Accounts

Palladium-Catalyzed Double and Single Carbonylation of Aryl Halides and Allylic Compounds

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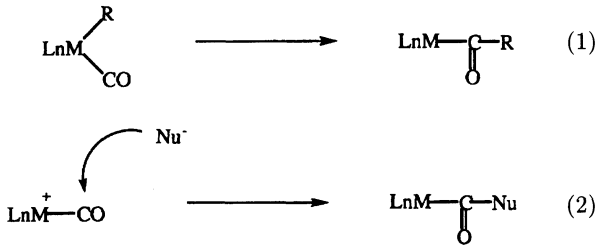
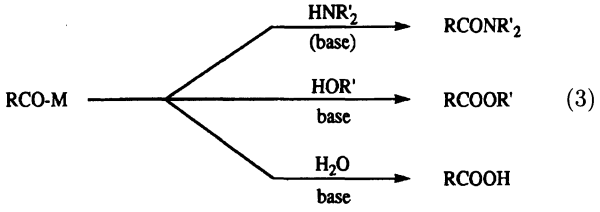
After a brief introduction summarizing the author's previous work concerning the double carbonylation of aryl halides catalyzed by palladium complexes, newly found catalytic processes (1) for converting allylic formates and chlorides into β,γ-unsaturated acids and (2) the double carbonylation of allylic chlorides to β,γ-unsaturated α-keto amides are described. Mechanisms which reasonably account for the catalytic processes are proposed on the basis of studies concerning the properties of the organopalladium complexes.

Carbonylation processes catalyzed by transition metal complexes have been used extensively in organic syntheses as well as in industrial processes.[1,2] Migratory insertion of carbon monoxide into the metal-carbon bond (Eq. 1) and the external attack of a nucleophile on the coordinated CO ligand (Eq. 2) are two fundamental processes involved in the catalytic reactions.



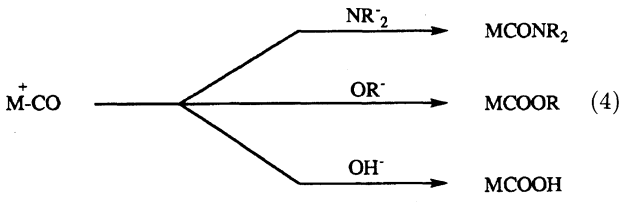
The mechanism of the CO insertion into a metal alkyl bond to give a metal acyl complex has been established to proceed by the migration of the alkyl ligand to the coordinated CO ligand. The thus-formed acyl ligand can possibly undergo a direct external attack by nucleophiles, such as amine, alcohol, or water, often in the



presence of a base, to give an amide, ester, or carboxylic acid, respectively, Eq. 3.

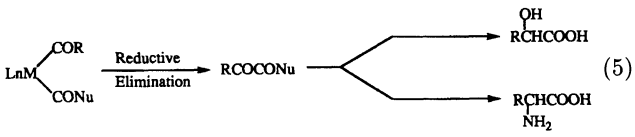
However, fundamental studies which have established the reaction courses of the acyl metal complex with nucleophiles to give the amide, ester and carboxylic acid have been quite limited.[3]

Other types of metal acyls may be formed according to Eq. 2 by an attack of amine, alcohol, or water, assisted by a base, on the coordinated CO ligand to give carbamoyl, alkoxycarbonyl, or carboxyl complexes, as represented in Eq. 4.[3,4]



If one can combine CO insertion into a metal alkyl or aryl to form a metal acyl together with a nucleophilic attack of the coordinated CO ligand to give another acyl type ligand, and can further cause a reductive elimination of the two acyl type ligands, α-keto acid derivatives can be formed (Eq. 5). The α-keto acid derivatives can be converted into biologically active compounds, such as α-hydroxy acids or α-amino acids. Since convenient routes to produce α-keto acid derivatives have been limited, the route through α-keto acid derivatives to α-amino acids or α-hydroxy acids have thus far been regarded as being unpractical; however, the realization of new synthetic methods to α-keto acid derivatives uti-

lizing CO may provide significant new routes to these biologically active carboxylic acids.



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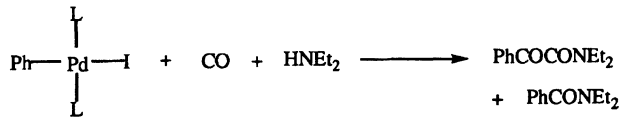
In the course of our studies concerning the mechanism of CO insertion into tertiary phosphine-coordinated *cis*- and *trans*-dialkylpalladium complexes we found that the distribution of the products derived from these dialkylpalladium complexes with CO varied, depending on the configuration of the starting complex (trans or cis) and the alkyl ligand (ethyl or methyl) (Scheme 1).[5]

The product distribution could be explained as shown in Scheme 1 by assuming alkyl ligand migration to the coordinated CO ligand to give alkyl-acyl type complexes, followed by a reductive elimination to give ketones or by a β-hydrogen elimination for the *cis*-diethylpalladium complex to yield ethylene and propionaldehyde. However, a question has remained concerning a mechanism to account for the formation of 2,3-butanedione (diacetyl) from the *cis*-dimethylpalladium complex upon its treatment with carbon monoxide. The formation of the dione could be accounted for either by assuming consecutive CO insertion to give an α-keto acylpalladium species, followed by reductive elimination of the α-ketoacyl ligand with the methyl ligand, or, alternatively, by respective insertions of two CO molecules into two Pd–methyl bonds to give bisacetyl palladium that releases the butanedione. The treatment of a reaction system containing the *cis*-dimethylpalladium complex and CO with diethylamine produced pyruvamide, the formation of which seemed to suggest an attack of diethylamine on the α-ketoacyl ligand, which was possibly formed by double insertion of CO molecules into the Pd–methyl bond. However, since the consecutive insertion into the Pd–methyl bond is considered to be thermodynamically less favored, and there were very limited precedents indicating the double insertion process,[6,7] we have further examined the reactions of nucleophiles with various organopalladium complexes in the presence of CO. Our studies on the reactions of arylpalladium complexes revealed that the phenylpalladium iodide complex upon a reaction with carbon monoxide in the presence of secondary amine also yielded α-keto amide together with some amide.[8]



(6)

Development of Catalytic Double Carbonylation Processes. Since the starting phenylpalladium iodide complex in Eq. 6 can be readily obtained by the oxidative addition of phenyl iodide to a Pd(0) complex that can be formed as the result of a reductive elimination of the bis-acyl type species, the obvious next step for us was to examine whether the catalytic process of converting phenyl iodide into α-keto amide in the presence of CO and a secondary amine could be realized.

It was, in fact, found that the catalytic process proceeded as had been anticipated when we used diethylamine as the nucleophile.[9] Our later studies revealed that the amine which we happened to use was the most suitable one for obtaining the α-keto amide selectively.

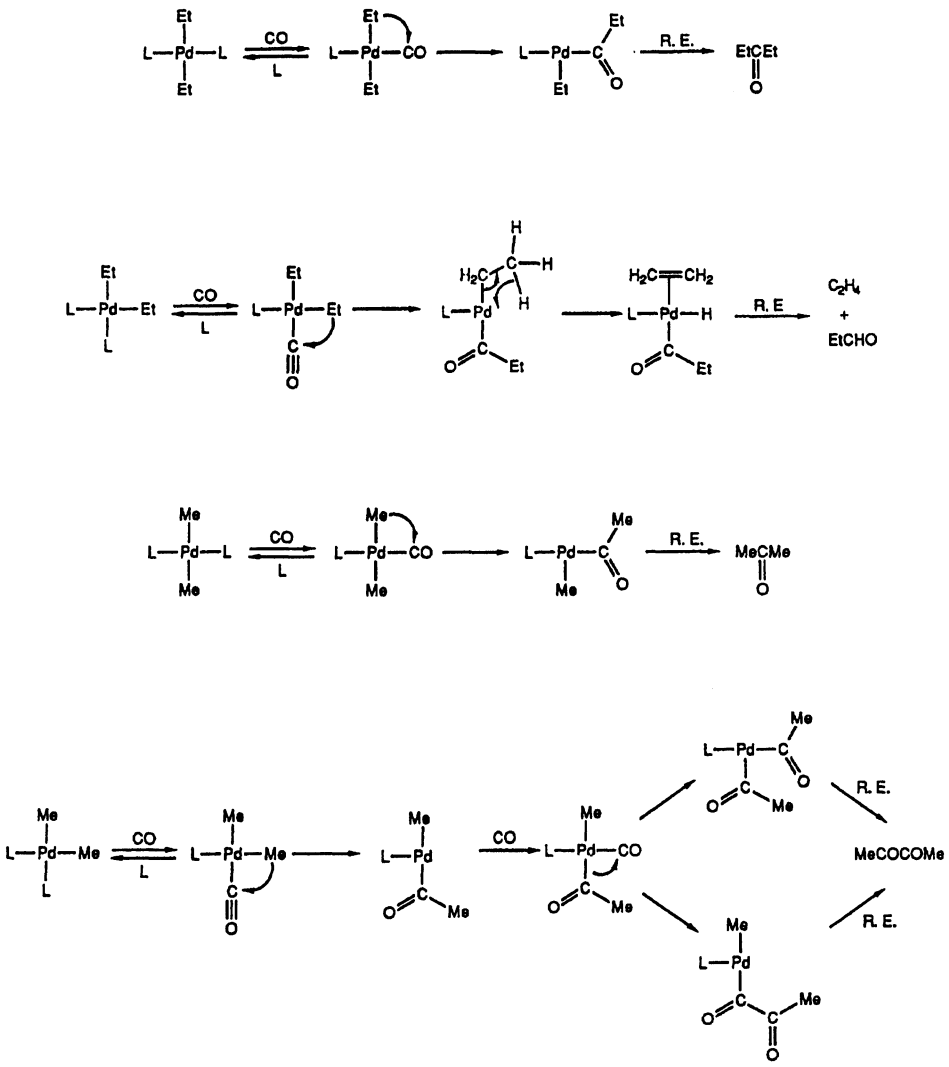
$$ArI + 2R_2NH + CO \xrightarrow[-R_2NH_2X]{[Pd]} ArCOCONR_2 + ArCONR_2 \quad (7)$$

Tanaka's group also discovered the same process at the same time.[10] They were involved in studies of the catalytic synthesis of ketones by the reactions of aryl halide, CO, and alkyltin compounds and were led to the same line of results as ours. As we have experienced in our discovery of the first cobalt-dinitrogen complex, it sometimes happens that some other groups are quite close to the same target.[11]

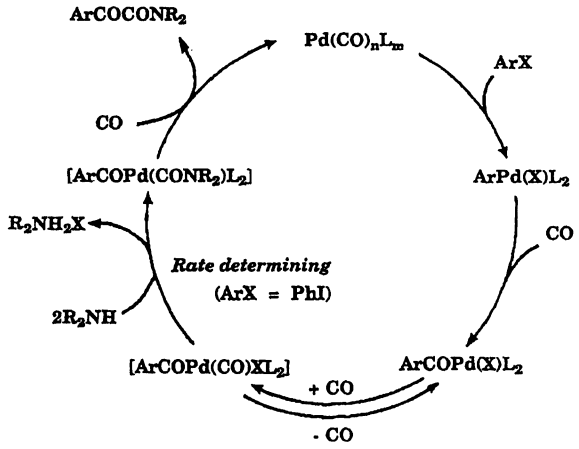
Our detailed studies as well as those by Tanaka's group led to the mechanism shown in Scheme 2.[12,13]

The mechanism involves: (a) the oxidative addition of aryl halide to Pd(0) species, (b) CO insertion into the aryl–palladium bond to give an acylpalladium complex, (c) CO coordination to the acyl complex, (d) a nucleophilic attack of a secondary amine on the coordinated cationic acylpalladium complex to yield an acyl(carbamoyl)palladium complex, (e) a reductive elimination of the acyl and carbamoyl ligands to release α-keto amide with regeneration of the palladium(0) species that carries the catalytic cycle. For a related double carbonylation process to give α-keto esters, a similar mechanism involving an attack of alcohol in the presence of tertiary amine to give an alkoxycarbonyl ligand that reductively eliminates the α-keto ester in combination with the aroyl ligand was proposed.[12c—14]

The proposed mechanism has been supported by studies on model complexes by our group as well as by Sen and Chen.[15,16] Particularly useful information was obtained by using trimethylphosphine as a ligand, since it does not readily dissociate from the palladium center because of its high basicity and small steric bulkiness. With other readily dissociating ligands such as triphenylphosphine, the isolation of organopalladium complexes sometimes encounters difficulties. By using trimethylphosphine we could isolate and characterize model compounds of important reaction intermediates. Thus, the attack of a CO ligand coordinated to an acylpalladium complex by a secondary amine to give an acyl(carbamoyl)palladium intermediate assumed in the catalytic cycle in Scheme 2 has been unequivocally established.[17,18] The possibilities of consecutive CO insertion to give an α-ketoacyl species that is attacked by a nucleophile to give α-keto acid derivatives were excluded based on studies concerning the properties of



Scheme 1. Mechanism to account for the product distribution in reactions of *cis*- and *trans*-dialkylpalladium complexes having two tertiary phosphine ligands with CO.



Scheme 2. Mechanism of palladium-catalyzed double carbonylation of aryl halides with secondary amines to afford α-keto amides.

the acyl(carbamoyl)palladium complexes as well as on the reactivities of α-ketoacyl-palladium and platinum complexes.[19,20]

For the palladium-catalyzed single carbonylation of aryl halides in combination with secondary amine to give amides and for alkoxycarbonylation with alcohol and tertiary amine to yield esters two different mechanisms have been proposed on the basis of model studies as well as of studies of catalytic systems. The amide has been concluded to be formed by a reductive elimination of the aryl and carbamoyl ligands[15d] whereas the ester is considered to be generated by a reductive elimination of the acyl and alkoxide ligands.[13,14]

The palladium-catalyzed double carbonylation can be applied to other substrates, such as *o*-iodoacetanilide, which can be converted into isatin and quinoline derivatives.[21] Double carbonylation of alkenyl halides can also be accomplished, although alkenyl halides that can be double-carbonylated were only those containing phenyl substituents.[22] Examination of the catalytic activities of other transition metal complexes than palladium for the double carbonylation of aryl halides re-

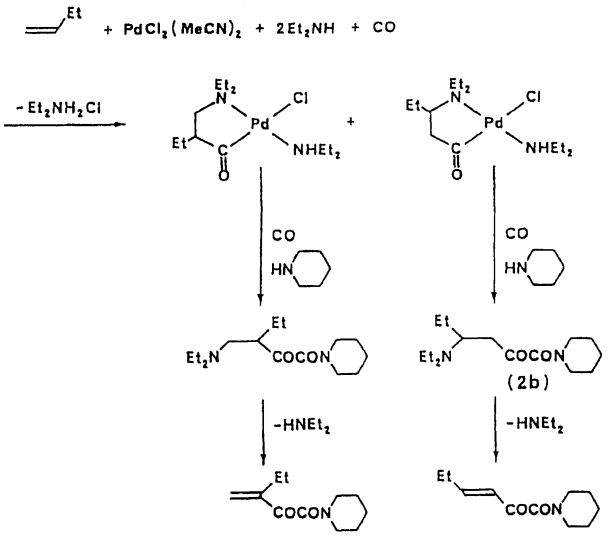
vealed that the palladium complexes are the most suitable catalysts.

Although stoichiometric reactions of CO-coordinated acyl-cobalt, manganese, and rhenium towards nucleophiles were examined, they afforded α-keto amides only upon treatment with bromine.[23] Acyl(carbonyl)-ruthenium(II)- and iron(II) complexes also reacted with amines to give acyl(carbamoyl)-type complexes, though catalytic double carbonylation was not realized.[24] As other examples of catalytic processes, the conversions of benzyl halides have been reported in patents[25,26] and the cobalt-catalyzed double carbonylation of benzyl as well as other phenylalkyl bromides has been briefly reported.[27]

As other attempts to introduce two CO molecules into organic compounds, a stoichiometric conversion of aminoaldehydes into α-keto amides has been accomplished.[28] Furthermore, the conversion of 1-butene into β,γ-unsaturated α-keto amide was achieved, but in only a stoichiometric manner by the processes shown in Scheme 3.[29]

The process is based on an external attack by amine on the olefin coordinated to Pd(II) and a subsequent CO insertion to give an aminoacylpalladium species. The coordination of CO to palladium followed by an attack by amine on the coordinated CO ligand gives the acyl(carbamoyl)palladium species. A reductive elimination of both of the acyl ligands liberates an α-keto amide having an amino group attached to the γ-position. Ready de-amination caused by a treatment of the product mixtures on a chromatographic column gives the unsaturated α-keto amide. Although the process is potentially interesting, since it gives unsaturated α-keto acid derivatives, we have not been able to make the process proceed catalytically.

The catalytic processes discussed in Scheme 2 include an oxidative addition of aryl halide to a Pd(0) species as a key step. An alternative approach, which is not dealt with here in detail, is to utilize the concept of an attack of nucleophiles on the CO ligands coordinated to Pd(II) to give a bis acyl type complex which reductively eliminates oxalate or oxamate type products to regenerate a Pd(0) species. The difference from the process (as illustrated in Scheme 2) is that the liberated Pd(0) species is to be reoxidized to Pd(II) so as to undergo further CO coordination and an attack of the bound CO by a nucleophile. The commercialized Ube process is based on this concept.[30] By using a similar concept, catalytic processes to synthesize oxamate derivatives have been developed.[31]



Scheme 3. Mechanism of stoichiometric double carbonylation of 1-butene with diethylamine.

Carbonylation and Double Carbonylation of Allylic Compounds. The work described above had been performed toward the end of my tenure at the Tokyo Institute of Technology. Before my compulsory retirement from TIT we could not realize the catalytic double carbonylation of aliphatic compounds and a project to realize the double carbonylation of aliphatic compounds remained to be pursued further at Waseda University, which accepted me after 1990.

Since double carbonylation of simple alkyl halides did not seem to be feasible in view of their reactivity with secondary amines, we sought other substrates suitable for introducing CO molecules to give carbonylation products. Allylic compounds seemed to be the most promising candidates to accomplish catalytic double carbonylation, because of their known reactivities with palladium to form π-allyl palladium complexes with the cleavage of carbon–halogen or carbon–oxygen bonds.[32—35] It seemed possible to realize the double carbonylation of allylic compounds if we could accomplish CO insertion into the allyl–palladium bond combined with the attack of a nucleophile on the CO coordinated to the palladium(II) species.

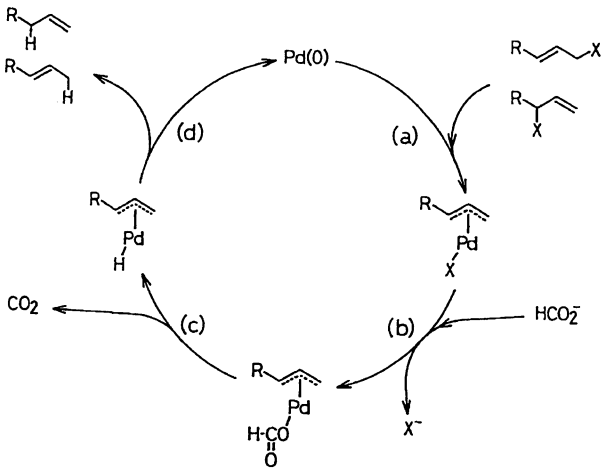
Another objective which we had when we started our study on the reactivities of allylic compounds with palladium complexes was to develop a halide-free catalytic process. As in the carbonylation of aryl halides, most processes of such palladium-catalyzed reactions as arylation of olefins employ aryl halides as the starting compounds because of the ease of oxidative addition of the aryl halides to the Pd(0) complex. However, as we have mentioned in the preceding section, the halide must eventually be removed from the system as a salt with the aid of a base. It would be much more favorable, if we could develop a catalytic process in which no use of organic halides and a base is required. It was hoped that such a halide-free process may be realized by using allylic esters that are known to oxidatively add to Pd(0) along with a cleavage of the C–O bond to form π-allylpalladium complexes.

There are some precedents concerning the carbonylation of allylic compounds catalyzed by palladium compounds. Allylic acetates,[36,37] halides,[38,39]

ethers,[40] alcohols,[41] and carbonates[42] have been carbonylated to their respective carboxylic acids, carboxylic esters or other derivatives using various combinations of palladium catalysts. The processes are considered to proceed through π-allylpalladium intermediates. However, the reported yields and selectivities are not so high and no example of double carbonylation has been reported.

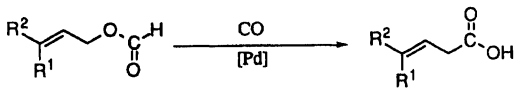
Shortly before I moved from Tokyo Institute of Technology to Waseda University I had started collaboration with Professor Isao Shimizu at Waseda University, who is experienced in the synthesis of complicated organic compounds using palladium complexes. The collaborative work to isolate and identify key intermediates in palladium-catalyzed reductive cleavage of allylic esters with formic acid[43,44] led us to the isolation of π-allyl palladium formates having one and two tertiary phosphine ligands, respectively.[45] On the basis of our study concerning the behavior of the isolated π-allylpalladium formate and acetate complexes, we proposed the catalytic cycle shown in Scheme 4 in order to account for the mechanism of the catalytic reductive cleavage of allylic esters.

The catalytic cycle comprises several elementary steps: (a) an oxidative addition of allylic ester to Pd(0) to form a π-allylpalladium carboxylate, (b) replacement of the carboxylate ligand with formate to give a π-allylpalladium formate, (c) decarboxylation of the formate ligand to give a π-allylpalladium hydride, (d) a reductive elimination of the hydride and allyl ligands to give terminal or internal olefins.[46] When allylic formates are used instead of allylic acetate, a reductive cleavage of the allylic formate can be accomplished by using a palladium catalyst. From these studies it was expected that we might be able to incorporate carbon monoxide into the catalytic system. To our surprise, studies using allylic formates as the starting material under the pressure of carbon monoxide led to the discovery of a



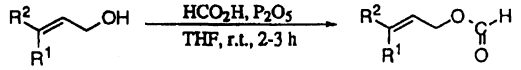
Scheme 4. Proposed mechanism to account for the reductive cleavage of allylic esters with a formate catalyzed by a palladium complex.

novel catalytic process to give β,γ-unsaturated carboxylic acids, Eq. 8.[47]



(8)

The starting allylic formates can be readily prepared by treating allylic alcohols with diphosphorus pentaoxide (Eq. 9).



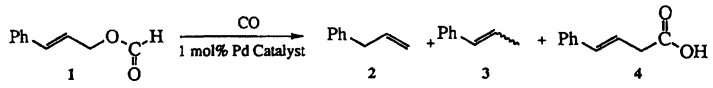
(9)

Since allylic alcohols can be prepared in chloride-free processes, the combination of Eqs. 8 and 9 provides a route to β,γ-unsaturated acids without using a chloride. This process does not require a base either. For examining the conditions used to give β,γ-unsaturated acids we have tested various combinations of the catalysts, solvents, and CO pressure using cinnamyl formate (**1**) as the substrate, as shown in Table 1 with Eq. 10. Nonpolar solvents such as toluene was found to be suitable for a process to give the β,γ-unsaturated acid **4**. The employment of polar solvents, such as DMSO and DMF (Entries 9 and 10 in Table 1), caused a decrease in the yield of the carboxylic acid and formed terminal and internal olefins (**2** and **3**) as the major products.

When the reaction was performed under argon, a palladium-catalyzed reductive cleavage took place at room temperature evolving carbon dioxide and giving only olefins **2** and **3**. Similarly, the olefins were formed when the reaction was carried out under atmospheric pressure of carbon monoxide (Entries 1 and 17 in Table 1). The reductive cleavage of cinnamyl formate to yield **2** and **3** can be accounted for by the mechanism shown in Scheme 4.

In contrast, when the reaction was performed in toluene under pressurized carbon monoxide of over 20 atm, 4-phenyl-3-butenoic acid **4** was produced almost exclusively, even at room temperature (Entries 2 to 6). Raising the reaction temperature caused an increase in the reaction rate. The unsaturated acid **4** could be prepared with a yield greater than 95% by heating a system containing **1** in toluene and carbon monoxide pressurized over 40 atm at 60 °C overnight in the presence of a palladium catalyst (Entries 5 to 7). As the catalyst, simple Pd(0) complexes in combination with triphenylphosphine or tricyclohexylphosphine could be used to give satisfactory results (Entries 5, 6, 12, and 15). Employment of a bidentate tertiary phosphine ligand, such as 1,2-bis(diphenylphosphino)ethane (dppe), was not suitable (Entries 13 and 14). A palladium(II) complex without tertiary phosphine was inactive while forming a precipitate of palladium black (Entry 16).

The carboxylation process (Eq. 8) to give the β,γ-unsaturated acid is quite clean, and virtually no by-products are produced in the reaction. Beside the olefins,



(10)

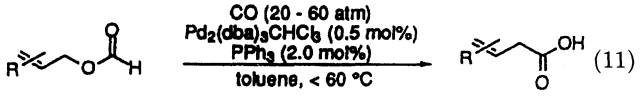
Table 1. Carboxylation of Cinnamyl Formate[a)]

Entry	Catalyst[b)]	CO Pressure	Solvent	Temp	Time	Conv.	Yield/%		
		atm		°C	h	%	**2**	**3**	**4**
1	A	1	Toluene	r.t.	96	79	40	36	tr.
2	A	20	Toluene	r.t.	96	99	1	2	87
3	A	35	Toluene	r.t.	96	100	1	1	92
4	A	60	Toluene	r.t.	96	100	Trace	1	92
5	A	60	Toluene	60	15	100	1	1	95(95)
6	A	40	Toluene	40	40	100	1	1	95
7	A	20	Toluene	60	15	91	16	14	56
8	B	60	CH_3CN	60	15	86	9	5	36
9	B	60	DMSO	60	15	56	42	7	Trace
10	A	60	DMF	60	15	100	48	36	Trace
11	A	60	THF	60	20	92	1	1	80
12	B	60	Toluene	60	15	100	5	2	93
13	C	60	Toluene	60	15	9	Trace	7	1
14	D	60	Toluene	60	15	79	3	12	30
15	E	60	Toluene	60	10	100	1	1	89
16	F	60	Toluene	60	15	<1	Trace	Trace	Trace
17	E	1	Toluene	50	4	100	56	43	Trace

a) Typical conditions: cinnamyl formate (4 mmol), $Pd_2(dba)_3CHCl_3$ (0.02 mmol), PPh_3 (0.08 mmol), toluene (10 ml). b) A = $Pd_2(dba)_3CHCl_3 + PPh_3$ (P/Pd = 2/1), B = $Pd_2(dba)_3CHCl_3 + P(c\text{-}C_6H_{11})_3$ (P/Pd = 2/1), C = $Pd_2(dba)_3CHCl_3$ + DPPE (P/Pd = 2/1), D = $Pd_2(dba)_3CHCl_3$ + DPPB (P/Pd = 2/1), E = $Pd(PPh_3)_4$, F = $[(1\text{-Ph-allyl})PdCl]_2$.

only very minor amounts of aldehydes and cinnamyl ester of **4** were detected as by-products. The process is in essence a molecular rearrangement of allylic formate to β,γ-unsaturated acid under carbon monoxide pressure where nothing is added to nor subtracted from the starting substrate.

This process is applicable to other allylic alcohols with various substituents, Eq. 11 (Table 2).



(11)

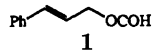
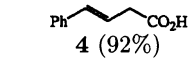
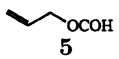
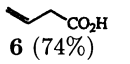
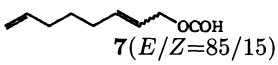
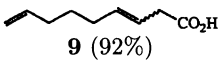
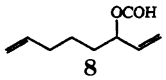
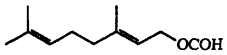
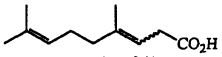
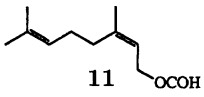
The formate ester of simple allyl alcohol **5** can be converted into 3-butenoic acid **6** selectively. Formates of higher allylic alcohols such as **7** and **8** also can be converted into unsaturated carboxylic acids. The results that products of similar stereochemistry (**9** in a *E*/*Z* ratio of about 82/18) were obtained starting from the formates of linear as well as branched alcohols (**7** and **8**) clearly indicates that the reaction proceeds via a common π-allylpalladium intermediate. When formates of trisubstituted allylic alcohols of *E*- and *Z*-isomers (**10** and **11**) were used, β,γ-unsaturated carboxylic acid **12** was obtained in similar yields along with a slight difference in the isomer ratio (Entries 5 and 6).

Although monodentate tertiary phosphines, such as triphenylphosphine and tricyclohexylphosphine, proved to be effective for producing 4-phenyl-3-butenoic acid **4** from cinnamyl formate **1**, only an unsatisfactory yield (about 5%) was obtained when a formate of allylic alcohols, such as geraniol **10** or nerol **11**, bearing a trisubstituted allylic double bond, were subjected to a catalytic carbonylation reaction with the catalyst system containing triphenylphosphine and $Pd_2(dba)_3CHCl_3$ (dba = dibenzylideneacetone). A significant increase in the yield of the unsaturated acid **12** was realized by using dppe. The influence of the monodentate and bidentate tertiary phosphines on the reaction course is presently being investigated. In all cases, the carbonyl group was introduced into a less substituted site in the presumed intermediate π-allylpalladium complex.

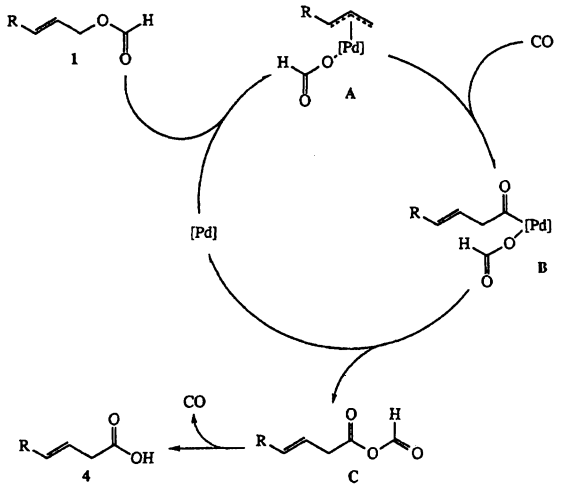
The process to produce the β,γ-unsaturated acids can be accounted for by the mechanism presented in Scheme 5, which shows the case for converting cinnamyl formate.

The first step in the catalytic cycle is an oxidative addition of cinnamyl formate **1** to a Pd(0) species to give π-allylpalladium formate **A**. A subsequent CO insertion into the allyl–palladium bond gives an acylpalladium formate **B**, which upon reductive elimination liberates a mixed anhydride **C**. The mixed anhydride **C** is relatively unstable and is converted into β,γ-unsaturated acid **4** upon decarbonylation.[48)] After a reductive elimination of the mixed anhydride a Pd(0) species is regenerated to carry the catalytic cycle. As shown in

Table 2. Carboxylation of Various Allylic Formates[a)]

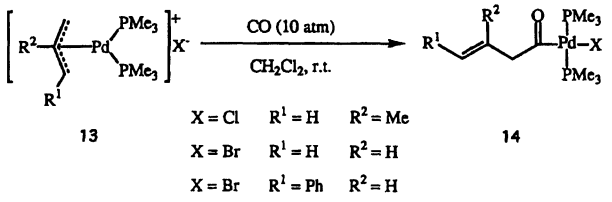
Entry	Allylic formate	Conditions	Product yield (%)
1	 **1**	35 atm, r.t., 96 h	 **4** (92%) (E/Z=100/0)
2	 **5**	30 atm, r.t., 90 h	 **6** (74%)
3	 **7**(E/Z=85/15)	40 atm, 40 °C, 50 h	 **9** (92%) (E/Z=83/17)
4	 **8**	60 atm, 60 °C, 25 h	**9** (94%) (E/Z=81/19)
5[b)]	 **10**	60 atm, 60 °C, 25 h	 **12** (52%) (E/Z=71/29)
6[b)]	 **11**	60 atm, 60 °C, 25 h	**12** (51%) (E/Z=41/59)

a) General conditions: $Pd_2(dba)_3CHCl_3$ (0.02 mmol), PPh_3 (0.08 mmol), allylic formates (4 mmol), and toluene (10 ml) were stirred in a 100 ml stainless autoclave under CO pressure. b) 1,2-Bis(diphenylphosphino)ethane (DPPE) was used in place of PPh_3.



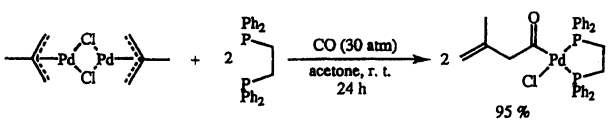
Scheme 5. Mechanism of conversion of allylic formate to β,γ-unsaturated carboxylic acid under CO catalyzed by a palladium complex.

Scheme 4, an oxidative addition of allylic carboxylate to a Pd(0) species has been well established. The subsequent CO insertion into the π-allylpalladium complex has had much less precedents until recently. We had previously shown that the CO insertion into the π-allyl-palladium bond takes place under appropriate conditions, depending on the nature of the allylic moiety as well as on the number and property of the tertiary phosphine ligand.[49)]



(12)

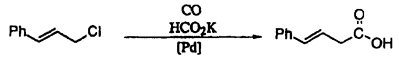
The nature of the halide ligand also has a strong influence to cause CO insertion. A particularly important factor here seems to be that of the halide ligand to hinder the decarbonylation of the acyl-palladium entity back to the π-allyl complex. Removal of the halide ligand in the *trans*-acylpalladium complex coordinated with two trimethylphosphine ligands (**14**), derived by CO insertion into π-allylpalladium complexes **13**, was observed to greatly facilitate decarbonylation, presumably by creating a vacant site to assist in the coordination of the allylic moiety. Our later studies also revealed that strongly coordinating ligands, such as dppe and trimethylphosphine, favor an insertion reaction, Eq. 13



(13)

Upon finding the catalytic formation of β,γ-unsaturated acids from allylic formates in the presence of

pressurized CO we have further studied whether a similar catalytic process can also be achievable with allylic halides, which are well known to undergo an oxidative addition to Pd(0) complexes involving carbon-halogen bond cleavage to give π-allylpalladium halide complexes. In fact, the reaction of cinnamyl chloride with potassium formate in the presence of a palladium complex catalytically produced β,γ-unsaturated carboxylic acid, Eq. 14.



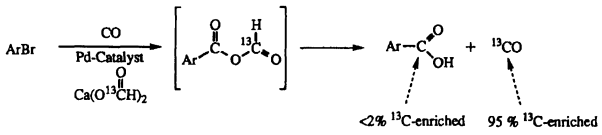
(14)

The reaction can be carried out at room temperature in benzene solutions containing water to dissolve the formate salts to give 4-phenyl-3-butenoic acid **4** quantitatively; however, the reaction also proceeds in the absence of water by using a catalyst system containing $PdCl_2(PPh_3)_2$. Employment of 18-crown-6 to activate the potassium formate gave 4-phenyl-3-butenoic acid quantitatively at 50 °C under a CO pressure of 50 atm.

On the Mechanisms of Formation of β,γ-Unsaturated Acids from Allylic Formates and Allylic Chlorides Catalyzed by Palladium Complexes. With respect to the mechanism for the formation of β,γ-unsaturated acids from allylic formates, an alternative possibility to the mechanism shown in Scheme 5 is a direct attack of water, inadvertently introduced into the system, on the acylpalladium complex. We consider this process to be unlikely, since the reaction of cinnamyl formate can be catalytically carried out in hydrocarbon solvents from which water has been carefully removed, and that acylpalladium complexes, such as **14**, are relatively insensitive to water. We consider that the probable route to β,γ-unsaturated acid is a decarbonylation of mixed anhydride produced by a reductive elimination of the acyl and formato ligands, as shown in Scheme 5. The formation of mixed anhydride, acetic butenoic anhydride, was reported by Tsuji in the carbonylation of allyl acetate in the presence of palladium dichloride under 150 atm of CO in benzene at 100 °C.[50] Further, the decarbonylation process may well be catalyzed by a palladium complex. The ready oxidative addition of carboxylic anhydrides to low valent transition metal complexes, such as Ir(I), Ni(0), and Pd(0), to form acyl-carboxylato type complexes are known.[51]

As a related process, Lee recently reported on the selective formation of optically active 2-arylpropanoic acids from 1-arylethyl esters by palladium catalysts.[52] The mechanism proposed by Lee also involves an acylformyl intermediate which reductively eliminates mixed anhydride. Later decarbonylation is assumed to yield 2-arylpropanoic acid. Thus, their mechanism is similar to ours (Scheme 5) with a difference in that we use allylic formates whereas they use 1-arylethyl esters.

A palladium-catalyzed formation of carboxylic acids from aryl iodide and salts of formic acids under CO pressure has also been reported;[53] and evidence in support of the release of CO from mixed anhydride originated from calcium formate has been provided by using ^{13}C-labelled calcium formate, Eq. 15

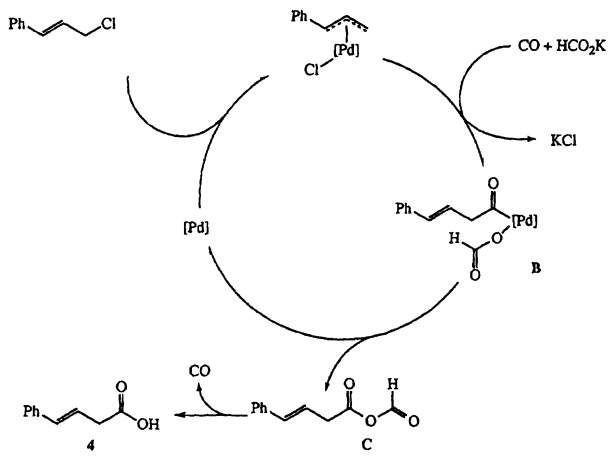


(15)

The conversion mechanism of cinnamyl chloride into 4-phenyl-3-butenoic acid can be accounted for similarly to Scheme 5 by the following several elementary steps: (a) an oxidative addition of allylic chloride to Pd(0) species to produce π-allylpalladium chloride, (b) insertion of CO into the allyl–palladium bond to form an acyl species, (c) replacement of the chloride ligand by the formate to give the acyl(formato)palladium complex, (d) a reductive elimination of the formato and the acyl ligands to produce the mixed anhydride **C**, and (e) decarbonylation of **C** to give the product **4** (Scheme 6).

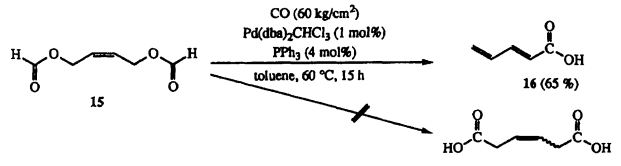
Although it is conceivable that cinnamyl formate may be formed by the reaction of cinnamyl chloride and potassium formate and the cinnamyl formate may be utilized in the succeeding catalytic process, this alternative route does not seem to be likely, since in the absence of a palladium catalyst cinnamyl chloride was recovered unreacted after its treatment with potassium formate at room temperature for 50 h. It is probable that a Pd(0) species may be formed by the reaction of $Pd(PPh_3)_2Cl_2$ and that potassium formate and the Pd(0) species serves as the catalyst.

An Attempt of Carrying out the Carboxylation Reaction to Obtain Dibasic Acids. As shown in Table 2, the new process converting formates of a variety of allylic alcohols into β,γ-unsaturated acids provides a convenient method for introducing one CO group under mild conditions to yield unsaturated acids. An obvious extension of the process is its application to bifunctional alcohols. Our attempt to examine the reaction of diformate of 2-betene-1,4-diol, **15**, to get dibasic



Scheme 6. Mechanism of palladium-catalyzed carboxylation of cinnamyl chloride.

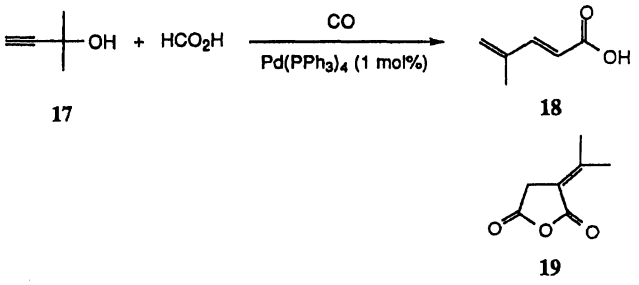
acid revealed that the CO was introduced into only one terminal of the diol entity to produce 2,4-pentadienoic acid, **16**, Eq. 16.



(16)

The reaction course may be accounted for as represented in Scheme 7. The first cleavage of the allylic formate on one terminal would give a half ester having a carboxyl group on the other end (**D**). The second oxidative addition of the allylic formate part in **D** produces a π-allylpalladium formate **E**. If β-hydrogen elimination takes place before CO insertion into the allyl-palladium bond, 2,4-pentadienoic acid **16** and formic acid will be produced. The formation of formic acid was confirmed. Although an attempt to obtain the adipic acid precursor **F** was unsuccessful, a further examination of the reaction conditions may reveal possibilities of application of the new process.

Carboxylation of Propargyl Alcohol and Its Analogs. As a logical extension of the carboxylation of allylic alcohols we have examined the palladium-catalyzed carbonylation of propargyl alcohol and its analogs. The representative results are given below.

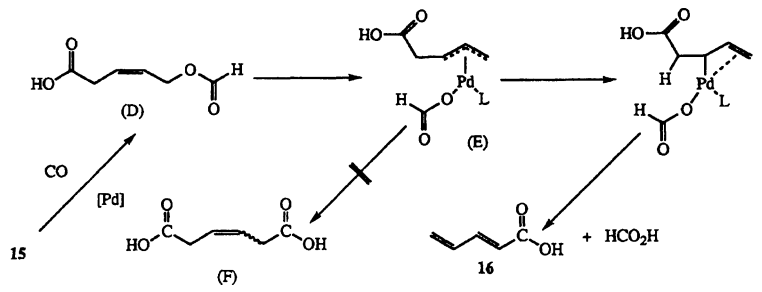


(17)

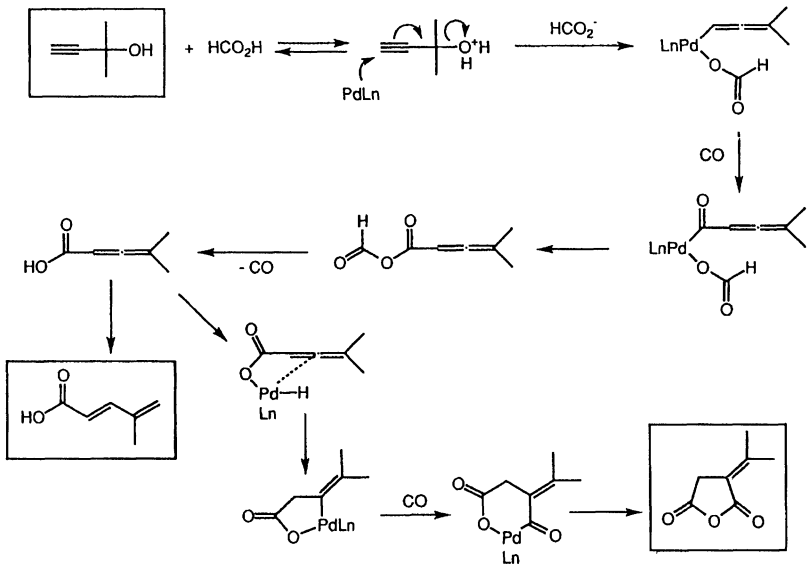
3-Methyl-1-butyne-3-ol, **17**, was converted under CO pressure over 20 atm at 50 °C overnight in the presence of $Pd(PPh_3)_4$ into 4-methyl-2,4-dienoic acid **18** and a cyclic anhydride with an exomethylene group **19** in yields of about 50 and 20%, respectively. Non-polar solvents, such as toluene, seems to be suitable as solvents. A monodentate tertiary phosphine, such as triphenylphosphine, seems to be appropriate; a bidentate ligand, such as dppe, was not suitable for the reaction. Although the examined examples are still limited, tertiary alkynyl alcohols have so far proved to be the only reactive substrates. Catalytic carbonylation of alkynols by a palladium catalyst without tertiary phosphine ligands to give esters of unsaturated carboxylic acids and cyclic anhydrides with an exomethylene group had previously been reported in the sixties by Tsuji.[54] The catalytic formation of dienoic acids and their esters from alkynes and CO under phase transfer conditions catalyzed by palladium complexes are also recently attracting attention.[55,56] Scheme 8 gives a tentative mechanism to explain the formation of the dienoic acid and the cyclic anhydride with the exomethylene group. The catalytic reaction may involve the formation of an intermediate allenylpalladium formate which undergoes CO insertion to afford an allenoyl(formato)-palladium complex. The reductive elimination of the allenoyl and the formato ligands would give a mixed anhydride of the formic and 4-methyl-2,3-pentadienoic acid. The mixed anhydride on decarbonylation would yield the dienoic acid **18** after double bond isomerization. A further oxidative addition of the dienoic acid to Pd(0) to give a hydrido(carboxylato)palladium intermediate followed by hydride migration and CO insertion would give a cyclic carboxylato(acyl)intermediate. The reductive elimination would produce the cyclic anhydride **19** with an exomethylene substituent.

Double Carbonylation of Allylic Halides to Give Unsaturated α-Keto Amides. Encouraged by our success in finding an unexpected, but novel carbonylation processes, we turned our attention back to the original target of realizing double carbonylation of allylic compounds. As we mentioned previously, if we assume that the catalytic double carbonylation proceeds in a way similar to that which we established for the double carbonylation of aryl halides, the following requirements must be fulfilled in order to achieve the double carbonylation of allylic compounds: (a) an oxidative addition of allylic compounds to Pd(0) to give π-allylpalladium(II) complexes, (b) insertion of CO into the allyl–palladium bond to generate acylpalladium complexes, (c) coordination of CO to the acylpalladium complexes, (d) an attack of the coordinated CO ligand by nucleophiles such as amine, alcohol, and water to give carbamoyl, alkoxycarbonyl, or carboxyl intermediates, (e) a reductive elimination of the two acyl ligands to liberate the α-keto acid derivatives with regeneration of the Pd(0) complex that carries the catalytic cycle. The oxidative addition of allylic compounds to palladium(0) complexes to give π-allylpalladium complexes is a well established process;[57] we have reported on the isolation and characterization of the π-allylpalladium complexes obtained by the oxidative addition of allylic acetates,[58] chalcogenides,[59,60] carbonates,[61] and formates.[62] We have already shown that CO insertion into the allyl–palladium bond is a feasible process, although its precedents have been limited. We have also established that the subsequent processes of CO coordination to Pd(II) species and an attack of the coordinated CO ligand by nucleophiles, such as amine, alkoxide, and hydroxide, are feasible processes.

What we were concerned with was that a nucleophilic attack of the nucleophile on the π-allyl ligand coordinated on palladium to yield an allylated nucleophile may be more facile than an attack of a nucleophile on the coordinated CO ligand to produce an acyl li-



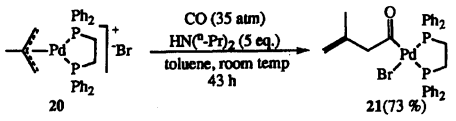
Scheme 7. Mechanism of formation of dienoic acid **16** from formate **15**.



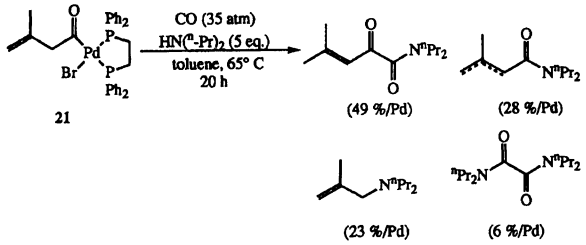
Scheme 8. A tentative mechanism to account for the formation of dienoic acid and a cyclic anhydride with an exo-methylene group with formic acid from methyl-substituted propargyl alcohol catalyzed by a palladium catalyst.

gand, and that this may prevent the catalytic reaction to proceed. Actually, our previous study indicated that nucleophiles attack the coordinated π-allyl ligand to produce allylation products of the nucleophiles.[63]

A synthetic chemist should not sit and worry without trying experiments. An examination of the reactivities of acylpalladium complexes obtained by CO insertion into the allyl–palladium bond (Eq. 18) revealed that the treatment of the acylpalladium complex **21** with a secondary amine under CO pressure at 65 °C in toluene produced the α-keto amide, amide, allylamine, and oxamide in the quantities shown in Eq. 19.



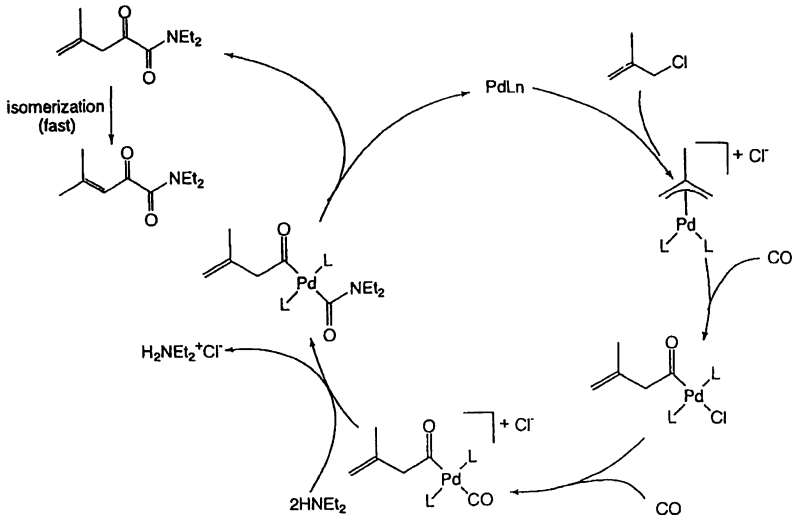
(18)



(19)

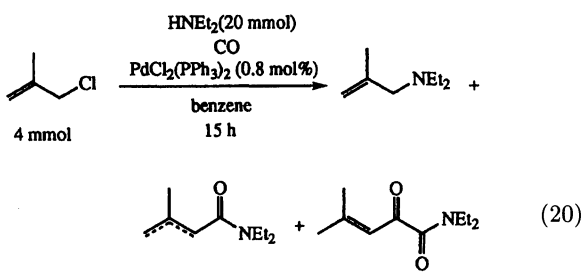
The fact that CO insertion into the π-allyl bond in **20** occurred under CO pressure, even in the presence of a secondary amine, indicates that under certain conditions CO insertion precedes the amine attack on the π-allyl ligand and that, once an acylpalladium species is formed, further CO coordination and a succeeding attack by amine to give a carbamoyl ligand can take place. A reductive elimination of the acyl and the carbamoyl ligands should produce the α-keto amide.

On the basis of these preliminary studies on the stoichiometric reactions of π-allylpalladium complexes and the acylpalladium complexes derived thereof by CO insertion, we attempted further to realize our long suspended goal of finding a double carbonylation process of allylic compounds. In fact, we were very pleased to



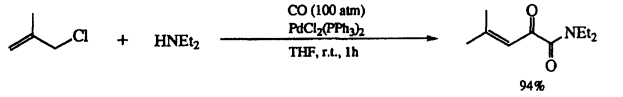
Scheme 9. A proposed mechanism to account for the double carbonylation of allylic chlorides catalyzed by a palladium complex.

see that the double carbonylation of 2-substituted allyl chlorides can be achieved under certain conditions by using simple catalyst precursors, such as $PdCl_2(PPh_3)_2$ in the presence of diethylamine, Eq. 20.

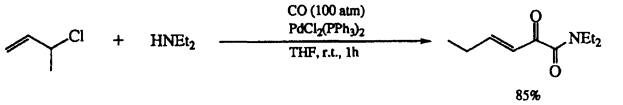


(20)

In this process, the application of a CO pressure was crucial in introducing CO molecules. Under 1 atm of CO only *N,N*-diethyl-2-methylallylamine was obtained, whereas an increase in the CO pressure favored the formation of the amide and the α-keto amide at the expense of the amine. Along with an increase in the CO pressure above 100 atm, the α-keto amide became the predominat product; a decrease in the reaction temperature further favored the double carbonylation process. Under suitable reaction conditions a yield of over 95% could be achieved at room temperature by carrying out the reaction overnight.[64] As the ligand, triphenylphosphine was quite effective, whereas palladium complexes coordinated with bidentate tertiary phosphines, such as dppe and 1,4-bis(diphenylphosphino)-butane (dppb), were inactive, and $PMePh_2$-coordinated complexes showed less activity and selectivity. Palladium chloride without a tertiary phosphine ligand showed some activity for producing single carbonylation products. Simple allyl chloride and cinnamyl chloride did not give a double carbonylation product, though substituted allylic chlorides afforded α-keto amides predominantly, as shown below.



(21)



(22)

A mechanism to account for the formation of α-keto amide is shown in Scheme 9.

The scheme is self-evident based on what we discussed in the former sections. The addition of allylic chlorides to the Pd(0) species to give π-allylpalladium chloride complexes is a well known process. We have established CO insertion into the allyl–palladium bond to give an acylpalladium species in our former and present studies. Further CO coordination to a cationic acylpalladium and a subsequent attack on the coordinated CO by amine are crucial steps in the catalytic process. In our previous studies on the double carbonylation of aryl halides we have established through model studies using trimethylphosphine ligands that the formation of a carbamoyl ligand by the attack of an amine on the coordinated CO in a cationic acylpalladium complex in fact gives an acyl(carbamoyl)palladium complex that reductively eliminates the α-keto amide under suitable conditions. Representation of the intermediate acyl(carbamoyl)palladium intermediate in the trans configuration in Scheme 9 is only for the sake of convenience of presentation. In the actual catalyst system one of the tertiary phosphine ligands may well be dissociated, or if a *trans* acyl(carbamoyl)complex is formed, it should somehow be transformed into the cis form where the acyl and carbamoyl ligands are suitably situated in mutually adjacent positions for the concerted reductive elimination to take place. After the generation of γ,δ-unsaturated α-

keto amide, double bond migration seems to be a rapid process because of the presence of two strongly electron-withdrawing carbonyl groups in the α-keto amide.

In retrospect, we did not have to be overly concerned about a nucleophilic attack of a secondary amine on the π-allyl ligand to produce allylamine, since recent papers report on the palladium-catalyzed carbonylation of allylamines to β,γ-unsaturated amides, although under somewhat drastic conditions.[65,66]

Concluding Remarks. In this account I have tried to describe how we were led to finding new catalytic carbonylation and double carbonylation processes on the basis of our fundamental studies on the chemistry of organopalladium complexes. Through our basic quest to find the reasons behind some unexpected reactions we happened to find unexpected results which may have some future possibilities involving applications that have not yet been imagined. The mechanisms of the catalytic reactions that I have described here can be accounted for reasonably as a combination of fundamental processes, such as oxidative addition, CO insertion, a nucleophilic attack on the coordinated CO, and reductive elimination. Many other processes, however, are still expected to be found by a combination of fundamental steps involving the insertion of other substrates, such as alkenes and alkynes, by the combination of a nucleophilic attack on the coordinated ligand and other conceivable processes together with yet-to-be found new reactions. Although new discoveries may result from the pursuit of practical applications, I believe that there are still ample opportunities that one may come across findings involving novel processes if one is prepared for the possible applications, even through curiosity-driven fundamental research, as shown in the present account.

First of all I would like to thank my previous and present co-workers who eagerly contributed to the line of work I have discussed in the present account. Particularly, the first part of the work on the double carbonylation of aryl halides has been chiefly driven by my former associate at Tokyo Institute of Technology, Professor Fumiyuki Ozawa, presently at Osaka City University. After I moved to Waseda University upon my official retirement from Tokyo Institute of Technology, I enjoyed the cooperation with my colleague, Professor Isao Shimizu. I would also like to mention that the second part I described in this article was achieved almost single-handedly by Tohru Terashima, a student for a Master's degree at Waseda University. I am particularly thankful to Nippon Zeon Company which made it possible to carry out the research project at Waseda University by the generous donation of a chair created for me. The grant support by the Ministry of Education, Science and Culture is gratefully acknowledged.

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