached to the metals on the basis of characterization by their thermolysis and treatment with protic reagents releasing the alkanes, the first reactions we attempted were with butadiene followed by reactions with various vinyl compounds.

The reactions of these complexes with butadiene proved that these complexes actually serve as the catalysts for oligomerization of butadiene in the same way as with the mixed catalyst systems. On the other hand, when we subjected these transition metal alkyls to vinyl compounds we observed that the ensuing processes varied depending on the transition metals employed. Coupling of the alkyl groups from nickel dialkyls was observed on treatment of the nickel alkyls with electron-deficient olefins, such as acrylonitrile and acrolein, whereas polymerization of vinyl monomers occurred with the iron alkyls. The reactions of $\mathrm{NiEt_2(bpy)}$ **1** with electron deficient olefins such as acrylonitrile at low temperatures were revealed to involve the co-ordination of the olefin to the nickel alkyls.[11] Raising the temperature led to activation of the nickel–alkyl bonds in **1** and to coupling of the two alkyl groups by a process now termed reductive elimination[12,13] [eqn. (2)].

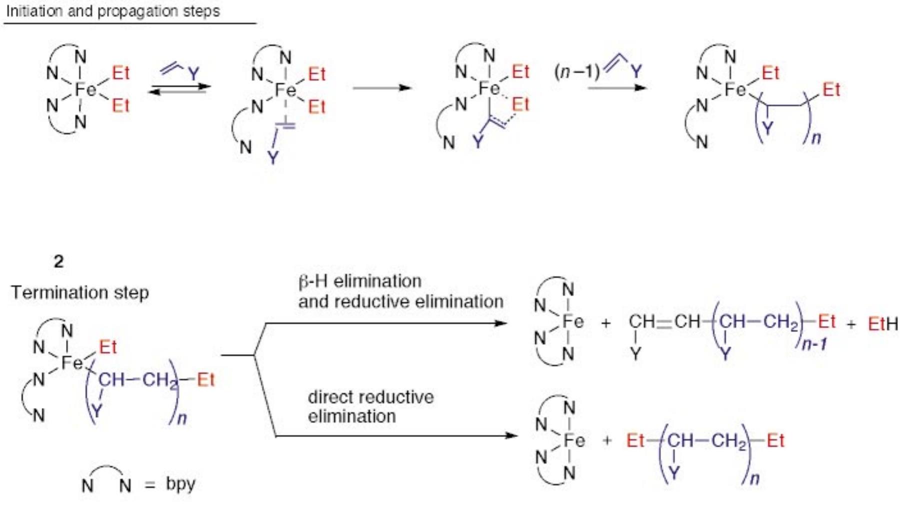


The bipyridine-co-ordinated nickel alkyls provided us with a good model to demonstrate how the transition metal–alkyl bonds are activated on interaction with olefins as was proposed in Cossee's original concept. It was revealed that the more back bonding is provided from the transition metal to the co-ordinated olefin, the stronger becomes the π bond between the metal and the co-ordinated olefin, and that the stronger the back bonding from the metal to the olefin, the stronger becomes the activation of the nickel–alkyl bond to enhance the reductive elimination.

On the other hand, the bipyridine-co-ordinated iron alkyl **2** was found to initiate the polymerization of electron-deficient vinyl monomers such as acrylonitrile and methyl methacrylate. This work was the first example of polymerization of polar monomers initiated by isolated alkyl complexes of late transition metals.[14] The results we obtained contained important conclusions in the light of our present knowledge regarding the mechanism of vinyl polymerization by transition metal alkyls as reiterated below.[15–20] (1) The polymerization is initiated by co-ordination of an olefin to a vacant site created by partial dissociation of the bipyridine ligands. (2) Competition reactions of various monomers indicate that olefin binding more strongly with the iron alkyl center by back donation is preferentially introduced into the copolymer and the feature of the copolymerization is similar to that of anionic polymerization. (3) The initiation by insertion of the co-ordinated olefin into the iron–alkyl bond is followed by rapid successive insertions of the monomers constituting the propagation steps. (4) Termination involves β-hydrogen elimination from the polymer attached to the iron propagation site or proceeds by reductive elimination of the iron-bound growing alkyl chain with the other remaining alkyl group (Scheme 2).[21]

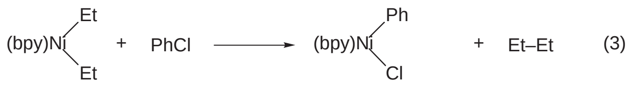
However, the iron alkyls we prepared showed a different behavior from the Ziegler Natta type catalysts composed of early transition metal compounds that showed high polymerization activity for non-polar α-olefins. Thus a question has remained if there is an intrinsic difference between the reactivities of early and late transition metal alkyls in their ability to polymerize olefins. Recent development of the chemistry of palladium and nickel alkyls shows that α-olefins such as ethylene and propylene also can be polymerized when a suitable ligand is employed.[22,23] Very recently, attainment of quite high activity for ethylene polymerization was reported by two groups using iron- and cobalt-based initiators.[24,25] The results indicate that high molecular weight polymers of α-olefins are available even with late transition metal complexes such as iron and cobalt by controlling chain transfer processes.

In the mean time, a study related to examination of the solvent effect in propylene dimerization with nickel complexes in



Scheme 2 Mechanism of olefin polymerization initiated by $\mathrm{FeEt_2(bpy)_2}$.

chlorobenzene led us to investigate the reaction of $NiEt_2(bpy)$ with chlorobenzene.[26] The nickel complex **1** exhibited a high activity for dimerization of propylene in chlorobenzene and the mechanism consisting of propylene insertions followed by β-hydrogen elimination was proposed to account for the formation of the linear and branched dimers. The investigation of the reaction of halogenoarenes with $NiEt_2(bpy)$ **1** to get information on the marked influence of chlorobenzene on the dimerization activity brought us an unexpected finding that the reaction caused the coupling of the two ethyl groups forming butane and gave arylnickel halide complexes **5** [eqn. (3)]. Without realizing the importance of this finding we reported the result simply as the preparation of a new arylnickel complex. The importance was not overlooked by those who were prepared to apply the new results to organic synthesis. Tamao and Kumada[27,28] at Kyoto University and Corriu and Masse[29] in Montpelier developed a new synthetic method to realize the coupling of aryl and alkyl groups by using aryl halides and alkyl Grignard reagents [eqn. (4)].



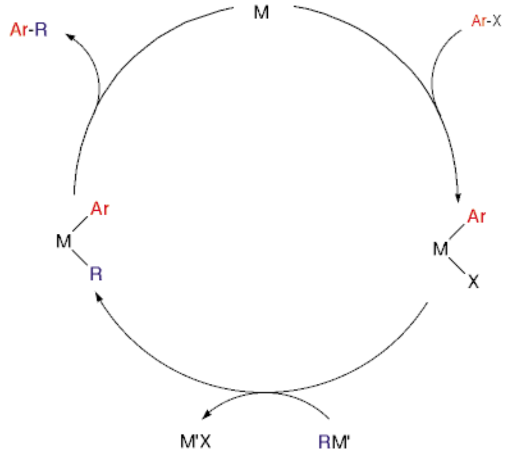
$$(bpy)Ni(Et)_2 + PhCl \longrightarrow (bpy)Ni(Ph)(Cl) + Et\text{–}Et \qquad (3)$$

5

$$ArX \quad + \quad RMgX \xrightarrow[\text{- }MgX_2]{[Ni]\text{ or }[Pd]} Ar\text{-}R \qquad (4)$$

The process was later developed to more convenient synthetic methods utilizing palladium complexes. Further modification of the process utilizing other alkylation agents such as alkylzinc, aluminium, boron, tin, and silicon compounds in place of the Grignard reagent led to development of extremely useful processes in organic syntheses for achieving various coupling processes.[30] I failed to see the applicability of the process represented in eqn. (4). At that time I did not feel much chagrin but later realized that I missed a pretty big catch because of my ignorance of the significance of the synthetic methodology.

The essence of the cross coupling process can be represented by Scheme 3. The process is composed of (1) oxidative addition of aryl halides (Ar–X) to zerovalent transition metal complexes to give arylmetal halides, (2) alkyl transfer (transmetallation) to give an aryl(alkyl)transition metal complex, (3) reductive elimination involving C–C coupling to liberate an alkyl–aryl coupling product.†[31,32]



Scheme 3 Mechanism of transition metal-catalysed cross coupling of aryl and alkyl groups.

Of the above three elementary processes in Scheme 3 the oxidative addition of aryl halides to complexes of Ni^0 or Pd^0 to give arylnickel and arylpalladium halide complexes had been well established. The other processes, namely alkyl transfer from a metal alkyl to arylnickel or arylpalladium halides to give alkyl(aryl)-nickel and -palladium complexes, had not been well examined. Our interest to find the reasons why some transition metal alkyls exist as thermally stable compounds, while the others do not, led us to study the thermolysis mechanisms of various diorgano-nickel and -palladium complexes.[33–36] Particularly interesting results were obtained by examining the thermolysis behavior of *cis*- and *trans*-dialkylpalladium complexes having monodentate tertiary phosphine ligands. It was revealed that the *trans* and *cis* isomers of the dialkylpalladium complexes having two monodentate tertiary phosphine ligands behave differently.

Thermolysis of *cis*-dialkylpalladium complexes in the absence of added ligand afforded coupling products, ethane from *cis*-$PdMe_2(PR_3)_2$ and butane from *cis*-$PdEt_2(PR_3)_2$ and the thermolysis was hindered by addition of PR_3 to the system, whereas the thermolysis of *trans*-$PdEt_2(PR_3)_2$ liberated ethylene and ethane in a 1:1 ratio. On the other hand, thermolysis of *trans*-$PdMe_2(PR_3)_2$ proceeded through *trans* to *cis* isomerization followed by reductive elimination. These results suggested the involvement of a three-co-ordinated, T-shaped intermediate having "*cis*" and "*trans*" configurations and existence of an energy barrier between them. Theoretical studies provided the support for the intermediacy of the T-shaped species.[34]

Further studies on reactions of square planar *cis*- and *trans*-dialkyl-nickel[37] and -palladium[38] complexes with carbon monoxide revealed intriguing behavior. In our studies on reactions of CO with dimethyl- and diethyl-palladium complexes toward carbon monoxide we found liberation of ketones, diketone, ethylene and propionaldehyde depending on the methyl and ethyl complexes, and also on the *cis* and *trans* configurations of the dialkylpalladium complexes. Generation of these different products in reactions of dialkylpalladium complexes with carbon monoxide was accounted for in a consistent manner by assuming the constraint of square planar geometry in the behavior of palladium complexes and by assuming alkyl migration in the CO insertion into palladium–alkyl bond in the square plane. Particularly, examination of the reason for production of only acetone from *trans*-$PdMe_2(PR_3)_2$ on the one hand, and generation of acetone and butane-2,3-dione on the other, in the reaction of *cis*-$PdMe_2(PR_3)_2$ with CO suggested operation of two routes (a) and (b) in Scheme 4.

The assumption prompted us to investigate the reaction of the dimethylpalladium complex with CO in the presence of diethylamine with the aim of trapping the acetyl group. The reaction afforded the α-keto amide $MeCOCONEt_2$ where two CO molecules were introduced. Further studies on the reactions using monomethylpalladium iodide and monophenylpalladium iodide with CO and diethylamine also showed liberation of α-keto amides $MeCOCONEt_2$ and $PhCOCONEt_2$ respectively together with monoamides, the single carbonylation products.[39] The latter process producing the α-keto amide on reaction of *trans*-$PdPh(I)(PR_3)_2$ **6** with CO and diethylamine [eqn. (5)] suggested the possibility of application of the finding to a catalytic process to convert aryl halides into α-keto amides, since the

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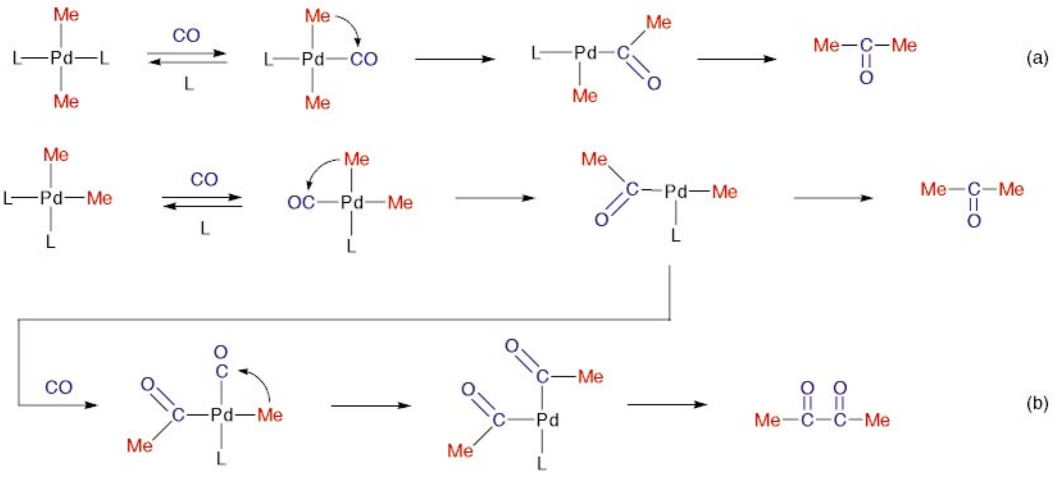
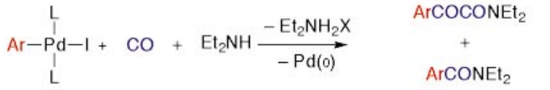
† In causing the reductive elimination of the alkyl–aryl coupling product, interaction of the aryl halide through the phenyl ring with the alkyl(aryl)metal complex may be involved, but this process is omitted from Scheme 3 to stress the most important concept. The mechanism is straightforward when a bidentate ligand is used but consideration of *trans* and *cis* isomers and of the isomerization processes between them is required when a monodentate tertiary phosphine is employed as the ligand.



Scheme 4 Formation routes of ketone and diketone form *cis*- and *trans*-$PdMe_2L_2$.



6

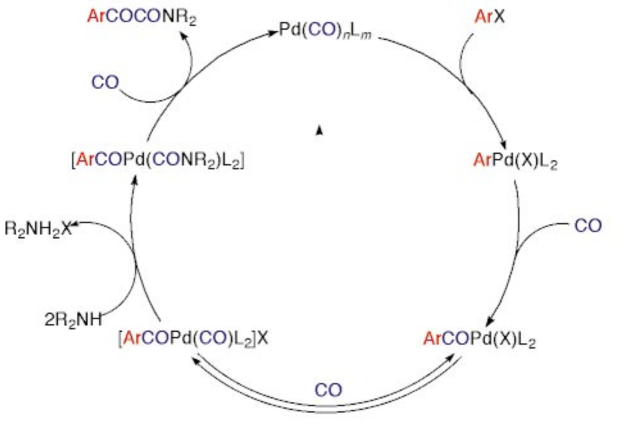
$$Ar{-}PdL_2{-}I + CO + Et_2NH \xrightarrow[-\,Pd(0)]{-\,Et_2NH_2X} ArCOCONEt_2 + ArCONEt_2 \qquad (5)$$

reaction (5) is expected to produce a palladium(0) complex together with NEt_2H_2X and such complexes are well known oxidatively to add aryl halide to yield an arylpalladium halide. In fact, the catalytic conversion of aryl halide into α-keto amide on treatment with CO and diethylamine in the presence of $Pd(PPh_3)_4$ was confirmed in the first attempt of the catalytic process [eqn. (6)].[40]

$$ArX + CO + R_2NH \xrightarrow[-\,R_2NH_2X]{[Pd]} ArCOCONR_2 + ArCONR_2 \qquad (6)$$

The lesson I learned in having missed the opportunity of devizing the cross-coupling process catalysed by a transition metal complex had some effect. It is interesting that Tanaka independently achieved the same catalytic process starting from a different question regarding the formation of ketone at about the same time.[41] It often happens that when one finds something new, there is always someone else quite close to the finding.

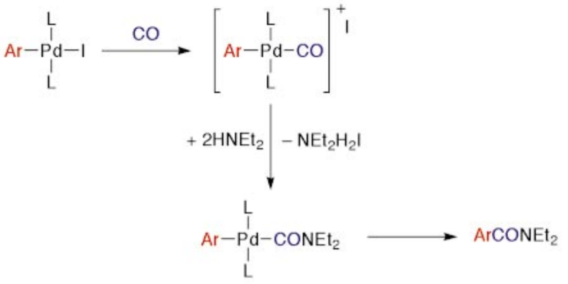
We have studied the scope of application of the double carbonylation to organic synthesis as well as the mechanism of the new process. It took us about 10 years to establish the reaction mechanism to a satisfying degree. The mechanism of α-keto amide formation from aryl halide and CO in the presence of secondary amine catalysed by a palladium complex is summarized in Scheme 5.[42] The catalytic cycle is composed of the following elementary processes: (1) generation of a palladium(0) species from a catalyst precursor; (2) oxidative addition of aryl halide to this species to yield arylpalladium halide; (3) insertion of CO into the palladium–aryl bond to afford an aroylpalladium complex; (4) CO co-ordination to the palladium center; (5) nucleophilic attack of the amine on the co-ordinated CO bound with a cationic center; (6) deprotonation by a base (secondary amine itself is included) to produce an aroyl(carbamoyl)palladium; (7) reductive elimination of the aroyl and the carbamoyl ligands to produce α-keto amide with regeneration of a palladium(0) species that drives the catalytic cycle further.



Scheme 5 Mechanism of palladium-catalysed α-keto amide formation from aryl halide and CO in the presence of a secondary amine.

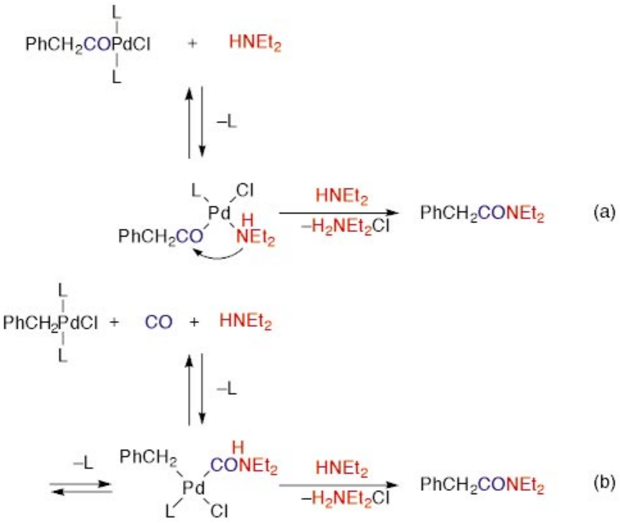
The key steps in the double carbonylation lie in CO insertion into the aryl–palladium bond to give an acylpalladium species and its further reactions to give the bis-acyl type palladium(II) intermediate that reductively eliminates the α-keto amide. The possibility of the consecutive CO insertion into the aryl–palladium bond to give an α-ketoacyl intermediate was excluded by studies involving the separately prepared α-ketoacyl-palladium and -platinum complexes.[43,44]

Further studies to increase the selectivity for the double carbonylation revealed a somewhat surprising mechanism for formation of amide as the single carbonylation product. It was established that arylpalladium halide dissociates the halide ligand in solution under CO pressure to have the CO ligand bound with a cationic arylpalladium center. In fact *trans*-$Pd(Ar)I(PMe_3)_2$ provides *trans*-$Pd(Ar)(CONEt_2)(PMe_3)_2$ on interaction with diethylamine under CO. Under certain conditions, amide $ArCONEt_2$ can be reductively eliminated from the aryl(carbamoyl)palladium complex [eqn. (7)].



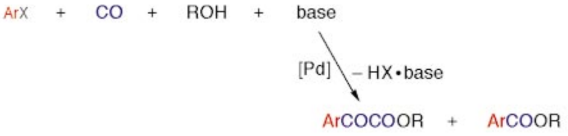
(7)

Our later study on the reactivities of benzylpalladium and phenylacetylpalladium complexes revealed involvement of another course to give the amide, the single carbonylation product, by the reaction of a phenylacetylpalladium complex with the secondary amine (route a in Scheme 6) as well as the formation of amide from the benzylpalladium species on reaction with CO and the amine[45] (route b in Scheme 6). The formation of the amide from the CO-co-ordinated benzylpalladium species *via* route b was concluded to take place in the presence of an excess of the amine to deprotonate the CO bound diethylamine to give the carbamoyl ligand prior to the CO insertion (Scheme 6).



Scheme 6 Two routes to give the amide from phenylacetylpalladium and benzylpalladium complexes.

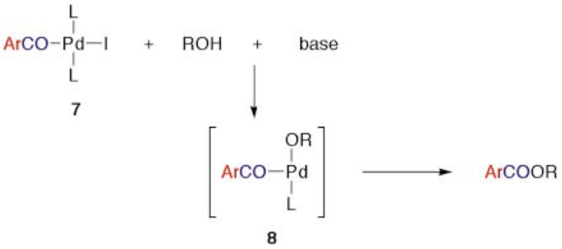
Since α-keto acids can readily be converted into biologically active compounds such as α-amino acids and α-hydroxy acids, the finding of the catalytic double carbonylation process was thought to provide a new route for synthesis of these useful derivatives. However, α-keto amides are usually resistant to hydrolysis and development of a synthetic route to more readily hydrolysable α-keto ester was desirable. Studies of our group and of Tanaka's group realized the double carbonylation of aryl halides to α-keto esters[46] [eqn. (8)].



(8)

Detailed studies on the mechanism of double carbonylation of aryl halides to α-keto esters revealed that the catalytic cycle comprises: (1) oxidative addition of aryl halide to a palladium(0) species to give an arylpalladium halide, (2) CO insertion into the Ar–Pd bond to afford an aroylpalladium complex, (3) attack of CO co-ordinated to a cationic palladium center by the alcohol and a base to yield aroyl(alkoxycarbonyl)palladium, (4) reductive elimination of the aroyl and the alkoxycarbonyl ligands to liberate the α-keto ester with regeneration of a palladium(0) species that carries the catalytic cycle.

Formation of the ester, the single carbonylation product, was found to be derived from an aroylpalladium complex not from the arylpalladium complex. Ester was found to be formed *via* a route involving the intermediacy of aroyl(alkoxy)palladium complex **8** by reductive elimination [eqn. (9)]. Later we have confirmed that a similar mechanism also operates in the ester formation from $PhCH_2COPdCl(PPh_3)_2$ and alcohols in the presence of NEt_3.[45]

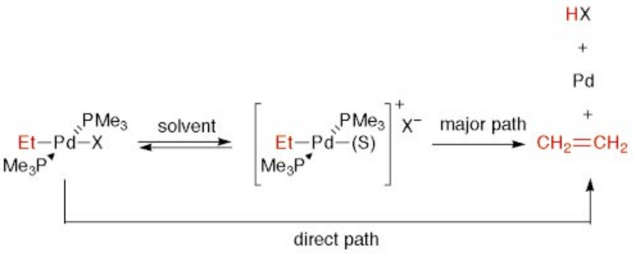


(9)

These studies indicated that the palladium-catalysed double carbonylation of aryl halides proceeds through a common mechanism involving CO insertion into an arylpalladium center and by reductive elimination of the acyl ligand with a carbamoyl or alkoxycarbonyl ligand, although the mechanisms to give the ester or amide differ from each other.

When we reached these conclusions the time for the compulsory retirement at Tokyo Institute of Technology for me approached and I had to terminate the research there. Fortunately, I was invited by Waseda University, my alma mater, to continue my work there under somewhat different research conditions in 1990 to build a new research group from scratch with one student.

The first project I started was to examine the properties of monoorganopalladium complexes having trimethylphosphine ligands. A kinetic study on thermolysis of *trans*-$PdEt(X)(PMe_3)_2$, where X is halide, phenoxide, and various carboxylato ligands, revealed that the anionic ligand dissociates in the rate-determining step to generate a cationic ethylpalladium species which is unstable and readily undergoes β-hydrogen elimination with liberation of ethylene (Scheme 7).[47] The result suggested involvement of a cationic monoorganopalladium species as an important reactive species in the reactions of neutral monoorganopalladium complexes with various substrates as well as in β-hydrogen elimination of monoalkylpalladium complexes. We have prepared a variety of monoorganopalladium complexes with mono- and di-tertiary phosphine ligands and examined their reactions with olefins, carbon monoxide, and alkyl isocyanides. During the effort of building a new research group at Waseda, the recent upsurge of interest regarding the alternating copolymerization of CO and α-olefins and homopolymerization of α-olefins catalysed by cationic palladium complexes spurred intensive research effort by a number of groups in the U. S. and Europe.[48] Fundamental studies on the properties of cationic organopalladium complexes, notably those led by Brookhart[49] and the Netherlands groups,[50] clarified various factors regarding the insertions of CO and olefins into the Pd–C bonds of cationic organo-palladium and -nickel complexes. Theoretical studies also contributed to support many of the observations found in the experimental studies.[51]

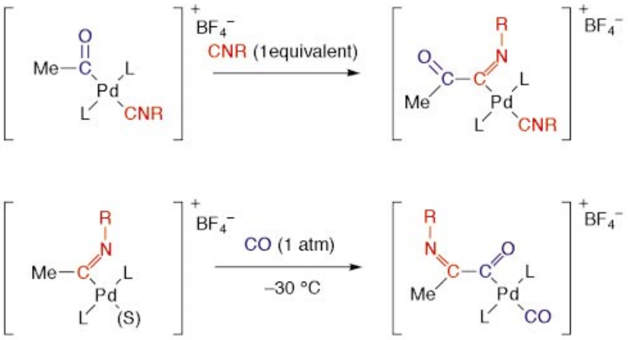


Scheme 7 β-Hydrogen elimination routes from *trans*-$PdEt(X)(PMe_3)_2$.

Since I have already reviewed our previous results dealing with comparison of the properties of neutral and cationic organopalladium and ruthenium complexes[52] and we are contributing another account including the later development concerning the organopalladium complexes,[53] I would like to restrict the discussion here on the properties of monoorganopalladium complexes to a minimum.

The studies comparing the reactivities of the neutral and cationic monoorganopalladium complexes having various supporting ligands revealed that the marked enhancement in the reactivities of the neutral monoorganopalladium complexes toward unsaturated compounds such as CO and olefins by their conversion into cationic monoorganopalladium complexes arises mainly by creation of an available co-ordination site *cis* to the alkyl or aryl ligand to allow the subsequent insertion reactions and not from the effect of the charge of the cationic palladium complex.[54] In fact, blocking the co-ordination site of a cationic monoorganopalladium complex with a strongly co-ordinating ligand caused a more pronounced inhibition of the insertion reaction than with the neutral complex having ligands of less co-ordinating abilities.[55–59] For example, examination of the CO insertion rates into *trans*-$[PdMe(L)(PMe_3)_2]^+BF_4^-$ revealed that the rate decreased in the order of L = acetone > NO_3 > $CNBu^t$. The rate of CO insertion into the Pd–Me bond was smaller with the cationic isocyanide-co-ordinated complex than into the Pd–Me bond in the neutral methylpalladium chloride complex. The reason for the remarkable rate enhancement by addition of a silver salt to the catalyst system in the olefin arylation reactions catalysed by palladium complexes[60] may be mainly ascribed to the generation of a cationic species having a readily available vacant site by removal of the halide ligand from a neutral arylpalladium halide intermediate in the catalytic cycle. It was also revealed that addition of an excess amount of a silver salt removes one of the co-ordinated tertiary phosphine ligands from the catalyst species leading to further enhancement of the reactivity.[58]

Another interesting observation in these studies of the insertion reactions into monoorganopalladium complexes is the finding of consecutive alternating insertion of CO and isocyanide into the Pd–C bond. It is well known that the consecutive CO insertion into the Pd–C bond is unfavorable, whereas isocyanides readily undergo consecutive insertion into the Pd–C bond. On the other hand, alternating insertion of the CO after isocyanide or *vice versa* has not been reported to our knowledge (Scheme 8).

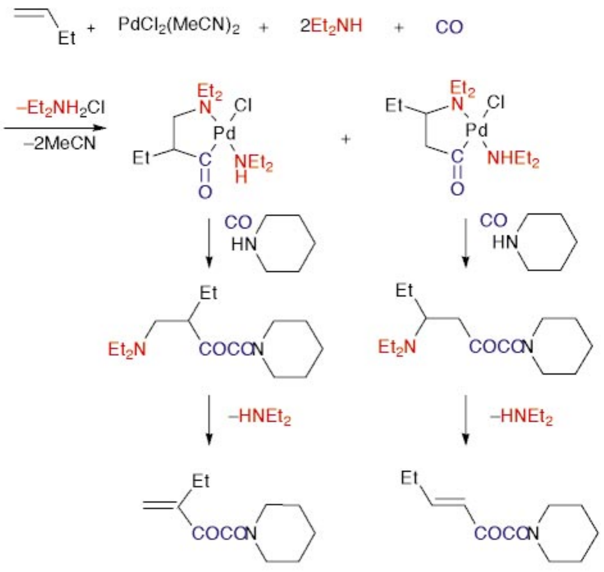


Scheme 8 Alternating insertion of CO and isocyanide into a Pd–C bond.

Among the supporting ligands used to stabilize organometallic compounds of late transition elements tertiary phosphines have been used most extensively. Recent reports indicate that employment of phosphite ligands or combination of the phosphine and phosphite donors as a specific ligand shows remarkable influence on the insertion rate and stereoselectivities of the insertion products, notably in the CO and α-olefin copolymerization.[61] Our own examination of the effect of trialkyl phosphite[59] showed that employment of the phosphite ligands favors the *cis* configuration whereas monoorganopalladium complexes having the tertiary phosphines often give *trans* complexes. Restriction of the research resources did not permit us further to examine the effect of the ligands more widely including the effect of steric bulkiness on the insertion processes. The recent reports using diimine-type ligands with large steric bulkiness seem to underline the importance of steric factors in controlling the olefin insertion and β-hydrogen elimination steps.[6,48]

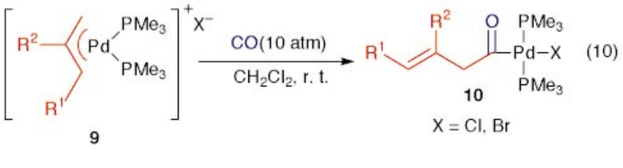
1 Catalytic double carbonylation of aliphatic substrates

Regarding the catalytic double carbonylation processes there remained one project unachieved before my retirement from Tokyo Institute of Technology. We could carry out the double carbonylation process to introduce two consecutive CO units into aromatic compounds but the process could not be applied to aliphatic systems as long as we use the principle of oxidative addition of alkyl halides to a palladium(0) species; alkyl halide reacts with a nucleophile quite readily and no catalytic cycle could be constructed by a similar mechanism as we discussed regarding Scheme 5. We could convert, however, alkenes into β,γ-unsaturated α-keto amides by stoichiometric double carbonylation, *i.e.* by aminopalladation of olefin followed by carbonylations (Scheme 9).[62]



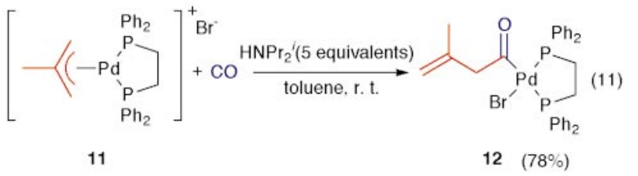
Scheme 9 Stoichiometric conversion of but-1-ene to α-keto amides.

In our quest for realization of double carbonylation of aliphatic compounds allylic compounds appeared to be a promising candidate as substrates. The key elementary process was the insertion of CO into an allylpalladium bond. The oxidative addition of allylic compounds with a palladium(0) complex to give an η^3-allylpalladium complex is well known. If the CO insertion into the allyl–palladium bond takes place to give an acylpalladium species before attack of the nucleophile at the η^3-allyl ligand there seems to be a chance of accomplishing the catalytic double carbonylation of allylic compounds. Precedents of the CO insertion into the η^3-allylpalladium bond had been quite limited.[63] Before my move to Waseda, we observed that employment of the PMe_3 helps to stabilize the CO-inserted acylpalladium complexes and CO insertion into the allyl–palladium bond can be accomplished under appropriate conditions [eqn. (10)].[64] Our later studies at Waseda revealed that the

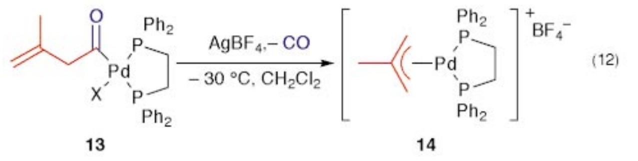


CO insertion process can take place under various conditions and that the CO insertion reaction into **11** proceeded even in the presence of a small amount of a secondary amine to give the acylpalladium complex **12** [eqn. (11)].

Employment of strongly co-ordinating ligands such as PMe_3 and dppe as well as the usage of a halide ligand of higher co-ordinating ability, such as chloride and bromide rather than iodide or non-co-ordinating anions, seems to favor the CO insertion reaction by preventing the reverse decarbonylation

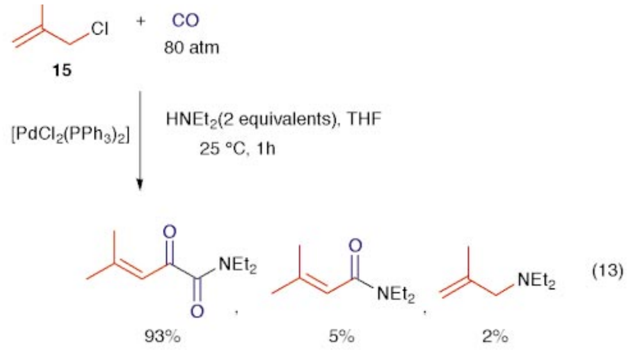


process. In fact removal of the halide from the acylpalladium complex **13** with $AgBF_4$ at −30 °C immediately afforded the decarbonylated η^3-allylpalladium complex **14** [eqn. (12)] and the

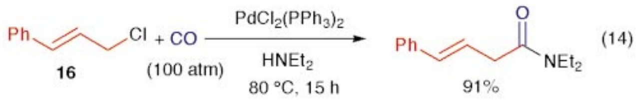


reaction of a cationic η^3-allylpalladium complex having BF_4 anion with CO did not give the acylpalladium complex.

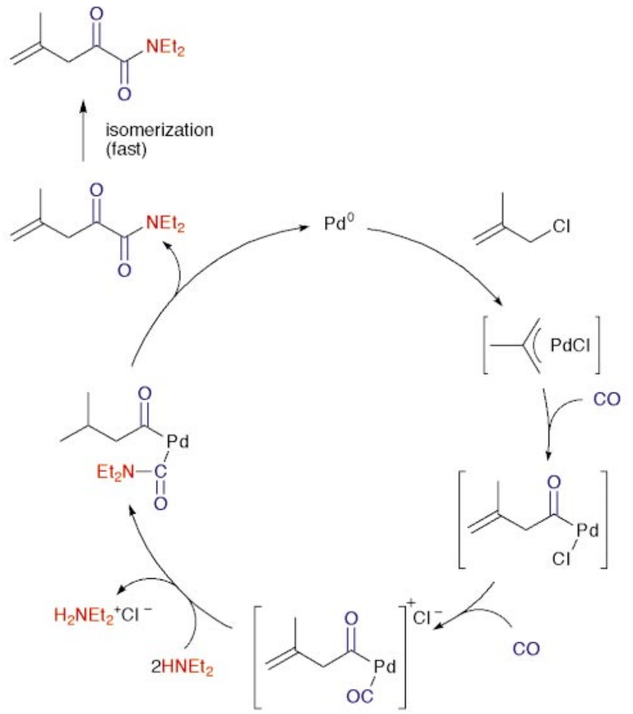
Examination of the reaction of the acylpalladium complex **12** with secondary amines under CO indicated that α-keto amides could be produced together with amide accompanied by formation of allylamines and oxamides. The results indicate that further CO co-ordination can take place to the acylpalladium complex **12** and the co-ordinated CO ligand can be attacked by a secondary amine to give a carbamoyl ligand. The subsequent reductive elimination of the acyl and the carbamoyl ligands gives an α-keto amide, as we proposed in the double carbonylation of aroylpalladium complexes. Application of the information obtained with these allyl- and acyl-palladium complexes to a catalytic process led us to realization of the double carbonylation of allylic chlorides catalysed by simple catalyst precursors such as $PdCl_2(PPh_3)_2$. Employment of polar solvents was not suitable for production of the double carbonylation products. The catalytic double carbonylation did not proceed under 1 atm of CO but application of CO pressure gave quite high yields of α-keto amides with high selectivities [eqn. (13)]. The catalytic double carbonylation process is applicable



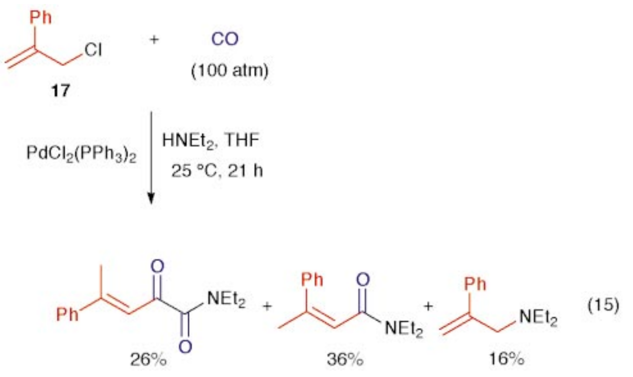
to allyl chloride, methallyl chloride **15**, and 2-chlorobut-1-ene but double carbonylation of cinnamyl chloride **16** gave only amide, the single carbonylation product, whereas 3-chloro-2-phenylpropene **17** afforded the double carbonylation product [eqns. (14) and (15)].



The mechanism presented in Scheme 10, composed of oxidative addition of methallyl chloride to Pd^0, CO insertion, CO co-ordination, nucleophilic attack on the co-ordinated CO, and reductive elimination of the acyl and carbamoyl ligands, seems reasonable on the basis of the behavior of the allylpalladium complexes described above.



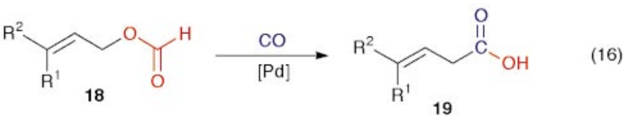
Scheme 10 Mechanism of the palladium-catalysed double carbonylation of methallyl chloride.



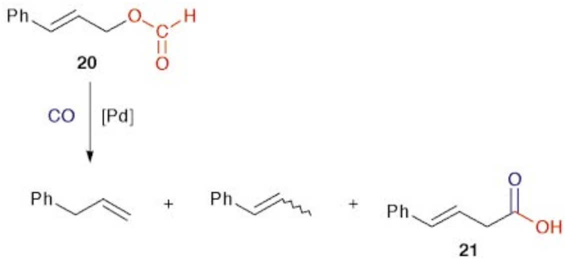
2 Other catalytic carbonylation processes

Another line of project I was interested in was the C–O bond cleavage promoted by transition metal complexes with an objective of realizing catalytic processes without using organic halides.[65,66] The presently known transition metal-catalysed processes use organic halides as substrates to prepare organic products but a base has to be used to remove the hydrogen halide to prepare products containing no halogen. Thus the total efficiency is not high and these processes are not environmentally benign. In the course of examination of the C–O bond cleavage of allylic formats[67] we discovered that the C–O bond in allylic formate **18** can be cleaved in the presence of a palladium catalyst and it can be converted into β,γ-unsaturated carboxylic acid **19** when the reaction is carried out under CO pressure [eqn. (16)].[68,69]

Since the starting allylic formates **18** can readily be prepared by treating the mixture of allylic alcohols and formic acid with

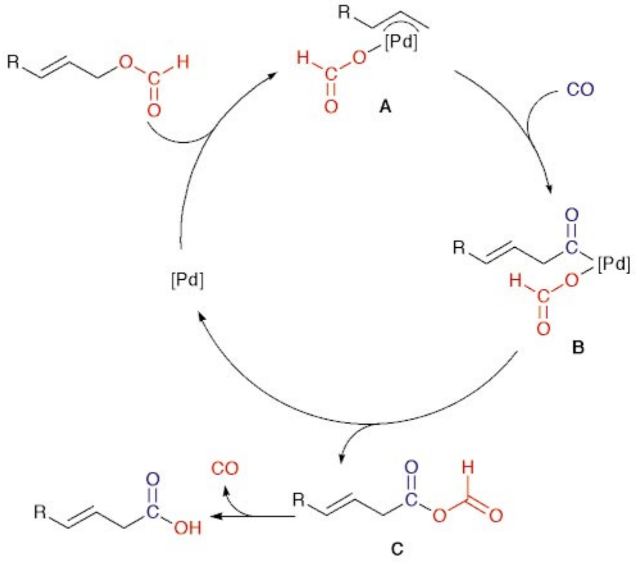


diphosphorus pentaoxide, the palladium-catalysed carbonylation of allylic formates provides a convenient means of synthesizing unsaturated carboxylic acids from allylic alcohols without starting from organic halides. For example, treatment of cinnamyl formate **20** with 0.01 mol equivalent of palladium(0) complex in the presence of triphenylphosphine under 1 atm of CO at room temperature yields terminal and internal olefins, allylbenzene and propenylbenzenes. Increasing the CO pressure above 20 atm completely changes the reaction course and gives 4-phenylbut-3-enoic acid **21** in excellent yields [eqn. (17)]. The process is in essence a molecular rearrangement of allylic formate to β,γ-unsaturated acid under the influence of CO pressure and provides a quite clean process to give various unsaturated acids. It can be performed in excellent yields and selectivity when carried out in non-polar solvents such as benzene and toluene, whereas use of polar solvents is unfavorable for getting the acids.



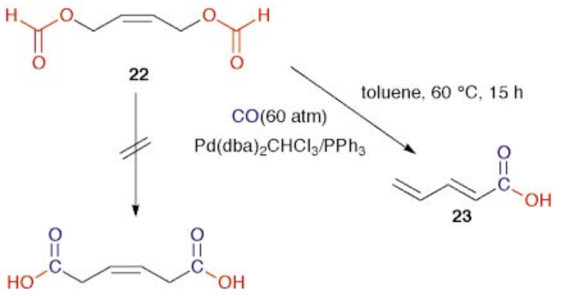
(17)

The mechanism of the catalytic process can be accounted for by a cycle as shown in Scheme 11 composed of (a) the C–O bond cleavage of allylic formate to give η^3-allylpalladium formate **A**, (b) CO insertion into the allyl–palladium bond to give the acylpalladium–formate intermediate **B**, (c) reductive elimination of the mixed anhydride **C** from **B** to regenerate the palladium(0) species to carry the catalytic cycle. The decarbonylation of the mixed anhydride **C** to give carboxylic acids is a known process. The application of CO pressure is critical in driving the catalytic cycle to yield the unsaturated carboxylic acids. Under 1 atm of CO, the insertion process to convert the allylic intermediate **A** into the acylpalladium **B** does not proceed well and the allylformatopalladium species **A** undergoes the decarboxylation to give allylhydridopalladium species that liberates olefins on reductive elimination. In an independent study we have established that the η^3-allylpalladium formate undergoes the decarboxylation and the subsequent reductive elimination to afford olefins.[67] The fact that the course of the reaction can be controlled from the one giving the reduction products of allylic formates to the carbonylation process giving the unsaturated carboxylic acids indicates the importance of the CO insertion process as a critical elementary process to determine the product selectivity.

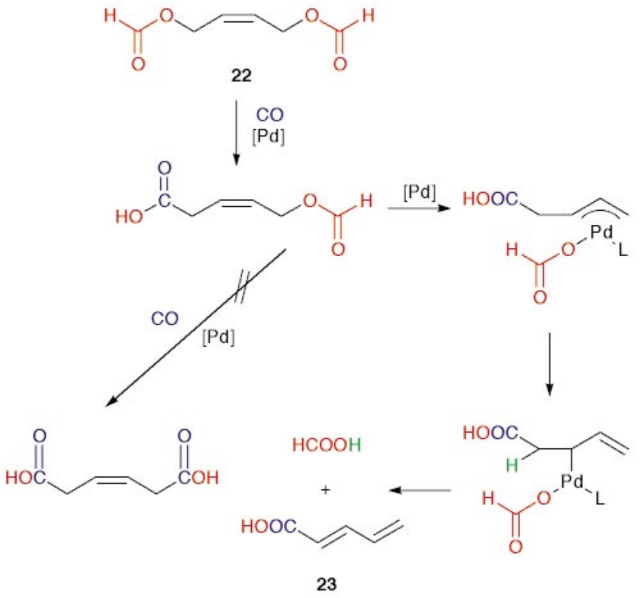


Scheme 11

In our attempt to find application of the above CO rearrangement we have examined the palladium-catalysed reaction of the diformate of but-2-ene-1,4-diol **22** to get an adipic acid precursor. However we found that the CO insertion took place at only one of the two allylic C–O bonds and the product was penta-2,4-dienoic acid **23** [eqn. (18)] The reaction course can be accounted for by Scheme 12 which involves the first carbonylation at one of the two allylic formate functionalities in **22** followed by the second allylic C–O bond cleavage to give an η^3-allylpalladium complex. Occurrence of the β-hydrogen elimination from the methylene group adjacent to the allylic entity would produce the α,γ-pentanedienoic acid **23** from the diformate **22** without giving the expected dibasic acid. Although the original intention of producing an adipic acid precursor from a butenediol derivative failed, the study revealed a new route to produce a dienoic acid from an unsaturated diol.[69]

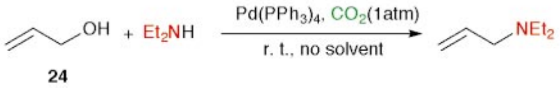


(18)



Scheme 12

Control of the cleavage of the allylic C–O bonds promoted by a palladium complex provides further opportunities of finding a new catalytic process. Although direct cleavage of the C–O bond in allylic alcohols is difficult to accomplish with a palladium catalyst, we have found a new allylation process of nucleophiles such as secondary amines catalysed by palladium complexes *under the influence of CO_2* [eqn. (19)].[70] The catalytic process is also applicable to allylation of various carbon nucleophiles such as acetylacetone, alkyl malonates, and β-ketoesters.



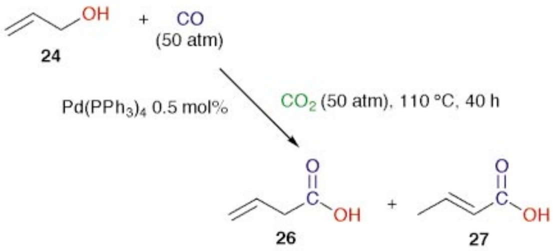
(19)

The effect of promotion of the allylic C–O bond cleavage by CO_2 can be accounted for by assuming the equilibrium (20) to

(20)

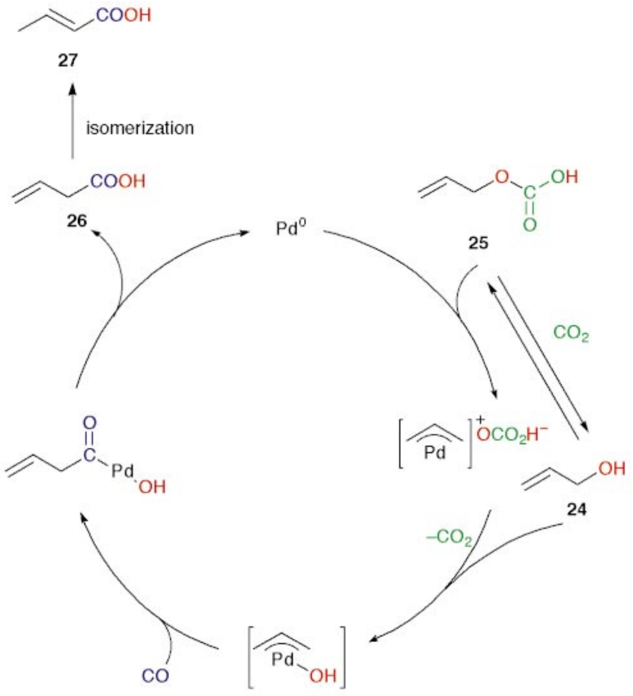
generate allyl hydrogencarbonate **25**, albeit in minor quantities, from allyl alcohol **24** and CO_2. The allyl hydrogencarbonate **25** is more susceptible than the parent allyl alcohol to the C–O bond cleavage on interaction with a palladium(0) species.

We have further found that the allyl alcohol **24** undergoes the CO insertion to give but-3-enoic acid **26** and its isomer **27** in the presence of palladium complexes and that the reaction is accelerated by CO_2 [eqn. (21)].



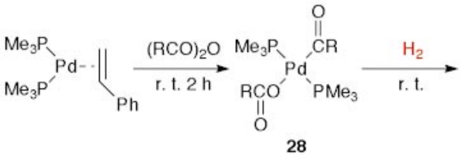
(21)

The palladium-catalysed carbonylation of allyl alcohol and the promotion effect of carbon dioxide can be accounted for by Scheme 13. A zerovalent palladium species formed from a catalyst precursor is considered to react with allyl hydrogencarbonate **25** formed from **24** to give a cationic η^3-allylpalladium complex having the hydrogencarbonate anion. In our previous study we have established the formation of a similar cationic η^3-allylpalladium complex by the allyl–oxygen bond cleavage in allyl alkyl carbonate complex.[71] Decarboxylation of the hydrogencarbonate anion gives the η^3-allylpalladium containing OH anion. Insertion of CO giving the acylpalladium intermediate followed by reductive elimination yields the butenoic acid **26**. An isomerization process, either from the but-3-enoic acid **26** or in the intermediate acyl complex, gives the but-2-enoic acid **27** as shown in Scheme 13.



Scheme 13

Another type of substrate amenable to C–O cleavage promoted by a transition metal complex is a carboxylic anhydride. As an extension of the previous studies on the C–O bond cleavage of carboxylic anhydrides by nickel complexes,[72] we examined the C–O bond cleavage of carboxylic anhydrides by a palladium complex and found their ready oxidative addition to give acyl(carboxylato)palladium complexes **28** [eqn. (22)].[73]



(22)

Treatment of **28** with dihydrogen liberated aldehydes and carboxylic acids. Based on the finding a new catalytic hydrogenation process of converting carboxylic anhydrides into aldehydes and carboxylic acids has been developed [eqn. (23)]. Combination of

$$(RCO)_2O + H_2 \xrightarrow[\text{THF, 80 °C, 15 h}]{Pd(PPh_3)_4} RCHO + RCOOH \qquad (23)$$

the C–O bond cleavage of acid anhydrides with olefin insertion into an aryl–palladium bond produced by decarbonylation of the acylpalladium complex led to development of a new type of olefin arylation process by DSM Research [eqn. (24)].[74]

$$(ArCO)_2O + R^1HC{=}CR^2R^3 \xrightarrow[\text{NMP, 160 °C}]{[Pd], NaBr} ArR^1C{=}CR^2R^3 + ArCOOH + CO \qquad (24)$$

NMP = *N*–methylpyrridinone

Further studies in our group to utilize the concept of the C–O bond cleavage of carboxylic anhydrides promoted by palladium complexes led to discovery of a novel direct catalytic hydrogenation of carboxylic acids into aldehydes in the presence of a dehydrating agent such as pivalic anhydride [eqn. (25)].[75] The process provides a quite convenient means of producing various aldehydes cleanly from a variety of carboxylic acids, including mono-, di-, and tri-basic acids. Aliphatic as well as aromatic and heteroaromatic carboxylic acids are converted into respective aldehydes in high yields and selectivities. However, since the process is not directly related with the central theme of the present Perspective, *i.e.* insertion processes, the account of the catalytic mechanism will not be dealt with here.[76]

$$RCOOH + H_2 \xrightarrow{[Pd],\ (^tBuCO)_2O} RCHO \ \left(+ \ HOH \right) \qquad (25)$$

3 Conclusion

As can be seen from the present Perspective our attempts to prepare new organometallic complexes and to understand the chemistry of these new complexes often led to findings of unexpected reactions, some of which could be applied to useful catalytic processes. It is my great pleasure that I have had the opportunity of working in the emerging and fertile organometallic field between inorganic and organic chemistry. I would like to invite younger people to join the field where they can satisfy both academic and practical interests.

4 Acknowledgements

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